The effect of $5f$ states on the $nd \rightarrow 5f$ transition energies and spectra of americium ions

N J Dala$^{1,2,*}$, Wu Zhong-Wen$^{1}$, Ding Xiao-Bin$^{1}$, Xie Lu-You$^{1}$ and Dong Chen-Zhong$^{1}$

1. Key Laboratory of Atomic and Molecular Physics and Functional Materials of Gansu Province, College of Physics and Electronic Engineering, Northwest Normal University, Lanzhou 730070, People’s Republic of China
2. University of Geneina, Western Darfur State, Sudan
* Author to whom any correspondence should be addressed.
E-mail: zhongwen.wu@nwnu.edu.cn and dongcz@nwnu.edu.cn

Abstract
The spectra originating from the electric dipole transitions of $nd$ ($n = 3 \rightarrow 5$) core excited states to the 5f valence states of Am$^{2+}$ to Am$^{8+}$ ions have been calculated using the Dirac-Hartee-Fock method, which are compared with the results from the Flexible Atomic Code for the explanation of accuracy. It is found that both the $N_{4,5}(3d \rightarrow 5f)$ and $N_{4,5}(4d \rightarrow 5f)$ spectra of these ions consist of two peaks that are well separated in energy respectively by 202.11 eV and 49.10 eV due to strong spin-orbit interaction of the $3d^{-1}$ and $4d^{-1}$ hole state, while the $O_{4,5}(5d \rightarrow 5f)$ spectra show a broad quasi-continuum profile.

1. Introduction

Americium (Am) is a radioactive element with atomic number $Z = 95$. It is the third element past uranium and the fourth element discovered after curium. The main isotopes of Am are known as $^{243}$Am (with a half-lifetime $\tau_{1/2} = 7,400$ yr), $^{241}$Am ($\tau_{1/2} = 433$ yr), and $^{242}$Am ($\tau_{1/2} = 152$ yr). Am is the product of a series of successive neutron captures plutonium, and its most common use is focused on smoke detectors

Recently, Moore et al [14] studied the $N_{4,5}$ a short-hand notation for the $4d \rightarrow 5f$ transition spectra of Am metal by using the electron energy-loss spectroscopy (EELS). Butterfield et al [15] examined the $O_{4,5}$ ($5d \rightarrow 5f$) edge structure of the ground state α-phase of Am metal using the same experimental technique as in [14]. Furthermore, Buck and Fortner [16] have measured the absorption edge energies of Am also with the use of the EELS.

In the present work, the relative intensities of spectra originating from the electric dipole transitions from the $nd$ ($n = 3 \rightarrow 5$) core states excited to the 5f valence states of Am$^{2+}$ to Am$^{8+}$ ions have been theoretically studied by using the multiconfiguration Dirac–Hartee–Fock (MCDHF) method [17, 18] and its corresponding computer code GRASP2K [19, 20]. However, GRASP2K is not the only code that can do MCDHF. The Breit interaction, and the quantum-electrodynamic (QED) effect have been taken into account.

2. Theoretical method

As the details of the theoretical procedure of the MCDHF method have been explained in the [21] by Grant, therefore, in the present paper we only present the main points of it. The Dirac–Coulomb Hamiltonian of an atom or ion with $N$-electron can be given by
Here, \( h_0(r_i) \) denotes one-electron Dirac Hamiltonian, while the second term is the electron-electron Coulomb interactions. In the MCDHF method, an atomic state function (ASF) of the system with parity \( P \), total angular momentum \( J \) and its component \( M \) is approximated by a linear combination of configuration state functions (CSFs) of the same symmetry \( PJM \),

\[
|\psi_\alpha(PJM)\rangle = \sum_{r=1}^{N} c_r(\alpha)|\gamma_r(PJM)\rangle,
\]

in which \( n_\gamma \) is the number of CSFs and \( c_r(\alpha) \) denotes the configuration mixing coefficients corresponding to each individual CSF.

The calculation is started from a single configuration Dirac-Fock solution with the nucleus described as an extended Fermi distribution. A single electron is excited from 3d, 4d, and 5d core hole-states to the 5f states. The trial radial wave functions are estimated by solving the Dirac equation either in the Thomas-Fermi potential or in the screened hydrogenic approximation. Furthermore, the contributions of the Breit interaction and QED effects are considered as a perturbation through relativistic configuration interaction (RCI) calculations.

In the calculations of transition energies \( \Delta E \), transition rates \( A \) [22], and weighted oscillator strengths \( g_f \) [23] of the \( nd \rightarrow 5f \) (\( n = 3 \rightarrow 5 \)) transitions of Am\(^{2+} \sim\)Am\(^{8+} \) ions, the configurations \( [\text{Rn}]5f^5, [\text{Rn}]5f^6, [\text{Rn}]5f^7, [\text{Rn}]5f^8, [\text{Rn}]5f^9, \) and \( [\text{Rn}]5f^{10} \) are adopted as the ground-state configurations corresponding to Am\(^{2+} \), Am\(^{3+} \), Am\(^{4+} \), Am\(^{5+} \), Am\(^{6+} \), Am\(^{7+} \), and Am\(^{8+} \) ions, respectively. For example, in order to perform calculations for the 3d\(^{10}5f^7 \rightarrow 3d^55f^8, 4d^55f^7 \rightarrow 4d^55f^8 \), and 5d\(^{10}5f^7 \rightarrow 5d^55f^8 \) transitions of Am\(^{2+} \) ions, \( 1s^22s^22p^63s^23p^63d^{10}...6s^66p^55f^3 \) is taken as the initial-state configuration, and \( 1s^22s^22p^63s^23p^63d^{10}4s^24p^64d^{10}...6s^66p^55f^3 \) and \( 1s^22s^22p^6...5d^66s^66p^55f^3 \) act as the final-state configurations. In table 1, the numbers of the relativistic CSFs generated for the initial- and final-state configurations of Am\(^{5+} \) \((q = 2, 3 ... 8)\) ions are presented.

### 3. Results and discussions

In table 2, the presently calculated transition energies \( \Delta E \), transition rates \( A \), and weighted oscillator strengths \( g_f \) for the \( M_4(3d_{3/2} \rightarrow 5f_{5/2}), M_4(3d_{5/2} \rightarrow 5f_{5/2}), N_4(4d_{3/2} \rightarrow 5f_{5/2}), N_4(4d_{5/2} \rightarrow 5f_{5/2}), O_4(5d_{3/2} \rightarrow 5f_{5/2}), \) and \( O_4(5d_{5/2} \rightarrow 5f_{5/2}) \) transitions of Am\(^{2+} \sim Am^{8+} \) ions are shown. To the best of authors knowledge, there are no other available data for Am ions in literature to compare with the present results. In order to justify the present GRASP2K results, similar calculations with the use of the Flexible Atomic Code (FAC) [24] are performed as well, which is also a fully relativistic package based on the Dirac equation for the calculations of atomic transition properties. Regarding the transition energies, the maximum relative discrepancies between the GRASP2K and the FAC results are 0.21 %, 0.41 %, and 3.34 % for the \( M, N, \) and \( O \) transitions, respectively. As for the \( A \) and \( g_f \) values, only relatively slight discrepancies between the GRASP2K and the FAC are found for most of the transitions, while for a few transitions such as the \( M_4 \) of Am\(^{4+} \) and Am\(^{5+} \) ions such a discrepancy is a little big. Since the same configurations have employed in both the GRASP2K and FAC calculations with an inclusion of the Breit interaction and QED

### Table 1. Numbers of the relativistic CSFs for Am\(^{q+} \) \((q = 2, 3 ... 8)\) ions considered in the calculations.

| Ions  | Ground config. | CSFs | Excited config. | CSFs |
|-------|----------------|------|----------------|------|
| Am\(^{2+} \) | \( d^{10}5f^7 \) | 327 | \( d^55f^8 \) | 2725 |
| Am\(^{3+} \) | \( d^{10}5f^8 \) | 295 | \( d^55f^7 \) | 3106 |
| Am\(^{4+} \) | \( d^{10}5f^5 \) | 198 | \( d^55f^8 \) | 2725 |
| Am\(^{5+} \) | \( d^{10}5f^4 \) | 107 | \( d^55f^3 \) | 1878 |
| Am\(^{6+} \) | \( d^{10}5f^3 \) | 41 | \( d^55f^4 \) | 977 |
| Am\(^{7+} \) | \( d^{10}5f^2 \) | 13 | \( d^55f^1 \) | 386 |
| Am\(^{8+} \) | \( d^{10}5f^1 \) | 2 | \( d^55f^2 \) | 107 |
Table 2. The presently calculated transition energies $\Delta E$ (eV), rates $A$ (s$^{-1}$), and gf values for $nd \rightarrow 5f$ ($n=3-5$) transitions of $\text{Am}^{2+}$--$\text{Am}^{4+}$ ions in both cases of the GRASP2K and FAC. While the entries in parentheses refer to the power of ten, the symbols $M$, $N$, and $O$ are x-ray notations used for inner-shell transitions.

| Ions $\text{Am}^{n+}$ | $M_s$  | $M_{ls}$ | $N_s$ | $N_{ls}$ | $O_s$ | $O_{ls}$ |
|------------------------|--------|----------|--------|-----------|--------|----------|
|                         | 4096.51 | 3892.94 | 885.26 | 834.91 | 129.59 | 112.92 |
| $A$                     | 1.08(12) | 1.07(12) | 9.28(10) | 1.62(11) | 2.42(09) | 4.13(09) |
| $gf$                    | 2.98(−03) | 3.24(−03) | 5.46(−03) | 1.07(−02) | 6.65(−03) | 1.49(−02) |
| $\text{Am}^{5+}$       | 4098.54 | 3895.93 | 887.46 | 836.79 | 133.09 | 113.17 |
| $A$                     | 9.45(11) | 1.63(12) | 1.91(11) | 9.52(11) | 1.21(09) | 1.60(09) |
| $gf$                    | 3.89(−03) | 7.44(−03) | 1.68(−02) | 9.40(−02) | 4.73(−03) | 8.59(−03) |
| $\text{Am}^{6+}$       | 4100.76 | 3897.60 | 887.51 | 838.71 | 136.75 | 114.32 |
| $A$                     | 5.37(12) | 9.67(09) | 2.80(10) | 3.74(11) | 3.72(11) | 6.47(08) |
| $gf$                    | 9.80(−03) | 2.94(−05) | 1.64(−03) | 2.45(−02) | 9.16(−01) | 2.28(−03) |
| $\text{Am}^{7+}$       | 4102.18 | 3900.24 | 889.93 | 841.98 | 140.17 | 116.49 |
| $A$                     | 5.03(12) | 4.87(11) | 1.74(10) | 1.62(09) | 6.65(09) | 3.17(08) |
| $gf$                    | 1.07(−02) | 2.21(−03) | 1.52(−03) | 1.58(−04) | 3.40(−02) | 1.62(−03) |
| $\text{Am}^{8+}$       | 4103.18 | 3903.20 | 892.14 | 843.83 | 142.20 | 118.69 |
| $A$                     | 9.23(12) | 8.62(12) | 4.94(10) | 9.05(10) | 2.89(10) | 1.31(−09) |
| $gf$                    | 2.52(−02) | 2.43(−02) | 2.86(−03) | 8.86(−03) | 6.32(−02) | 4.28(−03) |
| $\text{Am}^{9+}$       | 4108.80 | 3906.38 | 895.63 | 846.48 | 147.44 | 122.87 |
| $A$                     | 2.28(12) | 5.91(12) | 2.40(10) | 2.74(11) | 3.73(11) | 4.89(09) |
| $gf$                    | 9.35(−03) | 2.68(−02) | 2.07(−03) | 2.64(−02) | 2.82(00) | 2.24(−02) |
| $\text{Am}^{10+}$      | 4111.80 | 3911.93 | 899.11 | 848.36 | 150.57 | 122.68 |
| $A$                     | 8.47(12) | 4.86(13) | 1.49(12) | 1.43(11) | 1.75(12) | 4.66(09) |
| $gf$                    | 4.62(−02) | 2.92(−01) | 1.70(−01) | 1.83(−02) | 1.07(01) | 2.85(−02) |

**GRASP2K**

**FAC**

As can be seen from table 2, the transition energies corresponding to the same inner-shell hole-states are quite close in sequence to each other. For a specific ion, the corresponding transition energies decrease while the inner-shell hole moves towards outer shells. The energy difference between $M_s$ and $M_{ls}, N_s$, and $N_{ls}$ as well as $O_s$ and $O_{ls}$ indicates the splitting of the core states, i.e., the fine-structure splitting of $3d^{-1}2D_{3/2}$ and $2D_{5/2}$.

In figure 1, the presently calculated $O_{ls}(5d \rightarrow 5f)$ spectra of $\text{Am}^{2+}$--$\text{Am}^{8+}$ ions are shown, which are Gaussian line shapes and are obtained by convoluting the corresponding transition rates with the full width at half maximum (FWHM) 5 eV. However, since the separation of the 5f and 5d fine-structure energy levels is too small to be well separated, it appears like a quasi-continuum profile. With the decreasing number of the 5f effect, these discrepancies are mainly due to the difference of optimization techniques adopted by the two codes.
spectator electrons, such a quasi-continuum profile changes gradually to be a two-peak-like characteristics especially for Am$^{7+}$ and Am$^{8+}$ ions, and the width of the corresponding transition peaks becomes narrower and the intensity becomes weaker. Moreover, for all of the spectra the peak center shifts towards higher-energy region.

Moreover, the $\psi^{N}\rightarrow\phi^{df}$ spectra of these Am ions as shown in figure 2 are studied. While these spectrum are obtained by the same convolution as in figure 1, the results are ultimately different from the ones of the O$_{4,5}$ transition. In the latter case, the core spin-orbit interaction is dominant over the electrostatic interaction of the 4$d$ hole. Based on this fact, the two peaks are well separated in energies corresponding to the N$_4$ and N$_5$. The energy difference between these two peaks is approximately 49.10 eV on average. Moreover, the N$_4$ and N$_5$ peaks witness a reduction in intensity from Am$^{2+}$ to Am$^{8+}$. In figure 3, the ratio N$_4$:N$_5$ is plotted versus the number of the 5f electrons. It is found that the ratio N$_4$:N$_5$ increases with the decreasing number of the 5f vacancies. Also, it is found that the differences of the ratio N$_4$:N$_5$ corresponding to the GRASP2K and FAC results are relatively small for most of the Am ions.

The M$_{4,5}$(3$d$ $\rightarrow$ 5$f$) spectra are plotted in figure 4. M$_4$ and M$_5$ peaks corresponding respectively to the E1 transitions 3$d_{3/2}$ $\rightarrow$ 5$f_{3/2}$ and 3$d_{5/2}$ $\rightarrow$ 5$f_{5/2,7/2}$ are well separated from each other, which arises from the spin-orbit splitting of 3$d$ electrons. The energy separation of these two peaks is about 202.11 eV for all of the ions under study. Furthermore, the separation of energy levels are corresponding to the 3$d_{3/2}$ and 3$d_{5/2}$ states. Moreover, the peak intensity ratio M$_4$:M$_5$ is plotted in figure 5 as a function of the number of the 5f electrons. It is found that the ratio M$_4$:M$_5$ decreases as increasing number of the 5f spectator electrons.
Figure 2. The same as figure 1 but for the \( N_{4,5} (4d \rightarrow 5f) \) spectra.

Figure 3. Dependence of the ratio \( N_4/N_5 \) on the occupation number of the 5f electrons corresponding to Am\(^{2+}\)–Am\(^{8+}\) ions.
4. Conclusions

The spectra originating from $n d \rightarrow 5f$ ($n = 3 - 5$) transitions of $\text{Am}^{2+}$–$\text{Am}^{8+}$ ions have been calculated by using GRASP2K code. While the obtained $O_{4,5}(5d \rightarrow 5f)$ spectra show a broad quasi-continuum profile, both

---

**Figure 4.** The same as figure 3 but for the $M_{4,5}(3d \rightarrow 5f)$ spectra.

**Figure 5.** The same as figure 3 but for the ratio $M_{4}/M_{5}$. 
the $N_{d5}(4d \rightarrow 5f)$ and $M_{d5}(3d \rightarrow 5f)$ spectra consist of two peaks that are well separated with respect to energy because of the strong spin-orbit interactions of $3d^{-1}$ and $4d^{-1}$ hole state.

**Acknowledgments**

This work has been supported by the National Key Research and Development Program of China under Grant No. 2017YFA0402300 and the National Natural Science Foundation of China (NSFC) under Grant Nos. 11804280, 11 874 051, U1530742, 91 126 007, and the Scientific Research Program of the Higher Education Institutions of Gansu Province of China (Grant No. 2018A-002) and the Young Teachers Scientific Research Ability Promotion Plan of Northwest Normal University under No. NWNU-LKQN-15-3.

**Data availability statement**

All data that support the findings of this study are included within the article (and any supplementary information files).

**ORCID iDs**

N J Dala @ https://orcid.org/0000-0001-9091-9720  
Ding Xiao-Bin @ https://orcid.org/0000-0003-0004-3206

**References**

[1] Schulz W W 1976 *Chemistry of Americium* (Springfield Virginia: Technical Information Center) osti.gov-WW Schulz-1976 0-87079-040-4  
[2] Albers R C 2001 *Nature* **410** 759  
[3] Havela L, Gouder T, Wastin F and Rebizant J 2002 *Phys. Rev. B* **65** 235118  
[4] Hecker S S 2004 *Metall. Mater. Trans. A* **35** 2207  
[5] Tobin J G, Moore K T, Chung B W, Wall M A, Schwartz A J, van der Laan G and Kutepov A L 2005 *Phys. Rev. B* **72** 085109  
[6] Moore K T, van der Laan G, Haire R G, Wall M A and Schwartz A J 2006 *Phys. Rev. B* **73** 033109  
[7] Baer Y and Lang J K 1980 *Phys. Rev. B* **21** 2060  
[8] Lander G H, Fisher E S and Bader S D 1994 *Adv. Phys.* **43** 1  
[9] Savrasov S Y and Kotliar G 2000 *Phys. Rev. Lett.* **84** 3670  
[10] Wong I, Krisch M, Farber D L, Ocelli F, Schwartz A J, Chiang T C, Wall M, Borov C and Xu R 2003 *Science* **301** 1078  
[11] Heathman S, Haier R G, Bihan T L, Lindbaum A, Idiri M, Normile P, Li S, Ahuja R, Johansson B and Lander G H 2005 *Science* **309** 110  
[12] Moore K T, Soderlind P, Schwartz A J and Laughlin D E 2006 *Phys. Rev. Lett.* **96** 206204  
[13] Saber I A, Dong C Z, Wang X L, Zhou W D and Wu Z W 2014 *Chin. Phys. B* **23** 023101  
[14] Moore K T, van der Laan G, Wall M A, Schwartz A J and Haire R G 2007 *Phys. Rev. B* **76** 073105  
[15] Butterfield M T, Moore K T, van der Laan G, Wall M A and Haire R G 2008 *Phys. Rev. B* **77** 113109  
[16] Buck E C and Fortner J A 1997 *Ultramicroscopy* **67** 69  
[17] Jönsson P and Fischer C F 1997 *J. Phys. B* **30** 5861  
[18] Bieroński J, Gaigalas G, Gaidamaukas G, Fritzsche S, Indelicato P and Jönsson P 2009 *Phys. Rev. A* **80** 012513  
[19] Jönsson P, He X, Fischer C F and Grant I P 2007 *Comput. Phys. Commun.* **177** 597  
[20] Jönsson P, Gaigalas G, Bieroński J, Fischer C F and Grant I P 2013 *Comput. Phys. Commun.* **184** 2197  
[21] Grant I P 2007 *Relativistic Quantum Theory of Atoms and Molecules* 40 (New York: Springer) 10:0-387-34671-6  
[22] Grant I P 1974 *J. Phys. B* **7** 1458  
[23] Cowan R D 1981 *The Theory of Atomic Structure and Spectra* (Berkeley: University of California Press) 978-0-520-03821-9  
[24] Gu M F 2008 *Can. J. Phys.* **86** 675