The first-principles treatment of the electron-correlation and spin–orbital effects in uranium mononitride nuclear fuels†

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The DFT + U calculations were employed in a detailed study of the strong electron correlation effects in a promising nuclear fuel—uranium mononitride (UN). A simple method for solving the multiple minima problem in DFT + U simulations and insure obtaining the correct ground state is suggested and applied. The crucial role of spin–orbit interactions in reproduction of the U atom total magnetic moment is demonstrated. Basic material properties (the lattice constants, the spin- and total magnetic moments on U atoms, the magnetic ordering, and the density of states) were calculated varying the Hubbard U-parameter. By varying the tetragonal unit cell distortion, the meta-stable states have been carefully identified and analyzed. The difference in the magnetic and structural properties obtained for the meta-stable and ground states is discussed. The optimal effective Hubbard parameter $U_{\text{eff}} = 1.85$ eV reproduces correctly the UN anti-ferromagnetic ordering, and only slightly overestimates the experimental total magnetic moment of the U atom and the unit cell volume.

1. Introduction

Actinide compounds continue to attract great attention of both materials scientists and nuclear engineers. Their properties combine strong electron correlation and relativistic effects caused by 5f valence electrons. Reliable calculations of many properties of actinides and their compounds require better understanding of these materials at the atomic and electronic structure levels. In particular, low temperature magnetic properties and defects in the bulk and on surfaces were addressed in several recent papers on actinides.1–9 To treat properly strong electron correlation effects, advanced first principles methods are required, e.g. Hubbard-U (DFT + U) approach.7

Uranium nitride (UN) is one of the actinide compounds considered by the Generation IV forum10 as a perspective fuel for fast nuclear reactors. The standard DFT computations of a number of UN properties give the results which look, at the first glance, to be in good agreement with the experiment.11–13 The study of actinide nitrides by Atta-Fynn and Ray11 could serve as an example. A deviation of the calculated lattice constant in UN was <1% of the experimental value, the spin magnetic moment of the U atom $\mu_S$ was also in a good agreement with the experiment14 (0.96 $\mu_B$ against 0.75 $\mu_B$ respectively). However, the electron correlation effects were not completely incorporated (despite the spin–orbit interactions were included). As a result, the calculated ground state was ferromagnetic (FM), in contrast to the anti-ferromagnetic (AFM) order known experimentally.14

The DFT + U calculations are becoming a standard technique for studying strongly correlated actinide compounds. The most studied material is UO$_2$,2,15,16 in contrast to the much less investigated PuO$_2$.2,17,18 In particular, the so-called non-collinear 3-k magnetic structure and tiny oxygen cage distortion in UO$_2$ was confirmed by means of the first principles DFT + U calculations.2,8,9

It is well known also that the standard DFT calculations of insulators and semiconductors (including actinide oxides or transition metal oxides) considerably underestimate the band gap due to insufficient treatment of electron self-interaction. The DFT + U approach is capable to correct phenomenologically this disadvantage. However, it is more difficult to observe effects of the strong electron correlations in metallic systems, such as UN. (Another example is metallic Gd (ref. 19) where neglect of the correlation effects results in a wrong magnetic state and the position of f-electron bands.) The DFT + U method was applied also to calculate basic bulk properties of PuN.20 In the latter study the DFT + U method reproduced the experimental total magnetic moment provided the spin–orbit interactions were included. Recently, Petit et al.21 have demonstrated partial localization of 5f electrons in UN using the self-interaction corrected(SIC)-LSD approach. This conclusion is supported by the angle resolved photoemission spectroscopy (ARPES) measurements by Ito et al.22 and is also discussed below.

In the present paper, we employed the DFT + U technique combined with spin–orbit interactions (SOI). Using this approach, we were able to reproduce correctly the AFM ground state.
and reasonably well the experimentally observed unit cell volume and the total magnetic moments on U atoms.

The paper is organized as follows. Computation methods and our approach are discussed in Section 2, and main results in Section 3 (with and without SOI effects in two sub-sections). Conclusions are given in Section 4.

## 2. Modeling approach

### 2.1. Computational details

UN possesses a rock-salt structure\textsuperscript{14} without essential tetragonal distortion.\textsuperscript{23} The latter is expected, however, to exist for the AFM order observed at low temperatures (the Néel temperature $T_N = 53$ K). UN reveals a collinear magnetism, with the U magnetic moments alternating along the [001] direction.\textsuperscript{14} We calculated UN for both the FM and AFM orders, assuming for the latter an alternation of the magnetic moments along the [001] crystallographic direction. As a direct consequence of the AFM order, the symmetry of the crystal is reduced from cubic to tetragonal. Consequently, the same tetragonal unit cell with two UN formula units (4 atoms) was used for the AFM structure as well as for the FM one insuring consistency of simulations. As it is shown below, such a symmetry reduction appeared to be essential allowing separation and identification of the ground and meta-stable states found in our simulations.

The simplified rotationally-invariant Dudarev’s form for the DFT $+ U$ technique\textsuperscript{2} was used. In this approach the difference $U_{\text{eff}} = U - J$ of the Hubbard parameter $U$ and the exchange parameter $J$ is used. We fixed the value of exchange parameter $J = 0.125$ eV and did not vary it throughout the present simulations, so the only independent parameter in the employed form of DFT $+ U$ is $U_{\text{eff}}$ whose value was varied from 0 to 4.875 eV. This is equivalent to changes in the Hubbard parameter $U$ from 0.125 eV to 5 eV. The double counting correction in all our calculations was treated with account for spin-polarization.\textsuperscript{24}

The VASP (version 4.6) computer code\textsuperscript{25,26} with the projector augmented wave method\textsuperscript{27} was used. The exchange-correlation functional employed was that by Perdew, Burke and Ernzerhof (PBE)\textsuperscript{28} which is one of the commonly used functionals within generalized gradient approximation (GGA). The plane wave cut-off energy was fixed at 520 eV throughout all the calculations. The integration in the reciprocal space over the Brillouin zone (BZ) was performed using $10 \times 10 \times 8$ Monkhorst-Pack mesh.\textsuperscript{29} The applied mesh is sufficient to reach the convergence of $10^{-6}$ eV for one-electron energies. Fractional electronic occupations were estimated with the method of Methfessel and Paxton\textsuperscript{30} using the smearing parameter of 0.1 eV. The lattice parameters $a$ and $c$ of the tetragonal unit cell were optimized along with the electron wave functions until the total energy converged to $10^{-5}$ eV. Calculations without account for SOI were done keeping tetragonal symmetry of the system, but calculations with SOI were performed with lifted symmetry constraints.

### 2.2. Handling of meta-stable states

The DFT $+ U$ computations are known to converge often to meta-stable states\textsuperscript{15} what complicates finding the ground state of the electronic system and may lead to improper defect energetics.\textsuperscript{15,16} The meta-stable states were also found in the present UN calculations. Thus, for intermediate values of $U_{\text{eff}}$ (between 1.375 eV and 2.375 eV) we obtained two distinct local minima on the adiabatic energy surface. The energy difference between these two minima is of the order of 0.05 eV. One of these minima occurs for the tetragonal unit cell elongated along the $c$ axis ($c/a > 1$) whereas the second one corresponds to the compressed ($c/a < 1$) unit cell. In the present study the meta-stable states were carefully identified for all considered unit cells and both the AFM and FM orders.

Several techniques have been used so far to find the ground state among many possible meta-stable states within DFT $+ U$ modeling. Dorado \textit{et al.}\textsuperscript{15} proposed the occupation matrix control (OMC) scheme. In the OMC approach one has to enumerate all possible meta-stable states, to build occupation matrices (or, essentially, projectors) for reasonable approximations to these states, and to insure that many-electron wavefunction corresponds to a chosen state using these projectors. This approach requires identification of a large number of possible meta-stable states, building relevant occupation matrices (projectors), and performing computations for each significant state. The occupation matrices are not always available in the most plane-wave codes. In addition to the mentioned problems, the simulations with such a technique employed often use the initial atomic geometries having excessively high symmetry.\textsuperscript{15} The latter causes a necessity to consider too many possible states. Overall this is a brute-force approach, suggesting testing of large number of candidate states in an attempt to find the ground state of a system.

In particular, the OMC technique was applied to UO$_2$ in ref. 15 enforcing undisturbed fluorite structure, at least as a starting point of computations. Even in this situation, only 3 U5f orbitals have to be considered instead of all 7 due to splitting of the entire f multiplet of orbitals in a cubic crystal field. Further account for the AFM order (in the case of a collinear 1-k magnetic structure) will produce splitting of the remaining 3 U5f orbitals into a singlet and a doublet. Considering that (i) UO$_2$ is a semiconductor (ii) U atom has a non-zero magnetic moment, and (iii) only two electrons are available to occupy the U5f orbitals, a single occupation matrix is necessary to set the reasonable initial guess for the calculation of UO$_2$ ground state. Therefore, the OMC technique can be greatly simplified by appropriate symmetry analysis and account for the energy level splitting by the crystal field for relevant atomic orbitals. In our technique discussed below the same effect was achieved just by appropriate distortions of the crystals.

The Quasi Annealing (QA) approach\textsuperscript{31} uses repeated process of self-consistency and geometry optimization without imposing symmetry constraints. Small geometry distortions (shaking the system) at each optimization attempt are used to reach the ground state. The QA technique looks relatively computationally expensive because it requires repeated structure optimizations with lifted symmetry constraints.

Another, “$U$-ramping” technique\textsuperscript{32} suggests adiabatic increase of the Hubbard $U$ and exchange $J$ parameters from zero to their full magnitude. This is done by repeating computations while raising values of $U$ and $J$ by small increments. The electron density or the wavefunction obtained for a set of $U$ and $J$ is used as an initial guess for the next set of these parameters.
In this paper, we suggest the controlled symmetry reduction (CSR) method for solving the problem of multiple minima in the DFT+U calculations based on appropriate choice of symmetry and magnitude of unit cell deformations and/or atomic displacements. These displacements and/or deformations should be chosen in such a way that they produce sufficient splitting of the desirable state toward lower energies and ensure occupation of correct one-electron states. Then, the obtained electron density (or wavefunction) can be used as an initial guess for distortions and geometry optimizations. The same procedure can be used within any computational method for the electronic structure calculation, whatever it is DFT+U, hybrid functionals, or Hartree–Fock method.

It was straightforward to apply this approach in the present modeling: (i) experimentally known rock-salt crystal structure of UN and its collinear AFM order with alternation of atomic magnetic moments along the [001] direction suggests possibility of only two possible structures: elongated and compressed tetragonal crystal lattices. Therefore, we had to investigate consequences of only these two deformations of cubic structure. (ii) The initial electron density for each of these cases was obtained by performing computations for respective tetragonal deformations of the unit cell. The initial magnitudes of the distortion in the calculations were chosen to be large enough to guarantee convergence of the electronic densities to the desired state. (iii) Then, the computations with different deformations were performed using the obtained electron densities as the initial guesses. No additional efforts to keep specific populations of crystalline orbitals (as proposed in ref. 15) are necessary. Such computations begin from the largest considered tetragonal distortions in both directions (c/a < 1 and c/a > 1, see Fig. 1) and continue toward each other, until the adiabatic energy surfaces merge at the middle point.

All mentioned approaches for dealing with meta-stable states have shown promising results and could be effectively combined together. The CSR technique described here was already successfully applied by us in the investigation of 3-K magnetic structure stabilization in UO$_2$.

3. Results and discussion

3.1. Computations neglecting spin–orbit interactions

The total energies ($E_{\text{tot}}$) for three different $U_{\text{eff}}$ parameters are shown in Fig. 1 as functions of the tetragonal lattice parameter ratio c/a for both FM and AFM states. The curves were obtained by fixing the ratio c/a for every value of $U_{\text{eff}}$ (without SOI) while unit cell volume was optimized.

One can clearly see that for small $U_{\text{eff}}$ values (Fig. 1a) the only minimum at $c/a \approx 1$ exists for both the AFM and FM ordering of the magnetic moments. In contrast, larger values of $U_{\text{eff}}$ (Fig. 1b and c) lead to the appearance of the two minima which correspond to the ground and the meta-stable states. Thus, for $U_{\text{eff}} = 1.375$ eV both minima (at $c/a \approx 0.97$ and $c/a \approx 1$) appear for the AFM order and, while a single minimum occurs for the FM order, a precursor of another (meta-stable) minimum can be seen, too. For higher value of the effective Hubbard parameter $U_{\text{eff}} = 2.375$ eV both minima ($c/a \approx 0.97$ and $c/a \approx 1.02$) are well pronounced for the FM order, but the second minimum (with $c/a > 1$) disappears for the AFM order. Lastly, for larger values of $U_{\text{eff}}$ (see discussion below) a single minimum occurs for both the magnetic orders.

The dependencies of several basic properties (the total energy per UN molecule, the c/a ratio, the spin magnetic moment, and unit cell volume) are plotted in Fig. 2 as functions of $U_{\text{eff}}$. One can see again that the adiabatic surface profile along the tetragonal distortion of the unit cell has a

![Fig. 1](image-url)

The total energy (in eV per primitive cell) dependence on $c/a$ for the FM and the AFM magnetic orders (see the text for details) for (a) $U_{\text{eff}} = 0.875$ eV (b) $U_{\text{eff}} = 1.375$ eV (c) $U_{\text{eff}} = 2.375$ eV. No SOI effects were included.
single minimum for small $U_{\text{eff}} \leq 1$ eV. In this parameter range the unit cell retains the cubic shape ($c/a = 1$) for the FM state and slightly elongated tetragonal shape for the AFM one. Computations converge into two different minima with very small differences in the total energy, if $1 < U_{\text{eff}} < 2.375(1.875)$ eV for the FM(AFM) order. For the AFM order, the lowest energy state corresponds to the compressed unit cell ($c/a < 1$). Contrary, for the FM order the lowest energy state has the elongated unit cell ($c/a > 1$). The higher energy states disappear at larger values of $U_{\text{eff}}$ and self-consistent computations converge into the respective lower energy states.

The spin magnetic moments $\mu_S$ of U atoms plotted in Fig. 2b show growth with a $U_{\text{eff}}$ increase. They are close for both (AFM and FM) magnetic orders at small $U_{\text{eff}}$. For the larger Hubbard parameters ($U_{\text{eff}} > 1$ eV) the spin magnetic moment for the AFM order is slightly (by $\sim 0.1$–$0.2$ $\mu_B$) smaller than that for the FM order. It is important to stress here that even the smallest $\mu_S$ values are significantly larger than the experimental total magnetic moments $14$ ($0.75$ $\mu_B$). As it is demonstrated below, incorporation of the SOI induces orbital magnetic moments and brings the U atom total magnetic moments in good agreement with experiments.

The density of states (DOSs) projected on a single UN molecule in a [001] crystal plane were drawn in Fig. 3 with one spin polarization and for different values of $U_{\text{eff}}$. This is the easiest way to separate the DOSs for different spin orientations and to avoid summing of densities for majority and minority spin orientations occurring in the total DOS for the AFM states. According to the obtained DOS, spin polarization in UN occurs due to difference in the occupation of U5f orbitals by electrons with majority and minority spin orientations. Its decomposition into all contributions from the U5f orbitals are provided in Fig. S1, ESI.

For small $U_{\text{eff}}$ (= 0.875 eV) the one-electron majority-spin states located just below the Fermi energy contain mostly U5f$_{xyz}$ orbitals. However, the same peak has significant contribution from both U5f$_{y}$ ($3x^2/2$) and U5f$_{x}$ ($x^2/2$) orbitals. Another peak formed by U5f$_{xyz}$ orbitals is higher in energy than the first one by 0.38 eV and it is located above the Fermi level. Also, there is a small peak in this DOS, $\sim 1$ eV below the Fermi energy, which is formed by U5f$_{z}$ ($x^2/2$) orbitals. For this value of $U_{\text{eff}}$ the UN unit cell still retains a cubic shape. In the DOS for $U_{\text{eff}} = 1.875$ eV both mentioned peaks formed by U5f$_{xyz}$ orbitals are well pronounced and located below the Fermi energy. The splitting between these two peaks becomes 0.60 eV. The lowest in energy of the two peaks lies $\sim 1$ eV below the Fermi level and it coincides with the peak formed by U5f$_{z}$ orbitals. The peak formed by the U5f$_{z}$ orbitals moved above the
The DOS projected onto single UN molecule with both atoms in the same plane for 4 atom AFM unit cell in the ground state as a function of $U_{\text{eff}}$. The Fermi energy is taken as zero. SOI effects were neglected. The DOS was re-calculated with the tetrahedron method.\textsuperscript{34}

The DOSs for electrons with minority spin orientation are presented as negative values. Energy differences between peaks formed by U5f$_{xz}$ orbitals are represented by brackets like $\Box$ and between the lowest peaks formed by U5f$_{yz}$ and by both U5f$_{(3x^2-3y^2)}$ and U5f$_{((x^2-y^2)/C0)}$ orbitals are represented by brackets like $\Box$. Fermi energy. The UN unit cell for $U_{\text{eff}} = 1.875$ eV was already compressed. Finally, for $U_{\text{eff}} = 2.875$ eV the peak formed by both U5f$_{yz}$ and U5f$_{(3x^2-3y^2)}$ orbitals moves deeper below the Fermi energy (with the peak at $-1.7$ eV). The splitting between two U5f$_{yz}$ peaks increases to 0.95 eV. The magnitude of the upper peak becomes very small. The distance between the lower U5f$_{yz}$ peak and the peak formed by U5f$_{(3x^2-3y^2)}$ (U5f$_{(x^2-y^2)/C0}$) orbitals increases twice, becoming 2.1 eV. The latter peak moves to a higher energy side. The peaks for the respective electrons with minority spin orientation are located well above the Fermi level and move to higher energies as $U_{\text{eff}}$ increases. Such a behavior of electron bands usually correlates with increasing localization of electrons with increasing Hubbard’s parameter. The DOSs presented in Fig. 3 demonstrate also that an increase in the effective Hubbard parameter $U_{\text{eff}}$ and the localization of U5f electrons are accompanied by a decrease in the DOS at the Fermi energy. The trend of certain electron localization near the Fermi level has been indeed found in high-resolution ARPES measurements.\textsuperscript{22} Signs of dual localized/delocalized behavior of these electrons were presented in X-ray photoelectron spectroscopy and magnetic susceptibility measurements.\textsuperscript{33} This was also confirmed in the SIC-LSD simulations by Petit et al.\textsuperscript{34} The integrated DOS for electrons with majority spin orientation below the Fermi energy increases following an increase in $U_{\text{eff}}$.

The position of the lower band located between $-6.5$ eV and $-2.5$ eV under the Fermi energy remains insensitive to the $U_{\text{eff}}$. This band contains about the same contribution from N 2p orbitals and U spd orbitals (see Fig. S2 in ESI\textsuperscript{1}).

In an attempt to clarify the nature of higher and lower energy states for both magnetic orders, the spin density maps (Fig. 4) have been drawn for all elongated and compressed tetragonal states with the AFM and FM orderings. These maps could be compared with the detailed DOSs calculated for all the electron states and presented in Fig. S2–S5, ESI\textsuperscript{1}. These spin densities and DOSs were calculated for $U_{\text{eff}} = 1.875$ eV. According to presented results, the occupied bands are formed mostly by U5f$_{yz}$ orbitals with contribution from U5f$_{(3x^2-3y^2)}$ orbitals in the compressed tetragonal states for both magnetic orders. In the elongated states these bands become vacant and electrons occupy bands formed by U5f$_{(3x^2-3y^2)}$, U5f$_{(x^2-y^2)/C0}$, U5f$_{((x^2-y^2)/C0}$ and U5f$_{yz}$ orbitals.

From a comparison of the content of occupied bands in the compressed and elongated tetragonal states, one can expect that all states formed by the U5f orbitals (U5f$_{yz}$, U5f$_{(3x^2-3y^2)}$, U5f$_{(x^2-y^2)/C0}$, U5f$_{(x^2-y^2)/C0}$, U5f$_{((x^2-y^2)/C0})$) should be occupied in order to retain a nearly cubic shape of the UN unit cell. In particular, this condition appeared to be fulfilled in the computations with small $U_{\text{eff}}$ (Fig. 3 and S1, ESI\textsuperscript{1}) and the unit cell retains a cubic shape.

### 3.2. Effects of the spin–orbit interactions

In the next step, we included SOI into computer simulations. We started calculations using as the initial guess the geometries calculated one. This allows us to estimate the $U_{\text{eff}}$ values and the localization of U5f electrons.\textsuperscript{33} The position of the lower band located between $-1.7$ eV and $-2.5$ eV under the Fermi energy remains insensitive to the $U_{\text{eff}}$. According to presented results, the occupied bands are formed mostly by U5f$_{yz}$ orbitals with contribution from U5f$_{(3x^2-3y^2)}$ orbitals in the compressed tetragonal states for both magnetic orders. In the elongated states these bands become vacant and electrons occupy bands formed by U5f$_{(3x^2-3y^2)}$, U5f$_{(x^2-y^2)/C0}$, U5f$_{((x^2-y^2)/C0})$ and U5f$_{yz}$ orbitals.

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The differences between the total energies of the unit cells with the AFM and FM ordering are presented in Fig. 7. We used the energies obtained from calculations of ground states for both FM and AFM magnetic order with and without SOI. As mentioned above, UN is antiferromagnetic at low temperature. In our calculations, the AFM state turns out to be more stable (has lower energy) for $U_{\text{eff}} \geq 1.65$ eV in calculations without SOI and for $U_{\text{eff}} \geq 1.80$ eV in calculations with SOI. This suggests that for the reproduction of the experimental magnetic order the $U_{\text{eff}}$ value has to be larger than 1.80 eV. The U-atom total magnetic moment for this $U_{\text{eff}}$ is $\mu_{\text{tot}} = 0.79 \mu_B$, which is slightly larger than the experimental 0.75 $\mu_B$. Thus, the range of $U_{\text{eff}}$ between 1.8 eV to 1.9 eV seems to be the optimal to reproduce both right sequences of the magnetic states (the FM state must be higher in the total energy than the AFM state) and the total U atom magnetic moment. For example, for the intermediate $U_{\text{eff}} = 1.85$ eV the total magnetic moment $\mu_{\text{tot}} = 0.81 \mu_B$.

Lastly, the dependence of unit cell volume as a function of the effective Hubbard parameter (Fig. 5b) was analyzed. For $U_{\text{eff}} \approx 0$ eV the unit cell volume is slightly smaller than the experimental one (116.78 Å$^3$), which is consistent with previous calculations. For the proposed value of $U_{\text{eff}} = 1.85$ eV, the unit cell volume (118 Å$^3$) exceeds the experimental one less than by ~ 1%. This is good accuracy, comparing with the rough GGA

**Fig. 4** Spin-density iso-surfaces obtained at $U_{\text{eff}} = 1.875$ eV and correspond to the electron spin density of 0.008 electrons per unit cell volume. Light yellow surface corresponds to ‘spin up’ electron density. Light blue surface corresponds to ‘spin down’ electron density. (a) AFM, $c/a < 1$; (b) AFM, $c/a > 1$; (c) FM, $c/a < 1$; (d) FM, $c/a > 1$. The figure was drawn using Vesta code.
Furthermore, we obtained the correct ground state, reproducing the AFM order. The calculated value of U atom magnetic moment is only slightly overestimated. Thus, the value $U_{\text{eff}} = 1.85$ eV suggests sufficiently good description for the UN crystal.

The band structure and the total density of states obtained for $U_{\text{eff}} = 1.85$ eV and with account for SOI are plotted in Fig. 8. Overall both the band structure and the total DOS do not change much with respect to calculations without SOI. The main effect of SOI can be well seen in splitting of two...
UN lattice restrained to a cubic shape. Authors estimated the UN should be also noted. In this study SOI was neglected and obtained within the accuracy in the ligand-field calculations of UO$_2$ (ref. 9 and refs. therein).

Interaction. For instance, this was partly taken into account candidate for such a possible coupling is a configuration states (not taken into account here) may cause their mixing and suppress the tetragonal unit cell distortion predicted in our study. In fact, the experimental cubic structure$^2$ was obtained within the accuracy $c/a - 1 < 2 \times 10^{-4}$. The primary candidate for such a possible coupling is a configuration interaction. For instance, this was partly taken into account in the ligand-field calculations of UO$_2$ (ref. 9 and refs. therein).

Unfortunately, full account of the configuration interaction for solids is hardly possible nowadays. Besides, the barrier between these two states is very small (of the order of a few meV), suggesting easy jumping between these two states, even at very low temperatures. Both mentioned effects should be considered in the future, when such capabilities will be developed.

Lastly, recent attempt$^3$ to perform DFT + $U$ simulations of UN should be also noted. In this study SOI was neglected and UN lattice restrained to a cubic shape. Authors estimated the $U_{	ext{eff}} = 2 \, \text{eV}$ parameter by calculating only the unit cell volume and bulk modulus. In contrast, as the result of SOI consideration in the present simulations, we were able to evaluate the total magnetic moments of U atoms, where the orbital contribution appears to be crucial. Even if SOI would be accounted for in ref. 37, the value $U_{\text{eff}} = 2 \, \text{eV}$ suggested there would produce the total magnetic moment of U atom $\mu_{\text{tot}} = 1.01 \, \mu_{\text{B}}$ (Fig. 6a) which deviates from the experimental total magnetic moment$^3$ ($\mu_{\text{tot}} = 0.75 \, \mu_{\text{B}}$) more than the value $\mu_{\text{tot}} = 0.81 \, \mu_{\text{B}}$ obtained in the present work at $U_{\text{eff}} = 1.85 \, \text{eV}$. Modeling of the tetragonal distortion of the unit cell allowed us to detect the existence of two close energy states and the UN tetragonal instability. Anyway, the obtained values of the optimal Hubbard parameter ($U_{\text{eff}} = 1.85 \, \text{eV}$ here, and $U_{\text{eff}} = 2 \, \text{eV}$ in ref. 37) (accidentally) are surprisingly close. Thus, our present simulations have demonstrated that UN basic properties (the unit cell volume, the U-atom magnetic moments and the correct magnetic order) can be simultaneously reproduced employing the same Hubbard $U$-parameter.

4. Conclusions

We suggested a simple CSR method for detection and elimination of multiple minima in the electronic structure computations, commonly obtained in the DFT + $U$ calculations and show how to achieve the real ground state of a system with relatively little efforts. This technique could be useful for modeling numerous systems containing actinides, lanthanides and transition metals.

We applied this method in a study of the atomic, electronic and low temperature magnetic structure of a promising nuclear fuel—UN. Using Dudarev et al.’s form$^2$ of the DFT + $U$ method for strongly correlated systems, we have demonstrated a close relation between the on-site repulsion between the 5f electrons of U atoms and its magnetic structure. It is shown that only for the parameter $U_{\text{eff}} > 1.80 \, \text{eV}$ the AFM order turns out to be energetically more stable than the FM one, in agreement with low-temperature experiments.

Present simulations have revealed also instability of a UN cubic unit cell with respect to a tetragonal distortion. Surprisingly, the signs of the tetragonal distortion in the ground states have opposite trends in the AFM and the FM states: in the former case the unit cell is compressed but elongated in the latter case. Our simulations show the presence of (at least one) meta-stable states for each magnetic order at $U_{\text{eff}} > 1 \, \text{eV}$ with the energy being very close to that of the ground state. We have shown also that an improper treatment of meta-stable states could result in incorrect physical properties.

It is demonstrated that an incorporation of SOI plays a crucial role in a correct reproduction of the experimentally observed total magnetic moments on U atoms. Moreover, the orbital contributions to the total magnetic moments are shown to be large and having opposite signs to the spin moments.

Both improved descriptions of inter-electron interactions (through the DFT + $U$ method) and spin–orbital interactions were found necessary for achieving good agreement with experiments simultaneously for the magnetic order, magnetic moments and unit cell volume. The best overall agreement is obtained for the Hubbard parameter $U_{\text{eff}} = 1.85 \, \text{eV}$, which we suggest for future GGA + $U$ simulations of UN properties.

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Notes and references


Fig. 8 The band structure and the total DOS (the right panel) in calculations with account for spin–orbit interactions for UN. Zero energy is set at the Fermi energy.

U$_{5f_{xyz}}$ peaks into two components each with the total electron moments $j = 7/2$ and $5/2$.

Our simulations have clearly demonstrated the presence of the two states (for both the AFM and FM orders) with very close total energies (Fig. 1). Thus, a coupling between these states (not taken into account here) may cause their mixing and suppress the tetragonal unit cell distortion predicted in our study. In fact, the experimental cubic structure$^2$ was obtained within the accuracy $c/a - 1 < 2 \times 10^{-4}$. The primary candidate for such a possible coupling is a configuration interaction. For instance, this was partly taken into account in the ligand-field calculations of UO$_2$ (ref. 9 and refs. therein).

Unfortunately, full account of the configuration interaction for solids is hardly possible nowadays. Besides, the barrier between these two states is very small (of the order of a few meV), suggesting easy jumping between these two states, even at very low temperatures. Both mentioned effects should be considered in the future, when such capabilities will be developed.

Lastly, recent attempt$^3$ to perform DFT + $U$ simulations of UN should be also noted. In this study SOI was neglected and UN lattice restrained to a cubic shape. Authors estimated the $U_{\text{eff}} = 2 \, \text{eV}$ parameter by calculating only the unit cell volume and bulk modulus. In contrast, as the result of SOI consideration in the present simulations, we were able to evaluate the total magnetic moments of U atoms, where the orbital contribution appears to be crucial. Even if SOI would be accounted for in ref. 37, the value $U_{\text{eff}} = 2 \, \text{eV}$ suggested there would produce the total magnetic moment of U atom $\mu_{\text{tot}} = 1.01 \, \mu_{\text{B}}$ (Fig. 6a) which deviates from the experimental total magnetic moment$^3$ ($\mu_{\text{tot}} = 0.75 \, \mu_{\text{B}}$) more than the value $\mu_{\text{tot}} = 0.81 \, \mu_{\text{B}}$ obtained in the present work at $U_{\text{eff}} = 1.85 \, \text{eV}$. Modeling of the tetragonal distortion of the unit cell allowed us to detect the existence of two close energy states and the UN tetragonal instability. Anyway, the obtained values of the optimal Hubbard parameter ($U_{\text{eff}} = 1.85 \, \text{eV}$ here, and $U_{\text{eff}} = 2 \, \text{eV}$ in ref. 37) (accidentally) are surprisingly close. Thus, our present simulations have demonstrated that UN basic properties (the unit cell volume, the U-atom magnetic moments and the correct magnetic order) can be simultaneously reproduced employing the same Hubbard $U$-parameter.

4. Conclusions

We suggested a simple CSR method for detection and elimination of multiple minima in the electronic structure computations, commonly obtained in the DFT + $U$ calculations and show how to achieve the real ground state of a system with relatively little efforts. This technique could be useful for modeling numerous systems containing actinides, lanthanides and transition metals.

We applied this method in a study of the atomic, electronic and low temperature magnetic structure of a promising nuclear fuel—UN. Using Dudarev et al.’s form$^2$ of the DFT + $U$ method for strongly correlated systems, we have demonstrated a close relation between the on-site repulsion between the 5f electrons of U atoms and its magnetic structure. It is shown that only for the parameter $U_{\text{eff}} > 1.80 \, \text{eV}$ the AFM order turns out to be energetically more stable than the FM one, in agreement with low-temperature experiments.

Present simulations have revealed also instability of a UN cubic unit cell with respect to a tetragonal distortion. Surprisingly, the signs of the tetragonal distortion in the ground states have opposite trends in the AFM and the FM states: in the former case the unit cell is compressed but elongated in the latter case. Our simulations show the presence of (at least one) meta-stable states for each magnetic order at $U_{\text{eff}} > 1 \, \text{eV}$ with the energy being very close to that of the ground state. We have shown also that an improper treatment of meta-stable states could result in incorrect physical properties.

It is demonstrated that an incorporation of SOI plays a crucial role in a correct reproduction of the experimentally observed total magnetic moments on U atoms. Moreover, the orbital contributions to the total magnetic moments are shown to be large and having opposite signs to the spin moments.

Both improved descriptions of inter-electron interactions (through the DFT + $U$ method) and spin–orbital interactions were found necessary for achieving good agreement with experiments simultaneously for the magnetic order, magnetic moments and unit cell volume. The best overall agreement is obtained for the Hubbard parameter $U_{\text{eff}} = 1.85 \, \text{eV}$, which we suggest for future GGA + $U$ simulations of UN properties.

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Notes and references