Strong resonances in low-energy electron elastic total and differential cross sections for Hf and Lu atoms

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Very low-energy electron elastic total and differential cross sections for Hf and Lu atoms exhibit dramatically sharp resonances, whose energy positions are identified with their electron affinities, which are comparable in magnitude with those of Ca and Sr atoms, thus making Hf and Lu atoms suitable candidates for use in the quenching of Rydberg states. The calculation used the recent Regge-pole methodology which embeds the crucial electron correlation effects, with a Thomas-Fermi-type potential incorporating the vital core-polarization interaction. The near-threshold total cross sections for Hf and Lu are contrasted with those of Yb, Ca, and Sr atoms.

Resonances in very low-energy (below about 0.2 eV) electron elastic scattering total cross sections and differential cross sections are currently best investigated theoretically through the Regge-pole methodology since Regge poles, singularities of the S matrix, rigorously define resonances [1,2]. Additional to the important physics that we probe near threshold, such as the Ramsauer-Townsend minima, the Wigner threshold law, and the shape resonances, we also search for dramatically sharp long-lived resonances. These have recently been identified as signatures of the stable bound states of the relevant negative ions formed during the collision [3,4] through careful scrutiny of the imaginary part of the complex angular momentum L. Fundamental to the physical mechanism through which low-energy electron scattering deposits energy and induces chemical transitions is the existence and properties of temporary negative-ion states [5]. Shape resonances, resulting from electrons trapped by the centrifugal barrier, represent such temporary anion states [5].

The great need for understanding and delineation of the near-threshold resonance structures in the total and differential cross sections for tenuously bound atomic systems (those with electron affinities smaller than 0.1 eV), such as the Ca$^-$ ion, is in the context of the quenching of Rydberg states by ground-state atoms with small electron affinities [6,7]. Processes occurring during the collision may be sensitive to the value of electron affinity of the relevant ground-state atom (the electron affinity is numerically equal to the binding energy of the extra electron to the neutral system). These processes are typified by the ion-pair formation cross section, which peaks at a specific value of the principal quantum number n [8], and can be connected to the electron affinity of the target through the multiple-curve-crossing Landau-Zener model [9] or the decay model [10]. These methods have been used to obtain the electron affinities of several molecules, including confirmation of the most accurate value of the electron affinity of Ca [8,11].

Complex and subtle interactions among many diverse electron configurations have made accurate and reliable calculations of the electron affinities for tenuously bound and complex atomic systems very difficult. For such weakly bound negatively charged species, even *ab initio* calculations of the relevant electron affinities are no more reliable than those of simple models [9]. In this Rapid Communication, we have calculated elastic scattering total and differential cross sections for Hf and Lu in the electron impact energy range $0 < E < 0.1$ eV and extracted their electron affinities from the corresponding near-threshold resonances in these cross sections. Finally, we contrasted the calculated total cross sections for Hf, Lu, Yb, Ca, and Sr in the same electron impact energy range. All the results have been calculated using the recently developed Regge-pole methodology [12] with a Thomas-Fermi-type potential which incorporates the vital core-polarization interaction. The success of the Regge-pole methodology, which naturally embeds the essential electron correlation effects, in low-energy electron elastic scattering calculations is attributed mainly to the adequate replacement of the traditionally large and slowly converging expansion over partial waves used when the angular momentum is constrained to integer values by the contribution of a few poles.

Regge-pole analysis is a general method that has been successfully applied to atom-atom [13], electron-atom [3,4,12], and reactive atom–diatom [14,15] scattering through the Mulholland formula [16], to understand the low-energy oscillations in the elastic total cross section [12,13] (atomic units are used throughout):

$$\sigma_{\text{tot}}(E) = 4\pi k^{-2} \int_0^\infty \text{Re}[1 - S(\lambda)]\lambda \, d\lambda$$

$$- 8\pi^2 k^{-2} \sum_n \text{Im} \frac{\lambda_n \rho_n}{1 + \exp(-2\pi i \lambda_n)} + I(E), \quad (1)$$

where S is the scattering matrix, $k = \sqrt{(2mE)}$, with m being the mass, ρ_n is the residue of the S matrix at the nth pole, λ_n and $I(E)$ contains the contributions from the integrals along the imaginary λ axis. We calculated the $I(E)$ contribution to the total cross section and found that this term had neither a qualitative nor a quantitative effect on our results and therefore it will be omitted here. If the angular life of the complex formed during the collision, proportional to $1/\text{Im}(L)$, with $L = \lambda + 1/2$ being the complex orbital angular momentum, is
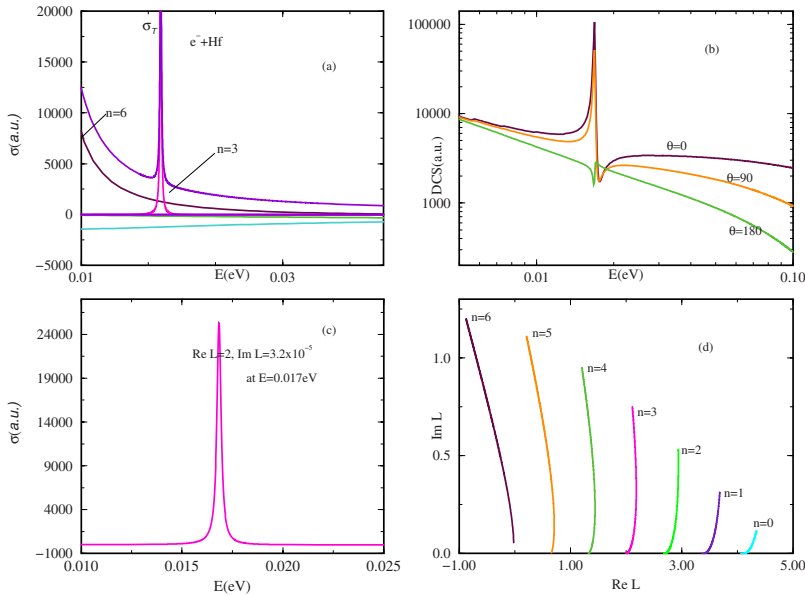
FIG. 1. (Color online) (a) Total, σ_T, and Mulholland partial elastic cross sections, in a.u., for e^--Hf scattering versus E (eV). The $n=6$ Mulholland partial cross section determines the Wigner threshold law. (b) Differential cross sections, in a.u., for elastic e^--Hf scattering versus E (eV) at $\theta=0°$, 90°, and 180° showing the differential cross section maxima at the resonance energy, corresponding to the electron affinity of the Hf atom at 0.017 eV for all the angles. (c) Mulholland contribution to the total cross section, in a.u., for e^--Hf scattering versus E (eV), corresponding to the Regge trajectory that passes near Re $L=2$ at $E=0.017$ eV, and hence responsible for the resonance in the total cross section at that energy. This is a long-lived resonance as seen from its large angular life, proportional to $(\mathrm{Im}\,L)^{-1}$, and corresponds to the electron affinity for the Hf atom. (d) Regge trajectories, viz., Im $L(E)$ versus Re $L(E)$, for the Hf$^-$ ion.

sufficiently long for the complex to return to the forward direction many times, then the condition Im $\lambda_n \ll 1$ must be satisfied [12], and for constructive addition, Re $L \approx 0, 1, 2, \ldots$.

The Thomas-Fermi potential [17] constitutes a suitable choice for use in Eq. (1), since its asymptotic behavior accounts properly for the polarization interaction at very low energies. Here we use the form of the Thomas-Fermi potential well investigated in another context [18]:

$$U(r) = \frac{-Z}{r(1 + aZ^{1/3}r)(1 + bZ^{2/3}r^2)}, \qquad (2)$$

where a and b are adjustable parameters. Clearly, Eq. (2) possesses the appropriate polarizationlike asymptotic behavior, viz., $-1/(abr^4)$.

In our approach, two independent calculations are performed. In the first one, the radial Schrödinger equation is numerically integrated for integer angular momenta to a sufficiently large r, the S matrix is determined, and the total elastic cross section evaluated as the traditional sum over partial waves, with the index of summation being the integer angular momentum. Similarly, the differential cross sections are evaluated using the partial wave sum and the numerical S matrix evaluated for (physical) integer angular momenta. In the second calculation, the S-matrix pole positions and residues in Eq. (1) are obtained following a method similar to that of Burke and Tate [19]. The Schrödinger equation is solved for an electron in the field of the atomic target and numerically integrated for complex values of the orbital angular momentum L and real, positive values of the impact energy E:

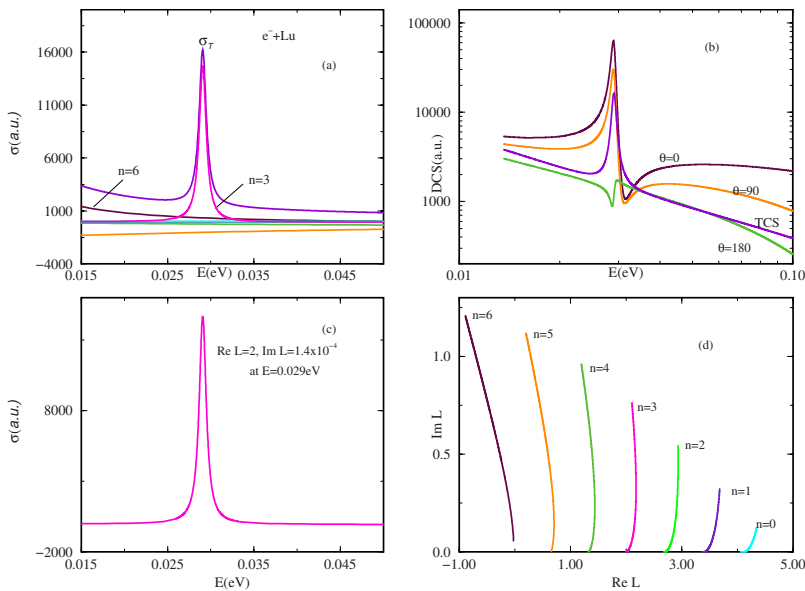$$\psi'' + 2\left(E - \frac{L(L+1)}{2r^2} - U(r)\right)\psi = 0. \qquad (3)$$

We note here that, while we have inadvertently omitted the factor of $1/2$ in the barrier term of Eq. (3) in some of our published papers (related to the present one), it is nevertheless properly accounted for in the calculations. To calculate the S matrix, which is defined by the asymptotic boundary condition of the solution of the Schrödinger equation, we evaluate the two linearly independent solutions of the Schrödinger equation as Bessel functions of complex order; the details are similar to those in [19].

As was demonstrated in [3,4], the calculation of the very low-energy electron scattering cross sections and the subsequent extraction of the electron affinities of the relevant atoms require only the optimized parameters a and b of the Thomas-Fermi potential above. The present results were obtained using the optimal values $b=0.0350$ and 0.0341 for Hf and Lu, respectively, and $a=0.2$ for both atoms.

Figure 1(a) presents the elastic total and the Mulholland partial cross sections (a.u.) versus E (eV) for e^--Hf scattering, demonstrating significant contributions from the $n=6$ and 3 Mulholland partial cross sections. The $n=6$ Mulholland partial cross section also clearly determines the Wigner threshold behavior, while the $n=3$ cross section, which passes near Re $L=2$ with Im $L=3.2\times10^{-5}$ at $E=0.017$ eV, is responsible for the dramatically sharp resonance at that energy. Since the angular life of a state is defined as proportional to $1/(\mathrm{Im}\,L)=1/(3.2\times10^{-5})$, corresponding to a long-lived stable negative ion, the energy position of this resonance is identified with the binding energy of the Hf$^-$ negative ion. The Ramsauer-Townsend minimum in the total cross section occurs at 0.015 eV, which does not correspond to the true Ramsauer-Townsend minimum, determined by the value of E where the $n=6$ Mulholland partial cross section crosses the real axis. It is the interference between the $n=6$ and 3 Mulholland partial cross sections that gives a nonzero Ramsauer-Townsend minimum to the total cross section. Figure 1(c) shows an expanded view of the sharp resonance of Fig. 1(a).

Figure 1(b) displays the elastic differential cross sections for e^--Hf scattering at the scattering angles $\theta=0°$, 90°, and 180°, showing the sharp resonance at $\theta=0°$ and 90° when $E=0.017$ eV. This resonance is still visible at 180°, but to a lesser extent. Clearly, the binding energy of the Hf$^-$ ion can

FIG. 2. (Color online) (a) Total, σ_T, and Mulholland partial elastic cross sections, in a.u., for e^--Lu scattering versus E (eV). The $n=6$ Mulholland partial cross section determines the Wigner threshold law. (b) Differential cross sections, in a.u., for elastic e^--Lu scattering versus E (eV) at $\theta=0°$, 90°, and 180° showing the maxima in the differential cross sections at the resonance energy, corresponding to the electron affinity of the Lu atom at 0.029 eV for all the angles. (c) Mulholland contribution to the total cross section, in a.u., for e^--Lu versus E (eV), corresponding to the Regge trajectory that passes near Re $L=2$ at $E=0.029$ eV, and hence responsible for the resonance in the total cross section at that energy. This is a long-lived resonance as seen from its large angular life proportional to $(\mathrm{Im}\,L)^{-1}$ and corresponds to the electron affinity for the Lu atom. (d) Regge trajectories, viz., Im $L(E)$ versus Re $L(E)$, for the Lu$^-$ ion.

also be determined through the measurement of the electron elastic differential cross sections at these angles. Figure 1(d) gives the Regge trajectories, namely, Re L versus Im L, demonstrating that indeed Re $L=2$ is responsible for the very sharp resonance at 0.017 eV, because of its closeness to an integer.

The corresponding results for the e^--Lu scattering covering the energy range $0 < E \leqslant 0.1$ eV are shown in Fig. 2. Figure 2(a) displays the sharp dominant resonance at 0.029 eV with Re $L=2$, corresponding to the formation of a stable bound state of the Lu$^-$ ion. The Wigner threshold behavior is determined by the $n=6$ Mulholland contribution as in the case of the e^--Hf scattering, while the Ramsauer-Townsend minimum in the total cross section appears at about 0.025 eV. Again here, as in the case of e^--Hf scattering, the interference between the $n=3$ and 6 Mulholland partial cross sections gives rise to a nonzero Ramsauer-Townsend minimum.

Figure 2(c) presents an expanded view of the resonance at 0.029 eV, with Im $L=1.4 \times 10^{-4}$, indicating a long-lived stable state of the Lu$^-$ ion. The differential cross sections for e^--Lu scattering at $\theta=0°$, 90°, and 180° are presented in Fig. 2(b), all exhibiting a maximum at 0.029 eV. This corresponds as before to a bound state of the Lu$^-$ ion. Also plotted for comparison is the total cross section. We note that the total cross section follows very closely the backward scattering differential cross section, except in the region of the resonance. This demonstrates that very low-energy electron scattering can be investigated reasonably well through the backward scattering differential cross sections. Figure 2(d) presents the Regge trajectories, i.e., Re L versus Im L, demonstrating that indeed Re $L=2$ is responsible for the very sharp resonance at 0.029 eV, because of its closeness to an integer.

In Table I the present electron affinities for Hf and Lu atoms are compared with those from laser photoelectron spectroscopy [20,21] and other studies [22–24]. For Lu the existing electron affinities vary from a value of 0.1 eV through 0.346(14) eV, while ours is 0.029 eV. Clearly, our

electron affinity is about an order of magnitude lower than the lowest available value. For Hf the latest measured electron affinity value is >0 [21], while that from accelerator mass spectroscopy [24] is >0.1 eV and the present value is 0.017 eV. Again here our value is between the two experimental limits [21,24].

We note that the theoretical results [22,23] are very sophisticated Dirac-Hartree-Fock density functional theory and relativistic coupled cluster theory with single and double excitations, respectively. The disturbing very large discrepancies among the existing experimental electron affinities on the one hand, and between the measured and the theoretical results on the other hand, call for a concerted effort to obtain reliable electron affinities for these atoms. Our results, which we believe to be reliable, represent a significant step toward obtaining accurate theoretical electron affinities for heavy elements. Work is almost complete on near-threshold resonance structure investigations in electron–lanthanide atom scattering and will be presented soon.

To provide a sense of the relative positions and magnitudes of the resonances in the total cross sections for the e^--Hf and e^--Lu scattering, we have compared in Fig. 3 the present results with the calculated total cross sections for Ca, Sr [3], and Yb. Although the Ca$^-$ ion has the second lowest binding energy, its resonance is the broadest. Interestingly, among the heavy atoms the Hf$^-$ ion has the lowest binding energy, followed by that for Yb$^-$ and Lu$^-$ ions in this order. The Sr$^-$ ion has the highest binding energy and its resonance

TABLE I. Present electron affinities (eV) of Hf and Lu atoms compared with those from laser photoelectron spectroscopy (LPES) and other studies.

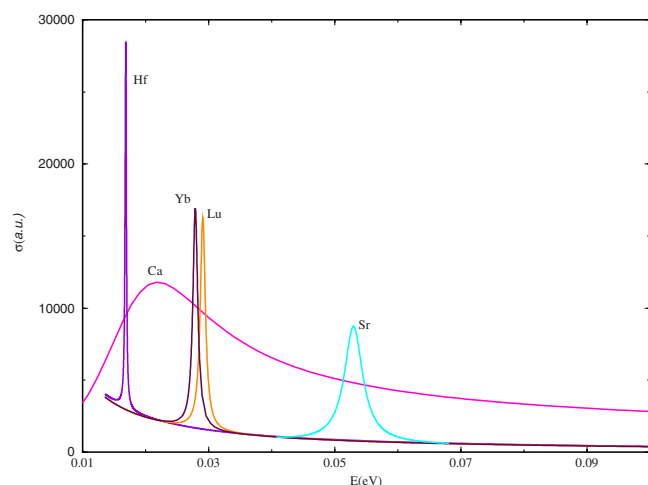| Atom	Present	LPES	Other studies
Lu	0.029	0.346(14) [20]	0.190(110) [22]
			0.257 [23]
			>0.1 [24]
Hf	0.017	>0 [21]	>0.1 [24]

FIG. 3. (Color online) Comparison of the electron elastic total cross sections for Hf, Lu, Yb, Ca, and Sr atoms near threshold. Note that Hf has the lowest electron affinity of the five atoms and the sharpest resonance.

is broader than that of any one of the three lanthanides. Clearly, the widths of the resonances decrease as we move from Ca $[Ar]4s^2$ through Sr $[Kr]5s^2$ through Lu $[Xe]4f^{14}5d^16s^2$, Yb $[Xe]4f^{14}6s^2$, and Hf $[Xe]4f^{14}5d^26s^2$. We note that the order follows no clear logical prescription.

The recent Regge-pole methodology has been used together with a Thomas-Fermi-type potential to explore very low-energy electron elastic scattering from Hf and Lu atoms.

Dramatically sharp resonances are predicted in the total cross sections for both e^--Hf and e^--Lu scattering, whose energy positions are identified with their electron affinities. The strength of the Regge-pole methodology lies in its extraction of the electron affinities from the near-threshold characteristic resonances, without prior knowledge of them. The present electron affinities for both Hf and Lu are among the lowest determined to date. Thus, they may be suitable candidates for the quenching of Rydberg states with ground state atoms, with the subsequent determination of their electron affinities [6,8].

Finally, we have further tested the predictive power of the Regge-pole methodology by calculating the near-threshold electron elastic scattering cross sections for Nd. From the resonance structure in the total cross section we extracted the value of 0.162 eV for the electron affinity of Nd, in excellent agreement with the most recently calculated value of 0.169 eV [25]. This further gives credence to the predictive power of the Regge-pole methodology when used with the appropriate core-polarization interaction to extract electron affinities for complicated and tenuously bound atomic systems without *a priori* knowledge of the electron affinity.

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