Hidden order and multipolar exchange striction in a correlated $f$-electron system

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The nature of order in low-temperature phases of some materials is not directly seen by experiment. Such “hidden orders” (HOs) may inspire decades of research to identify the mechanism underlying those exotic states of matter. In insulators, HO phases originate in degenerate many-electron states on localized $f$- or $d$-shells that may harbor high-rank multipole moments. Coupled by intersite exchange, those moments form a vast space of competing order parameters. Here, we show how the ground-state order and magnetic excitations of a prototypical HO system, neptunium dioxide NpO$_2$, can be fully described by a low-energy Hamiltonian derived by a many-body ab initio force theorem method. Superexchange interactions between the lowest crystal-field quadruplet of Np$^{4+}$ ions induce a primary noncollinear order of time-odd rank 5 (triakontadipolar) moments with a secondary quadrupole order preserving the cubic symmetry of NpO$_2$. Our study also reveals an unconventional multipolar exchange striction mechanism behind the anomalous volume contraction of the NpO$_2$ HO phase.

Significance

Second-order phase transitions in solids occur due to spontaneous symmetry breaking with an order parameter continuously emerging from the disordered high-temperature phase. In some materials, the phase transitions are clearly detected in thermodynamic functions (e.g., specific heat), but the microscopic order parameters remain “hidden” from researchers, in some cases for decades. Here, we show how such hidden-order parameters can be unambiguously identified and the corresponding ordered phase fully described using a first-principles many-body linear response theory. Considering the canonical “hidden-order” system neptunium dioxide, we also identify an unconventional mechanism of spontaneous multipolar exchange striction that induces an anomalous volume contraction of the hidden-order phase in NpO$_2$.

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The authors declare no competing interest.

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analysis of low-temperature susceptibility and INS data (24, 25). The full structure of this Hamiltonian cannot be extracted from experiment due to a large number of possible superexchange interactions (SEIs). The measured CF splitting of 55 meV between the \( \Gamma_8 \) ground state and first exited CF level \((8, 9, 32)\) is much larger than \( T_0 \), suggesting SEI between \( \Gamma_8 \) states on neighboring Np ions as the origin of its exotic ordered phase. Such low-energy superexchange Hamiltonian has not been so far derived theoretically. Previous theoretical density functional theory (DFT) + \( U \) studies have confirmed the stability of a triakontadipolar order in NpO\(_2\) \((15, 33)\); however, they imposed an initial symmetry breaking consistent with the \( 3k \) rank 5 order inferred experimentally.

In this work, we apply a first-principles many-body framework to the problem of “hidden” multipolar orders in correlated insulators as exemplified by NpO\(_2\). It consists of evaluating the full low-energy superexchange Hamiltonian from an ab initio description of the symmetric paramagnetic phase. We start with charge self-consistent DFT + dynamical mean-field theory (DMFT) \((34–36)\) calculations for paramagnetic NpO\(_2\) treating Np \( 5f \) within the quasiatomic Hubbard-I (HI) approximation \((37)\) (this method is abbreviated below as DFT + HI) to obtain its electronic structure and the composition of a CF-split Np \( 5f^n \) shell. A force theorem within HI (FT-HI) approach \((38)\) is subsequently employed to derive SEIs between the calculated CF \( \Gamma_8 \) ground-state quadruplets. In summary, we perform an ab initio electronic structure calculation of a complete superexchange Hamiltonian for high-rank magnetic multipoles in an \( f \)-electron crystalline material. By solving this Hamiltonian, we find a \( 3k \) rank 5 primary magnetic multipolar order (MMO) accompanied by a secondary longitudinal quadrupole order. The calculated time-odd splitting of \( \Gamma_8 \) and magnetic excitation spectra are in a good agreement with experiment. The lattice contraction effect \((20)\) is shown to be not related to quadrupole ordering as suggested before \((39)\) but rather, to stem from the volume dependence of leading time-odd SEIs. This multipolar “exchange spring” effect is quite unique and has not been, to our awareness, discussed previously in the literature. Overall, we show that within our first-principles scheme, which treats all competing order parameters on the equal footing, high-rank multipolar orders in correlated insulators can be captured both qualitatively and quantitatively.

**Results**

**CF Splitting and Superexchange Hamiltonian.** We start with evaluating the Np CF splitting in paramagnetic NpO\(_2\): as discussed above, this splitting determines the space of low-energy states forming the MMO. The CF splitting of the Np \( 5f^9 \) ground-state multiplet \( J = 9/2 \) calculated by DFT + HI is shown in Fig. 1. The ground-state \( \Gamma_8 \) quartet is separated from another excited \( \Gamma_8 \) quartet by 68 meV, in agreement with the experimental range for this splitting, 30 to 80 meV, inferred from INS measurements \((19, 32, 40)\). The broad experimental range for the excited \( \Gamma_8 \) energy is due to the presence of a dispersive phonon branch in the same range \([this overlap has been a major source of difficulties for the phenomenological analysis of NpO\(_2\) in the framework of effective CF model model \((8)\)]\). The third exited level, \( \Gamma_6 \) doublet, is located at much higher energy above 300 meV \((see Fig. 1A)\).

Our calculated CF corresponds to \( x = -0.54 \) parameterizing the relative magnitude of the four- and six-order contributions to the cubic CF \((41)\). Our values are in good agreement with \( x = -0.48 \) inferred from INS measurements \((19)\) and analysis of CF excitation energies along the actinide dioxide series \((31)\). The CF-level energies calculated within DFT + HI are

![Fig. 1. Np 5f on-site splitting and Np–Np inter-site interactions in NpO\(_2\).](https://doi.org/10.1073/pnas.2025317118)
also in good agreement with previous DFT + DMFT calculations by Kolorenč et al. (42) employing an exact diagonalization approach to Np 5f\textsuperscript{7}. The calculated wave functions (WFs) of the CF ground-state Γ\textscript{s} quartet (SI Appendix, Table S1) feature a small admixture of the excited \(J = 11/2\) and 13/2 multipoles.

The space of CF GS Γ\textscript{s} quadruplet is conveniently represented by the effective angular momentum quantum number \(J_{\text{eff}} = 3/2\), with the Γ\textscript{s} WFs labeled by the corresponding projection \(M = -3/2, -1/2, +1/2, +3/2\) and the phases of WFs chosen to satisfy the time-reversal symmetry (SI Appendix, Table S1). The on-site degrees of freedom within the GS quadruplet are (pseudo-)dipole, quadrupole, and octupole moments defined for \(J_{\text{eff}} = 3/2\) in the standard way (8). Hence, the most general form for a superexchange coupling between Γ\textscript{s} quadruplets on two Np sites reads

\[
\sum_{KK'Q'Q} V^{QQ'}_{KK'}(R) \hat{O}^{Q'}_{K}(R_0) \hat{O}^{Q}_{K'}(R_0 + R), \tag{1}
\]

where \(\hat{O}^{Q}_{K}(R_0)\) and \(\hat{O}^{Q'}_{K'}(R_0 + R)\) are the real spherical tensor operators (8) for \(J = 3/2\) of rank \(K = 1, 2, 3\), \(-K \leq Q \leq K\) acting on the sites \(R_0\) and \(R_0 + R\), respectively. \(V^{QQ'}_{KK'}(R)\) is the SEI that couples them, and due to the translational invariance, \(V^{QQ'}_{KK'}\) depends only on the intersite lattice vector \(R\).

We employed the FT-HI approach (38) to evaluate all interactions \(V^{QQ'}_{KK'}(R)\) from the converged DFT + HI NpO\textsubscript{2} electronic structure for the several first Np coordination shells. Only NN SEIs are significant, with longer-distance ones being more than an order of magnitude smaller. All SEIs \(V^{QQ'}_{KK'}(R)\) for a given bond \(R\) form a matrix, designated below as the SEI matrix, with the rows and columns labeled by the moments \(KK'\) and \(Q'Q\) on the sites \(R_0\) and \(R_0 + R\), respectively. The NN SEI matrix \(\hat{V}(R)\) is graphically represented in Fig. 1B (SI Appendix, Table S2) using a local coordinate system with the quantization axis \(z[R]\). This \(15 \times 15\) matrix is of a block-diagonal form since the interactions between time-even and time-odd moments are zero by symmetry. It can thus be separated into the dipole–dipole (DD), quadrupole–quadrupole (QQ), octupole–octupole (OO), and dipole–octupole (DO) blocks. Despite this simplification, the SEI matrix \(\hat{V}\) can in principle contain 70 distinct elements. The number of distinct nonzero matrix elements in \(\hat{V}\), while reduced by the cubic symmetry to 38, remains rather large.

Our calculations predict the largest values for the diagonal DD \(x-x\) (AF, 1.6 meV) SEI. However, the off-diagonal OO \(xyz\) to \(y(x^2 - 3yz^2)\) (ferro, \(-1.5\) meV) and DO \(z\) to \(z^3\) (AF, 0.95 meV) couplings are of about the same magnitude as the DD \(x-x\) one. Overall, the calculated \(\hat{V}\) matrix shown in Fig. 1B features many negligible DD, OO, and DO interactions of a comparable magnitude. The QQ interactions are weaker, reflecting the secondary nature of the quadrupole order. Our calculations thus predict a complex and frustrated superexchange in NpO\textsubscript{2}, which may give rise to multiple competing time-odd orders. Therefore, as has been previously noted (8, 25), extracting a full superexchange Hamiltonian of NpO\textsubscript{2} from experimental (e.g., INS) data is virtually impossible due to a large number of parameters entering into the fit of an exciton spectra. The same difficulty is encountered by ab initio approaches based on total energy calculations for symmetry broken phases (15, 33, 43), which require a large number of very precise calculations to extract multiple nonnegligible matrix elements of \(V\), with the magnitude of 0.5 meV and above. Within the present framework, all interactions are extracted from a single ab initio calculation for paramagnetic NpO\textsubscript{2}.

**Ordered State of NpO\textsubscript{2}.** The calculated superexchange Hamiltonian for NpO\textsubscript{2} reads

\[
H_{SE} = \frac{1}{N} \sum_{\text{R} \in \text{NN}} \hat{O}(\text{R}_0) \hat{V}(\text{R}) \hat{O}(\text{R}_0 + \text{R}), \tag{2}
\]

where \(\text{R}\) runs over all NN bonds in the Np face-centered cubic (fcc) sublattice and \(N\) is the number of Np sites; we also introduce the obvious vector notation \(\hat{O} = [O_1, \ldots, O_{27}]\) for multipole tensors. The SEI matrix \(\hat{V}(\text{R})\) in the local frame \(\hat{R}\) (Eq. 1, see also Fig. 1B) is rotated to align \(\hat{R}\) along the corresponding Np NN bond. We solved [2] numerically within the mean-field (MF) approximation (44), obtaining a second-order transition at \(T_c = 37\) K, in good agreement with its experimental value of 26 K taking into account the usual MF overestimation of ordering temperatures. The numerical results were verified by a linearized (MF) theory, derived by a first-order expansion of MF equations in the order parameters \(\langle \hat{O} \rangle\) (Methods).

The resulting GS order of NpO\textsubscript{2} in the \(J_{\text{eff}}\) space consists of a primary (pseudo-)DO order combined with secondary (pseudo-)quadrupole one (SI Appendix, Table S3 lists the values of all \(J_{\text{eff}}\) order parameters; see also SI Appendix, Fig. S1). The pseudodipole order is a complex 3k planar AF structure, with four inequivalent simple-cubic sublattices forming two pairs with different moment magnitude; the moments of those two pairs are aligned along the \(\{1,1,0\}\) and \(\{3,1,0\}\) directions in the fcc lattice, respectively. The origin of this inclined AF structure of pseudodipoles is in the DO SEI, similar to physical AF magnetic orders found in some materials with large spin-orbit coupling that are likely induced by higher-order magnetic multipoles interactions. The pseudotetrapoles order is also oriented in nonsymmetrical directions. The secondary pseudotetrapole order is of a 3k type, which we analyze in detail below.

We subsequently mapped the moment calculated in the \(J_{\text{eff}} = 3/2\) space into the observable multipolar moments that are defined in the physical \(J = 9/2\) space of Np 5f\textsuperscript{7} GS multiplet (Methods). The calculated physical multipole order of NpO\textsubscript{2} is displayed in Fig. 2. Notice that observable moments up to \(K = 7\) can exist on an \(f\)-electron shell (8); we show the largest primary (odd) and secondary (even) order parameters as well as the physically important quadrupole order. All nonzero multipole moments are listed in SI Appendix, Table S4. The physical dipole magnetic moments are found to completely vanish since their contribution into the \(\langle O_3 \rangle\) and \(\langle O_5 \rangle\) pseudodipole \(J_{\text{eff}} = 3/2\) moments is exactly canceled by that due to the \(\langle T_3 \rangle\) and \(\langle T_5 \rangle\) pseudotetrapoles. The primary order parameter is of rank 5 (triakontadipole); the physical octupole moment is an order of magnitude smaller, and the magnitude of rank 7 moments is about 1/3 of that for triakontadipoles, in agreement with previous estimates for the relative contribution of those multipoles into the MOO order in NpO\textsubscript{2} (24). The magnetic triakontadipoles on different sublattices are oriented in four different directions (forming mutual angles corresponding to the angles between the cube’s main diagonals), thus structured similarly to the 3k-AMF dipole order in UO\textsubscript{2} (Fig. 2A). The secondary order is dominated by hexadecapole (rank 4) (Fig. 2B). The ordered quadrupole moments (Fig. 2C) are roughly twice smaller. The quadrupole order is directly related to the pseudotetrapole order since the \(\Gamma_5\) (or \(I_{5z}\)) pseudotetrapoles directly map into the physical ones, apart from swapping \(xy \leftrightarrow yz\) and \(x^2 - y^2\) \(\leftrightarrow z^2\). The resulting physical quadrupole order can be represented, in the space of \(\Gamma_5\) quadrupoles \([O_{1x}, O_{2y}, O_{3z}]\) by four directions \([111], [1\bar{1}1], [1\bar{1}1], [1\bar{1}1]\) for four inequivalent Np sublattices \([0,0,0], [1/2,1/2,0], [1/2,0,1/2], [0,1/2,1/2]\), respectively. These quadrupoles can be depicted as \(\langle O_{2z} \rangle\) moments with the principal axes \(z\) along the corresponding direction at each given
Exchange Splitting and Magnetic Excitations. Having obtained the MMO of NpO$_2$, we subsequently calculated its excitation spectra, which have been previously measured, in particular, by INS (19, 25).

The MMO lifts the degeneracy of CF GS $\Gamma_5$ quartet; the resulting exchange splitting calculated from the ab initio superexchange Hamiltonian (2) is depicted in Fig. 1A. Right. The ground state is a $\Gamma_5$ singlet with the first excited doublet found at 6.1 meV above the GS $\Gamma_5$ singlet and the second excited level, singlet, located at 12.2 meV. The calculated position of first excited doublet is in excellent agreement with the location of a prominent peak in INS spectra at about 6.4 meV (19) in the ordered phase; another broad excitation was observed in the range of 11 to 18 meV (25) (see below).

Previously, an exchange splitting of the $\Gamma_8$ was obtained in ref. 24 assuming a diagonal uniform SEI between $\Gamma_5$ triakontadipole. The value of this SEI was tuned to reproduce the magnitude of the first excited doublet. The fact that the splitting of high-energy peak was clearly observed at all in the measured INS spectra, after experimental broadening is shown in Fig. 3B. The high-energy feature, however, is clearly split in experiment into two broad peaks centered at about 12 and 16 meV. In order to understand whether the relative weights of the low- and high-energy features are captured in the theory, we employed the same analysis as Magnani et al. (25). Namely, we evaluated, as a function of the momentum transfer, the ratio of high-energy feature spectral weight to that of the low-energy one. The calculated ratio is in excellent agreement with experiment up to $|q|=2.5$ Å$^{-1}$. As noticed in ref. 25, a phonon contribution to INS appears below 18 meV for large $|q|$, thus rendering the separation of magnetic and phonon scattering less reliable for $|q| > 2$ Å$^{-1}$. The splitting of high-energy peak was clearly observed at all measured $|q|$; it was not reproduced by the simplified semiempirical SEI employed by Magnani et al. (25). They speculated that this splitting might stem from complex realistic Np–Np SEIs, which could not determine from experiment. In the present work, we determined the full superexchange Hamiltonian for the GS CF $\Gamma_5$ quadruplet. Hence, the fact that the splitting of INS high-energy feature is still not reproduced points out to its origin likely being a superexchange coupling between the ground-state and first excited $\Gamma_5$ quadruplets (a significant contribution of the very high-energy $\Gamma_5$ CF doublet is unlikely). This interquadruplet coupling can be in principle derived using the present framework; we have not attempted to do this in the present work.

Alternatively, lattice-mediated interactions might be also considered as the origin of the high-peak splitting. These interactions couple time-even moments (i.e., the quadrupoles within the $\mathcal{J}_{qq}$ space). However, the QQ coupling is rather expected to impact the shape of the low-energy peak in Fig. 3B because the corresponding lowest on-site excitation in the ordered phase...
the volume contraction and we evaluated the volume dependence of $NpO_2$ magnetic multipoles. Rather stems from the volume-dependent SEI coupling high-rank order coupling to the lattice. As we show below, this is not the case, and the volume contraction in $NpO_2$ rather stems from the volume-dependent SEI coupling high-rank magnetic multipoles.

**Multipolar Exchange Striction.** The onset of the HO phase $NpO_2$ is marked by an anomalous volume contraction vs. decreasing temperature (anti-Invar anomaly). The estimated total volume contraction in the ordered state as compared with the paramagnetic phase is 0.018% at zero temperature (20). This effect cannot be attributed to the conventional volume magnetostriction since ordered magnetic moments are absent in $NpO_2$. Hence, this anomaly was speculated (39) to be induced by a (secondary) quadrupole order coupling to the lattice. As we show below, this is not the case, and the volume contraction in $NpO_2$ rather stems from the volume-dependent SEI coupling high-rank magnetic multipoles.

In order to make a quantitative estimation for this anomaly, we evaluated the volume dependence of $NpO_2$ ordering and elastic energies. To that end, we adopted the elastic constants calculated for $NpO_2$ in the framework of the DFT + U approach (45): $C_{11} = 404$ GPa, $C_{12} = 143$ GPa. The corresponding parabolic volume dependence of elastic energy $E_{\text{elas}} = 1/2 \left( C_{11}/2 + C_{12} \right) \epsilon^2 \equiv K \epsilon^2$, where $\epsilon = (V - V_0) / V_0$ is the volume contraction and $V_0$ is the $NpO_2$ equilibrium volume (45), is depicted in Fig. 4. The dependence of MMO energy vs. volume was obtained by calculating the SEIs at a few different volumes and then evaluating the MF order and ordering energy vs. volume expansion or contraction. The superexchange ordering energy remains linear vs. $\epsilon$ in a rather large range ($\epsilon = \pm 1\%$); its dependence upon $\epsilon$ for the relevant range of small $\epsilon$ is thus easily obtained.

As is seen in Fig. 4, the superexchange contribution shifts the equilibrium volume in the ordered state toward smaller volumes. The negative slope for the ordering energy vs. volume is expected as the SEIs become larger with decreasing $Np$-$Np$ distance. Thus, the multipolar SEIs act as springs (scheme in Fig. 4, Inset) pulling $Np$ atoms closer as the order parameters increase below $T_0$. Our approach is thus able to qualitatively capture this very small in magnitude subtle effect: The calculated spontaneous multipolar exchange striction is 0.023% (Fig. 4) at zero $T$ as compared with the experimental estimate of 0.018% (20, 39).

We also performed the same calculations suppressing the QQ superexchange, obtaining only a very minor change, by about 0.5%, in the slope of MMO energy vs. volume. Hence, the secondary quadrupole order plays virtually no role in the anomalous volume contraction. The physical origin of this effect is the volume dependence of leading, time-odd SEIs.

To analyze the temperature dependence of the anomalous contraction, one may recast the linear in volume MMO energy (Fig. 4) into a general form of $K_{\text{SEI}}^\ell \xi^\ell(T) + K_{\text{SEI}}^2 \xi^2_\text{SEI}(T)$, where $\xi(T)$ and $\xi^2_\text{SEI}(T)$ are primary and secondary order parameters, respectively, and $K_{\text{SEI}}^\ell$ and $K_{\text{SEI}}^2$ are the slopes of volume dependence for the corresponding contributions to MMO energy. The temperature dependence of the anomalous volume contraction is thus given by that of squares of the order parameters, $\xi^2_\text{SEI}(T)$ and $\xi^2_\text{SEI}(T)$. As shown in SI Appendix, Fig. S2, secondary quadrupole $\xi^2_\text{SEI}(T)$ exhibits a smooth evolution across $T_0$ and rather slowly increases vs. decreasing $T$, while primary time-odd $\xi^2_\text{SEI}(T)$ features a discontinuity in the slope at $T_0$, as expected, with a rapid growth for $T < T_0$, reaching about 60% of total magnitude at $3/4 T_0$. This behavior of $\xi_\text{SEI}^2(T)$ is in a perfect agreement with the shape of temperature dependence of the volume anomaly (20), thus confirming that it is induced directly by the time-odd primary order.
Discussion
In conclusion, we have applied an advanced ab initio framework to the HO phase of neptunium dioxide NpO$_2$. Our framework is based on the density functional + DMFT (DFT + DMFT) in conjunction with a quasistatic approximation to local correlations on Np 5f. Its crucial part is a force theorem method (38) that we employ to calculate SEIs between all multipole moments of the Np f$^3$ lowest CF manifold. From the resulting superexchange Hamiltonian, we derive all order parameters of the HO phase, its ordering temperature, magnetic excitations, and volume effect. In fact, numerous properties of the NpO$_2$ HO phenomenon that have been painstakingly determined in experiments over several decades—absence of conventional magnetic order, the CF-level scheme, the primary triadcapole order and secondary longitudinal 3k quadrupole order, the singlet–doublet–singlet exchange splitting of the CF ground state, the two-peak structure of the magnetic quadrupole order, the singlet–doublet–singlet exchange splitting of symmetric paramagnetic phase combined with the force theorem—can be predicted and their interplay with various parameters—external or chemical pressure, applied field, lattice distortions—identified, thus opening up an avenue for theoretical search of new exotic phases of matter.

Methods

DFT + Hi First-Principles Calculations. Our charge self-consistent DFT + DMFT calculations using the Hi approximation for Np 5f, abbreviated as DFT + Hi, were carried out for the CaF$_2$-type cubic structure of NpO$_2$ with the experimental lattice parameter $a = 5.434$ Å. We employed the Wien-2k full-potential code (47) in conjunction with “TRIQS” library implementations for the DMFT cycle (36, 48) and Hi. The spin-orbit coupling was included in Wien2k within the standard second-variation treatment. The Brillouin zone (BZ) integration was carried out using 1,000 k points in the full BZ, and the local density approximation (LDA) was employed as DFT exchange correlation potential.

The Wannier orbitals representing Np 5f states were constructed by the projective technique of refs. 49 and 50 using the Kohn–Sham bands enclosed by the energy window $[−2.04:2.18]$ eV around the Kohn–Sham Fermi energy; this window thus encloses all Np 5f-like bands. The use of a narrow window enclosing only the target (5f-like) band for the construction of local orbitals results in a so-called “extended” Wannier basis. By employing such a basis within DFT + Hi, one may effectively include the contribution of hybridization to the CF splitting on localized shells, as discussed in ref. 51. The same choice for the local 5f basis was employed in our previous DFT + Hi study (52) of UO$_2$, resulting in a good quantitative agreement of the calculated CF splitting with experiment.

The on-site Coulomb interaction between Np 5f was specified by the Slater parameter $F_0 = 4.5$ eV and the Hund’s rule coupling $J_H = 0.6$ eV; the same values were previously employed for UO$_2$ (52). The double-counting correction was computed using the fully localized limit (53) with the atomic occupancy of Np f$^3$ shell (54). The DFT + DMFT charge self-consistency was implemented as described in ref. 55. In our self-consistent DFT + Hi calculations, we employed the spherical averaging of the Np 5f charge density, following the approach of Delange et al. (56), in order to suppress the contribution of LDA self-interaction error to the CF. The DFT + Hi calculations were converged to 5 mRy in the total energy.

CF and SEIs. The self-consistent DFT + Hi calculations predict a CF split $^{1}I_{8/2}$ atomic multiplet to have the lowest energy, in agreement with Hund’s rules for an f$^3$ shell; the calculated spin-orbit coupling $\lambda = 0.27$ eV. The CF splitting of the $^{1}I_{8/2}$ multiplet predicted by these calculations is shown in Fig. 1A, rank multipole moments. HOs, stemming from coupling between those moments, can be predicted and their interplay with various parameters—external or chemical pressure, applied field, lattice distortions—identified, thus opening up an avenue for theoretical search of new exotic phases of matter.

Fig. 4. Multipolar exchange striction in NpO$_2$. The curves represent the DFT + U elastic energy (green) and the ordering energy of the multipolar ground state vs. volume (blue); the latter is calculated from the volume-dependent ab initio SEIs. The multipolar order is seen to induce the contraction of the equilibrium volume (total energy; red curve) due to the two-site multipolar striction effect, analogously to the two-site volume magnetostriction in conventional magnetically ordered materials. The “springs” in Inset schematically illustrate the action of the intersite superexchange energy upon the onset of NpO$_2$ multipolar order.
and the corresponding CF WFs are listed in SI Appendix, Table S1. The cubic CF parameters—$A^M_{ij}(r^M)$ = $-152$ meV, $A^R_{ij}(r^R) = 5A^M_{ij}(r^M)$, $A^A_{ij}(r^A) = 32.6$ meV, and $A^B_{ij}(r^B) = 21A^A_{ij}(r^A)$—were extracted by fitting the converged DFT + Hf one-electron $5f$-level positions (56).

Within this method, matrix elements of intersite coupling $V^K$ for the Np–Np bond R read

$$
(M_i M_j | V^K | M_i M_k) = \text{Tr} \left\{ \left( V^S_{M_i M_j} a^\dagger_{M_i M_k} - R^0_{M_i M_j} \right) G_{R^0_{M_i M_j}} G_{R^0_{M_i M_k}} a^\dagger_{M_i M_k} \right\},
$$

where $R^0_{M_i M_j}$ is the corresponding element of the $J_{eff} = 3/2$ density matrix on site $R_0$, $V^K_{M_i M_j}$ is the derivative of atomic (HI) self-energy $\Sigma^{\text{CF}}$ over a fluctuation of the $R^M_{M_j}$ element, and $G_{R^0_{M_i M_j}}$ is the inter-site Green’s function for the Np–Np bond R evaluated within the DFT + Hf. After all matrix elements (3) are calculated, they are transformed to the couplings $V^K_{M_i M_j}$ on site $R_0$ by

$$
V^K_{M_i M_j} = \sum (M_i M_j | V^K | M_i M_k) \delta_{kk'},
$$

where $\delta_{kk'}$ is the Kronecker delta. $V^K_{M_i M_j}$ is the $M_i M_j$ matrix element of the real spherical tensor defined in accordance with equation 10 in Santini et al. (8). The SE matrix $V$ shown in Fig. 18 was subsequently obtained by rotating calculated $V$ by 45° about the [010] axis, thus aligning one of the NN bonds R with z.

### MF Calculations and Analysis of Order Parameters

We solved the obtained superexchange Hamiltonian (2) using the numerical MF package MCMFPHASE (44) including all 1k structures up to $4 \times 4 \times 4$ unit cells. We have also verified the numerical solution by an analytical approach. Namely, the MF equations read

$$
\left\{ \left. \bar{\rho}_{\alpha \beta}(q) \right| \sum_{\varepsilon} \left( \bar{\rho}_{\alpha \beta}(\varepsilon) - \chi_{\alpha \beta}^{\text{eff}}(q, \varepsilon) \right) \phi_{\alpha}(q) \right\} = \frac{1}{Z} \left\{ \left. \bar{\rho}_{\alpha \beta}(q) \right| \sum_{\varepsilon} \left( \bar{\rho}_{\alpha \beta}(\varepsilon) - \chi_{\alpha \beta}^{\text{eff}}(q, \varepsilon) \right) \phi_{\alpha}(q) \right\},
$$

where $\bar{\rho}_{\alpha \beta}(q)$ is the MF Hamiltonian for sublattice a, $\phi_{\alpha}(q)$ is the SE matrix between sublattices a and b ($\bar{\rho}_{\alpha \beta}(q) = 1/\sum_{\varepsilon} |R_0| \bar{\rho}_{\alpha \beta}(q) \psi_\varepsilon$ with $R_0 \in a$), $\phi_{\alpha}(q)$ is the corresponding Boltzmann weight.

After the $J_{eff}$ susceptibility matrix $\chi_{\alpha \beta}(q, E)$ is calculated, it is “upfolded” to the physical $J = 9/2$ space similarly to the $\psi_{\alpha}(q)$ density matrix as described above. The magnetic susceptibility $\chi_{\alpha \beta}(q, E)$ is given by the DD blocks of the upfolded $\chi(q, E)$ summed over the sublattice indices.

### Data Availability

All relevant data are available within the manuscript and SI Appendix. Raw computational data have been also deposited in the publicly accessible Materials Cloud Archive (10.24435/materialscloud:12-7q) (60).

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