

Electron affinities and hyperfine structure for U^- and $U\ I$ obtained from relativistic configuration-interaction calculations

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Valence-shell relativistic configuration-interaction calculations predict one U^- bound state, viz., $5f^3 6d 7s^2 7p\ J = \frac{13}{2}$, with an electron affinity of 0.175 eV. We found no other J 's for this configuration to be bound, nor are any $5f^3 6d^2 7s^2$ levels expected to be bound. Attachment of a $5f$ electron is even more unlikely. The hyperfine structure (hfs) constants for the $^{235}U^-$ state, in MHz, are, respectively, $A, B = -72.4, 2644$. Although core polarization effects are absent, the valence hfs results for $^{235}U\ I$ are in generally good agreement with experiment and represent a modest improvement compared to existing semiempirical values. An LS analysis is provided for the bound state.

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I. INTRODUCTION

Recently, most of the lanthanide [1–3] and several of the actinide negative ions [4,5], viz., Th^- , Pa^- , U^- , and Pu^- , have been detected using accelerator mass spectrometry. Other than relative yields, no experimental results exist, except for Tm^- [6], e.g., for electron affinities, or characterization (configuration J) of the negative-ion states.

Theoretically, the earliest work [7–9] on the rare-earth elements, done with local density methods, suggested formation of X^- by attachment of f electrons; however, this is not supported by more modern work [10,11]. Instead, the common attachment mechanism is associated with the p electron, as originally suggested by Vosko, Chevary, and Mayer [12]. Since then, there has been work on the lanthanides La^- [13], Ce^- [14], Pr^- [15], Tm^- [11], Yb^- [12,16], and Lu^- [17], the first two of which also exhibit $5d$ attachment. There has been less work on the lanthanides in the middle of the row because they are more complicated (more $4f$ electrons or holes) and because experimental yields are smaller or non-existent [1–3], as for Ho^- , Pm^- , and Er^- .

For the actinides, there has been theoretical work on Ac^- [13] and Th^- [18], both of which attach $7p$ and $6d$ electrons. Here we report work on a third actinide, U^- , which is found to attach only the $7p$ electron. This is the most complicated species theoretically studied so far, as it has the greatest number of open subshell electrons.

II. METHODOLOGY

A. Multiconfiguration Dirac-Fock

To provide a starting point for our relativistic configuration-interaction (RCI) calculations, we do smaller multiconfiguration Dirac-Fock (MCDF) calculations, using Desclaux's program [19], which we have expanded to handle 1000 vectors and up to 500 000 extra Coulomb integrals. The MCDF basis includes the largest contributors to the electron affinity, treated in a balanced way.

To simplify presentation, we group together all relativistic configurations reducing to a common nonrelativistic manifold. Specifically, for $U\ I\ J=6$, the MCDF solution contains

the manifolds $5f^3(6d 7s^2 + 6d^2 7s + 6d^3 + 6d 7p^2 + 7s 7p^2)$. For the $7p$ attachments, the MCDF solution contains the manifolds $5f^3(6d 7s^2 7p + 6d 7p^3 + 6d^3 7p + 6d^2 7s 7p + 7s 7p^3)$. For the $6d$ attachment, the MCDF solution is built from the manifolds $5f^3(6d^2 7s^2 + 6d^3 7s + 6d^4 + 6d^2 7p^2 + 7s^2 7p^2 + 6d 7s 7p^2)$.

Comparing the threshold to the $7p$ attachment, we see that the latter is formed by adding a $7p$ electron to the former. This is done so that whatever correlation effects are present in the threshold can also appear in the negative ion, in addition to the contributions from the $7p$ electron. In the $6d$ attachment we included the $7p$ correlation because it has a substantial energy and weight contribution, particularly $7s^2 \rightarrow 7p^2$ and $6d 7s \rightarrow 7p^2$. This is what we mean by balance.

The manifolds contain more than 1000 vectors in total; to avoid having to increase the dimension of the program [19] again, and also realizing that the current RCI version [20] can treat up to 7000 vectors, we seek additional limits on the MCDF manifolds. We begin by observing that $\langle r \rangle_{5f} \sim 1.0$ a.u., where $\langle r \rangle_{6d} \sim 3.1$ a.u. and $\langle r \rangle_{7s} \sim 4.4$ a.u. This illustrates the well-known localized or "corelike" character of the $5f$ electrons, as compared to the valence space, and suggests a relatively moderate interaction of the $5f$ electrons with the valence space. We take advantage of this by separately imposing restrictions on the J ranges associated with the $5f^3$ and valence electrons. Blaise and Wyart [21] label the $U\ I$ ground state $5f^3(^4I)6d(^2D)7s^2\ ^5L_6$, which we confirm. The J range corresponding to $5f^3\ ^4I$ is $2J_f=9-15$ and that of the valence electrons is $2J_v=3-5$. However, these $U\ I$ manifolds will also provide a threshold for the $6d$ attachment, labeled [21] $5f^3(^4I)6d(^3F)7s\ ^7M_6$, which suggests that the valence range be expanded to $2J_v=3-9$. We do impose these restrictions on $U\ I$ and maintain the $2J_f$ range for all U^- calculations. For the $7p$ attachment, we use $2J_v=0-8$, which is also used for the $6d$ attachment. To illustrate, for $U\ I$, the full $2J_f$ range is [1–17] and since $2J=12$, this implies that the full valence range is $2J_v=1-29$.

Even with these restrictions, manifold sizes frequently exceed 1000 vectors. To illustrate, the final MCDF sizes for $U\ I$

are 1041 vectors, for $U^- 7p J = \frac{13}{2}$, 2377 vectors, and for $U^- 6d J = \frac{13}{2}$, 1827 vectors. To fit our dimensioning restrictions we have “pushed” the least important part of the J range ($2J_f = 13-15$) into the RCI part of the calculations. This has been done “self-consistently,” i.e., first we include the largest contributions from the couplings with $2J_f = 9-11$ for our MCDF calculation and use these radial functions as input to the RCI calculation with $2J_f = 9-15$. Then the RCI result is used to select the largest MCDF parents and a new MCDF calculation is done, if necessary. This is justified also by the weight of the RCI “parents” (basis functions): less than or equal to 0.01 for parents with $2J_f = 13-15$.

For very large atoms, the original version of the Desclaux program [19], which we use here, can yield results that exhibit a significant lack of self-consistency, e.g., up to a few tenths of an eV, as in [10] Md^- . This problem can be reduced by using a small (0.2) acceleration factor [19] for the MCDF weights. Ultimately, this problem will be removed once we install the more recent version [22] of the program. For this work, the largest lack of self-consistency is for $U^- 6d J = \frac{13}{2}$ and is 0.079 eV. This tends to differentially unbind this state, if left uncorrected. We do correct for this through symmetry preserving single excitations in the RCI calculation.

B. RCI calculations

To generate the rest of the wave function, we make single and double excitations from the valence subshell of the MCDF manifolds, thus selecting a first-order *form*. Subshells not occupied in the MCDF function are called virtual functions; their unorthogonalized radial parts are represented as relativistic screened (Z^*) hydrogenic spinors. This choice avoids [23] potential variational collapse problems. The Z^* are determined during application of the variational principle to the configuration-interaction (CI) matrix. We restrict $l \leq 4$; we will see that g symmetry plays a modest role. With the choice $n = l + 1$, a single virtual function is able to capture about 90% of the correlation energy [15] for a given symmetry (κ). For all but the largest contributions, we use only one virtual.

Due to the increased number of open subshells and/or greater number of higher l 's present, an average CI manifold generates more vectors than the average MCDF manifold. Practically, this means the 7000-parent limit [24] would be quickly exceeded. We avoid this difficulty by introducing the REDUCE procedure [10,25,26], in which a CI manifold's vectors are rotated so as to generate a new basis having the maximum number of zero interactions with the reference function. These “zero” vectors are then discarded. Here we use the most dominant MCDF manifold's wave functions as reference. Specifically, for U I we used $5f^3 6d 7s^2$ and $5f^3 6d^2 7s$ vectors, as determined by the MCDF calculation. Both are needed, as a single U I RCI calculation will provide two thresholds. The multireference REDUCE is discussed in Ref. [26]. For U^- we use $5f^3 6d 7s^2 7p$ for $7p$ attachment and $5f^3 6d^2 7s^2$ for $6d$ attachment, as REDUCE reference functions. The use of REDUCE has the effect of replacing a CI matrix of approximate order 100 000 with one of order 7000. It is also responsible for our CI matrix having fewer [24] zero elements than usual (90%).

TABLE I. Contributions to the $7p$ EA of U^- . Contributions are in eV. Dirac-Fock (DF) contributions are given relative to the U I DF energy. CI contributions are given relative to their own DF. NA denotes not available.

Excitation	U I $J=6$, ground	$U^- J = \frac{13}{2}$	$U^- J = \frac{11}{2}$
	$5f^3 6d 7s^2$	$5f^3 6d 7s^2 7p$	$5f^3 6d 7s^2 7p$
DF ^a	0	+0.1187	+0.2517
$7p \rightarrow vp$	NA	-0.0031	-0.0065
$7p \rightarrow vf$	NA	-0.0018	-0.0043
$7s \rightarrow 6d$	-0.1727	-0.5163	-0.4298
$7s \rightarrow vs$	-0.0050	-0.0072	-0.0055
$7s \rightarrow vd$	-0.0105	-0.0669	-0.0690
$7s \rightarrow vg$	-0.0328	-0.0009	-0.0008
$6d \rightarrow vs$	~ 0	-0.0001	-0.0001
$6d \rightarrow vd$	-0.0128	-0.0518	-0.0457
$6d \rightarrow vg$	-0.0006	-0.0037	-0.0096
$7s^2 \rightarrow vs^2$	-0.0033	-0.0061	-0.0031
$7s^2 \rightarrow 7p^2$	-0.4387	-0.2278	-0.2365
$7s^2 \rightarrow 7pvp$	+0.0020	-0.0225	-0.0002
$7s^2 \rightarrow vp^2$	-0.0014	-0.0089	-0.0019
$7s^2 \rightarrow 6d^2$	-0.1206	-0.1407	-0.1353
$7s^2 \rightarrow 6dvd$	-0.0203	-0.0130	-0.0116
$7s^2 \rightarrow vd^2$	-0.0011	-0.0010	-0.0009
$7s^2 \rightarrow vf^2$	-0.0091	-0.0078	-0.0063
$7s^2 \rightarrow vg^2$	-0.0039	-0.0031	expected small
$6d 7s \rightarrow 7p^2$	-0.0986	-0.0285	-0.0315
$6d 7s \rightarrow 7pvp$	-0.0029	-0.0200	-0.0173
$6d 7s \rightarrow vp^2$	-0.0003	-0.0022	-0.0001
$6d 7s \rightarrow vd^2$	+0.0011	+0.0014	+0.0005
$6d 7s \rightarrow vf^2$	+0.0001	+0.0008	+0.0001
$6d 7s \rightarrow vsvd$	-0.0112	-0.0247	-0.0188
$6d 7s \rightarrow 7pvf$	-0.1334	-0.1146	-0.1221
$6d 7s \rightarrow vpvf$	-0.0047	-0.0191	-0.0143
$6d 7s \rightarrow vg^2$	-0.0003	+0.0001	~ 0
$6d 7s \rightarrow vdv g$	-0.0044	-0.0011	-0.0001
$7s 7p \rightarrow vsvp$	NA	-0.0226	-0.0095
$7s 7p \rightarrow 6dvp$	NA	-0.0010	-0.0054
$7s 7p \rightarrow vpv d$	NA	-0.0041	-0.0038
$7s 7p \rightarrow 6dvf$	NA	-0.0177	-0.0223
$7s 7p \rightarrow vdv f$	NA	-0.0020	-0.0038
$6d 7p \rightarrow vsvp$	NA	~ 0	~ 0
$6d 7p \rightarrow vpv d$	NA	-0.0401	-0.0347
$6d 7p \rightarrow vdv f$	NA	-0.0070	-0.0067
$6d 7p \rightarrow vsv f$	NA	-0.0001	-0.0001
CI (total)	-1.0854	-1.3854	-1.2569
Breit ^b	0.0	+0.006	+0.002
EA	NA	0.175	-0.074

^aRadial functions are generated from $5f^3(6d 7s^2 + 6d^2 7s + 6d^3 + 6d 7p^2 + 7s 7p^2)$ for U I and from $5f^3(6d 7s^2 7p + 6d 7p^3 + 6d^3 7p + 6d^2 7s 7p + 7s 7p^3)$ for U^- . For the purposes of energy analysis, only the first is used in each case.

^bAverage Breit energy (relative to U I) for the DF configuration (see the text).

While REDUCE is very efficient in limiting CI matrix size, each REDUCE vector may involve up to 5000 determinants, which makes matrix element construction greater than 70% of the total run time. This is after introducing [20] the effi-

TABLE II. Contributions (as derived from Table I) to the EA of $U^- 5f^3 6d 7s^2 7p$ $2J=13$.

Excitation	Contribution (meV)
Dirac-Fock ^a	-119
7s	+370 (+344 for 7s→6d)
7s ²	-165 (-211 for 7s ² →7p ²) (+20 for 7s ² →6d ²) (+25 for 7s ² →7pvp)
6d	+42
7s7p	+48
6d7p	+47
6d7s	-47
other	+5
total	+181

^aSingle configuration.

ciency of processing pairs of determinants once only (on average there are ten vectors per determinant here). To gain further efficiency, we have created a parallel version of RCI, which splits the matrix element construction's outer loop over n machines. This has been implemented for $n=2$ on dissimilar computers (SPARC 10 and SPARC 20), using the Argonne National Laboratory p4 software [27]. With some balancing, including allowing for a different memory size, each machine spent nearly the same time [28] setting up the structure (approximately 20 h each for the worst case).

To further trim the size of the CI calculation, we remove any vectors whose CI coefficient is less than 0.001 in magnitude and whose energy contribution is less than 0.0001 eV before proceeding, if necessary, to include more correlation configurations. For U I both thresholds must satisfy these conditions.

One can assign an energy contribution to each vector, to first order, using intermediate normalization. We write the CI wave function as

$$\psi_{CI} = c_0 \Phi_0 + \sum_i c_i \mathcal{R}_i. \quad (1)$$

As written, each of the functions is normalized; Φ_0 consists of all the vectors in the dominant manifold. We define an intermediately normalized CI function $\Psi_{CI} \equiv \psi_{CI}/c_0$, which satisfies the condition $\langle \Phi_0 | \Psi_{CI} \rangle = 1$. The CI energy can then be written as

$$E_{CI} = \langle \Phi_0 | H | \Psi_{CI} \rangle = E_0 + \sum_i (c_i/c_0) \langle \Phi_0 | H | \mathcal{R}_i \rangle. \quad (2)$$

We then assign the correlation vector \mathcal{R}_i an energy $E_i = (c_i/c_0) \langle \Phi_0 | H | \mathcal{R}_i \rangle$, which is used as a removal criterion (above) and a diagnostic. Later, we will see instances where $E_i > 0$, which directly signifies the presence of higher-order effects.

For the purposes of analysis and presentation, it is useful to be able to express, approximately, the vectors of a manifold as LSJ eigenstates. To do this [29], we set the radial minor components equal to zero and assume the radial major

TABLE III. Contribution to the 6d EA of $U^- 5f^3 6d^2 7s^2$. Contributions are in eV. DF contributions are given relative to the U I of energy. CI contributions are given relative to their own DF. NA denotes not available.

Excitation	U I $J=6$ $5f^3 6d^2 7s^b$	$U^- J=\frac{13}{2}$ $5f^3 6d^2 7s^2$
DF ^a	0.0	+0.1681
7s→6d	-0.0027	-0.0435
7s→vs	-0.0059	-0.0440
7s→vd	-0.0028	-0.0022
7s→vg	-0.0207	-0.0440
6d→7s	+0.0098	NA
6d→vs	-0.0006	-0.0006
6d→vd	-0.0746	-0.0022
6d→vg	-0.0222	-0.0224
7s ² →vs ²	NA	-0.0138
7s ² →7p ²	NA	-0.4173
7s ² →7pvp	NA	+0.0086
7s ² →vp ²	NA	-0.0038
7s ² →6d ²	NA	-0.0370
7s ² →6dvd	NA	-0.0072
7s ² →vd ²	NA	-0.0039
7s ² →vf ²	NA	-0.0093
6d7s→7p ²	-0.0036	-0.2898
6d7s→7pvp	-0.0014	-0.0052
6d7s→vp ²	~0	-0.0016
6d7s→vd ²	~0	-0.0003
6d7s→vf ²	~0	-0.0038
6d7s→vsvd	-0.0124	-0.0510
6d7s→7pvf	-0.1292	-0.1794
6d7s→vppv	-0.0014	-0.0148
6d7s→vdrv	-0.0033	-0.0024
6d ² →vs ²	~0	~0
6d ² →7svs	~0	~0
6d ² →7p ²	-0.0014	-0.0035
6d ² →7pvp	~0	-0.0003
6d ² →vp ²	~0	~0
6d ² →vd ²	-0.0297	-0.0454
6d ² →vf ²	-0.0205	-0.0175
6d ² →7svd	~0	~0
6d ² →vsvd	~0	~0
6d ² →7pvf	-0.0218	-0.0146
6d ² →vppv	-0.0010	-0.0020
6d ² →vg ²	-0.0048	-0.0029
6d ² →vdrv	-0.0003	-0.0004
CI (total)	-0.3509	-1.2775
Breit ^c	0.0	~0
relative to the ground state ^d	+0.7747	
EA ^e	NA	-0.016

^aRadials are generated from $5f^3(6d7s^2+6d^27s+6d^3+6d7p^2+7s7p^2)$ for U I and from $5f^3(6d^27s^2+6d^37s+6d^4+6d^27p^2+7s^27p^2+6d7s7p^2)$ for U^- . For the purposes of energy analysis, only the first is used in each case.

^bThis is the second excited state ($J=6$), both theoretically and experimentally, and is labeled ${}^7M_6^o$ at 6249.029 cm^{-1} by Blaise and Wyart [21].

^cAverage Breit energy (relative to U I) for the DF configuration (see the text).

^dExperimental [21] difference between $5f^3 6d^2 7s {}^7M_6^o$ threshold at 6249 cm^{-1} and the $5f^3 6d 7s^2 {}^5L_6^o$ ground state.

^eComputed as $\text{CI}(U\text{ I})-\text{CI}(U^-)-\text{DF}(U^-)-0.7747\text{-Breit}(U^-)$.

TABLE IV. Hyperfine structure constants A and B , in MHz, for ^{235}U $I=6$ levels and the $^{235}\text{U}^-$ bound state. For mass number 235, $\mu = -0.38$, $Q = 4.55$ b, $2I = 7$, and $1 \text{ MHz} = 0.033\,356 \text{ mK}$. The EAs should be nearly insensitive to the mass number. The hfs constant A should scale as μ/I and B with the value of Q .

Level	E^a (cm^{-1})	A			B		
		Expt. ^b	RCI ^c	Semiempirical ^b	Expt. ^b	RCI ^c	Semiempirical ^b
$\text{U } 5f^3 6d 7s^2 \ ^5L_6^0$	0	-60.52	-65.2	-74.38	4102	3200	3901
$\text{U } 5f^3 6d 7s^2 \ ^5K_6^0$	4276	-59.09	-60.4	-60.92	447	469	622
$\text{U } 5f^3 6d^2 7s \ ^7M_6^0$	6249	+67.80	+50.7	+45.7 ^d	2364	2328	2087 ^d
$\text{U } 5f^3 6d 7s^2 \ J=6$	7006	-54.35	-64.0	-61.67	609	460	134
$\text{U}^- \ J=\frac{13}{2} \ 5f^3 6d 7s^2 7p$	-0.175 eV		-72.4	-87.1 ^d		2644	2994 ^d

^aFrom Ref. [21].

^bFrom Ref. [31].

^cThis work. Valence relativistic configuration-interaction calculation.

^dThis work. Single-configuration Dirac-Fock result.

components to be independent of j in each manifold analyzed. We then simultaneously diagonalize L^2 , S^2 , and J^2 matrices.

III. RESULTS

We initially chose $2J=13$ for our $7p$ attachment to the $\text{U } I=6$ ground state. This is what one would expect for a predominantly $7p_{1/2}$ attachment and is consistent with our choices for Ce^- [14] and Pr^- [15]. The results are presented in Table I. From Table II we observe that, as before [14,15], the $7s \rightarrow 6d$ excitation is the largest contributor to binding the system, whereas the Dirac-Fock excitations $7s^2 \rightarrow 7p^2$ and $6d 7s \rightarrow 7p^2$ make the largest contribution to unbinding U^- . The $\text{U } I=6$ RCI matrix is of order 6640, that for $\text{U}^- \ 2J=13$ of order 6820, and for $\text{U}^- \ 2J=11$ of order 5654. MCDF solutions for U were self-consistent to 0.024 eV, for $\text{U}^- \ 2J=13$ to 0.005 eV, and for $\text{U}^- \ 2J=11$ to 0.019 eV. A portion of the $7p \rightarrow vp$, $7s \rightarrow vs$, and $6d \rightarrow vd$ contributions partially correct for the lack of self-consistency.

The Breit contribution to the electron affinity (EA) is expected to be modest: the attached electron is outermost, with a large value for $\langle r \rangle$. We calculate this at the MCDF level, for the average energy. The effect is only 0.006 eV, quite small.

We also explore $2J=11,15$ and the first excited state for $2J=13$ for the $7p$ attachment. None of these is bound, the first being the least (-0.074 eV) unbound. Table I also contains an analysis for this state. The largest error associated with the EAs is undoubtedly the neglect of core-valence correlation effects. Little is known of such effects in the high- Z species. However, in Ca^- , a $4p$ attachment, it seems [30] that core-valence effects can reduce the EA by approximately 30 meV. This does not encourage one to believe there is more than one $7p$ bound state for U^- .

To investigate $6d$ attachment, we avoid direct comparison with the $\text{U } I$ ground state as the nd -core pair correlation can make large contributions to the EA (greater than 0.5 eV). The U^- configuration involved, $5f^3 6d^2 7s^2$, can also be considered as being formed by $7s$ attachment to $5f^3 6d^2 7s$. This has the advantage that the ns -core pair correlation to the EA is much reduced as compared to the nd -core contributions. In Cs^- , for example [14], the $6s$ -core correlation reduces the EA by approximately 97 meV. In $\text{U } I$ there is a

$5f^3 6d^2 7s \ ^7M_6$ state at [21] 6249 cm^{-1} , which is the second $J=6$ excited state and is computationally a convenient choice for a threshold to directly compare with $5f^3 6d^2 7s^2 \ \text{U}^-$ states. With the closure of $7s$, either a $2J=11$ or $2J=13 \ \text{U}^-$ state is possible and both have been investigated. The $2J=13$ energy is the lower of the two and is bound by 0.7587 eV to the 7M_6 threshold. But this threshold is [21] 0.7747 eV above the $\text{U } I$ ground state, making $\text{U}^- \ 5f^3 6d^2 7s^2 \ 2J=13$ unbound by 0.016 eV. As noted, core-valence effects would be likely to make this state even more unbound. An analysis of both states is provided in Table III. The U^- state contained 5059 vectors and its MCDF lack of self-consistency was 0.079 eV.

Using the above logic, we can estimate whether a $5f$ electron can be attached. The following thresholds in [21] $\text{U } I$ are of interest: $5f^4 7s^2 \ ^5I_4$ at 7021 cm^{-1} (approximately 0.87 eV), $5f^4 6d 7s \ ^7L_5$ at $14\,839 \text{ cm}^{-1}$ (approximately 1.84 eV), and $5f^4 7s 7p \ ^7K_4^0$ at $22\,792 \text{ cm}^{-1}$ (approximately 2.83 eV). To the first we might attach a $6d$ or $7p$ electron, but neither is likely to produce greater than 0.87 eV energy lowering. For 7L_5 , we would attach a $7s$ or $6d$ electron, but neither would be expected to yield greater than 1.84 eV lowering. Successful attachment of a $7s$ or a $7p$ electron to 7K_4 is even more unlikely. Thus we conclude that it is unlikely that any $\text{U}^- \ 5f^4 6d^a 7s^b 7p^c$ state lies below the $\text{U } I$ ground state.

In Table IV we present results for the A and B hyperfine structure constants of all the bound states of U and U^- : these are obtained from the preceding RCI calculations. These results are the first *ab initio* ones available for these states and are generally in better agreement with experiment [31] than either semiempirical or Dirac-Fock results. Including core polarizations such as $5s \rightarrow s$ and $5p \rightarrow p$ should further improve the agreement.

We believe that the largest error in our calculations comes from neglect of core-valence correlation effects. If the $4p$ attachment to Ca can be used as a guide, this may be approximately 0.03 eV, tending to unbind the system. The uncorrected part of the self-consistency error, which is largest for $\text{U } I$, would tend to unbind the system. This is probably smaller and would be taken care of by performing single symmetry-preserving, "Brillouin"-type excitations from the core. There is still some error associated with restriction of the J ranges, but probably this is smaller than the missing

TABLE V. Percent *LS* analysis of $U\ I$ and U^- levels for the dominant configuration (Dirac-Fock) only. Absent percentages are small.

Root ^a	$U\ I\ (5f^3 6d 7s^2)\ J=6$									Total
	³ H ^o	⁵ H ^o	³ I ^o	⁵ I ^o	³ K ^o	⁵ K ^o	⁵ G ^o	⁵ L ^o	¹ I ^o	All ^b
Ground	0.08	0.01	0.59	0.05	14.51	0.09	0.00	83.90	0.78	100
$5f^3\ ^4I$					3.9			83.9		88.1 ^c
$5f^3\ ^2H$					10.5					11.0 ^c
First	0.23	0.06	8.03	0.11	1.00	90.42	0.00	0.07	0.09	100
$5f^3\ ^4I$			3.1			90.4				94.7 ^c
$5f^3\ ^2H$			4.9							4.9 ^c
Third	9.02	2.55	22.48	3.37	36.84	0.03	0.47	10.79	14.46	100
$5f^3\ ^4I$			14.4		21.7			10.8		53.2 ^c
$5f^3\ ^2H$					14.1				9.6	26.7 ^c
$5f^3\ ^2G$			6.3						4.4	11.9 ^c

	$U\ I\ (5f^3 6d^2 7s)\ J=6$			Total
	⁷ M ^o	⁵ L ^o	Others	
Second	88.3	11.1		100
$5f^3\ ^4I$	88.3	3.9	1.6	92.4 ^c
$5f^3\ ^2H$		7.1		7.4 ^c

	$U^- (5f^3 6d 7s^2 7p)\ J=\frac{13}{2}$				Total
	⁶ M ^o	⁴ L ^o	² K ^o	Others	
Bottom	53.9	36.9	5.2		100
$5f^3\ ^4I$	53.9	5.6	1.1	4.0	60.6 ^c
$5f^3\ ^2H$		31.2	3.6		34.8 ^c

^aIn order of increasing energy.

^b*LS* for all electrons.

^c*LS* for $5f^3$ electrons.

TABLE VI. Energies and *LS* composition of $U\ I$ states.

$E\ (\text{cm}^{-1})$	Experimental ^a		$E\ (\text{cm}^{-1})$	Theory ^b	
	Configuration label	<i>LS</i>		<i>LS</i> ^c	DF wt. ^d
0	$5f^3 6d 7s^2$	⁵ L ^o	0	⁵ L ^o (84%), ³ K ^o (15%)	87%
4276	$5f^3 6d 7s^2$	⁵ K ^o	4611	⁵ K ^o (90%), ³ I ^o (8%)	89%
6249	$5f^3 6d^2 7s$	⁷ M ^o	5582	⁷ M ^o (88%), ⁵ L ^o (11%)	96%
7006	$5f^3 6d 7s^2$		8690	³ K ^o (37%), ³ I ^o (23%), ¹ I ^o (14%), ⁵ L ^o (11%) ³ H ^o (9%)	88%

^aReference [21].

^bThis work. The configuration label is the same as the experimental one.

^c*LS* composition of the single configuration ("Dirac-Fock") from Table IV.

^dTotal weight (%) of the single configuration in the RCI vector.

core-valence correlations. The LS analysis of Table V shows that $5f^3$ are mainly coupled to 4I or 2H , both of which are completely spanned by $2J_f=9-15$. Our largest known error is for the 3rd excited state of U I (see Table V), but this state is not used to determine the EAs. Excited states tends to have progressively higher errors because the MCDF radial set was optimized for the ground state.

In Tables V and VI we present an LS analysis of all bound states. Table VI confirms the dominant term assigned by Blaise and Wyart [21] for the bottom three U I $J=6$ states and establishes the analysis for the U I $J=6$ state at 7006 cm^{-1} and for the U⁻ $2J=13$ state.

In conclusion, we find only one bound state for U⁻, that due to $7p$ attachment with $2J=13$, and believe this is con-

sistent with the relatively modest experiment yields obtained [4].

Note added in proof. A recent measurement [D. Berkovits, E. Boaretto, S. Ghelberg, O. Heber, and M. Paul, Phys. Rev. Lett. **75**, 414 (1995)] on the EA of Sr suggests that core-valence effects may tend to unbind p attachment by 50–60 meV.

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