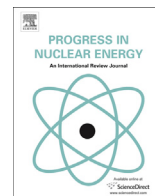




Contents lists available at ScienceDirect

Progress in Nuclear Energy

journal homepage: www.elsevier.com/locate/pnuceneDFT + U as a reliable method for efficient *ab initio* calculations of nuclear materials[☆]George Beridze^{a, b}, April Birnie^{a, b, c}, Sarah Koniski^{a, b, d}, Yaqi Ji^{a, b}, Piotr M. Kowalski^{a, b, *}^a Institute of Energy and Climate Research, Nuclear Waste Management and Reactor Safety (IEK-6), Forschungszentrum Jülich GmbH, Wilhelm-Johnen-Straße, 52425, Jülich, Germany^b JARA High-Performance Computing, Schinkelstraße 2, 52062, Aachen, Germany^c Department of Chemistry, Smith College, Northampton, MA, 01063, USA^d Department of Pathology and Laboratory Medicine, Children's Hospital of Philadelphia, Philadelphia, PA, 19104, USA

ARTICLE INFO

Article history:

Received 14 August 2015

Received in revised form

15 April 2016

Accepted 11 July 2016

Keywords:

Nuclear materials

ab initio modeling

Density functional theory

f-electrons

Actinide chemistry

Nuclear waste management

ABSTRACT

Density functional theory (DFT)-based *ab initio* methods become standard research tools in various research fields, including nuclear materials science. However, having strongly correlated *f*-electrons, lanthanide- and actinide-bearing nuclear materials are computationally challenging for DFT methods and straightforward DFT calculations of these materials can easily produce false results. In this contribution we benchmark the DFT + U method, with the Hubbard U parameter derived *ab initio*, for prediction of structural and thermochemical parameters of nuclear materials, including various actinide-bearing molecular complexes and lanthanide-bearing monazite- and xenotime-type prospective ceramic nuclear waste host forms. Our studies show that the applied DFT + U method improves significantly prediction of DFT by producing results with uncertainties similar to those of the higher order, but computationally unfeasible *ab initio* methods, and the experimental data, and thus allows for reliable and feasible *ab initio* computation of even chemically complex nuclear materials.

© 2016 Elsevier Ltd. All rights reserved.

1. Introduction

The growing availability of computational power increases the role of *ab initio* atomistic modeling calculations in various research fields, including nuclear materials science (Chronos et al., 2013; Jahn and Kowalski, 2014). The methods of computational quantum chemistry, mainly Density Functional Theory (DFT), are applied on regular basis in nuclear research, including research on nuclear waste forms (e.g. Chronos et al. (2013), Li et al. (2014), Jiang et al. (2009)). Unfortunately, the standard DFT approaches such as LDA or GGA approximations often fail to adequately describe the properties of *f*-electrons-bearing molecules and crystalline solids (Shamov et al., 2007; Schreckenbach and Shamov, 2010; Wen et al., 2013a; Beridze and Kowalski, 2014). For instance, the error of the reaction enthalpies predicted by DFT is

usually unacceptably large (~ 100 kJ/mol for U-bearing molecular complexes (Shamov et al., 2007; Schreckenbach and Shamov, 2010; Iche-Tarrat and Marsden, 2008; Beridze and Kowalski, 2014)). DFT also fails on qualitative level describing even the simplest actinide oxides (AnO_2) as metals instead of semiconductors (Wen et al., 2013a).

Several benchmarking theoretical studies were performed to show the performance of different *ab initio* methods for actinide-bearing molecular complexes and crystalline solids (e.g. Wen et al. (2013b); Schreckenbach and Shamov (2010); Iche-Tarrat and Marsden (2008); Shamov et al. (2007); Beridze and Kowalski (2014); Odoh and Schreckenbach (2010); Schreckenbach (2000); de Jong et al. (2001)). For the reaction enthalpies it has been shown that DFT often fails, giving large errors and thus application of more accurate but computationally intensive methods of computational quantum chemistry, such as hybrid functionals (PBE0, B3LYP or HSE), MP2 or CCSD(T), is suggested (Wen et al., 2013a; Shamov et al., 2007; Schreckenbach and Shamov, 2010). The dramatic increase in the computational cost required by these methods, comparing to efficiency of DFT, limits the applicability of *ab initio* simulation techniques to studies of only simple molecular or solid compounds. This prevents calculation of chemically complex

[☆] Paper presented at SBNFC III: symposium F, EMRS spring meeting, Lille, 11–15 May 2015.

* Corresponding author. Institute of Energy and Climate Research, Nuclear Waste Management and Reactor Safety (IEK-6), Forschungszentrum Jülich GmbH, Wilhelm-Johnen-Straße, 52425, Jülich, Germany.

E-mail address: p.kowalski@fz-juelich.de (P.M. Kowalski).

systems, such as, for instance, solid solutions that are of special interest in nuclear waste management. In our previous studies we extensively tested the DFT + U method (Anisimov et al., 1991; Liechtenstein et al., 1995; Cococcioni and de Gironcoli, 2005), which is a computationally cheap extension of DFT that accounts for electronic correlations using the Hubbard model (Himmotoglu et al., 2014). We obtained excellent results for the enthalpies of reactions involving uranium-bearing molecular complexes and solids (Beridze and Kowalski, 2014) and the structural and thermodynamic properties of monazite- and pyrochlore-type ceramics (Blanca-Romero et al., 2014; Li et al., 2015; Kowalski and Li, 2016), with errors of the computed quantities that are comparable to results of above-mentioned higher order *ab initio* methods. In this contribution we performed subsequent benchmarking studies of the performance of DFT + U method, with the Hubbard U parameter derived *ab initio* using the linear response approach of Cococcioni and de Gironcoli (2005) (hereafter we name the method DFT + U_{LR}), for the prediction of structural and thermodynamic parameters of simple, actinide-bearing molecular complexes containing actinides other than U, namely Np, Pu and Am. We also extended our previous studies of monazite-type ceramics (Blanca-Romero et al., 2014) into calculations of xenotime-type phosphates, a stable $LnPO_4$ phase for late lanthanides (beyond Tb). The main goal was to perform further tests of the performance of DFT + U_{LR} method for the actinide- and lanthanide-bearing compounds in order to check the general applicability of this method for calculation of materials relevant for nuclear waste management.

2. Computational details

The calculations were performed using plane-wave DFT Quantum-ESPRESSO code (Giannozzi et al., 2009). We applied the PBE (Perdew et al., 1996) and PBEsol (Perdew et al., 2008) exchange-correlation functionals. We chose these particular functionals because they are real *ab initio*, i.e. not empirically designed, functionals that are also most commonly used. The scalar relativistic ultrasoft pseudopotentials were used to represent the core electrons and the $6s^2 6p^6 5f^3 6d^1 7s^2$ electrons of uranium atom, $6s^2 6p^6 5f^4 6d^1 7s^2$ electrons of neptunium atom, $6s^2 6p^6 5f^6 7s^2$ of plutonium atom and $6s^2 6p^6 5f^7 7s^2$ electrons of americium atom were treated explicitly. We applied 50 Ryd plane-waves energy cut-off. The atomic systems and molecules were relaxed to equilibrium positions with the maximum component of residual forces on the ions being less than 0.005 eV/Å. The equilibrium molecular geometries were confirmed by supplementary calculations of the vibrational frequencies in a similar way as in the studies of Beridze and Kowalski (2014). For the purpose of DFT + U calculations the atomic f -orbitals produced by uspp-736 package (Vanderbilt, 1990) were used as projectors and the elements of response matrices needed for calculation of the Hubbard U parameter values were derived by the finite differences following the procedure of Cococcioni and de Gironcoli (2005). The Hubbard U parameter values were derived for all molecular and solid compounds discussed in this paper. We computed a monazite series ($LnPO_4$) with different lanthanide $Ln = Tb, Dy, \dots, Yb$ using $2 \times 2 \times 2$ k -points grids. The calculations of solids were performed by relaxing the lattice parameters and the ionic positions so that the resulting pressure was 0 GPa with a tolerance of 0.01 GPa and all the calculations details are identical to the ones used by Blanca-Romero et al. (2014). Because spin-orbit interaction can be significant for actinides we computed the spin-orbit contributions to the total energies and the reaction enthalpies using the non-collinear spin-polarized approach implemented in Quantum-ESPRESSO code. For the studies of monazite and xenotime we performed two types of standard DFT calculations: (1) f -in-the-valence (FV) approach

treating f -electrons explicitly and (2) f -in-the-core (FC) approach modeling f -electrons by the pseudopotential, i.e. not computing them explicitly. The abbreviations of the two pseudopotential approaches will be used through the paper.

3. Results and discussion

3.1. Actinide-bearing molecular complexes

The aim of these studies was to test if the DFT + U_{LR} approach, which was shown by Beridze and Kowalski (2014) to significantly improve the predicted enthalpies of reactions involving uranium-bearing complexes, also performs so well for other actinide elements. Therefore, we have studied the reactions between various fluorides, chlorides and oxides containing U, Np, Pu and Am in different valence state (U(I–VI), Np(I–IV,VI), Pu(I–IV,VI), Am(III,VI)). The considered reactions are given in Table 1. We selected the reactions and the molecular compounds for which there exist the structural and the thermochemical data: the experimental measurements (Guillaume et al., 2003; Morss et al., 2011; Hay and Martin, 1998; Seip, 1965; Kimura et al., 1968) and the theoretical calculations (Averkiev et al., 2011; Zaitsevskii et al., 2013; Shamov et al., 2007; Han, 2001), which allows us for a meaningful benchmarking of the computational method.

In Table 2 we provide the Hubbard U parameter values derived for each actinide compound by the linear response approach of Cococcioni and de Gironcoli (2005). As illustrated in Fig. 1, the Hubbard U parameter value decreases with decreasing the oxidation state of the actinide, with a potential minimum for $An(II)$ and slight increase for $An(I)$. This shows that the trend we found for uranium-complexes (Beridze and Kowalski, 2014) holds also for the other actinides.

The considered hexafluorides and tetrahalogenides of U, Pu and Np were optimized in O_h and T_d symmetry respectively. Trihalogenides of the four actinides were optimized in C_{3v} symmetry (see Fig. 2). All dioxide molecules have planar geometry with the 180° oxygen-actinide-oxygen bond angle. The UO_3 and PuO_3 molecules have T shaped geometry with the dihedral angle of 180° . There are only few experimentally measured structures of the molecules in the gas phase that are available for comparison. The structural parameters of UF_6 , PuF_6 and NpF_6 are presented in Table 3. Out of the considered computational methods PBE functional gives the worst agreement for the actinide-fluoride bond distance, which is consistent with the previous finding for U–F bond length (Beridze and Kowalski, 2014). PBEsol functional results in much better agreement with the experiment, which is expected as discussed by Csonka et al. (2009) and Beridze and Kowalski (2014). The differences between the experimental and the computed values are only 0.010 Å for UF_6 , 0.015 Å for NpF_6 and 0.023 Å for PuF_6 which is at the accuracy level of more computationally intensive hybrid

Table 1

List of the 22 considered reactions involving the gas-phase actinide-bearing molecules.

(1) $UF_6 \rightarrow UF_4 + 2F$	(12) $PuF_4 \rightarrow PuF_3 + F$
(2) $UF_4 \rightarrow UF_3 + F$	(13) $PuF_3 \rightarrow PuF_2 + F$
(3) $UF_3 \rightarrow UF_2 + F$	(14) $PuF_2 \rightarrow PuF + F$
(4) $UF_2 \rightarrow UF + F$	(15) $PuCl_4 \rightarrow PuCl_3 + Cl$
(5) $UCl_4 \rightarrow UCl_3 + Cl$	(16) $AmF_6 \rightarrow AmF_3 + 3F$
(6) $NpF_6 \rightarrow NpF_4 + 2F$	(17) $UO_3 \rightarrow UO_2 + O$
(7) $NpF_4 \rightarrow NpF_3 + F$	(18) $UO_2 \rightarrow UO + O$
(8) $NpF_3 \rightarrow NpF_2 + F$	(19) $NpO_2 \rightarrow NpO + O$
(9) $NpF_2 \rightarrow NpF + F$	(20) $PuO_3 \rightarrow Pu_2 + O$
(10) $NpCl_4 \rightarrow NpCl_3 + Cl$	(21) $PuO_2 \rightarrow PuO + O$
(11) $PuF_6 \rightarrow PuF_4 + 2F$	(22) $AmO_2 \rightarrow AmO + O$

Download English Version:

<https://daneshyari.com/en/article/1740279>

Download Persian Version:

<https://daneshyari.com/article/1740279>

[Daneshyari.com](https://daneshyari.com)