

Calculations of Hf^- electron affinity and photodetachment partial cross sections

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Abstract. Relativistic configuration interaction calculations show Hf^- has only one bound state, $5d^26s^26p$ $J=5/2$. The electron affinity is determined to be 0.114 eV. Using a fixed photon energy of 2.34 eV (~ 532 nm), the partial cross sections to energetically accessible neutral thresholds are calculated. It is found that the 6p detachment into the Hf I ground state $5d^26s^2$ 3F_2 dominates the photoelectron spectrum. The effect of resonances is included using Mies's formalism.

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1. Introduction

Negative ions are important in many branches of physics, ranging from astrophysics, plasma physics to surface physics, etc. An important quantity for negative ions is the electron affinity (EA). Experimentally, the electron affinity can be measured by the technique of laser photodetachment electron spectroscopy (LPES), laser photodetachment threshold spectroscopy (LPTS), accelerator mass spectrometry (AMS), and photodetachment microscopy, etc. Computationally, EA can be calculated by finding the energy difference between the ground states of the negative ion and the neutral atom. The accurate prediction for EA requires the careful treatment of correlation effects, which are the dominant mechanism in binding the excess electron.

Hafnium is the transition metal (TM) atom at the right edge of the Lanthanides. It is one of the few TM elements whose EA has not been determined [1]. Several experimental investigations have been made for the EA of Hafnium [1, 2, 3, 4], providing some lower limits for its EA: ≥ 0.1 eV [1] based on AMS, > 0 eV [4] based on LPES. On the theory side, no calculation has yet been conducted to help further determine the EA.

The output of a LPES experiment [2, 4] is the photoelectron spectrum, which gives the electron counts as a function of photoelectron energy. Analysis of this spectrum will be greatly facilitated with the information about the negative ion, such as bound state configurations, their number, and binding energies. A straightforward way would be to compare the spectrum with the calculated plot of partial cross section versus photoelectron energy. It is known [5] that at the magic angle (when $P_2(\cos\theta) = 0$), the electron counts or electron intensity is directly proportional to the partial cross section σ . We were thus motivated to perform a partial cross section calculation for Hf^- , in addition to the calculation of its EA.

Our calculation will help establish the EA for Hafnium, or at least its lower limit. The calculation is also our initial step toward incorporating the effect of resonances in the cross section calculation, within the formalism of configuration interaction in the continuum.

2. Methodology

2.1. Bound States

The method employed is the Relativistic Configuration Interaction (RCI) formalism. The details of this method can be found elsewhere [6]. Briefly, a Dirac-Coulomb-Breit hamiltonian is employed. The basis set is made up of reference functions and correlation functions. The reference functions represent the configurations of interest, e.g., $\text{Hf I } 5d^26s^2$. Their one-electron radial functions are numerical solutions [7] of the Multi-Configuration Dirac-Fock (MCDF) equations. The correlation functions represent the correlation configurations, obtained by replacing one or two electrons in the reference configuration(s). When making the replacements, the subshells that are not occupied in

the reference configuration(s) are represented by virtual orbitals, vl . The radial function for each virtual orbital is in the form of the relativistic screened hydrogenic function with one adjustable parameter, the effective charge, which is determined during the energy variational process. For each symmetry (l), usually at least two virtuals are needed to capture the compact portion of the whole Rydberg series $n'l$ ($n' > n$, nl being the highest subshell that is occupied in the reference configurations) and the continuum.

In this work, the wave function for all the bound states are constructed using the RCI method.

2.2. Photodetachment Cross Section

The following process represents the photodetachment of a negative ion by a photon:



where A^- represents the initial bound state of the negative ion. The righthand side is the final continuum state, which consists of the neutral atom A plus a detached free electron. Its wave function is constructed as follows.

We assume the wave function of the free electron takes the same angular form as that of a bound electron. Its radial function is numerically generated using a modified version [8] of the relativistic continuum wave solver code of Perger *et al.* [9, 10]. The wave function of a continuum electron thus prepared is then coupled to the RCI wave function for the neutral atom A [8], following the frozen core approximation, to generate the wave function for the continuum state.

The cross section is calculated using [11]:

$$\sigma = 4\pi^2\alpha a_0^2 \frac{df}{dE} = 8.067 \times 10^{-18} \frac{df}{dE} \text{ (cm}^2\text{)}, \quad (2)$$

where α is the fine-structure constant, a_0 is the radius of the first Bohr orbit, $\frac{df}{dE}$ is the differential oscillator strength for the electric dipole (E1) transition from the initial bound state to the final continuum state. The $\frac{df}{dE}$ is evaluated using a modified version [12] of our code for bound states [13], the core of which is to compute the transition matrix element. The codes include the effects of non-orthonormality (NON).

Resonances are known to be responsible for some pronounced features in the absorption spectrum. In this work, the impact of some potentially important resonance configurations has been incorporated using Fano's [14] and Mies's [15] theory. Suppose for an atomic system, some discrete states ϕ_n are embedded in a range of continuum states $\psi_{\beta E}$. The CI matrix element between them is,

$$(\phi_n | H - E | \psi_{\beta E}) = V_{n\beta} \quad (3)$$

The total wave function should now bear the form of a linear combination of the two sets of states:

$$\Psi_{\alpha E} = \sum_n B_{\alpha n} \phi_n + \sum_{\beta} \int_0^{\infty} dE' C_{\alpha\beta} \psi_{\beta E'}, \quad (4)$$

where $B_{\alpha n}$ and $C_{\alpha\beta}$ are mixing coefficients. The explicit expression for this wave function, together with the transition matrix element were first proposed by Fano [14] for several cases, i.e., one discrete state and one continuum, one discrete state and two continua, many discrete states and one continuum. The expression for the general case of multiple discrete states with multiple continua was provided later by Mies [15] and Davis *et al* [16]. The Mies's solution allows one to calculate the partial cross section to an individual channel. The main results from Mies's work used in the calculation are summarized below.

In solving for B 's and C 's, a symmetric matrix F is introduced,

$$F_{nm}(E) = E_n \delta_{nm} + P \int_0^\infty dE' \sum_\beta \frac{V_{n\beta} V_{m\beta}}{E - E'}. \quad (5)$$

and is then diagonalized,

$$F = \tilde{G} \varepsilon G. \quad (6)$$

The eigenvalues ε_n give the ‘‘positions’’ of the transformed discrete states,

$$\Phi_n^{shift} = \sum_m G_{nm} \phi_m. \quad (7)$$

Accordingly, the CI matrix V is transformed into:

$$v_{n\beta}(E, E') = \sum_m G_{nm} V_{m\beta}. \quad (8)$$

With the definition of a ‘‘modified resonance state’’,

$$\Phi_n = \Phi_n^{shift} + \sum_\beta P \int_0^\infty dE' \frac{v_{n\beta} \psi_{\beta E'}}{E - E'}, \quad (9)$$

the total wave function is solved to be:

$$\Psi_{\alpha E} = \sum_\beta Z_{\alpha\beta} (\psi_{\beta E} + \sum_n \frac{v_{n\beta}}{E - \varepsilon_n} \Phi_n). \quad (10)$$

where Z is the normalization matrix, obtained by finding the inverse of the matrix $I + iK$, with

$$K_{\alpha\beta}(E) = \sum_n \frac{\pi v_{n\alpha} v_{n\beta}}{E - \varepsilon_n}. \quad (11)$$

The principle integral in eqn. (9) represents the admixture of the continuum states into the discrete state. This admixture is neglected in our calculation, as does Martins [17].

The transition matrix element for excitation from the initial bound state Ψ_i into the continuum state, or channel α is:

$$t_\alpha^c = (\Psi_{\alpha E} | T | \Psi_i). \quad (12)$$

with T the electric dipole transition operator.

3. Calculation

3.1. Electron Affinity

The electron affinity (EA) is calculated by doing separate calculations for the ground states of Hf I and Hf^- , then finding their energy difference. Since it is the energy difference that counts, the two ground states must be correlated with the same type of electron-replacements and to the same extent (in terms of the number of virtual orbitals and saturation of the radial basis sets). Replacements which make similar contribution to the correlation energy in both states will not contribute to EA and are therefore left out.

3.1.1. Hf I Ground State The ground state of Hf I is $5d^26s^2\ ^3F_2$. The radial functions for 1s, 2s, \dots , 5d, 6s, 6p are generated by doing a MCDF calculation including $5d^26s^2$, $5d^36s$, $5d^4$ and $5d^26p^2$. The average radius of 5d and 6s differs by ~ 1.4 a.u, suggesting at least two sets of virtuals will be needed in a valence calculation. The first set is for the one- and two- electron replacements of the valence electron 5d and 6s. The second set is to make up any deficiency in capturing correlations involving a 5d electron, like $5d6s \rightarrow vp^2$, $vlv(l+2)$. The maximum symmetry of the virtuals included is $l = 5$.

Intermediate calculations show both $5d^36s$ and $5d^26p^2$ have a significant weight (> 0.04) in the ground state. Though they represent levels higher in the spectrum, their correct positioning relative to the $5d^26s^2$ level will help lower the latter. Therefore, they are correlated similarly to $5d^26s^2$. Another correlation configuration, $5d^26svd$, has a large (magnitude ~ 347 meV) correlation energy in the $5d^36s$ level. However, correlating it makes only a small change (≤ 50 cm^{-1}) in the relative position of $5d^36s$.

To assess the quality of the RCI wave function, the Landé g value is calculated and found to be 0.691. This is in good agreement with the experimental value of 0.695 [18], indicating the LS compositions are accurately mixed in the RCI wave function.

3.1.2. Hf^- Bound State The negative ion can be formed by attaching one more electron to an unfilled subshell or unoccupied subshell. Given the Hf I ground state configuration $5d^26s^2$, there are two possible candidates for Hf^- , $5d^36s^2$ and $5d^26s^26p$. Only the latter is found to form a Hf^- bound state.

Dirac-Fock calculations using Desclaux's code [7] show the lowest $5d^26s^26p$ state has $J=5/2$. Not surprisingly, there is a large mixing of $5d^36s6p$, $5d^26p^3$ in it, each being a 6p attachment to the large components $5d^36s$, $5d^26p^2$ in the Hf I ground state. The radial functions for 1s, 2s, \dots , 5d, 6s, 6p are numerically generated by the MCDF calculation including $5d^26s^26p$, $5d^36s6p$, $5d^46p$ and $5d^26p^3$.

As for Hf I, two sets of virtuals are introduced in the radial basis set. They describe correlations from replacing one or two valence electrons of 5d, 6s or 6p. In addition to $5d^26p^3$ and $5d^36s6p$, $5d6s6p^2vf$ is found to have a non-trivial weight (> 0.001) and large correlation energy (absolute value > 0.2 eV). However, after the second set of virtuals is added, these three configurations show a different amount of decrease in both weight

and correlation energy. To recover the “loss”, they are correlated with replacements that contribute more than 20 meV in magnitude to the correlation energy. This helps lower the Hf^- ground state by ~ 72 meV. The above valence calculations produce an EA of 0.158 eV for Hf^- . The dominant LS terms of Hf^- ground state are $^4\text{G}_{5/2}$ (68%) and $^2\text{F}_{5/2}$ (27%).

Similar calculations are then conducted for other J 's of $\text{Hf}^- 5d^26s^26p$, but none of them seems to be bound. For example, $J=3/2, 7/2$ is 0.392 eV, 0.423 eV above $J=5/2$, thus unbound by 0.234 eV, 0.265 eV respectively.

Next, the possibility of a bound $\text{Hf}^- 5d^36s^2$ state is explored. Valence calculations show the lowest $\text{Hf}^- 5d^36s^2$ state has $J=3/2$, and it is about 1.5 eV below the $\text{Hf I } 5d^36s \ ^5\text{F}_5$ level and 0.7 eV above the Hf I ground state. Separate calculations indicate correlation involving the shallow core subshell 5p has no significant contribution to make up the 0.7 eV difference. Based on these observations, we conclude $5d^36s^2$ does not form a bound state.

3.1.3. Electron Affinity The 0.158 eV EA obtained above is from valence calculation only. To take into account the correlation contribution from the shallow core of 5s, 5p, we compute separately (thus using a much smaller basis set) the correlation energy of one-electron replacement of 5p, two-electron replacements of 5s(5p, 5d, 6s), 5p(5d, 6s, 6p), and $5p^2$. These correlations were not included in the final wave function due to the following concerns. First, the size of the RCI energy matrix would have expanded well beyond the current 20 K limit [20]. Second, these replacements preferentially correlate the $5d^26s^2$ state in Hf I and $5d^26s^26p$ in Hf^- . The subtotal of their correlation energy is more than 5 eV, much larger than the correlation energy of about 2 eV at the valence stage. If added, the balanced mixing of those important configurations would be disturbed. Though the correct mixing could in principle be restored by correlating those configurations similarly, the greatly expanded size of the RCI matrix would have made this impractical. On the other hand, the separate calculations have the advantage of providing a more accurate estimate of the size of the specific correlation. Since we are dealing with a smaller basis set, we can begin with the two sets of virtuals in the valence calculation, then introduce additional virtuals to well saturate the radial space. As a check, we have computed that, for the 5p5d replacement, the estimated contribution to EA by these separate calculations can be achieved in the big calculation when more virtual orbitals are introduced.

Our calculations show the correlation involving a 5s subshell has a trivial contribution to the EA and therefore is neglected. The 5p correlation makes a net contribution of about -0.044 eV. This lowers the 0.158 eV at the valence stage to about 0.114 eV. This value falls within the limits set by both experiments: ≥ 0.1 eV [1], > 0 eV [4].

3.2. Photodetachment Partial Cross Sections

The photon energy is fixed to be 2.34 eV (about 532 nm), which is what was used in the LPES experiment [3].

3.2.1. Neutral Thresholds For the photon energy given, the accessible neutral thresholds are listed in table 1. Omitted in the table are three lowest 5d³6s levels. These thresholds correspond to a multi-electron process from the initial state Hf⁻ 5d²6s²6p and are not expected to produce major features in the photoelectron spectrum [2].

Table 1. Energy value (in eV) and Landé g value of accessible Hf I neutral thresholds in photodetachment of Hf⁻ at given photon energy 2.34 eV.

Threshold	LS designation ^a	Energy value ^a	Expt. Landé g ^b	RCI Landé g
5d ² 6s ²	³ F ₂	0	0.695	0.691
	³ F ₃	0.292	1.083	1.083
	³ F ₄	0.566	1.240	1.245
	³ P ₀	0.685	0.000	0
	¹ D ₂	0.699	1.165	1.138
	³ P ₁	0.815	1.500	1.500
	³ P ₂	1.114	1.300	1.338
	¹ G ₄	1.306	1.008	1.005
5d6s ² 6p	³ F ₂	1.303	NA	0.820
	³ D ₁	1.738	0.55	0.540
	¹ D ₂ ^c	1.790	0.89	0.916
	³ F ₃	1.803	1.08	1.097
	³ D ₂	2.004	1.17	1.138

^a From NIST database [19], converted from cm⁻¹ to eV.

^b From Moore's tabulation [18]. The 5d6s²6p levels were incorrectly designated as 5d²6s6p in [18]. As a result, the configurations and the Landé g values were mismatched. Here, this has been corrected by matching the LS designations and energy values in [18] to those in [19].

^c This level was labeled as ³F₂ by Moore [18], which is wrong as shown in [19] and by our RCI calculation.

The wave function for each neutral threshold is generated by doing a valence RCI calculation. In the even parity 5d²6s² states, 5d³6s and 5d²6p² usually have a large mixing and are correlated with large one- and two- electron replacements. In the odd parity 5d6s²6p states, there is a large mixing of 19% – 32% of 5d²6s6p, depending on the specific J . The two configurations have been correlated similarly in the wave function. The Landé g values are calculated to check the quality of the wave functions. As can be seen from table 1, the agreement with Moore's tabulation [18] is good.

3.2.2. Resonance Candidates It is obvious that the resonances should have a non-zero transition matrix element with the Hf^- ground state. In other words, they should be reached by electric dipole transition from $\text{Hf}^- 5d^26s^26p$. Therefore, $5d^36s^2$, $5d6s^26p^2$ and $5d^26s6p^2$ are possible resonance candidates (ϕ_n 's).

While the above resonance configurations produce a large number of configuration state functions, we select only the most promising ones based on eqn. (10). First, they must have the right J value. Given the initial state to be $\text{Hf}^- J=5/2$, the selection rule allows only $J' = 3/2, 5/2$ and $7/2$ for the final state in an E1 transition. Secondly, they need to have a large transition matrix element to produce a significant contribution. Thirdly, their ‘‘positions’’ (ε_n) must not be too far away from E , the photon energy. In the calculation, the deviation from the photon energy is within about 1 eV.

For each allowed J' , a valence RCI calculation is conducted for reference configurations $5d^36s^2$, $5d6s^26p^2$ and $5d^26s6p^2$. The details of the Dirac-Fock radials are mentioned in the next subsection. The $5d^36s^2$ states are positioned relative to the neutral $5d^36s \ ^5F_5$ state first, while the $5d6s^26p^2$ and $5d^26s6p^2$ states are positioned relative to the neutral $5d6s^26p \ ^3F_2$ state. Their positions relative to the Hf^- ground state are then calculated using the Hf I spectrum and EA. Table 2 gives a list of the final candidates and their leading LS terms.

Table 2. Candidates for the resonance states of Hf^-

J	Dominant configuration(s) & leading ($\geq 20\%$) LS term(s)	Position ^a (eV)	Dipole matrix element	
			Babuskin gauge	Coulomb gauge
3/2	$5d6s^26p^2 \ ^2D$	2.081	-7.213×10^{-4}	-6.053×10^{-4}
	$5d^36s^2 \ ^2D, \ ^2P$	2.434	-3.191×10^{-4}	-2.415×10^{-4}
	$5d^26s6p^2 \ ^4F; 5d6s^26p^2 \ ^2D$	3.503	1.074×10^{-3}	9.029×10^{-4}
5/2	$5d6s^26p^2 \ ^2F$	2.177	-2.151×10^{-4}	-2.384×10^{-4}
	$5d6s^26p^2 \ ^2D$	2.682	-1.784×10^{-4}	-1.514×10^{-4}
	$5d^26s6p^2 \ ^4G$	3.430	-1.526×10^{-4}	-1.399×10^{-4}
7/2	$5d6s^26p^2 \ ^4D, \ ^2F$	2.041	3.192×10^{-4}	3.897×10^{-4}
	$5d6s^26p^2 \ ^2G$	2.323	-6.385×10^{-4}	-7.775×10^{-4}
	$5d^26s6p^2 \ ^4H$	3.184	-1.476×10^{-3}	-1.549×10^{-3}

^a Energy value relative to Hf^- ground state, no shift by the continua is included.

3.2.3. Partial Cross Section For the photon energy (2.34 eV) given, Hf^- can undergo both 6p detachments and 5d detachments. The relativistic channels in the 6p detachments are $(5d^26s^2)\varepsilon_{s_{1/2}}, \varepsilon_{d_{3/2,5/2}}$. The relativistic channels in the 5d detachments are $(5d6s^26p)\varepsilon_{p_{1/2,3/2}}, \varepsilon_{f_{5/2,7/2}}$. In the independent channel approximation, each

relativistic channel is computed separately, without mixing from other channels. The differential oscillator strength is calculated first using our own code [12]. Then it is converted to cross section using eqn. (2). The partial cross section to each neutral threshold is obtained by adding up the cross sections of all the corresponding relativistic channels. The results are shown in table 3, the first number in each entry.

To take into account the effect of resonances, Mies's formalism is employed. This involves evaluating the CI matrix element between a resonance state and an unperturbed continuum state (see eqn. (3)) and tabulating it as a function of the photon energy E . The energy E is removed from $V_{n\beta}$ by excluding the equivalent basis functions that dominate the continuum states. For example, in the wave function for Hf⁻ 5d³6s² (ϕ_n), the correlation function 5d²6s² vs , 5d²6s² vd are omitted because they are equivalent to 5d²6s² εs , 5d²6s² εd in the continuum state ($\psi_{\beta E}$).

The NON between the radial functions in ϕ_n and $\psi_{\beta E}$ is treated partially. We assume the noncorresponding radials are orthogonal. The corresponding radial functions are treated in a partially common way. Specifically, for the CI matrix elements involving the 5d6s²6p channels, the resonances and the neutral thresholds share a common set of Dirac-Fock radial functions taken from Hf I 5d6s²6p ¹D₂, and a common first set of virtual orbitals consisting of vs , vp , vd , vf and vg , with vp 's being the 6p's taken from 5d6s²6p² $J=5/2$. The second set of virtuals are optimized separately to the specific state. For the CI matrix elements involving the 5d²6s² channels, the neutral thresholds and the resonances have their own Dirac-Fock radial functions except for a common 6p radials. However, they share a common first set of virtuals, with vs being actually the 6s radial taken from 5d³6s² $J=5/2$, vp 's being the 6p's from 5d6s²6p² $J=5/2$. The second set of virtuals are again optimized separately. In all the cases, the radial overlaps between the corresponding radials are larger than 0.90.

For each $V_{n\beta}$, the angular structure of all the R^k and I integrals are generated by the RCI code [20]. The radial integrals are then evaluated using the continuum integral solver code of Perger *et al.* [21]. A logarithmic-like grid is used when tabulating the $V_{n\beta}$'s as a function of photon energy. Following the Mies's formalism, it is then straight forward to obtain the normalization matrix $Z_{\alpha\beta}$, $v_{n\beta}$ and the ε 's. The electric dipole matrix element of the resonance state, $(\phi_n|T|\Psi_i)$, is extracted from the bound state code [13]. These are then plugged into eqn. (10) and eqn. (12) to obtain the total dipole matrix element for channel α , i.e., t_α^c (eqn. (12)). From there, the partial cross section is calculated.

4. Results

RCI calculations show Hf⁻ has only one bound state, 5d²6s²6p (68% ⁴G_{5/2}, 27% ²F_{5/2}) which is a 6p attachment to the Hf I ground state. The electron affinity is 0.114 eV. The result for the partial cross sections from independent channel approximation and the Mies's theory are listed in table 3.

In the independent channel approximation, the dominantly strong detachment is

Table 3. Hf^- partial photodetachment cross sections at photon energy 2.34 eV

Threshold	Gauge	$J=3/2$ ^a	$J=5/2$ ^a	$J=7/2$ ^a	Total ^a
5d ² 6s ² ³ F ₂	Babuskin	1.7479, 2.3584	6.2278, 5.6792	15.3724, 14.7353	23.3481, 22.7729
	Coulomb	1.3088, 1.6676	5.9387, 5.3212	15.7227, 15.3030	22.9702, 22.2918
³ F ₃	Babuskin	0.0037, 2.6014	0.0061, 0.0682	0.0053, 0.0856	0.0151, 2.7552
	Coulomb	0.0026, 1.7707	0.0050, 0.0500	0.0058, 0.1320	0.0134, 1.9527
³ F ₄	Babuskin	0.0286, 0.0645	0.0211, 0.6868	0.0305, 0.0534	0.0802, 0.8047
	Coulomb	0.0204, 0.0435	0.0189, 0.5590	0.0240, 0.0744	0.0633, 0.6769
³ P ₀	Babuskin	0.0016, 0.0701	0.0000, 0.0164	0.0000, 0.0000	0.0016, 0.0865
	Coulomb	0.0001, 0.0543	0.0000, 0.0151	0.0000, 0.0000	0.0001, 0.0694
¹ D ₂	Babuskin	0.0231, 0.9003	0.1025, 0.1099	0.2672, 0.3121	0.3928, 1.3223
	Coulomb	0.0170, 0.6245	0.0699, 0.0648	0.2096, 0.2614	0.2965, 0.9507
³ P ₁	Babuskin	0.0002, 0.4997	0.0025, 0.0068	0.0080, 0.0075	0.0107, 0.5140
	Coulomb	0.0005, 0.3319	0.0012, 0.0058	0.0060, 0.0055	0.0077, 0.3432
³ P ₂	Babuskin	0.0006, 0.8773	0.0042, 0.0632	0.0066, 0.0264	0.0114, 0.9669
	Coulomb	0.0007, 0.6042	0.0024, 0.0563	0.0039, 0.0478	0.0070, 0.7083
¹ G ₄	Babuskin	0.0473, 0.2703	0.0465, 0.0675	0.0753, 2.6571	0.1691, 2.9949
	Coulomb	0.0245, 0.1680	0.0250, 0.0406	0.0480, 3.7868	0.0975, 3.9954
5d6s ² 6p ³ F ₂	Babuskin	0.0118, 0.2065	0.0845, 0.1007	0.2243, 0.3184	0.3206, 0.6256
	Coulomb	0.0315, 0.2507	0.1021, 0.1567	0.2282, 0.3784	0.3618, 0.7858
³ D ₁	Babuskin	0.0048, 0.0143	0.0017, 0.0043	0.0123, 0.0056	0.0188, 0.0242
	Coulomb	0.0049, 0.0310	0.0011, 0.0018	0.0083, 0.0032	0.0143, 0.0360
¹ D ₂	Babuskin	0.0005, 0.2564	0.0011, 0.1221	0.0031, 0.2181	0.0047, 0.5966
	Coulomb	0.0021, 0.1861	0.0013, 0.0958	0.0014, 0.3672	0.0048, 0.6491
³ F ₃	Babuskin	0.0010, 0.3257	0.0012, 0.0457	0.0023, 0.2034	0.0045, 0.5748
	Coulomb	0.0001, 0.2354	0.0010, 0.0581	0.0002, 0.3511	0.0013, 0.6446
³ D ₂	Babuskin	0.0000, 0.0023	0.0003, 0.0012	0.0001, 0.0053	0.0004, 0.0088
	Coulomb	0.0001, 0.0022	0.0001, 0.0009	0.0000, 0.0093	0.0002, 0.0124

^a The first number is from independent channel approximation (without resonances).
The second number is from Mies's Theory (with resonances).

the 6p detachment into the Hf I ground state. All the other detachments are dwarfed by this strong one and are very weak themselves.

After mixing in the resonances and allowing the channels to mix, the Hf^- ground state to Hf I ground state detachment still dominates and is only slightly changed. This is not surprising considering all the other channels are very weak, and the resonances are all energetically far away. As for the other detachments, almost all of them are increased, by up to two orders of magnitude. However, despite the large increase, only two of them become comparable to the dominant one. Both are 6p detachments, one to the first excited state $5d^26s^2\ ^3F_3$, the other to $5d^26s^2\ ^1G_4$. Let's take a closer look at them. As shown in table 3, the bulk of the partial cross section to $5d^26s^2\ ^3F_3$ comes from $J=3/2$, the bulk of which comes from $(5d^26s^2\ ^3F_3)\varepsilon d_{5/2}$. This relativistic channel has a relatively strong interaction with the first $J=3/2$ resonance state $5d6s^26p^2\ ^2D$ in table 2, as indicated by the transformed CI matrix element $v \sim -0.0220$. Moreover, the shifted position of this resonance is very close to the photon energy used. Combination of these two factors give the resonance a large mixing coefficient in the total wave function (see eqn.(10)). The bulk of the partial cross section to $5d^26s^2\ ^1G_4$ comes from $J=7/2$, the bulk of which comes from $(5d^26s^2\ ^1G_4)\varepsilon s_{1/2}$. The second $J=7/2$ resonance state, $\text{Hf}^- 5d6s^26p^2\ ^2G$ in table 2, interacts strongly with this relativistic channel and has a mixing coefficient of about 3.2 in the total wave function.

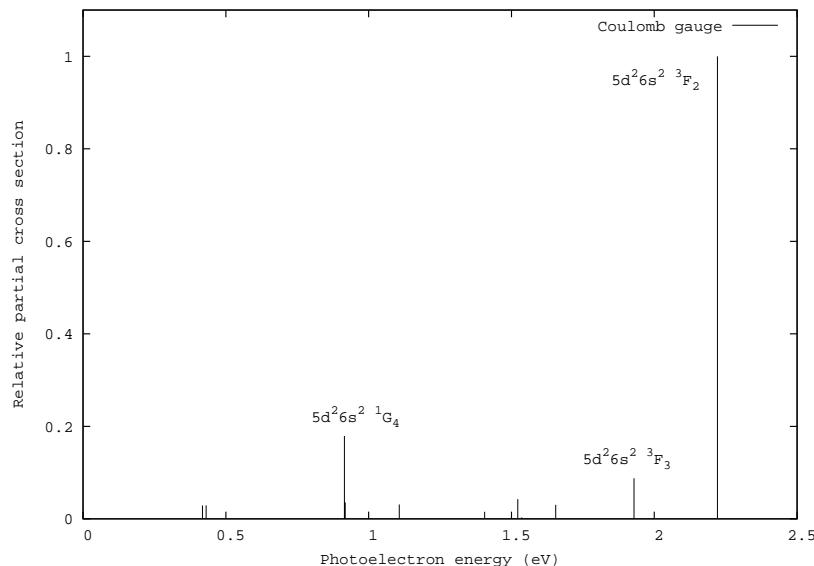


Figure 1. Relative partial cross section (Coulomb gauge) with respect to the Hf^- ground state to Hf I ground state detachment.

From table 3, the $J=5/2$ channels do not produce large partial cross sections even with the inclusion of resonances. This is due to the lack of strong resonances nearby, as indicated by the dipole matrix elements listed in table 2. Among the three $J=5/2$ resonances, the second one has the largest mixing coefficient (~ 1.5 in the relatively large channels). However, due to its moderate dipole matrix element, its mixture does

not lead to large cross sections.

Considering the approximations used in the calculation, we do not claim high accuracy in the absolute values of the cross sections in table 3. Instead, relative partial cross sections to that of the ground state to ground state detachment are calculated and plotted in figure 1. This plot shows a qualitative description of how the photoelectron spectrum would look like for given photon energy 2.34 eV. Since the Babuskin gauge and the Coulomb gauge have similar plot, only the Coulomb gauge plot is given. The height of the vertical lines are equal to the ratios. The horizontal axis gives the energy of the detached electron. The higher the threshold in the neutral spectrum, the smaller energy the photoelectron carries. When comparing with future experimental plot, the vertical lines need to be convoluted using the resolution of the experiment.

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