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Symmetry Breaking and the Ground State of UO_2 in DFT+U Approach

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Abstract

It turns out that in the ground state of some systems, the symmetry of some property is broken. It has already been shown that the energy functional of a strongly-correlated electron system is a multi-minima function of the input parameters. The methods already introduced to single out the ground state among the local minima set, are not able to determine all such minima states and thereby one may lose the "true" ground state of the system and identify a false minimum as the ground state which may have quite different properties. In this work, we introduce a simple and straight-forward method of SMC to find the ground state as well as the meta-stable states of 1k-order anti-ferromagnetic configuration of UO_2 .

Keywords: Symmetry-Breaking, DFT+U, Ground State, Meta-Stable State.

Introduction

Experimental studies had shown that UO_2 has a 3k-order antiferromagnetic (AFM) crystal structure at T<30K, and paramagnetic structure at higher temperatures [1]. The low temperature structure is shown in Fig. 1 in which the U atoms occupy the sites of an FCC structure with a lattice constant of 5.47 Angstrom, and the O atoms occupy positions with $Pa\bar{3}$ symmetry [2].

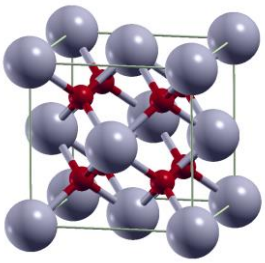

Figure 1. Low temperature structure of UO_2 crystal with lattice constant equal to 5.47 Angstrom. U and O atoms are presented with grey and red balls, respectively.

The electronic structure of UO_2 has already been investigated and shown that using the LDA or GGA approximations for the exchange-correlation functional in the density functional theory (DFT) [3] leads to incorrect metallic behavior [4], while it is experimentally found to be an insulator, and so it is called as "Mott insulator". The energy functional in the DFT+U method is a multi-minima functional of input parameters, the lowest energy state among them is the ground state (GS). The methods so far introduced to determine the local minima (meta-stable states) were not able to find all possible states and therefore identifying the "true" GS in DFT+U was a challenging problem. In this work, we introduce a simple and straight-forward method of "Starting Magnetization Control" (SMC) which gives more meta-stable states compared to other methods, and used the method to show that the true GS of UO_2 is a spin-symmetry broken state [5].

Calculation methods

Calculations are based on the DFT method using the QE code package [6]. For the interactions of ions with electrons we used ultra-soft pseudo-potentials (USPP) generated by the *atomic* code (for details ref. to [5]). To apply the SMC method, we take the starting magnetization of O atoms as a degree of freedom and vary in the steps of 0.1 from -1 to +1. For the U atoms, we assign the values of +0.5 and -0.5 to construct the 1k-order AFM structure. By scanning different values of magnetizations for O atoms, we determine a subset of local minima containing the lower energy state which is the true GS. This GS is shown to be a spin-symmetry broken state, that is, the spin-up and spin-down electron densities are not symmetrically distributed. By taking the O atoms as two inequivalent sets, we obtain more meta-stable states which also include the minima determined by previous methods.

Results and discussion

We take the crystal cell containing three types of atoms, as shown in Fig. 2. In this model, the spin-polarized Kohn-Sham equations were solved for all possible starting magnetizations for O atoms, while those of U atoms were kept at the fixed values of +0.5 and -0.5 Bohr-Magnetons.

Table 1. Equilibrium properties of the UO_2 ground state.

a (c) Ang.	*a*(Exp.) Ang.	Tot. mag. BM	Abs. mag. BM	E_g eV
5.509(5.480)	5.470	0.00	2.165	2.10

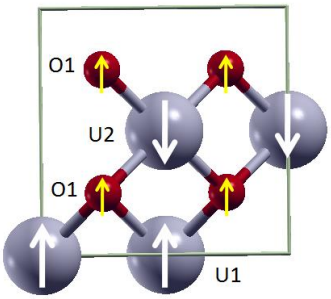

Figure 2. All-equivalent oxygen atoms scheme. In this scheme, the magnetizations of O atoms are varied simultaneously with the same amount.

In Table 1, the equilibrium properties of the GS are shown. The values are in excellent agreement with experiment.
Applying the SMC method, the GS is shown to be a spin-symmetry broken state of the electron density. In Fig. 3, the GS and meta-stable states are shown schematically.

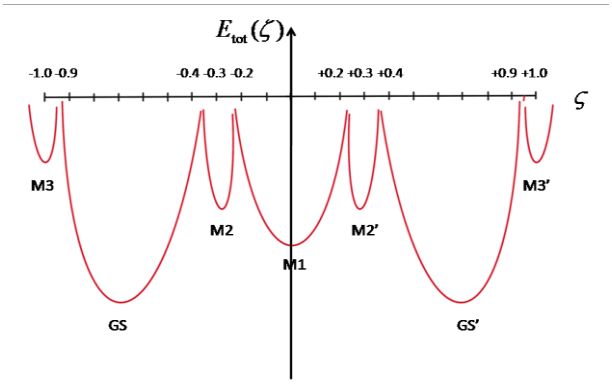

Figure 3. Schematic plot of local minima and their corresponding magnetizations.

As is shown in Fig. 3, the GS has non-zero magnetization and is doubly degenerate. This means that the spin-up and spin-down electron densities are not symmetrically distributed in the GS. So far the M1 meta-stable state was taken as the GS which has different properties.
In Table 2, the properties of the minimum energy states are listed. As is seen, the lattice constants of M1 state is higher than those of the true GS.

Conclusions

In this work, we have shown that the "true" GS of 1k-order AFM UO_2 system is a spin-symmetry broken state of the electron spin magnetizations of oxygen atoms.

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Table 2. Ground state and meta-stable states' properties in the all-equivalent oxygen atom model. The energies are in Ry/(unit formula) and are compared to the GS. Lattice constants are in Angstrom, and the magnetizations are in Bohr-magneton/(unit formula).

state.	ΔE Ry	Tot. mag. BM	Abs. mag. BM	*a*(c) Ang.
GS	0.0000	0.00	2.165	5.509(5.480)
M1	0.0027	0.00	2.155	5.522(5.456)
M2	0.0118	0.00	2.165	5.530(5.440)
M3	0.0588	0.04	2.240	5.469(5.510)

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