



Comparison of SMC and OMC results in determining the ground-state and meta-stable states solutions for UO_2 in the DFT+U method

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Abstract

Correct prediction of the behavior of UO_2 crystal, which is an anti-ferromagnetic system with strongly correlated electrons, is possible by using a modified density functional theory, the DFT+U method. In the context of DFT+U, the energy of the crystal turns out to be a function with several local minima, the so-called meta-stable states, and the lowest energy state amongst them is identified as the ground state. OMC was a method that was used in DFT+U to determine the ground state. The SMC method, by leveraging only the oxygen electronic spin-polarization degrees of freedom, has indeed uncovered the multi-minima energy structure within the DFT+U approach and produced results consistent with the experimental data. In this work, we compare the SMC and OMC results and show that although the ground states of the two methods have similar energies and geometries, the electronic structures have significant differences. Moreover, we show that the GS obtained from SMC is by $0.0022 \text{ Ry}/(\text{formula unit})$ above that of OMC. The discrepancy in GS results between the two methods suggests that they explore minimum-energy states across different electron densities subspaces. Neither method alone is sufficient to identify the global minimum energy state. Therefore, to obtain the global-minimum state of energy one has to search over larger subspaces that involve both occupation matrices of U atoms and starting magnetization of O atoms.

Keywords: density-functional theory, strongly-correlated electrons, anti-ferromagnetism, occupation-matrix control, starting-magnetization control

1. Introduction

Uranium dioxide is a common fuel used in nuclear power reactors. It has a 3k-order anti-ferromagnetic (AFM) crystal structure at temperatures less than 30 K and a paramagnetic structure at higher temperatures [1-2]. From earlier experimental results [3] it was concluded that the uranium and oxygen atoms occupied respectively the octahedral (4a) and tetrahedral (8c) symmetry positions of cubic space group $Fm\bar{3}m$ (No. 225) with lattice constant of 5.47 Angstrom, which is shown in fig. 1(a). This space group can be represented by a simple tetragonal unit cell with 6 atoms, as shown in fig. 1(b). However, a later XRD experiment [4] indicated that UO_2 crystallizes with a less symmetric cubic space group $Pa\bar{3}$ (No. 205) with oxygen atoms slightly displaced inside the cube. The use of ordinary approximations in density-functional theory (DFT) [5-6] description of the system leads to incorrect metallic behavior while it is

experimentally found [7] to be an insulator with a gap of 2.10 eV. The incorrect metallic prediction arises from the partially-filled "localized" 5f or 6d valence electrons in uranium atoms that are treated on the same footing as other delocalized ones in the atom. One of the ways to overcome this problem is the method of DFT+U [8-11] in which the DFT contributions of the Hubbard orbitals (E_{dc}), are subtracted from the DFT energy and a better contribution, which is borrowed from Hubbard model (E_{Hub}), is added to DFT energy, leading to the DFT+U energy functional:

$$E_{DFT+U} = E_{DFT} - E_{dc} + E_{Hub}, \quad (1)$$

In equation (1), the first term in the right hand side is the LDA/GGA [6, 12] total energy of the system. E_{Hub} depends on the elements of the occupation matrices of highly correlated f and d electrons of

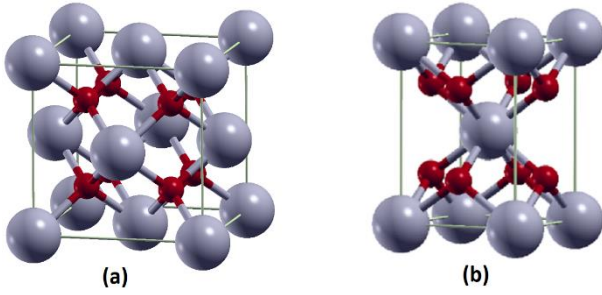


Figure 1. (a) UO_2 crystal structure with cubic space group $Fm\bar{3}m$ (No. 225) and lattice constant of 5.47 Angstrom, and (b) description by a simple tetragonal crystal structure with six atoms. Gray and small red balls represent uranium and oxygen atoms, respectively.

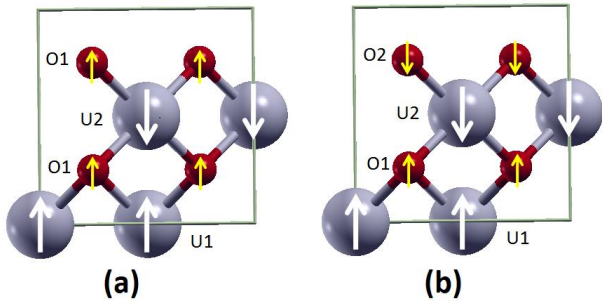


Figure 2. (a) All-equivalent oxygen atoms scheme, and (b) two-inequivalent oxygen atoms scheme. In the all-equivalent oxygen atoms model, all oxygen atoms are treated as the same type, O1, and assume the same starting magnetizations within the SMC method, while in the two-inequivalent oxygen atoms model, the O1 and O2 oxygen atoms are treated as different types and assume independent values for the starting magnetizations in the SMC method [13].

uranium atoms. It turns out that E_{DFT+U} is a functional having several local minima, the so-called meta-stable states. To determine the ground state (GS) of the system, one has to carefully determine all such local minimum states and then identify the lowest energy state as the GS of the system. Two of the methods that determine the meta-stable states are called the occupation-matrix control [10] (OMC) and the starting magnetization control [13] (SMC). In this work, we briefly describe these methods and primarily show, by comparing the results, that the number of metastable states depends on the method and the computational details. Then, it is shown that even though the GS states determined by these two methods have similar energies, the electronic structure of the two GS's have significant differences. Moreover, we have shown that the SMC-GS is by 0.0022 Ry/(formula unit) above the OMC-GS. This difference implies that the two methods search for the minimum-energy state over different subspaces of electron densities, and each method alone is not capable to explore the global minimum of the energy. Therefore, to locate the global-minimum state of energy, we have searched over a larger subspace which involves at the same time both occupation matrices of Hubbard f orbitals of U atoms and the starting magnetization of O atoms and shown that the number of metastable states varies with starting magnetization.

The organization of this paper is as follows: In Section 2, we present the computational details; in Section 3 the calculated results are presented and discussed; Section 4 concludes this work.

2. Computational details

All DFT+U calculations are based on the solution of the KS equations using the Quantum-ESPRESSO code package [14, 15]. For the atoms U and O, we have employed the ultra-soft pseudo-potentials (USPP) generated by the atomic code, using the generation inputs (with small modifications for more desired results) from the pslibrary [16]. For the USPP generation, we have used the valence configurations of U(6s2 6p6, 7s2, 7p0, 6d1, 5f3) and O(2s2, 2p4); and to take into account the dominant relativistic effects of the electrons [17], we have adopted the scalar-relativistic (SR) method [18]. For the exchange-correlation, we have chosen the Perdew-Zunger [19] (PZ) LDA, which gives excellent geometric properties whenever the Hubbard on-site parameter U is set to 4.53 eV and the projection onto Hubbard orbitals are chosen to be atomic ones that are not orthogonalized. Performing convergence tests, the appropriate kinetic energy cutoffs for the plane-wave expansions were chosen as 90 and 720 Ry for the wavefunctions and densities, respectively. To avoid the self-consistency problems, the Methfessel-Paxton smearing method [20] for the occupations with a width of 0.01 Ry is used. For the Brillouin-zone integrations in geometry optimizations, a $8 \times 8 \times 6$ grid was used; while for density-of-states (DOS) calculations, we used a denser grid of $10 \times 10 \times 7$ in reciprocal space and "tetrahedron" method [21] for the occupations. All geometries were fully optimized for total residual pressures on unit cells to within 0.5 kbar, and residual forces on atoms to within 10^{-3} mRy/a.u.

2.1. OMC method

In this method, the starting magnetization for oxygen atoms is set to zero values, and for U atoms they are set to ± 0.5 for making anti-ferromagnetic (AFM) configuration along the z direction. Moreover, the initial values for the diagonal elements of occupation matrices in Hubbard correction are set to zero and unity ($n_\sigma = 0, 1$; $\sigma = \uparrow, \downarrow$).

Since in the present work we apply on-site Hubbard corrections to only 5f localized orbitals, the dimension of the occupation matrices are equal to 7. On the other hand, since in our employed U-atom pseudo-potential the 5f orbital is occupied by 3 electrons, then we can have $C_3^7 = 35$ different ways for occupying the diagonal elements of 7×7 matrix by 3 electrons: [1110000], [1101000], [1100100], ..., [0001011], [0000111]. Among these occupation configurations, the ones which lead to the lowest energy are taken as the initial occupations for GS. All others lead to metastable states. On the other hand, some researchers have argued that only two f orbitals of U atoms should be filled [10], and therefore ending up with a $C_2^7 = 21$ different ways for occupying the diagonal elements: [1100000], [1001000],

[1000100], ... , [0000101], [0000011]. We have considered both cases in our calculations.

2. 2. SMC method

In the SMC method [13], the starting magnetization for the U atoms is set to ± 0.5 as in the OMC method, but the starting magnetization for the O-atoms, ζ , is considered as a new degree of freedom. For the initial configurations of electrons, different values for starting magnetization in the interval $-1.0 \leq \zeta \leq +1.0$ with step $\Delta\zeta = 0.1$ were considered. This new degree of freedom may be taken into account in two ways: a) All-equivalent O atoms, and b) Two inequivalent O atoms. In the former case, all oxygen atoms in the unit cell take the same values for ζ , and in the latter case, since there are two inequivalent uranium atoms with magnetizations ± 0.5 , we may consider two independent degrees of freedom for oxygen atoms which are denoted by ζ_1 and ζ_2 . The situation is shown in fig. 2.

In this method the number of SCF calculations, 441, is much higher than that in OMC, which equals at most 35.

3. Results and discussions

3. 1. OMC results

3. 1. 1. C_3^7 – occupations :

The self-consistent solutions in the OMC method with C_3^7 occupations resulted in 12 local minima, the lowest energy one is identified as the GS. The results are summarized in table 1. It was already shown [10] that when the symmetries of wavefunctions were not included in the solutions of the KS equations, all metastable states turned into insulators with different gaps. In the case of OMC- C_3^7 method, we solved the KS equations without any symmetries for the wavefunctions other than time-reversal symmetry, and most of the metallic metastable states turned into insulators. These calculations were done for a cubic structure with experimental lattice constant of 5.47 Angstrom. The results are shown in table 2. The states tabulated in table 2 are named according to the configuration order and not the energy order.

3. 1. 2. C_2^7 – occupations :

To test the validity of arguments [10] which led to C_2^7 configurations, we have performed the calculations and tabulated the results in table 3. Comparison of table 1 and table 3 reveals that the GS and first two metastable states are the same in C_3^7 and C_2^7 schemes. However, the latter scheme predicts two more metastable states with a gap. So, C_2^7 is not the only scheme to find the GS. In addition, we see that the predicted lattice constant for the GS, 5.4656 (5.4787) Angstrom is in excellent agreement with experimental value, 5.47 Angstrom. However, the predicted KS band gap, 2.91 eV, is about 0.7 eV larger than the experimental gap.

3. 2. SMC results

It was shown [13] that for the all-equivalent-O scheme, one obtains seven different classes of energetic and structural properties. Also, the calculated total magnetizations, $M_{tot} = \int_{cell} (n_{\uparrow} - n_{\downarrow}) d^3r$, had shown that

the GS as well as the six meta-stable states had zero total magnetizations. The important result in the SMC method is that, in contrast to that of OMC method, for the GS the spin-up and spin-down electrons of O atoms are not symmetrically distributed. That is, the GS has a value $\zeta \neq 0$. The situation is schematically shown in fig. 3.

In the two-inequivalent-O scheme, we optimized the structures for 441 different combinations of ζ_1 and ζ_2 values and obtained 16 local minima for the energies. The energy results are shown in fig. 4. As is seen from fig. 4, there are 16 local-minimum states and most of ζ_1 and ζ_2 combinations lead to the GS. This figure also shows that the properties are invariant under the transformation $(\zeta_1, \zeta_2) \rightarrow (-\zeta_1, -\zeta_2)$. More details (complementary to fig. 4) on the result for the two-inequivalent-O atoms scheme are presented in table 4.

Here, we have also performed SCF calculation with no symmetry (other than the time-reversal) for the wavefunctions, and did not find any significant differences in the number of "insulator" metastable states, and therefore do not report the results.

Finally, we address the most important differences in the ground state properties in the two schemes of OMC and SMC. Firstly, the GS energy obtained in SMC is slightly higher than that of OMC by 0.0022 Ry/(formula unit). Secondly, the KS gap in SMC-GS, 2.18 eV, is very close to the experimental value compared to that of OMC-GS, 2.91 eV; and thirdly, as is seen from the plots of density of states (DOS) in fig. 5, in the GS of OMC scheme the up-spin and down-spin electrons are symmetrically distributed over the states while in the SMC scheme even though the total magnetization vanishes but the symmetry between up and down spins is broken.

3. 3. Searching for global minimum over larger subspaces

The differences between OMC-GS and SMC-GS imply that the two methods span different subspaces of electron densities, suggesting that one may search for the global minimum over larger subspaces. Here, we have considered two different extended subspaces: i) applying OMC independently for up-spin and down-spin uranium atoms, ii) applying OMC for each starting magnetization of O atoms.

3. 3. 1. Independent OMC for U1 and U2 atoms

In this method, we have solved the KS equations using all $C_2^7 \times C_2^7 = 441$ different initial occupation matrices and obtained 80 different metastable states closely lying within 0.2467 Ry energy interval.

Table 1. GS and meta-stable (MS) states' properties in the OMC- C_3^7 method. The energies are in Ry/(formula unit) and are compared to the GS. Equilibrium lattice constants are in Angstrom, total magnetizations are in Bohr-magneton/(formula unit), and the energy gap is in eV.

State	initial occupations	ΔE	a (c)	Tot. mag.	E_{gap}
GS	[111000],[0110010],[0110001]	0.00000	5.4656 (5.4787)	0.00	2.91
MS1	[1000011],[0100011],[0010011]	0.00464	5.4888 (5.4327)	0.00	2.22
MS2	[1001100],[0101100],[0011100],[0001110],[0001101]	0.00838	5.4755 (5.4526)	0.00	2.15
MS3	[1001010],[1001001],[0101010],[0011010],[0001011]	0.05790	5.4354 (5.4628)	0.00	metal
MS4	[1010010]	0.06170	5.4479 (5.4543)	0.00	metal
MS5	[1000110],[1000101],[0100110],[0010110]	0.06203	5.4362 (5.4694)	0.00	metal
MS6	[0111000],[1101000],[0101001],[0011001],[1011000]	0.06206	5.4444 (5.4882)	0.00	metal
MS7	[0100101],[1100100],[0010101],[1010100]	0.06865	5.4588 (5.4571)	0.00	metal
MS8	[0000111]	0.06979	5.4446 (5.4418)	0.00	metal
MS9	[0110100]	0.08088	5.4703 (5.4248)	0.00	metal
MS10	[1100001]	0.09682	5.4151 (5.4954)	0.00	metal
MS11	[1100010],[1010001]	0.11800	5.4022 (5.4818)	0.00	metal

Table 2. Band gaps of metastable states for OMC- C_3^7 method when the symmetry of the wavefunctions were not included in the solutions of the KS equations. The states are sorted by the initial configurations of occupation matrices.

State	initial occupations	E_{gap} (eV)
GS*	[1110000]	2.90
MS*1	[1101000]	2.19
MS*2	[1100100]	2.51
MS*3	[1100010]	2.83
MS*4	[1100001]	1.89
MS*5	[1011000]	2.58
MS*6	[1010100]	2.51
MS*7	[1010010]	1.89
MS*8	[1010001]	2.79
MS*9	[1001100]	2.15
MS*10	[1001010]	2.36
MS*11	[1001001]	2.36
MS*12	[1000110]	2.38
MS*13	[1000101]	2.36
MS*14	[1000011]	2.21
MS*15	[0111000]	not conv.
MS*16	[0110100]	not conv.
MS*17	[0110010]	2.84
MS*18	[0110001]	2.84
MS*19	[0101100]	2.57
MS*20	[0101010]	2.57
MS*21	[0101001]	2.21
MS*22	[0100110]	2.82
MS*23	[0100101]	not conv.
MS*24	[0100011]	metal
MS*25	[0011100]	2.57
MS*26	[0011010]	2.21
MS*27	[0011001]	2.57
MS*28	[0010110]	not conv.
MS*29	[0010101]	2.86
MS*30	[0010011]	metal
MS*31	[0001110]	2.35
MS*32	[0001101]	2.35
MS*33	[0001011]	metal
MS*34	[0000111]	not conv.

Table 3. The same as in table 1 but for the OMC- C_2^7 method.

State	initial occupations	ΔE	a (c)	Tot. mag.	E_{gap}
GS	[110000]	0.00000	5.4656 (5.4787)	0.00	2.91
MS1	[1000001],[0000011]	0.00464	5.4888 (5.4327)	0.00	2.22
MS2	[0001100]	0.00838	5.4754 (5.4523)	0.00	2.15
MS3	[0010010]	0.02426	5.5068 (5.3983)	0.00	metal
MS4	[0001010],[0001001]	0.05790	5.4354 (5.4628)	0.00	metal
MS5	[0000110],[0000101]	0.06203	5.4362 (5.4694)	0.00	metal
MS6	[0101000],[0011000]	0.06206	5.4444 (5.4882)	0.00	metal
MS7	[1000100]	0.06370	5.5209 (5.5176)	0.00	1.00
MS8	[1001000]	0.06608	5.5265 (5.5020)	0.00	0.82
MS9	[0100100],[0010100]	0.06865	5.4588 (5.4571)	0.00	metal
MS10	[0100001]	0.09682	5.4151 (5.4954)	0.00	metal
MS11	[0100010],[0010001]	0.11800	5.4022 (5.4818)	0.00	metal
MS12	[1100000],[1010000]	0.13873	5.4992 (5.5028)	0.00	metal

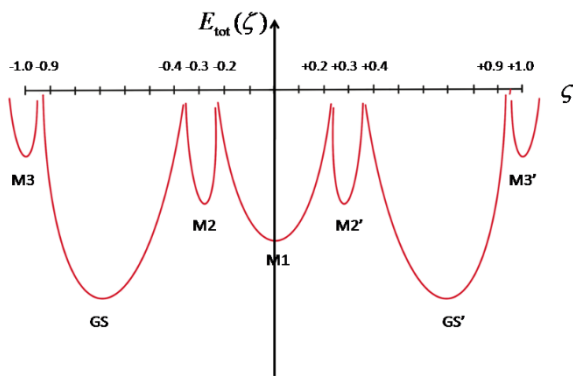
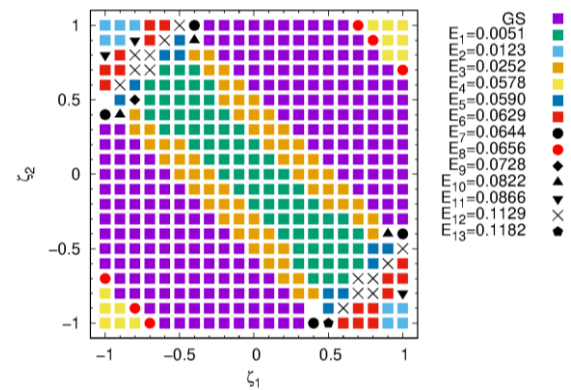
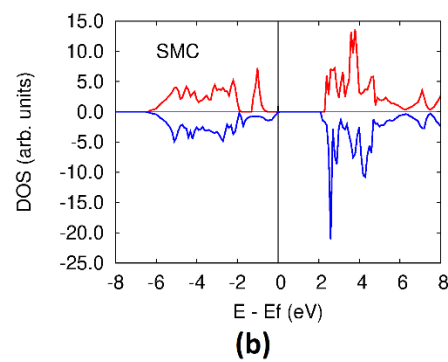
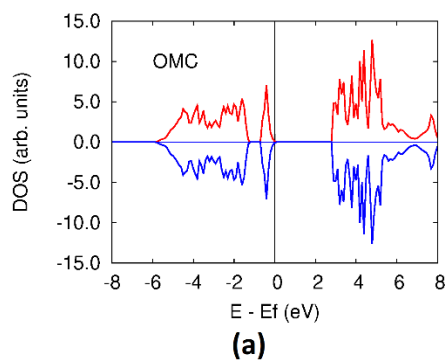
**Figure 3.** Schematic plot of local minima and their corresponding starting magnetizations. The depths of the minima (in arbitrary units) are consistent with their energy values. As seen, the GS and GS' cover the largest interval, but away from the zero starting magnetization.**Figure 4.** Local-minimum states in two-inequivalent-O scheme. It is seen that for the GS, the values of ζ_1 and ζ_2 are not simultaneously zero and most of ζ_1 and ζ_2 combinations lead to the GS than the other 15 metastable states. Also invariance under $(\zeta_1, \zeta_2) \rightarrow (-\zeta_1, -\zeta_2)$ transformation is clearly seen.**Figure 5.** Density of states (DOS) for spin-up (purple color) and spin-down (green color) for (a) OMC, and (b) SMC methods. In OMC it is symmetric but in SMC the symmetry is broken.

Table 4. GS and meta-stable (MS) states' properties in the SMC method with two-inequivalent-O atoms. The energies are in Ry/(formula unit) and are compared to the GS. Equilibrium lattice constants are in Angstrom, total magnetizations are in Bohr-magneton/(formula unit), and energy gap is in eV. Because of $(\zeta_1, \zeta_2) \rightarrow (-\zeta_1, -\zeta_2)$ symmetry in properties, they are not brought here.

State	$\{(\zeta_1, \zeta_2)\}$	ΔE	a (c)	Tot. mag.	E_{gap}
GS	(-1.0, [-0.7,+0.2]), (-0.9, [-0.8,+0.3]), (-0.8, [-0.9,+0.3]), (-0.7, [-1.0,+0.1]), (-0.6, [-1.0,0.0]), (-0.5, [-1.0,-0.1]), (-0.4, [-1.0,-0.2]), (-0.3, [-1.0,-0.3]), (-0.3, [+0.8,+0.9]), (-0.2, [-1.0,-0.4]), (-0.2, [+0.8,+1.0]), (-0.1, [-1.0,-0.5]), (-0.1, [+0.7,+1.0]), (0.0, [-1.0,-0.6]), (0.0, [+0.6,+1.0])	0.00000	5.4765 (5.4566)	0.00	2.18
MS1	(-0.7, [+0.4,+0.6]), (-0.6, [+0.3,+0.7]), (-0.5, [+0.2,+0.7]), (-0.4, [+0.2,+0.7]), (-0.3, [+0.1,+0.6]), (-0.2, [0.0,+0.5]), (-0.1, [-0.1,+0.4]), (0.0, [-0.2,+0.2])	0.00240	5.4888 (5.4327)	0.00	2.22
MS2	(-1.0, [+0.9,+1.0]), (-0.9, [+0.9,+1.0]), (-0.8,+1.0)	0.00614	5.4755 (5.4526)	0.00	2.15
MS3	(-0.8,+0.4), (-0.7, [+0.2,+0.3]), (-0.6, [+0.1,+0.2]), (-0.5, [0.0,+0.1]), (-0.4, [-0.1,+0.1]), (-0.4,+0.8), (-0.3, [-0.2,0.0]), (-0.3, +0.7), (-0.2, [-0.3,-0.1]), (-0.2, [+0.6,+0.7]), (-0.1, [-0.4,-0.2]), (-0.1, [+0.5,+0.6]), (0.0, [-0.5,-0.3]), (0.0, [+0.3,+0.5])	0.01218	5.4981 (5.4150)	0.00	1.90
MS4	(-1.0, [-0.9,-0.8]), (-0.9, -1.0), (-0.8, -1.0)	0.02848	5.4504 (5.4746)	0.00	metal
MS5	(-0.8, +0.5), (-0.5, +0.8)	0.029225	5.4621 (5.4485)	0.00	metal
MS6	(-1.0, [+0.6,+0.7]), (-0.9, +0.8), (-0.7, +1.0), (-0.6, +1.0)	0.031185	5.4562 (5.4578)	0.00	metal
MS7	(-1.0, +0.3)	0.031215	5.4719 (5.4516)	0.00	metal
MS8	(-0.9, +0.4), (-0.4, +0.9)	0.031775	5.4533 (5.4720)	0.00	metal
MS9	(-0.9, -0.9)	0.032190	5.4552 (5.4590)	0.00	metal
MS10	(-0.3, +1.0)	0.038175	5.4705 (5.4507)	0.00	metal
MS11	(-1.0, +0.8)	0.042295	5.4559 (5.4330)	0.00	metal
MS12	(-0.9, [+0.5,+0.7]), (-0.8, [+0.6,+0.8]), (-0.7, [+0.7,+0.9]), (-0.6, [+0.8,+0.9]), (-0.5, +0.9)	0.055675	5.4354 (5.4628)	0.00	metal
MS13	(-1.0, [+0.4,+0.5]), (-0.5, +1.0), (-0.4, +1.0)	0.058130	5.4257 (5.4870)	0.00	metal
MS14	(-0.8, +0.9)	0.064050	5.4390 (5.4467)	0.00	metal
MS15	(-1.0, -1.0)	0.066290	5.4315 (5.5120)	0.00	metal

Table 5. Initial occupations of diagonal elements of f Hubbard orbitals that lead to GS for the corresponding given starting magnetization of O atoms (column one). The Third and fourth columns specify the number of corresponding metastable states and the range, in Ry, over which they are distributed.

starting mag. ζ	GS initial occupations	number of MS states	energy range (Ry)
0.0	[1110000],[0110100],[0110010],[0110001]	16	0.21922
0.1	[1110000],[0110100],[0110010],[0110001]	13	0.21922
0.2	[1110000],[1100010],[1100001],[0110010]	20	0.21922
0.3	[1100010],[1100001]	22	0.16105
0.4	[1100010],[1100001]	19	0.14337
0.5	[1100010],[1100001]	23	0.15528
0.6	[1100010],[1100001]	21	0.13946
0.7	[1100010]	19	0.12196
0.8	[1100010],[1100001]	25	0.13387
0.9	[1100010],[1100001]	18	0.13930
1.0	[1110000],[1101000],[1100100],[1100010],[1100001]	17	0.16590

The GS was obtained for two different combinations of occupations for up-spin and down-spin uranium atoms, respectively: ([0110000], [0110000]) and ([0100001], [0110000]), which is energetically identical to the symmetric OMC result explained above.

3. 3. 2. OMC on top of SMC

Here, we apply the OMC method on U atoms for each value of $0 \leq \zeta \leq 1$ with step $\Delta\zeta = 0.1$ for O atoms. The results show that the occupation matrices leading to the GS are not independent of the starting magnetizations of O atoms. The results are presented in table 5.

As is seen from table 5, depending on the initial magnetization of oxygen atoms, the diagonal elements of the initial occupation matrices for GS vary. This result crucially shows that ignoring the starting magnetization for oxygen atoms in the OMC method may result in a metastable state. Moreover, as is seen from the third and fourth columns of table 5, the number of metastable states, as well as the range of energy that they are spread out, depend on the starting magnetization of O atoms. Finally, whenever no symmetry applies to the cell (due to a defect, for example), to find the best candidate for the GS, one

has to consider occupation matrices for all Hubbard atoms independently.

4. Conclusion

To overcome the incorrect prediction of metallic behavior for UO_2 by the ordinary DFT method, one may use a Hubbard correction for the energy contributions of localized orbitals, which is called the DFT+U method. However, the application of DFT+U to determine the GS properties is somewhat tricky, as one should take care not to stuck in higher-energy metastable states which may have very different structural and electronic properties. The occupation-matrix-control (OMC) method was one way to search for the global minimum among lots of local minimum states. In the OMC method, people constrain the starting magnetization of O atoms to be zero and use different possible initial occupation matrices for the localized orbital. However, in the SMC method we release the constraint used in the OMC method and allow the starting magnetizations of O atoms vary between -1.0 and +1.0. It turns out that in this way one reproduces different sets of metastable states. It was shown that in the SMC method, one obtains more metastable states than in OMC.

Comparing the GS properties in the two methods showed very similar lattice constants and total magnetizations. However, even though the KS gap in SMC-GS, 2.18 eV, is very close to the experimental value compared to that of OMC-GS, 2.91 eV, the GS energy obtained in SMC is slightly higher than that of OMC by 0.0022 Ry/(formula unit). The differences between the two ground states imply that the two methods span different subspaces of electron densities, suggesting that one may search for the global minimum over larger subspaces involving both the initial magnetization of O atoms and the occupation matrices of U atoms. Finally, for a unit cell with no symmetry, to find the best candidate for the GS, one has to deal with the occupation matrices of all Hubbard atoms independently.

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Data Availability

The raw or processed data required to reproduce these results can be shared with anybody interested upon sending an E-mail to M. Payami.

References

1. G Amoretti, A Blaise, R Caciuffo, J M Fournier, M T Hutchings, R Osborn, and A D Taylor, *Phys. Rev. B* **40**, 3 (1989) 1856.
2. J Faber, G H Lander, and B R Cooper, *Phys. Rev. Lett.* **35**, 26 (1975) 1770.
3. M Idiri, T Le Bihan, S Heathman, and J Rebizant, *Phys. Rev. B* **70**, 1 (2004) 14113.
4. L Desgranges, Y Ma, Ph Garcia, G Baldinozzi, D Simeone, and H E Fischer, *Inorg. Chem.* **56**, 1 (2017) 321.
5. P Hohenberg and W Kohn, *Phys. Rev.* **136** (3B) (1964) B864.
6. W Kohn and L J Sham, *Phys. Rev.* **140** (4A) (1965) A1133.
7. J Schoenes, *J. Appl. Phys.* **49**, 3 (1978) 1463.
8. M Cococcioni and S de Gironcoli, *Phys. Rev. B* **71**, 3 (2005) 035105.
9. B Himmetoglu, A Floris, S de Gironcoli, and M Cococcioni, *Int. J. Quantum Chem.* **114**, 1 (2014) 14.
10. B Dorado, B Amadon, M Freyss, and M Bertolus, *Phys. Rev. B* **79**, 23 (2009) 235125.
11. M Freyss, B Dorado, M Bertolus, G Jomard, E Vathonne, Ph Garcia, and B Amadon, *Ψ_k scientific highlight of the month*. **113** (2012).
12. J P Perdew, A Ruzsinszky, G I Csonka, O A Vydrov, G E Scuseria, L A Constantin, X Zhou, and K Burke, *Phys. Rev. Lett.* **100**, 13 (2008) 136406.
13. M Payami, *Iranian J. Phys. Res.* **22**, 3 (2022) 175.
14. P Giannozzi et. Al., *J. Phys.: Condensed Matt.* **21**, 39 (2009) 395502.
15. P Giannozzi, O Baseggio, P Bonfa, D Brunato, R Car, I Carnimeo, C Cavazzoni, S de Gironcoli, P Delugas, F Ferrari Ruffino, A Ferretti, N Marzari, I Timrov, A Urru, and S Baroni, *J. Chem. Phys.* **152**, 15 (2020) 154105.
16. A Dal Corso, *Comput. Mater. Sci.* **95** (2014) 337.
17. M Payami and S Sheykhi, *Iranian J. Phys. Res.* **23**, 2 in press (2023).
18. D D Koelling and B N Harmon, *J. Phys. C: Sol. State Phys.* **10**, 16 (1977) 3107.
19. J P Perdew and A Zunger, *Phys. Rev. B* **23**, 10 (1981) 5048.
20. M Methfessel and A T Paxton, *Phys. Rev. B* **40**, 6 (1989) 3616.
21. P E Blochl, O Jepsen and O K Andersen, *Phys. Rev. B* **49**, 23 (1994) 16223.