Assessment of the Accuracy of Shape-Consistent Relativistic Effective Core Potentials Using Multireference Spin−Orbit Configuration Interaction Singles and Doubles Calculations of the Ground and Low-Lying Excited States of U^{4+} and U^{5+}[†]

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Multireference spin−orbit configuration interaction calculations were used to determine the accuracy of 60-, 68-, and 78-electron shape-consistent relativistic effective core potentials (RECPs) for uranium V and VI ground and low-lying excited states. Both $5f^n$ and $(5f6d)^n$, ($n = 1, 2$) reference spaces were investigated using correlation-consistent double-ζ quality basis sets. Accuracy was assessed against gas-phase experimental spectra. The 68-electron RECP calculations yielded low relative and rms errors and predicted the empirical ordering of states most consistently.

Introduction

The chemistry of uranium continues to be of intense interest in many applications. Design, performance, aging, and disposal of nuclear fuel and weapon components and the environmental transport of uranium compounds in ore processing waste, as well as depleted uranium munitions, all require a thorough understanding of the chemistry of uranium. Spectroscopic measurements, in particular, electronic spectroscopy, can provide a window into relevant chemical processes.[1]

Interpretation of actinide spectra is complicated by several difficulties. First, because of the high density of states available to actinide compounds arising from the interaction of the open-shell 5f orbitals with varying ligand species, unique identification of spectroscopic features can prove difficult, without resorting to theoretical calculations to serve as a guide. Second, uranium behaves differently from lighter elements because of the magnitude of relativistic effects.[2,3]

One relativistic effect of particular importance to spectroscopic calculations is spin−orbit splitting of the energy levels. This splitting can be treated in a theoretical method in two ways: one-step or two-step.[4] In a one-step method, the spin−orbit interactions are computed with the electronic correlation. In a two-step method, the electronic correlation is calculated then a spin-orbit contribution is computed. One-step methods are particularly attractive, especially in systems that exhibit intermediate coupling.[5−11] Working with a two-component wave function introduces additional computational complexity when symmetry is considered, due to the need to include the additional irreducible representations of the full double group.

Accurate assessment of uranium calculations is hindered by a sparsity of well-characterized gas-phase experimental measurements. Interpretation of the spectroscopy of solids can be complicated by crystal field effects or by the purity of the samples involved. For example, the uranyl ion, UO_2^{2+}, has received intense theoretical scrutiny, and it is often used to benchmark theoretical methods involving uranium.[12−22] The chemical stability of the uranyl ion, its presence in a majority of uranium compounds found in nature, and the relative insensitivity of its electronic spectrum to the local chemical environment make it an excellent candidate for these benchmarking studies. However, the lack of precise gas-phase measurements of the spectrum of the uranyl ion limits its usefulness in assessing the accuracy of calculations, with variations on the order of 1000 cm^{-1} occurring from ligand influences.[23] Attempts have been made to calculate the electronic spectra of uranyl in crystalline environments, but the problem quickly becomes computationally intractable.[14,24,25]

One solution is to use calculations of atomic uranium species to assess the performance of theoretical methods, for which accurate experimental measurements have been performed, and in some cases, the spectra are well-characterized. Using these data, an accurate assessment of the theoretical method can be performed and used to guide the choice of ab initio methods, basis sets and reference and active spaces. In addition, understanding the electronic structure of an atomic system can yield some insight into the molecular structure of uranium compounds. A search through the literature reveals surprisingly few computational studies of atomic uranium species,[26,27] especially of their excited states.[25,28−33]

Theoretical calculations of the spectra of heavy elements, and the actinides in particular, show that the effects of relativity and electronic correlation are roughly of the same order of magnitude. Thus, adequately treating both is critical. Unfortunately, the currently tractable general computational methods require a trade-off between modeling core relativistic effects

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TABLE 1: Valence Electrons Included in Uranium PAC-RECPs

PAC-RECP	valence space
60e	$5s^2 5p^6 5d^{10} 6s^2 6p^6 5f^3 6d^1 7s^2$
68e	$5d^{10} 6s^2 6p^6 5f^3 6d^1 7s^2$
78e	$6s^2 6p^6 5f^3 6d^1 7s^2$

and valence electronic effects, especially the spin–orbit coupling. The relativistic effective core potential (RECP) approach to heavy-element quantum chemistry provides one way to selectively probe the relative importance of both effects on the accuracy of spectroscopic calculations.

This work investigates the accuracy of the P. A. Christiansen, W. C. Ermler, and co-workers shape-consistent RECPs[34,35] by examining the ground and low-lying excited states of the U^{4+} and U^{5+} atomic cations. These species were chosen because of the tractable sizes of the multireference spin–orbit configuration interaction singles and doubles (MR-SOCISD) expansions when using a correlation-consistent double-ζ quality basis set.

Three RECP core sizes were investigated for both cations: a 60-electron core, a 68-electron core, and a 78-electron core. The 78-electron core produces the valence electron configuration $6s^2 6p^6 5f^1$ for U^{5+}. The 68-electron core promotes the 5d shell from the core to the valence space, while the 60-electron core also frees the 5s and 5p shells. The performance of the 62-electron core potential was assumed to be similar to the 60-electron core, as shown in preliminary work,[36] in that the inclusion of the $5s^2$ together with the $5p^6$ was important, and that there would be minimal savings in computational effort in neglecting the 5s shell. For these ionic uranium species, experimental measurements find the lowest-energy electronic transitions to be weak and sharp, which is characteristic of electric dipole forbidden f←f transitions. This suggests that, at a minimum, the 5f electrons must be present in the valence space. Table 1 lists the valence electrons for each PAC-RECP for the ground-state neutral uranium atom.

Theory

Relativistic Effective Core Potentials. Relativistic effects in chemistry have been studied since the 1970s, with pioneering work by Pitzer,[2] Pyykkö, and Desclaux.[3] Relativistic effects in chemistry have been reviewed numerous times.[37−44] Three main effects are observed: (1) direct relativistic contraction and stabilization of s and p shells which have a higher probability of being found near the nucleus, (2) indirect expansion and destabilization of d and f shells due to increased screening of the nucleus by contracted s and p shells, and (3) spin–orbit splitting in all but s shells, with the largest splitting observed in p shells. Many methods exist for treating relativity in ab initio calculations, but one particularly effective and popular choice is RECPs.

The development and application of RECPs have been thoroughly reviewed in the literature.[38,45−51] Shape-consistent core potentials and pseudo-orbitals are generated from the two-component spinor resulting from a Dirac–Hartree–Fock calculation.[52−54] Two terms are frequently employed, a spin-free averaged REP

$$U^{\mathrm{AREP}} = U_L^{\mathrm{AREP}}(r) + \sum_{l=0}^{L-1} \sum_{m=-l}^{l} (U_l^{\mathrm{AREP}}(r) - U_L^{\mathrm{AREP}})(r)|lm\rangle\langle lm| \quad (1)$$

where L is the maximum l value of the core plus one, and a spin-dependent term

$$H_{\mathrm{SO}} = \sum_{l=1}^{L} \left(\frac{2}{2l+1}\right) \Delta U_l^{\mathrm{REP}}(r) \sum_{m'=-l}^{l} \sum_{m=-l}^{l} |lm'\rangle\langle lm'|\vec{s}\cdot\vec{l}\,|lm\rangle\langle lm| \quad (2)$$

where $\Delta U_l^{\mathrm{REP}}(r) = U_{l,l+1/2}^{\mathrm{REP}}(r) - U_{l,l-1/2}^{\mathrm{REP}}(r)$. The AREP term contains all the relativistic effects included by the Dirac–Coulomb Hamiltonian except the spin–orbit coupling, which is included in the SO term. Both the U^{AREP} and the H_{SO} potentials are fit to Gaussian-type functions of the form

$$\frac{1}{r^2} \sum_i C_{li} r^{n_{li}} \exp(-\zeta_{li} r^2) \quad (3)$$

The averaged RECPs obtained above are widely encountered in quantum chemical calculations, due to the ease of inclusion of these one-component pseudopotentials in existing one-component algorithms. The spin–orbit potential, however, is a two-component operator, and its use requires a two-component wave function, which is one reason why spin–orbit potentials are much less frequently used in quantum chemistry calculations.

Shape-consistent pseudopotentials and pseudo-orbitals are particularly attractive for two reasons. One reason is that the shape-consistent pseudopotentials are completely ab initio. A second reason is that the spin–orbit operator develops quite naturally from their derivation.

Basis Sets for Use with PAC-RECPs. Generally contracted[55] double-ζ Gaussian basis sets are generated by variationally optimizing each exponent in restricted open-shell Hartree–Fock atomic calculations.[56] This procedure can yield a shell-averaged description of a particular spin state(s) of the atom or ion. To produce correlation-consistent quality basis sets, cc-pVDZ, polarization functions are added,[57] and the exponents are optimized using MR-SOCISD calculations, typically involving correlation of only the 5f electrons for uranium. The resulting basis sets are designed for efficient CI computations.

Because exponent collapse can occur frequently when using 1*s* primitives in optimization of the exponents for heavy-element atom basis sets,[58] Cartesian d functions are frequently used, with an additional linear combination of Cartesian 3d primitives added to represent the 3s functions. Such functions vanish at the origin, making them quite useful with shape-consistent pseudo-orbitals, which go smoothly and nodelessly to zero at the origin. Exponent collapse can also occur during the development of 2p basis functions, though less often. In this case, Cartesian f functions can be used to circumvent the exponent collapse that can occur in the exponent optimization in larger basis sets. When 2p function primitives are used, an extra primitive is typically added to ensure the vanishing of the derivative of the contracted function at the origin.[59] When Cartesian functions of higher principal quantum number are used (3sd, 4pf, etc.), the resulting contracted functions do not need their functional behavior at the origin compensated with an additional primitive.

Method

The COLUMBUS program suite[8,60−63] was used to compute MR-SOCISD ground and excited electronic states of the U^{5+} and U^{4+} atomic uranium cations. Calculations were performed using the D_{2h} Abelian point group. The 60- and 68-electron core

TABLE 2: U^{5+} MR-SOCISD/cc-pVDZ Energy Levels with a 5f^1 Reference Space[a]

J	principal LS component	60e PAC-RECP cc-pVDZ	68e PAC-RECP cc-pVDZ	78e PAC-RECP cc-pVDZ	experiment[68]
(5 / 2)u	$^2F^o_{5/2}$	0	0	0	0
(7 / 2)u	$^2F^o_{7/2}$	7977 (+4.8)	7560 (−0.6)	6598 (−13.3)	7609
(3 / 2)g	$^2D_{3/2}$	102642 (+12.8)	103246 (+13.5)	114999 (+26.4)	91000
(5 / 2)g	$^2D_{5/2}$	112459 (+11.9)	112030 (+11.5)	125463 (+24.8)	100511
(5 / 2)u	$^4F^o_{5/2}$	124443	116683	117376	
(7 / 2)u	$^4F^o_{7/2}$	129006	121025	121261	
(1 / 2)g	$^2S_{1/2}$	154042 (+8.9)	156038 (+10.3)	166266 (+17.5)	141448
rms error		11.7%	11.8%	24.5%	

[a] Energies are in cm^{-1}. Relative errors in percent are listed in parentheses.

TABLE 3: U^{5+} MR-SOCISD/cc-pVDZ Energy Levels with a (5f6d)^1 Reference Space[a]

J	principal LS component	60e PAC-RECP cc-pVDZ	68e PAC-RECP cc-pVDZ	78e PAC-RECP cc-pVDZ	experiment[68]
(5 / 2)u	$^2F^o_{5/2}$	0	0	0	0
(7 / 2)u	$^2F^o_{7/2}$	7990 (+5.0)	7578 (−0.4)	6641 (−12.7)	7609
(3 / 2)g	$^2D_{3/2}$	87760 (−3.6)	92570 (+1.7)	115240 (+26.6)	91000
(5 / 2)g	$^2D_{5/2}$	97593 (−2.9)	101403 (+0.9)	125704 (+25.1)	100511
(5 / 2)u	$^4F^o_{5/2}$	124554	116809	117588	
(7 / 2)u	$^4F^o_{7/2}$	129116	121471	121471	
(1 / 2)g	$^2S_{1/2}$	140841 (−0.4)	146989 (+3.9)	166507 (+17.7)	141448
rms error		3.9%	2.5%	24.6%	

[a] Energies are in cm^{-1}. Relative errors in percent are listed in parentheses.

uranium shape-consistent RECPs were developed by P. A. Christiansen.[36,64] The 78-electron RECP is from the literature.[35] cc-pVDZ quality basis sets for U(II) or higher oxidation-state ions were developed for use with the various shape-consistent RECPs by the Pitzer group at the Ohio State University.[64] For the 78-electron PAC-RECP, a (4sd4p4f1g)/[3sd2p2f1g] basis set was used;[22] for the 68-electron PAC-RECP a (5sd4p4f1g)/[4sd2p2f1g] basis set, and for the 60-electron PAC-RECP a (7sd5p4f1g)/[5sd3p2f1g] basis set were employed;[36] note that for all three there were postpublication changes to the most diffuse p contraction coefficients to follow the Christiansen augmentation scheme.[59]

For the 60-electron PAC-RECP calculations, the 5s, 5p, and 5d electrons were treated as frozen core electrons, with similar treatment of the 5d electrons in the 68-electron PAC-RECP calculation. Both (5f6d)^1 and 5f^1 reference spaces were used. The occupied molecular orbitals were obtained from one-component restricted open-shell Hartree−Fock average-of-configuration calculations that included scalar relativistic effects via the RECPs. To provide a balance between the quality of the molecular orbitals for both ground and excited states, the unoccupied molecular orbitals were improved virtual orbitals.[65,66]

For U^{5+}, only 2 MR-SOCISD calculations of 15 eigenvalues were necessary to fully characterize the ground and excited states, one for ungerade states, the other for gerade states. States of this odd-electron system transform like the two-dimensional irreducible representations of the D_{2h} double group.[67] Identification of state *J* values was made through analysis of the degeneracy and parity of the computed eigenvalues, while assignment of the principal LS component was made by analysis of spin-multiplicity and orbital occupation of the component with the largest CI coefficient. Results of the calculations were compared with experimental measurements of the excited states of the uranium systems.[68]

For U^{4+}, 4 MR-SOCISD calculations were necessary. One calculation of 28 eigenvalues for A_g symmetry and one calculation of 21 eigenvalues for B_{1g} symmetry fully characterized the 91 even states arising from the 5f^2 electronic configuration. For odd states, 2 calculations of 35 eigenvalues each, one in A_u symmetry and another in B_{1u} symmetry, completely characterized the 140 odd states arising from the 5f^{1}6d^1 electronic configurations. State assignment proceeded in a similar fashion to the U^{5+} calculations.

Results and Discussion

Table 2 lists the results for those calculations on U^{5+} using all seven references arising from a 5f^1 active space. The ^{2}F states exhibit relative errors of roughly 10% when compared with experiment, but the D and S states show larger relative errors of 10−30%. The ^{4}F states were not reported in the experimental references. The 78-electron core yields particularly high errors. The 68-electron PAC-RECP cc-pVDZ performs nearly as well as the 60-electron core calculation overall. In fact, the relative error for the first excited state is lower in the 68-electron core calculation.

Table 3 lists the results for those calculations on U^{5+} resulting from the twelve possible references arising from a (5f6d)^1 active space. Including the five references arising from 6d^1 electronic configurations markedly improved the relative errors in the ^{2}D and ^{2}S states for the 60- and 68-electron cores. However, the 78-electron core still yields particularly high errors.

Table 4 lists the results for those calculations on U^{4+} resulting from a 5f^2 reference space with a cc-pVDZ basis set. Overall, the 68-electron core outperforms the others. The difference is especially noticeable for the gerade states where the relative errors for all but two states are under 5% for the 68-electron core. Of course, the results of all calculations for the ungerade states are poor due to the inadequate reference space.

Table 5 lists the results for those calculations on U^{4+} with the larger (5f6d)^2 reference space. The 68-electron core calculations outperform the 60-electron core in both relative and rms error. However, the 78-electron core results are now equal in rms error to those with the 68-electron core. Using a larger active/reference space had little impact on the overall results for the even U^{4+} states, all of which arise from 5f←5f transitions, while it substantially improved the results for the odd U^{4+} states which arise from 6d←5f transitions. Note the large change of 40% rms error for the 78-electron core.

Overall, the best results, when compared with established experimental data, occur when the 68-electron core PAC-RECP

TABLE 4: U^{4+} MR-SOCISD/cc-pVDZ Energy Levels with a $5f^2$ Reference Space.[a]

J	principal LS component	60e PAC-RECP cc-pVDZ	68e PAC-RECP cc-pVDZ	78e PAC-RECP cc-pVDZ	experiment[68]
4g	${}^{3}H_{4}$	0	0	0	0
2g	${}^{3}F_{2}$	5019 (+20.6)	4153 (−0.2)	3966 (−4.7)	4161
5g	${}^{3}H_{5}$	6734 (+9.7)	5854 (−4.6)	5174 (−15.7)	6137
3g	${}^{3}F_{3}$	10132 (+12.8)	8605 (−4.2)	7850 (−12.6)	8984
4g	${}^{3}F_{4}$	10483 (+11.1)	9372 (−0.7)	8336 (−11.6)	9434
6g	${}^{3}H_{6}$	12717 (+10.5)	11150 (−3.2)	9862 (−14.3)	11514
2g	${}^{1}D_{2}$	**19356 (+17.6)**	**16579 (+0.7)**	**15477 (−6.0)**	16465
4g	${}^{1}G_{4}$	**18363 (+10.3)**	**16417 (−1.4)**	**14515 (−12.9)**	16656
0g	${}^{3}P_{0}$	20301 (+18.5)	17478 (+2.0)	16498 (−3.7)	17128
1g	${}^{3}P_{1}$	23308 (+17.6)	19978 (+0.8)	18727 (−5.5)	19819
6g	${}^{1}I_{6}$	26509 (+19.0)	24509 (+10.0)	22354 (+0.3)	22276
2g	${}^{3}P_{2}$	28520 (+15.7)	24619 (−0.1)	22771 (−7.6)	24653
0g⁻	${}^{1}S_{0}$	50436 (+15.6)	47848 (+9.7)	43928 (+0.7)	43614
rms error		15.4%	4.6%	9.5%	
4u	${}^{3}H^{o}_{4}$	77954 (+31.7)	77043 (+30.2)	86202 (+45.7)	59183
2u	${}^{3}F^{o}_{2}$	78674 (+31.9)	77837 (+30.5)	89539 (+50.1)	59640
3u	${}^{3}G^{o}_{3}$	82614 (+31.0)	82027 (+30.1)	**95937 (+52.2)**	63053
4u	${}^{1}G^{o}_{4}$	84451 (+28.9)	83288 (+27.1)	**93903 (+43.3)**	65538
3u	${}^{3}F^{o}_{3}$	86065 (+28.4)	85180 (+27.1)	**99217 (+48.0)**	67033
5u	${}^{3}H^{o}_{5}$	86773 (+28.4)	85406 (+26.3)	**94417 (+39.7)**	67606
1u	${}^{3}D^{o}_{1}$	88130 (+29.5)	86972 (+27.8)	**101407 (+49.0)**	68054
2u	${}^{1}D^{o}_{2}$	88692 (+28.0)	87244 (+25.9)	**99436 (+43.5)**	69277
4u	${}^{3}G^{o}_{4}$	89435 (+28.3)	88519 (+27.0)	**102701 (+47.3)**	69700
2u	${}^{3}D^{o}_{2}$	**92909 (+27.8)**	91102 (+25.2)	**105130 (+44.6)**	72689
3u	${}^{3}D^{o}_{3}$	**92887 (+27.6)**	91591 (+26.0)	**107000 (+47.0)**	72773
4u	${}^{3}F^{o}_{4}$	93079 (+26.0)	91721 (+24.2)	**105760 (+43.2)**	73845
1u	${}^{3}P^{o}_{1}$	**94763 (+26.8)**	**93179 (+23.8)**	**107406 (+43.7)**	74740
5u	${}^{3}G^{o}_{5}$	**95130 (+26.8)**	**93928 (+24.9)**	**110250 (+47.0)**	75009
0u⁺	${}^{3}P^{o}_{0}$	95125 (+26.5)	93403 (+25.0)	**107142 (+42.5)**	75208
6u	${}^{3}H^{o}_{6}$	**94686 (+25.8)**	**92939 (+23.9)**	**102422 (+36.1)**	75273
2u	${}^{3}P^{o}_{2}$	99472 (+25.6)	97085 (+22.6)	**101186 (+39.1)**	79219
3u	${}^{1}F^{o}_{3}$	101355 (+25.1)	99903 (+23.3)	116176 (+43.4)	80997
5u	${}^{1}H^{o}_{5}$	104755 (+25.6)	103164 (+23.7)	121095 (+45.2)	83416
1u	${}^{1}P^{o}_{1}$	110404 (+24.2)	108896 (+22.5)	124628 (+40.2)	88914
rms error		27.8%	26.0%	44.7%	

[a] Energies are in cm^{-1}. Relative errors in percent are listed in parentheses. Values in bold were ordered incorrectly by the calculation with respect to experiment.

is used. Although the 68-electron core did not always yield the lowest relative or rms errors in the calculations of the ground and excited states of the two cationic species, it did always produce comparable results to the PAC-RECP with the lowest error. The large range of relative and rms errors observed when using the 78-electron core PAC-RECP suggests that it should only be used for qualitative insight into the nature of the ground and excited states. The 60-electron core PAC-RECP showed a smaller range of rms errors than the 78-electron core. However, a large range of relative errors was observed in the U^{4+} calculations.

One possible explanation for the relative success of the 68-electron core RECP may lie in the nature of the core and valence electron shell treatments. Incorporation of an electron shell in the core allows for a relativistic treatment of those electrons, while relativity is treated indirectly, via interaction with the core potential, in the valence electrons. Electrons in the core p-shells are known to exhibit the largest spin−orbit splitting; so, inclusion of the uranium 5p shell in the core in order for an accurate relativistic description seems warranted, as is done in the 68- and 78-electron core potentials. Removal of the uranium 5d shell from the valence space, as is done in the 78-electron shape-consistent core potential, does not allow the 6d electron shell to adequately relax. At the MR-SOCISD/cc-pVDZ level of theory, the 68-electron core PAC-RECP strikes an acceptable balance between relativity and correlation, with a relativistic treatment of the 5p shell, and a valence treatment of the 5d shell. This is consistent with other RECP and pseudopotential work.[10,45,69−73] In addition, the near-degeneracy of the 5f and 6d shells in many uranium atomic species seems to require an accurate treatment of the 6d electronic excitations, which is facilitated by freeing the 5d shell from the core and into the valence electron space, allowing the 6d shell to relax.

Another factor impacting the accuracy of these calculations is the size of the reference space used in the MR-SOCISD calculation, as the relative and rms errors in the calculations based on the $5f^n$ reference space were larger than those calculations using the larger $(5f6d)^n$ reference spaces. For example, the relative error in the energy of the ${}^{2}F_{7/2}$ state when computed using the $5f^1$ reference space were on the order of 3−10%. Errors in the energies of the D and S states, which arise from $6d^1$ and $7s^1$ electronic configurations, exhibited errors on the order of 10−20%. When the 6d orbitals were included in the reference space, the errors in the energies of the D states became consistent with the F-state energy relative error. For states that arose exclusively from $5f^n$ configurations, there was little or no change in the relative error of the energy of the calculated state.

Conclusions

In summary, applying 60-, 68-, and 78-electron Christiansen et al. shape-consistent relativistic effective core potentials in MR-SOCISD/cc-pVDZ calculations of the ground and excited states of U^{5+} and U^{4+} ions show that the 68-electron PAC-RECP yields the best overall accuracy. The lowest relative errors in

TABLE 5: U^{4+} MR-SOCISD/cc-pVDZ Energy Levels with a (5f6d)^2 Reference Space[a]

J	principal LS component	60e PAC-RECP cc-pVDZ	68e PAC-RECP cc-pVDZ	78e PAC-RECP cc-pVDZ	experiment[68]
4g	$^{3}\mathrm{H}_{4}$	0	0	0	0
2g	$^{3}\mathrm{F}_{2}$	5186 (+24.6)	4180 (+0.5)	4007 (−3.7)	4161
5g	$^{3}\mathrm{H}_{5}$	6764 (+10.2)	6357 (+3.6)	5606 (−8.6)	6137
3g	$^{3}\mathrm{F}_{3}$	10287 (+14.5)	9085 (+1.1)	8292 (−7.7)	8984
4g	$^{3}\mathrm{F}_{4}$	10510 (+11.4)	9678 (+2.6)	8640 (−8.4)	9434
6g	$^{3}\mathrm{H}_{6}$	12776 (+11.0)	12017 (+4.4)	10622 (−7.7)	11514
2g	$^{1}\mathrm{D}_{2}$	18405 (+11.8)	17088 (+3.8)	15183 (−7.8)	16465
4g	$^{1}\mathrm{G}_{4}$	19794 (+18.8)	17096 (+2.6)	15974 (−4.1)	16656
0g	$^{3}\mathrm{P}_{0}$	20983 (+22.5)	18068 (+5.5)	17296 (+1.0)	17128
1g	$^{3}\mathrm{P}_{1}$	24052 (+21.4)	20854 (+5.2)	19841 (+0.1)	19819
6g	$^{1}\mathrm{I}_{6}$	26976 (+21.1)	25463 (+14.3)	23385 (+5.0)	22276
2g	$^{3}\mathrm{P}_{2}$	29139 (+18.2)	25754 (+4.5)	23999 (−2.7)	24653
0g^{-}	$^{1}\mathrm{S}_{0}$	50373 (+15.5)	48194 (+10.5)	43856 (+0.6)	43614
rms error		17.4%	6.1%	5.7%	
4u	$^{3}\mathrm{H}^{o}_{4}$	44465 (−24.9)	63245 (+6.9)	57259 (−3.3)	59183
2u	$^{3}\mathrm{F}^{o}_{2}$	44957 (−24.6)	63732 (+6.9)	59720 (+0.1)	59640
3u	$^{3}\mathrm{G}^{o}_{3}$	48433 (−23.2)	67511 (+7.1)	**66033 (+4.7)**	63053
4u	$^{1}\mathrm{G}^{o}_{4}$	50826 (−22.4)	69338 (+5.8)	**64437 (−1.7)**	65538
3u	$^{3}\mathrm{F}^{o}_{3}$	52288 (−22.0)	71074 (+6.0)	**68894 (+2.8)**	67033
5u	$^{3}\mathrm{H}^{o}_{5}$	53305 (−21.2)	71681 (+6.0)	**65503 (−3.1)**	67606
1u	$^{3}\mathrm{D}^{o}_{1}$	54314 (−20.2)	72814 (+7.0)	**71593 (+5.2)**	68054
2u	$^{1}\mathrm{D}^{o}_{2}$	54922 (−20.7)	73195 (+5.7)	**69693 (+0.6)**	69277
4u	$^{3}\mathrm{G}^{o}_{4}$	55222 (−20.8)	74003 (+6.2)	72833 (+4.5)	69700
2u	$^{3}\mathrm{D}^{o}_{2}$	**59080 (−18.7)**	76910 (+5.8)	**75256 (+3.5)**	72689
3u	$^{3}\mathrm{D}^{o}_{3}$	**58964 (−19.0)**	77336 (+6.3)	**76915 (+5.7)**	72773
4u	$^{3}\mathrm{F}^{o}_{4}$	59309 (−19.7)	77645 (+5.1)	75375 (+2.1)	73845
1u	$^{3}\mathrm{P}^{o}_{1}$	**61189 (−18.1)**	**79316 (+6.1)**	**77730 (+4.0)**	74740
5u	$^{3}\mathrm{G}^{o}_{5}$	**60926 (−18.8)**	**79434 (+5.9)**	**79799 (+6.4)**	75009
0u^{+}	$^{3}\mathrm{P}^{o}_{0}$	**61607 (−18.1)**	**79618 (+5.9)**	77788 (+3.4)	75208
6u	$^{3}\mathrm{H}^{o}_{6}$	**61172 (−18.7)**	**79208 (+5.2)**	**73430 (−2.4)**	75273
2u	$^{3}\mathrm{P}^{o}_{2}$	65918 (−16.8)	83219 (+5.0)	80570 (+1.7)	79219
3u	$^{1}\mathrm{F}^{o}_{3}$	67439 (−16.7)	85690 (+5.8)	86134 (+6.3)	80997
5u	$^{1}\mathrm{H}^{o}_{5}$	70851 (−15.1)	89121 (+6.8)	91604 (+9.8)	83416
1u	$^{1}\mathrm{P}^{o}_{1}$	76764 (−13.7)	94920 (+6.8)	94705 (+6.5)	88914
rms error		17.9%	5.9%	5.2%	

[a] Energies are in cm^{-1}. Relative errors in percent are listed in parentheses. Values in bold were ordered incorrectly by the calculation with respect to experiment.

excitation energies were achieved when the reference space included all the electron configurations spawning the states of interest. The 78-electron PAC-RECP had more difficulty than the 60-electron core providing correct ordering of states, even when the relative errors for those states were low with respect to experiment, as was the case in the U^{4+} odd-state calculation using a (5f6d)^2 active space.

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Supporting Information Available: For the 78-electron PAC-RECP, a (4sd4p4f1g)/[3sd2p2f1g] cc-pVDZ basis set was used. For the 68-electron PAC-RECP a (5sd4p4f1g)/[4sd2p2f1g] cc-pVDZ basis set and for the 60-electron PAC-RECP a (7sd5p4f1g)/[5sd3p2f1g] cc-pVDZ basis set were employed. This material is available free of charge via the Internet at http://pubs.acs.org.

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