Hybrid Density Functional Study on Plutonium Dioxide

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(Received September 30, 2013)

We perform hybrid density functional calculations taking account of spin-orbit couplings on plutonium dioxide in order to numerically obtain its observed ground state, i.e., the paramagnetic insulating state. We show that hybrid density functional calculations with spin-orbit couplings yield the paramagnetic insulating states similar to those obtained by LDA+U.

KEYWORDS: Plutonium dioxide, hybrid DFT, DFT, LDA+U

1. Introduction

Plutonium dioxide ($\text{PuO}_2$) is one of components of nuclear fuels. In order to develop more secure and more efficient nuclear fuels, it is important to have a detailed knowledge of $\text{PuO}_2$. In particular, simulations for $\text{PuO}_2$ are effective since the determination of the properties through experiments is not easy owing to the handling of nuclear materials.

First-principles calculations are suitable to estimate materials properties by numerical simulation, because they do not need empirical parameters. Recently, density functional theory (DFT) with local density approximation (LDA) or generalized gradient approximation (GGA) is popular as a first-principles method. However, LDA and GGA are known to be inappropriate for strongly-correlated electronic systems. Actually, LDA and GGA predict that plutonium dioxide is a metal though it is observed to be an insulator.

A few methods beyond LDA have succeeded in reproducing the paramagnetic insulating state of $\text{PuO}_2$, such as SIC-LDA [1], LDA-DMFT [2] and LDA+U [3]. In all successful methods, spin-orbit coupling (SOC) is properly included. As pointed out in Ref. [3], SOC is critical to obtain the correct insulating states.

In this paper, we evaluate the electronic state of plutonium dioxide by hybrid-DFT [4] with SOC. Hybrid-DFT is a combination of Hartree-Fock method and LDA or GGA and often applied to the strongly-correlated systems. Hybrid-DFT does not need material-dependent parameters, while most of other methods beyond LDA have parameters depending on atomic species, such as Hubbard $U$ for LDA+U method. Therefore, application of hybrid-DFT for the other materials can be more convenient than that of LDA+U.

2. Materials and Methods

Plutonium dioxide has a fluorite structure as shown in Fig. 1. Its space group is $Fm\bar{3}m$, and Pu and O atoms are located at Wyckoff position $a$ and $c$, respectively [5]. The electronic state of this material is known to be insulating and paramagnetic, while most of actinide dioxides have complex magnetic order in their ground states. For instance, uranium dioxide has a triple-$q$ antiferromagnetic state [6]. However, plutonium dioxide does not have any magnetic order, and therefore it is suitable...
Fig. 1. Crystal structure of PuO$_2$. Large and small spheres denote Pu and O atoms, respectively.

for the first trial of evaluation of actinide dioxides.

In the hybrid-DFT, exchange energy is described as a combination of LDA(GGA) and Hartree-Fock exchange energies. Several types of hybrid-DFT have been suggested. For instance, in the case of PBE0 [7], exchange energy is expressed as

$$E_{x}^{\text{PBE0}} = \frac{1}{4}E_{x}^{\text{HF}} + \frac{3}{4}E_{x}^{\text{PBE}},$$  \hspace{1cm} (1)

where $E_{x}^{\text{HF}}$ and $E_{x}^{\text{PBE}}$ are exchange energies of Hartree-Fock and PBE [8] (one of GGA), respectively. Calculation of $E_{x}^{\text{HF}}$ takes a large computational cost. To reduce this cost, HSE functional was suggested [9], where screened Coulomb potential is used for calculation of exchange energy. In this method, Coulomb potential are divided into two components,

$$\frac{1}{r} = \frac{\text{erf}(\omega r)}{r} + \frac{\text{erf}(\omega r)}{r}. \hspace{1cm} (2)$$

The first and second terms in the right-hand side correspond to the short-range (SR) and long-range (LR) components, respectively. In SR, hybrid exchange energy like PBE0 is adopted and GGA exchange energy (PBE) dominates in LR. Using this decomposition, exchange energy is written as

$$E_{x}^{\text{HSE}} = \frac{1}{4}E_{x}^{\text{HF,SR}} + \frac{3}{4}E_{x}^{\text{PBE,SR}} + E_{x}^{\text{PBE,LR}}. \hspace{1cm} (3)$$

In both cases of PBE0 and HSE, the PBE correlation energy is used in the entire region. We also use B3LYP [10] which is a more complicated and popular hybrid functional for evaluation of insulating gap sizes.

In this paper, we calculate band structure and density of states of PuO$_2$ by HSE hybrid-DFT. We also evaluate the optimized structure and bulk modulus, and gap sizes are estimated for several types of functionals. Throughout this paper, we employ VASP [11] code for DFT and hybrid-DFT calculations. In all calculations, we adopt the primitive cell and $k$-points are set to $6 \times 6 \times 6$. 
Table I. Lattice constants and bulk moduli for various functionals. The numbers in parentheses denote the difference from experimental value.

<table>
<thead>
<tr>
<th></th>
<th>HSE</th>
<th>LDA+U</th>
<th>GGA</th>
<th>experiment</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lattice constant (Å)</td>
<td>5.383</td>
<td>5.355</td>
<td>5.379</td>
<td>5.396 [5]</td>
</tr>
<tr>
<td></td>
<td>(-0.12 %)</td>
<td>(-0.8 %)</td>
<td>(-0.3 %)</td>
<td></td>
</tr>
<tr>
<td>Bulk modulus (GPa)</td>
<td>221</td>
<td>228</td>
<td>220</td>
<td>–</td>
</tr>
</tbody>
</table>

Table II. Insulating gap sizes for various functionals.

<table>
<thead>
<tr>
<th></th>
<th>HSE</th>
<th>PBE0</th>
<th>B3LYP</th>
<th>LDA+U</th>
<th>experiment</th>
</tr>
</thead>
<tbody>
<tr>
<td>Gap size (eV)</td>
<td>2.7</td>
<td>3.5</td>
<td>2.6</td>
<td>1.8</td>
<td>1.8 [12]</td>
</tr>
</tbody>
</table>

3. Results

Figure 2 shows the band structure and density of states calculated by HSE. We successfully obtain the insulating electronic states with a gap. These results are very similar to those by LDA+U [3], while the calculated gap size (2.7 eV) is slightly larger than the observed one (1.8 eV [12]). We also evaluate the optimized lattice constant and bulk moduli as shown in Table I. The lattice constant calculated by HSE are similar to those by LDA+U and GGA and agrees well with the experimental value. The calculated bulk modulus is also comparable to other results.

In Table II, we tabulate the calculated gap sizes for various functionals. The hybrid functionals such as HSE, PBE0 and B3LYP tend to overestimate the gap size. Though the gap size obtained by LDA+U agrees with experiments, we should note that Hubbard $U$ can be a parameter to fit the gap size.

![Band structure and density of states of PuO$_2$ obtained by HSE.](image_url)

Fig. 2. Band structure and density of states of PuO$_2$ obtained by HSE.
4. Discussions

Spin-orbit coupling is necessary to obtain the correct insulating state of PuO$_2$, as discussed in Ref. [3]. Here, we briefly review this discussion. Pu$^{4+}$ in PuO$_2$ has four electrons in its $f$ orbital. The $f$-orbitals are split into several degenerated levels due to the crystal field. Only when spin-orbit coupling exists, a four-folded level appears and is occupied by 4 $f$-electrons. Thus, insulating state is possible because of spin-orbit coupling, and strong-correlation effect introduced by LDA+U or hybrid functionals opens the insulating gap. Actually, we confirm that hybrid DFT without spin-orbit coupling cannot obtain the paramagnetic insulating state of PuO$_2$.

Here, we discuss the functional dependences of the gap size. The Hartree-Fock approximation is known to overestimate gap sizes of insulators and semi-conductors, while LDA and GGA underestimates them. Improvement of gap sizes by hybrid DFT is caused by mixture of their contrary properties. In table II, PBE0 yields the largest gap size, and HSE and B3LYP follow it. The ratio of Hartree-Fock exchange energy to the total one in PBE0 reaches 25 %. On the other hand, that of B3LYP is almost 20 %. Thus, higher ratio of Hartree-Fock energy gives larger gap size. In the case of HSE, the effect of Hartree-Fock approximations is reduced by the screened potential, though the ratio of Hartree-Fock energy is similar to PBE0 in the short range. In order to improve the gap-size estimations, we may have to develop new hybrid functionals appropriate to actinide materials.

5. Conclusion

We calculate the electronic state of PuO$_2$ by hybrid DFT with spin-orbit coupling and successfully obtain the proper insulating state. The calculated lattice constant and bulk modulus are reasonable, while the gap size is slightly overestimated. We confirm that the combination of the spin-orbit coupling and strong correlation are necessary to obtain the proper electronic states in this material.

Acknowledgment

The authors thank Tatssumi Arima, Nanako Tamari, Masato Kato and Hiroyuki Serizawa for valuable discussions. This work was partially supported by JSPS KAKENHI Grant Number 23246174.

References