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Ionization potentials and electron affinities of the superheavy elements 115–117 and their sixth-row homologues Bi, Po, and At

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Calculations of the first and second ionization potentials and electron affinities of superheavy elements 115–117 are presented. The calculations are performed in the framework of the Dirac-Coulomb Hamiltonian, and the results are corrected for the Breit and QED contributions. Correlation is treated by the relativistic coupled cluster approach with single, double, and perturbative triple excitations [CCSD(T)]. The same approach is used to calculate the ionization potentials and electron affinities of the lighter homologues, Bi, Po, and At. Comparison of the available experimental values for these atoms, namely, the first ionization potentials (IPs) of Bi, Po, and At and the second IP and EA of Bi, with our results shows excellent agreement, within a few hundredths of an eV, lending credence to our predictions for their superheavy homologues. High-accuracy predictions are also made for the second ionization potentials and electron affinities of Po and At, where no experiment is available.

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I. INTRODUCTION

Theoretical investigations of atomic properties of superheavy elements are important in assigning these atoms their place in the periodic table and in predicting their chemical and spectroscopic behavior [1]. The influence of relativistic effects on the electronic structure may be studied by comparing the calculated properties of the superheavy elements to those of their lighter homologues. In addition, high quality predictions of atomic properties can assist in future experimental research, such as spectroscopic measurements or gas-phase chromatography experiments [as ionization potentials (IPs) can be linked to adsorption properties on various surfaces [2]].

IPs and electron affinities (EAs) are among the most basic and most important atomic properties. They reflect the electronic structure of the elements, and provide insight into their chemical behavior and reactivity. A successful measurement of the first ionization potential of astatine, using laser ionization spectroscopy, has been reported recently [3]. This measurement filled the last gap in the list of experimental IPs of the naturally occurring elements. Less is known about the second IPs and EAs, which are more difficult to measure, and experimental data are still lacking for many heavy elements.

The spectroscopic measurement in Ref. [3] was accompanied by a theoretical calculation of the astatine IP. We performed this calculation using the relativistic coupled cluster approach with single, double, and perturbative triple excitations [CCSD(T)]. The calculated IP was 9.307(25) eV, in remarkable agreement with the newly measured experimental value of 9.31751(8) eV. The successful performance of the relativistic CCSD(T) approach prompted the current study, where the same method is applied to the calculation of EAs and the first two IPs of the $6p$ elements, Bi, Po, and At. While experimental first IPs of these atoms are known [3,4], the second IP and the EA were only measured for Bi [4,5]. Thus, we provide consistent high-accuracy predictions of these properties for Po and At. Another major goal of these calculations is the assessment of their quality; good agreement with experiment where available will allow making reliable predictions of the IPs and EAs of the $7p$ elements 115, 116 (Lv), and 117, also obtained in the present work.

Calculations of the properties studied here have been attempted in the past, employing a variety of methods. The multiconfigurational Dirac Fock (MCDF) approach has been applied to the IPs and EAs of most of the atoms studied here [6–8], as was the four-component relativistic density functional theory (4c-DFT) [9–11]. Relativistic multireference configuration interaction (4c-MRCI) calculations were performed for the three superheavy elements [12]. Other methods used include the combination of relativistic effective core potentials (RECPs) with the correlation consistent composite approach (ccCA) [13], relativistic many body perturbation theory (4c-MBPT) [14], the combination of the Douglas-Kroll Hamiltonian with complete active space perturbation theory (DK+CASPT2) [15], and relativistic Hartree-Fock-Slater (HFS) calculations [16]. The relativistic multireference Fock space coupled cluster (4c-FSCC) approach was applied to the properties of Bi and element 115 and to the EA of element 117 [17–19], and a combination of RECPs and the CCSD(T) method was used to calculate the electron affinities of Po and At [20].

The next section gives a brief description of the methods used. The calculated IPs and EAs of the elements are given and compared with experiment (when available) and with previous calculations in Sec. III.

II. METHOD AND COMPUTATIONAL DETAILS

The calculations were carried out using the DIRAC13 computational program package [21], in the framework of the relativistic Dirac-Coulomb Hamiltonian,

$$H_{DC} = \sum_i h_D(i) + \sum_{i<j} (1/r_{ij}). \tag{1}$$

Here, h_D is the one-electron Dirac Hamiltonian,

$$h_D(i) = c\boldsymbol{\alpha}_i \cdot \mathbf{p}_i + c^2\beta_i + V_{\text{nuc}}(i), \tag{2}$$

where $\boldsymbol{\alpha}$ and β are the four-dimensional Dirac matrices. The nuclear potential V_{nuc} takes into account the finite size of the nucleus, modeled by a Gaussian charge distribution. The root mean square radii used for the nuclei are listed in Ref. [22].

Electron correlation was included by the relativistic CCSD(T) approach. The Faegri dual family basis sets of uncontracted Gaussian-type orbitals [23] were used. The basis sets were augmented by high angular momentum and diffuse functions until convergence of the calculated IPs and EAs was achieved. The final basis sets consist of $27s25p19d14f6g3h1i$ functions for Bi, Po, and At, and $30s26p19d14f8g4h2i$ functions for elements 115–117. Virtual orbitals with energies above 50 a.u. were omitted; 34 and 66 electrons were left in the core for the $6p$ and $7p$ elements, respectively. The number of correlated electrons in the neutral species is thus 49–51.

Due to the noninstantaneous interaction between particles limited by the speed of light in the relativistic framework, a correction to the two-electron part of H_{DC} (1) is added (in Coulomb gauge), in the form of the zero-frequency Breit interaction:

$$B_{ij} = -\frac{1}{2r_{ij}}\left[\boldsymbol{\alpha}_i \cdot \boldsymbol{\alpha}_j + (\boldsymbol{\alpha}_i \cdot \mathbf{r}_{ij})(\boldsymbol{\alpha}_j \cdot \mathbf{r}_{ij})/r_{ij}^2\right]. \tag{3}$$

To further enhance precision, we also include the lowest order QED corrections, namely, the vacuum polarization, electron self-energy, and the frequency dependent contribution to the Breit term (3). The Breit and QED contributions were computed perturbatively in the framework of the MCDF wave function, using the recent implementation of the self-energy contribution [24,25] in GRASP (general-purpose relativistic atomic structure program) package [26,27]. In the course of GRASP calculations the MCDF wave function was computed numerically using an extensive radial grid with the initial radius $RNT = 10^{-8}$ a.u. and the exponent $H = 0.008$ (producing over 5000 grid points), while a wave-function convergence threshold was set to 10^{-9}. The calculated Breit and QED contributions were then added to the DIRAC13 CCSD(T) results.

III. RESULTS AND DISCUSSION

Table I lists the calculated first IPs. In addition to the CCSD(T) results, CCSD values are given, to show the contribution of the triple excitations, which raise the IPs slightly, by 24–97 meV. This contribution increases from group 15 to group 17, probably due to the larger number of p triples, and is larger for $7p$ compared to $6p$ elements, as the $7p_{3/2}$ orbital is more diffuse, and thus its electrons are more available for excitations than the $6p_{3/2}$ ones. The contribution of the Breit term is very small, up to 4 meV. QED contributions are also small and fairly constant, between 6 and 7 meV. The CCSD(T) results, corrected for Breit interaction and QED effects, are taken as the final recommended values. Table I also lists the available experimental IPs and the results of earlier theoretical studies.

TABLE I. Calculated first IPs (eV), compared to experiment and to earlier calculations.

Bi	Po	At	Method	Ref.
7.242	8.381	9.230	4c + CCSD	Present
7.266	8.427	9.308	4c + CCSD(T)	Present
7.266	8.426	9.307[a]	4c + CCSD(T) + Breit	Present
7.272	8.432	9.313	4c + CCSD(T) + Breit + QED	Present
7.183			4c-FSCC + Breit	[17]
7.284			4c-MSIH[b] + Breit	[18]
7.467	8.473	10.004	RECP-ccCA	[13]
7.259	8.242	8.965	4c-MBPT	[14]
7.370	8.290	9.130	DK + CASPT2 + SO[c]	[15]
		9.35	MCDF + empirical[d]	[7]
6.84			4c-DFT	[9]
		9.24	DK6[e] + DFT	[10]
7.286	8.414	9.318[a]	Expt.	[4]
115	Lv	117	Method	Ref.
5.496	6.775	7.548	4c + CCSD	Present
5.563	6.845	7.645	4c + CCSD(T)	Present
5.567	6.848	7.647	4c + CCSD(T) + Breit	Present
5.574	6.855	7.654	4c + CCSD(T) + Breit + QED	Present
5.583			4c-FSCC + Breit	[17]
5.342	6.629	7.380	4c + MRCI[f]	[12]
5.9	6.8	8.2	HFS[g]	[16]
4.65	5.96	6.51	MCDF	[6]
		7.64	MCDF + empirical[d]	[7]
5.33		7.601	4c-DFT	[9,11]
		7.57	DK6[e] + DFT	[10]

[a] Reference [3].

[b] Mixed sector intermediate Hamiltonian variant of the FSCC approach.

[c] DK Hamiltonian combined with CASPT2 and corrected for spin-orbit (SO) effects. For details, see Ref. [15].

[d] MCDF results corrected through a semiempirical extrapolation procedure. For details, see Ref. [7].

[e] Sixth-order Douglas-Kroll Hamiltonian.

[f] The results were extrapolated to the basis set limit.

[g] Hartree-Fock-Slater calculations combined with extrapolations in the groups. For details see Ref. [16].

Our calculated first IPs of Bi, Po, and At are in excellent agreement with experiment, with errors of 0.005–0.020 eV. The increase of triple excitation contributions in the series Bi, Po, At is not accompanied by a corresponding increase of errors in the calculated IPs. Similar accuracy, of a few hundreths of an eV, may be expected for the superheavy homologues.

The early exploratory MCDF values [6], based on minimal sets of configuration state functions due to the computer power limitations at the time, are lower by 1 eV or more than the current results. The relativistic MRCI IPs [12] are closer to our values, but still lower by ∼0.2 eV, due to a less extensive treatment of correlation. The best agreement for Bi and element 115 is obtained with the 4c-FSCC results of Eliav *et al.* [17]; the method used there is rather similar to the present scheme, but the basis sets were smaller. The results of Chang *et al.* [7]

TABLE II. Calculated second IPs (eV), compared to experiment and to earlier calculations.

Bi	Po	At	Method	Ref.
16.581	16.148	17.710	4c + CCSD	Present
16.672	16.179	17.749	4c + CCSD(T)	Present
16.642	16.173	17.740	4c + CCSD(T) + Breit	Present
16.653	16.186	17.753	4c + CCSD(T) + Breit + QED	Present
16.655			4c-FSCC + Breit	[17]
		17.88	MCDF + empirical[a]	[7]
16.25			4c-DFT	[9]
16.703			Expt.	[4]

115	Lv	117	Method	Ref.
18.397	13.467	15.093	4c + CCSD	Present
18.431	13.534	15.161	4c + CCSD(T)	Present
18.360	13.534	15.158	4c + CCSD(T) + Breit	Present
18.360	13.550	15.174	4c + CCSD(T) + Breit + QED	Present
18.168			4c-FSCC + Breit	[17]
18.190	13.262	14.896	MRCI[b]	[12]
17.84	12.56	14.17	MCDF	[6]
		15.33	MCDF + empirical[a]	[7]
17.94		15.247	4c-DFT	[9,11]

[a] MCDF results corrected through a semiempirical extrapolation procedure. For details, see Ref. [7].

[b] The results were extrapolated to the basis set limit.

for At and element 117 include empirical corrections obtained by fitting calculated values for the lighter homologues Cl–I to experiment, and are close to the *ab initio* values presented here. The 4c-DFT predictions [9–11] show good agreement with our values for element 117, but differ by 0.1–0.4 eV for other elements.

Table II shows the second IPs of the atoms under study. The experimental IP2 is available for Bi only, and our calculated result is 0.05 eV lower. The triple excitation contributions to the second IPs are small, as in the case of the first IPs. It is largest for Bi (0.09 eV), and smaller in Po and At (0.03–0.04 eV). The second IPs of the superheavy atoms show an opposite trend, with low triple contribution in element 115 (0.03 eV) and a larger effect in Lv and element 117 (0.07 eV).

The Breit contribution decreases the calculated second IP by 0.03 eV for Bi and by 0.07 eV for element 115. The effect on the other atoms is small, below 0.01 eV. The second IPs in Bi and E115 involve the removal of an $np_{1/2}$ electron, which penetrates closer to the nucleus than $np_{3/2}$ and experiences stronger relativistic effect, hence the larger Breit contribution. The QED contributions are in the range of 0.01–0.02 eV for all atoms except E115, where they are negligible.

The very good agreement of the calculated second IP of Bi with experiment indicates that the values obtained for the other atoms, for which no measurements are available, are of high quality. Comparing with previous calculations, we see good agreement with the Bi value in Ref. [17]; the prediction there for element 115 is not as good, 0.2 eV off the present calculation, which we ascribe to the smaller basis used there. The MRCI results [12] for the second IPs of elements 115–117 are lower by 0.2–0.3 eV than ours. The MCDF values [6] are again lower by 0.5–1 eV than present results. The empirically corrected MCDF results of Ref. [7] for At and element 117 are in good agreement with present numbers, higher by just 0.17 eV. Finally, 4c-DFT performed well for element 117 [11], but differed by 0.4 eV from present results for element 115 [9].

TABLE III. Calculated electron affinities (eV), compared to experiment and to earlier calculations.

Bi	Po	At	Method	Ref.
0.883	1.362	2.314	4c + CCSD	Present
0.953	1.461	2.404	4c + CCSD(T)	Present
0.957	1.464	2.407	4c + CCSD(T) + Breit	Present
0.961	1.469	2.412	4c + CCSD(T) + Breit + QED	Present
	1.9(3)	2.8(2)	SE[a]	[28]
	1.911	3.115	RECP + CCSD(T)	[20]
1.034			4c-FSCC + Breit	[17]
0.720	1.930	3.183	RECP-ccCA	[13]
0.731	1.225	2.110	4c-MBPT	[14]
0.75	1.25	2.22	DK + CASPT2 + SO[b]	[15]
		2.38	MCDF + empirical[c]	[7]
	1.405	2.416	MCDF	[8]
1.09			4c-DFT	[9]
		2.30	DK6[d] + DFT	[10]
0.942			Expt.	[5]

115	Lv	117	Method	Ref.
0.249	0.657	1.474	4c + CCSD	Present
0.308	0.769	1.594	4c + CCSD(T)	Present
0.311	0.773	1.598	4c + CCSD(T) + Breit	Present
0.313	0.776	1.602	4c + CCSD(T) + Breit + QED	Present
0.232	0.620	1.403	MRCI[e]	[12]
0.378		1.369	FSCC + Breit	[17,19]
		1.45	MCDF + empirical[c]	[7]
0.47		1.595	4c-DFT	[9,11]
		1.47	DK6[d] + DFT	[10]

[a] Semiempirical results.

[b] DK Hamiltonian combined with CASPT2 and corrected for spin-orbit (SO) effects. For details, see Ref. [15].

[c] MCDF results corrected through a semiempirical extrapolation procedure. For details, see Ref. [7].

[d] Sixth-order Douglas-Kroll Hamiltonian.

[e] The results were extrapolated to the basis set limit.

Table III shows the calculated electron affinities. The contribution of the triple excitations to the calculated EAs

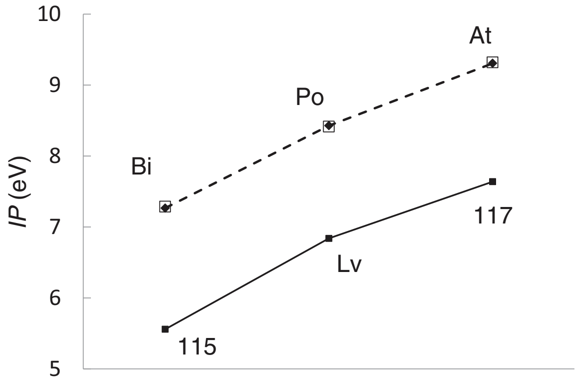

FIG. 1. First IPs of Bi to At [CCSD(T) values: solid rhomboids, dashed line; experimental values: empty squares) and of element 115 to 117 [CCSD(T) values: solid squares, solid line].

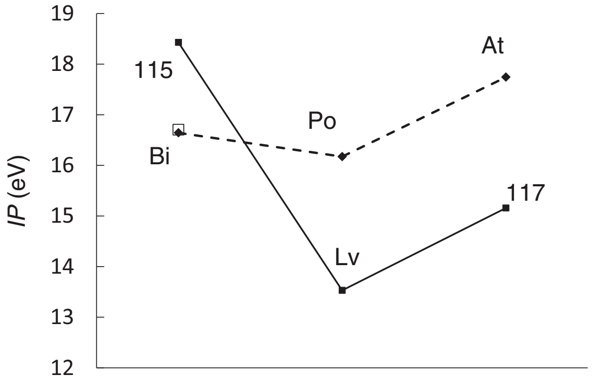

FIG. 2. Second IPs of Bi to At [CCSD(T) values: solid rhomboids, dashed line; experimental value: empty square) and of element 115 to 117 [CCSD(T) values: solid squares, solid line].

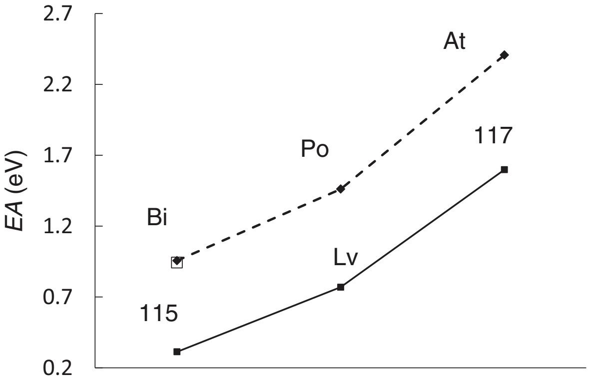

FIG. 3. EAs of Bi to At [CCSD(T) values: solid rhomboids, dashed line; experimental value: empty square] and of element 115 to 117 [CCSD(T) values: solid squares, solid line].

is close in magnitude to that in the IPs, but is more significant in relative terms, in particular for elements 115 and Lv, where it provides 15%–20% of the total EA. The Breit and QED contributions are below 0.005 eV in all cases.

The only EA available experimentally is that of Bi, which is reproduced to 0.02 eV by our CCSD(T) result. Assuming similar quality for Po and At, the commonly quoted semiempirical values for Po [1.9(3) eV] and At]2.8(2) eV] [28] seem overestimated by about 0.5 eV. The RECP + CCSD(T) values of Ref. [20] for Po and At are also too high. The error is probably due to correlating only the outer-shell *ns* and *np* electrons. Note that the "experimental" EAs of Po and At quoted in [20] from the compilation of Hotop and Lineberger [29] are, in fact, the 1969 semiempirical estimates of Zollweg [28]. The MBPT [14] and the CASPT2 [15] results for the $6p$ elements are lower than the present values by 0.2–0.3 eV. The MCDF results with empirical corrections [7] are close to the CCSD(T) values for At and 117; the recent MCDF study of Li *et al.* [8] is of better quality, with results close to ours for Po and At without using corrections. The FSCC results for Bi and element 115 [17] are close to the present values; larger disagreement is seen for element 117 [19], due to the limited basis set used. The MRCI EAs [12] again appear too low, and the performance of DFT for Bi [9], At [10], element 115 [9], and element 117 [10,11] looks satisfactory.

Figures 1 and 2 show the first and second IPs, respectively, and the EAs appear in Fig. 3. In general, these properties increase from left to right and from bottom to top of the Periodic Table. The properties calculated here follow this behavior, with the exception of the second IPs of Bi and element 115, which are larger than those of Po and Lv, respectively. The second ionization of Bi and 115 involves removing an $np_{1/2}$ electron, whereas the other elements lose an $np_{3/2}$ electron. The $np_{1/2}$ electron is bound more strongly because of relativistic stabilization, leading to higher IPs. The effect is stronger in the superheavy element 115, which shows the highest IP2 of the elements discussed here, 5 eV above that of Lv and 1.7 eV above Bi.

IV. SUMMARY AND CONCLUSION

We have calculated the first two IPs and the EAs of the superheavy elements 115, Lv, and 117, as well as their lighter homologues, Bi, Po, and At. The calculations were performed within the framework of the Dirac-Coulomb Hamiltonian, combined with the CCSD(T) approach for treatment of correlation. The Breit and QED corrections to the IPs and EAs were calculated at the MCDF level, and added to the CCSD(T) results.

The reported calculations present unprecedented levels of accuracy. The mean absolute error of our calculated first IPs of Bi, Po, and At is 12 meV, compared with 309 [13], 184 [14], and 132 [15] meV in other works that treated the three atoms. The calculated EA of Bi, the only EA known experimentally, has an error of 19 meV; except for our earlier work [17], the smallest error of calculations is 0.15 eV [9]. No previous method showed consistent accuracy at the level reported here. Similar accuracy may be expected for the properties which have yet to be measured.

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