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The role of atomic correlations in the theoretical study of minor actinide ions

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ABSTRACT

This paper aims to demonstrate the recent possibilities to account for correlation and relativistic effects in studying the electronic structure and energy spectra of actinide ions. The fine structure of lowest term ^7F of tetravalent curium (Cm^{4+}) is considered as an example, as part of an ongoing project to understand the unexpected ground-state properties of this peculiar ion. The calculations were performed in multiconfiguration Hartree–Fock (including relativistic effects in the Breit–Pauli approach) and multiconfiguration Dirac–Fock approximations. The results obtained demonstrate that, whilst core–valence and core–core correlations are essential to assess correctly the Cm^{4+} term energy, their role in the determination of the fine structure is much less important compared to that of valence–valence correlations.

1. Introduction

Apart from being intensively studied for energy generation purposes, transuranium actinide elements are also extremely interesting for their peculiar magnetic properties. The latter, however, have not yet been completely understood in the light of a comprehensive general model [1], partly because of the difficulty in making measurements and the resulting paucity of experimental data [2] (due to the strict safety and handling requirements for radioactive materials) and partly because the theoretical study of heavy chemical elements is a great challenge in itself; extremely complex models and lengthy calculations are required [3].

Whilst the contribution of *f*-electron states to the magnetic properties of metallic elements is the subject of considerable debate (see for example recent work on curium [4] and its rare-earth analog gadolinium [5]), the situation for typical 'toy compounds' such as oxides and fluorides is still not completely clear either. As an example of the spectacular failure of simple models, the large effective magnetic moments measured in the several compounds containing tetravalent curium [6] still remain unexplained, since Cm^{4+} ions in a $5f^6$ configuration are expected to display a $J = 0$ nonmagnetic singlet as ground-state. Density functional theory (DFT) is able to reproduce the correct value of the magnetic moment for CmO_2 only if 5*f* electrons are considered to be itinerant [7], while a localized picture has been shown to be more appropriate for the whole series of actinide dioxides [8]. It must be noticed that the failure of DFT in correctly describing strongly correlated systems (such as *f* electrons!) is widely known, although some useful ideas on how to overcome this difficulties have been suggested [9].

To clarify the above situation, we have undertaken a project to calculate the energy spectra and ground-state composition of Cm^{4+} from ab-initio methods. However, the complexity of the calculations and the fact that very few experimental data are available make it difficult to assess which fundamental interactions, correlations and relativistic effects have the largest impact on the spectral and magnetic properties and which are, on the other hand, negligible. The results reported here are an assessment of the valence–valence, core–valence and core–core correlation effects for Cm^{4+}.

2. Calculation methods

For the calculation of energy spectra of Cm^{4+} we used multiconfiguration Hartree–Fock (MCHF) and configuration interation (CI) methods accounting for relativistic effects in Breit–Pauli approach [10]. In these approaches, the atomic state function (ASF) $\Psi(\gamma LS)$ is expressed as a linear combination of *symmetry-adapted configuration state functions* (CSFs) $\Phi(\gamma_{i\ LS})$ i.e.

$$\Psi(\gamma LS) = \sum_i c_i \Phi(\gamma_i LS). \qquad (1)$$

The energy functional on which the orbitals are optimized is found using the linear combination of the configuration states of the main configuration of the Cm^{4+}:

$$AS_0 = 1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^6 4d^{10} 4f^{14} 5s^2 5p^6 5d^{10} 6s^2 6p^6 5f^6.$$

Configuration state function of the multiconfigurational calculations additionally include single and double substitutions from the valence shell (VV correlation). Thus, ASFs, are generated using the following sets of the orbitals:

$$AS_6 = AS_0 + \{6d\} \text{ (ASF with } \mathbf{1628} \text{ CSFs)},$$
$$AS_7 = AS_6 + \{6f, 7s, 7p, 7d\} \text{ (ASF with } \mathbf{15028} \text{ CSFs)},$$

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Table 1
The six lowest energy levels of *Cm*$^{4+}$ calculated in multiconfiguration Hartree–Fock approach. AS$_n$ indicates the set of orbitals chosen for the calculations (see main text for details). The columns labelled VV refer to calculations performed with valence–valence correlations only, while those labelled CV include valence–valence, core–valence and core–core correlations (the latter calculations have been performed only for $n = 6$).

States	*J*	Total energy (a.u.)			Energy levels (cm^{-1})		
		AS$_6$ VV	AS$_7$ VV	AS$_6$ CV	AS$_6$ VV	AS$_7$ VV	AS$_6$ CV
$5f^6\ ^7F$	0	−30582.01	−30582.06	−30582.12	0	0	0
	1	−30582.00	−30582.05	−30582.11	1788	2020	1792
	2	−30581.99	−30582.04	−30582.10	4838	5465	4841
	3	−30581.97	−30582.02	−30582.09	8189	9222	8173
	4	−30581.96	−30582.01	−30582.07	11107	12423	11063
	5	−30581.95	−30581.99	−30582.06	13656	15143	13607

Table 2
The six lowest energy levels of *Cm*$^{4+}$ calculated in multiconfiguration Dirac–Fock (relativistic) approach. The columns labelled VV refer to calculations performed with valence–valence correlations only, while those labelled CV include valence–valence, core–valence and core–core correlations. AS$_n$ indicates the set of orbitals chosen for the calculations (see main text for details).

J	Total energy (a.u.)			Energy levels (cm^{-1})				
	AS$_6$ VV	AS$_7$ VV	AS$_6$ CV	AS$_7$ CV	AS$_6$ VV	AS$_7$ VV	AS$_6$ CV	AS$_7$ CV
0	−31247.83	−31247.86	−31247.95	−31248.05	0	0	0	0
1	−31247.82	−31247.85	−31247.94	−31248.04	2692	2898	2812	2886
2	−31247.81	−31247.83	−31247.92	−31248.03	5569	5897	5710	5821
3	−31247.80	−31247.82	−31247.91	−31248.02	8238	8622	8352	8476
4	−31247.79	−31247.81	−31247.90	−31248.00	10640	11040	10719	10846
5	−31247.78	−31247.80	−31247.89	−31248.00	12727	13109	12779	12902

Core–valence and core–core correlations were also taken into account using CI approach. Additional CSFs were generated by single and double substitutions from core 6*s*, 6*p* and valence 5*f* shells.

In order to reduce the size of the multiconfiguration expansion the LS reduce technique was applied [11] in nonrelativistic and the *jj* reduce technique was applied in relativistic approaches. Then for example in the nonrelativistic case the number of CSF was reduced from 87262 to 4269 in the $n = 6$ and from 1105881 to 21243 in the $n = 7$ calculations.

3. Results and conclusions

Tables 1 and 2 list the six lowest energy levels of the Cm^{4+} in multiconfigurational Hartree–Fock and Dirac–Fock approaches, respectively, with both AS$_6$ and AS$_7$ orbital sets. Whilst valence–valence correlation effects have been taken into account in all cases, the calculations were performed both with and without core–valence and core–core correlations. An inspection of the results demonstrates that, even if core–valence and core–core correlations are essential to assign the correct Cm^{4+} term energies, their role in the fine structure calculations is small compared to that of valence–valence correlations. Therefore the latter are the most important correlations which should be accounted for while studying the ground-state properties of Cm^{4+} compounds. Essentially the same conclusion follows from both multiconfiguration Hartree–Fock and multiconfuguration Dirac–Fock approaches. The behaviour of correlation and relativistic effects has a complex character, therefore further theoretical studies are necessary and experimental spectroscopic data would be of great help.

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