Relativistic coupled cluster calculations of spectroscopic and chemical properties for element 120

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The coupled cluster calculations with accounting for relativistic effects to study spectroscopic and chemical properties of element 120 (E120) are performed. Similar calculations for Ba are also done and they are in a good agreement with the experimental data. Dissociation energies of diatomic X-H and X-Au molecules, where X=E120, Ba, are calculated; for E120 they are found to be 1.5 ± 2 times smaller than those for Ba.

INTRODUCTION

At present all the relatively long-lived superheavy elements (SHEs) up to the seventh period of the Periodic table were synthesized in FLNR JINR (see [1, 2] and references) and their synthesis was mainly confirmed in LBNL [3] and GSI [4]. The new challenge for nuclear references) and their synthesis was mainly confirmed in

GRECP generation and atomic calculations

The GRECP for E120 was generated in the framework of the present work. To check performance of the GRECP method for such a heavy element, relativistic correlation calculations on the E120 atom and its cations were carried out. We used four-component calculations with Dirac-Coulomb-Breit (DCB) Hamiltonian and Fermi nuclear charge distribution (A = 304) as the reference calculations. This Hamiltonian takes into account the great bulk of the relativistic effects including the relativistic corrections to the Coulomb interaction between electrons. The 1−5s, 2−5p, 3−5d, and 4−5f shells were frozen from the ground state E1202+ calculation. The 28 electrons (occupying the 6spd, 7spd, 8sp shells) were correlated in the [12,14,16,19,21] basis set of 6−17s1/2, 6−19p1/2, 6−19p3/2, ... 6−16h11/2 numerical spinors localized in the same radial space region as the 6spd, 7spd, 8sp spinors. The correlations were taken into account with the help of the FS-RCCSD method. The closed-shell ground state of E1202+ was the reference state and the Fock-space scheme was

\[ E120^{2+} \rightarrow E120^+ \rightarrow E120, \]

with electrons added to the 8s1/2, 8p1/2, 8p3/2, 7d3/2, and 7d5/2 spinors (the relativistic configurations corresponding to the nonrelativistic 8p2, 7d2, and 8p57d1 ones were excluded from the model space).

The leading configurations and terms for the lowest-lying states of the E120 atom and its cations are presented in the first and second columns of table [1]. The results of the semiempirically-fitted CI/MBPT calculations with Dirac-Coulomb Hamiltonian [5, 14] are compared with our FS-RCCSD results in the third and fourth columns. They are in a reasonable agreement. The absolute errors due to decrease in the number of the correlated electrons, the neglect of a finite nuclear size or Breit interactions are listed in the last four columns. One can see that a finite nuclear size should be taken into account, whereas the correlations with the 6spd electrons and Breit interactions can be neglected for the accuracy within 2 kcal/mol ≈ 700 cm−1 for one-electron excitations.

We have generated the GRECP for only 10 explicitly

CALCULATION METHOD

To calculate properties of E120, the generalized relativistic effective core potential (GRECP) method [9] was employed. For relativistic correlation calculations, the fully-relativistic Fock-space coupled cluster code with single and double cluster amplitudes (FS-RCCSD) [2, 10] was applied. To calculate corrections on enlargement of the basis set and higher cluster amplitudes, the Cfour [11] and MRCC [12, 13] codes were used.
treated electrons of E120 (i.e. with the 7spd, 8sp, 6f, 5g
GRECP components) following the scheme [15] just
to reduce unnecessary computational efforts at the
stage of correlation molecular calculations (see below);
similar GRECP version was generated earlier for Ba
[16]. The results for 10 correlated electrons (occupying
the 7spd, 8sp shells) in the [9,11,11,9,8,7] basis set
of 7−15s1/2, 7−17p1/2, 7−17p3/2, ... 6−12b1/2 numerical
spinors localized in the same radial space region as the
7spd, 8sp spinors are presented in Table I. Transition
energies from the DCB/FS-RCCSD calculations with Fermi
nuclear model and the absolute errors of their reproducing
in the GRECP calculations are tabulated in the third
and fourth columns.

Different approximations to the “full” GRECP calcula-
tions are considered in the last four columns. If one
neglects the difference between the outercore (7sp) and
valence (8sp) GRECP components, two extreme GRECP
versions can be derived with the conventional semi-local
RECP operator: only valence or only outercore GRECP
components acting on both the valence and outercore
electrons. These cases are referred to as the valence or
core GRECP versions, respectively [9]. One can see that
the full and valence GRECP versions are suitable for
the accuracy of 2 kcal/mol ≈ 700 cm⁻¹ whereas the core
GRECP version is not. It should be noted that the er-
rors of neglecting the innercore correlations with the 6sp
d shells and the errors of the GRECP approximation
are partly compensating each other, thus, it additionally jus-
tifies our choice of the 10-electron GRECP for the present
molecular calculations.

The scalar-relativistic (SR) calculations, i.e. without
spin-orbit (SO) part of the valence GRECP operator, are
presented in the seventh column. The SO contributions
are large and should be taken into account. The scalar-
relativistic SCF calculations followed by the FS-RCCSD
calculations with the SO part of the valence GRECP op-
erator are presented in the last column. These errors are
comparable with the errors of the valence GRECP cal-
culations in the fifth column. It should be emphasized
that the GRECP calculations in the 4–6-th columns were
carried out with the SO part at both the SCF and FS-
RCCSD stages. The computational versions used in the
last two columns (the SR SCF calculation followed by the
scalar-relativistic or fully-relativistic coupled cluster
study) are also used in the molecular correlation calcula-
tions discussed below.

### Table I: Transition energies (TE) from DCB/FS-RCCSD
calculations of the lowest-lying states of the E120 atom and its
cations for 28 correlated electrons with Fermi nuclear model
and Breit interactions taken into account. Absolute errors of
reproducing the TE in the different versions of the four-
component calculations. All values are in cm⁻¹.

| Leading conf. | Term | SCF TE | Ref. Point without nucl. | Breit Abs. errors |
|---------------|------|--------|--------------------------|------------------|
| 8s1/2         | (J=1/2) | 24551 | [5, 14] | 5372 1299 -51 |
| 7d1/2         | (J=3/2) | 25355 | -151 1714 135 |
| 7d1/2         | (J=5/2) | 27529 | -481 1661 152 |
| 8p1/2         | (J=3/2) | 38057 | -401 1632 62 |
| E120⁺⁺       | (J=0) | 89331 | -620 1592 77 |
| 8s1/2         | (J=0) | 16061 | 975 -45 |
| 8s1/2,8p1/2   | (J=0) | 18008 | 1015 30 |
| 8s1/2,7d1/2   | (J=1) | 23066 | 1242 101 |
| 8s1/2,7d1/2   | (J=2) | 23231 | 1212 101 |
| 8s1/2,7d5/2   | (J=3) | 23872 | 1186 108 |
| 8s1/2,7d5/2   | (J=2) | 25457 | 1186 42 |
| 8s1/2,7d5/2   | (J=1) | 27477 | 1347 100 |
| 8s1/2,7d5/2   | (J=0) | 27685 | 1024 39 |
| 8s1/2         | (J=1/2) | 47296 | 906 40 |

To compare with the E120 transition energies, the cor-
responding experimental data for Ba from Ref. [17] are
listed in Table II. One can see that the barium excitation
energies are smaller in general. It also indicates that
E120 will possibly be more inert in general than Ba.

### Table II: Transition energies (TE) from DCB/FS-RCCSD
calculations of the lowest-lying states of the E120 atom and its
cations for 10 correlated electrons with Fermi nuclear model
and Breit interaction are taken into account. Absolute errors of
reproducing the TE with different versions of the GRECP
 calculations. All values are in cm⁻¹.

| Leading conf. | Term | SCF TE | Ref. Val. SR-SCF | Val. SR-GRECP abs. errors |
|---------------|------|--------|------------------|--------------------------|
| 8s1/2         | (J=1/2) | 24142 | 247 306 2761 9255 393 |
| 7d1/2         | (J=3/2) | 25241 | 436 -1766 1316 358 |
| 7d1/2         | (J=5/2) | 27071 | 447 -1765 -514 447 |
| 8p3/2         | (J=3) | 37194 | 392 -1937 -3797 257 |
| E120⁺⁺       | (J=0) | 88907 | 554 -1701 -739 -417 |
| 8s1/2         | (J=0) | 15012 | 310 -2354 6060 -100 |
| 8s1/2,8p1/2   | (J=1) | 17064 | 295 -2341 4908 -171 |
| 8s1/2,7d1/2   | (J=1) | 22207 | 416 -1632 585 316 |
| 8s1/2,7d1/2   | (J=2) | 22259 | 428 -1629 533 483 |
| 8s1/2,7d3/2   | (J=3) | 22968 | 436 -1617 -176 484 |
| 8s1/2,8p1/2   | (J=2) | 25009 | 297 -1842 -3037 384 |
| 8s1/2,7d5/2   | (J=2) | 27271 | 394 -1813 -262 291 |
| 8s1/2,8p3/2   | (J=1) | 27834 | 351 -1820 -1171 563 |
| 8s1/2         | (J=1/2) | 47120 | 385 -1661 -687 381 |

Molecular calculations

In two-component molecular relativistic calculations and
high-level correlation treatment only relatively small
TABLE III: The experimental transition energies (TE) from Ref. [17] for the lowest-lying states of the Ba atom and its cations. All values are in cm⁻¹.

| Leading conf. | Term | TE        | Ref.  |
|--------------|------|-----------|-------|
| 6s_{1/2}   | (J=1/2) | → |       |
| 5d_{3/2}   | (J=3/2) | 4874 |       |
| 5d_{5/2}   | (J=5/2) | 5675 |       |
| 6p_{1/2}   | (J=1/2) | 20262 |     |
| 6p_{3/2}   | (J=3/2) | 21952 |     |
| Ba^{+}     | (J=0) | 80686 |       |
| 6s_{1/2}   | (J=0)   | → |       |
| 6s_{3/2}   | (J=1)   | 9034 |       |
| 6s_{1/2} + 6s_{1/2} | (J=2) | 9216 |       |
| 6s_{1/2} + 5d_{5/2} | (J=3) | 9597 |       |
| 6s_{1/2} + 5d_{5/2} | (J=2) | 11395 |      |
| 6s_{1/2} + 6p_{1/2} | (J=0) | 12266 |     |
| 6s_{1/2} + 6p_{1/2} | (J=1) | 12637 |     |
| 6s_{1/2} + 6p_{3/2} | (J=2) | 13515 |     |
| 6s_{1/2} + 6p_{3/2} | (J=1) | 18060 |     |

basis sets can be used for diatomics like E120Au. At the same time, rather large basis sets can be employed in scalar-relativistic calculations of diatomic molecules. Therefore, the following scheme for the basis set generation was used in this work: (i) For each atom (E120, Ba and Au), a large set of primitive Gaussian functions capable of describing wave-functions of the ground and excited states of the corresponding atoms was generated. These basis sets will be referred as LBAs below. LBAs(E120) and LBAs(Ba) consist of 15s, 15p, 8d, 8f, 6g, 6h-type functions, which slightly can be written as [15,15,8,8,6,6]. (ii) Then scalar relativistic CCSD calculation is performed with the large basis set for an atom and its compound (E120, E120-H, E120-Au, etc.). (iii) Generation of a compact basis set of contracted Gaussian functions was performed in a manner similar to that employed for generating atomic natural basis sets [13]: the atomic blocks from the density matrix calculated at stage (ii) were diagonalized to yield atomic natural-like basis set. The functions with the largest occupation numbers were selected from these natural basis functions. The results obtained with the given basis set approximately reproduce those with the large basis set. Besides, the functions required for accurately reproducing the essentially different radial parts of the 7p_{1/2} and 7p_{3/2} spinors, as well as the 8p_{1/2}, 8p_{3/2}, 7d_{5/2}, and 7d_{3/2} spinors, have also been included to the new bases. These compact basis sets will be referred as CBAs.

Finally, the following scheme to evaluate ionization potentials and dissociation energies of molecules was employed: (i) Calculation using two-component Fock-Space coupled cluster method with single and double amplitudes in the CBAs basis set. (ii) Calculation of corrections on enlargement of the basis set and contribution of triple cluster amplitudes by the scalar-relativistic coupled cluster method with single, double and non-iterative triple cluster amplitudes, CCSD(T), using LBAs. (iii) Calculation of corrections on higher (iterative triple and non-iterative quadruple) cluster amplitudes by the scalar-relativistic coupled cluster method with single, double, triple and non-iterative quadruple cluster amplitudes, CCSDT(Q), using CBAs.

Equilibrium internuclear distances in the considered diatomic molecules were calculated using the scalar-relativistic CCSD(T) method and LBAs.

RESULTS AND DISCUSSIONS

Ionization potentials

Some properties of E120, of which the first (IP1) and second (IP2) ionization potentials are examples, are considered here in comparison with the corresponding properties of Ba. As was described above, the two-component FS-RCCSD method was used to calculate the main contributions to IP1 and IP2. These calculations were performed in compact basis sets, CBAs, consisting of 5s, 6p, 4d, and 3f functions for E120 and of 5s, 5p, 3d, and 3f for Ba. The computed values for E120 are IP1 = 47236 cm⁻¹ and IP2 = 8061 cm⁻¹, while for Ba IP1 = 42340 cm⁻¹ and IP2 = 80326 cm⁻¹. Contributions from enlargement of the basis set up to 15s, 15p, 8d, 8f and 6h ([15,15,8,8,6,6]) functions and non-iterative triple cluster amplitudes for E120 are -462 cm⁻¹ for IP1 and 31 cm⁻¹ for IP2 [23]. For Ba these values are -579 cm⁻¹ and -65 cm⁻¹. Contributions of higher cluster amplitudes estimated using CCSDT(Q) method and [15,15,8,8,6] basis set (h functions were excluded) are negligible (less than 30 cm⁻¹). The final values of the ionization potentials for E120 and Ba are given in Table VII together with the corresponding experimental values for Ba.

The theoretical uncertainty of the ionization potentials of E120 can be estimated from the corresponding atomic calculations (tables II and III) and is suggested to be within 1 kcal/mol ≈ 350 cm⁻¹.

X-H dissociation energies, X=E120, Ba

In order to estimate the stability of compounds of E120 compared to those of Ba we have first considered the dissociation energies of the corresponding hydrides since the experimental data are available for BaH [19]. Another often considered characteristic of SHE is the dissociation energy of its fluorides, X-F. However, the X-F bonding is not so illustrative qualitatively because almost all the elements (except light noble gases) are known to react in
a fluorine atmosphere yielding rather stable fluorides. At the same time the dimer systems such as Ba$_2$, Hg$_2$, Xe$_2$, E112$_2$ are all the van der Waals systems with small dissociation energies.

By contrast, the ground state of the XeH molecule is not observed in the gas phase, whereas BaH was observed and characterized [20, 21].

To calculate E120H and BaH, the scheme similar to that for the calculation of the ionization potentials was used. Compact basis sets for E120, Ba and H were [5,6,4,2], [5,5,3,2] and [4,3,1], respectively. Large basis sets for E120 and Ba were [15,15,8,8,6], i.e. without h-functions. The aug-cc-pvqz [22] basis set was used as the large basis set for H. To exclude the basis set superposition errors, the diatomic molecules and atoms were calculated in the same two-center basis, i.e. the counterpoise corrections [23] were used.

The dissociation energy of E120H calculated within FS-RCCSD using the CBas(E120) and CBas(H) basis sets is 8258 cm$^{-1}$, while the correction on the large basis and triple cluster amplitudes is -261 cm$^{-1}$. For BaH the former contribution is 17061 cm$^{-1}$, while the correction gives -430 cm$^{-1}$.

The calculated spectroscopic properties of the BaH molecule are in a good agreement with the experimental data (see table IV).

| Calculation | Experiment |
|-------------|------------|
| $w_c$, cm$^{-1}$ | 1158 | 1168 [20] |
| $w_c x_c$, cm$^{-1}$ | 14.1 | 14.5 [20] |
| $D_0$, cm$^{-1}$ | 16053 | 15728 [19] |
| $R_e$, Å | 2.238 | 2.232 [20] |

The final values for the dissociation energies, $D_e$, of E120H and BaH are given in table V. The equilibrium internuclear distance in BaH is on 0.2 Å shorter than that in E120H.

The theoretical uncertainty of the dissociation energy of E120H is estimated to be 500 cm$^{-1}$.

It follows from table V that $d$ functions (and higher harmonics) significantly contribute to bonding of the monohydrides under consideration. At the CCSD(T) level of theory, this contribution is 5280 cm$^{-1}$ to the Ba-H bond, while is only 1601 cm$^{-1}$ in E120H. These values confirm the qualitative discussion above based on the atomic transitions. However, even without $d$ basis functions the BaH bond energy at the CCSD(T) level is twice stronger than that in E120H. This observation is in a qualitative agreement with the fact that the states with the valence $sp$ ($p$) configurations in E120 (E120$^+$) lies higher than the corresponding states in Ba (Ba$^+$). It should be noted that the bonding in E120H is in essence due to the correlation effects when the CBasNoD basis set is used.

### X-Au dissociation energies, X=E120, Ba

As the first stage of modelling interaction of E120 element with gold surface, the simplest comparative model, E120Au vs. BaAu, is considered here.

The 19-electron GRECP was used for Au. Thus, 29 electrons were treated in the correlation calculation. For E120Au, the relativistic two-component FS-RCCSD calculation in the Au[7,7,4,2] and E120[5,5,2,1] basis sets gives the dissociation energy of 11732 cm$^{-1}$. Correction on the larger basis set ([15,15,8,8,7] for Au and [15,15,8,4] for E120) is 510 cm$^{-1}$, contribution of non-iterative triple cluster amplitudes [25] is 2264 cm$^{-1}$ and correction on higher amplitudes (calculated as the difference between CCSDT(Q) and CCSD(T) energies in the compact Au[6,6,4,2,1] and E120[6,5,2,1] basis sets) is less than 100 cm$^{-1}$. Similar calculations were performed for BaAu. The final calculated values are given in table V.

The equilibrium distance for BaAu is on 0.1 Å shorter than that in E120Au.

The theoretical uncertainty of the dissociation energy of E120Au is estimated to be 1000 cm$^{-1}$.
TABLE VI: Calculated properties of E120 in comparison with Ba: the first and second ionization potentials (IP1 and IP2), dissociation energies ($D_e$) of hydrides and aurides (X-Au) and the corresponding equilibrium distances ($R_e$).

|            | E120-calc | Ba-calc | Ba-exp |
|------------|-----------|---------|--------|
| IP1, cm$^{-1}$ | 47046     | 41932   | 42035  |
| IP2, cm$^{-1}$ | 89286     | 80442   | 80686  |
| $D_e$(X-H), cm$^{-1}$ | 7997       | 16632   | 16308  |
| $R_e$(X-H), Å  | 2.45       | 2.24    | 2.23   |
| $D_e$(X-Au), cm$^{-1}$ | 14428      | 22608   | -      |
| $R_e$(X-Au), Å  | 3.1        | 3.0     | -      |

Conclusion

Properties of E120 and its compounds are considered in comparison with their Ba analogues. The monohydride and monoauride of E120 are found to be less stable than the corresponding analogues of the Ba compounds. Nevertheless, E120 can be rather considered as a “typical” representative of the second group.

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