Parameterisation of an LSDA+$U$ model for non-collinear magnetic configurations: Multipolar magnetism in UO$_2$

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Unraveling the complexity of non-collinear magnetism in materials with strongly correlated electrons is a considerable task that requires developing and applying state of the art theories and computational methods. Using the Coury model Hamiltonian, which includes spin and orbital degrees of freedom and generalizes the collinear Stoner Hamiltonian, we derive an extension of the collinear LSDA+$U$ approximation to non-collinear magnetic configurations and explore the magnetic ground state of the archetypal spin-orbit correlated oxide UO$_2$. We show that parameterizing a non-collinear LSDA+$U$ model requires only one parameter $U$, as opposed to the difference between the Hubbard and Stoner parameters $U-J$ found in an earlier derivation based on a collinear model Hamiltonian. To find the magnetic ground state of UO$_2$ in the non-collinear configuration space, we combine LSDA+$U$ with a spin adiabatic occupation matrix approach, involving the construction of a magnetic energy surface that follows the adiabatic evolution of the occupation matrix as a function of the spin canting angle. Our results show that the strong spin-orbit coupling (SOC) is the key factor stabilizing the so-called $3k$ spin ordered magnetic ground state of UO$_2$. Using a relativistic atomic Hamiltonian we find that the SOC strength is colossal, 1.45 eV per uranium atom, the largest value ever found in relativistic materials. This unusually strong SOC implies that the spin and orbital degrees of freedom are virtually inseparable. As a result, to derive and quantify spin-spin interactions it is necessary to adopt the pseudospin picture. By constructing an extended effective multipolar pseudospin Hamiltonian, we prove the significance of octupolar and dipole-dipole exchange couplings in establishing the $3k$ magnetic phase, consistent with the non-collinear spin arrangement, and associated with the canted orbital ordering of uranium $f$-orbitals. Importantly, our study reveals that despite the presence of strong spin-lattice interaction in UO$_2$, the cooperative Jahn-Teller instability does not contribute to the onset of the non-collinear $3k$ state, which remains the most favorable ground state even in the undistorted lattice. Finally, we discuss the part played by parameter $U$ in the LSDA+$U$ scheme and provide evidence that the choice of this parameter has a substantial quantitative effect on the predicted properties of the oxide, in particular the magnetic exchange interactions and, perhaps trivially, on the band gap: the value of $U$ computed fully ab initio by the constrained random phase approximation, $U=3.46$ eV, delivers a band gap of 2.11 eV in good agreement with experiment, and a balanced account of the other relevant energy scales.

I. INTRODUCTION

A realistic treatment of magnetic properties by ab initio methods requires using approaches that do not artificially constrain the orientation of magnetic moments to a specific direction. This is achieved by means of the so-called non-collinear density functional theory approximation [1, 2]. In the non-collinear approximation, the direction of local magnetic moments varies from point to point in real space, and the fact that magnetic non-collinearity does indeed occur in real materials is confirmed by direct experimental observations and first principles calculations [3–8]. Non-collinear spin orderings is particularly evident in heavy element compounds where it results from strong spin-orbit coupling effects. Examples include $f$-electron systems [9–11] and $5d$ transition metal oxides [12, 13]. Fluctuations of magnetic non-collinearity is a factor contributing to electrical and thermal resistivity of alloys [14] and may offer a clue to understanding electronic and magnetic phase transitions [15, 16]. It has also been discovered that non-collinear magnetic fluctuations may be responsible for the observed anomalous thermal conductivity of uranium dioxide [17], a material of considerable technological significance. Indeed, while in metallic alloys, magnetic fluctuations represent just one of the types of electronic excitations associated with the electric and thermal resistivity of the material, in a semiconducting oxide like UO$_2$, where thermal conductivity is dominated by the transport of phonons, the strong spin-orbit coupling (SOC) linking atomic displacements with magnetic degrees of freedom provides an additional and potentially significant channel of dissipation. The fact that lattice and magnetic degrees of freedom in uranium dioxide are strongly coupled has been confirmed.

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by observations of piezo-magnetism [18]. The observations were modeled phenomenologically, assuming the occurrence of direct coupling between atomic displacements and magnetic moments. On the electronic structure level, such a coupling stems from the relativistic SOC between the magnetic moments of uranium ions and their orbital degrees of freedom, where the relatively weak but still notable directional character of bonds involving valence \( f \)-orbitals of uranium ions generates inter-atomic forces that depend on the orientation of magnetic moments.

The fundamental difference between a magnetic metal and an actinide oxide like UO\(_2\) is that while the spin-orientation-dependent forces in a metal stem from the coordinate dependence of the Heisenberg exchange [19], in an antiferromagnetic semiconducting actinide oxide the forces result from a combination of Anderson’s superexchange [20, 21], the strong correlations between electrons occupying \( f \)-shells of uranium atoms [22], and the relativistic spin-orbit interaction [23–25] coupling magnetic configurations to forces acting on the nuclei. In what follows, we shall focus on exploring the electronic and magnetic aspects of the problem using a suitably adapted \textit{ab initio} LSDA+\( U \) model.

The subtlety of the problem is associated with the fact that an \textit{ab initio} treatment of directional magnetic degrees of freedom in materials with strongly correlated electrons requires a non-collinear formulation of the electronic structure model, which at the same time must be suitable for the evaluation of the total energy of the electronic system. A LSDA+\( U \) model, often applied to total energy calculations [26], was derived from a collinear model Hamiltonian, similar to the Hamiltonians used earlier by Anisimov et al. [27] and by Kotani and Yamazaki [22]. It can be readily shown that these model Hamiltonians are identical to the Hamiltonian of the collinear Stoner model [28], and hence do not provide a suitable foundation for the treatment of non-collinear magnetism. A LSDA+\( U \) model that can in principle be applied to the treatment of non-collinear magnetism was proposed by Liechtenstein et al. [29]. However the choice of the double counting term, which has the same form as in the collinear case, \textit{cf.} equation (4) of Ref. [29] and equation (3) of Ref. [28], introduces an element of uncertainty in the total energy part of the analysis.

The choice of the LSDA+\( U \) model for the analysis below is stimulated by the extensive application of \textit{ab initio} approaches to the simulation of materials with strongly correlated electrons [30–35]. In what follows, we explore a generalization of the collinear LSDA+\( U \) model [26] to non-collinear magnetic configuration.

The new development has been stimulated and enabled by a recent work by Coury et al. [36], who found a way of transforming, through an exact calculation, the general four-index matrix form of the second-quantized Hamiltonian for interacting electrons, into a simpler form, resembling the Hamiltonian used earlier for the derivation of simplified versions of the LSDA+\( U \) model [26, 27]. The relative simplicity of the Coury Hamiltonian enables performing a more accurate derivation of the LSDA+\( U \) model, suitable for the treatment of non-collinear magnetism in materials with strongly correlated electrons, at the same time providing the means for deriving a double counting term for evaluating the total energy.

Below we apply the method to the investigation of electronic structure and non-collinear magnetism in uranium dioxide. This oxide, despite the fact that it has been studied for several decades [10, 37–44], remains a subject of extensive research as the scope of \textit{ab initio} methods expands to include the treatment of defects [45] and their diffusion [46–48]. It is known that in metals the structure of defects [49] and atomic diffusion [50] are highly sensitive to magnetism. The experimental observation showing the effect of magnetic fluctuations on the thermal conductivity of UO\(_2\) [17] suggests that other high-temperature transport properties may also be affected by the magnetic degrees of freedom.

The magnetic ground state of defect-free UO\(_2\) has been extensively investigated both experimentally and theoretically [10, 37–41, 51]. However, a definitive verdict on the stability of the 3k magnetic ground state structure and the form of a low-energy spin excitation Hamiltonian suitable, for example, for spin-lattice dynamics simulations [19, 52, 53], still remains outstanding. Partly, the difficulty is associated with the fact that an \textit{ab initio} treatment of the oxide requires exploring the complexity of the energy landscape involving multiple local energy minima, which impedes applications of conventional energy minimization algorithms [54]. Also, it is necessary to take into account relativistic effects, giving rise to large SOC [42] and the emergence of multipolar spin interactions. Furthermore, it is necessary to determine the population of uranium \( f \)-orbitals, which result in the formation of orbital magnetic moments on uranium ions that are twice the magnitude of the spin moment [55]. Finally, magnetism is intimately linked to distortions of the underlying crystal structure, manifested in UO\(_2\) via the Jahn-Teller (JT) instabilities [56], and non-collinear spin arrangement in the form of a 3k-ordered magnetic state. In this paper, we address the outstanding issues noted above using a consistent theoretical and methodological framework, aiming to uncover the ultimate quantum origin of the magnetic ground state in UO\(_2\).

An important aspect of application of LSDA+\( U \) models to \textit{ab initio} simulations of materials is the proper choice of values of the Coulomb repulsion and Hund’s coupling parameters \( U \) and \( J \). Owing to the difficulties inherent in evaluating the magnitude of these interactions, these quantities are generally treated as tunable parameters, and are chosen according to how well they reproduce some specific properties such as the band gap, the equilibrium volume, the magnetic moment or the formation energy [57]. In an attempt to improve the predictive capacity of LSDA+\( U \) models, several approaches have been proposed that aim to compute \( U \) and \( J \) without relying on phenomenological considerations [58–61]. Among them, the constrained random phase approxima-
tion (cRPA) allows one to take into account the effect of screening of the Coulomb interaction between correlated electrons and to estimate the magnitude of parameters $U$ and $J$ in the correlated subspace. The cRPA method has been successfully applied to a large variety of systems, and now represents a reliable and computationally viable method of obtaining accurate values of $U$ and $J$ \[62-65\]. In the analysis below, we apply this approach to computing $U$ and $J$ in the correlated $f$ subspace, in this way providing a solid reference for the choice of values of these parameters in actinide compounds, and allowing for a fully \textit{ab initio}-based application of the LSDA+$U$ model. In particular, the possibility to selectively compute $U$ and $J$ enables making an estimate of the role played by $U$ in the parametrization of the LSDA+$U$ model for non-collinear spin systems.

The manuscript is organized as follows. We start from deriving a non-collinear magnetic LSDA+$U$ model, giving equations for the effective correcting one-electron potential and the double counting term, showing that the relevant formulae require only one parameter $U$ as opposed to the difference $U - J$ found in the collinear version of the model. We then use cRPA to compute the value of $U$ and compare the results with the available data. Subsequently, we address the question of stability of the non-collinear $3\text{k}$ magnetic structure and, by using an adiabatic occupation matrix approach, prove that the $3\text{k}$ structure represents the lowest energy configuration of UO$_2$ even in a perfect cubic lattice. Finally, we perform a detailed analysis of effective spin Hamiltonians and spin-spin interactions, concluding with the assessment of potential applications of the proposed methodology to computing high temperature properties, including simulations of atomic and magnetic dynamics.

II. A NON-COLLINEAR LSDA+$U$ MODEL

The existing collinear LSDA+$U$ model, which aims to provide an improved description of the electronic structure of materials characterized by strong electron correlations in spatially localized $d$ and $f$ shells, adds a correction term to the effective single particle electron potential \[26, 27, 29\]

$$V_{ij}^\sigma = \frac{\delta E_{\text{LSDA}+U}}{\delta \rho_{ij}^\sigma} = \frac{\delta E_{\text{LSDA}}}{\delta \rho_{ij}^\sigma} + (U - J) \left[ \frac{1}{2} \delta_{ij} - \rho_{ij}^\sigma \right], \quad (1)$$

and a double counting correction to the total electronic energy \[26\]

$$E_{\text{LSDA}+U}^{dc} = \frac{(U - J)}{2} \sum_{\sigma,j,l} \rho_{jl}^\sigma \rho_{ij}^\sigma. \quad (2)$$

The latter is required to take into account the fact that a simple sum of single particle energies in a system of interacting electrons does not represent the correct contribution to the total energy, see e.g., Eq. (15) and Eq. (16) of Ref. \[66\]. In Eq. (1) and Eq. (2), indexes $j,l$ refer to orbitals associated with a lattice site, and $\sigma$ is the spin index.

Eq. (1) and Eq. (2) were derived from a model tight-binding Hamiltonian \[22, 67\], where the on-site electron interaction terms have the form

$$\hat{H} = \frac{U}{2} \sum_{l,l',\sigma} \hat{n}_{l\sigma} \hat{n}_{l'\sigma} - \frac{(U - J)}{2} \sum_{l,l',\sigma} \hat{n}_{l\sigma} \hat{n}_{l'\sigma}. \quad (3)$$

It can be shown \[28, 36\] that the above Hamiltonian is identical to the Hamiltonian of the collinear Stoner model

$$\hat{H} = \frac{U}{2} \left( \hat{N}^2 - \hat{N} \right) - \frac{J}{4} \left( \hat{N}^2 - 2\hat{N} \right) - \frac{J}{4} \hat{M}^2, \quad (4)$$

where $\hat{N}_\sigma = \sum_l \hat{n}_{l\sigma}$, $\hat{N} = \hat{N}_\uparrow + \hat{N}_\downarrow$ and $\hat{M} = \hat{N}_\uparrow - \hat{N}_\downarrow$. Using the procedure outlined in Ref. \[26\], Eq. (1) and Eq. (2) can be derived by evaluating the expectation values of either Eq. (3) or Eq. (4).

Despite the relative success of the LSDA+$U$ model \[31\], there are two points in the derivation that remain elusive. It is unclear to what extent the approximations associated with Hamiltonian (3) affect the form of Eq. (1) and Eq. (2), and also how to generalize these equations to non-collinear magnetic configurations, significant to applications \[17, 19, 41\]. The brief analysis given below addresses these two points.

First, we note that there is a major term missing in collinear Hamiltonians (3) and (4). This missing term has been identified in Ref. \[36\], and we show below that this term contributes to the LSDA+$U$ correction, changing its form. Second, we note that the correction itself is not invariant in the extended space of spin and orbital indexes, a point that can be readily rectified using a suitable definition of the convolution of the full spin and orbital-dependent electron density matrix.

To derive a non-collinear form of the LSDA+$U$ model, we start by considering a model Hamiltonian, different from and more general than Eq. (3) or Eq. (4), and apply it to the parametrization of the LSDA+$U$ equations, simplifying the full matrix representation of electron interactions. The treatment is based on a recent study by Coury et al. detailed in Ref. \[36\]. We find that application of the same methodology as what was followed in Ref. \[26\], to a more complete Hamiltonian \[36\], results in the LSDA+$U$ equations that require only one parameter $U$ as opposed to the two parameters $U$ and $J$ entering the formula derived in \[26\]. The general functional form of the LSDA+$U$ correction remains the same.

An on-site Hamiltonian, describing interaction between electrons occupying orbitals $i,j,k,l$, is given by a sum of combinations of four creation and annihilation operators multiplied by a four-index matrix $V_{ij,kl}$:

$$\hat{H} = \frac{1}{2} \sum_{i,j,k,l} \sum_{\sigma,\xi} V_{ij,kl} \hat{c}_{i\sigma,j,\xi}^\dagger \hat{c}_{k,\xi} \hat{c}_{l,\sigma}. \quad (5)$$

Matrix $V$ has $(2l+1)^4$ elements, which in the case of $p$ ($l=1$) electrons amounts to $3^4=81$ elements, and $5^4=625$
elements in the case of $d$ electrons. Symmetry constraints show that all the elements of $V_{ij,kl}$ can be parameterized using only two independent constants in the $p$-electron case, three constants in the $d$-electron case, and four in the $f$-electron case. In the $p$-electron cubic harmonic orbital case, using an analogy with the theory of isotropic elasticity [68], where the four-index matrix of elastic constants $C_{ijkl}$ has the same symmetry as $V_{ij,kl}$, Hamiltonian (5) can be written exactly as [36]

$$\hat{H} = \frac{1}{2} \left( U - \frac{J}{2} \right) : \hat{N}^2 : + \frac{J}{4} : \hat{M}^2 : + \frac{J}{2} \sum_{i,j} : (\hat{n}_{ij})^2 : .$$

Here, $\hat{N} = \sum_{m,\sigma} \hat{c}_{m,\sigma}^\dagger \hat{c}_{m,\sigma}$ is the operator of the total number of electrons on a site, $\hat{c}_{kl} = \sum_{\sigma} \hat{c}_{k,\sigma}^\dagger \hat{c}_{l,\sigma}$, and

$$\hat{M} = \sum_{m,\xi,\xi'} \hat{c}_{m,\xi}^\dagger \sigma_{\xi\xi'}^\sigma \hat{c}_{m,\xi'},$$

is the total vector magnetic moment operator associated with the site. In Eq. (6), $\cdot \cdot$ denotes normal ordering of creation and annihilation operators. The normally ordered terms in Eq. (6), expressed using conventional notations, have the form

$$\hat{N}^2 : = \hat{N}^2 - \hat{N},$$

$$\hat{M}^2 : = \hat{M}^2 - 3 \hat{N},$$

$$\hat{N}_{\xi} \equiv \hat{N}_{\xi} : = \sum_{\sigma} \hat{c}_{k,\sigma}^\dagger \hat{c}_{l,\sigma},$$

$$\hat{n}_{kl} : = \sum_{\sigma} \hat{c}_{k,\sigma}^\dagger \hat{c}_{l,\sigma}.$$

The first two terms in Eq. (6) are identical to those entering Eq. (4), with the natural exception that now the magnetic moment operator is a vector quantity. Most significantly, in addition to the terms contained in Eq. (4), Hamiltonian (6) includes an extra third term, required by symmetry and absent in Eq. (4). This term is related to the orbital momentum of electrons on a lattice site [36]. In the collinear approximation, where operator $\hat{M}$ in Eq. (6) is replaced by its projection $\hat{M}_z = \hat{N}_{\uparrow} - \hat{N}_{\downarrow}$ on a quantization axis, and the third term in Eq. (6) is neglected, Hamiltonian (6) is identical to Eq. (4). We note that Hamiltonian (6) is exact in the sense that no procedure of “directional” averaging is involved in the transformation from Eq. (5) to Eq. (6).

We now follow the derivation given in Refs. [26, 27] and deduce the LSDA+$U$ model from Hamiltonian (6). We identify the terms in Hamiltonian (6) that contain two creation and two annihilation operators acting on the same electronic state $(m, \sigma)$. In the mean-field approximation, these terms provide contribution to the total energy proportional to $n_{m,\sigma}^2$ whereas their exact expectation value is proportional to $n_{m,\sigma}$. The LSDA+$U$ model correction equals the difference between the exact and mean-field expectation values of these terms, resulting in

$$E_{\text{LSDA}+U} - E_{\text{LSDA}} = \left[ \frac{1}{2} \left( U - \frac{J}{2} \right) - \frac{J}{4} + \frac{J}{2} \right] \sum_{m,\sigma} (n_{m,\sigma} - n_{m,\sigma}^2).$$

In the above expression, each term in square brackets corresponds to a respective term in Hamiltonian (6), and $n_{m,\sigma}$ is the electron occupation number of an orbital state $m$ with spin index $\sigma$.

We see that the terms in Eq. (8), which contain parameter $J$, cancel each other, and only the term proportional to parameter $U$ remains. The sum of the first two terms in square brackets ($U - J/2)/2 - J/4 = (U - J)/2$ gives the coefficient found in the LSDA+$U$ derivation given earlier [26], which was based on a collinear model Hamiltonian (4). The third term in square brackets in Eq. (8) stems from the last term in Hamiltonian (6), which is missing in the Hamiltonians [22, 67] used earlier. The full cancellation of the terms containing parameter $J$ is perhaps not surprising, given the original form of the Hubbard Hamiltonian (69) that contains no $J$ terms and is still able to generate a variety of magnetic solutions, originating solely from strong on-site electron correlations.

A general form of Eq. (8), invariant with respect to the choice of electronic orbitals and spin quantization axis, is now:

$$E_{\text{LSDA}+U} - E_{\text{LSDA}} = \frac{U}{2} \left[ \text{Tr} \rho - \text{Tr} \rho^2 \right]$$

$$= \frac{U}{2} \left[ \sum_{m,\sigma} \rho_{mm}^{\sigma\sigma} - \sum_{m,\sigma,\sigma'} \rho_{m'm'}^{\sigma\sigma'} \rho_{m'm}^{\sigma'\sigma} \right],$$

where $\rho$ is the full orbital and spin-dependent one-electron density matrix.

In the collinear approximation, where the density matrix is assumed to be diagonal with respect to the subset of its spin indexes $\rho_{m'm'}^{\sigma\sigma'} = \rho_{mm'}^{\sigma\sigma'}$, Eq. (9) is identical to equation (5) of Ref. [26]. In this limit, the only difference between equation (5) of Ref. [26] and Eq. (9) given above is the prefactor that, due to the presence of the third term in Hamiltonian (6), now equals $U/2$ as opposed to $(U - J)/2$ derived from Hamiltonian (3).

An invariant orbital- and spin-dependent non-collinear form of LSDA+$U$ (1) and (2) is now:

$$V_{ij}^{\sigma\sigma'} = \frac{\delta E_{\text{LSDA}+U}}{\delta \rho_{ij}^{\sigma\sigma'}} = \frac{\delta E_{\text{LSDA}}}{\delta \rho_{ij}^{\sigma\sigma'}} + U \left[ \frac{1}{2} \delta_{ij} \delta_{\sigma\sigma'} - \rho_{ij}^{\sigma\sigma'} \right],$$

and

$$E_{\text{LSDA}+U}^{\text{de}} = \frac{U}{2} \sum_{\sigma,\sigma',i,j} \rho_{ij}^{\sigma\sigma'} \rho_{ij}^{\sigma'\sigma'}.$$
convoluting the density matrix over the full set of its orbital and spin indexes, a point that was not addressed in earlier derivations [26, 27, 29].

Similarly to Eq. (8), the terms containing parameter $J$ also cancel exactly if we perform the above derivation for the $d$-electron case [36]. The most direct way of carrying out the derivation is to start from equation (22) of Ref. [36] and note that in the $d$-electron case, all the terms containing parameter $J$ can be expressed in terms of a renormalised parameter $J = 6\Delta J$, resulting in Eq. (9) given above, plus small terms proportional to $\Delta J$, which together amount to a small fraction of an electron-volt per atom and are normally neglected in applications [31]. This suggests that the single-parameter form of the LSDA+$U$ correction given by Eq. (10) and Eq. (11) remains sufficiently accurate and applicable to $d$-electron orbitals, and other types of shells containing correlated electrons. Parameter $U$, according to the analysis given in [30, 62], is an effective quantity, characterizing the strength of electron-electron interactions, modified by effects of many-body self-screening. The significance of the above equations, in addition to the fact that they have been derived from a more accurate form of the on-site interaction Hamiltonian, is in that they can be used for treating non-collinear magnetic configurations.

III. AB INITIO METHODOLOGY

This section details the set of theoretical and methodological approaches adopted in this study. All the calculations were carried out using the Vienna $ab$ initio simulation package (VASP) [70, 71], where the non-collinear extension of the Dudarev et al. LSDA+$U$ scheme is implemented [72] with the full inclusion of relativistic effects (e.g., a full self-consistent treatment of spin-orbit coupling) [7]. A robust energy cut off up to 700 eV with the convergence precision of $10^{-6}$ eV was used in all the calculations, and the Brillouin zone was sampled using a $6\times6\times6$ $k$-point mesh. Atomic positions were optimized with the lattice parameters fixed at its observed value ($a=5.469$ Å) [73]. In what follows, we explore in considerable detail (A) the evaluation of interaction parameters $U$ and $J$ within the cRPA, (B) magnetically constrained density functional theory (DFT), (C) spin adiabatic occupation matrix approach to the calculation of magnetic energy landscape, (D) effective multipolar pseudospin Hamiltonian and exchange coupling, and (E) a strategy for estimating the strength of the SOC.

A. Constrained random phase approximation

Interaction parameters $U$ and $J$ were computed from first principles using the constrained random phase approximation [58]. In the cRPA, the Coulomb repulsion and Hund’s coupling parameters $U$ and $J$ are derived from the matrix elements of $U_{ijkl}$ written in terms of Wannier basis functions representing the correlated subspace (in this case, the uranium $f$ states)

$$U_{ijkl} = \lim_{\omega \to 0} \int d\mathbf{r} d\mathbf{r}' w_i^*(\mathbf{r}) w_j^*(\mathbf{r}') \mathcal{U}(\mathbf{r}, \mathbf{r}', \omega) w_k(\mathbf{r}) w_l(\mathbf{r}')$$

(12)

More precisely, $U$ and $J$ are the average matrix elements $U_{ijkl}$ (intra- and inter-orbital interactions of the different spins) and $U_{ijji}$ (inter-orbital interactions of the same spins), respectively. In Eq. (12), $\mathcal{U}$ is the partially screened interaction kernel, which is calculated by solving the Dyson-like equation

$$\mathcal{U}^{-1} = \mathcal{V}^{-1} - \chi_r$$

(13)

where $\mathcal{V}$ is the bare (unscreened) interaction kernel and $\chi_r = \chi - \chi_r$ is the polarizability, excluding contributions from the “target” correlated $f$ subspace, $\chi_r$. Following this procedure, we have found $U_{\text{cRPA}}=3.46$ eV and $J_{\text{cRPA}}=0.30$ eV, corresponding to the effective interaction parameter $U_{\text{eff}}=3.16$ eV. These values are expectedly smaller than those extracted from experimental estimates, adopted in previous LSDA+$U$ studies of UO$_2$ [74]: $U=4.50$ eV and $J=0.54$ eV, $U_{\text{eff}}=3.96$ eV. In order to verify the role played by the prefactor $U/2$ entering Eq. (9) in the description of magnetic properties of UO$_2$, we have tested four different choices of interaction parameters, namely

1. $U=3.16$ eV (i.e. $U_{\text{eff}}$)
2. $U=3.46$ eV (i.e. $U_{\text{cRPA}}$)
3. $U=3.96$ eV (i.e. ‘Expt.’ $U_{\text{eff}}$)
4. $U=4.50$ eV (i.e. ‘Expt.’ $U$)

![FIG. 1. Schematic plots of the (001)-AFM, 3k (longitudinal) and (110)-AFM non-collinear spin configurations considered in this study.](image)

B. Magnetically constrained non-collinear DFT+$U$

To determine the non-collinear magnetic ground state of UO$_2$, we have minimized the total energy, treating it as a function of the direction of spin moments and using the magnetically constrained non-collinear DFT+$U$ [7, 13, 75]. In particular, we have inspected spin rotations that transform the system from a characteristic
non-collinear $3\mathbf{k}$ state into collinear antiferromagnetically (AFM) ordered (001) and (110) configurations [41], illustrated in Fig. 1. A non-collinear $3\mathbf{k}$ phase is described by three independent wave vectors and can be represented by a combination of three different phases, one longitudinal and two equivalent transverse. To facilitate the construction of the canted magnetic energy landscape, we used the longitudinal $3\mathbf{k}$ ordered magnetic structure shown in Fig. 1 as a starting configuration. The two other ordered AFM configurations, (001) and (110), belong to the $1\mathbf{k}$ (one wave-vector) and $2\mathbf{k}$ (two wave-vectors) categories, respectively.

The (001)–3$\mathbf{k}$–(110) magnetic structure transformation pathway can be defined by a concerted variation of angle $\theta$ on the four inequivalent uranium sites in a UO$_2$ magnetic unit cell [see Fig. 2(a) and (c)]. Constrained energy minimization as a function of $\theta$ along the transformation pathway is achieved by considering the energy penalty arising from constraining the direction of the spin magnetic moment, defined by the formula

$$E = E_0(\{M_i\}) + \sum_i \gamma_i |M_i - M_i^0|^2 \cdot M_i|.$$  \hspace{1cm} (14)

Here $E_0$ is the unconstrained DFT total energy, whereas the second term is a penalty contribution defined as a non-collinear directional constraint on the direction of local moments $M_i$ with respect to an arbitrary set of unit vectors $M_i^0$ on sites $i$. $M_i$ is the magnetic moment computed by integrating over a Wigner-Seitz cell centered on atom $i$ (the effective Wigner-Seitz radius is 1.588 Å for a U ion and 0.82 Å for an O ion). Parameter $\gamma$ defines the magnitude of the energy penalty term, where by progressively increasing $\gamma$, functional (14) is driven to convergence towards the DFT total energy [75]. We used the value $\gamma=10$ that guarantees that the expectation value of the energy penalty term is lower than $10^{-5}$ eV.

C. Adiabatic spin occupation matrix approach

A known drawback of DFT+$U$ approaches is the difficulty associated with finding the lowest energy state of a strongly correlated magnetic material. In most cases a DFT+$U$ functional exhibits a multitude of local minima corresponding to a variety of spin and orbital occupations in the correlated electronic subspace [41, 76–78]. The difficulty with finding a global minimum stems from the curvature of the energy surface as a function of orbital occupations [77]. In standard DFT calculations the energy surface is typically convex, but the global minimum might correspond to a physically unreasonable partial fractional orbital occupation, e.g. a metallic state of the material that in reality is an insulator. DFT+$U$ corrects this by adding a term that penalizes fractional occupations, but this correction changes the curvature of the energy surface from convex to concave, unavoidably giving rise to many local minima [77]. Dorado and coworkers proposed to address this point by performing a search involving a large number of self-consistent calculations, each starting from different initial occupation matrices, and to select the outcome corresponding to the lowest total energy [76]. This procedure can be accelerated by adiabatically “turning on” the value of parameter $U$ starting from the DFT limit $U=0$ and gradually converging to the true ground state with integral orbital occupations [77]. The above issue is particularly pertinent to non-collinear spin systems, where small rotations of spin moments could give rise to many local minima, all lying in a few meV energy range.

Bearing in mind this aspect of energy minimization, we have combined the occupation matrix approach with a gradual adiabatic change of the spin moment direction, using the magnetically constrained non-collinear DFT+$U$ functional described in the previous subsection [7, 13, 75]. Starting from the 3$\mathbf{k}$-type non-collinear spin ordered state of UO$_2$ [10, 41] shown in Fig. 2(a), we gradually change the canting angle $\theta$, moving adiabatically from the non-collinear 3$\mathbf{k}$ state to the energetically comparable AFM collinearly ordered (001) and (110) configurations shown in Fig. 2(c). At each cant-
ing step, we initialize the occupation matrix to the one obtained at the preceding step and perform a fully self-consistent calculation. In this way, by gradually perturbing the wave function of the $3\mathbf{k}$ state, we are able to construct a smooth total energy curve $E(\theta)$ as a function of the canting angle $\theta$, shown in Fig. 2(c). The absence of cups and sudden jumps guarantees that this energy curve represents the lowest energy path linking the spin configurations considered here, and also that the $3\mathbf{k}$ state is indeed the global minimum with respect to spin rotations. Probing other spin configurations (not shown here) confirmed this analysis and did result in finding spin configurations with lower total energies. We note that the orbital moment $\mathbf{m}_o$ remains anti-parallel to the spin moment everywhere on the transformation pathway, and the magnitudes of both moments are almost independent of the canting angle: $m_s \approx 1.5 \mu_B$ and $m_o \approx 3.2 \mu_B$ [see Fig. 2(b) and (c)].

D. Effective pseudospin Hamiltonian and exchange interactions

To characterize magnetic properties of a material and to understand the origin of the specific spin ordered configuration that it adopts, it is necessary to quantify the dominant spin-spin interactions. For systems conserving the total spin moment, magnetic coupling parameters can be analyzed in terms of an effective Heisenberg spin Hamiltonian involving conventional spin operators. In materials with strong spin-orbit coupling, the spin moments alone are not conserved and it is more appropriate to use the pseudospin operators and pseudospin Hamiltonian [79] suitable for the treatment of multipolar interactions [80–82].

In the pseudospin picture, spin and orbital degrees of freedom are not independent, and the operator set is formed by a unit multipole (tensor) operators $T_{K_i}^{Q_j}(J)$ [25, 83, 84] (here $J$ is the angular moment, $K$ the rank and $Q = -K, \ldots, K$). In a general form, a multipolar exchange Hamiltonian can be written as [25, 84]

$$H = \sum_{i,j} \sum_{KQ} C_{K_i,K_j}^{Q_iQ_j} T_{K_i}^{Q_i} T_{K_j}^{Q_j},$$  \hspace{1cm} (15)$$

where $i,j$ are the site indexes, and $C_{K_i,K_j}^{Q_iQ_j}$ are the coupling constants describing how the energy of the system changes as a result of variation of the two multipole moments $T_{K_i}^{Q_i}$ and $T_{K_j}^{Q_j}$.

$\text{UO}_2$ adopts a non-collinear $3\mathbf{k}$-ordered magnetic configuration, and the two-electrons ($f^2$) ground state of a uranium ion is a $\Gamma_5$ triplet, corresponding to the effective spin (pseudospin) $\tilde{S} = 1$ [23]. The $\Gamma_5$ ground state is associated with cooperative quadrupolar interactions that cannot be accounted for by using a $S = 1/2$ Heisenberg model [11, 23, 25, 51, 85], but can be modeled by means of a suitable pseudospin Hamiltonian.

To compute the spin-spin interactions in $\text{UO}_2$, we adopt the multipolar spin Hamiltonian derived by Mironov et al. [23], describing superexchange interactions between neighboring $U^{4+}$ ions in the $5f^2$ configuration. The general form of the Mironov exchange Hamiltonian reads

$$H = A_0 + H_1 + H_2 + H_3 + H_4,$$

where $A_0$ is a spin-independent parameter, whereas the remaining terms accounts for various types of spin interactions, which can be written using the conventional spin variables as

$$H_1 = D[(S_A^x)^2 + (S_B^x)] + E[(S_A^y)^2 + (S_B^y)^2 - (S_B^y)^2]$$

$$H_2 = J x S_A^x S_B^x + J y S_A^y S_B^y + J z S_A^z S_B^z ,$$

$$H_3 = j_1 S_A^z S_B^z [ (S_A^x)^2 + (S_B^x)^2 ] + 2j_2 S_A^y S_B^y S_A^z S_B^z + j_2 S_A^z S_B^z [ (S_A^x)^2 + (S_B^x)^2 ] + 2j_2 S_A^z S_B^z S_A^z S_B^z$$

$$H_4 = q_1 O_A^{(1)} O_B^{(1)} + q_2 O_A^{(2)} O_B^{(2)} + q_3 O_A^{(3)} O_B^{(3)}$$

$$+ q_4 [O_A^{(1)} O_B^{(2)} + O_A^{(2)} O_B^{(1)}].$$

Here, $H_1$ is a single-spin term, quadratic in the spin components and accounting for the zero field splitting (ZFS) dipolar interactions; the ZFS parameters $D$ and $E$ describe the axial and transversal components of magnetic dipole-dipole (DD) interaction, respectively. $H_2$ is bilinear in spins (and isotropic under rotations) and describes spin exchange interactions (sometimes called the Heisenberg exchange), parameterized by $J_x$, $J_y$ and $J_z$. The term $H_3$ describes four-spin exchange interactions with $j$ as the corresponding coupling constant. Finally, $H_4$ accounts for biquadratic quadrupole-quadrupole (QQ) interactions, where $O_A^{(n)}$ and $O_B^{(n)}$ are the components of the
quadrupole operator, specifically:

\[
O^{(3)} = (S^z)^2 - S(S + 1)/3 \\
O^{(2)}_k = (S^x_k)^2 - (S^y_k)^2 \\
O^{(3)}_k = S^z_k S^x_k + S^y_k S^y_k,
\]

where \( k = A, B \). Labels A and B refer to the interacting nearest neighbour uranium ions, see Fig. 3 for details. There are four inequivalent sites in a magnetic unit cell of UO\(_2\) [U1–U4, see Fig. 2(a)] producing six inequivalent nearest neighbor AB pairs: A=U1, B=U2; A=U1, B=U3; A=U1, B=U4; A=U2, B=U3; A=U2, B=U4; A=U3, B=U4. \( S_A \) and \( S_B \) are the two spins forming a distinct inequivalent AB pair, and \( x, y, \) and \( z \) are the local quantization axes illustrated in Fig. 3. Cartesian components of spins \( S_A \) and \( S_B \) in the local quantization axis representation are given in the Supplementary Material [86].

A fully \textit{ab initio} evaluation of the above superexchange parameters is a difficult task [24, 25]. We also note that depending on the specific definition of tensor operators, slightly different forms of superexchange coupling can be found in literature [11, 23, 25, 85], impeding an accurate quantitative comparison with existing data.

In formulating the effective pseudospin Hamiltonian we followed the procedure by Mironov [23]. To estimate the magnitude of effective magnetic interactions, Mironov \textit{et al.} used a second-order perturbation approach, using free-ion and cubic crystal-field parameters and limiting the interaction to the two nearest-neighbor U atoms only. In our analysis, we estimate the dominant exchange couplings by means of a controlled fitting procedure, involving the mapping of \( \Delta E(\theta) \) onto DFT+U+SOC total energies using Eq. (16). To achieve this, we have rewritten the four terms entering Eq. (16) as functions of the canting angle \( \theta \), replacing components of spins by their explicit expressions in terms of local Cartesian components and arriving at the total magnetic energy expressed as a function of \( \theta \). After some algebra, we find that \( \Delta E(\theta) \) has the form

\[
\Delta E(\theta) = B_0 + B_1 \cos(\theta) + B_2 \cos(2\theta) + B_3 \cos(3\theta) + B_4 \cos(4\theta) + C_1 \sin(\theta) + C_2 \sin(2\theta) + C_4 \sin(4\theta),
\]

where the coefficients are given in terms of the eleven superexchange parameters entering the Mironov Hamiltonian \((D, E, J_x, J_y, J_z, j_1, j_2, q_1, q_2, q_3, \) and \( q_4 \)):

\[
B_0 = 6D + 3/2J_x + 3/2J_y + 3J_z + 3j_1 + 3j_2 \\
B_1 = + 3q_1 + 3/2q_2 + 3q_4 - 4q_1 S + (4D - 2E) \\
B_2 = - 2j_1 - 2j_2 - 3/2J_x - 5/2J_y + 2J_z \\
B_3 = + 4/3q_1 - 4q_2 - 4q_4 + 1/24(11q_1 + 42q_2 + 33q_3 + 4q_4 \\
B_4 = - 42j_1 - 42j_2)S^4
\]

\[
B_1 = (4D + 2J_x + 2j_1 + 2j_2 + 4q_1 + 2q_4)S \\
B_2 = - 4/3q_1 S^2 - (j_1 + j_2 - 5/3q_1 + 3q_4)S^3 \\
B_3 = (j_1 + j_2 + q_1 + 3q_4)S^3 \\
B_4 = 1/8(6j_1 + 6j_2 + 3q_1 - 6q_2 + 9q_3 + 4q_4)S^4
\]

\[
C_1 = (4D + 2j_1 + 2j_2 + 2j_3 + 4q_1 + 2q_4)x\sqrt{2}S \\
C_2 = (-4E + J_x - J_y - 2q_4)\sqrt{2}S^2 \\
C_3 = + 4\sqrt{2}/3q_4S^3 + \sqrt{2}/3q_4S^4 \\
C_4 = \sqrt{2}/2q_4S^4.
\]

\[E. \text{ Calculation of the spin-orbit coupling strength}
\]

We conclude the methodological section with an estimate of the strength of SOC in UO\(_2\). To produce this estimate, we relate the relativistic total energies obtained from first principles calculations to the relativistic atomic Hamiltonian for \( f \) orbitals:

\[
H_{SOC} = \lambda \mathbf{L} \cdot \mathbf{S},
\]

where \( \lambda \) defines the SOC strength. By using the 14 \( f \) \((l = 3)\) spinors as a basis in the following order: \( |x y z, \uparrow \rangle, |x(5x^2 - 3y^2), \uparrow \rangle, |y(5y^2 - 3x^2), \uparrow \rangle, |z(5z^2 - 3x^2), \uparrow \rangle, |x(y^2 - z^2), \uparrow \rangle, |y(x^2 - z^2), \uparrow \rangle, |z(x^2 - y^2), \uparrow \rangle \) (and the corresponding \( \uparrow \rightarrow \downarrow \) spinors), the atomic Hamiltonian \( H_{SOC} \) can be written as a \((14 \times 14)\) matrix, see Eq. (34) below [87].

The diagonalization of matrix (34) yields the following eigenvalues \(-\lambda, -\lambda, -\lambda, -\lambda, -\lambda, \lambda, 3\lambda/4, 3\lambda/4, 3\lambda/4, 3\lambda/4, 3\lambda/4, 3\lambda/4, 3\lambda/4, 3\lambda/4\). From the eigenvalues of the SOC Hamiltonian, it is possible to extract the contribution to the total energy from the SOC effects, \( \Delta E_{soc} \), by considering either the SOC-induced splitting (\( \frac{\lambda}{4} \)) or the energy contribution arising from the occupied states. We have followed the latter route, as in this case a suitable mapping can be constructed between the atomic limit \((H_{SOC})\) and realistic \textit{ab initio} calculations. Specifically, considering that U\(^{4+}\) ions in UO\(_2\) are in the \( 5f^2 \) electronic configuration, the two electrons occupy the lowest two eigenvalues \((-\lambda)\) resulting
in $\Delta E_{\text{soc}} = -2\lambda$. An estimate of $\Delta E_{\text{soc}}$ can be obtained from the DFT total energy difference between a relativistic (with SOC) and a non-relativistic calculation (no SOC), i.e., $\Delta E_{\text{soc}} = E_{\text{SOC}} - E_{\text{noSOC}}$. To exclude the spurious energy contributions arising from differences in the electronic ground states (insulating vs. metallic), this estimate was obtained using $U = 0$ and the $3k$ spin ordered configuration. In this limit $U=0$, both reference states (with and without SOC) are metallic. On the other hand, a DFT+$U$+SOC calculation delivers an insulating solution, where DFT+$U$ (without SOC) stabilizes an insulating ground state: this would include terms other than SOC to the energy balance affecting a proper valuation of the SOC energy. Using the above approach, we find that $\Delta E_{\text{soc}} = -2.90$ eV per uranium ion, corresponding to $\lambda = -\Delta E_{\text{soc}}/2 = 1.45$ eV. We should mention that in the metallic solution, the values of spin and orbital moments are greatly reduced with respect to those found in the DFT+$U$+SOC ground state (referred to in Table 1), specifically $m_s \approx 1 \mu_B$ and $m_o \approx 1.5 \mu_B$. 

Further support for this large value of $\lambda$ comes from an approximate scaling of the magnitude of SOC at atomic level, where it is known that the SOC parameter $\lambda$ is proportional to $Z^4$, where $Z$ is the atomic number. By rescaling the SOC strength of iridium (0.5 eV) [88] with the relative nuclear charge of Ir ($Z_{\text{Ir}}$) and U ($Z_{\text{U}}$) we find

$$\lambda_U \approx \lambda_{\text{Ir}}(Z_U/Z_{\text{Ir}})^4 = 0.5 \text{ eV} \times (92/77)^4 = 1.02 \text{ eV},$$
confirming the very large expected value of the SOC parameter in uranium dioxide.

### IV. RESULTS AND DISCUSSION

The large SOC in UO$_2$ is responsible for the formation of a $\Gamma_5$ triplet described by an effective pseudospin $S = 1$ [23] state, where the spin and orbital moments are ordered in a $3k$ magnetic structure [10, 89], see Fig. 2(a) and (b). Moreover, the various types of (multipolar) superexchange interactions acting in the $3k$ magnetic configuration are coupled with the cooperative Jahn-Teller (JT) effect, manifested by a distortion of the oxygen cage around the U$^{4+}$ ions [11, 18, 38, 84]. The computational verification of these experimental observations and their interpretation on a quantum level is a difficult task due to a variety of factors: (i) magnetic non-collinearity, (ii) self-interaction acting in the U-$f$ manifold, and (iii) existence of multiple local minima in a narrow energy interval [40, 41, 76]. As was noted above, a combination of fully relativistic and magnetically constrained DFT+$U$ with the adiabatic evolution of the occupation matrix is able to predict the ground state of UO$_2$ [Fig. 2(c)] and should help decipher the subtleties of electronic and magnetic effects in UO$_2$.

To gain insight into the nature of magnetic interactions, we compute the magnetic energy curves similar to the one shown in Fig. 2, but this time performing the calculations for several different values of parameter $U$ used in the DFT+$U$ formalism. The curves shown in Fig. 4 suggest that the non-collinear $3k$ ordering remains the lowest energy state for any value of $U$, but the energy difference between the $3k$ phase and the competing AFM collinear phases (001) and (110), illustrated in Fig. 1, depends sensitively on the choice of $U$. As the value of parameter $U$ increases, the relative stability of the $3k$ state decreases, and it becomes progressively less energetically costly to rotate the spins. This implies that the value of the magnetic exchange interactions is also sensitive to the choice of $U$. We shall discuss this later in the section.

The role of parameter $U$ is also reflected in the fundamental electronic and magnetic properties of the $3k$ ground state. Table 1 gives values of the spin moment
and Supplemental Material [86]). This unequivocally demonstrates that the JT effect is not the mechanism that drives the system towards the $3k$ ground state [94]. On the other hand, rescaling the SOC strength to half the original value ($\lambda = 0.75$ eV) causes a huge energy change, favorable for both the $\langle 001 \rangle$-AFM and $\langle 110 \rangle$-AFM configurations, where the latter as a result of halving the SOC value becomes the most favorable one by more than 11 meV/f.u. This provides a clear indication that SOC is the major driving force responsible for the stabilization of the $3k$ state; reducing the SOC strength leads to the over-stabilization of collinear magnetic structures.

TABLE II. Relative energies (in meV/f.u.) of the $\langle 001 \rangle$-AFM and $\langle 110 \rangle$-AFM with respect to $3k$ phases as a function of the Jahn-Teller distortion ($\delta_{JT}$, Å) and the strength of SOC, rescaled to a half of the self-consistent value $\lambda = 1.45$ eV. The phases with $\delta_{JT} = 0$ and $\delta_{JT} = 0.003$ are almost degenerate in energy within $10^{-5}$ eV/f.u., whereas the experimental structure ($\delta_{JT} = 0.014$) is $0.84$ meV/f.u. less stable than the self-consistently optimized one (see Supplemental Material [86]). All the data given in the table were computed for $U=3.46$ eV.

| $\delta_{JT}$ | $E_{\langle 001 \rangle}$-AFM - $E_{3k}$ | $E_{\langle 110 \rangle}$-AFM - $E_{3k}$ |
|--------------|---------------------------------|----------------------------------|
| $\delta_{JT} = 0$ | 3.86                           | 1.01                             |
| $\delta_{JT} = 0.003$ | 3.87                           | 1.03                             |
| $\delta_{JT} = 0.014$ | 3.88                           | 0.94                             |

To discern how SOC stabilizes the $3k$ ordering of moments, we have explored the differences between electronic and magnetic properties of these three phases. Surprisingly, there are only marginal changes in the magnitude of spin and orbital moments (see Table III), in the band structure (see Fig. 5), as well as in the occupation...
All the values were computed assuming \( U = 3.46 \) eV.

| Configuration | (001)-AFM | (110)-AFM | 3k |
|---------------|-----------|-----------|----|
| \( m_\sigma \) | -1.55 | -1.51 | -1.53 |
| \( m_\sigma \) | 3.26 | 3.24 | 3.19 |
| \( m_t \) | 1.70 | 1.73 | 1.66 |

The results show that the 3k configuration is the only spin arrangement exhibiting a visible orbital anisotropy at the uranium sites, associated with the canting ordering of \( f \) orbitals. The \( f \)-orbitals are rotated towards the nearest oxygen sites, following the same chessboard configuration of the 3k spin ordering as that shown in Fig. 2(a) and (b). Remarkably, the effect of SOC, critical to the stabilization of the 3k phase, is manifested primarily in the shape of \( f \)-orbitals rather than in the total orbital occupation, as illustrated in Table IV.

The exchange parameters in Mironov’s model fall into four different categories, namely (i) single-spin parameters \( D \) and \( E \), (ii) bilinear parameters \( J_x, J_y \) and \( J_z \), (iii) parameters describing the four-spin terms \( J_1 \) and \( J_2 \) and (iv) parameters of biquadratic interactions \( q_1, q_2, q_3 \) and \( q_4 \). The accuracy of Mironov’s approach can be improved by noting that, according to the calculations by Savrasov and coworkers, the strength of quadrupolar (QQ) interactions computed by Mironov is underestimated by about 50%.

To better understand the significance of this change in the topology of band structure, in Fig. 6 we plot charge-density isosurfaces for the occupied \( f \) orbitals in the energy interval (-2, 0) eV, projected onto a (110) plane containing both uranium and oxygen ions. The results show that the 3k configuration is the only spin arrangement exhibiting a visible orbital anisotropy at the uranium sites, associated with the canting ordering of \( f \) orbitals. The \( f \)-orbitals are rotated towards the nearest oxygen sites, following the same chessboard configuration of the 3k spin ordering as that shown in Fig. 2(a) and (b). Remarkably, the effect of SOC, critical to the stabilization of the 3k phase, is manifested primarily in the shape of \( f \)-orbitals rather than in the total orbital occupation, as illustrated in Table IV.

To handle this complication, we rely on the analysis by Mironov et al. [23] that can be summarized as follows. First, we note that using the values of parameters evaluated by Mironov (collected in Table V) in the pseudospin Hamiltonian, already leads to an overall fairly good account of the first principles magnetic energy, as illustrated graphically in Fig. 7. Even though the two curves do not match well, Mironov’s parameters predict the correct position of the energy minimum, located at the 3k position, suggesting that all the relevant magnetic coupling terms are correctly included in the theoretical treatment. However, Mironov’s parameters deliver a curve that varies over a significantly narrower energy interval than the curve derived from the first principles data, and as a result the relative stability of the 3k state with respect to the collinear 1k and 2k states is underestimated by about 50%.

The exchange parameters in Mironov’s model fall into four different categories, namely (i) single-spin parameters \( D \) and \( E \), (ii) bilinear parameters \( J_x, J_y \) and \( J_z \), (iii) parameters describing the four-spin terms \( J_1 \) and \( J_2 \) and (iv) parameters of biquadratic interactions \( q_1, q_2, q_3 \) and \( q_4 \). The accuracy of Mironov’s approach can be improved by noting that, according to the calculations by Savrasov and coworkers, the strength of quadrupolar (QQ) interactions computed by Mironov is underestimated by an order of magnitude [25]. Following this argument, we have fitted \( \Delta E(\theta) \) by varying the two largest quadrupolar terms \( (q_1, q_2) \) only, and keeping all the other superexchange parameters fixed to the original Mironov’s values.
FIG. 6. Charge densities of UO$_2$ in a (110) plane computed for the ⟨001⟩-AFM, 3k and ⟨110⟩-AFM spin ordered configurations. All the three plots were computed assuming that $U=3.46$ eV.

The resulting curve is in excellent agreement with first principles energies ($\chi^2_R=0.9989$, see Fig. 7), and this improvement is associated with a very large increase of the magnitude of the quadrupolar terms, approximately by an order of magnitude $(q_1+q_2)/2=4.56$ meV, see Table V. However, this is in very good agreement with the earlier DFT+$U$ data (3.1 meV [25]) and the values extracted from experimental spin-wave spectra (1.9 meV) [51]. As expected, the values of $q_1$ and $q_2$ are sensitive to the choice of parameter $U$, see Table VI. The strength of the QQ interaction increases as a function of $U$, this in particular applies to the the anisotropic biquadratic interaction $q_2$. Nevertheless, the resulting values do not depend on the Jahn-Teller distortions; using the undistorted cubic phase one obtains essentially the the same values of parameters, further demonstrating the fairly negligible role played by the JT effect in stabilizing the 3k non-collinear state.

We conclude the discussion of magnetic properties of UO$_2$ by analyzing the individual contributions of various types of superexchange mechanisms to the stabilization of the 3k state. As was noted in the section on computational methods, the total magnetic Hamiltonian is expressed as a sum of four terms, each corresponding to a specific type of superexchange interaction: $H_1$ accounts for the DD interaction [Eq. (17)], $H_2$ describes the bilinear exchange [Eq. (18)], $H_3$ represents the four-spin exchange [Eq. (19)], and finally $H_4$ takes care of the quadrupolar coupling [Eq. (20)]. The data, summarized in Fig. 8, clearly show that the formation of the 3k state occurs as a result of a concerted action of the DD and octupolar interactions. The contributions of bilinear exchanges ($H_2$, $J's$) and four spin exchanges ($H_3$, $J's$) are essentially independent of the canting angle, resulting in the rather flat curves. On the other hand, the DD interactions have a quadratic-like trend with a marked minimum at 3k and the fit-corrected quadrupolar term (the right panel of Fig. 8) is not only minimum at 3k, but also correctly describes the energy pathway from the 3k to the 1k and 2k states, following the trend exhibited by the first principles energies (see Fig. 7).

Based on the above results, we can conclude that the onset of the 3k state in UO$_2$ is driven, at the quantum level, by a concerted action of the DD and QQ spin interactions. These interactions are active in the undistorted and JT-distorted crystal lattices, clearly indicating that, despite the existing coupling between the spin and lattice degrees of freedom, the JT instabilities do not contribute to the formation of the non-collinear 3k ordered magnetic state, which is present also in the undistorted cubic phase.

FIG. 7. Comparison between the calculated (DFT+$U$+RPA+SOC) and fitted (out fit using Mironov’s parameters) magnetic canting energies $\Delta E(\theta)$. In our fit we employed an extension of the Mironov model to all the U-U interactions and optimized the fit with respect to the dominant quadrupolar terms $q_1$ and $q_2$, by keeping all the other terms fixed to the corresponding values obtained by Mironov [23] (see Table V).
TABLE V. Magnetic coupling parameters (meV) estimated by Mironov [23] shown together with the fitted values of the dominant QQ terms obtained by mapping the DFT+U\textsuperscript{cRPA}+SOC energies onto the extended Mironov’s Hamiltonian. $\chi_{R}^{2}$ serves as an indication of the quality of the fit in terms of the reduced chi-squared test.

| $U$ (eV) | $D$ | $E$ | $J_{s}$ | $J_{q}$ | $J_{0}$ | $j_{1}$ | $j_{2}$ | $q_{1}$ | $q_{2}$ | $q_{3}$ | $q_{4}$ | $\chi_{R}^{2}$ |
|---------|-----|-----|---------|---------|---------|--------|--------|--------|--------|--------|--------|--------|
| Mironov [23] | -0.57 | 0.64 | 1.82 | 2.74 | 2.33 | -0.04 | 0.05 | 0.22 | 0.32 | 0.07 | -0.02 | 7.18 |
| Fit (QQ) | 6.55 | 0.36 | 3.46 | 4.56 | 5.71 | 7.18 | 1.94 | 0.07 | 0.68 | 1.54 | 2.33 | 0.9989 |

TABLE VI. Fitted quadrupolar parameters $q_{1}$ and $q_{2}$ (and their average, in meV) as a function of $U$.

| $U$ (eV) | $q_{1}$ (meV) | $q_{2}$ (meV) | $(q_{1}+q_{2})/2$ (meV) |
|---------|---------------|---------------|-------------------------|
| 3.16 eV | 6.55          | 0.36          | 3.46                    |
| 3.46 eV | 7.18          | 1.94          | 4.56                    |
| 3.96 eV | 7.64          | 3.77          | 5.71                    |
| 4.50 eV | 7.81          | 5.19          | 6.50                    |

FIG. 8. Decomposition of the magnetic energy $\Delta E(\theta)$ into four components $H_{1}$ [DD interaction, $D$ & $E$, Eq. (17)], $H_{2}$ [bilinear exchange, $J$’s, Eq. (17)], $H_{3}$ [four-spin exchange, $j$’s, Eq. (19)], and $H_{4}$ [quadrupolar, $q$’s, Eq. (20)]. The right panel shows the difference between the quadrupolar term derived directly from Mironov’s data and our fitted curve.

V. SUMMARY AND CONCLUSIONS

In conclusion, in this study we have addressed the issue of parametrization of the LSDA+$U$ approximation for non-collinear spin systems and explained the origin of the canted 3$k$ state in UO$_{2}$ by combining an array of advanced computational techniques including the constrained random phase approximation to compute the Coulomb repulsion parameter $U$ and the Hund’s coupling parameter $J$, thus rendering the LSDA+$U$+SOC fully \textit{ab initio}, magnetic constraints to study the dependence of the total energy on the direction of the spin moment, adiabatic propagation of the occupation matrix to avoid the multiple minima problem in constructing the accurate magnetic energy landscape, and two different effective Hamiltonians to extract from the \textit{ab initio} data the value of the spin-orbit interaction $\lambda$ (achieved using an atomic-like relativistic Hamiltonian for $f$ orbitals) and the quadrupole-quadrupole exchange interactions (using an effective pseudospin Hamiltonian).

The outcome of our study is threefold. First, we have derived an invariant orbital- and spin-dependent formalism for the LSDA+$U$ model for non-collinear spins that involves a spin and orbital convolution of the density matrix, and have shown that, unlike in collinear LSDA+$U$, the non-collinear LSDA+$U$ potential and double counting correction depend on one parameter $U$ only, and is independent on Hund’s coupling parameter $J$. Second, our data suggest that the spin-orbit interaction parameter in UO$_{2}$ is as large as 1.45 eV, which is among the largest SOC strengths ever observed in a bulk material, and this represents the origin of many exotic physical phenomena emerging from the unusually intricate interplay between the spin, charge and orbital degrees of freedom, explicated by the formation of a multipolar magnetic state associated with tilted orbital ordering in the $f$-orbital manifold. Finally, we have uncovered the role of dipole-dipole and quadrupole-quadrupole spin interactions in the formation of the non-collinear 3$k$ state and ruled out Jahn-Teller distortions as a factor in stabilizing the 3$k$ magnetic ordering. The most relevant energy scales defining the properties of UO$_{2}$ are summarized in Table VII.

Besides elucidating the complexity of exotic physical scenarios, these results provide a solid reference for future studies of relativistic non-collinear materials (in particular 5$d$ transition metal oxides), and open the way to a quantitatively reliable exploration of technologically relevant aspects of UO$_{2}$ such as spin and orbital magnetic dynamics, formation and evolution of structural defects and their diffusion, which is a topic of significant importance to applications. From this perspective, the study represents an example on how an accurate account of fundamental microscopic interactions derived from a direct application of laws of quantum mechanics can provide an accurate quantitative account of a number of physical processes and extract values of critical parameters (see Table VII) that can then be used as input for phenomenological schemes describing macroscopic phenomena such as transport and dissipation.
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