

Article



Low-Energy Electron Elastic Total Cross Sections for Ho, Er, Tm, Yb, Lu, and Hf Atoms

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Abstract: The robust Regge-pole methodology wherein is fully embedded the essential electron-electron correlation effects and the vital core polarization interaction has been used to explore negative ion formation in the large lanthanide Ho, Er, Tm, Yb, Lu, and Hf atoms through the electron elastic total cross sections (TCSs) calculations. These TCSs are characterized generally by dramatically sharp resonances manifesting ground, metastable, and excited negative ion formation during the collisions, Ramsauer-Townsend minima, and shape resonances. The novelty and generality of the Regge-pole approach is in the extraction of the negative ion binding energies (BEs) of complex heavy systems from the calculated electron TCSs. The extracted anionic BEs from the ground state TCSs for Ho, Er, Tm, Yb, Lu, and Hf atoms are 3.51 eV, 3.53 eV, 3.36 eV, 3.49 eV, 4.09 eV and 1.68 eV, respectively. The TCSs are presented and the extracted from the ground; metastable and excited anionic states BEs are compared with the available measured and/or calculated electron affinities. We conclude with a remark on the existing inconsistencies in the meaning of the electron affinity among the various measurements and/or calculations in the investigated atoms and make a recommendation to resolve the ambiguity.

Keywords: generalized bound states; electron correlations; anionic binding energies; polarization interaction; lanthanide atoms

PACS: 34.80. Bm; electron elastic scattering

1. Introduction

There is a great need to understand and clarify the measured and/or calculated electron affinities (EAs) of the large lanthanide and Hf atoms. Reliable atomic and molecular affinities are crucial for understanding the vast chemical reactions involving negative ions [1]. In addition, single atoms play an essential role in catalysis through negative ion formation in low-energy electron elastic collisions.

Calculated low-energy electron elastic TCSs for complex heavy systems, including fullerene molecules, are characterized generally by ground, metastable and excited negative ion formation, shape resonances, and Ramsauer-Townsend (R-T) minima. The presence of metastable and excited anions in the TCSs for the lanthanide and actinide atoms impacts significantly the reliability of both the measured and the calculated EAs in addition to leading to ambiguous EAs. The fundamental mechanism underlying atomic negative-ion catalysis and requiring reliable EAs was proposed by our group in the context of muon catalyzed nuclear fusion involving a negative muon, a deuteron, and a triton [2,3]. The mechanism involves anionic molecular complex formation in the transition state, with the atomic negative ion weakening/breaking the hydrogen bonding strength. Indeed, the negative ion catalysis mechanism requires the delineation and identification of the ground, metastable, and excited states anionic binding energies (BEs) of the formed negative ions during the collision of

the electron with the complex heavy systems. Unfortunately, for most of the lanthanide and actinide atoms, producing sufficient anions with known anionic BEs that can be used in photodetachment experiments is very challenging [4]. The lanthanide and Hf atoms provide clear cases of the ambiguous and confusing measured and/or calculated EA values [5,6]. Fundamental to the reliable investigation and understanding of negative ion formation in complex heavy systems is the use of theoretical methods that account adequately for the essential physics, viz. electron-electron correlation effects and core-polarization interaction. These are embedded fully in our Regge-pole methodology.

The EAs provide a stringent test of theoretical methods when the calculated EAs are compared with those from reliable measurements. For the complex heavy systems Au, Pt, and At, the agreement between our Regge-pole calculated ground-state anionic BEs and the measured EAs of Au [7–9], Pt [7,10,11] and, most recently, At [12] as well as of the fullerene molecule C_{60} [13,14] is outstanding. Very recently, the ground state anionic BEs extracted from our Regge-pole calculated electron elastic TCSs for the fullerene molecules C_{20} through C_{92} have been found to match in general excellently the measured EAs [15,16]. These results give great credence to the power and ability of the Regge-pole methodology to produce reliable ground state BEs of complex heavy systems through the TCSs calculation. Indeed, the Regge-pole methodology requires no assistance whatsoever from either experiment or other theories to achieve the remarkable feat.

Interest in the investigation of low-energy electron scattering from the large lanthanide atoms has been motivated mainly by: (1) The experiment [17] searched in vain for the EA of Yb and concluded that, if it existed, it must be less than 3 meV; (2) For the Tm atom, the measured EA value of 1.029 eV [18] agrees excellently with our anionic metastable state BE of 1.02 eV [5]; (3) The EA of atomic Eu was measured to be 0.116 ± 0.013 eV [4], which is in outstanding agreement with the calculated values using the Regge-pole [19] and MCDF-RCI [20] methods. However, the Regge-pole value corresponds to the BE of an excited Eu⁻ negative ion [19]. In addition, the previously measured EA value of 1.053 \pm 0.025 eV for Eu [21] agrees excellently with the Regge-pole value of 1.08 eV [22]. The conundrum in the two measured EAs [4,21] for Eu has been discussed recently and resolved [5] and (4) In [23], differential and integral electron elastic cross sections for Hf and Lu were investigated in the very narrow electron impact energy range $0.0 \le E \le 0.1$ eV and found to be characterized by dramatically sharp resonances. For the atomic Lu laser, photoelectron spectroscopy measurement obtained the EA value of 0.346 eV [24], while the calculated EAs are 0.190 eV [25] and 0.257 eV [26]. Under the results section, it will be demonstrated that these values may correspond to the BE of an excited Lu⁻ anionic state. Recently, it has been concluded that the existing calculations incorrectly identified the BEs of the metastable/excited anions with the EAs of the actinide atoms [27]. For the Eu, Tm, and other lanthanide atoms, including Nb, the resultant conundrum between our calculated ground state anionic BEs and the measured EAs has been discussed recently. It has been concluded that the measured EAs for some of the lanthanide atoms, including the recently measured EAs for Eu [4] and Nb [28], require reinterpretation [5].

The recently measured EA value of 0.917 ± 0.006 eV for the Nb atom [28] agreed generally well with the existing theoretical EAs [29,30] and the previously measured EA value of 0.894 ± 0.025 eV [31]. Our Regge-pole calculated BE of the Nb⁻ anion is 0.905 eV. Although agreeing with the measured EAs, this value corresponds to the BE of an excited state of Nb⁻; its ground state BE has been calculated to be 2.48 eV [5]. The investigation of the Hf atom is included here because of the existing outstanding agreement between the MCDF-RCI EA value (0.114 eV) [32] and our Regge-pole calculated excited state anionic BE (0.113 eV) [33]. However, our value corresponds to the BE of an excited state of the Hf⁻ anion. Indeed, the analysis above conveys a sense of uncertainty and ambiguity in the meaning of the EA values for many of the lanthanide atoms. This is the reason for the present investigation. It is noted here that our previous investigation of resonances in the electron scattering TCSs for the lanthanide atoms was limited to the narrow electron impact energy range $0.0 \le E \le 1.0$ eV [19], way below the energy region of the ground state negative ion formation in the lanthanide atoms. The reason is now clear for increasing the energy range of our current investigation to 10 eV.

2. Method of Calculation

Most existing theoretical methods used for calculating the anionic BEs of complex heavy systems are structure-based. Therefore, the results obtained through these methods are often riddled with uncertainties and lack definitiveness for complex heavy systems. Their general weakness lies in the fact that they employ large configuration interaction expansions demanded by the diffuseness of the wave functions for negative ions

In [34], it was confirmed that Regge poles formed during low-energy electron elastic scattering become stable bound states. Here, we adopt the Regge-pole methodology, also known as the complex angular momentum (CAM) method for the calculation of the electron scattering TCSs. Regge poles, singularities of the S-matrix, rigorously define resonances [35,36]; consequently, they are appropriate for use in this investigation. Being generalized bound states, they can be used to calculate reliably the anionic BEs of the ground and metastable states of complex heavy systems, provided the essential physics has been accounted for adequately as in our case here. In the Regge pole methods, the important and revealing energy-dependent Regge trajectories are also calculated. Their effective use in low-energy electron scattering has been demonstrated in, for example, [19,37].

The Mulholland formula [38] is used here to calculate the near-threshold electron–atom/fullerene collision TCSs resulting in negative ion formation as resonances. In the form below, the TCS fully embeds the essential electron–electron correlation effects [39,40] (atomic units are used throughout):

$$\sigma_{tot}(E) = 4\pi k^{-2} \int_{0}^{\infty} \operatorname{Re}[1 - S(\lambda)] \lambda d\lambda -8\pi^{2} k^{-2} \sum_{n} \operatorname{Im} \frac{\lambda_{n} \rho_{n}}{1 + \exp(-2\pi i \lambda_{n})} + I(E)$$
(1)

In Equation (1), $S(\lambda)$ is the S-matrix, $k = \sqrt{2mE}$, *m* being the mass and *E* the impact energy, ρ_n is the residue of the S-matrix at the *n*th pole, λ_n and *I*(*E*) contains the contributions from the integrals along the imaginary λ -axis (λ is the complex angular momentum); its contribution has been demonstrated to be negligible [19].

As in [41], here we consider the incident electron to interact with the complex heavy system without consideration of the complicated details of the electronic structure of the system itself. Therefore, within the Thomas-Fermi theory, Felfli et al. [42] generated the robust Avdonina-Belov-Felfli (ABF) potential which embeds the vital core–polarization interaction

$$U(r) = -\frac{Z}{r(1 + \alpha Z^{1/3}r)(1 + \beta Z^{2/3}r^2)}$$
(2)

In Equation (2), *Z* is the nuclear charge, and α and β are variation parameters. Note also that the ABF potential has the appropriate asymptotic behavior, viz. $\sim -1/(\alpha\beta r^4)$ and accounts properly for the polarization interaction at low energies. The strength of this extensively studied potential [43] lies in the fact that it has five turning points and four poles connected by four cuts in the complex plane. The presence of the powers of *Z* as coefficients of *r* and r^2 in Equation (2) ensures that spherical and non-spherical atoms and fullerenes are correctly treated. Small and large systems are also appropriately treated. The effective potential $V(r) = U(r) + \lambda(\lambda + 1)/2r^2$ is considered here as a continuous function of the variables *r* and complex λ . The details of the numerical evaluations of the TCSs have been described in [40] and further details of the calculations may be found in [44].

The novelty and generality of the robust Regge-pole approach lies in the fact that the crucial electron–electron correlation effects are fully embedded in the Mulholland formula. In addition, the ABF potential contains the vital core–polarization interaction. These two important effects have been identified as the major physical effects mostly responsible for electron attachment in low-energy electron scattering from complex heavy systems, leading to stable negative ion formation. Crucial in the CAM methods are the Regge trajectories, viz. Im $\lambda_n(E)$ versus Re $\lambda_n(E)$ ($\lambda_n(E)$ is the CAM). These probe electron attachments at the fundamental level near the threshold thereby allow for the

determination of reliable EAs. Thylwe [37] investigated Regge trajectories, using the ABF potential, and demonstrated that, for Xe atom, the Dirac Relativistic and non-Relativistic Regge trajectories yielded essentially the same Re λ_n (E) when the Im λ_n (E) was still very small. This clearly demonstrates the insignificant difference between the Relativistic and non-Relativistic calculations at near threshold electron impact energies, if the appropriate physics is accounted for adequately as in our case.

The potential (2) has been used successfully with the appropriate values of α and β , see [19]. In all the calculations, the optimal value here is $\alpha = 0.2$; it determines the optimum value of β for a resonance in the TCS [19]. The effective use of Im $\lambda(E) \rightarrow 0$ is also demonstrated in [19] and carefully explained there. Connor [45] and Regge himself [46] have given the physical interpretation of Im $\lambda(E)$. For a true bound state, namely E < 0, Im $\lambda(E) = 0$ and therefore the angular life, $1/(\text{Im } \lambda(E)) \rightarrow \infty$, implying that the system can never decay. We limit the calculations of the TCSs to the near-threshold energy region, namely below any excitation thresholds to avoid their effects.

We emphasize here that the investigation of the Regge trajectories allows us to readily determine the electron impact energy range, where Relativity is unimportant in the calculation of the TCSs, i.e., at small electron impact energies. In addition, the use of the Im λ_n (E) allows us to differentiate among the important ground, metastable, and excited negative ion formation as well as the shape resonances. The very small value of Im λ_n (E) is indicative of the ground state negative ion formation.

3. Results

In the paper [23], we investigated resonance structures in the electron scattering differential and integral cross sections for tenuously bound atomic systems, E < 0.1 eV in the context of the quenching of Rydberg states by ground state atoms with small EAs [47,48]. In the Au, Pt, and At atoms as well as the C₆₀ and other fullerene molecules, the meaning of the EAs was in the context of electron attachment to the ground state of neutral complex heavy systems. Consequently, in this paper, the EAs of the lanthanide and Hf atoms are determined and discussed in this context, namely electron attachment to the ground state of the neutral atoms resulting in stable negative ion formation. Hopefully, this will minimize the proliferation of the ambiguous meaning of the EAs of the complex heavy systems in the published literature.

Figure 1 (top left) presents the electron elastic TCSs for atomic Ho. The pink, red, and green curves represent respectively the ground, metastable, and excited states TCSs. Generally, these TCSs are characterized by dramatically sharp resonances representing negative ion formation during the collisions, R-T minima, and shape resonances. These characteristic R-T minima, also observed in the Dirac R-matrix low-energy electron elastic scattering cross sections' calculations for the heavy alkali-metal atoms Rb, Cs, and Fr [49], manifest that the important polarization interaction has been accounted for adequately in our calculation consistent with the conclusion by Johnson and Guet [50]. The energy positions of the sharp resonances correspond to the anionic BEs of the formed negative ions during the electron collision with the ground, metastable, and excited Ho atoms. The extracted from the TCSs shape resonances and the anionic BEs are summarized in Table 1 where they are also compared with the available EAs. As seen from Table 1, the anionic BEs for the Ho⁻ anions are unavailable to compare our results with. In addition, to our knowledge, there are no experimental and/or theoretical EAs to compare with our data. This is a strong justification for the investigation of the TCSs for the Ho atom.

The physics underlying the TCSs of Figure 1 is similar to that explained in our paper [5]; consequently, here it will be explained briefly. For a better understanding and appreciation of the physics underlying the TCSs, we first focus upon the ground state TCS for Ho (red curve). From near threshold, the ground state TCS decreases monotonically with the increase of the electron impact energy, reaching the first R-T minimum at about 1 eV. With the further increase in energy, the electron becomes trapped by the centrifugal barrier manifested by the appearance of the shape resonance (SR) at about 1.7 eV. As the electron leaks out of the barrier, it polarizes the Ho atom, strongly reaching maximum polarization at about 3.43 eV. Here, the Ho atom is transparent and the electron becomes

attached to it, forming the stable Ho⁻ anion with the BE value of 3.51 eV. The electron spends many angular rotations as the Ho⁻ anion decays, with the angular lifetime determined by $1/(\text{Im}\lambda(\text{E})) \rightarrow \infty$, since for the ground state negative ion formation Im $\lambda(\text{E}) \rightarrow 0$.

The brown curve represents the TCS for the Ho metastable state. As the incident electron approaches the Ho atom in the metastable state, it polarizes the atom significantly, as manifested through the appearance of the first deep R-T minimum at about 0.07 eV. With increase in energy, the electron becomes trapped by the centrifugal potential, evidenced through the appearance of the SR at about 0.21 eV. As the electron leaks out of the barrier, it becomes trapped forming the metastable Ho⁻ anion with BE value of 0.338 eV. The continuing Ho⁻ anionic decay results in the outgoing electron polarizing the Ho atom further, reaching maximum polarization at about 0.57 eV. This TCS behavior is typical of metastable state TCSs and resembles those of complex heavy atoms such as Au and Pt. The green curve corresponds to the TCS for an excited state of the Ho atom. Near threshold, it is characterized by an SR at about 0.034 eV. This behavior of the excited state TCS is similar to that found in the TCSs for the other lanthanide atoms Eu, Tm, Gd, etc.

Minor and subtle differences among the various TCSs in Figures 1 and 2, notwithstanding, the fundamental physics used to analyze the results of Ho in Figure 1 is applicable to all the remaining TCSs of Figures 1 and 2. Consequently, the results in the remaining Figures will be described only briefly. Figure 1 (top right) presents the TCSs for the Er atom; the red, brown and green curves represent respectively the ground, metastable and excited states TCSs. The explanation of the behavior of the various TCSs is similar to that for the electron-Ho scattering, described above. The SRs and the anionic BEs are summarized in Table 1, where they are compared with those of the other complex heavy lanthanide atoms as well as of Hf. It is noted here that the ground state anionic BE for the Er⁻ anion is also large, 3.53 eV comparable to that of the Ho⁻ anion and located at the second R-T minimum of the TCS. For the Er atom, like for the Ho atom, there are no SRs and EAs available, to our knowledge, to compare our data with. The TCSs for the electron-Tm scattering, presented also in Figure 1 (left bottom), also resemble those of the Ho and Er atoms. Together with the associated SRs, the anionic BEs for Tm are summarized in Table 1 where they are compared with those for the other atoms. Notably, they all have ground state anionic BEs greater than 3 eV; therefore, they could be useful as nanocatalysts and in organic solar cells. Significantly, the metastable TCS, brown curve has a relatively large anionic BE value of 1.02 eV compared to those for the Ho and Er atoms. This is attributed to the collapse of the 5d orbital to the 4f orbital, impacting the polarization interaction significantly [51]. Indeed, the measured EA value of Tm is 1.029 eV [18], which is in outstanding agreement with the Regge-pole value above. However, as seen from Figure 1, our value corresponds to the anionic BE of the metastable Tm⁻ anion and not of its ground state. The rest of the results for the Tm atom are presented in Table 1, where they are compared with those of the rest of the atoms and available EAs.

In the electron impact energy range of interest here, the TCSs for the Yb atom, shown in Figure 1 (bottom right), resemble those of the Ho, Er, and Tm atoms. It is noted here, however, that, for Yb, the anionic BE of the metastable state is comparable to those for Ho and Er atoms. The large BE of the anionic ground state Yb⁻ anion is comparable to those of the Ho⁻, Er⁻, and Tm⁻ anions. Here, we observe the appearance of an excited anionic state of Yb⁻ near threshold with BE value of 0.028 eV due to the size effect. The anionic BEs and the SRs for the Yb atom are compared in Table 1 with those for the other atoms. It is worth pointing out that the Yb atom was investigated experimentally [17] searching for its EA, with the conclusion that, if the EA existed, then it must be less than 3 meV. According to our investigation, the TCSs for the Yb atom are characterized by both SRs and dramatically sharp resonances manifesting the formation of stable negative ions, ground, metastable, and excited. If the experiment was searching for the ground state of the Yb⁻ anion, then the search was in the wrong direction. The BE values of the sharp resonances in the TCSs for the Yb atom should help experiments search for the ground and metastable negative ion formation. Indeed, it appears to us that the best investigation for negative ion formation in these systems and others is the use of low-energy electron scattering as was described many years ago [52]. Namely, ground state formation of a negative ion

is identifiable through the appearance of a sharp resonance peak in the low-energy electron-atom scattering TCS [52]. This facilitates the extraction of the EA from the TCS. It is interesting that the experiment [18] found the EA of Tm in agreement with the Regge-pole BE value of the metastable state of the Tm⁻ anion. However, the experiment [17] could not detect the Regge-pole predicted metastable anionic BE value of 0.485 eV or the excited anionic BE value of 0.204 eV for Yb⁻.



Figure 1. Total cross sections (a.u.) for Ho (Top Left) and Er (Top Right). The red, brown, and green curves in both atoms represent the TCSs for the ground, metastable, and the excited states, respectively. Bottom left and right figures are for Tm and Yb, respectively. In both figures, the red, orange, brown, and green curves represent the TCSs for the ground, metastable, and the two excited states, respectively. The dramatically sharp resonances in the figures correspond to the anionic formation during the collisions.

Figure 2 presents the TCSs for the Lu atom. The red, blue, brown, and green curves represent the TCSs for the ground, metastable, and the two excited states, respectively. These TCSs resemble those for the other atoms already considered here. Notably, the Lu's highest excited state TCS (green curve) has the near-threshold sharp resonance with the BE value of 0.029 eV; it resembles and is comparable in magnitude to that already found in the TCSs for Tm and Yb. Importantly, the Lu ground state TCS has a large BE value of 4.09 eV; it is the largest anionic BE found in the lanthanide atoms thus far. It could be very useful in nanocatalysis and organic solar cells to name a few applications. Its metastable TCS has an unusually large negative ion BE value of 1.92 eV; this needs verification because it could easily be mistaken for the ground state anionic BE of the Lu⁻ anion. The data for the Lu atom are summarized in Table 1, where they are compared with those for the other atoms and the available EAs as well. Again, here we see the measured EA value of 0.346 eV [24] being close to our anionic BE value of the first excited Lu⁻ anion and the calculated EA values [25,26], see Table 1. Our calculated anionic ground state and metastable state BEs are, respectively, 4.09 eV and 1.92 eV. From our perspective, the experiment appears to identify the BE of the excited anionic state with the EA of Lu similarly to the case of atomic Tm.



Figure 2. Total cross sections (a.u.) for electron elastic scattering from Lu. The red, blue, brown, and green curves represent the TCSs for the ground, metastable, and the two excited states, respectively. The dramatically sharp resonances correspond to the Lu^- anionic formation during the collisions.

The TCSs for the electron scattering from the Hf atom are presented in Figure 3. The pink, green, orange, and purple curves represent the TCSs for the ground, metastable, and the two excited states, respectively. Recall that the Hf atom has been selected for investigation because our anionic BE value of 0.113 eV [33] agreed excellently with the calculated EA value of 0.114 eV by Pan and Beck [32]. Clearly from Figure 3, the 0.113 eV value corresponds to the BE of an excited negative ion of Hf⁻. The TCSs resemble those of the Tm, Yb, and Lu atoms; the highest excited state anionic BE of Hf⁻ is 0.017 eV. Notably, the TCSs for the Hf atom like those of the large lanthanide atoms are characterized by ground, metastable, and excited ionic states formation. The extracted from the TCSs anionic BEs and the SRs are compared in Table 1 with those from the large lanthanide atoms. Interestingly, the ground state anionic BE of the Hf⁻ anion is, by comparison, small, viz. 1.68 eV; it is almost a factor of two smaller than the BEs of the lanthanide atoms. Indeed, the delineation and identification of the resonance structures in the TCSs are important for the understanding and the determination of the ground state negative ion formation during the electron collision with the Hf atom.

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Figure 3. Total cross sections (a.u.) for electron elastic scattering from Hf. The pink, green, orange, and purple curves represent the TCSs for the ground, metastable, and the two excited states, respectively. The dramatically sharp resonances correspond to the Hf⁻ anionic formation during the collisions.

E(eV)

0.1

Since our 0.113 eV BE corresponds to the anionic BE of an excited state of the Hf⁻ anion, the 0.114 eV value [32] cannot be considered as the EA of Hf; it should be simply viewed as the anionic BE of a highly excited state of the Hf⁻ anion. Figure 3 indicates that the anionic BE value of 1.68 eV belongs to the ground state of the Hf⁻ anion; therefore, it should be considered as the EA of atomic Hf consistent with the determination of the EAs of Au, Pt, and At atoms as well as the fullerene molecules. Consequently, experiments and theory alike should search for the anionic BE of the ground state of the Hf⁻ anion of the EA of Hf. The data from Figure 3 are summarized in Table 1 where they are contrasted with those of the large lanthanide atoms.

Clarification of the meaning of the measured and/or calculated EAs of Tm, Lu, and Hf atoms is appropriate. This is in the context of the measured and/or calculated EAs of Au, Pt, and At atoms as well as of the C_{60} and other fullerene molecules, being equivalent to the BEs of the formed negative ions in the ground states. For the Tm atom, the experiment [18] measured its EA to be 1.029 eV which is in outstanding agreement with the Regge-pole calculated value of 1.02 eV. However, as seen from Figure 1, this value corresponds to the anionic BE of a metastable Tm⁻ anion. The measured EA for atomic Lu is 0.346 eV [24,53]; it should be contrasted with the Regge-pole calculated anionic BE value of 0.292 eV, which is for an excited state of the Lu⁻ anion and the theoretical EA values of 0.257 eV [26] and 0.190 eV [25]. These theoretical values are reasonably close to the measured EA of Lu. For the Hf atom, the most recent measurement of its EA is 0.178 eV [54]. Our Regge-pole calculated BE value of 0.113 eV for the excited Hf⁻ anionic state is in outstanding agreement with the EA value of 0.114 eV [32], and these values are reasonably close to the measured and/or calculated EAs presented in Table 1 are contrasted with the measured/calculated EAs of the Au, Pt and At atoms as well as of the C_{60} fullerene molecule [13,14], it can be safely concluded that the meaning of the EAs for the large lanthanide and Hf atoms is both ambiguous and confusing as well.

Table 1. Negative ion binding energies (BEs), in eV obtained from the TCSs for the large lanthanide and Hf atoms. GRS, MS-1, and EX-*n* (n = 1, 2) represent respectively ground, metastable, and excited states. The experimental EAs, EXPT; theoretical EAs, Theory; and shape resonances, SR-*n* (n = 1-3) in eV are also presented. N/A denotes not available. Table 1 demonstrates the importance of determining the ground state BEs of the formed negative ions during the collisions. R-T Min is the energy position of the ground state R-T minimum in eV.

| Atom. | BEs | EAs | BEs | BEs | BEs | EAs | SR-1 | SR-2 | SR-3 | R-T Min |
|-------|------|---------------|-------|-------|-------|------------------|-------|-------|--------|---------|
| | GRS | EXPT | MS-1 | EX-1 | EX-2 | Theory | | | | GRS |
| Но | 3.51 | N/A | 0.338 | 0.124 | - | 0.338 [19] | 1.73 | 0.205 | 0.0331 | 3.43 |
| Er | 3.53 | N/A | 0.362 | 0.119 | - | 0.362 [19] | 1.8 | 0.191 | 0.0343 | 3.49 |
| Tm | 3.36 | 1.029 [18] | 1.02 | 0.274 | 0.016 | 0.032 [55] | 1.81 | 0.273 | 0.042 | 3.38 |
| | | | | | | 0.027-0.136 [56] | | | | |
| | | | | | | 1.02 [5] | | | | |
| Yb | 3.49 | <0.003 [17] | 0.485 | 0.204 | 0.028 | 0.036 [57] | 1.76 | 0.231 | 0.039 | 3.51 |
| | | | | | | 0.054 [58] | | | | |
| Lu | 4.09 | 0.346 [24,53] | 1.92 | 0.292 | 0.029 | 0.257 [26] | 2.01 | 0.801 | 0.046 | 4.07 |
| | | | | | | 0.190 [25] | | | | |
| Hf | 1.68 | 0.178 [54] | 0.525 | 0.113 | 0.017 | 0.114 [32] | 0.821 | 0.252 | 0.021 | 1.67 |
| | | | | | | 0.113 [33] | | | | |

4. Summary and Conclusions

We have used our robust Regge-pole methodology wherein the essential electron–electron correlation effects and the vital core polarization interaction are fully embedded to investigate negative ion formation in the large lanthanide atoms Ho, Er, Tm, Yb, and Lu as well as in atomic Hf through the electron elastic TCSs' calculations. The main objective has been the determination of reliable energy positions of the negative ions formed during the collisions, paying particular attention to the ground state anionic formation. We found that the TCSs for these atoms are characterized generally by ground, metastable, and excited negative ion formation; these requiring careful delineation and identification have been used to understand the measured and/or calculated EAs of these complex heavy atoms. We have also found that, essentially, the metastable and/or excited anionic BEs of the formed stable negative ions have been considered by existing measurements and/or calculations to correspond incorrectly to the EAs of the investigated atoms. Thus, the lack of unambiguous definition of the EAs for these atoms has led to the proliferation of confusing EA values in the published literature, see also Ref. [5]. Notably, both the measured EA of Hf [54] and the recent first measurement of the EA of the radioactive Th atom [59] do not correspond to the ground state anionic BEs of the formed negative ions during the collisions.

In conclusion, our calculated anionic BEs of the large lanthanide and Hf atoms can now be used to guide sophisticated theoretical methods such as the Dirac R-matrix, MCHF, MCDF-RCI, etc., to construct the appropriate wave functions and for fine-structure energy calculations. Importantly, here we have determined the theoretically challenging anionic BEs of the ground states of the formed negative ions during the collisions. These should be important for the unambiguous definition and determination of the EAs of the lanthanide and Hf atoms. The remarkable agreement between the recent first measured EA of the highly radioactive At atom [12] and sophisticated theoretical EAs [60] is worth pointing out here. Extensive comparisons of the theoretical EAs are also found in [60]. Indeed, our Regge-pole calculation demonstrated long ago that the EA of atomic At corresponds to the ground state anionic BE consistent with the calculated EAs [61,62]. In addition, it will continue to produce reliable electron elastic TCSs and anionic BEs of complex heavy systems, including fullerene molecules.

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