



Conundrum in Measured Electron Affinities of Complex Heavy Atoms

Research Article

Zineb Felfli and Alfred Z. Msezane*

Department of Physics and Center for Theoretical Studies of Physical Systems,
Clark Atlanta University, Atlanta, Georgia 30314, USA

*Corresponding author: amsezane@cau.edu

Abstract. Low-energy electron scattering from the lanthanide atoms Eu, Tb, Tm, Gd, and Nd including Nb is investigated through calculated electron elastic total cross sections using our robust Regge-pole methodology. The extracted binding energies of the resultant ground and metastable anions formed during the collisions are contrasted with the measured electron affinities (EAs). It is concluded that the measured EAs for these atoms require reinterpretation and new recommended values are presented.

Keywords. Electron affinities; Complex heavy atoms; Regge pole methodology; Anionic binding Energies; Lanthanide atoms

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1. Introduction

Calculated electron affinities (EAs) of atoms provide a stringent test of theoretical methods when the results are compared with those from reliable measurements. A strong motivation for the present investigation is the following: (i) Recently, the electron affinity of atomic Eu was measured to be 0.116 ± 0.013 eV [1]. This value is in outstanding agreement with the values calculated using the Regge pole [2] and MCDF-RCI [3] methods. Previously, the EA of Eu was measured to be 1.053 ± 0.025 eV [4], which agrees very well with the Regge pole value of 1.08 eV [5]. Here we have a conundrum because an atom can have only a single

EA value. (ii) A recent experiment [6] measured the EA of Nb to be 0.917 ± 0.006 eV and obtained generally good agreement with existing theoretical EAs [7, 8] and the previously measured EA of 0.894 ± 0.025 eV [9]. However, our Regge-pole calculated binding energy (BE) of the resultant Nb⁻ anion during the collision 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. (iii) Very recently, the Regge pole methodology has been used to calculate low-energy electron scattering total cross sections (TCSs) for the fullerenes from C₂₀ through C₂₄₀ [10, 11]. The extracted BEs of the resultant fullerene anions from the TCSs matched excellently the measured EAs for the considered fullerenes [12–16]; this is an unprecedented theoretical accomplishment. Importantly, correlation and polarization induced long-lived metastable anionic formations were identified as well.

The quandary arising in both (i) and (ii) above requires clarification as well as resolution. Measured EAs for atomic Eu [1, 4], Tb [17], Tm [18], Nd [17] and Nb [6, 9] are available and, except for Nb, have been compared with other data in [2]. It is noted that ref. [2] did not go sufficiently high in energy to reveal the current structure in the TCSs for these atoms. For Gd there is a great need for data, hence its inclusion here. In this communication we have explored through the total cross sections (TCSs) calculations electron scattering from the complex atoms Eu, Tb, Tm, Gd, Nd and Nb in the electron impact energy range $0.0 \leq E \leq 10.0$ eV. We searched for the appearance of the characteristic dramatically sharp resonances manifesting ground and excited states negative ion formation in these systems. The extracted BEs for the resultant anions are compared with the measured EAs.

2. Method of Calculation

For the near-threshold electron-neutral atom collisions resulting in negative ion formation as resonances, we calculate TCSs using the Mulholland formula [19]. In the form below, the TCS fully embeds the electron-electron correlation effects [20] (atomic units are used throughout):

$$\sigma_{tot}(E) = 4\pi k^{-2} \int_0^\infty Re[1 - S(\lambda)]\lambda d\lambda - 8\pi^2 k^{-2} \sum_n Im \frac{\lambda_n \rho_n}{1 + \exp(-2\pi i \lambda_n)} + I(E). \quad (1)$$

In eq. (1), S is the S -matrix, $k = \sqrt{2mE}$, with 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; its contribution has been demonstrated to be negligible [2].

As in [21] here we consider the incident electron to interact with the fullerene without consideration of the complicated details of the electronic structure of the fullerene itself. Therefore, within the Thomas-Fermi theory, Felfli *et al.* [22] generated the robust potential

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

where Z is the nuclear charge, α and β are variation parameters. Notably, our choice of the potential, eq. (2), is adequate as long as we limit our investigation to the near-threshold energy regime, where the elastic cross section is less sensitive to short-range interactions and is

determined mostly by the polarization tail. Note also that the potential (2) has the appropriate asymptotic behavior, *viz.* $U(r) \sim -1/(\alpha\beta r^4)$ and accounts properly for the crucial polarization interaction at low energies. The advantage of the well-investigated [23–25] potential (2) is that it is a good analytic function that can be continued into the complex plane and has five turning points and four poles that are connected by four cuts there. The presence of the powers of Z as coefficients of r and r^2 in eq. (2) ensures that spherical and non-spherical atoms are correctly 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 potential (2) has been used successfully with the appropriate values of α and β . It has been found that when the TCS as a function of β has a resonance [2], corresponding to the formation of a stable bound negative ion, this resonance is longest lived for a given value of the energy, which corresponds to the EA of the system (for ground state collisions) or the BE of the excited anion. This was found to be the case for all the systems, including fullerenes [10, 11] we have investigated thus far. This fixes the optimal value “ β ” in eq. (2) when the optimum value of $\alpha = 0.2$. The use in this paper of different values of the optimal parameter “ β ” for the ground and the excited atoms is supported by the study of low-energy electron scattering from Cu atoms [26]. There it was demonstrated that the ground and excited states are polarized differently as expected, namely both the dipole polarizability and quadrupole polarizability for the ground and the excited atomic Cu were found to be different.

The details of the numerical evaluations of the TCSs have been described in [20] and further details of the calculations may be found in [27]. In the Regge pole description of low-energy electron scattering from complex atomic, molecular and cluster systems leading to negative ion formation as resonances, Regge trajectories, *viz.* $\text{Im } \lambda$ versus $\text{Re } \lambda$ are the crucial calculated quantities. The Regge trajectories approach close to the atomic/molecular/cluster core and for the methodology to work very well, it is required that we stay close to the real axis of the complex angular momentum (CAM). This implies that $\text{Im } \lambda$ should remain small within the electron impact energy of interest.

For a better understanding and appreciation of the use of the Regge trajectories, here we explain the effective use of the pole λ (CAM) in the Mulholland formula, eq. (1). From the pole λ , where $\text{Re } \lambda$ is an integer and $\text{Im } \lambda \rightarrow 0$, we can determine from eq. (1) shape resonances, long-lived metastable anions and ground state anionic resonances. The effective use of $\text{Im } \lambda \rightarrow 0$ is demonstrated in our paper [2]. Although we have previously referred to Connor [28] for the physical interpretation of $\text{Im } \lambda$, the original interpretation was given by Regge himself [29]. The resonance width in energy is Γ ; $\text{Im } \lambda$ represents its width in angular momentum. The conjugate variable to energy is time, and the lifetime Δt of the resonance satisfies the relation $\Delta t = \hbar/\Gamma$. Similarly, the conjugate variable in angular momentum is angle, and the angle $\Delta\theta$ through which the particle orbits during the course of the resonance satisfies the relation $\Delta\theta = \hbar/\text{Im } \lambda$. For a long lived resonance the lifetime $\text{Im } \lambda$ is small and $\Delta\theta$ is large. For a true bound state,

negative E , $\text{Im} \lambda$ vanishes and the orbit becomes permanent. Obviously, in our calculations $\text{Im} \lambda$ is not identically zero, but small – this can be clearly seen in the figures: the long-lived resonances hardly have a width as opposed to shape resonances for instance (see also our paper ref. [2] for comparison). This means that technically the corresponding state is not a true bound state. This is acceptable, since most negative ions do not have an infinite lifetime, i.e. they eventually decay.

3. Results

Low-energy electron scattering TCSs for ground, metastable and excited states of atomic Eu, Tb, Tm and Gd are displayed in Figure 1. Table 1 summarizes the data for the investigated atoms, viz. Eu, Tb, Tm, Gd, Nd and Nb. At a glance the TCSs for each atom in the figure appear to be complicated. However, these TCSs are readily understood and interpreted if we focus on a single color-coded curve at a time since each color-coded curve in each figure represents scattering from different states resulting in negative ion formation; a ground, metastable and higher excited states. We first focus on the Figure 1(a) which contrasts the ground state TCS (red curve) with the polarization induced metastable TCS (blue curve) and the higher excited state TCS (green curve) for the e-Eu scattering. Generally all the TCSs in the figure are characterized by R-T minima, SRs and dramatically sharp resonances corresponding to the Eu^- anionic formation.

We briefly explain the physics behind the ground state curve of Figure 1(a); the explanation will be applicable to all the results presented in the figure. As the incident electron approaches the ground state Eu atom closer, the atom becomes polarized, reaching maximum polarization manifested through the appearance of the first R-T minimum in the TCS at about 0.86 eV. With the increase in energy, the electron becomes trapped by the centrifugal potential whose effect is seen through the appearance of the SR at about 1.43 eV. As the electron departs from the Eu atom, the strong polarizability of the Eu atom leads to the creation of the second deep R-T minimum at 2.64 eV. At the absolute minimum the long-lived ground state Eu^- anion is formed; its BE is seen to be 2.63 eV. At this R-T minimum the Eu atom is transparent to the incident electron and the electron becomes attached to it forming the stable ground state Eu^- anion. The electron spends many angular rotations about the Eu atom as it decays. The long angular life time of the ground state Eu^- anion is determined by $1/\text{Im} \lambda \rightarrow \infty$, since $\text{Im} \lambda \rightarrow 0$, see eq. (1). Indeed, the appearance of the R-T minima in the electron scattering cross sections in Figure 1, demonstrating the crucial importance of the polarization interaction, manifests that the polarization interaction has been accounted for adequately in the calculation, consistent with the conclusion in [30].

The blue and green curves can be analyzed similarly. Of great importance in the results of Figure 1(a) is that the 0.116 eV and the 1.13 eV resonances agree with the measured EAs [1] and [4], respectively. But these energies correspond to the BEs of the excited/metastable anionic states of the Eu^- anion formed during the collision and not to the EA of Eu. Our calculated BE

of the ground state of the Eu^- anion is 2.63 eV; this value is recommended as the EA of Eu. It is supported by our findings in the e-Au scattering [31] and most recently in the e-fullerenes scattering [10, 11].

Similar analysis for the other atoms applies as in the case of e-Eu scattering. Notably, the anionic BEs of the resonances at 1.20 eV for the e-Tb, Figure 1(b) and at 1.02 eV for the e-Tm, Figure 1(c) scattering agree excellently with the measured EAs [17, 18], respectively. Here too the ground state BEs of the resultant anions are 3.04 eV and 3.36 eV, respectively and these should be taken as the EAs of the Tb and Tm atoms. Figure 1(d) presents calculated TCSs for the unexplored Gd atom; the general structures of the TCSs, particularly the ground state, are similar to those for the Eu, Tb and Tm atoms. The results in Figure 1 are summarized for convenience in Table 1 where they are compared with the data for the other atoms not plotted because of space constrain.

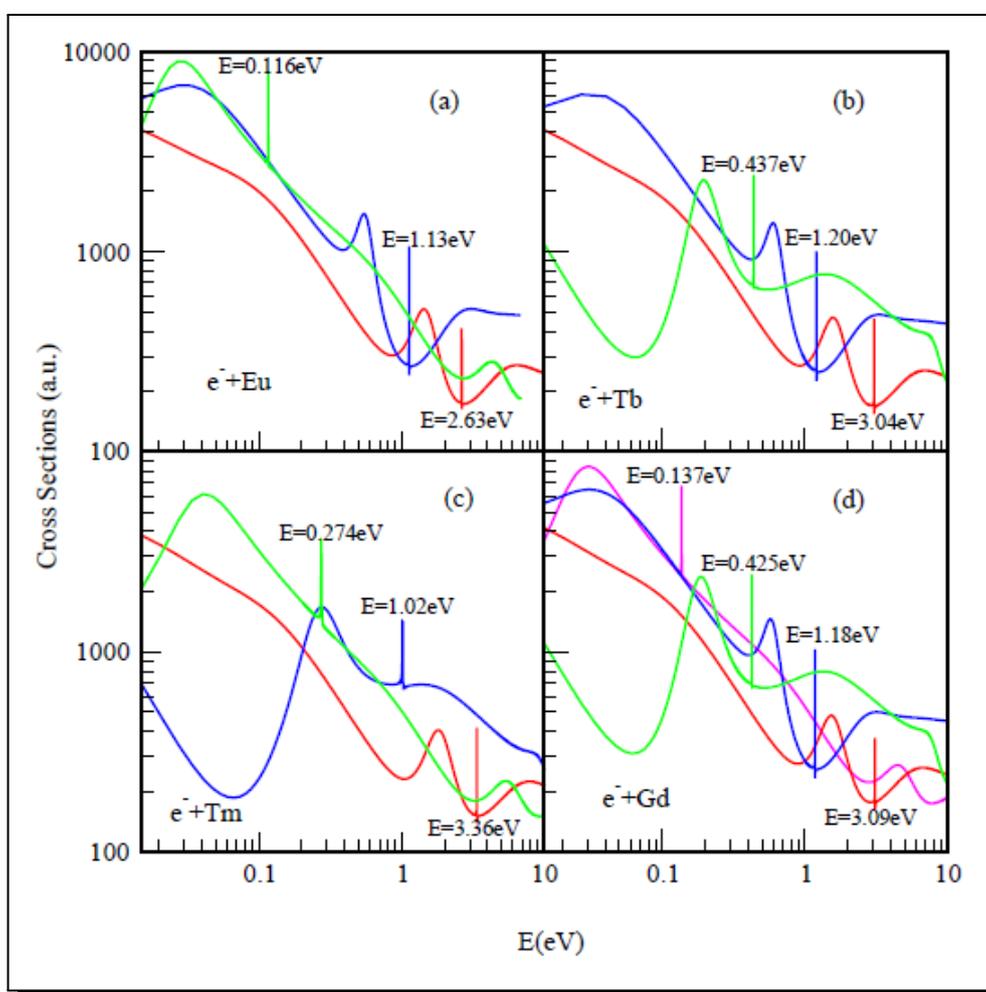


Figure 1. Total cross sections (a.u.) for electron elastic scattering from Eu (a), Tb (b), Tm (c) and Gd (d). The red, blue and green curves represent TCSs for the ground, first and second metastable states, respectively; the pink curve for Gd corresponds to an excited state. The dramatically sharp resonances represent the anionic formation during the collisions

Table 1. Ramsauer–Townsend (R-T) minima and shape resonances (SRs) in the electron scattering TCSs for the atoms Eu, Tb, Tm, Gd, Nd and Nb as well as our binding energies (BEs) of their resultant anions. RT-1 and RT-2 represent respectively the first and second R-T minima. Experimental (Expt.) and previous theoretical EAs are also included; N/A stands for not available

| Atom | RT-1 | SR | RT-2 | BE | EA Expt. | EA Theory |
|------|--------|-------|-------|-------|-------------|------------|
| Eu | 0.859 | 1.43 | 2.64 | 2.63 | 0.116 [1]; | 0.116 [2] |
| | 0.387 | | | 1.13 | 1.053 [4] | 0.117 [3] |
| | N/A | 0.029 | N/A | 0.116 | | 1.08 [5] |
| Tb | 0.917 | 1.57 | 3.05 | 3.04 | >1.165 [17] | |
| | 0.421 | 0.598 | 1.21 | 1.20 | >0.1 [32] | |
| | 0.068 | 0.197 | N/A | 0.437 | | |
| Tm | 1.05 | 1.81 | 3.37 | 3.36 | 1.029 [18] | 0.027– |
| | 0.068 | 0.274 | N/A | 1.02 | | 0.136 [33] |
| | N/A | 0.041 | 3.26 | 0.274 | | |
| Gd | 0.0524 | 1.81 | 3.37 | 3.09 | >0.1 [32] | 0.137 [2] |
| | 0.0351 | 0.279 | N/A | 1.18 | | |
| | 0.0457 | 0.041 | 3.26 | 0.425 | | |
| Nd | 0.0761 | 1.209 | 2.324 | 1.88 | >1.916 [17] | 0.167 [3] |
| | | | | | | 0.162 [2] |
| | N/A | 0.028 | N/A | 0.162 | | |
| Nb | 0.068 | 0.470 | N/A | 0.902 | 0.9174 [6] | 0.82 [7] |
| | | | | | 0.894 [9] | 0.99 [8] |
| | 0.047 | 0.146 | N/A | 0.356 | | |
| | 0.727 | 1.325 | 2.426 | 2.481 | | |

4. Conclusion

The conundrum in the measured electron affinities of the complex heavy atoms Eu, Tb, Tm, Nd and Nb has been clarified and resolved through the scrutiny of the calculated electron scattering TCSs using our robust Regge pole methodology. It is concluded that the measured and previously calculated EAs for the investigated atoms, including the most recent measurements of the EAs of Eu [1] and Nb [6] correspond to the BEs of excited anions of these atoms. We therefore recommend the reinterpretation of the previously measured and calculated EAs of all the investigated atoms in this communication. The newly calculated BEs of the ground state anionic resonances of the Eu, Tb, Tm, Gd, Nd and Nb atoms are recommended as the EAs for these atoms.

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Competing Interests

The authors declare that they have no competing interests.

Authors' Contributions

All the authors contributed significantly in writing this article. The authors read and approved the final manuscript.

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