

Electron affinities of six bound states of Ce^- formed by attachment of $6p$ and $5d$ electrons to Ce

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Valence-shell relativistic configuration-interaction calculations for Ce^- ($6p$ attachment to the $4f5d6s^2$ ground state) have yielded the following electron affinities (EA): $(2J, EA \text{ (eV)}) = (9, 0.259), (7, 0.147), (5, 0.105), (3, 0.043), \text{ and } (7, 0.055)$. We also find the electron affinity for $5d$ attachment in the $4f5d^26s^2$ $2J=7$ state to be 0.178 eV. This is possibly the second species (La^- being the first) with opposite parity bound states. The existence of several bound states is consistent with the high yields of Ce^- achieved in recent accelerator mass spectrometry experiments.

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I. INTRODUCTION

Recently [1–3] most of the lanthanide negative ions have been detected in accelerator mass spectrometry (AMS) experiments. For two species, La^- and Ce^- , yields have been high, indicating that these ions have either one highly bound state (>0.6 eV) or several more moderately bound states [3].

Some of these species (La^- , Lu^- , Yb^-), have been examined by Vosko *et al.* [4–6] using a combination of Dirac-Fock calculations, density-functional theory, and semiempirical isoelectronic extrapolation. Their results suggest that $6p$ electrons can be attached in these cases by a few tenths of an eV and that in the case of La^- , a $5d$ attachment is also possible [5].

In Sec. II we outline the methodology used to carry off our calculations. Section III discusses the results obtained for various levels of Ce^- .

II. METHODOLOGY

The calculations reported here are valence-shell relativistic configuration-interaction ones, which start from zeroth-order multiconfigurational Dirac-Fock (MCDF) solutions obtained using the program of Desclaux [7]. The formalism employs the Dirac-Breit Hamiltonian, and the wave function is expanded in Slater determinants whose elements are four component spinors.

For the ground state of Ce , labeled $4f5d6s^2 1G_4^o$ by Martin, Zalubas, and Hagan [8], our MCDF solutions contain eigenvectors from the configurations $4f(5d+6s)^3$ viz.,

$$4f(5d^3+5d^26s+5d6s^2).$$

Due to the well-known highly localized nature of the $4f$ radial ($\langle r \rangle_{4f} \approx 1.0$ a.u.) and the dominance ($\approx 82\%$) of $4f5d6s^2$, the most important MCDF eigenvectors are those where the $(5d+6s)^3$ electrons are coupled to $J=1.5$ or 2.5 . We confirm that MCDF radial functions generated from just the $J=1.5$ and 2.5 couplings are good approximations to MCDF radials obtained from the set of all possible $(5d+6s)^3$ couplings. We do so by generating both sets of MCDF radials, following them with

relativistic configuration-interaction (RCI) calculations, and find that the final RCI energies are essentially indistinguishable.

Currently, it is important that this be so, because the number of MCDF vectors that can be handled is 1000 (prior to this work, it was 350), and for some of the most complicated lanthanides, e.g. Tb^- , a single “nonrelativistic manifold” may have >1000 vectors. Current RCI capacity is ≤ 7000 vectors, which is quite adequate for the $Ce-Ce^-$ problem, where the size of the final CI matrix is 2000–3000 vectors.

For $6p$ attachments, MCDF calculations based on the nonrelativistic manifolds $4f(5d+6s)^3$ are not adequate—the lowest state is not dominated by $4f5d6s^26p$ as would be expected ($4f5d^26s6p$ is dominant). The situation is corrected by also including $4f5d6p^3$ (and of lesser importance, $4f6s6p^3$) in the MCDF basis. Here the dominant MCDF coupling for the valence electrons range from $J=0$ to 4 ($5d \times 6p$ has $J \leq 4$).

The RCI nonrelativistic manifolds are created by single and double excitations from the valence subshells ($5d$, $6s$, $6p$) of the dominant (weights $\geq 72\%$) MCDF manifold: $4f5d6s^2$ for Ce and $4f5d6s^26p$ for Ce^- . Radial functions for the previously unoccupied subshells (called *virtals*) are screened relativistic (four-component) hydrogenic functions, (with $n=l+1$), where the effective charge Z^* is determined by minimizing the appropriate root during the CI process. The specific nonrelativistic manifolds used are shown with the Tables accompanying Sec. III. In the calculations reported here, we found that restricting azimuthal symmetries $l \leq 4$ introduces errors of <0.010 eV in the calculated electron affinities (EA’s). Similarly, only for the largest EA contributors was it necessary to include a second virtual for each l . These change the EA by ≤ 0.04 eV. Additional virtals would be expected to have a considerably smaller effect. A small set of virtals is thus able to represent the essential, localized pattern of the full range of Rydberg and continuum series [9]. Further methodology details are given in previous publications [10–14].

During the CI calculations, all possible couplings are examined for the most important nonrelativistic manifolds. Matrix sizes are kept under control by removing

all vectors whose coefficients are <0.001 in magnitude and whose energies are <0.0001 eV. (Cumulative energy errors were <0.002 eV under these conditions.)

Previously, the great variety of relativistic configurations and angular-momentum couplings associated with a single nonrelativistic manifold having open d or f electrons meant a lot of “people time” was spent in data preparation. As part of this project, we have created new software which reads in just the nonrelativistic manifold, and any coupling restrictions desired, and generates all possible relativistic configurations with their desired couplings.

The calculations reported here ignore core-valence (and core-core) correlation effects. For attachment of s and p electrons, this is probably not too severe a restriction, if the EA's are not too small (>0.1 eV), as is mostly the case here. To illustrate, in Table I we report a study of the $6s$ EA of Cs⁻ ($Z=55$). Defining the valence electrons to be $6s^2$, we find that valence correlation effects bind the extra electron by 0.5076 eV (this includes extrapolation of the partial waves to infinity), which, when added to the Dirac-Fock value (0.0605 eV), produces an EA of 0.5681 eV. The experimental value [15], on the other hand, is 0.471 630 eV, implying that the remaining correlation effects tend to unbind the system by 96.5 meV.

In a study [16] of the attachment of a $4p$ electron to Ca, it is found that core-polarization effects (a form of core-valence correlation) unbind the system by ≈ 40 meV. Such effects are quite critical here, because the final EA is only [17,18] 17–18 meV.

In Ce and Ce⁻ we might expect these effects to be several tens of meV, tending to unbind Ce⁻ (perhaps the second $4f5d6s^26p$ $J=7/2$ and $3/2$ states would no longer be bound). Ultimately, of course, a combination of experiment and more thorough calculations will be needed to finally resolve this issue. It should be noted that the valence correlation calculations reported here are some of the largest *ab initio* ones currently available for the lanthanides.

TABLE I. Energy contributions to the EA of Cs⁻.

Type	Value (meV)
Dirac-Fock	60.5
$6s^2 \rightarrow vs^2$	56.9 ^a
$6s^2 \rightarrow vp^2$	427.8 ^a
$6s^2 \rightarrow vd^2$	17.8 ^a
$6s^2 \rightarrow vf^2$	3.3 ^b
$6s^2 \rightarrow vg^2$	0.96 ^b
$6s^2 \rightarrow \sum_{l \geq 5} vl^2$	0.88 ^c
Total	568.1
Experiment	471.6 ^d

^aTwo virtuals are used for this l .

^bOnly one virtual is used for this l .

^cAssuming higher l ($l \geq 4$) contributions decrease as l^{-4} , a Riemann zeta function is evaluated to complete the sum.

^dReference [15].

For attachment of d electrons [to create Ce⁻ $4f5d^26s^2$], core-valence effects cannot be ignored, as our work [19] in Sc⁻ indicates. There individual core-valence effects were found to be as large as 0.5 eV. It seems possible to alleviate this difficulty by theoretically attaching a $6s$ electron to a $4f5d^26s$ state, and then use the *experimental* [8] difference between the $4f5d^26s$ threshold and the $4f5d6s^2^1G_4$ ground state (which includes all correlation effects exactly, of course) to produce a reliable result. This rests on the proposition that core-valence effects are considerably reduced for $6s$ vs $5d$ attachment, and has been used by Vosko *et al.* [5] in their study of La⁻ and Ac⁻.

In Ce, the lowest level with $6s$ singly occupied is [8] $4f5d^26s^2^5H J=3$ at 2369 cm^{-1} . This is the second excited state [8] for this J ($4f5d6s^2^3G$ is at 1389 cm^{-1} and $4f5d6s^2^3F$ is at 1663 cm^{-1} ; $44\,672 \text{ cm}^{-1} = 5.5387 \text{ eV}$). Attaching a $6s$ electron produced $J=7/2$ and $5/2$. Dirac-Fock calculations on Ce⁻ $4f5d^26s^2$ for these two J 's places the $5/2$ level ≈ 0.49 eV above $J=7/2$, indicating that it is not bound. A complication arising at the RCI stage is that the Ce $4f5d^26s$ $J=3$ state is the first (not the second [8]) $J=3$ excited state (these are separated by [8] 0.0875 eV). Theoretically, 81% of the second state is associated with $4f5d^26s$, so we have used this state as a threshold for Ce⁻ $4f5d^26s^2 J=7/2$. To be conservative, we then use the experimental difference between the third $J=3$ and the $J=4$ ground state ($2369 \text{ cm}^{-1} = 0.294 \text{ eV}$). At this point, the alternative of an incorrect experimental assignment cannot be confirmed due to our failure to include core-valence effects which might reorder these two levels.

TABLE II. Correlation contributions in Ce I $4f5d6s^2^1G_4^o$ ground state. Note: All energies in eV, signs reversed.

Configuration	Weight	Energy
$4f5d6s^2$	0.8530	0.0000
$4f5d^26s$	0.0525	0.1107
$4f5d^3$	0.0128	0.0751
$4f5d6svs$	0.0015	0.0010
$4f5d6sud$	0.0043	0.0237
$4f6s^2vs$	0.0000	0.0000
$4f6s^2vd$	0.0005	0.0011
$4f5d^2vs$	0.0000	0.0000
$4f5d^2vd$	0.0042	0.0478
$4f5dvs^2$	0.0001	0.0027
$4f5dvp^2$	0.0556	0.5034
$4f5dvd^2$	0.0001	0.0090
$4f5dvsud$	0.0000	0.0000
$4f5dvpvf$	0.0010	0.0000
$4f5dvf^2$	0.0001	0.0054
$4f6sups^2$	0.0072	0.0750
$4f6svd^2$	0.0000	-0.0007
$4f6svsud$	0.0004	0.0086
$4f6svpvf$	0.0056	0.1617
$4f6svf^2$	0.0000	-0.0005
$4f6svs^2$	0.0000	0.0000
$4f5d^2vg$	0.0000	0.0000
$4f6s^2vg$	0.0000	0.0002

III. RESULTS AND CONCLUSIONS

Writing the normalized wave function Ψ in terms of its normalized Dirac-Fock part Φ and N normalized correlation vectors χ_i , we have $\Psi = c_0\Phi + \sum_{i=1}^N c_i\chi_i$, where the c 's are the configuration-interaction coefficients. By converting to the intermediate normalization $\langle \Psi' | \Phi \rangle = 1$, [$\Psi' = c_0^{-1}\Psi$], it is possible, for the purpose of analysis, to assign an energy contribution ε_i to each χ_i , i.e.

$$\varepsilon_i = \frac{c_i}{c_0} \langle \Phi | H | \chi_i \rangle .$$

For the most part, the χ_i are constructed by single or double subshell valence excitation from the relativistic configurations present in Φ , i.e., Ψ has a first-order form. Some correlation vectors are also added which don't interact with Φ ; these are chosen because they were thought to interact strongly with an existing χ_i , which in turn interacted strongly with Φ (i.e., we anticipate that they are important second-order vectors).

In Tables II and III we present our valence RCI results for the $4f5d6s^2$ $J=4$ ground state of Ce and $J=9/2$, $7/2$ (two roots), $5/2$, and $3/2$ states of Ce^-

TABLE III. Valence correlation effects to first order in $4f5d6s^26p$ Ce^- . Note: All energies in eV, signs reversed. Total number of vectors (J , number) (9/2,1456); (7/2,3439); (5/2,1994); (3/2,1621).

Configuration	$J=9/2$		$J=7/2(1)$		$J=7/2(2)$		$J=5/2$		$J=3/2$	
	Weight	Energy	Weight	Energy	Weight	Energy	Weight	Energy	Weight	Energy
$4f5d6s^26p^a$	0.7324	0.2934	0.7152	0.5173	0.6555	0.8007	0.7195	0.4754	0.7573	0.4925
$4f5d^26s6p$	0.1577	0.5407	0.1444	0.5638	0.1501	0.5605	0.1654	0.5365	0.1273	0.4669
$4f5d^36p$	0.0297	0.1321	0.0260	0.1265	0.0245	0.1226	0.0288	0.1278	0.0257	0.1182
$4f5d6p^3$	0.0317	0.3003	0.0354	0.2923	0.0264	0.2447	0.0317	0.2923	0.0329	0.3046
$4f6s6p^3$	0.0036	0.0458	0.0064	0.0690	0.0073	0.0719	0.0057	0.0576	0.0061	0.0649
$4f5d6svs6p$	0.0002	0.0016	0.0009	0.0030	0.0009	0.0045	0.0005	0.0028	0.0007	0.0044
$4f5d6svd6p$	0.0092	0.0964	0.0097	0.0732	0.0157	0.1273	0.0091	0.0943	0.0103	0.1005
$4fvs6s^26p$	0.0000	0.0000	0.0000	0.0002	0.0000	0.0002	0.0000	0.0001	0.0001	0.0005
$4fvd6s^26p$	0.0079	0.0865	0.0185	0.1554	0.0100	0.1006	0.0093	0.0982	0.0093	0.1020
$4f5d6s^2vp$	0.0003	0.0054	0.0107	0.0470	0.0635	0.2627	0.0011	0.0154	0.0011	0.0124
$4f5d6s^2vf$	0.0000	0.0013	0.0003	0.0114	0.0007	0.0205	0.0003	0.0083	0.0006	0.0132
$4f5d^2vs6p$	0.0005	0.0000	0.0005	0.0000	0.0005	0.0000	0.0004	0.0000	0.0005	0.0000
$4f5d^2vd6p$	0.0048	0.0265	0.0036	0.0195	0.0064	0.0286	0.0053	0.0277	0.0055	0.0312
$4f5d^26svp$	0.0002	-0.0014	0.0042	-0.0044	0.0096	-0.0135	0.0004	-0.0053	0.0005	0.0020
$4f5d^26svf$	0.0007	0.0157	0.0007	0.0119	0.0004	0.0099	0.0006	0.0133	0.0007	0.0131
$4f5d^3vp$	0.0000	0.0000	0.0002	0.0000	0.0014	0.0000	0.0000	0.0000	0.0000	0.0000
$4f5d^3vf$	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
$4fvs6p^3$	0.0000	0.0000	0.0001	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
$4fvd6p^3$	0.0005	0.0000	0.0010	0.0000	0.0006	0.0000	0.0006	0.0000	0.0006	0.0000
$4f5d6svsvp$	0.0016	0.0219	0.0014	0.0195	0.0023	0.0200	0.0013	0.0200	0.0019	0.0239
$4f5d6svdvp$	0.0012	0.0095	0.0010	0.0077	0.0013	0.0100	0.0011	0.0085	0.0011	0.0105
$4f5d6svdvpf$	0.0002	0.0030	0.0002	0.0017	0.0002	0.0017	0.0002	0.0027	0.0002	0.0038
$4f6s^2vsup$	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0001
$4f6s^2vpud$	0.0022	0.0373	0.0025	0.0255	0.0014	0.0134	0.0021	0.0338	0.0020	0.0305
$4f6s^2vdf$	0.0003	0.0098	0.0002	0.0079	0.0003	0.0129	0.0003	0.0097	0.0004	0.0123
$4f5dvs^26p$	0.0004	0.0066	0.0004	0.0062	0.0004	0.0072	0.0004	0.0065	0.0004	0.0066
$4f5dup^26p$	0.0005	0.0149	0.0006	0.0172	0.0008	0.0149	0.0004	0.0146	0.0007	0.0180
$4f5dvd^26p$	0.0002	0.0021	0.0003	0.0022	0.0004	0.0058	0.0002	0.0019	0.0002	0.0029
$4f5dvf^26p$	0.0001	0.0062	0.0000	0.0064	0.0001	0.0060	0.0001	0.0063	0.0000	0.0069
$4f5dvsvd6p$	0.0002	0.0000	0.0001	0.0000	0.0002	0.0000	0.0003	0.0000	0.0002	0.0000
$4f5dvpvf6p$	0.0000	0.0000	0.0002	0.0000	0.0003	0.0000	0.0001	0.0000	0.0001	0.0000
$4f5dup6p^2$	0.0020	0.0294	0.0044	0.0567	0.0078	0.0752	0.0026	0.0415	0.0018	0.0270
$4f5dvf6p^2$	0.0024	0.0000	0.0018	0.0000	0.0016	0.0000	0.0023	0.0000	0.0020	0.0000
$4f6svs^26p$									0.0000	0.0000
$4f6sup^26p$	0.0000	0.0017	0.0001	0.0033	0.0001	0.0032	0.0000	0.0027	0.0000	0.0020
$4f6svd^26p$	0.0007	-0.0028	0.0006	-0.0022	0.0006	-0.0009	0.0008	-0.0019	0.0007	-0.0020
$4f6svf^26p$			0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
$4f6svsvd6p$	0.0011	0.0186	0.0008	0.0149	0.0009	0.0155	0.0011	0.0185	0.0011	0.0186
$4f6svpvf6p$	0.0007	0.0266	0.0011	0.0340	0.0014	0.0363	0.0009	0.0312	0.0009	0.0301
$4f6svp6p^2$	0.0010	0.0213	0.0012	0.0199	0.0017	0.0256	0.0012	0.0232	0.0014	0.0255
$4f6svf6p^2$	0.0044	0.1188	0.0033	0.0964	0.0026	0.0878	0.0041	0.1155	0.0039	0.1078
$4fvgs^26p$			0.0000	0.0010	0.0000	0.0022				
$4f5d6svg6p$			0.0000	0.0008	0.0000	0.0014				
EA (eV)	0.259		0.147		0.055		0.105		0.043	

^aDF energies (in eV) are given with respect to the neutral DF ground state (Table II).

$4f5d6s26p$ —all of which we predict to be bound [EA (meV) = 259, 147, 55, 105, and 43]. We also examined the $J=11/2$ and second-lowest $J=9/2$ states of this configuration, but do not find them to be bound.

For the ease of analysis, we have collected all relativistic configurations belonging to a common nonrelativistic manifold into a single entry. The weight entry is $\sum_i c_i^2$ for all i belonging to the manifold. In Table IV, we compress information of Tables II and III for the $J=9/2$ attachment, for the purpose of understanding the major contributions to its EA; we can see that at the DF level, the system is unbound. According to perturbation theory [13] the $6s^2 \rightarrow$ and $5d6s \rightarrow$ contributions would be zero (as a consequence of $6s$ being closed in both Ce and Ce⁻) if the radials do not change. But, characteristically, when a $6p$ is added [13], the $6s$ becomes more diffuse in Ce⁻, tending to reduce the $6s^2$ correlation energy, thus tending to unbind Ce⁻; the $6s6p$ and $5d6p$ pair excitations exist only in the negative ion and thus tend to bind the ion. By far the biggest contributor to the binding is the $6s \rightarrow 5d$ excitation, with the $6s \rightarrow vd$ and $5d \rightarrow vd$ excitations playing more moderate binding roles.

It is of some interest to see if any single LS component dominates the $6p$ Ce⁻ Ψ as sometimes happens [8] in Ce. Focusing just on Φ , we find this not to be the case, though each of the $6p$ Ce⁻ Φ is dominated ($\geq 60\%$) by the $4f_{5/2}5d_{3/2}6s^26p_{1/2}$ configuration.

Our results for $5d$ attachment to the ground state (based on $6s$ attachment to Ce $4f5d^26s$) are shown in Table V. Combining the results of Table V with the experimental [8] Ce $4f5d^26s$ $J=3$ position relative to the ground state (see Sec. II), we predict an EA of 178 meV. We also examined $J=\frac{5}{2}$ and $\frac{9}{2}$ and the second $J=7/2$ root, but none of these is bound.

In analyzing the results, we see Ce⁻ is unbound at the DF level, and that the $6s^2$ pair excitation (not present in Ce) and $5d6s$ pair excitations (present to a greater extent in Ce⁻) are major contributors to the binding. On the other hand, $5d^2$ pair excitations tend (moderately) to unbind the system (as a result of changing $5d$ radials), as do $5d \rightarrow 6s$ excitations (absent in Ce⁻).

For Ce⁻ $J=7/2$ an LS analysis [10] shows that 67% of the wave function is in $4f5d^26s^2^4H_{7/2}$ and 15% in $4f5d^26s^2^2G_{7/2}$. This very closely parallels the assignments made [8] to the $4f5d^26s$ $J=3$ threshold.

TABLE IV. Contribution to the EA of Ce⁻ $4f5d6s^26p$ $J=9/2$.

Excitation type	Contribution (meV)
Dirac-Fock	-293
$6s \rightarrow$	430
$6s^2 \rightarrow$	-117
$5d \rightarrow vd$	86
$6s \rightarrow vd$	73
$6s6p \rightarrow$	50
$5d6p \rightarrow$	47
$5d6s \rightarrow$	-13
Total	262

Although we have made no investigation of possible $4f$ attachment, in an earlier work [13] on Tm⁻ and Md⁻ (f^{14} configurations), we showed that these species were quite unbound. For $4f$ attachment to Ce, we look for low-lying $4f^2$ thresholds in Ce (so that we may attach a $6s$ or $6p$ electron to it—processes whose correlation energy is better understood than $5d$ or $4f$ attachment). There is a state in CeI $4f^26s^2^4H_4$ at [8] 4763 cm^{-1} ($=0.59 \text{ eV}$) to which we could try to attach a $6p$ electron. But this work suggests this would yield energies $<0.3 \text{ eV}$ —well below what is needed. There is also a state $4f^25d6s^2^5I_4$ at 12114 cm^{-1} ($=1.50 \text{ eV}$) to which we could attach a $6s$, but the energy gained is likely to be $\approx 0.5 \text{ eV}$, again well below what is needed. Based on these considerations, we cannot be sanguine about attaching a $4f$ to Ce. We be-

TABLE V. Energy contributions to Ce $4f5d^26s^2^5H_3^0$ and Ce⁻ $4f5d^26s^2^4H_{7/2}$. Note: Individual contributions to energy given with reversed signs. EA($^4H_{7/2}$)=178 meV. (EA = [Energy(Ce⁻)] - [Energy(Ce)] - 294.0 meV; see text.)

Excitation ^a	Ce	Ce ⁻
Dirac-Fock ^b	0	-230
$6s \rightarrow vs$	0	NC ^c
$6s \rightarrow 5d$	9	25
$6s \rightarrow vd$	4	6
$5d \rightarrow 6s$	35	
$5d \rightarrow vs$	3	NC ^c
$5d \rightarrow vd$	5	4
$5d \rightarrow vg$	19	20
$5d6s \rightarrow vs^2$	0	NC ^c
$5d6s \rightarrow vp^2$	7	152
$5d6s \rightarrow vd^2$	0	0
$5d6s \rightarrow vf^2$	NC ^c	5
$5d6s \rightarrow vsvd$	55	113
$5d6s \rightarrow vpvf$	157	251
$5d^2 \rightarrow 6svs$	0	
$5d^2 \rightarrow vs^2$	0	NC ^c
$5d^2 \rightarrow vp^2$	-2	1
$5d^2 \rightarrow vd^2$	41	32
$5d^2 \rightarrow vf^2$	30	11
$5d^2 \rightarrow 6svd$	0	
$5d^2 \rightarrow vsvd$	0	0
$5d^2 \rightarrow vpvf$	15	6
$5d^2 \rightarrow 6svg$	0	
$6s^2 \rightarrow vs^2$		33
$6s^2 \rightarrow vp^2$		391
$6s^2 \rightarrow 5d^2$		11
$6s^2 \rightarrow 5dvd$		2
$6s^2 \rightarrow vd^2$		6
$6s^2 \rightarrow vf^2$		10
Total	377	849

^aFrom DF configuration.

^bAdd $-8861.11268357 \text{ a.u.}$ to get the total DF energy. We take $1 \text{ a.u.} = 27.20976 \text{ eV}$.

^cNot calculated, expected to be negligible.

lieve the major uncertainty in our calculated EA's to be due to the failure to include core-valence correlation effects. Based on Cs⁻ and Ca⁻ examples noted in the text, such effects may decrease 6*p* EA's by ≈0.040 eV and the 5*d* EA by ≈0.097 eV.

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- [1] D. Berkovitz, E. Obaretto, M. Paul, and G. Hollos, *Rev. Sci. Instrum.* **63**, 2825 (1992).
- [2] M. A. Garwan, X. L. Zhao, M. J. Nadeau, A. E. Lietherland, and L. R. Kilius, *Bull. Am. Phys. Soc.* **37**, 1148 (1992).
- [3] M. A. Garwan, A. E. Lietherland, M. J. Nadeau, and X. L. Zhao, *Nucl. Instrum. Methods B* **79**, 631 (1993).
- [4] S. H. Vosko, J. A. Chevary, and I. L. Mayer, *J. Phys. B* **24**, L225 (1991).
- [5] S. H. Vosko, J. B. Lagowski, I. L. Mayer, and J. A. Chevary, *Phys. Rev. A* **43**, 6389 (1991).
- [6] S. H. Vosko and J. A. Chevary, *Bull. Am. Phys. Soc.* **37**, 1089 (1992).
- [7] J. P. Desclaux, *Comput. Phys. Commun.* **9**, 31 (1975).
- [8] *Atomic Energy Levels*, Natl. Bur. Stand. Ref. Data Ser., Natl. Bur. Stand. (U.S.) Circ. No. 60, edited by W. C. Martin, R. Zalubas, and L. Hagan (U.S. GPO, Washington, DC, 1978).
- [9] D. R. Beck and C. A. Nicolaides, in *Excited States in Quantum Chemistry*, edited by C. A. Nicolaides and D. R. Beck (Reidel, Dordrecht, 1979), p. 105.
- [10] D. R. Beck, *Phys. Rev. A* **37**, 1847 (1988).
- [11] Z. Cai, D. R. Beck, and W. F. Perger, *Phys. Rev. A* **43**, 4660 (1991).
- [12] D. R. Beck and D. Datta, *Phys. Rev. A* **48**, 182 (1993).
- [13] D. Datta and D. R. Beck, *Phys. Rev. A* **47**, 5198 (1993).
- [14] K. D. Dinov and D. R. Beck, *Bull. Am. Phys. Soc.* **38**, 1097 (1993).
- [15] H. Hotop and W. C. Lineberger, *J. Phys. Chem. Ref. Data* **14**, 731 (1985).
- [16] H. W. van der Hart, C. Laughlin, and J. E. Hansen, *Phys. Rev. Lett.* **71**, 1506 (1993).
- [17] C. Walter and J. R. Peterson, *Phys. Rev. Lett.* **68**, 2281 (1992).
- [18] M. J. Nadeau, X. L. Zhao, M. A. Garwan, and A. E. Lietherland, *Phys. Rev. A* **46**, R3588 (1992).
- [19] D. R. Beck, Z. Cai, and G. Aspromallis, *Int. J. Quantum Chem. Symp.* **21**, 457 (1987).