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Discussion

Electronic and optical properties of (U,Th)O_2 compound from screened hybrid density functional studies

Chongjie Mo [a], Yu Yang [b], Wei Kang [a], Ping Zhang [a,b,*]

[a] Center for Applied Physics and Technology, Peking University, Beijing 100871, China
[b] Institute of Applied Physics and Computational Mathematics, Beijing 100088, China

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ABSTRACT

The electronic structure and optical properties for the (U,Th)O_2 compound are systematically studied by employing the Heyd–Scuseria–Ernzerh method (HSE) of screened hybrid density functional. The electronic band gap of (U,Th)O_2 is predicted to be 3.06 eV, in the middle of the values of UO_2 and ThO_2. Based on wavefunction analysis, we conclude (U,Th)O_2 to be a Mott insulator in its ground state. The frequency dependent dielectric functions and optical properties are then calculated and compared with those of ThO_2 and UO_2. At the visible light frequency range, the adsorption coefficients for ThO_2, UO_2 and (U,Th)O_2 are totally different, which gives an accessible method to predict the proportion of U atoms in an arbitrary unknown (U,Th)O_2 compounds from the adsorption spectrum of visible lights.

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1. Introduction

In order to avoid dealing with radioactive reaction wastes from burning cycles of UO_2 within fission reactors, it is proposed to use mixed actinide oxides (MOX) as fission fuels instead of pure UO_2 [1–7]. As an example, the (U,Th)O_2 alloys are used as advanced fuel materials for fission reactors [8,9]. For efficient processing of admixtures in new generation nuclear fuels, a thorough understanding of the structural and electronic properties of (U,Th)O_2 alloys is crucial. Therefore in the present paper, we systematically study the electronic as well as optical properties of UO_2, ThO_2 and their alloy, by using the screened hybrid density functional theory.

Besides of the practical significance, studying the electronic properties of the (U,Th)O_2 alloys is also scientifically interesting. In the solid state with similar fluorite structures, UO_2 and ThO_2 have very different electronic structures. With localized uranium $5f$ electronic states distributing around the Fermi energy, UO_2 is a Mott insulator with an electronic band gap of around 2.50 eV [10–19]. At another side, ThO_2 is an ionic insulator with the band gap of around 5.75 eV [17,20], and the valence band maximum (VBM) and conduction band minimum (CBM) states are mainly the O-$2p$ and Th-$5f$ electronic states respectively [11,17]. We can see that because of the different $5f$ orbital occupancies of Th and U elements, ThO_2 and UO_2 are divided into different solid categories. ThO_2 is a large-gap charge-transfer insulator, while UO_2 is a small-gap Mott insulator. From basic point of view, it would be very interesting to look into the electronic structures of the alloys of these two actinide oxides.

Scientifically, the biggest problem when studying the electronic properties of actinide dioxides from UO_2 to AmO_2 is how to accurately describe the localized $5f$ electronic states, whose strong on-site Coulomb repulsion interaction is severely underestimated in standard density functional theory (DFT) calculations. This wrongness leads to the consequence that standard DFT calculations describe them to be incorrect conductors [21–26]. In order to conquer this difficulty, several approaches like DFT + U [27,28], self-interaction corrected local spin density (SIC–LSD) models [5], and dynamical mean-field theory [15] have been applied on the ground-state calculations of PuO_2 and UO_2. Although some questions still exist, sizable electronic band gaps have been successfully obtained in these studies for the actinide dioxides. For ThO_2, although standard DFT calculations yields a valuable electronic band gap (because it is a charge-transfer insulator instead of Mott insulator), the calculated electronic band gap is much smaller than the experimental value [16]. The underestimation of the electronic band gap comes from the inaccurate description of the excited electronic states. To conquer this difficulty, several approaches have also been successfully developed to accurately reproduce the band gap of charge-transfer insulators, like the hybrid density functional of (Heyd, Scuseria, and Enzerhof) HSE [29–31] and the *ab initio* GW

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* Corresponding author at: Institute of Applied Physics and Computational Mathematics, Beijing 100088, China.
E-mail address: zhang_ping@iapcm.ac.cn (P. Zhang).

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method [32,33]. Due to the different difficulties when describing the electronic structures of UO_2 and ThO_2, it is a hard task to find a way to accurately describe the Th and U electronic states at the same time. Here in the present work, we find that the HSE method can successfully reproduce the electronic band gaps for Mott-type insulator UO_2 and charge-transfer insulator ThO_2, the obtained band gap values accord well with latest experiments. Therefore, we further use the HSE method to study the ground-state electronic properties for their alloy $(U,Th)O_2$. The direction-dependent optical properties are then calculated for ThO_2, UO_2, and $(U,Th)O_2$ based on their ground-state electronic structures.

2. Calculation methods

The calculations in this work are carried out using the Vienna *ab initio* simulations package (VASP) [34] with the projected-augmented-wave potential (PAW) method [35]. For standard DFT calculations, the exchange-correlation energy is treated within the generalized gradient approximation (GGA) using the parameterization of Perdew, Burke, and Ernzerhof (PBE) [36,37] to compare with previously published calculations. For screened hybrid functional calculations, the HSE06 [38] formula is employed, in which a certain portion of the nonlocal Hartree–Fock (HF) exchange energy is added to the GGA exchange-correlation functional. Specifically,

$$E_{xc}^{\mathrm{HSE}} = \frac{1}{4}E_x^{\mathrm{HF}}(\mathrm{SR}) + \frac{3}{4}E_x^{\mathrm{PBE}}(\mathrm{SR}) + E_x^{\mathrm{PBE}}(\mathrm{LR}) + E_c^{\mathrm{PBE}}. \tag{1}$$

The HSE functionals benefit from the range separation of the HF exchange into a short- (SR) and long-range (LR) contribution and replaces the latter by the corresponding DFT exchange part, and the range separation parameter is set to 0.2 Å^{-1} for the HSE06 functional. Electron wave functions are expanded in plane wave basis up to a cutoff energy of 500 eV and all atoms are fully relaxed until the Hellmann–Feynman forces on them are less than 0.005 eV/Å^2. A $5 \times 5 \times 5$ k-point mesh by using the Monkhorst–Pack [39] scheme is used for integrations over the Brillouin Zone of UO_2, ThO_2 and the alloy $U_{\frac{1}{2}}Th_{\frac{1}{2}}O_2$. Convergence of the electronic degrees of freedom is achieved when the total energy change between two electronic steps is smaller than 1.0×10^{-6} eV. The thorium $6s^27s^26p^66d^2$, uranium $6s^27s^26p^66d^25f^2$, and oxygen $2s^22p^4$ electrons are treated as valence electrons. Our previous study finds that spin–orbit coupling (SOC) induces little modifications on the electronic structures of actinide dioxides [16]. Therefore in the present study, SOC is not considered.

The frequency dependent dielectric matrices are calculated based on the ground state electronic structures of ThO_2, UO_2 and $(U,Th)O_2$ compounds, according to the method proposed by Gajdoš et al. [40]. This method is derived from the PAW methodology, and the frequency-dependent symmetric dielectric matrix in the random phase approximation (RPA) [40,41]. The derived imaginary part of the dielectric matrix can be determined by a summation over empty states using the following equation:

$$\varepsilon_2^{\alpha\beta}(\omega) = \frac{4\pi^2e^2}{\Omega}\lim_{q\to 0}\frac{1}{q^2}\sum_{c,v,k}2w_k\delta(\varepsilon_{ck} - \varepsilon_{vk} - \omega) \times \langle u_{ck+e_{\alpha q}}|u_{vk}\rangle\langle u_{ck+e_{\beta q}}|u_{vk}\rangle^*, \tag{2}$$

where Ω is the volume of the primitive cell, w_k is the k-point weights that sum to 1, w is the frequency, the indices c and v refer to conduction and valence band states respectively, and u_{ck} is the cell periodic part of the wave functions at the k point. The real part of the dielectric tensor is then calculated by the usual Kramers–Kronig transformation:

$$\varepsilon_1^{\alpha\beta} = 1 + \frac{2}{\pi}P\int_0^{\infty}\frac{\varepsilon_2^{\alpha\beta}(\omega')\omega'}{\omega'^2 - \omega^2 + i\eta}d\omega'. \tag{3}$$

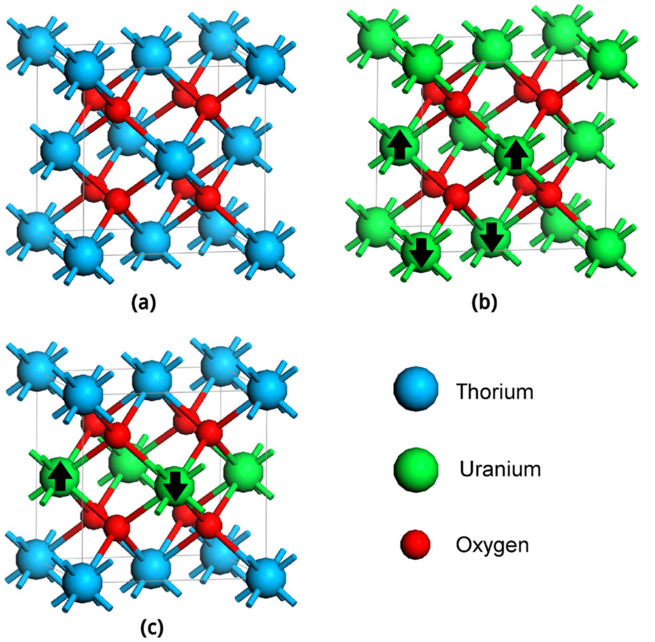

Fig. 1. (Color online.) Atomic structures of ThO_2 (a), UO_2 (b) and $U_{\frac{1}{2}}Th_{\frac{1}{2}}O_2$ compounds (c). Large blue and green balls represent for Th and U atoms, while small red balls represent for O atoms.

The optical properties, adsorption coefficient $I(\omega)$, energy loss spectrum $L(\omega)$, reflectivity $R(\omega)$, and refractive index $n(\omega)$ are calculated from the dielectric matrices following:

$$I(\omega) = \sqrt{2}\omega[\sqrt{(\varepsilon_1(\omega)^2 + \varepsilon_2(\omega)^2)} - \varepsilon_1(\omega)]^{1/2}, \tag{4}$$

$$L(\omega) = \varepsilon_2(\omega)/[(\varepsilon_1(\omega)^2 + \varepsilon_2(\omega)^2)], \tag{5}$$

$$R(\omega) = |\frac{\sqrt{\varepsilon(\omega)} - 1}{\sqrt{\varepsilon(\omega)} + 1}|^2, \tag{6}$$

$$n(\omega) = (1/\sqrt{(2)})[\sqrt{(\varepsilon_1(\omega)^2 + \varepsilon_2(\omega)^2)} + \varepsilon_1(\omega)]^{1/2}, \tag{7}$$

respectively [42,43], where $\varepsilon(\omega) = \varepsilon_1(\omega) + i\varepsilon_2(\omega)$ is the frequency dependent dielectric function, and $\varepsilon_1(\omega)$ and $\varepsilon_2(\omega)$ are the real and imaginary parts of $\varepsilon(\omega)$.

3. Results and discussions

Most actinide dioxides in their ground states crystallize into the CaF_2-like fluorite structures [as depicted in Fig. 1(a)], belonging to the space group of $Fm\overline{3}m$ (No. 225). For example in ThO_2, each Th atom is surrounded by eight O atoms forming a cube and each O atom connects with four nearest Th atoms to build a tetragon. Earlier studies reveal that ThO_2 is nonmagnetic (NM), while UO_2 is antiferromagnetic (AFM) in their ground states [17]. To avoid too large calculation consumptions (especially for the HSE method), here we only consider the 1-k AFM state for UO_2 [44], as depicted in Fig. 1(b). The 3-k AFM state with a small energy reduction [45–47] is not considered here.

For the alloy of $(U,Th)O_2$, we only consider the simple 1:1 ratio alloy also because of the large computation consumption of the HSE method. This simple sample, nevertheless, gives us quite a knowledge on the chemical bonding characters within MOX materials and their influences on the optical properties. The ferromagnetic (FM), AFM, and NM states have all been considered for the ordered $Th_{\frac{1}{2}}U_{\frac{1}{2}}O_2$ alloy. We find that the AFM state depicted in Fig. 3(c) is the most stable. Its electronic energy is 1.77 eV lower than the NM, and 0.89 eV lower than the FM states.

Our calculated lattice constant, atomic magnetization and electronic band gaps for ThO_2, UO_2, and $Th_{\frac{1}{2}}U_{\frac{1}{2}}O_2$ are summarized

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