All-order calculations of the spectra of superheavy elements E113 and E114

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We apply a recently developed method (V. A. Dzuba, PRA \textbf{90}, 012517 (2014); J. S. M. Ginges and V. A. Dzuba, PRA \textbf{91}, 042505 (2015)) to calculate energy levels of superheavy elements Uut (Z = 113), Fl (Z = 114), and Fl\textsuperscript{+}. 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\textsuperscript{+} are used to gauge the accuracy of the calculations.

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\textbf{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 synthesised (see, e.g., Refs. \cite{18, 20}), and evidence for naturally-occurring E122 was reported \cite{6}.

Apart from huge activity in the theoretical and experimental nuclear physics there are also many theoretical works in atomic physics and quantum chemistry with attempts to predict the chemical propertises of the superheavy elements and their electron structure and spectra (see, e.g., \cite{18, 20}).

Superheavy elements E113 and E114 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 closed-shell core which ends with the 7s\textsuperscript{2} subshell. Its lighter analog is Tl. The E114 atom can be considered as a system with two valence electrons.

There is a number of calculations of electron spectra of elements E113 and E114 using multi-configuration Dirac-Fock, coupled-cluster, configuration interaction methods and their combinations \cite{10–17}. The results of different approaches agree in general trends caused by 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 the recently developed technique \cite{18} which combines the all-order correlation potential method \cite{19}, supplemented by ladder diagrams \cite{20} with the configuration interaction method \cite{21}. The technique gives very accurate results for energy levels of Cs, Tl, Ba, Lu, Ra and those ions of these elements which have one or two valence electrons above closed shells \cite{18, 20}. It was used to calculate energy levels of superheavy elements E119, E120 and E120\textsuperscript{+} \cite{22, 23}. We demonstrate that the method also works for Pb and Pb\textsuperscript{+}. Then we apply it to calculate energy levels of E113, E114 and E114\textsuperscript{+}.

\textbf{II. METHOD OF CALCULATIONS}

The method was described in detailed in our previous papers \cite{18, 20, 23, 24}. Here we repeat its main points with the focus on the details specific for current calculations.

\textbf{A. Atoms with one valence electron}

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

\begin{equation}
\hbar \psi_\ell = \epsilon \psi_\ell ,
\end{equation}

using the B-spline technique \cite{23, 20}. Here \(h_0\) is the relativistic Hartree-Fock Hamiltonian

\begin{equation}
h_0 = c \alpha \cdot p + (\beta - 1) mc^2 - \frac{Ze^2}{r} + V^{N-1} .
\end{equation}

B-spline basis set and Feynman diagram technique are used to calculate the all-order correlation potential (CP) \(\Sigma\) \cite{19, 20}. The CP operator \(\Sigma\) 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: \(\delta \epsilon_v = \langle v|\Sigma|v\rangle\). Perturbation theory expansion for \(\Sigma\) starts from the second order, we use the \(\Sigma^{(2)}\) notation for corresponding CP. Then we include three classes of the higher-order correlations into the all-order CP \(\Sigma^{(\infty)}\) \cite{19}: a) screening of Coulomb interaction, b) hole-particle interaction, and c) ladder diagrams \cite{20}. States and energies of the valence electron are found by solving the equation

\begin{equation}
(h_0 + \Sigma) \psi_v = \epsilon_v \psi_v .
\end{equation}
Here  $\Sigma$ can be either the second-order CP $\Sigma^{(2)}$ or all-order CP $\Sigma^{(\infty)}$. Note that by iterating the Eq. (3) we include one more class of higher-order correlations, the iterations of $\Sigma$ (contributions proportional to $\Sigma^2$, $\Sigma^3$, etc.). The wave-functions $\psi_i$ of the valence electron found by solving the Eq. (3) are often called Brueckner orbitals. Corresponding energies $\epsilon_i$ include correlations. Breit and quantum electrodynamic corrections are also included (see below).

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 from our earlier paper [20], the results for Pb$^+$ are obtained in this work. Contributions of the ladder diagrams are presented separately because it is the latest section. We introduce index 1 to stress that this is a single-electron operator. Tl and Pb$^+$ have similar electron structure, 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 stronger Coulomb potential leading to smaller relative value of the correlation correction. Indeed, the correlation correction to the energy is equal to the difference between the relativistic Hartree-Fock results (the RHF column 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%.

\[
\begin{array}{cccccccc}
\text{State} & \text{RHF} & \Sigma^{(2)} & \Sigma^{(\infty)} & \text{Ladder} & \text{Final} & \Delta & \text{Expt.} \\
6p_{1/2} & 42823 & 51597 & 50815 & -1215 & 49600 & 336 & 49264 \\
6p_{3/2} & 36636 & 43524 & 42491 & -794 & 41697 & 226 & 41471 \\
7s_{1/2} & 21109 & 23375 & 22887 & -43 & 22844 & 58 & 22786 \\
\text{Pb}^+ & 114360 & 123612 & 122547 & -1421 & 121126 & -119 & 121245 \\
6p_{3/2} & 100731 & 109451 & 108108 & -987 & 107121 & -43 & 107164 \\
7s_{1/2} & 58660 & 62793 & 61895 & -104 & 61791 & -5 & 61796 \\
\end{array}
\]

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## B. Atoms with two valence electrons

We use the configuration interaction (CI) technique combined with the all-order methods to include correlation-valence correlations [18, 21, 23]. The effective CI Hamiltonian for the system of two valence electrons has the form

\[
\hat{H}^{\text{CI}} = \hat{h}_1(r_1) + \hat{h}_1(r_2) + \hat{h}_2(r_1, r_2),
\]

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 $\hat{\Sigma}_1$

\[
\hat{h}_1 = \hat{h}_0 + \hat{\Sigma}_1.
\]

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 Coulomb interaction and the correlation operator $\hat{\Sigma}_2$ [18]

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

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 which comes from solving the single-double (SD) coupled-cluster equations [18]. Note that solving the SD equation produce both, single-electron CP $\hat{\Sigma}_1$ and two-electron correlation operator $\hat{\Sigma}_2$. However, for many atomic systems, including those considered in present work and those considered previously [18, 24], using the all-order CP $\Sigma^{(\infty)}$ which was discussed in previous section, leads to better results than using the SD operator $\Sigma_1$.

Table I 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. 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 quantum electrodynamic (QED) corrections.

The Breit operator in the zero energy transfer approximation has the form:

\[
h^B = -\frac{\alpha_1 \cdot \alpha_2 + (\alpha_1 \cdot \mathbf{n})(\alpha_2 \cdot \mathbf{n})}{2r},
\]

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

We use the radiative potential method introduced in Ref. 29 to include QED corrections to the energies. The radiative potential has the form

\[
V_{\text{rad}}(r) = V_U(r) + V_g(r) + V_e(r),
\]

where $V_U$ is the Uehling potential and $V_g$ is the potential arising from the magnetic formfactor, and $V_e$ is the potential arising from the electric formfactor. Both, Breit and QED operators are included to the Hartree-Fock iterations so that an important relaxation effect is taken into account [30, 32].
TABLE II: Calculated excitation energies (E, cm$^{-1}$), and g-factors for lowest states of Pb atom.

| State | This work | Experiment |
|-------|-----------|------------|
| 6p$^2$ | $^1$S$_0$ | 0 | 0.0000 | 0 | 0.0 |
| 6p$^2$ | $^3$P$_1$ | 7922 | 1.4999 | 7819 | 1.501 |
| 6p$^2$ | $^3$D$_2$ | 10940 | 1.2916 | 10650 | 1.269 |
| 6p$^2$ | $^3$D$_2$ | 21924 | 1.2085 | 21458 | 1.230 |
| 6p$^2$ | $^1$S$_0$ | 29177 | 0.0000 | 29467 | 0.0 |
| 7s6p | $^1$S$_0$ | 35109 | 0.0000 | 34959 | 0.0 |
| 7s6p | $^3$P$_1$ | 35536 | 1.3509 | 35287 | 1.349 |
| 6p7p | $^3$D$_1$ | 43236 | 0.6707 | 42919 |
| 6p7p | $^1$S$_0$ | 44449 | 0.0000 | 44401 | 0.0 |
| 6p7p | $^3$P$_1$ | 44873 | 1.4690 | 44675 |
| 6p6d | $^3$F$_2$ | 44896 | 0.7962 | 45443 | 0.798 |
| 6p7p | $^3$D$_2$ | 44997 | 1.1739 | 44809 |
| 6p6d | $^1$P$_1$ | 46132 | 0.8186 | 46068 | 0.864 |
| 6p6d | $^3$D$_2$ | 46162 | 1.2715 | 46061 | 1.247 |
| 6p6d | $^3$F$_2$ | 46324 | 1.1184 | 46328 | 1.116 |
| 7s6p | $^3$P$_2$ | 48765 | 1.4814 | 48188 | 1.496 |
| 8s6p | $^1$S$_0$ | 48874 | 0.0000 | 48726 |
| 8s6p | $^3$P$_1$ | 48811 | 1.3238 | 48867 | 1.304 |
| 7s6p | $^1$P$_1$ | 49892 | 1.1014 | 49440 | 1.131 |
| 6p9p | $^3$D$_1$ | 51422 | 0.6690 | 51321 |
| 6p9p | $^1$S$_0$ | 51683 | 0.0000 | 51786 |

III. RESULTS AND DISCUSSION

Table III shows the results of calculations for Uut (Z = 113) and Fl$^+$ (Z = 114) calculated in different approximations. Notations like in Table II.

| State | RHF | $\Sigma^{(2)}$ | $\Sigma^{(\infty)}$ | Ladder | Final | Other $^a$ |
|-------|-----|---------------|-----------------|--------|-------|-----------|
| 7p$_{1/2}$ | 54901 | 61929 | 61953 | -2183 | 59770 | 60154 |
| 7p$_{3/2}$ | 31557 | 38498 | 36623 | -497 | 36126 | 34938 |
| 8s$_{1/2}$ | 22913 | 24653 | 23761 | -32 | 23729 | 21313 |
| 7p$_{1/2}$ | 130420 | 138110 | 138105 | -2333 | 135772 | 137710 |
| 7p$_{3/2}$ | 89802 | 99170 | 96708 | -667 | 96041 | 97329 |
| 8s$_{1/2}$ | 60844 | 65316 | 63832 | -82 | 63750 | 63964 |

$^a$Reference 17

perheavy 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. $\sim 0.5\%$.

The results of present calculations are in a reasonable agreement with previous SD+CI calculations of Ref. 15 (see Table III). However, they are closer to the results of coupled-cluster calculations of Ref. 10. This is true for both, ionization potential and excitation energies.

The results for Fl (E114) are presented in Table IV and compared with previous calculations of Refs. 12, 17. In most of the cases the results of 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 previous section).

IV. CONCLUSION

We apply a recently developed advanced method of atomic structure calculation which combines three different all-order techniques to calculate energy levels of superheavy elements E113, 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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