PHYSICAL REVIEW A **110**, 022817 (2024)

Relativistic coupled-cluster calculations of the electron affinity and ionization potentials of lawrencium

Yangyang Guo,[1,2,*] Lukáš F. Pašteka,[2,3] Yuichiro Nagame,[4] Tetsuya K. Sato,[4] Ephraim Eliav,[5] Marten L. Reitsma,[2] and Anastasia Borschevsky[2,†]

[1]*Institute of Quantum Materials and Physics, Henan Academy of Sciences, Zhengzhou 450046, China*
[2]*Van Swinderen Institute for Particle Physics and Gravity, University of Groningen, Nijenborgh 4, 9747 Groningen, The Netherlands*
[3]*Department of Physical and Theoretical Chemistry & Laboratory for Advanced Materials, Faculty of Natural Sciences, Comenius University, Mlynská dolina, Bratislava 84215, Slovakia*
[4]*Advanced Science Research Center, Japan Atomic Energy Agency (JAEA), Tokai, Ibaraki 319-1195, Japan*
[5]*School of Chemistry, Tel Aviv University, Tel Aviv 6997801, Israel*

(Received 30 May 2024; accepted 12 August 2024; published 27 August 2024)

The calculations of the first and the second ionization potentials of lawrencium and lutetium and the electron affinity of lawrencium are performed within the relativistic coupled-cluster framework. These results are corrected by including the contributions of extrapolation to the complete basis set limit and higher-order contributions due to relativity and electron correlation. The excellent agreement between our predictions of the ionization potentials of Lu and Lr and experimental values supports the accuracy of our predictions of the second ionization potential and the electron affinity of Lr.

DOI: 10.1103/PhysRevA.110.022817

I. INTRODUCTION

The discovery of superheavy element oganesson ($Z = 118$) completes the seventh row of the Periodic Table [1–3]. At the same time, atomic spectroscopy of the heaviest elements is notoriously challenging and our experimental knowledge of electronic structure presently terminates at the later actinides.

Actinides were investigated via a variety of experimental approaches, such as laser spectroscopy, ion chemistry, and surface ionization techniques; see Refs. [4–8]. Such studies allow the exploration of the fascinating behavior of these heavy species, where the relativistic effects play a major role [9].

At the very end of the actinide series, lawrencium ($Z = 103$) was synthesized for the first time in 1961 by bombardment of californium with boron ions [10]. Due to the strong relativistic effects that stabilize the outermost $7p_{1/2}$ orbital, the electronic configuration of the ground state of Lr is predicted to be $[\mathrm{Rn}]5f^{14}7s^27p_{1/2}$ [11–16], in contrast to its lighter homologue Lu, $[\mathrm{Xe}]4f^{14}6s^25d$. The ionization potential (IP_1) of Lr was first measured on an atom-at-a-time scale using the surface ionization technique by Sato *et al.* [6,7]. These measurements were accompanied by the state-of-the-art relativistic calculations. Recently the lower limit on the second ionization potential (IP_2) of Lr was established in a gas-phase ion chemistry experiment [17]. Electron affinity (EA) is another fundamental electronic property that determines chemical behavior and reactivity. So far, the electron affinity of Lr has not been measured, but the development of novel, specially designed experimental techniques brings this goal closer to our reach.

Recently, the EA of the radioactive astatine (At, atomic number $Z = 85$) isotope, ^{211}At (half-life, $T_{1/2} = 7.2$ h) produced in a spallation reaction of thorium (Th) with 1.4 GeV protons at the CERN-ISOLDE radioactive ion beam facility was successfully measured by laser photodetachment threshold spectroscopy [18]. In this innovative experiment, 3.75×10^6 particles per second of $^{211}\mathrm{At}^-$ ions were produced. The ^{211}At isotope was mass separated by ISOL (Isotope Separator On-Line) and guided into the GANDALPH (Gothenburg ANion Detector for Affinity measurements by Laser PHotodetachment) apparatus which is designed for measurements of the EAs of radioactive elements [19]. The EA of astatine was determined to be 2.41578(7) eV, in excellent agreement with the accompanying state-of-the-art relativistic coupled-cluster calculations that predicted an EA of 2.414(16) eV.

However, measurement of EA of still heavier elements, especially those heavier than fermium (Fm, $Z = 100$), is an extremely challenging task since these elements must be produced using accelerator-based heavy-ion-induced nuclear reactions [20,21]. Production rates of these elements, thus, are minuscule and the half-lives of the produced isotopes are very short; they are usually available only in very small quantities that require one-atom-at-a-time scale experiments and measurements in the approximate half-life range of the isotopes under investigation [4,22,23].

The isotopes ^{256}Lr ($T_{1/2} = 27$ s) and ^{255}Lr ($T_{1/2} = 31$ s) with sufficiently long half-lives, produced at rates of a few atoms per second, will be possible candidates for the EA measurements of Lr. ^{256}Lr produced in the bombardment of a ^{249}Cf target with ^{11}B beams was exploited for the measurement of the first ionization potential of Lr. In the experiment,

---

[*] Contact author: lisaguo1208@gmail.com

[†] Contact author: a.borschevsky@rug.nl

the Lr atoms were extracted as Lr^+ ions using ISOL at JAEA (Japan Atomic Energy Agency) [6]. ^{255,256}Lr synthesized in the reactions of ^{48}Ca ions with a ^{209}Bi target were employed in the direct mass measurements of these nuclides using the Penning trap mass spectrometer SHIPTRAP at GSI (GSI Helmholzzentrum für Schwerionenforshung) [24].

For the measurement of the electron affinity of Lr, effective production of negative Lr^- ions is indispensable. This can be achieved using strong electron donors, such as cesium, with low IP_1. A Cs-sputter negative ion source was applied in the past to produce negative ions of lutetium (Lu^-), lanthanide homologue of Lr [25]. Similarly, the production of Lr^- ions could be achieved via the charge exchange reaction $\mathrm{Lr}^+ \rightarrow \mathrm{Lr}^-$ by passing the Lr^+ ion beams through Cs vapor. While the measurement of EA is rendered challenging by the difficulty in obtaining Lr atoms on the scale of more than one atom at a time, an efficient detection system of radioactive α decays of Lr isotopes event by event could provide a significant advantage for such measurements [26]. Efficient production of negative ions, coupled to laser photodetachment spectrometry and α-decay spectrometry, could thus open up the possibility of measuring electron affinities of heavy elements, including Lr. Another component crucial for the success of these challenging experiments on short-lived and rare species are accurate and reliable theoretical predictions of the EA of Lr.

The present work aims to provide benchmark values of the first and second IPs and EAs of Lr, using the state-of-the-art relativistic coupled-cluster approach. An extensive computational study is used to estimate the uncertainties of our predictions, following the scheme developed in our earlier works [18,27,28]. Alongside the calculations for Lr, we also carried out equivalent investigations of the first and second IPs of its lighter homologue, Lu. The accuracy of our predictions for the EA and the IP_2 of Lr is confirmed by comparison of both IPs of Lu and the IP_1 of Lr to the experimental values [6,29–31].

Several earlier accurate calculations of atomic properties of Lr are available, based on different approaches. Transition energies and ionization potentials were calculated using the Fock-space coupled-cluster (FSCC) method [13,15,32], the configuration-interaction approach combined with many-body perturbation theory (CI + MBPT) [16], and the combination of the configuration-interaction method and all-order single-double coupled-cluster technique (CI+ all-order); in the latter work also static dipole polarizabilities were presented [12]. The only EA prediction so far was carried out within the FSCC method [13,15]. A higher accuracy prediction of this property, along with reliable error bars, is important for providing solid support for future experiments.

II. METHOD AND COMPUTATIONAL DETAILS

The overall computational methodology and the scheme for the evaluation of the uncertainties is similar to that used in our recent works (see Refs. [18,27,28]). The calculations were carried out in the framework of the relativistic single-reference coupled-cluster approach with single, double, and perturbative triple excitations [DC-CCSD(T)]. The Dirac-Coulomb (DC) Hamiltonian is (in atomic units)

$$H_{\mathrm{DC}} = \sum_i h_{\mathrm{D}}(i) + \sum_{i<j} (1/r_{ij}), \tag{1}$$

where h_{D} is the relativistic one-electron Dirac Hamiltonian,

$$h_{\mathrm{D}}(i) = c\boldsymbol{\alpha}_i \cdot \mathbf{p}_i + c^2\beta_i + V^n(i), \tag{2}$$

and α and β are the four-dimensional Dirac matrices. The nuclear potential $V^n(i)$ is modeled by a Gaussian charge distribution [33].

The DC-CCSD(T) calculations were carried out using the DIRAC19 computational program package [34]. In the coupled-cluster calculations, all electrons were correlated and virtual orbitals with energies above 70 a.u. were omitted. We have carried out test calculations with a higher active-space cutoff and used the results in the error estimate (see below).

All calculations were performed using Dyall's relativistic basis sets [35–37], consisting of uncontracted Gaussian functions, namely the valence (v*N*z), the core-valence (cv*N*z), and the all-electron (ae*N*z) basis sets, with N the basis set cardinality, $N = 2, 3, 4$. We found in our previous studies that diffuse functions of different angular momenta have a significant effect on the calculated atomic properties, especially on the electron affinity [27]. Thus the basis sets were augmented with diffuse functions until convergence of the calculated IPs and EA was achieved. These augmented basis sets are designated (x-aug)-cv*N*z, where the prefix x stands for the number of layers of diffuse functions added to the basis set.

We performed extrapolations to the complete basis set (CBS) limit, using the scheme of Feller *et al.* [38] for the DHF values (three-point extrapolation using 2z, 3z, and 4z results) and the scheme of Helgaker [39] for the correlation contribution (two-point extrapolation using the 3z and the 4z results).

In the DC Hamiltonian, the electronic repulsion is taken in its nonrelativistic form. Due to the noninstantaneous interaction between particles being limited by the speed of light in the relativistic framework, a correction to the two-electron part of H_{DC} is added (in Coulomb gauge), in the form of the zero-frequency Breit interaction:

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

To account for the QED corrections, and thus further improve the accuracy of our results, we applied the model Lamb shift operator (MLSO) of Shabaev and co-workers [40] to the atomic no-virtual-pair many-body Dirac-Coulomb-Breit (DCB) Hamiltonian as implemented into the QEDMOD program. This model Hamiltonian uses the Uehling potential and an approximate Wichmann-Kroll term for the vacuum polarization (VP) potential [41] and local and nonlocal operators for the self-energy (SE), the cross terms (SEVP), and the higher-order QED terms [42]. The implementation of the MLSO formalism in the Tel Aviv atomic computational package [43] allows us to obtain the VP and SE contributions beyond the usual mean-field level, namely at the FSCC level. The FSCC methodology within the same code was also used to calculate the Breit interaction. These contributions were then added to the DIRAC19 CCSD(T) IPs and EAs and the

TABLE I. IP_1, IP_2 and EA (eV) of Lr and IP_1 and IP_2 of Lu on the DC-CCSD(T) level of theory using different quality of basis sets.

	Lu		Lr		
Basis set	IP_1	IP_2	IP_1	IP_2	EA
v4z	5.305	13.962	4.943	14.502	0.424
cv4z	5.332	13.988	4.947	14.536	0.421
ae4z	5.332	13.988	4.947	14.542	0.420
(1-aug)-cv4z	5.333	13.988	4.947	14.536	0.428
(3-aug)-cv2z	5.259	13.945	4.908	14.475	0.389
(3-aug)-cv3z	5.308	13.979	4.924	14.481	0.408
(3-aug)-cv4z	5.336	13.988	4.947	14.534	0.426
(3-aug)-CBS-cv$N$z	5.356	13.995	4.963	14.573	0.439

resulting values are designated DCB-CCSD(T) and DCB-CCSD(T) + QED.

We improved the accuracy of our calculations further by going beyond the standard CCSD(T) approach and considering higher-order excitations. The full triple contributions ΔT were calculated with the EXP-T program [44]. Dyall's (2-aug)-v3z basis sets were used for the calculation of ΔT. For Lr the valence $7s$ and $7p$ and core $5d$, $5f$, $6s$, and $6p$ electrons were correlated, while the virtual space comprised of 99 orbitals (up to 70 a.u.). For Lu the valence $6s$ and $5d$ and core 4-5s, 4-5p, and $4f$ electrons were correlated, while the virtual space comprised of 94 orbitals (up to 70 a.u.). We have found in our earlier investigations that higher-order excitations are generally localized in the valence-shell region [45], justifying our use of a limited active space. The differences between the full triples and the perturbative triples [$\Delta T = T - (T)$] were added to the DCB-CCSD(T) + QED results (extrapolated to the CBS limit) to obtain the final recommended values, DCB-CCSDT + QED.

III. RESULTS AND DISCUSSION

The calculated IP_1, IP_2, and EA of Lr and IP_1 and IP_2 of Lu are presented in Table I for different basis sets; these calculations were carried out on the DC-CCSD(T) level of theory. The first three lines explore the effect of the core-correlating functions, using the 4z quality basis sets. Since, in our calculations, all the electrons are correlated, such functions have a significant effect on the quality of the results. The difference between cv4z and v4z ionization potentials is especially notable; for EAs the effect is less significant. Switching to the all-electron (ae4z) basis set yields negligible changes in the calculated properties, with the exception of IP_2 of Lr, where it increases the calculated value by 6 meV, representing a mere 0.04% difference. Thus we proceed with further calculations using the cv4z basis sets and accounting for this difference in the estimated uncertainty.

The ionization potentials of both Lr and Lu are not sensitive to the addition of diffuse functions, while for the EA of Lr we observe an increase of 2% upon the addition of the first augmentation layer [(1-aug)-cv4z]. This is expected; the electron affinity represents the energy associated with a loosely bound extra electron, rendering the quality of the description of the outer part of the wave function important. Adding two further augmentation layers has a small effect of 2 meV on the obtained electron affinity [(3-aug)-cv4z]. We thus use the (3-aug)-cv$N$z basis set family for the extrapolation of the results to the complete-basis-set limit [(3-aug)-CBS-cv$N$z].

TABLE II. IP_1, IP_2 and EA (eV) of Lr and IP_1 and IP_2 of Lu with higher-order corrections contributions (eV).

	Lu		Lr		
Basis set	IP_1	IP_2	IP_1	IP_2	EA
CCSD	5.260	13.831	4.903	14.394	0.329
CCSD(T)	5.356	13.995	4.963	14.573	0.439
CCSDT	5.370	13.995	4.961	14.574	0.448
CCSDT+Breit	5.376	13.987	4.949	14.558	0.447
CCSDT+Breit+QED	5.387	14.023	4.954	14.618	0.446

Table II summarizes the results including higher-order correction contributions. Among them, the perturbative triple contributions are between 60 and 170 meV, making it the largest term. In particular, in the case of the electron affinity of Lr, perturbative triples comprise about a quarter of the total value. Transitioning from perturbative to full triple excitations increases the IP_1 of Lu by 15 meV and the EA of of Lr by 9 meV, respectively, while the changes for the other properties remain within 2 meV. The Breit correction increases the IP_1 of Lu by 6 meV while decreasing the IP_2 of Lu and the IPs of Lr by 8 to 16 meV. QED corrections notably boost the IPs of both Lu and Lr, particularly elevating the IP_2 of Lr by 60 meV. Both Breit and QED corrections have a negligible effect on the EA of Lr. The significant QED contribution to the IPs, compared with the size of the Breit effect, should stimulate further investigation into the QED effects in heavy elements [46].

Several sources of uncertainty arise from the approximation inherent to the computational approach and from the computational limitations; these are the incompleteness of the basis set, the neglect of electron correlation beyond triple excitation, the restriction of the correlation space, and the neglect of higher-order QED corrections.

The uncertainty stemming from the basis set arises from three main factors: the extrapolation to a complete basis set using a semiempirical scheme, the limited augmentation of the basis set, and the absence of inner layer electron description in the core-valence basis set. The presented calculations of the last line in Table I are performed with the Helgaker scheme; here we compare the Helgaker, Lesiuk, and Martin schemes

TABLE III. First and second IPs and EA of Lr and IP_1, IP_2 of Lu obtained using different extrapolation schemes together with the resulting 95% confidence interval, in eV.

	Lu		Lr		
Scheme	IP_1	IP_2	IP_1	IP_2	EA
Helgaker	5.356	13.995	4.963	14.573	0.439
Lesiuk	5.361	13.997	4.967	14.583	0.443
Martin	5.351	13.993	4.960	14.565	0.437
95% c.i.	0.009	0.004	0.007	0.017	0.006

TABLE IV. Main sources of uncertainty in the calculated IP$_1$, IP$_2$ and EA of Lr and IP$_1$ and IP$_2$ of Lu, in meV.

	Lu		Lr		
Error source	IP$_1$	IP$_2$	IP$_1$	IP$_2$	EA
Basis set					
CBS scheme	9.4	3.8	7.2	17.4	6.1
augmentation	3.4	0.1	0.0	2.5	1.8
(ae4z–cv4z)	0.2	0.0	0.6	5.7	0.5
Correlation					
virtual cutoff	4.0	3.0	0.9	3.5	0.3
higher excitations	13.8	0.3	2.2	0.8	9.0
QED	5.7	18.7	3.8	45.0	0.8
Total	18	19	9	49	11

[39,47–49] for extrapolation, respectively, as detailed in [28] and determine the 95% confidence interval of the standard deviation among the three schemes to represent the complete basis set (CBS) uncertainty, as shown in Table III. Additionally, we consider the difference between the (3-aug)-cv4z and (1-aug)-cv4z results as the augmentation uncertainty and the difference between the values obtained with the ae4z and cv4z basis sets as uncertainty due to basis set incompleteness in the core region. The latter is also added as a correction to the final recommended values in Table V.

The uncertainty arising from the treatment of electron correlation is due to the cutoff of the virtual correlation space (we correlate all the electrons) and the neglect of higher-order excitations beyond CCSDT. To verify the effect of energy cutoff in virtual space, we increased the cutoff from 70 a.u. to 2000 a.u. using the v4z basis set and took the difference as the corresponding uncertainty. This correction was also added to the final recommended values in Table V. The neglected higher-order excitations beyond the triple level were estimated to be no greater than ΔT.

Regarding relativity, we assume that the neglected higher-order QED contributions are not larger than the second-order contributions. Based on the expansion of the bound-state propagator [50], the leading order and next-to-leading order QED contributions scale as $\sim Z\alpha^2$ and $\sim Z^2\alpha^3$, respectively, where α is the fine-structure constant. We thus used the calculated QED contributions scaled with the ratio $Z\alpha$ as the corresponding uncertainties.

The absolute values of the individual contributions to the uncertainty are detailed in Table IV. One can assume that the uncertainty contributions stemming from different sources are independent to a large degree; this assumption should be valid as long as we are dealing with higher-order contributions. Thus the total uncertainty is obtained by adding the individual sources of uncertainty using the usual Euclidean norm. The final recommended values of the first and second IPs of Lu and Lr, as well as the EA of Lr, are summarized in Table V, along with recent-high accuracy calculations and the existing experimental values.

Our calculated IP$_1$ of Lu is 34 meV below the experimental value, with this difference exceeding the uncertainty we set on our prediction. It is not clear whether the source of this discrepancy is in the computational scheme or whether it is experimental in origin. Our prediction of IP$_2$ of Lu agrees well with the recently proposed semiempirical values [51] and within the combined uncertainties of the two results. The present IP$_1$ value for Lr stands at 4.955 eV with an uncertainty of ±9 meV, in good agreement with the earlier CCSD(T) prediction from 2015. Remarkably, both these findings align well with experimental data, which reports an IP$_1$ of $4.96^{+0.05}_{-0.04}$ eV [6]. These values are also consistent with the prediction obtained using the CI+all order technique [12]. The earlier result obtained using the FSCC method is approximately 0.07 eV lower than the experimental value. This discrepancy can be attributed to the omission of electron correlation beyond double excitations in the earlier work.

Utilizing the one-atom-at-a-time gas-phase ion chemistry technique, the lower limit on the IP$_2$ of Lr was set at 13.3(3) eV [17]. The current predictions surpass this value by more than an eV and align with the earlier FSCC value [32].

In this work, we did not address the electron affinity of Lu. The electron configuration of Lu$^-$ is [Xe] $4f^{14}6s^2 5d6p$ [25] and thus not analogous to the [Rn] $5f^{14}7s^2 6p^2$ configuration of Lr$^-$. Furthermore, the single reference coupled-cluster approach used in this work is less suited for treatment of multiple open shells than, for example, the Fock-space coupled-cluster (FSCC) method which was applied to Lu$^-$ in Ref. [13].

Our prediction for the EA of Lr is in good agreement with the 2007 FSCC result, but expected to be more accurate due to the basis set extrapolation and to the inclusion of higher excitations and QED corrections. The proposed error bars on

TABLE V. Final recommended values of the IPs (eV) and EA (eV) of Lr and Lu compared with previous calculations and experiment, where available.

		Lu		Lr			
Method	Year	IP$_1$($6s^2$)	IP$_2$($6s^1$)	IP$_1$($7s^2$)	IP$_2$($7s^1$)	EA($7s^2 7p^2$)	Reference
CBS-CCSDT+Breit+QED		5.391(18)	14.026(19)	4.955(9)	14.627(49)	0.446(11)	Present
FSCC	2007	5.301		4.894		0.476	[13]
CI+all order	2014			4.934			[12]
CCSD(T)	2015			4.963(15)			[6]
FSCC	2021		13.973		14.500(48)		[32]
Experiment		5.4259(13)	14.13(10)[a]	$4.96^{+0.05}_{-0.04}$	>13.3(3)[b]		[6,7,17,30,31,51]

[a] Indirectly derived from experimental data in the lanthanide series.

[b] Only lower limit is predicted.

this value should be used with caution, however, due to the possible underestimation of uncertainty for the IP_1 of Lu.

IV. CONCLUSION

We carried out relativistic coupled-cluster calculations of the first and second ionization potentials and electron affinity of lawrencium, as well as the first and second ionization potentials of lutetium, the latter allowing comparison with experimental data. We have extrapolated our results to the complete basis set limit and corrected the calculated properties for higher-order correlation effects and for the Breit and QED contributions.

Our calculations are in good agreement with the available experimental values for the first ionization potential of Lr and the second ionization potential of Lu, confirming the accuracy and reliability of the selected computational approach. Future efforts aimed at determining the electron affinity and the second ionization potential of Lr will benefit from our theoretical prediction, which includes uncertainty estimation, providing a detection range to guide the measurements.

ACKNOWLEDGMENTS

We would like to thank the Center for Information Technology of the University of Groningen for their support and for providing access to the Peregrine and Hábrók high-performance computing clusters. L.F.P. acknowledges the support from Project No. VI.C.212.016 of the talent programme VICI financed by the Dutch Research Council (NWO) and from the Slovak Research and Development Agency Projects No. APVV-20-0098 and No. APVV-20-0127.

[1] Y. Oganessian, Heaviest nuclei from ^{48}Ca-induced reactions, J. Phys. G: Nucl. Part. Phys. **34**, R165 (2007).

[2] P. J. Karol, R. C. Barber, B. M. Sherrill, E. Vardaci, and T. Yamazaki, Discovery of the element with atomic number Z= 118 completing the 7th row of the periodic table (IUPAC technical report), Pure Appl. Chem. **88**, 155 (2016).

[3] Y. T. Oganessian and V. Utyonkov, Super-heavy element research, Rep. Prog. Phys. **78**, 036301 (2015).

[4] A. Türler and V. Pershina, Advances in the production and chemistry of the heaviest elements, Chem. Rev. **113**, 1237 (2013).

[5] Y. Nagame, J. V. Kratz, and M. Schädel, Chemical studies of elements with $Z \geqslant 104$ in liquid phase, Nucl. Phys. A **944**, 614 (2015).

[6] T. Sato *et al.*, Measurement of the first ionization potential of lawrencium, element 103, Nature (London) **520**, 209 (2015).

[7] T. K. Sato *et al.*, First ionization potentials of Fm, Md, No, and Lr: Verification of filling-up of 5f electrons and confirmation of the actinide series, J. Am. Chem. Soc. **140**, 14609 (2018).

[8] P. Chhetri *et al.*, Precision measurement of the first ionization potential of nobelium, Phys. Rev. Lett. **120**, 263003 (2018).

[9] V. Pershina, Relativity in the electronic structure of the heaviest elements and its influence on periodicities in properties, Radiochim. Acta **107**, 833 (2019).

[10] A. Ghiorso, T. Sikkeland, A. E. Larsh, and R. M. Latimer, New element, lawrencium, atomic number 103, Phys. Rev. Lett. **6**, 473 (1961).

[11] J.-P. Desclaux and B. Fricke, Relativistic prediction of the ground state of atomic lawrencium, J. Phys. France **41**, 943 (1980).

[12] V. A. Dzuba, M. S. Safronova, and U. I. Safronova, Atomic properties of superheavy elements No, Lr, and Rf, Phys. Rev. A **90**, 012504 (2014).

[13] A. Borschevsky, E. Eliav, M. Vilkas, Y. Ishikawa, and U. Kaldor, Transition energies of atomic lawrencium, Eur. Phys. J. D **45**, 115 (2007).

[14] Y. Zou and C. F. Fischer, Resonance transition energies and oscillator strengths in lutetium and lawrencium, Phys. Rev. Lett. **88**, 183001 (2002).

[15] E. Eliav, U. Kaldor, and Y. Ishikawa, Transition energies of ytterbium, lutetium, and lawrencium by the relativistic coupled-cluster method, Phys. Rev. A **52**, 291 (1995).

[16] E. V. Kahl, S. Raeder, E. Eliav, A. Borschevsky, and J. C. Berengut, *Ab initio* calculations of the spectrum of lawrencium, Phys. Rev. A **104**, 052810 (2021).

[17] J. T. Kwarsick *et al.*, Assessment of the second-ionization potential of lawrencium: Investigating the end of the actinide series with a one-atom-at-a-time gas-phase ion chemistry technique, J. Phys. Chem. A **125**, 6818 (2021).

[18] D. Leimbach *et al.*, The electron affinity of astatine, Nat. Commun. **11**, 3824 (2020).

[19] S. Rothe *et al.*, Laser photodetachment of radioactive $^{128}I^-$, J. Phys. G: Nucl. Part. Phys. **44**, 104003 (2017).

[20] Y. T. Oganessian, A. Iljinov, A. Demin, and S. Tretyakova, Experiments on the production of fermium neutron-deficient isotopes and new possibilities of synthesizing elements with $Z > 100$, Nucl. Phys. A **239**, 353 (1975).

[21] V. Zagrebaev *et al.*, Gas-cell-based setup for the production and study of neutron rich heavy nuclei, Hyperfine Interact. **227**, 181 (2014).

[22] C. Le Naour, D. Trubert, and D. C. Hoffman, Fundamental and experimental aspects of single atom-at-a-time chemistry, in *The Chemistry of Superheavy Elements*, edited by M. Schädel and D. Shaughnessy (Springer, Berlin, Heidelberg, 2014).

[23] M. Schädel, Chemistry of the superheavy elements, Philos. Trans. R. Soc. A **373**, 20140191 (2015).

[24] E. M. Ramirez *et al.*, Direct mapping of nuclear shell effects in the heaviest elements, Science **337**, 1207 (2012).

[25] V. Davis and J. Thompson, Measurement of the electron affinity of lutetium, J. Phys. B: At. Mol. Opt. Phys. **34**, L433 (2001).

[26] J. Khuyagbaatar *et al.*, $^{48}Ca + ^{249}Bk$ fusion reaction leading to element Z= 117: Long-lived α-decaying ^{270}Db and discovery of ^{266}Lr, Phys. Rev. Lett. **112**, 172501 (2014).

[27] Y. Guo, L. F. Pašteka, E. Eliav, and A. Borschevsky, Ionization potentials and electron affinity of oganesson with relativistic coupled cluster method, *Advances in Quantum Chemistry* (Academic Press, New York, 2021).

[28] Y. Guo, A. Borschevsky, E. Eliav, and L. F. Pašteka, Relativistic coupled cluster calculations of the electron affinity and ionization potential of Nh (113), J. Phys. B: At. Mol. Opt. Phys. **55**, 155003 (2022).

[29] P. Camus and F. S. Tomkins, Absorption-line series in Lu I, J. Phys. France **33**, 197 (1972).

[30] H. Maeda, Y. Mizugai, Y. Matsumoto, A. Suzuki, and A. Takami, Highly excited even Rydberg series of Lu I studied by two-step laser photoionisation spectroscopy, J. Phys. B: At. Mol. Opt. Phys. **22**, L511 (1989).

[31] R. Li, J. Lassen, Z. P. Zhong, F. D. Jia, M. Mostamand, X. K. Li, B. B. Reich, A. Teigelhofer, and H. Yan, Even-parity Rydberg and autoionizing states of lutetium by laser resonance-ionization spectroscopy, Phys. Rev. A **95**, 052501 (2017).

[32] E. V. Kahl, J. C. Berengut, M. Laatiaoui, E. Eliav, and A. Borschevsky, High-precision *ab initio* calculations of the spectrum of Lr^+, Phys. Rev. A **100**, 062505 (2019).

[33] L. Visscher and K. G. Dyall, Dirac-fock atomic electronic structure calculations using different nuclear charge distributions, At. Data Nucl. Data Tables **67**, 207 (1997).

[34] DIRAC, a relativistic *ab initio* electronic structure program, release DIRAC19 (2019), written by A. S. P. Gomes, T. Saue, L. Visscher, H. J. Aa. Jensen, and R. Bast, with contributions from I. A. Aucar, V. Bakken, K. G. Dyall, S. Dubillard, U. Ekström, E. Eliav, T. Enevoldsen, E. Faßhauer, T. Fleig, O. Fossgaard, L. Halbert, E. D. Hedegård, B. Heimlich–Paris, T. Helgaker, J. Henriksson, M. Iliaš, Ch. R. Jacob, S. Knecht, S. Komorovský, O. Kullie, J. K. Lærdahl, C. V. Larsen, Y. S. Lee, H. S. Nataraj, M. K. Nayak, P. Norman, G. Olejniczak, J. Olsen, J. M. H. Olsen, Y. C. Park, J. K. Pedersen, M. Pernpointner, R. di Remigio, K. Ruud, P. Sałek, B. Schimmelpfennig, B. Senjean, A. Shee, J. Sikkema, A. J. Thorvaldsen, J. Thyssen, J. van Stralen, M. L. Vidal, S. Villaume, O. Visser, T. Winther, and S. Yamamoto (available at http://dx.doi.org/10.5281/zenodo.3572669; see also http://www.diracprogram.org).

[35] K. G. Dyall, Relativistic double-zeta, triple-zeta, and quadruple-zeta basis sets for the actinides Ac-Lr, Theor. Chem. Acc. **117**, 491 (2007).

[36] A. S. Gomes, K. G. Dyall, and L. Visscher, Relativistic double-zeta, triple-zeta, and quadruple-zeta basis sets for the lanthanides La-Lu, Theor. Chem. Acc. **127**, 369 (2010).

[37] K. G. Dyall, Core correlating basis functions for elements 31-118, Theor. Chem. Acc. **131**, 1 (2012).

[38] D. Feller, Application of systematic sequences of wave functions to the water dimer, J. Phys. Chem. **96**, 6104 (1992).

[39] T. Helgaker, W. Klopper, H. Koch, and J. Noga, Basis-set convergence of correlated calculations on water, J. Chem. Phys. **106**, 9639 (1997).

[40] V. Shabaev, I. Tupitsyn, and V. Yerokhin, Qedmod: Fortran program for calculating the model lamb-shift operator, Comput. Phys. Commun. **189**, 175 (2015).

[41] J. Blomqvist, Vacuum polarization in exotic atoms, Nucl. Phys. B **48**, 95 (1972).

[42] V. M. Shabaev, I. I. Tupitsyn, and V. A. Yerokhin, Model operator approach to the lamb shift calculations in relativistic many-electron atoms, Phys. Rev. A **88**, 012513 (2013).

[43] TRAFS-3C code (Tel-Aviv Relativistic Atomic Fock-Space coupled cluster code), written by E. Eliav, U. Kaldor, and Y. Ishikawa (1990–2013), with contributions by A. Landau.

[44] A. V. Oleynichenko, A. Zaitsevskii, and E. Eliav, Towards high performance relativistic electronic structure modelling: The exp-t program package, in *Russian Supercomputing Days*, edited by V. Voevodin and S. Sobolev (Springer International Publishing, Cham, 2020), Vol. 1331, pp. 375–386.

[45] L. F. Pašteka, E. Eliav, A. Borschevsky, U. Kaldor, and P. Schwerdtfeger, Relativistic coupled cluster calculations with variational quantum electrodynamics resolve the discrepancy between experiment and theory concerning the electron affinity and ionization potential of gold, Phys. Rev. Lett. **118**, 023002 (2017).

[46] A. V. Malyshev, D. A. Glazov, V. M. Shabaev, I. I. Tupitsyn, V. A. Yerokhin, and V. A. Zaytsev, Model-qed operator for superheavy elements, Phys. Rev. A **106**, 012806 (2022).

[47] M. Lesiuk and B. Jeziorski, Complete basis set extrapolation of electronic correlation energies using the Riemann Zeta function, J. Chem. Theory Comput. **15**, 5398 (2019).

[48] J. M. Martin, *Ab initio* total atomization energies of small molecules—towards the basis set limit, Chem. Phys. Lett. **259**, 669 (1996).

[49] J. M. M. Amir Karton, Comment on "Estimating the Hartree–Fock limit from finite basis set calculations" [Jensen F (2005) Theor Chem Acc 113:267], Theor. Chem. Acc. **115**, 330 (2006).

[50] A. Sunaga, M. Salman, and T. Saue, 4-component relativistic Hamiltonian with effective QED potentials for molecular calculations, J. Chem. Phys. **157**, 164101 (2022).

[51] D. A. Johnson and P. G. Nelson, Lanthanide ionization energies and the sub-shell break. part 1. The second ionization energies, J. Phys. Chem. Ref. Data **46**, 013108 (2017).