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Electronic energies of americium from multiconfiguration Dirac-Fock calculations

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A sophisticated theoretical description of the electronic states of americium has been hindered by the need to treat the half-filled $5f$ shell. We present here *ab initio* calculations for americium on a multiconfiguration Dirac-Fock level. The calculations were possible because only the dominant configuration state functions were used. The results give a reasonable description of the energy of the electronic ground states for the various total angular momenta and parity of americium. The results indicate some corrections for the spectroscopic assignments. [S1050-2947(96)00212-0]

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I. INTRODUCTION

During the past 25 years the relativistic multiconfiguration Dirac-Fock (MCDF) method for atoms proved to be a powerful method for obtaining a description of the ground state as well as excited states of complicated many-electron atoms [1–10]. From the work to generate atomic MCDF computer programs, two programs emerged that are now generally available and can be used to perform calculations for a large number of atoms and ions. One of these is the program by Desclaux [11] and the other is by Grant and Quiney [12,13]. Several nonrelativistic codes are also available, but they are for application to low atomic number atoms only.

Most of the applications have been made at the level of the inclusion of all possible configuration-state functions [14] that can be constructed from a specified set of valence single-particle orbitals. In many cases, such as in the middle of the transition elements series, inclusion of all possible configuration-state functions is at the borderline of or even beyond available computer capabilities. This situation is even worse for the elements in the middle of the lanthanides and actinides series. For these elements the full application of the MCDF method is far from practical on current computers.

To treat such systems as the lanthanide and actinide elements, we used a subset of the configuration-state functions that can be constructed from a specified set of valence single-particle orbitals. An example of such a treatment is presented here. This is the treatment of the $5f$ element americium for which the dominant electron configuration is $(5f)^7(7s)^2$. There are other reasons to treat americium. Apparently, only the $5f$ and $7s$ valence orbitals have been used in calculations for americium [15]. No $6d$ or $7p$ orbitals have been used. The $6d$ and $7p$ orbitals are energetically close to the $5f$ and $7s$ orbitals, thus their contribution to the ground-state wave function is expected to be significant.

The method of choosing the configuration-state functions is described in Sec. II. The Desclaux code was used to obtain MCDF results. Results are presented and discussed in Sec. III. Section IV contains some conclusions.

II. METHOD

The MCDF method is well known and was formulated over 25 years ago [12]. We used the MCDF computer program that was written by Desclaux [11] to perform the calculations. The americium nucleus was treated as a point charge. The Breit interaction was determined using first-order perturbation. The self-energy and vacuum polarization energy were not included. Further calculations have shown that including the self-energy and vacuum polarization energy does not significantly change the transition energies presented below. This finding is in agreement with results presented in Ref. [6]. A conclusion presented in Ref. [6] is that self-energy and vacuum polarization energy has little effect on the fine-structure splittings.

An excellent summary of the MCDF method is given in Ref. [13]. The total wave function ψ of a relativistic many-electron atom is represented as a sum of configuration-state functions. The wave function is given by

$$\psi=\sum_{i=1}^{N} a_i|(\mathcal{F})_i\rangle,$$

where N is the number of configuration-state functions used to construct the total wave function and a_i is the configuration coefficient for configuration-state function i, $|(\mathcal{F})_i\rangle$. The configuration weights that will be used below are the squares of the configuration coefficients. A configuration-state function is an eigenfunction of the total and z component of the angular momentum operators that consists of a linear combination of Slater determinants [16]. Results improve as the completeness of the basis set increases, so as many configuration-state functions are used in calculations as is practical. The Slater determinants are constructed from single-particle relativistic atomic orbitals φ_j, which are eigenfunctions of angular momentum and parity. Each Slater determinant corresponds to a configuration of electrons in single-particle orbitals.

In the MCDF method both the coefficients a_i and the single-particle orbitals φ_j are optimized with respect to the minimum of the total energy of the whole atom. Two

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TABLE I. Electron orbital configurations for the first choice for the wave-function basis set for americium. The seven numbers in the parentheses give the number of electrons in the seven single-particle orbitals $5f^*$, $5f$, $6d^*$, $6d$, $7s$, $7p^*$, and $7p$.

Total angular momentum and parity	Choice 1		
$(\frac{1}{2})^-$	(5,2,0,0,2,0,0),	(5,2,1,0,1,0,0),	(6,1,0,1,1,0,0)
	(5,2,2,0,0,0,0),	(6,1,1,1,0,0,0),	(6,1,0,2,0,0,0)
	(5,2,0,0,0,2,0),	(5,2,0,0,0,1,1),	(5,2,0,0,0,0,2)
	(6,0,0,0,2,1,0),	(5,1,0,0,2,0,1),	(6,0,1,0,1,1,0)
	(5,1,0,1,1,1,0),	(6,0,1,0,1,0,1),	(6,0,0,1,1,0,1)
	(6,0,2,0,0,1,0),	(6,0,1,1,0,1,0),	(6,0,0,2,0,1,0)
	(6,0,2,0,0,0,1),	(6,0,1,1,0,0,1),	(6,0,0,2,0,0,1)
	(5,1,0,0,0,2,1),	(6,0,0,0,0,1,2),	(5,1,0,0,0,0,3)
$(\frac{3}{2})^-$	(5,2,0,0,2,0,0),	(6,1,1,0,1,0,0),	(6,1,0,1,1,0,0)
	(6,1,2,0,0,0,0),	(6,1,1,1,0,0,0),	(6,1,0,2,0,0,0)
	(5,2,0,0,0,2,0),	(6,1,0,0,0,1,1),	(6,1,0,0,0,0,2)
	(5,1,0,0,2,1,0),	(6,0,0,0,2,0,1),	(6,0,1,0,1,1,0)
	(6,0,0,1,1,1,0),	(6,0,1,0,1,0,1),	(6,0,0,1,1,0,1)
	(6,0,2,0,0,1,0),	(6,0,1,1,0,1,0),	(6,0,0,2,0,1,0)
	(6,0,2,0,0,0,1),	(6,0,1,1,0,0,1),	(6,0,0,2,0,0,1)
	(6,0,0,0,0,2,1),	(6,0,0,0,0,1,2),	(6,0,0,0,0,0,3)
$(\frac{5}{2})^-$	(5,2,0,0,2,0,0),	(6,1,1,0,1,0,0),	(6,1,0,1,1,0,0)
	(6,1,2,0,0,0,0),	(6,1,1,1,0,0,0),	(6,1,0,2,0,0,0)
	(5,2,0,0,0,2,0),	(6,1,0,0,0,1,1),	(6,1,0,0,0,0,2)
	(5,1,0,0,2,1,0),	(5,1,0,0,2,0,1),	(6,0,1,0,1,1,0)
	(6,0,0,1,1,1,0)	(6,0,1,0,1,0,1),	(6,0,0,1,1,0,1)
	(6,0,2,0,0,1,0),	(6,0,1,1,0,1,0),	(6,0,0,2,0,1,0)
	(6,0,2,0,0,0,1),	(6,0,1,1,0,0,1),	(6,0,0,2,0,0,1)
	(5,1,0,0,0,2,1),	(6,0,0,0,0,1,2),	(5,1,0,0,0,0,3)
$(\frac{7}{2})^-$	(6,1,0,0,2,0,0),	(6,1,1,0,1,0,0),	(6,1,0,1,1,0,0)
	(6,1,2,0,0,0,0),	(6,1,1,1,0,0,0),	(6,1,0,2,0,0,0)
	(6,1,0,0,0,2,0),	(6,1,0,0,0,1,1),	(6,1,0,0,0,0,2)
	(5,1,0,0,2,1,0),	(5,1,0,0,2,0,1),	(5,1,1,0,1,1,0)
	(6,0,0,1,1,1,0),	(6,0,1,0,1,0,1),	(6,0,0,1,1,0,1)
	(5,1,2,0,0,1,0),	(6,0,1,1,0,1,0),	(6,0,0,2,0,1,0)
	(6,0,2,0,0,0,1),	(6,0,1,1,0,0,1),	(6,0,0,2,0,0,1)
	(5,1,0,0,0,2,1),	(5,1,0,0,0,1,2),	(5,1,0,0,0,0,3)
$(\frac{25}{2})^-$	(3,4,0,0,2,0,0),	(4,3,1,0,1,0,0),	(4,3,0,1,1,0,0)
	(4,3,2,0,0,0,0),	(5,2,1,1,0,0,0),	(5,2,0,2,0,0,0)
	(3,4,0,0,0,2,0),	(4,3,0,0,0,1,1),	(4,3,0,0,0,0,2)
$(\frac{1}{2})^+$	(5,2,0,0,1,1,0),	(5,2,0,0,1,0,1),	(5,2,1,0,0,1,0)
	(6,1,1,0,0,0,1),	(6,1,0,1,0,1,0),	(6,1,0,1,0,0,1)
	(5,1,1,0,2,0,0),	(5,1,0,1,2,0,0),	(6,0,2,0,1,0,0)
	(6,0,1,1,1,0,0),	(6,0,0,2,1,0,0),	(5,1,3,0,0,0,0)
	(6,0,2,1,0,0,0),	(6,0,1,2,0,0,0),	(6,0,0,3,0,0,0)
	(6,0,0,0,1,2,0),	(6,0,0,0,1,1,1),	(6,0,0,0,1,0,2)
	(5,1,1,0,0,2,0),	(6,0,1,0,0,1,1),	(6,0,1,0,0,0,2)
	(5,1,0,1,0,2,0),	(6,0,0,1,0,1,1),	(6,0,0,1,0,0,2)
$(\frac{3}{2})^+$	(5,2,0,0,1,1,0)	(6,1,0,0,1,0,1),	(6,1,1,0,0,1,0)
	(6,1,1,0,0,0,1),	(6,1,0,1,0,1,0),	(6,1,0,1,0,0,1)
	(6,0,1,0,2,0,0),	(5,1,0,1,2,0,0),	(6,0,2,0,1,0,0)
	(6,0,1,1,1,0,0),	(6,0,0,2,1,0,0),	(6,0,3,0,0,0,0)
	(6,0,2,1,0,0,0),	(6,0,1,2,0,0,0),	(6,0,0,3,0,0,0)
	(5,1,0,0,1,2,0),	(6,0,0,0,1,1,1),	(6,0,0,0,1,0,2)
	(6,0,1,0,0,2,0),	(6,0,1,0,0,1,1),	(6,0,1,0,0,0,2)
	(5,1,0,1,0,2,0),	(6,0,0,1,0,1,1),	(6,0,0,1,0,0,2)
$(\frac{5}{2})^+$	(6,1,0,0,1,1,0),	(6,1,0,0,1,0,1),	(6,1,1,0,0,1,0)
	(6,1,1,0,0,0,1),	(6,1,0,1,0,1,0),	(6,1,0,1,0,0,1)
	(5,1,1,0,2,0,0),	(6,0,0,1,2,0,0),	(6,0,2,0,1,0,0)
	(6,0,1,1,1,0,0),	(6,0,0,2,1,0,0),	(5,1,3,0,0,0,0)
	(6,0,2,1,0,0,0),	(6,0,1,2,0,0,0),	(6,0,0,3,0,0,0)
	(5,1,0,0,1,2,0),	(6,0,0,0,1,1,1),	(6,0,0,0,1,0,2)
	(5,1,1,0,0,2,0),	(6,0,1,0,0,1,1),	(6,0,1,0,0,0,2)
	(6,0,0,1,0,2,0),	(6,0,0,1,0,1,1),	(6,0,0,1,0,0,2)
$(\frac{7}{2})^+$	(6,1,0,0,1,1,0),	(6,1,0,0,1,0,1),	(6,1,1,0,0,1,0)
	(6,1,1,0,0,0,1),	(6,1,0,1,0,1,0),	(6,1,0,1,0,0,1)
	(5,1,1,0,2,0,0),	(5,1,0,1,2,0,0),	(5,1,2,0,1,0,0)
	(6,0,1,1,1,0,0),	(6,0,0,2,1,0,0),	(5,1,3,0,0,0,0)
	(6,0,2,1,0,0,0),	(6,0,1,2,0,0,0),	(6,0,3,0,0,0,0)
	(5,1,0,0,1,2,0),	(5,1,0,0,1,1,1),	(5,1,0,0,1,0,2)
	(5,1,1,0,0,2,0),	(6,0,1,0,0,1,1),	(6,0,1,0,0,0,2)
	(5,1,0,1,0,2,0),	(6,0,0,1,0,1,1),	(6,0,0,1,0,0,2)

approximations were made in choosing the single-particle orbitals used. First, the number of single-particle orbitals that should be included is infinite, so the first approximation in every MCDF calculation is the choice of the specific basis. A natural choice in the numerical MCDF code [11,14] are single-particle atomic wave functions. The calculation should include all of those wave functions that have their maxima in the region of the valence shell. Highly excited orbitals are usually left out.

Second, configuration-state functions that contain excitations of occupied inner-shell orbitals contribute, but they are usually left out because of impracticability and convergence problems that often occur in such calculations. We therefore restrict ourselves to the single-particle orbitals $5f$, $7s$, $6d$, and $7p$ as the valence orbitals. All the inner orbitals from $1s$ to $6p$ are taken as occupied and not involved in the explicit MCDF procedure. In addition, we do not consider here higher orbitals such as $8s$ and $7d$.

Since we are using a relativistic treatment, the valence orbitals used in the MCDF treatment are $5f^*$, $5f$, $7s$, $6d^*$, $6d$, $7p^*$, and $7p$, where the asterisk denotes the orbital with total angular momentum equal to $L-\frac{1}{2}$ and the orbital without the asterisk has a total angular momentum equal to $L+\frac{1}{2}$. Here L is the orbital angular momentum. For example, the orbitals $5f^*$ and $5f$ are also denoted as $5f_{5/2}$ and $5f_{7/2}$, respectively. In the case of americium the 7 valence orbitals are occupied by 9 electrons and the radon core has 86 electrons. The problem for americium is now well defined:

TABLE II. Electron orbital configurations for the second and third choices for the wave-function basis set for americium. The seven numbers in the parentheses give the number of electrons in the seven single-particle orbitals $5f^*$, $5f$, $6d^*$, $6d$, $7s$, $7p^*$, and $7p$.

Total angular momentum and parity	Choice 2	Choice 3
$(\frac{1}{2})^-$	(6,0,0,0,2,1,0)	(6,0,0,0,2,1,0)
	(5,1,0,0,2,1,0)	(5,1,0,0,2,1,0)
	(4,2,0,0,2,1,0)	(4,2,0,0,2,1,0)
	(3,3,0,0,2,1,0)	(6,0,1,0,1,1,0)
	(2,4,0,0,2,1,0)	(6,0,1,0,1,0,1)
	(1,5,0,0,2,1,0)	(6,0,0,1,1,0,1)
	(0,6,0,0,2,1,0)	(6,0,2,0,0,1,0)
		(6,0,1,1,0,1,0)
		(6,0,0,2,0,1,0)
		(6,0,2,0,0,0,1)
		(6,0,1,1,0,0,1)
		(6,0,0,2,0,0,1)
		(6,0,0,0,0,1,2)
$(\frac{3}{2})^-$	(6,0,0,0,2,0,1)	(6,0,0,0,2,0,1)
	(5,1,0,0,2,0,1)	(5,1,0,0,2,0,1)
	(4,2,0,0,2,0,1)	(4,2,0,0,2,0,1)
	(3,3,0,0,2,0,1)	(3,3,0,0,2,0,1)
	(2,4,0,0,2,0,1)	(6,0,1,0,1,1,0)
	(1,5,0,0,2,0,1)	(6,0,0,1,1,1,0)
	(0,6,0,0,2,0,1)	(6,0,1,0,1,0,1)
		(6,0,0,1,1,0,1)
		(6,0,2,0,0,1,0)
		(6,0,1,1,0,1,0)
		(6,0,0,2,0,1,0)
		(6,0,2,0,0,0,1)
		(6,0,1,1,0,0,1)
		(6,0,0,2,0,0,1)
		(6,0,0,0,0,2,1)
		(6,0,0,0,0,1,2)
		(6,0,0,0,0,0,3)
$(\frac{5}{2})^-$	(6,0,1,0,1,1,0)	(6,0,1,0,1,1,0)
	(5,1,1,0,1,1,0)	(5,1,1,0,1,1,0)
	(4,2,1,0,1,1,0)	(4,2,1,0,1,1,0)
		(6,0,0,1,1,1,0)
		(6,0,1,0,1,0,1)
		(6,0,0,1,1,0,1)
		(6,0,2,0,0,1,0)
		(6,0,1,1,0,1,0)
		(6,0,0,2,0,1,0)
		(6,0,2,0,0,0,1)
		(6,0,1,1,0,0,1)
		(6,0,0,2,0,0,1)
		(6,0,0,0,0,1,2)
$(\frac{7}{2})^-$	(6,1,0,0,2,0,0)	(6,1,0,0,2,0,0)
	(5,2,0,0,2,0,0)	(5,2,0,0,2,0,0)
	(4,3,0,0,2,0,0)	(4,3,0,0,2,0,0)
	(3,4,0,0,2,0,0)	(3,4,0,0,2,0,0)
	(2,5,0,0,2,0,0)	(2,5,0,0,2,0,0)
	(1,6,0,0,2,0,0)	(1,6,0,0,2,0,0)
	(0,7,0,0,2,0,0)	(0,7,0,0,2,0,0)
		(6,1,1,0,1,0,0)
		(6,1,0,1,1,0,0)
		(6,1,2,0,0,0,0)
		(6,1,1,1,0,0,0)
		(6,1,0,2,0,0,0)
		(6,1,0,0,0,2,0)
		(6,1,0,0,0,1,1)
		(6,1,0,0,0,0,2)
$(\frac{25}{2})^-$	(3,4,0,0,2,0,0)	(3,4,0,0,2,0,0)
		(4,3,1,0,1,0,0)
		(4,3,0,1,1,0,0)
		(4,3,2,0,0,0,0)
		(5,2,1,1,0,0,0)
		(5,2,0,2,0,0,0)
		(3,4,0,0,0,2,0)
		(4,3,0,0,0,1,1)
		(4,3,0,0,0,0,2)
		(3,4,0,0,0,0,2)
$(\frac{1}{2})^+$	(5,1,1,0,2,0,0)	(5,1,1,0,2,0,0)
	(4,2,1,0,2,0,0)	(4,2,1,0,2,0,0)
	(3,3,1,0,2,0,0)	(3,3,1,0,2,0,0)
	(2,4,1,0,2,0,0)	(5,1,0,1,2,0,0)
	(1,5,1,0,2,0,0)	(5,1,3,0,0,0,0)
	(0,6,1,0,2,0,0)	(5,1,1,0,0,2,0)
		(5,1,0,1,0,2,0)
$(\frac{3}{2})^+$	(6,0,1,0,2,0,0)	(6,0,1,0,2,0,0)
	(5,1,1,0,2,0,0)	(5,1,1,0,2,0,0)
	(4,2,1,0,2,0,0)	(4,2,1,0,2,0,0)
	(3,3,1,0,2,0,0)	(6,0,2,0,1,0,0)
	(2,4,1,0,2,0,0)	(6,0,1,1,1,0,0)
	(1,5,1,0,2,0,0)	(6,0,0,2,1,0,0)
	(0,6,1,0,2,0,0)	(6,0,3,0,0,0,0)
		(6,0,2,1,0,0,0)
		(6,0,1,2,0,0,0)
		(6,0,0,3,0,0,0)
		(6,0,0,0,1,1,1)
		(6,0,0,0,1,0,2)
		(6,0,1,0,0,2,0)
		(6,0,1,0,0,1,1)
		(6,0,1,0,0,0,2)
		(6,0,0,1,0,1,1)
		(6,0,0,1,0,0,2)
$(\frac{5}{2})^+$	(5,1,1,0,2,0,0)	(5,1,1,0,2,0,0)
	(4,2,1,0,2,0,0)	(4,2,1,0,2,0,0)
	(3,3,1,0,2,0,0)	(3,3,1,0,2,0,0)
	(2,4,1,0,2,0,0)	(2,4,1,0,2,0,0)
	(1,5,1,0,2,0,0)	(5,1,3,0,0,0,0)
	(0,6,1,0,2,0,0)	(5,1,0,0,1,2,0)
		(5,1,1,0,0,2,0)
$(\frac{7}{2})^+$	(5,1,0,1,2,0,0)	(5,1,1,0,2,0,0)
	(4,2,0,1,2,0,0)	(5,1,0,1,2,0,0)
	(3,3,0,1,2,0,0)	(4,2,0,1,2,0,0)
		(3,3,0,1,2,0,0)
		(5,1,2,0,1,0,0)
		(5,1,3,0,0,0,0)
		(5,1,0,0,1,2,0)
		(5,1,0,0,1,1,1)
		(5,1,0,0,1,0,2)
		(5,1,1,0,0,2,0)
		(5,1,0,1,0,2,0)

construct all configuration-state functions that have 9 electrons in the 7 valence orbitals and have a given total angular momentum and parity. This leads to a very large number of configuration-state functions. Even with the restriction of state functions to eigenfunctions of the parity and total angular momentum operators, the number of configuration-state functions is too large to be handled by current computers and this is the reason why no full-scale MCDF calculations exist for americium and other such elements.

Our choice 1 for the americium configuration-state functions includes configurations with every allowable distribution of 2 or 3 electrons in the $7s$, $6d^*$, $6d$, $7p^*$, and $7p$ orbitals. The distribution of the remaining 7 or 6 electrons in the $5f^*$ and $5f$ orbitals are restricted. The restriction consists of selecting the allowed configurations with a maximum number of electrons in the $5f^*$ orbital. Choice 1 is given in Table I as a function of the total angular momentum. Each configuration in choice 1 is denoted by a set of seven ordered numbers. For example, the set (6,1,1,0,1,0,0) denotes the configuration $(5f^*)^6(5f\ )^1(6d^*)^1(6d)^0(7s)^1(7p^*)^0(7p)^0$. Choice 1 is only a first approximation and, as it will be shown in Sec. III, does not lead to results that are suitably accurate, so other choices need to be considered.

The configuration in a choice-1 set with the largest weight is a function of the total angular momentum. This configuration for a given total angular momentum will be called the principal configuration for that total angular momentum. A principal configuration has a specific number of electrons in the $5f^*$ and $5f$ orbitals and a specific number in the $7s$, $6d^*$, $6d$, $7p^*$, and $7p$ orbitals. Choice-2 basis sets contain the principal configuration plus configurations that are derived from the principal configuration by changing the distribution of electrons in the $5f^*$ and $5f$ orbitals with the number of electrons in the $7s$, $6d^*$, $6d$, $7p^*$, and $7p$ orbitals fixed. Choice-3 basis sets contain the principal configuration plus all of the allowed configurations that are derived from the principal configuration by changing the distribution of electrons in the $7s$, $6d^*$, $6d$, $7p^*$, and $7p$ orbitals with the number of electrons in the $5f$ orbitals fixed plus some of the configurations that are derivable from the principal configuration by changing the distribution of electrons in the $5f^*$ and $5f$ orbitals with the number of electrons in the $7s$, $6d^*$, $6d$, $7p^*$, and $7p$ orbitals fixed. The number of configurations selected for choice 3 is influenced by the computation time required to obtain energies using it. Several hundred hours of computation time were required for some choices. Choices 2 and 3 for the wave-function basis set for americium as a function of total angular momentum are presented in Table II. Table III contains the number of configuration-state functions that are associated with choices 1, 2, and 3 as a function of total angular momentum and parity.

For any large angular momentum, the number of configuration-state functions that can be constructed with 9 electrons in the $5f$, $7s$, $6d$, and $7p$ shells becomes small enough that a calculation that uses all of these configuration-state functions can be performed. Results from this calculation can be compared with the results from using the choice-1, -2, and -3 basis sets. For the value of the total angular momentum equal to $(\frac{25}{2})^-$ only 196 configuration-state functions are obtained when 7 electrons are in the $5f$ shell. A full-scale MCDF calculation with this basis set for neutral americium leads to a total energy of 827 617.482 eV. The choice-3 basis gives a total energy of 827 617.394 eV. In this case the choice-3 basis contains only 27 configuration-state functions. The energy from the choice-3 basis set differs by just 0.09 eV from the full MCDF value. Of course, this comparison is not a proof of the reliability of the choice-3 basis sets, but it is a strong argument in favor of some degree of reliability of the results that we obtain with the configuration-state functions of choice 3.

TABLE III. Number of configuration-state functions used in the MCDF calculations for the neutral americium atom for the three choices of subsets discussed in the text.

Total angular momentum and parity	Number of configuration-state functions Choice 1	Choice 2	Choice 3
$(\frac{1}{2})^-$	61	33	19
$(\frac{3}{2})^-$	39	107	79
$(\frac{5}{2})^-$	53	102	117
$(\frac{7}{2})^-$	86	50	68
$(\frac{25}{2})^-$	21	1	27
$(\frac{1}{2})^+$	47	56	38
$(\frac{3}{2})^+$	48	107	41
$(\frac{5}{2})^+$	48	139	130
$(\frac{7}{2})^+$	93	115	175

III. RESULTS

Using the configuration-state functions that we described in Sec. II, we were able to perform various MCDF calculations for neutral americium. Table IV shows the ground-state values of the total energy as a function of the total angular momentum for neutral americium with choices 1, 2, and 3 for the basis functions. Choice 1 for the basis set was used only to determine the dominant weights of the various configuration-state functions in order to find out which configuration-state functions should be included in choices 2 and 3. It is interesting that the choice-1 basis set yields a

TABLE IV. Total energies obtained using the basis sets given in Tables I and II.

Total angular momentum and parity	Energy (eV) Choice 1	Choice 2	Choice 3
$(\frac{1}{2})^-$	−827 621.902	−827 621.986	−827 622.481
$(\frac{3}{2})^-$	−827 620.998	−827 621.256	−827 621.618
$(\frac{5}{2})^-$	−827 620.627	−827 620.892	−827 621.283
$(\frac{7}{2})^-$	−827 620.207	−827 623.625	−827 623.642
$(\frac{25}{2})^-$	−827 617.147	−827 616.866	−827 617.394
$(\frac{1}{2})^+$	−827 621.822	−827 622.387	−827 622.501
$(\frac{3}{2})^+$	−827 622.493	−827 623.071	−827 623.159
$(\frac{5}{2})^+$	−827 622.055	−827 622.777	−827 622.786
$(\frac{7}{2})^+$	−827 621.278	−827 621.872	−827 622.130

TABLE V. Term symbols and dominant electron configuration of the lowest-energy states of americium as a function of the total angular momentum. For the calculated energies the weights of several dominant configurations are given. No term symbols are associated with the calculated values.

Total angular momentum and parity	Experiment		Calculations	
	Term	Configuration	Dominant configurations	Weight
$(\frac{1}{2})^-$			(6,0,0,0,2,1,0)	0.71
			(4,2,0,0,2,1,0)	0.15
$(\frac{3}{2})^-$			(6,0,0,0,2,0,1)	0.70
			(4,2,0,0,2,0,1)	0.17
$(\frac{5}{2})^-$	$^{10}D_{5/2}$	$(5f)^7(5d)^1(7s)^1$	(6,0,1,0,1,1,0)	0.61
			(4,2,1,0,1,1,0)	0.15
$(\frac{7}{2})^-$	$^8S_{7/2}$	$(5f)^7(7s)^2$	(4,3,0,0,2,0,0)	0.62
			(5,2,0,0,2,0,0)	0.17
$(\frac{1}{2})^+$			(5,1,1,0,2,0,0)	0.77
			(3,3,1,0,2,0,0)	0.14
$(\frac{3}{2})^+$			(6,0,1,0,2,0,0)	0.74
			(4,2,1,0,2,0,0)	0.17
$(\frac{5}{2})^+$		$(5f)^7(7s)^1(7p)^1$	(5,1,1,0,2,0,0)	0.42
			(4,2,1,0,2,0,0)	0.29
			(3,3,1,0,2,0,0)	0.11
$(7/2)^+$	$^{10}P_{7/2}$	$(5f)^7(7s)^1(7p)^1$	(5,1,0,1,2,0,0)	0.67
			(3,3,0,1,2,0,0)	0.14

ground state with a positive parity and with the total angular momentum equal to $\frac{3}{2}$. This clearly demonstrates that choice-1 basis sets are not suitable. In column 3 of Table IV the results for the total energies are given for choice 2. Column 4 lists the results for the total energies using choice 3. To show that the configurations that give the dominant contributions are different for different values of the total angular momentum, the weights of the one, two, or three dominant configurations are given in Table V. Note that only the spectroscopic assignment of the ground-state configuration with $(5f)^7(7s)^2$ is in agreement with the calculated results. The calculated results indicate that the assignments are probably $(5f)^6(6d)^1(7s)^1(7p)^1$, $(5f)^6(6d)^1(7s)^2$, and $(5f)^6(6d)^1(7s)^2$ for the lowest-energy states with a total angular momentum and parity of $(\frac{5}{2})^-$, $(\frac{5}{2})^+$, and $(\frac{7}{2})^+$, respectively. To see the results on a relative scale we have listed in Table VI the calculated total energies for several total angular momentum eigenvalues relative to the ground-state eigenvalue. The experimental values [17,18] for the energy levels of neutral americium along with the spectroscopic assignments of these configurations are given also.

TABLE VI. Experimental [17,18] and calculated energy differences between several total angular momentum eigenvalues and the ground-state eigenvalue. The calculated values were obtained using the choice-3 basis sets.

Total Angular Momentum and Parity	Experiment		Calculations
	Term	Energy (eV)	Energy (eV)
$(\frac{1}{2})^-$			1.16
$(\frac{3}{2})^-$			2.02
$(\frac{5}{2})^-$	$^{10}D_{5/2}$	1.95	2.36
$(\frac{7}{2})^-$	$^8S_{7/2}$	0	0
$(\frac{1}{2})^+$			1.14
$(\frac{3}{2})^+$			0.48
$(\frac{5}{2})^+$		2.21	0.86
$(\frac{7}{2})^+$	$^{10}P_{7/2}$	1.94	1.51

It is difficult to assess the accuracy of the calculated results on the basis of a comparison with experimental results since only a few experimental values are available. The comparison of the calculated and experimental values for the energies for a total angular momentum and parity of $(\frac{5}{2})^+$ and $(\frac{7}{2})^+$ indicates that one or both of these experimental absorption lines may have been misassigned. This follows because the uncertainty in the differences between calculated values of the same parity in Table VI is probably less than 0.5 eV and the experimental value for a total angular momentum and parity of $(\frac{5}{2})^+$ minus the experimental value for a total angular momentum and parity of $(\frac{7}{2})^+$ is not within 0.5 eV of the corresponding value that is determined from calculated transition energies. This experimental difference and the corresponding difference based on calculations is 0.27 and -0.65 eV, respectively. The estimate of 0.5 eV for the uncertainty of the differences between transition energies of the same parity in Table VI is based on the performance of the MCDF method with Breit interactions for some excitation energies of the lanthanide elements [10]. The results for energies show that the choice-3 basis sets usually give the best results. Further work indicated that good results are obtainable for total angular momentum values of $\frac{9}{2}$ and $\frac{11}{2}$, but these require very long computation times. The computation time decreases for total angular momentum values that are greater than $\frac{11}{2}$.

IV. CONCLUSION

We have performed the largest quantum-mechanical calculations yet completed for the neutral atom of americium on the relativistic MCDF level. We have considered three choices for the basis set. The first basis was used to determine which configuration-state functions should be included in the largest calculations. The configurations included are the dominant ones. The second choice made it clear that it is important to include more than one distribution of the electrons in the $6d$, $6d*$, $7s$, $7p*$, and $7p$ subshells. The third choice gave the most accurate results. The basis functions for choice 3 are given in Table II. Although we were only able to consider a certain subspace of the possible configuration-state functions, the comparison with the few experimental results that are available shows a quantitative agreement with the experiment. This seems to be the first large-scale MCDF calculation on an f element with 9 valence electrons.

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