Ab Initio Determination of Americium Ionization Potentials

Jeffrey L. Tilson Mathematics and Computer Science Division Argonne National Laboratory, Argonne, IL 60439

Ron Shepard, Conrad Naleway, Albert F. Wagner Chemistry Division Argonne National Laboratory, Argonne, IL 60439

Walter C. Ermler Department of Chemistry and Chemical Biology Stevens Institute of Technology, Hoboken, NJ 07030

Abstract

The first three ionization potentials of americium are calculated using ab initio spin-orbit configuration interaction techniques. These results are favorably compared with experimental and theoretical work. The lowest two ionization potentials are accurately determined using wavefunctions constructed as simple single and double substitutions from a self-consistent field reference configuration with scalar relativistic effects included through an averaged relativistic pseudopotential. A determination of the third ionization potential to comparable accuracy requires inclusion of the spin-orbit operator and significant intermediate coupling, with a resulting configuration expansion length in excess of 1.9 million double-group adapted functions. This problem was solved by application of a new parallel spin-orbit configuration interaction component to the COLUMBUS program system. A decomposition of the ionization potential calculation into parts either sensitive or largely insensitive to the spin-orbit operator was favorably tested, leading to hybrid calculations of improved accuracy.

I. Introduction

Fundamental gas-phase properties of many actinide atoms and, especially, their ions are difficult to measure. The ionization potentials (IP) of americium are an example of such a property and are the main thrust of this paper. Only for the first ionization potential for the neutral atom (IP1) has a definitive direct experimental measurement been made.¹ The IPs of the singly and doubly charged ions, IP2 and IP3 respectively, have been estimated from thermodynamic cycles, from early semi-empirical calculations, or from very recent configuration interaction (CI) and density functional theory (DFT) calculations. This paper reports more extensive CI calculations and compares them with all these previous results.

For the lighter elements, properties such as ionization potentials can be readily calculated to a high degree of accuracy by a variety of theoretical methods.² The IP1 of a series of heavier elements (through Xe) at a consistent level of theory has been determined using numerical Hartree-Fock (HF) with a perturbation correction for the spin-orbit (SO) effects.³ For the larger atoms, relativistic corrections amount to 0.5 - 1.0 eV. Relativistic HF calculations⁴ for IP1 of selected lanthanides indicated errors on the order of 0.3-1.0 eV. In both cases relativistic corrections can be as significant as the electron corrections.

Recently, advances in relativistic pseudopotentials^{5,6,7,8} and CI software have permitted solutions of the two-component spin-orbit CI (SOCI) problem constructed from an orbital basis generated with conventional (non-SO) methods and a list of atomic orbital (AO) occupations. A pseudopotential, or relativistic effective core potential (RECP), in the form of an averaged RECP (ARECP) plus spin-orbit operator, dramatically reduces the number of explicit electrons in the CI calculation, in turn dramatically reducing the computational effort. (The averaging in the ARECP is over different angular momentum couplings that are possible with SO interactions.) Configuration interaction calculations with ARECPs have been carried out on heavy elements with good results, many of which are have been reviewed recently.⁹ In this study, even with the incorporation of RECPs, the amercium calculations performed are the largest CI applications known to date that also directly incorporate a SO operator. The large size is due to the presence of so many open-shell f electrons in the valence These calculations would not have been possible without a space of americium. massively parallel SOCI code. Such a code has recently been produced,¹⁰ and this work is the first of a series of publications using the code to solve problems in the chemistry of f electrons. While this paper focuses on atomic and ionic properties, future papers in the series will examine the chemical binding of americium ions to other atoms and ions in the gas phase and in solution. The relative roles of ionic and covalent bonding in some of these cases will require an accurate treatment of the IPs such as that reported here.

The next section of this paper outlines the basic methodology used in the calculations. Following that is a discussion of the results for the first three ionization potentials and a comparison of these results with other calculations. Conclusions are discussed in the final section.

II. Methodology

The ab initio SOCI procedure used here consists of five basic steps: (1) the construction of an RECP to represent the core electrons followed by transformation to an ARECP with associated SO operators, (2) the development of an appropriate basis set for the remaining valence electrons, (3) the generation of AOs, (4) the selection of the configuration expansion, and (5) the construction and diagonalization of the resulting two-component Hamiltonian. The orbital generation and configuration selection steps are both based on standard non-SO coupled AOs. The subsequent SOCI step explicitly includes the SO operator and constructs a Hamiltonian in terms of double-group-adapted functions. Each of these steps is now briefly described.

Americium has 95 electrons, but explicitly including all these electrons in the calculation for determination of the IPs is not necessary and greatly increases the complexity of the calculation. Instead, 78 core electrons are replaced with an ARECP developed by Nash et al..¹¹ This ARECP includes the scalar relativistic effects but does not include certain higher-order corrections such as core polarization, which is expected to be unimportant in determining the IP. Use of this ARECP reduces the number of explicitly treated electrons to 17, which occupy in the simplest model the filled 6s, 6p, and 7s subshells and the half-filled 5f subshell. References to specific orbital occupations always refer to non-SO atomic orbitals and configurations. The SO operator is generated from the ARECPs in the standard way.¹²

In the calculations reported here, the atomic orbitals for the valence electrons are expanded in a typical Gaussian basis set of either triple-zeta or double-zeta quality. The correlation consistent polarized-valence triple-zeta basis set consists of [5p,6sd,3f,2g,1h] basis functions.¹³ The double-zeta basis set consists of [4p,4sd,2f,1g] basis functions.¹⁴

Both of these basis sets are too large for the largest of SOCI calculations on Am^{+2} and Am^{+3} . Thus, a recontracted double-zeta basis set consisting of [2p3sd,2f,1g] basis functions was generated with negligible loss in total energies. The reliability of all three of these basis sets will be discussed later in this section. With any of these basis sets, all AO integrals, including those necessary for subsequent SO calculations, were computed using the program ARGOS.¹⁵ ARGOS is limited to D_{2h} point groups and its subgroups, such as D₂. In all calculations performed here, either the D₂ or D_{2h} point groups were used.

The second step is the generation of a set of orthogonal AOs for use in the SOCI calculations. These orbitals are generated by one of three choices. The first choice is by using the multiconfiguration self-consistent field (MCSCF) method modified for use with pseudopotentials as found in the program MCSCF.¹⁶ The MCSCF program is flexible but can produce AOs that break the spherical symmetry of the atom. This breaking of symmetry is an important characteristic of dissociation and bond formation but requires careful use when these orbitals are to be used subsequently for a SOCI procedure that is not a full-CI. This symmetry breaking does not occur for Am, Am^{+1} , and Am^{+2} because, in each case, the ground state terms are all of S momentum arising from a completely half-filled 5f subshell and a spherical 7s in various states of occupation. In contrast, the Am⁺³ 5f subshell is not exactly half-filled, and non-SO symmetry breaking occurs. Since a more compact configuration expansion can be built with orbitals that do not break symmetry, for Am⁺³ two other choices of generating AOs were examined. The first of these two additional choices simply uses for the Am⁺³ a SOCI procedure, the AOs optimal for the Am⁺² MCSCF. Although a reasonable choice and carrying the proper symmetry, these orbitals are not optimal for the Am⁺³ SOCI because they are adapted for the wrong charge and their use may greatly extend the SOCI configuration length for a particular accuracy in the IP. The third choice is to generate AOs using a restricted-SCF approach in which AOs for Am⁺³ are energy optimized subject to the constraint of f orbital radial equivalence. This procedure is implemented in the program SCFPQ.¹⁷ The choice of which of these orbital selection schemes to use will be discussed in detail in the next section.

The CI calculations took the form of either a multireference SOCI or a non-SO singles and double excitations from the atomic SCF configuration. The SOCI configuration list is generated as a list of spatial configurations constructed from atomic orbitals using the program CGDBG.¹⁸ The SOCI reference spaces are each constructed from a full-CI among the valence f electrons (VFCI). As will be discussed below, VFCI multireference wavefunctions used in this study are composed of as many as 393 configurations. For the generation of AOs for the SOCI procedure and for the reference space of the non-SO CI, only the high-spin atomic SCF configurations are used. Single or single and double excitations are then permitted out of the selected SO or non-SO reference spaces. Because the americium atom nominally has 7 half-filled orbitals in the 5f subshell, appropriate SOCI single excitations from the filled 6s, 6p, or 7s subshells from the VFCI reference space can produce 9 open shells, and the appropriate double excitation can produce 11 open shells. Such a large number of open shells is not normally encountered in theoretical studies of atoms and molecules in the first few rows of the periodic table.

All of the above information is used to construct the SOCI Hamiltonian matrix for the valence electrons, which is iteratively solved for a selected number of the lowest eigenvalues and eigenvectors. This Hamiltonian matrix explicitly includes the spin-orbit operator, which means that various eigenvalues of the square of the total spin momentum and the projection of the total spin momentum are mixed together. A version of the program CIDBG¹⁹ has been extensively modified to allow efficient parallelization over hundreds of processors. This modified program, called P-SOCI, is extensively described elsewhere.¹⁰ Because of the large number of open shells, and because the presence of the spin-orbit operator leads to a wavefunction that is not an eigenfunction of the square of the total spin angular momentum operator, the configuration expansion can be very large (~2 million configurations) even for these atomic systems. As a result, these more extensive calculations are among the largest ever attempted for actinides. All of the indicated codes are part of the COLUMBUS programing system.²⁰

Now that the methodology has been described, the implications of the three different basis sets can be examined. As discussed in the next section, the first three ionization potentials (IP1, IP2, and IP3) will be calculated. A measure of the basis set error is the change of these three quantities with basis set as determined in non-SO CI calculations. By this measure, relative to the triple-zeta basis set, the double-zeta and recontracted double-zeta basis sets underestimate IP1 by 0.01 eV and 5.11 eV, IP2 by 0.05 eV and 2.54 eV, and IP3 by 0.36 eV and 0.38 eV, respectively. Clearly the contracted basis set is not useful for IP1 and IP2, while the full double-zeta and the triple-zeta basis set are essentially the same results. For IP3, the contracted and full double-zeta basis set are essentially the same and give results only a third of an eV from the triple-zeta basis set. Thus the contracted double-zeta basis set will be used only for IP3 calculations. Taken together, these results indicate that residual basis set errors at the triple-zeta basis level are probably less than 0.1 eV for all three IPs.

Both SOCI and non-SO CI calculations can suffer from size extensivity errors.²¹ This error can be fully corrected at a full CI level, which is not now feasible. However, two approximate methods were used to correct this error: the Davidson correction²² and the correction within the average coupled pair functional (ACPF) method²³. These corrections are currently available only for non-SO CI calculations. Results specific to each IP will be reported in the next section. The size of the IP corrections varied from 0.1 to 0.4 eV, with the Davidson correction always smaller than that from the ACPF. The available experimental evidence will show that these small corrections are important in obtaining more than qualitative agreement with experiment.

III. Results

The First Ionization Potential

IP1 measures the energy for the process $Am(^{8}S_{7/2}) \rightarrow Am^{+}(^{9}S_{4})$. In Fig. 1 the non-SO CI IP1 is compared with experimental values and early theoretical results. The abscissa of the figure indicates the extent of the CI expansions ordered from the smallest to the largest. These begin at the reference (ref) wavefunction, proceed to single excitations (S) from the reference space excluding 6s6p (no 6s6p) or including 6s6p excitations, and end at the single and double excitations (SD) excluding 6s6p (no 6s6p) or including 6s6p excitations. The final label entry refers to the experimental result and also to any earlier theoretical results. In this selection of expansions, excitations from the 6s6p electrons are allowed or forbidden to test their effect. This effect is important because the length of the CI expansion, and thus the time to solution, is dramatically increased with the inclusion of the 6s6p excitations. At the SOCI level, SD including 6s6p excitations is far too large even for the current P-SOCI code with all the selected basis sets.

Displayed in the figure under the experimental column are three published measurements of IP1. The earliest result²⁴ is based on an approximate solution for the IP derived from relativistic SCF solutions. The next earliest result is semi-empirical and

based upon some assumptions regarding the similarities between the actinide and lanthanide series.²⁵ The remaining value is a recent direct measurement of spectroscopic accuracy and is the most reliable gas-phase ionization potential of any order for americium. As the figure shows, excitations out of the 6s6p have almost no effect on IP1, while double excitations increase IP1 by more than 0.5 eV. These changes are quite small relative to the changes in the absolute energies of approximately 0.5 eV and 8.2eV, respectively. The triple- or double-zeta basis sets produce essentially the same IP1 values even while the absolute energies change by approximately 2.9 eV. The Davidson correction increases IP1 by about half that of the ACPF correction. The large basis set ACPF-corrected value of IP1 is about 0.3 eV below the direct experimental value of 5.97 eV. Overall, the figure shows at the non-SO CI level, increasing the wavefunction quality by extending the CI expansion generally increases the IP1. This result is expected because the lower-energy, more electron-rich, less charged species of the IP1 pair should benefit more by the larger CI expansions and larger basis sets. This is true if the essential nondynamical correlation, such as near-degeneracy effects, are included in the CI reference space.

Although the results in Fig. 1 are for non-SO CI calculations, the SO effect should be quite small because both Am and Am⁺¹ ground states have no orbital angular momentum. Nonetheless, SOCI calculations were also carried out using two different SOCI wavefunctions. The first calculation used only the small VFCI references for the SOCI, while the larger calculations included all single excitations in the virtual orbitals. The singles SOCI were further subdivided into those that included excitations from the 6s6p5f7s orbitals and those that permitted excitations only from 5f7s (no 6s6p). The maximum deviation of the SOCI from the non-SO CI results in the figure was 0.03 eV. Calculations for IP3 discussed later in this section suggest that additional doubles excitations do not alter the SOCI/non-SO CI comparisons. Thus, as expected, the SO effect is essentially negligible for IP1.

The best result is obtained using the triple-zeta basis ACPF calculation, yielding an error of 0.3 eV. This residual error is expected to be a combination of small errors in many aspects of the calculation. In addition to the ones described above, the core potential (ARECP) used in this calculation could contribute to the error. As will be discussed for IP3, this core potential does exhibit some limitations, but quantifying its effect on IP1 is beyond the scope of this paper.

The Second Ionization Potential

IP2 measures the energy required for the process $Am^+({}^{9}S_4) \rightarrow Am^{+2}({}^{8}S_{7/2})$. Analogous to Fig. 1, in Fig. 2 the non-SO CI IP2 is compared with an indirect experimental value of 12.0 eV²⁶ and an early theoretical value of 12.15 eV.²⁴ The computed non-SO IP2 increases with increasing wavefunction complexity and approaches the experimental value from below. Compared with Fig. 1, the results are quite similar in form and scale, with the best calculation (triple-zeta, non-SO ACPF) being again about 0.3 eV below the experimental result. As in IP1, non-SO excitations out of 6s6p have a negligible effect, as does the change from a double- to a triple-zeta basis. The Davidson and ACPF corrections are about half of what they were for IP1.

Even though the results in Fig. 2 are for non-SO CI calculations, the SO effects should be quite small for the same reasons as for the IP1 calculation. As a verification, SOCI calculations were again carried out through single excitation calculations with and without including excitations from the 6s6p electrons for comparison. The maximum deviation from the non-SO results in Fig. 2 was 0.06 eV. This is twice as large as

observed in IP1 but still quite modest on the scale of the figure. The difference between the experimental value and our best calculated value is expected to be a combination of small errors as indicated for IP1.

The Third Ionization Potential

IP3 measures the energy required for the process $Am^{+2}(^{8}S_{7/2}) \rightarrow Am^{+3}(^{7}F_{0})$. In contrast to the simplicity of calculating the first two ionization potentials, it is much more difficult to determine IP3 because of the splitting of the lowest-lying $Am^{+3}(^{7}F)$ term yielding the $Am^{+3}(^{7}F_{0})$ ground state. This is not an S term like the previous oxidation states and has implications for the selection of the orbital basis and the resulting necessary level of CI excitation. The different ways to generate the AOs has been discussed in an earlier section and were tested here using both SOCI and non-SO CI wavefunctions.

The first series of tests were for non-SO CI calculations. The MCSCF method for orbital selection, used for the lower charged states of americium, produces symmetry broken orbitals for Am⁺³. However, the non-SO 5f orbitals should be radially equivalent even though they are partially filled, a difficulty not encountered for the lower charged states of americium where the 5f shell is always half-filled. As discussed previously, appropriately symmetric orbitals to be used in a CI can be produced in two ways: the Am^{+2} -orbital method where the symmetric orbitials of $Am^{+2}(^{8}S_{7/2})$ are used and the restricted-SCF method that enforces spherical symmetry on the Am^{+3} 5f orbitals. All of these approaches have been examined at the non-SO CI level with the following results. CI calculations using the MCSCF symmetry-broken orbitals or the restricted-SCF orbitals produce IP3 values that never differ by more than 0.02 eV. This is true for both the double-zeta and recontracted double-zeta basis sets. In both cases, increasing the configuration expansion tends to increase the value of IP3, as expected if both Am^{+2} and Am⁺³ are comparably described at the SCF level. This result suggests the restricted-SCF AOs are close to being energy optimized at the non-SO CI level. In contrast, with Am⁺² orbitals, calculation of a frozen orbital SCF energy leads to an IP3 value 2.14 eV higher than that using the restricted-SCF orbitals. (Note that an unfrozen orbital SCF calculation would relax the initial Am orbitals to the symmetry broken orbitals already discussed.) Upon singles excitation, the IP3 level drops significantly, such that it falls below that of the other two methods by about 0.25 eV if single excitations are included out of the 6s6p orbitals. Upon double excitations, the IP3 value does rise, and if doubles out of 6s6p are included, the final value of IP3 is about 0.5 eV above that of the other two methods. This suggests that Am⁺³ calculations with Am⁺² orbitals do not produce, at the reference space level, comparable descriptions of the two charge states involved in IP3. Excitations, especially single excitations, are then used to recover a more comparable description, resulting in a configuration expansion that inefficiently builds in correlation.

SOCI calculations using the restricted-SCF and Am^{+2} orbitals were also compared. In SOCI calculations using restricted-SCF and Am^{+2} orbitals, we find that the Am^{+2} orbitals yields an IP3 value about 2 eV larger at the VFCI level than that using the restricted-SCF orbitals. Additionally, as with the non-SO CI, IP3 values are lower by a few tenths of an eV when including all singles excitations and higher by a few tenths of an eV at the singles plus doubles excitations level when using the Am^{+2} orbitals relative to the restricted-SCF orbitals. Consequently, all final results reported here use either the energy-optimized symmetry-broken orbitals for the non-SO CI or spherically averaged restricted-SCF orbitals for the SOCI. Analogous to Figs. 1 and 2, in Fig. 3 the non-SO CI IP3 is compared with experimental and theoretical values. In contrast to results for IP1 and IP2, the four previous experimental/theoretical estimations of IP3 are widely different. The first previous result shown on the figure is that of Morss,²⁶ obtained by scaling the result of Carlson et al.²⁴ for consistency with previously reported IP1 values.²⁵ A second result was an unpublished value of Mann²⁷ at 20.45 eV using the method of Cowen,²⁸ which includes SO effects as a perturbation. Lastly, an experimental estimation based on Born-Haber cycles of 21.9 eV²⁹ is also shown on the figures. While the basis set effect of about 0.35 eV is larger than that of IP1 and IP2, the ACPF and Davidson corrections are similar to each other (as in IP2) and in size in between that for IP1 and IP2. However, the most striking feature of Fig. 3 relative to Figs. 1 and 2 is that the non-SO CI results are converging on a substantially higher value for IP3 than the experimental and semi-empirical estimations.

A second major feature that distinguishes IP3 calculations from calculations of IP1 and IP2 is that the SOCI results are much different from non-SO CI results. The non-SO CI results converge to a much higher IP3 resulting from the importance of SO splitting in Am⁺³, indicating the necessity of using the SOCI method. The SOCI calculations cannot be carried out to quite the same configuration expansion as shown in The VFCI reference space for Am⁺² results in 393 spatial the previous figures. configurations and that for Am⁺³ results in 357 spatial configurations. A full SOCI single and double excitation including the 6s6p from these VFCI reference spaces is currently not feasible for any of the selected basis sets even with the P-SOCI program running on hundreds of processors. Therefore, while single excitations can include 6s6p, only partial double excitations from the 5f subshell into the virtual space were included. With this restriction indicated by an asterisk in the absissca label, Fig. 4 is the SOCI equivalent of Fig. 3. The SOCI calculations in the figure use the recontracted double-zeta basis set and restricted-SCF orbitals while the non-SO CI results in Fig. 3 use the full double-zeta basis and symmetry broken orbitals. Nonetheless, prior discussion has shown that these differences should amount to a few hundredths of an eV variation in IP3.

The SOCI results in the figure are qualitatively different from the non-SO CI results. At the reference level, the SOCI IP3 is about 0.6 eV below the corresponding non-SO CI value. Single excitations from only the 5f subshell (no 6s6p) have little influence on the IP3, just as in the non-SO CI results. The set of complete single excitations, however, lowers the IP3 by about another 0.3 eV. This lowering runs counter to the expectation that increasing the flexibility of the wavefunction preferentially benefits the lower, more electron-rich state, thus increasing the IP. This expectation is largely realized in all non-SO CI calculations carried out in this study (see Figs. 1-3). However, when SO effects are strong, configurations with different spins can couple to lower the energy of a given charge state. We speculate that the upper Am⁺³(⁷F₀) state can use relatively low-lying excitations out of the 6s6p subshells that without SO coupling are spin forbidden but with SO coupling can build in the character *and stabilization* of half-filled 5f orbitals. Thus, even though the upper state has fewer electrons to correlate, its energy is preferentially lowered relative to Am⁺²(⁸S_{7/2}).

Double excitations substantially increase the IP3 in a way quite similar for both SOCI and non-SO CI calculations. When 6s6p is excluded from single and double excitations, the additional effect of doubles is 0.09 eV larger in the non-SO CI calculation. When 6s6p is included fully in the non-SO CI but only partially (as described above) in the SOCI, the additional effect of doubles is 0.06 eV larger in the non-SO CI calculation. Furthermore, the additional effect of doubles excitations with and without 6s6p in the non-SO CI calculations varies by only 0.09 eV. All of this suggests

that double excitations from 6s6p are not important in either SOCI or non-SO CI calculations and the inclusion of double excitations from the 5f subshell in Fig. 4 introduces an error measured in hundredths of an eV.

The end result of the SOCI calculation is that the IP3 value approaches quite closely the indirect experimental estimation. Furthermore, the reported error (+/- 0.5eV) for the experimental result would accommodate much, if not all, of the increase in the calculated IP3 due to basis set deficiency and size extensivity errors as estimated from the non-SO CI results in Fig. 3. Thus, the best direct ab initio results fully support the highest experimental estimation over the lower theoretical estimations.

IV. Comparison with Ab Initio Results

Only recently have comprehensive calculations become available for comparison with the results discussed above. Liu, Kuchle, and Dolg (LKD) have published³⁰ ab initio pseudopotential values and a variety of all electron DFT values for IP1, IP2, and IP3 for all the actinides. The density functional calculations of LKD are four-component all-electron calculations with a self-interaction correction and with either a local density approximation or one of two gradient exchange-correlation functionals. They also compare with previous DFT results.

For the non-DFT ab initio calculations, LKD used a small-core pseudopotential incorporating 1s - 4f shells and designed³¹ to reproduce the valence total energies of a large number of low-lying electronic states of the neutral atom and its ions. Included in this assortment of energies are, in effect, ionization potentials and f-f spectroscopic The total energies being reproduced are calculated by all electron transitions. calculations but with the approximate first-order Wood-Boring³² Hamiltonian. The orbitals were described by the equivalent of a quadruple-zeta basis set. The complete active-space self-consistent field (CASSCF) reference space included all excitations within an active space of 5f, 6d, and 7s state averaged orbitals. Non-SO CI calculations involved the ACPF method for all single and double excitations out of the CASSCF reference, including excitations out of 5d, 6s, and 6p orbitals. The SOCI calculations were complete CI calculations within all open-shell orbitals (equivalent to our VFCI). For the lowest LS labeled term state in each Am atom or ion, the SOCI difference is calculated between the lowest level emerging from that term and the center of gravity (COG) of all the levels emerging from that term. The resulting SOCI difference is then added to the ACPF results for the final estimate of the energy. In effect, the final result is a hybrid of SOCI and non-SO ACPF calculations.

This approach contrasts with what we have reported here in four major ways. First, our pseudopotentials include shells of quantum number 5 or lower, are optimized via orbital shapes and energies, and include spin orbit effects from a full order Dirac-Hamiltonian.⁸ Second, our basis set is only triple-zeta, whereas the basis set of LKD is quadaruple-zeta. Third, our orbital optimizations are unrestricted by state averaging. Fourth, SO effects are explicitly included in the SOCI calculations beyond the VFCI level. This means that the hybrid mix of reference SOCI calculations and highly corrrelated non-SO CI calculations can be directly tested.

A comparison of these previous results with those reported here and with measured or theoretical results is given in Table I. The spread of values for the DFT results of LKD encompass the extremes of values for the different DFT calculations they report. In general, our ab initio results have the smallest values, with the LKD ab initio results higher and the LKD DFT results higher still. For the IP1 and IP2 results in Table

I, SO effects are unimportant, and sensitivity to basis sets, as discussed earlier, is rather minimal. The difference between the two ab initio results in Table I is less than 0.1 eV, smaller than the differences of either from experiment. All these differences are most likely due to imperfect pseudopotentials used here and by LKD, but further calculations are needed to clarify this. The differences between DFT results are larger, and it is hard to discern any trends.

The IP3 value in Table I is sensitive to the treatment of SO effects, and the two ab initio results handle SO effects very differently. LKD determine additive SO corrections only at the equivalent of our VFCI level, while we explicitly include SO effects in all our CI calculations. Nonetheless, the resulting two ab initio values are within 0.17 eV of each other in Table I. However, this agreement is somewhat deceptive because our SOCI calculations do not take into account likely basis set or size extensivity errors as presented in Fig. 3, while LKD include these errors through a hybrid mix of calculations.

This hybrid scheme can be directly tested at various levels by our SOCI calculations. In particular, we can decompose all of our SOCI calculations into two parts: (1) the separations between the COG of each oxidation state in the IPn and (2) the separation of the lowest state of each oxidation state from its COG. The hybrid scheme of LKD approximates the first part of the decomposition by a high-order non-SO ACPF calculation and the second part by a small SOCI calculation. As discussed in the preceding section, for IP1 and IP2, the non-SO CI and SOCI calculations of the first part never differ by more than 0.06 eV, consistent with the second part of the decomposition being identically zero. Thus, the hybrid scheme is quite accurate. However, for IP3, the second part of the decomposition for Am^{+3} is not identically zero. The lowest LS term of Am^{+3} is ⁷F, which the SO operator splits into seven levels with J = 0, 1,..., 6 of which the ground state is ⁷F₀. In Table II, the decomposition is reported for IP3 for all the SOCI calculations performed. In Table III a variety of non-SO CI calculations are displayed to compare with the first part of the decomposition in Table II.

The results in Table II show that the separation energy between Am^{+2} and the COG of the lowest ⁷F term of Am⁺³ is relatively insensitive to single excitations. The separation energy decreases by 0.19 eV with excitations from the 6s6p and 5f subshells but decreases 0.02 eV with only 5f excitations. However, subsequent double excitations that exclude 6s6p cause this separation energy to go up by 1.34 to 1.38 eV. This is quite consistent with the results in Fig. 4, which display IP3 directly (i.e., separation from the lowest state in Am^{+3} , not the COG of Am^{+3}). The degree to which the separation energy can be reproduced by non-SO CI calculations is found by a comparison of Table II and Table III. In Table III, non-SO CI calculations for IP3 are listed as a function of the number of basis functions and the nature of the orbitals that undergo excitations for Am⁺³. The SOCI results of Table II are for the contracted double-zeta basis set and for restricted-SCF orbitals. Those selections are found in Table III along with the full double-zeta basis set and symmetry-broken Am⁺³ orbitals. Table III shows that the basis set and nature of the orbitals have almost no effect on the calculated IP3, producing changes that are on the order of a few hundredths of an eV. However, variations in excitations do cause significant changes in the IP3 value. A comparison between Table II and Table III shows that, to a large degree, these changes with excitation mirror quite well the SOCI calculated separation energy of Am⁺² and the COG of the lowest term of Am⁺³. The maximum error is about 0.26 eV, occurring in all non-SO CI calculations that involve single excitations from 6s6p. The comparison between Tables II and III of calculations with 6s6p excitations is imperfect because the non-SO CI calculations allow single and double excitations from the 6s6p and 5f while SOCI calculations allow 6s6p and 5f single excitations and 5f double excitations only. Nonetheless, arguments discussed previously suggest that double excitations out of 6s6p are not particularly important. Thus, the results in Table III suggest that the non-SO CI calculations will overestimate the SOCI results by about 0.25 eV.

For the second part of the decomposition, in Table II, the separation from the COG to the lowest state in Am⁺³ varies by no more that 0.15 eV with additional excitations. The presence of single excitations out of the 6s6p changes this energy by 0.05 eV. Part of the reason for the small absolute change is that this energy is small to begin with. A 0.15 eV change in its value with excitation is greater than a 20% relative change. Thus, a very modestly correlated SOCI calculation appears to get about 80% of a relatively small number. However, unlike the first part of the decomposition, the second part of the decomposition can be compared with experiment. The highest-level calculations in Table III, namely, [S+D(no6s6p)], are significantly too small, about 70%, relative to the measured Am⁺³ f-f spectroscopy in LaCl₃ crystals³³. In principle, the decomposition is not specifically detailed in their publication. However, additional calculations we have performed, which will be the subject of a future publication, indicate that both the LKD pseudopotential and the pseudopotential used here result in errors in the description of the second part of the decomposition.

The results in Tables II and III lend support to a decomposition of IP3 into a large part that is approachable by non-SO CI calculations and a second part that is determined from f-f spectroscopy. This would imply that the largest non-SO CI calculation that can be done with the largest basis set can be combined with the best *measured* f-f spectroscopy for Am^{+3} to obtain the most reliable estimate of IP3. If the contrast between Tables II and III is any guide, this calculation could be about 0.25 eV too large. Figure 3 gives the best non-SO ACPF result of 23.63 eV for the triple-zeta basis set. The SO correction based on measured f-f spectroscopy in crystals is -1.16 eV \pm 0.01 eV, where the uncertainty is due to crystal field splittings not relevant to our gas phase calculations. Combining these two values gives an IP3 of 22.47 eV \pm .25 eV with an overestimation being more likely than an underestimation. This value is listed in Table I as the semi-empirical value under the current study. It represents the best estimate of IP3 to emerge from this study. Even with an enlarged uncertainty, the previous semi-empirical value of Morss receives the most support from the work reported here and from that of LKD.

V. Conclusions

In the first application of a new massively parallel spin-orbit configuration interaction code, P-SOCI, the first three ionization potentials of americium have been calculated. The computed values have an absolute error of less than 0.3 eV from the only direct experimental value, that for the first ionization potential. The second ionization potentials is within 0.3 eV of indirect experimental results, while the third ionizaton potential is within 0.6 eV. Differences of a similar but smaller size are also found between the computed results and recently published theoretical calculations.

The first two ionization potentials of americium are readily determined with non-SO CI wavefunctions that include only the scalar relativistic effects through a spin-orbit averaged relativistic effective core potential. The third ionization potential requires the direct incorporation of the spin-orbit operator in the calculation. Single excitations have little effect on any of the ionization potentials, but double excitations out of at least the 5f subshell are crucial. For IP3, the number of configurations required in the CI depends strongly on the choice of AOs. If the orbital basis is derived from a typical MCSCF calculation, the 5f orbitals will be symmetry broken but correlated well enough so that 6s6p excitations are largely unimportant in computing the IP. The same is true for the restricted-SCF procedure that produces spherically averaged 5f orbitals of the correct symmetry. However, if the orbital basis has the correct symmetry but is derived from another oxidation state, for example, Am⁺², the 6s6p single excitations appear necessary to substantially relax this basis.

Tests were carried out for the decomposition of our calculated SO and non-SO IPs into a component that contains the separation between the centers of gravity of the lowest atomic terms and a component that connects the separation of each term's lowest level with its center of gravity. Comparison of SOCI and non-SOCI center of gravity separation energies shows less than a 0.06 eV difference for IP1 and IP2 and a somewhat larger 0.25 eV difference for IP3. The second component is nonzero only for IP3 but show that the SOCI is significantly converged for IP calculations at low levels of CI. SOCI calculations with correlation in excess of the VFCI cause absolute changes of no more than about 0.15 eV. However, the best SOCI values are only 70% of experiment for this component. This decomposition suggests that a semi-empirical result generated using the best non-SO CI calculations for the first component and the experimental value for the second component gives the best estimate of IP3.

If 6s6p excitations can be excluded from the atomic IP calculations, very large pseudopotential cores may be formulated to simplify the electronic structure calculations and significantly reduce the time to solution. Molecular calculations involving actinides present the possibility of the actinide species exhibiting an intermediate in-situ oxidation state resulting from partial charge transfer to a ligand. Since it is possible that the amount of electron transfer at the SOCI level may differ significantly from that obtained during the generation of the orbitals, we believe incorporation of 6s6p single excitations into the SOCI will need to be tested to determine whether orbital relaxation will be necessary. Alternatively, core/valence potentials³⁴ may enable the necessary orbital relaxation without introducing those 6s6p electrons into the active space. We are actively pursuing this direction of development.

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	IP1	IP2	IP3
Current Study			
Ab Initio Semi-Empirical	5.66	11.69	21.82 $22.47 \pm .26$
LKD			
Ab Initio Hybrid	5.75	11.73	21.99
DFT	5.58 - 5.82	11.89 - 12.04	22.70 - 22.84
Measurement			
Direct	5.97a		
Exp./Theor.		12.00b	18.80c
1		12.15c	19.90b
			20.45d
			21.89e
a Ref 1			

Table I. Comparison of calculated and measured first through third ionization potentials in eV. (See text for details)

^b Ref. 26.

c Ref. 24.

d Ref. 27.

e Ref. 29.

Type of Calculation	Am ⁺³ (COG)–Am ⁺² eV	Am ⁺³ ([⁷ F ₀]-COG) eV
VFCI	21.47	-0.65
S(no6s6p)	21.45	-0.66
SD(no6s6p)	22.83	-0.75
VFCI	21.47	-0.65
S	21.28	-0.72
S+D(no6s6p)	22.62	-0.80

Table II. Decomposition of SOCI IP values. See text for details.

Type of Calculation $Am^{+3} - Am^{+2}$					
excitation	orbitals	eV			
Re-contracted double-zeta basis set results (47 basis functions)					
VFCI	sym broken	21 47			
S(no6s6p)	sym. broken	21.47			
SD(no6s6p)	sym. broken	22.86			
VFCI	sym. broken	21.47			
S	sym. broken	21.53			
SD	sym. broken	22.85			
VFCI	restricted-SCF	21.49			
SD	restricted-SCF	22.85			
Double-zeta basis set results (59 basis functions)					
VFCI	sym. broken	21.46			
S(no6s6p)	sym. broken	21.46			
SD(no6s6p)	sym. broken	22.85			
VFCI	sym. broken	21.46			
S	sym. broken	21.56			
SD	sym. broken	22.87			
VFCI	restricted-SCF	21.48			
SD	restricted-SCF	22.87			

Table III. The calculated value of IP3 in eV for non-SO CI calculations as a function of orbital type and the number of basis functions.

- Figure 1. Comparison of the experimental first ionization potential of americium with ab initio results. The horizontal axis characterizes the CI expansion used in the calculations. Experimental results are Ref. 1 (filled Δ), Ref. 24 (filled ◊), Ref. 25 (filled □). Theoretical results are: double-zeta basis (O), triple-zeta basis (□), triple-zeta with Davidson correction (◊), and triple-zeta ACPF (Δ). (See the text for details.)
- Figure 2. Comparison of the experimental second ionization potential of americium ab initio results. The axes are analogous to those in Fig. 1. Experimental results are Ref. 26 (filled Δ), Ref. 24 (filled \Diamond). The theoretical results are as labeled in Fig. 1. (See the text for details.)
- Figure 3. Comparison of the experimental third ionization potential of americium ab initio results. The axes are analogous to those in Fig. 1. Experimental results are Ref. 29 (filled □), Ref. 27 (filled ◊), Ref. 26 (filled Δ). The theoretical results are as labeled in Fig. 1. (See the text for details.)
- Figure 4. Comparison of the experimental third ionization potential of americium ab initio results. The axes are analogous to those in Fig. 1 with the exception of SD* on the absissca (see text for details). Experimental results are Ref. 29 (filled □), Ref. 27 (filled △), Ref. 26 (filled ◊). Theoretical results are SOCI (O),. (See the text for details)