Quadrupolar Superexchange Interactions, Multipolar Order and Magnetic Phase Transition in UO₂

Leonid V. Pourovskii1,2 and Sergii Khmelevskyi3

1CPHT, Ecole Polytechnique, CNRS, Université Paris-Saclay, Route de Saclay, 91128 Palaiseau, France
2Collège de France, 11 place Marcelin Berthelot, 75005 Paris, France
3Center for Computational Materials Science, IAP, Vienna University of Technology, Vienna, Austria

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The origin of non-collinear magnetic order in UO₂ is studied by an ab initio dynamical-mean-field-theory framework in conjunction with a linear-response approach for evaluating inter-site superexchange interactions between U 5f² shells. The calculated quadrupole-quadrupole superexchange interactions are found to unambiguously resolve the frustration of face-centered-cubic U sublattice toward stabilization of the experimentally observed non-collinear 3k-magnetic order. Therefore, the exotic 3k antiferromagnetic order in UO₂ is fully accounted for by a purely electronic exchange mechanism acting in the undistorted cubic lattice structure. The quadrupolar short-range order above magnetic ordering temperature T_N is found to qualitatively differ from the long-range order below T_N.

The magnetic structure of UO₂ has been experimentally and theoretical puzzle for a long time. The magnetic AFM unit cell of UO₂ coincides with the crystallographic one. Then the geometrical frustration of the U fcc sublattice results in three distinct AFM structures shown in Fig. 1 being degenerate in energy with respect to the usual spin-spin anisotropic Heisenberg exchange [14]. These structures are described, respectively, by a) the single propagation vector k = [0, 0, 1] (1k - collinear structure in the upper panel of Fig. 1), b) two propagation k-vectors (2k, middle panel of Fig. 1) with mutually perpendicular orientations of the magnetic moments in the cubic face plane parallel to the plane of the k-vectors and, c) three perpendicular k-vectors (3k, lower panel) with the moments oriented in different (111) directions [14]. All three AFM structures have been observed in different cubic uranium monopnictides (UX with X=N,P,As,Sb) [14]. The 3k structure has been finally confirmed to be the magnetic ground state of UO₂ by neutron diffraction and nuclear magnetic resonance experiments [10, 15, 16].

The mechanism leading to the stabilization of non-collinear 3k AFM in UO₂ has not been clearly identified to date. The crystal field splitting obtained in various experiments suggests that the ground state of the U⁴⁺ ions in UO₂ is a spherically symmetric Σ₅ triplet well separated from excited CF states [15, 17] thus the observed AFM structure cannot be due to the single-ion anisotropy. The lattice induced quadrupole-quadrupole (QQ) coupling might explain the first-order nature of the magnetic transition in UO₂, however, it seems to favor 1k-structure rather than 3k one [18, 19]. Hence, the 3k AFM should be rather due to a purely electronic mechanism with lattice distortions subsequently induced by the magnetic ordering [18]. The electronic quadrupolar superexchange (SE) can in principle stabilize the 3k-magnetic order in the structurally undistorted high-temperature phase as suggested by Ref. 20. They

The interplay of local spin and orbital degrees of freedom (DOF) in strongly correlated electron systems is at the origin of such remarkable phenomena as the multiferroic behavior [1], dynamical single-ion and cooperative Jahn-Teller effects [2], and colossal magnetoresistance [3]. In rare-earth and actinides compounds with native Jahn-Teller effects [2], and colossal magnetoresistance [1], dynamical single-ion and cooperative Jahn-Teller effects [2], and colossal magnetoresistance [3], due to a large number of multipolar DOF and a rather small magnitude of relevant energy scales compared to the conventional Heisenberg dipole-dipole couplings [7].

The uranium dioxide is a prototypical example of the MO in actinide magnetic insulators [3, 7]. It has a simple cubic fluorite structure, where U atoms occupy the fcc sublattice (see Fig. 1). Due to its importance as a nuclear fuel [8] and chemical catalyst [9] it has been thoroughly studied experimentally. UO₂ undergoes a first-order phase transition into an antiferromagnetically (AFM) ordered state at the Néel temperature, T_N of 30.8 K [10]. This transition is accompanied by an onset of MO [11] affecting both phonons and magnons dynamics [4, 7, 12, 13]. Dynamical Jahn-Teller effects associated with a spin-lattice quadrupolar coupling is also observed well above T_N [10, 12].
supported this conjuncture with a rather crude estimation of SE interactions (SEI) within a semi-empirical kinetic exchange model.

A reliable estimation of the QQ superexchange couplings in UO$_2$ is thus crucial to unravel the origin of its unusual noncollinear order. The theoretical evaluation of MIs by ab initio density-functional-theory (DFT) methods have a recognized vital importance in the field (see Refs. [21] [22] for review). However, the standard DFT framework in conjunction with local or semi-local exchange correlation functionals is not applicable to localized U 5$f$ states in UO$_2$. The DFT+U method, which was extensively employed to study UO$_2$ [23][25], is able to capture this localization, but only in the symmetry-broken ordered state. Pi et al. [26] has recently developed an approach for evaluating MIs based on a simultaneous flip of multipolar moments on two sites in a MO state described within DFT+U. Pi et al. [26] predicted the spin-wave spectra of UO$_2$ in reasonable agreement with experiment, but their calculated SE QQ interactions are ferromagnetic and would favor the 1$k$ AFM magnetic order instead of the 3$k$ one.

Both the high-temperature paramagnetic phase and ordered states of correlated $f$ compounds can be in principle quantitatively described by combining DFT with the dynamical mean-field theory (DMFT) [28] treatment of localized $f$ shells. This DFT+DMFT method [29][31] has been extensively employed to study the electronic structure of paramagnetic UO$_2$ [32][33]. However, low symmetries, small energy scales and a vast configurational space of MO phases render a direct application of DFT+DMFT to the symmetry-broken phase of UO$_2$ difficult.

In this work we first derive the ab initio electronic structure and CF splitting of UO$_2$ in its paramagnetic cubic phase and then apply the linear-response post-processing of Ref. [34] to these converged DFT+DMFT results evaluating all relevant dipole and multipole SEIs for the CF ground state. Our self-consistent in the charge density DFT+DMFT calculations were carried out employing the approach of Refs. [35][36], which combines a linearized augmented plane-wave band structure method [37] and the DMFT implementation [38][39]. The DMFT quantum impurity problem was solved in the quasi-atomic Hubbard-I approximation [40], which is expected to be reasonable for the paramagnetic high-$T$ phase of the Mott insulator UO$_2$. Wannier orbitals representing U 5$f$ states were constructed from the manifold of 14 Kohn-Sham 5$f$-like bands located in the vicinity of the Fermi level. The rotationally-invariant on-site Coulomb repulsion between these orbitals was parametrized by the Slater parameter $F^0$ =4.5 eV and Hund’s rule coupling $J_H$ = 0.6 eV obtained for UO$_2$ in recent constrained random-phase calculations [41]. SEIs can exhibit a strong sensitivity to the value of $J_H$, hence, to verify the robustness of our results we also performed calculations with $J_H$ = 0.7 eV previously employed in Ref. [26]. The double-counting correction was calculated in the fully-localized limit [42] using the atomic occupancy [43] of the U 5$f^2$ shell. The DFT+DMFT self-consistent calculations were carried out enforcing the uniform occupancy of U 5$f^2$ states within its ground-state multiplet (GSM) in order to suppress the impact of DFT self-interaction error onto the CF splitting [44].

Our calculated valence-band spectral function [45] is in a good agreement with photoemission and bremsstrahlung isochromat measurements [46] thus demonstrating the ability of Hubbard-I approximation to capture main features of the Mott insulating state of UO$_2$. We obtain the $^3H_4$ ground-state multiplet (GSM) of U 5$f^2$ shell with the $\Gamma_5$ triplet being the CF ground state; the exited doublet $\Gamma_3$, triplet $\Gamma_4$, and singlet $\Gamma_1$ predicted to be 193, 197, and 207 meV higher in energy, respectively. Our theoretical CF splitting is thus in good agreement with experimental measurements [47] that found the splitting of 150 to 180 meV between the $\Gamma_5$ ground state and densely-spaced exited CF levels, as well as with previous DMFT calculations of Ref. [32]. This CF splitting is much higher than $T_N$ of UO$_2$, hence, the impact of exited multiplets on the magnetic order can be neglected.
The calculated \( \Gamma_5 \) eigenstates in the \( |J; m_J\rangle \) basis

\[
\begin{align*}
|1\rangle &= 0.908|4; +3\rangle - 0.343|4; -1\rangle - 0.032|5; -5\rangle \\
|0\rangle &= 0.686|4; +2\rangle - 0.686|4; -2\rangle - 0.033|5; -2\rangle \\
&- 0.033|5; +2\rangle \\
| -1\rangle &= -0.908|4; -3\rangle + 0.343|4; +1\rangle - 0.032|5; +5\rangle
\end{align*}
\]

feature a small admixture of high-energy multiplets.

The \( \Gamma_5 \) triplet (effective \( J = 1 \)) can support both dipole and quadrupole moments. In order to evaluate the corresponding dipole and quadrupole SEIs acting between \( U \) shells in the \( \Gamma_5 \) state we employed the method of Ref. [34]. Namely, one evaluates the linear response of DFT+DMFT grand potential \( \Omega \) to small fluctuations of the on-site density matrix on two neighboring sites \( R \) and \( R' \) with respect to its symmetry unbroken state, 

\[
\delta^{\alpha\beta} \Omega \text{ (} \delta_{\rho\rho}' \text{) (} \delta_{\rho\rho}' \text{) (} \delta_{\rho\rho}' \text{) ,}
\]

where the lower case Greek letters designate the states \( \text{[1]} \) within the \( \Gamma_5 \) triplet, \( \hat{\rho} \) is the density matrix of the CF \( \Gamma_5 \) triplet. As shown in Ref. [34], 

\[
\delta^{\alpha\beta} \Omega \text{ (} \delta_{\rho\rho}' \text{) (} \delta_{\rho\rho}' \text{) (} \delta_{\rho\rho}' \text{) } = \frac{1}{\pi} T \text{Tr} \left[ G_{RR'} \delta^{\alpha\beta} \delta_{\rho\rho}' G_{RR'} \delta^{\alpha\beta} \delta_{\rho\rho}' \right],
\]

where the variational derivative of the local self-energy \( \Sigma \) with respect to a given fluctuation \( \rho^{\alpha\beta} \) is evaluated analytically within the Hubbard-I approximation. The inter-site Green’s function (GF) \( G_{RR'} \) is obtained by a Fourier transform of the lattice GF projected to the basis of correlated \( 5 \) orbitals.

The matrix element of \( \text{SE} \) \( V(R' - R) \) between given \( \Gamma_5 \) CF states on two \( U \) sites is defined as \( \langle \alpha\gamma | V(R' - R) | \beta\delta \rangle = \frac{1}{\delta_{\rho\rho}'} \delta^{\alpha\beta} \Omega \text{ (} \delta_{\rho\rho}' \text{) (} \delta_{\rho\rho}' \text{) (} \delta_{\rho\rho}' \text{) ,} \rangle \) where the dependence of \( V \) on \( R' - R \) only is due to the translational invariance. There are in total \( 3^4 = 81 \) SEIs \( \langle \alpha\gamma | V(R' - R) | \beta\delta \rangle \) for each \( U-U \) bond. We have subsequently transformed these interactions to more conventional SE couplings between the spherical tensor dipole and quadrupole moments [57] using 

\[
\sum_{\alpha\beta\gamma\delta} \langle \beta\delta | V(R' - R) | \alpha\gamma \rangle O_{\alpha\beta}^{LM} O_{\gamma\delta}^{LM'} = V_{LM}^{LL'}(R' - R),
\]

where \( O_{\alpha\beta}^{LM} = \alpha \beta \) is the \( \alpha \beta \) matrix element of the real spherical tensor for \( J = 1 \) [34] of the rank \( L = 1 \) (dipole) or \( 2 \) (quadrupole) and projection \( M \). \( V_{LM}^{LL'}(R' - R) \) is the resulting SE between the multipoles \( LM \) and \( L'M' \) located at the sites \( R \) and \( R' \), respectively.

Thus calculated SE Hamiltonians for the nearest-neighbor (NN) \( U-U \) bond \( R' - R = [1/2, 1/2, 0] \) is of the form 

\[
H_{\text{DD}} = V \sum_{\text{M} = \text{x}, \text{y}, \text{z}} \hat{O}_R^{\text{M}} \hat{O}_{R'}^{\text{M}} + V' \hat{O}_R^{\text{z}} \hat{O}_{R'}^{\text{z}},
\]

\[
H_{\text{QQ}} = \sum_{\text{M} = \text{z}, \text{y}, \text{z}} V_{\text{M}}^{\text{z}} \hat{O}_R^{\text{z}} \hat{O}_{R'}^{\text{z}} + V_{\text{z}, \text{y}, \text{z}}^{\text{z}, \text{y}, \text{z}} \hat{O}_R^{\text{z}} \hat{O}_{R'}^{\text{y}} \hat{O}_R^{\text{z}}.
\]

| \( J_H \) (eV) | \( V \) | \( V' \) | \( V_{x,y} \) | \( V_{x,xy}^{\text{z}} \) | \( V_{y,y}^{\text{x}} \) | \( V_{x,xy}^{\text{z}} \) |
|-------------|-----|-----|--------|--------|--------|--------|
| 0.6         | 1.42 | 3.85 | -0.67  | 0.18   | 0.01   | -0.16  |
| 0.7         | 1.39 | 3.73 | -0.69  | 0.20   | 0.01   | -0.18  |

The number of independent SE couplings is seen to be significantly reduced due to the cubic symmetry of the problem. Hence, for brevity we omit the rank \( L \) in the real tensors, as the projection \( M \) is sufficient to identify them unambiguously, and suppress superfluous indices for \( V \). The QQ SEI are labeled by the superscript \( q \). SE Hamiltonians for other NN bonds are easily obtained from (2) and (3) by symmetry. The interactions of next-nearest neighbors (NNN) are an order of magnitude smaller and induce no qualitative changes, they are listed in Supplementary Material [55]. More distant SEIs are negligible. The calculated NN SEIs for two values of \( J_H \) are listed in Table I. One may see that the variation in \( J_H \) has a rather insignificant impact on the SEIs. Unless explicitly mentioned otherwise, we use the SEIs for \( J_H = 0.6 \) eV in all calculations below.

We have subsequently solved the calculated \( ab \) \textit{initio} SE Hamiltonian including NN and NNN couplings within the mean-field approximation (MFA) implemented in Ref. [47]. We considered three structures shown in Fig. 1 as well as all single-\( k \) magnetic structures realizable within the \( 4 \times 4 \times 4 \) fcc supercell. A clear phase transition is observed in the evolution of specific heat at about \( T_N = 56 \) K accompanied by appearance of a non-zero on-site dipole moment oriented along the \( (111) \) direction and quadrupole moments of the \( t_{2g} \) irreducible representation (IREP) as shown in Fig. 2. The obtained magnetic and quadrupole orders correspond to the 3k-structure plotted the lower panel of Fig. 1 which is the experimental ordered structure of \( \text{UO}_2 \). Predicted \( T_N \) is substantially higher than the experimental first-order transition temperature of 30.8 K. A large overestimation of \( T_N \) in the MFA is expected for the fcc lattice due to its geometric frustration [48, 49].

Let us now analyze the calculated SEIs in order to identify the origin of the 3k-structure stabilization with respect to the competing 1k and 2k ones. The DD interactions are antiferromagnetic and very asymmetric. With \( J' < J < 0 \) all three AFM structures shown in Fig. 1 become degenerated with respect to \( H_{\text{DD}} \) [18, 30] having the same ordering energy \( E_{\text{mag}} = -V' = -3.85 \) meV/f.u. in the mean-field approximation. The quadrupole orders shown in the rhs of Fig. 1 are obtained by solving the full SE NN Hamiltonian for the AFM state of a given type. With the calculated SE QQ interactions from Table I the QQ contribution to the ground state energies is equal to 0.010, -0.047, and -0.060 meV/(f.u.) for the 1k, 2k, and 3k orders, respectively. Therefore, we conclude that the
QQ SEIs are stabilizing the experimentally observed non-collinear 3k magnetic structure; this order of a purely electronic origin subsequently results in the Jahn-Teller distortion.

In Table I we compare our results to previous theoretical and experimental estimates of SEIs in UO$_2$. Our DD SE is very close to the fit of experimental spin-waves spectra of Ref. [7], however, our QQ SEIs are much smaller. The qualitative difference with the DFT+U results [27] is in the sign of the QQ interactions. The negative sign predicted in Ref. [27] would stabilize 1k-order having NN \( \langle \hat{O}_M^M \hat{O}_R^R \rangle = 0 \) for all M belonging to the \( t_{2g} \) IREP (xy, xz, yz). AF \( t_{2g} \) SEIs favor the 3k-structure because of a larger angle between ordered quadrupoles in this case as compared to the 2k-structure, where one third of NN pairs have parallel quadrupole moments and the 1k-structure, where all quadrupole moments are parallel (see Fig. 1).

The magnitude of SEIs acting between the \( e_g \) quadrupoles has not been evaluated in Ref. [27] neither can it be estimated from the spin-wave dispersion, as \( \langle \hat{O}_M^M \hat{O}_R^R \rangle = 0 \) for \( M = z^2 \) and \( x^2 - y^2 \) in the experimental 3k AFM structure. However, the contribution of \( e_g \) SEIs is non-zero for the 1k and 2k competing orders thus impacting the relative stability of magnetic structures. We calculated the ordering energy of three structures employing the QQ SEIs \( \hat{V}_{e_g}^q (1 - r) \) and \( \hat{V}_{t_{2g}}^q (1 + r) \) with \( r \in [-1 : 1] \). Hence, \( r = 0 \) corresponds to the actual calculated QQ SEIs, while at \( r = -1 \) (1) only SEIs acting between \( e_g \) (\( t_{2g} \)) quadrupoles are non-zero. One sees that the 1k is stabilized with \( r \rightarrow -1 \), while the actual 3k is stabilized in the opposite limit. At \( r \approx -0.73 \) all 3 structures are degenerate in energy due to isotropic QQ ISEs. Therefore, it is the particular anisotropy of QQ SEIs of UO$_2$ with a larger magnitude of positive \( V_{t_{2g}}^q \) that is at the origin of 3k-order in UO$_2$.

The phase transition in UO$_2$ is of the first order and dynamical Jahn-Teller effects are also observed well above \( T_N \) [10] [12] hinting at a non-negligible short-range order (SRO) present in UO$_2$. We have analyzed SRO effects above the Néel temperature using an Oguchi-like method [31]. To this end we diagonalized the \( ab \) \( \text{initio} \) SE Hamiltonian, eqs. [3] and [3], with the SEIs from Table I for each NN pair of U ions. We then calculated the DD and QQ pair correlation functions \( \langle \hat{O}_M^M \hat{O}_R^R \rangle \) by averaging them over all NN bonds. The calculated NN pair correlation functions vs. \( T/T_N \) are shown in Fig. 3. Strong DD SRO effects are clearly observed well above Néel temperature as expected for the frustrated fcc lattice [52]. The dominating AFM DD SRO forces a ferroquadrupole SRO for both the \( t_{2g} \) and \( e_g \) quadrupoles for \( T > T_N \) as one sees in Fig. 3. The constrain of antiparallel orientation of the neighboring dipole moments is lifted in the ordered state by the AFM frustration. The \( t_{2g} \) quadrupole order is then antiferro due to the corresponding sign of QQ SEIs, while the \( e_g \) pair correlation functions are zero. Hence, the structure of QQ pair correlation function below and above the phase transition is qualitatively different. This observation has two important consequences. First, a SRO that is opposite

![FIG. 2: a. The expectation values of dipole and \( t_{2g} \) quadrupole tensors as a function of temperature. A phase transition at \( T = 56 \) K is clearly seen. b. The mean-field magnetic energy \( E_{mag} \) at zero temperature as a function of the anisotropy parameter \( r \) of the QQ SE, see text.](image)

![FIG. 3: The dipole-dipole and quadrupole-quadrupole nearest-neighbor pair correlation functions above \( T_N \). The quadrupole-quadrupole pair correlation functions are multiplied by 10.](image)

| TABLE II: Comparison of the SEIs calculated in the present work with previous DFT+U calculations of Ref. [27], and the values of Ref. [7] from a fit of the experimental spin-wave spectra. Following Refs. [7] [27] we define the isotropic part of DD and QQ SEIs as \( V' \) and \( V_{e_g}^q \), respectively, and the corresponding dimensionless anisotropy parameters \( \delta^d/\delta^q \) defined as \( \delta^d = V'/V' \) and \( \delta^q = V_{e_g}^q/V_{e_g}^q \), respectively. Refs. [7] [27] estimated only the SEI relevant for the 3k-structure, thus only those four parameters are available for comparison (Note that Ref. [7] assumed \( \delta^q = \delta^d \)). |
|-----------------|------|-----|-----|-----|
|                 | \( V' \) | \( \delta^d \) | \( V_{e_g}^q \) | \( \delta^q \) |
| This work       | 3.84 | 0.37 | 0.18 | 0.22 |
| Ref. [7]        | 3.1  | 0.25 | 1.9  | 0.25 |
| Ref. [27]       | 1.70 | 0.3  | -3.10| 0.9  |
to the corresponding pair correlation function in the ordered state is associated with a first-order magnetic phase transition \[^{53-55}\]. This hints at a purely electronic SE mechanism for the observed first-order type of magnetic transition in UO\(_2\). Second, the dynamical Jahn-Teller distortions above \(T_N\) might be quite different from the static one in the AFM phase. The last prediction can be possibly verified in future experimental studies.

In conclusion, our calculations point out at the anisotropy of quadrupole superexchange as the origin of non-collinear \(3k\) antiferromagnetic order in UO\(_2\) and the first-order type of the corresponding Néel transition. The present \textit{ab initio} approach seems to be highly promising for studies of other localized \(f\)-electron systems featuring complex unexplained magnetic or "hidden" orders and local multipole degrees of freedom.

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[57] The observable dipole magnetic and quadrupole moments are related to the corresponding tensor moments defined in the $\Gamma_5$ basis by the prefactors 2.88, 0.153 and 0.217 for the dipole, quadrupole $e_{g}$ and quadrupole $t_{2g}$, respectively.
[58] Using the SEIs evaluated with $J_H = 0.7$ eV we obtain the same ordered structures at almost identical temperature of 54 K.
Supplemental material of "Quadrupolar Superexchange Interactions, Multipolar Order and Magnetic Phase Transition in UO2"

by Leonid V. Pourovskii and Sergii Khmelevskyi

DFT+DMFT SPECTRAL FUNCTION OF UO₂ WITHIN THE HUBBARD-I APPROXIMATION

Our calculated DFT+DMFT spectral function of UO₂ calculated within the Hubbard-I approximation (HIA) and using \( J_H = 0.6 \) eV is plotted in Fig. S1 together with recent photoemission (PES) and bremsstrahlung isochromat spectra (BIS) of Ref. [46]. The experimental measurements of Ref. [46] employed high photon energies thus enhancing the relative spectral weight of 5f features. One sees an overall good agreement between the experimental and theoretical positions of the lower (LHB) and upper (UHB) Hubbard bands formed by localized U 5f states. The width of LHB seems to be underestimated by the theory due to a highly simplified treatment of the hybridization between 5f and conduction states by the HIA [56]. The width of UHB is mainly due to multiplet effects, which are fully included by the HIA, and thus well reproduced.

FIG. S1: The DFT+DMFT spectral function of UO₂ within the Hubbard-I approximation. The black, red, and green lines are the total, partial U 5f and O 2p spectral functions, respectively. The experimental emission and bremsstrahlung isochromat spectra of Ref. [46] are displayed by blue circles.
NEXT-NEAREST-NEIGHBORS SUPEREXCHANGE INTERACTIONS IN UO$_2$

The calculated SE Hamiltonian for the next-nearest-neighbor bond [001] $H_{SE}^{NNN} = H_{DD}^{NNN} + H_{QQ}^{NNN}$ reads

$$H_{DD}^{NNN} = V \sum_{M=x,y} \hat{O}_R^M \hat{O}_R^M + V' \hat{O}_R^x \hat{O}_R^z$$  \hspace{1cm} (S1)

$$H_{QQ}^{NNN} = \sum_{M \in \{g, e\}} V_q^M \hat{O}_R^M \hat{O}_R^M$$  \hspace{1cm} (S2)

where the dipole-dipole (DD) and QQ contributions take a simpler form compared to the nearest-neighbor SE Hamiltonian (eqs. 2 and 3 of the main text) due to the absence of off-diagonal terms. The SE Hamiltonians for other NNN bonds are obtained from that for [001] by the corresponding rotations, that amounts in the case of $H_{DD}^{NNN}$ to permutations of the $x$, $y$ and $z$ labels. The $L = 2$ tensors in $H_{QQ}^{NNN}$ transform upon these rotations like the corresponding $l = 2$ real spherical harmonics.

The calculated values of the NNN SEIs are listed in Table III. By comparing it with Table I of the main text one sees that the NNN SEIs are about one order of magnitude smaller compared to the NN ones.

| $V$  | $V'$ | $V_{x'y'}^y$ | $V_{x'y'}^z$ | $V_{x'y'}^{x^2-y^2}$ | $V_{x'y'}^z$ |
|------|------|-------------|-------------|---------------------|-------------|
| 0.143| 0.156| 0.004       | -0.015      | -0.003              | 0.053       |

TABLE III: Calculated U-U next-nearest-neighbor interactions for the [0,0,1] bond (meV) for $J_H = 0.6$ eV.