Structure of the hidden order and multipolar exchange springs in NpO₂

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The nature of order in low-temperature phases of some materials is not directly seen by experiment. Such “hidden orders” (HO) may inspire decades of research to identify the mechanism underlying those exotic states of matter. The dioxide of neptunium NpO₂ is a prototypical HO system, where the primary order parameter is believed to be of rank-5 (triakontadipolar), but the microscopic interactions driving this order are still not resolved. Here, we show how the exotic HO physics in NpO₂ can be fully described by a low-energy Hamiltonian derived by a many-body ab initio force-theorem method. Superexchange interactions for the lowest Γ₈ crystal-field quadruplet of Np⁴⁺ ions induce a primary 3k time-odd rank-5 order with a secondary quadrupole order preserving the cubic symmetry of NpO₂. The calculated on-site exchange splitting and magnetic excitation spectra of the HO phase agree well with experiment. An observed anomalous volume contraction in the NpO₂ HO phase is shown to be induced by a two-site multipolar exchange striction.

INTRODUCTION

Spontaneous symmetry breaking, or a phase transition, in extended systems is associated with emergence of a macroscopic order parameter, which is the statistical average over some physical observable. In some systems the onset of order is clearly observed in the behavior of thermodynamic functions, however, the order parameter is not detectable by standard probes like neutron scattering or magnetic susceptibility measurements. In metals such phenomena are typically associated with strongly correlated heavy-fermion behavior, as in the case of enigmatic URu₂Si₂. In correlated insulators HO phases typically originate in high-rank multipolar degrees of freedom on localized f and d-electron shells. It has been realized long time ago that in correlated magnetic insulators with strong spin-orbit coupling, apart from the ordinary Heisenberg interaction between localized spins, there may also exist inter-site interactions coupling higher order spin operators (magnetic multipoles). If those interactions are essentially large this might lead to a new state of matter - a multipolar order without any associated magnetic order. So far a purely multipolar order due to high-rank multipoles has been suggested only for few systems each such case attracting considerable interest.

Cubic insulating NpO₂ is the oldest known candidate for a purely high-rank magnetic multipolar order (MMO). A sharp second order phase transition at T₀ ≈26 K was detected in NpO₂ more than half-century ago, with no evidence for underlying magnetic order and structural transformations, apart from a small anomalous contraction of the cubic unit cell volume observed below T₀. At the same time, NMR measurements detect two inequivalent oxygen sites in the unit cell below T₀, due to lowering of the cubic symmetry from high-temperature Fm3m to Pn3m by a longitudinal order of Np quadrupoles. However, a primary quadrupolar order parameter initially suggested is excluded since muon spin-rotation measurements detect a non-zero magnetic density. Moreover, the crystal-field (CF) ground state quadruplet Γ₈ is split in the HO phase into two singlets and a doublet suggesting a time-odd primary order parameter. There is a multitude of possible high-rank odd order parameters realizable within the J =9/2 ground state multiplet of Np⁴⁺ (J =3.5, 7, i.e. octupolar, triakontadipolar, etc.). A lot of efforts has been directed over the last two decades to identify a possible primary order able to reconcile various experimental facts. In particular, assumption of a triakontadipolar AF 3k order of the Γ₅ symmetry was shown to lead to the best agreement with X-ray scattering and inelastic neutron scattering (INS) spectra. The same hypothesis is also strongly supported by estimates of the relative strength of odd Γ₅ multipole moments on the Np f⁵ shell in the presence of CF splitting.

Though there are substantial experimental evidences to support the 3k rank-5 order in NpO₂, the mechanism of its formation is still not well understood. The simplest possible form of the superexchange (SE) Hamiltonian, consisting of diagonal nearest-neighbor interactions between three Γ₅ triakontadipoles and between three dipole moments, has been employed in analysis of low-temperature susceptibility and INS data. The full structure of this Hamiltonian cannot be extracted from experiment due to a large number of possible SE interactions (SEI). The measured CF splitting of 55 meV between the Γ₈ ground-state and first exited CF level is much larger than T₀, suggesting SEI between Γ₈ states on neighboring Np ions as the origin of its exotic ordered phase. Such low-energy SE Hamiltonian has not been so far derived theoretically. Previous theoretical density-functional-theory+U (DFT+U) studies have confirmed the stability of a triakontadipolar order in NpO₂, however, they imposed an initial symmetry breaking con-
FIG. 1: Np 5f on-site splitting and Np-Np inter-site interactions in NpO₂. (a) Calculated crystal-field (CF) splitting of Np 5f₃/2 J=9/2 multiplet in paramagnetic state (left) and exchange splitting of the ground state quartet in the predicted ordered phase at zero temperature (right). Note the energy rescaling for the Γ₆ level on the CF splitting plot. Inset: crystal structure of the NpO₂. Positions of the Np-atoms is surrounded by the polar plot of the calculated primary order parameter (triacontadipoles) in the ground state. Different colors indicate four non-equivalent Np positions in the ordered state. The orange spheres are oxygen atoms. (b) SEI matrix between nearest-neighbor Np in NpO₂. These SEI couple multipolar operators \( \hat{O}_{lm} \) in the \( J_{\text{eff}} = 3/2 \) space of the Γ₈ CF ground state. Their values in the local coordinate system (with z-axis directed along the given bond direction and y-axis along the edge of the fcc lattice) are presented as a temperature map with the warm and cool colors representing, respectively, antiferromagnetic and ferromagnetic coupling of the corresponding multipoles.

consistent with the 3k rank-5 order inferred experimentally.

In this work we apply a novel framework to the problem of "hidden" multipolar orders in correlated insulators as exemplified by NpO₂. It consists in evaluating the full low-energy SE Hamiltonian from an ab initio description of the symmetric paramagnetic phase. We start with charge-self consistent DFT+dynamical mean-field theory \(^{30–32}\) calculations for paramagnetic NpO₂ treating Np 5f in the quasi-atomic Hubbard-I (HI) approximation \(^{33}\) (this method is abbreviated below as DFT+HI) to obtain its electronic structure and the composition of a CF-split Np 5f³ shell. A force theorem approach \(^{34}\) abbreviated FT-HI, is subsequently employed to derive SEIs between the calculated CF Γ₈ ground-state quadruplets. Our study represents first, to our awareness, ab initio electronic structure calculation of a complete SE Hamiltonian for high-rank magnetic multipoles in an f-electron crystalline material. By solving this Hamiltonian, we find a 3k rank-5 primary MMO accompanied by a secondary longitudinal quadrupole order. The calculated time-odd splitting of Γ₈ and magnetic excitation spectra are in a good agreement with experiment. The lattice contraction effect \(^{19}\) due to the MMO in NpO₂ is shown to stem from a volume dependence of the calculated SEI, which describes this small peculiarity with a quantitative precision. 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
Crystal-field splitting and super-exchange Hamiltonian

We start with evaluating the Np CF splitting in paramagnetic NpO₂; as discussed above, this splitting determines the space of low-energy states forming the MMO. The CF splitting of the Np 5f³ ground state multiplet \( J = 9/2 \) calculated by DFT+HI is shown in Fig[1]. The ground state Γ₈ quartet is separated from another, excited, Γ₈ quartet by 68 meV, in agreement with the experimental range for this splitting, 30-80 meV, inferred from INS measurements \(^{11,12,14}\). The broad experimental range for the excited Γ₈ 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 the NpO₂ in the framework of crystalline effective field model \(^{15}\)).
Our calculated CF corresponds to $x = -0.54$ parameterizing the relative magnitude of the 4 and 6-order contributions to the cubic CF. Our values are in good agreement with $x = -0.48$ inferred from INS measurements and analysis of CF excitation energies along the actinide dioxide series. The calculated wavefunctions of the CF ground-state quartet (see Supplementary Table I) feature a small admixture of the excited $J=11/2$ and $13/2$ multiplets.

The space of CF GS $\Gamma_8$ quadruplet is conveniently represented by the effective angular momentum quantum number $J_{eff}=3/2$, with the $\Gamma_8$ wave functions (WFs) labeled by the corresponding projection $M = -3/2 \ldots +3/2$ and the phases of WFs chosen to satisfy the time-reversal symmetry (see Supplementary Table I). The on-site degrees of freedom within the GS quadruplet are (pseudo) dipole, quadrupole, and octupole moments defined for $J_{eff}=3/2$ in the standard way. Hence, the most general form for a SE coupling between $\Gamma_8$ quadruplets on two Np sites reads

$$
\sum_{K,Q,K',Q'} V^{QQ'}_{KK'}(\mathbf{R}) O^Q_K(\mathbf{R}_0) O^{Q'}_{K'}(\mathbf{R}_0 + \mathbf{R}),
$$

where $O^Q_K(\mathbf{R}_0)$ and $O^Q_K(\mathbf{R}_0 + \mathbf{R})$ are the real spherical tensor operators for $J = 3/2$ of rank $K = 1$, 2, or 3, $-K \leq Q \leq K$, acting on the site $\mathbf{R}_0$ and $\mathbf{R}_0 + \mathbf{R}$, respectively, $V^{QQ'}_{KK'}(\mathbf{R})$ is the SEI that couples them; due to the translational invariance, $V^{QQ'}_{KK'}$ depends only on the intersite lattice vector $\mathbf{R}$.

We employed the FT-HI approach to evaluate all interactions $V^{QQ'}_{KK'}(\mathbf{R})$ from the converged DFT+HubI NpO$_2$ electronic structure for several first Np coordination shells. Only nearest-neighbor (NN) SEIs are significant, with longer distance ones being more than an order of magnitude smaller. The NN SEI matrix $\hat{V}(\mathbf{R})$ is graphically represented in Fig. 1b (see also Supplementary Table II) using a local coordinate system with the quantization axis $z || \mathbf{R}$. 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. In spite of this simplification, the SEI matrix $\hat{V}$ can in principle contain 70 distinct elements. The number of distinct non-zero 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 $y(x^2-3y^2)$ (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 non-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 SE in NpO$_2$, which may give rise to multiple competing time-

FIG. 2: Calculated multipolar order in NpO$_2$. This order of the physical multipoles in NpO$_2$ derived by mapping of the $J_{eff}=3/2$ space to the full $J=9/2$ space. The physical magnetic dipoles (magnetic moments) are exactly canceled on all Np sites, resulting in a purely multipolar order. (a) The primary physical order parameter, $K=5$ triakontadipole (b) The largest secondary “slave” order parameter, $K=4$ hexadecapole. The displayed isovalues for the primary and secondary order parameters is normalized with respect to the maximum possible value of a given moment in the $\Gamma_8$ crystal-field ground-state quartet. Hence the relative size of plotted moments indicates their relative magnitude. Black dashed lines are the primitive lattice translations of the original Np cubic face-centered sublattice, which in the ordered phase connect inequivalent Np sublattices. (c) Longitudinal 3k order of “slave” quadrupole moments, which are scaled on the plot by a factor of 4. Np-O bonds in ordered NpO$_2$ are indicated by dashed lines. One sees that in the Np tetrahedron around each O all ordered Np quadrupoles are directed either along the Np-O bonds, or form the same angle with those bonds. This longitudinal 3k quadrupolar order preserves the cubic positions of oxygen sites in the ordered phase of NpO$_2$, in contrast to the transverse 3k quadrupole order in UO$_2$. 

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odd orders. Therefore, as has been previously noted extracting a full SE Hamiltonian of NpO$_2$ from experimental (e.g., INS) data is virtually impossible due to a large number of parameters entering into the fit of an excitation spectra. The same difficulty is encountered by ab initio approaches based on total energy calculations for symmetry broken phases which require a large number of very precises calculations to extract multiple non-negligible matrix elements of $\hat{V}$, 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$_2$.

**Ordered state of NpO$_2$**

The calculated SE Hamiltonian for NpO$_2$ reads

$$H_{SE} = \frac{1}{N} \sum_{\mathbf{R} \in \text{NN}} \hat{O}(\mathbf{R}_0) \hat{V}(\mathbf{R}) \hat{O}(\mathbf{R}_0 + \mathbf{R}), \quad (2)$$

where $\mathbf{R}$ runs over all NN bonds in the Np fcc sublattice, $N$ is the number of Np sites, and we also introduced the obvious vector notation $\hat{O} = [O_{-1}^- \ldots O_{-3}^-]$ for multipole tensors. The SEI matrix $\hat{V}(\mathbf{R})$, eq. (1), is that in the local frame $\mathbf{R}||z$ (Fig. 1b) rotated to align $\mathbf{R}$ along the corresponding Np NN bond. We solved numerically within the mean-field (MF) approximation, obtaining a second-order transition at $T_0 \approx 38$ K, in good agreement with its experimental value of 26 K taking into account the usual mean-field overestimation of ordering temperatures. The numerical results were verified by a linearized (MF) theory, derived by first-order expansion of MF equations in the order parameters $\langle \hat{O} \rangle$, see Method section.

The resulting GS order of NpO$_2$ in the $J_{eff}$ space consists of a primary (pseudo) dipole-octupole order combined with secondary (pseudo) quadrupole one (see Supplementary Table III for the values of all $J_{eff}$ order parameters and Supplementary Figure 1). The pseudo-dipole 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 $\langle 1,1,0 \rangle$ and $\langle 3,1,0 \rangle$ directions in the fcc lattice, respectively. The origin of this inclined AF structure of pseudo-dipoles is in the dipole-octupole SEI; similarly to physical AF magnetic orders found in some materials with large SO that are likely induced by higher-order magnetic multipolar interactions. The pseudo-octupoles order is also oriented in non-symmetrical directions. The secondary pseudo-quadrupole order is of a $3k$ type, which we analyze in details below.

We subsequently mapped the moments calculated in the $J_{eff} = 3/2$ space into the observable multipolar moments that are defined in the physical $J = 9/2$ space of Np $5f^3$ GS multiplet (see Methods). The calculated physical multipole order of NpO$_2$ is displayed in Fig. 2a. Notice, that observable moments up to $K = 7$ can exist on an $f$-electron shell we show the largest primary (odd) and secondary (even) order parameters as well as the physically important quadrupole order. All non-zero multipole moments are listed in Supplementary Table IV. The physical dipole magnetic moments are found to completely vanish, since their contribution into the $\langle O_x \rangle$ and $\langle O_y \rangle$ pseudo-dipole $J_{eff} = 3/2$ moments is exactly canceled by that due to the $\langle T_x \rangle$ and $\langle T_y \rangle$ pseudo-octupoles. The primary order parameter is of rank-5 (triakontadipole); the physical octupole moments 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 multipole into the MIMO order in NpO$_2$. 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 structure similarly to the $3k$-AFM dipole order in UO$_2$, see Fig. 3a. 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 pseudo-quadrupole one, since the $\Gamma_5$ (or $t_{2g}$) pseudo-quarupoles directly map into the physical ones, apart from swapping $xy \leftrightarrow yz$ and $x^2-y^2 \leftrightarrow xx$. The resulting physical quadrupole order can be represented, in the space of $\Gamma_5$ quadrupoles $[O_{xz}, O_{yz}, O_{xy}]$, by four directions [111], [111], [111], and [111] 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 $\langle O_{zz} \rangle$ moments with the principal axes $z$ along the corresponding direction at each given site (Fig. 2). One sees that the ordered quadrupoles on the four Np sites forming the tetrahedron around each oxygen can either have their principal axes directed along the Np-O bonds towards the central O, or form the same angle of 70.5° with respect to those bonds. In both cases the tetrahedron symmetry is preserved. The first case is realized for two O along one of the principal cubic diagonals, while the second one is found for 6 others, resulting in the lowering of NpO$_2$ symmetry to $Pn3m$ from $Fm3m$ without any distortion of the cubic structure. This longitudinal $3k$ quadrupole order, previously proposed on the basis of resonant x-ray scattering and subsequently confirmed by the splitting of $^{17}$O-NMR spectra in ordered NpO$_2$ is thus predicted by our ab initio SE Hamiltonian.

**Exchange splitting and magnetic excitations**

Having obtained the MIMO of NpO$_2$ we subsequently calculated its excitation spectra, which has been previously measured, in particular, by INS.

The MIMO lifts the degeneracy of CF GS $\Gamma_5$ quartet, the resulting exchange splitting calculated from the ab initio SE Hamiltonian is depicted on the right panel of Fig. 1a. 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.
FIG. 3: Inelastic neutron-scattering (INS) spectra in ordered NpO$_2$. (a) INS cross-section $S(q, E)$ with the momentum transfer $q$ along a high-symmetry path in the fcc Brillouin zone. The special points are $\Gamma = [0,0,0]$, $X = [1,0,0]$, $W = [1, \frac{1}{2}, 0]$, $L = [\frac{1}{2}, \frac{1}{2}, \frac{1}{2}]$, in units of $2\pi/a$. (b) Powder (spherically averaged) INS cross-section vs. energy transfer $E$ for $|q| = 2.5$ Å$^{-1}$. The theoretical spectra was broadened with the Gaussian resolution function of 1.5 meV. The experimental points are from Magnani et al. and high-energy (10-20 meV) features vs. momentum transfer in the powder INS spectra (panel b). The experimental points are from Magnani et al. Theoretical points from the same work are calculated with a semi-empirical SE Hamiltonian, see text.

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$^{14}$ in the ordered phase; another broad excitation was observed in the range of 11-18 meV$^{20}$ see below. Previously, an exchange splitting of the $\Gamma_5$ was obtained assuming a diagonal uniform SEI between $\Gamma_5$ triakontadipoles tuned to reproduce the 5 GS to the excited doublet$^{20}$ thus obtained energy for the excited singlet is in agreement with our $ab$ initio result.

We also calculated the theoretical INS cross-section, $$\frac{d^2\sigma(q,E)}{dE dq} = S(q,E) \propto \sum_{\alpha,\beta} \left( \delta_{\alpha,\beta} - \frac{q_\alpha q_\beta}{q^2} \right) \text{Im}\chi_{\alpha\beta}(q,E),$$ where $E$ ($q$) the energy (momentum) transfer, respectively, $\alpha,\beta = x, y, z$, and $\chi_{\alpha\beta}(q,E)$ is the dynamical magnetic susceptibility. The latter was evaluated within the random-phase approximation (RPA) from the full calculated $ab$ initio SE Hamiltonian$^{[2]}$, see Methods. The resulting INS spectra $S(q,E)$ for $q$ along high-symmetry directions of the fcc lattice is displayed in Fig. 3. Along the $\Gamma - X$ path it is similar to that previously calculated from the simplified empirical SE Hamiltonian of Ref. 19. The $S(q,E)$ structure is richer along other directions showing multiple branches in the $E$ range from 4 to 8 meV. The experimental INS spectra $S(q,E)$ has not been measured so far due to lack of large single-crystal samples$^{[5]}$ hence, our result represents a prediction for future experiments. The calculated spherically averaged INS cross-section $\int S(q,E)dq$ is compared in Fig. 3, with that measured$^{[20]}$ on powder samples at the same $|q| = 2.5$ Å$^{-1}$. The theoretical INS spectra exhibits prominent peaks at around 6 meV and at about 12.5 meV, corresponding to the transition from the $\Gamma_5$ GS to the excited doublet and singlet, respectively.

The theoretical low-energy feature agrees very well with the measured INS spectra, once experimental broadening is taken into account, see Fig. 3b. The high-energy feature, though, is clearly split in experiment into two broad peaks centered at about 12 and 16 meV, respectively. In order to understand whether the relative weights of the low and high energy features is captured in the theory we employed the same analysis as Magnani et al.$^{20}$ 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 an excellent agreement with experiment up to $|q| = 2.5$ Å$^{-1}$. As noticed in Ref. 20, 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 semi-empirical SEI employed by Magnani et al. They speculated that this splitting might stem from complex realistic Np-Np SEIs, which they could not determine from experiment. In the present work we determined the full SE Hamiltonian for
the GS CF \( \Gamma_8 \) quadruplet. Hence, the fact that the splitting of INS high-energy feature is still not reproduced points out to its origin likely being a SE coupling between the ground-state and first excited \( \Gamma_8 \) quadruplets (a significant contribution of the very high-energy \( \Gamma_8 \) CF doublet is unlikely). This inter-quadruplet 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. Those interactions couple time-even moments, i.e., the quadrupoles within the \( J_{eff} \) space. However, the QQ coupling is rather expected to impact the shape of low-energy peak in Fig. 3b, since the corresponding lowest on-site excitation in the ordered phase (inset in Fig. 1) is due to reverting of the on-site quatorpole moment. Indeed, we recalculated the theoretical INS spectra (Fig. 3b) with the magnitude of QQ block in the SEI (Fig. 1) scaled by a factor from 0 to 5. These variations of the QQ coupling strength do modify the shape of low-energy peak but have no impact on the high-energy one. Since the lattice-mediated coupling is expected to modify exclusively the QQ block, it is thus quite unlikely to be the origin of the splitting.

**Multipolar exchange striction**

The onset of the “hidden order” phase \( \text{NpO}_2 \) is marked by an anomalous volume contraction vs. decreasing temperature (anti-Invar anomaly). The estimated total volume contraction in the ordered state as compared to the paramagnetic phase is 0.018\% at zero temperature.\textsuperscript{15} This effect cannot be attributed to the conventional volume magnetostriction, since ordered magnetic moments are absent in \( \text{NpO}_2 \). The volume contraction in \( \text{NpO}_2 \) may instead stem from the SEI coupling high-rank magnetic multipoles.

In order to make a quantitative estimation of the effect we evaluated the volume dependence of \( \text{NpO}_2 \) ordering and elastic energies. To that end we adopted the elastic constants calculated for \( \text{NpO}_2 \) in the framework of DFT+U+SOC approach.\textsuperscript{33} \( C_{11} = 404 \text{ GPa}, \ C_{12} = 143 \text{ GPa} \). The corresponding parabolic volume dependence of elastic energy \( E_{\text{elast}} = 1/3 (C_{11}/2 + C_{12}) \epsilon^2 \) where \( \epsilon = (V - V_0)/V_0 \) is the volume contraction, \( V_0 \) is the \( \text{NpO}_2 \) equilibrium volume 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 mean-field order and ordering energy vs. volume expansion or contraction. The SE 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 SE contribution shifts the equilibrium volume in the ordered state towards 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 (see scheme in Fig. 4 inset) pulling Np atoms closer as the order parameters increase below \( T_0 \). Interestingly, our approach is 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 to experimental estimate of 0.018\%\textsuperscript{14,39}

**DISCUSSION**

In conclusion, we have applied an advanced \textit{ab initio} framework to the “hidden-order” phase of Neptunium dioxide \( \text{NpO}_2 \). Our framework is based on the density-functional+dynamical mean-field theory (DFT+DMFT) in conjunction with a quasi-atomic approximation to local correlations on Np 5f. Its crucial part is a force-theorem method\textsuperscript{33} that we employ to calculate super-exchange interactions between all multipoles moments of the Np 5f\textsuperscript{3} lowest crystal-field (CF) manifold. From the resulting super-exchange Hamiltonian we derive all order parameters of the “hidden-order” phase, its ordering temperature, magnetic excitations and volume effect. In fact, numerous properties of the \( \text{NpO}_2 \)-“hidden-order” phenomenon that have been painstakingly determined
in experiments over several decades – absence of conventional magnetic order, the CF level scheme, the primary triandicapole 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-excitation spectra, the very small anti-Invar peculiarity of NpO2 thermal expansion – all of them are reproduced by our calculations that contain essentially no adjustable parameters. Hence, the present scheme is shown to provide full, parameter-free and quantitatively correct description of super-exchange in complex realistic correlated insulators. On the basis of our theory we may also identify the features that are not stemming from the inter-site coupling between the ground-state CF levels. For example, the splitting of the high-energy peak in NpO2 inelastic neutron scattering spectra likely stems from a super-exchange interaction with excited CF levels. This first-principles methodology – a dynamical mean-field treatment of symmetric paramagnetic phase combined with the force-theorem extraction of the full complex inter-site exchange responsible for the spontaneous symmetry breaking – can be applied to a wide range of rare-earth, actinide and heavy transition-metals correlated systems, in which the interplay of a large spin-orbit coupling with crystalline environment gives rise to a large degeneracy of the crystal-field ground state and high-rank multipole moments. “Hidden” orders, 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.

**METHOD**

**DFT+HI first-principles calculations.** Our charge self-consistent DFT+DMFT calculations using the Hubbard-I (HI) approximation for Np 5f, abbreviated as DFT+HI, were carried out for the CaF2-type cubic structure of NpO2 with the experimental lattice parameter \(a = 5.434\ \text{Å}\). We employed the Wien-2k full-potential code in conjunction with TRIQS library implementations for the DMFT code 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 1000 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. 44 and 45 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 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 UO2. The double-counting correction was computed using the fully localized limit (FLL) with the atomic occupancy of Np f3 shell. The DFT+DMFT charge self-consistency was implemented as described in Ref. 46. 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. in order to suppress the contribution of LDA self-interaction error to the crystal field. The DFT+HI calculations were converged to 5 \(\mu\)Ry in the total energy.

**Crystal-field and superexchange interactions.** The self-consistent DFT+HI calculations predict a crystal-field (CF) split \(4\)\(I_9/2\) atomic multiplet to have the lowest energy, in agreement with Hund’s rules for an f3 shell; the calculated spin-orbit coupling \(\lambda = 0.27\) eV. The predicted in these calculations CF splitting of the \(4\)\(I_9/2\) multiplet is shown in Fig. 1a and the corresponding CF wavefunctions are listed in Supplementary Table I. The cubic CF parameters \(A_0^0(r^s) = -152\) meV, \(A_2^0(r^s) = 5A_0^0(r^s)\), \(A_4^0(r^s) = 32.6\) meV, and \(A_6^0(r^s) = 21A_0^0(r^s)\) were extracted by fitting the converged DFT+HI one-electron 5f level positions.

The states of the CF ground-state quadruplet \(\Gamma_3\) were labeled by projection \(M\) of the pseudo-angular quantum number \(J_{eff} = 3/2\) as specified in Supplementary Table I. We subsequently employed the FT-HI method to evaluate all SEIs between the \(J_{eff} = 3/2\) quadruplet for several first Np-Np coordination shells. Previously the FT-HI method has been applied to systems with conventional magnetic primary order. Within this method matrix elements of inter-site coupling \(V_R\) for the Np-Np bond \(R\) read:

\[
\langle M_1M_3|V_R|M_2M_4 \rangle = Tr \left[ G_R \frac{\delta G_{\rho_{R_0}+R}^{\Sigma_{\rho_{R_0}}} \delta G_{\rho_{R_0}}^{\Sigma_{\rho_{R_0}}}}{\delta \rho^{M_0}_{R_0}} \left( - \frac{\delta R_0^{M_0}}{\delta \rho^{M_0}_{R_0}} \right) \right],
\]

where \(\rho^{M_0}_{R_0}\) is the corresponding element of the \(J_{eff} = 3/2\) density matrix on site \(R_0\), \(\delta G_{\rho_{R_0}}^{\Sigma_{\rho_{R_0}}}\) is the derivative of the atomic (Hubbard-I) self-energy \(\Sigma_{\rho_{R_0}}\) over a fluctuation of the \(\rho^{M_0}_{R_0}\) element, \(G_R\) is the inter-site Green’s function for the Np-Np bond \(R\) evaluated within the DFT+HI. Once all matrix elements \(\epsilon_{R_0}^{M_0}\) are calculated, they are transformed to the couplings \(V_{K'K}^{Q'Q}\) between on-site moments the following:

\[
V_{K'K}^{Q'Q}(R) = \sum_{M_1M_2} \langle M_1M_3|M_R\rangle \langle M_2M_4|V_{K'K}^{Q'Q} \rangle [O_{K}^{Q'}(J)]_{M_2M_1} [O_{K}^{Q}(J)]_{M_1M_3},
\]

where \([O_{K}^{Q}(J)]_{M_1M_2}\) is the \(M_1M_2\) matrix element of the real spherical tensor defined in accordance with eq. 10 in Santini et al. The SEI matrix \(V\) shown in Fig. 1b was subsequently obtained by rotating calculated \(V\) by 45°.
about the [010] axis thus aligning one of the NN bonds R with z.

Mean-field calculations and analysis of order parameters. We solved the obtained SE Hamiltonian \( \mathcal{H} \) using the numerical mean-field package MCPHASE 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 mean-field equations read

\[
\langle \hat{O} \rangle_a = \frac{1}{Z} \text{Tr} \left[ \hat{O}_a \exp(-\beta \hat{H}_{MF}^a) \right],
\]

where \( \hat{H}_{MF}^a = \sum_{b \neq a} \hat{O}_a \hat{V}_{ab} \langle \hat{O}_b \rangle \) is the mean-field Hamiltonian for sublattice \( a \), \( \hat{V}_{ab} \) is the SEI matrix between sublattices \( a \) and \( b \) \( \langle \hat{V}_{ab} \rangle = \frac{1}{2} \sum_{\mathbf{R}_a + \mathbf{R} \in a} \hat{V}_{a,\mathbf{R}} \) with \( \mathbf{R}_a \in a \), \( Z = \text{Tr} \left[ \exp(-\beta \hat{H}_{MF}^a) \right] \), \( \beta = 1/T \). Expanding the RHS of \( \langle \hat{O} \rangle \) to the linear order in \( \langle \hat{O} \rangle \) and allowing for four inequivalent simple-cubic Np sublattices, which is a minimal number needed to cover all possible ordered states on fcc lattice with a NN coupling, one obtains a system of 60 linear equations. Solutions of the linearized MF equations unambiguously identify primary order parameters. With both numerical and analytical MF approaches we obtained the highest ordering temperature (T=38K) and lowest free energy for the primary dipole-octupole order displayed in Supplementary Fig. 1.

This order in the \( J_{eff} = 3/2 \) space was subsequently mapped into the physical \( J = 9/2 \) space. The \( J_{eff} \) density matrix on the inequivalent site \( a \) reads \( \rho_a(J_{eff}) = \hat{O}_a \langle \hat{O} \rangle_a \), where \( \langle \hat{O} \rangle_a \) are the corresponding (pseudo) moments. This density matrix is unfolded into the one in the \( J = 9/2 \) space, neglecting small contributions of the excited \( J = 11/2 \) and \( 13/2 \) multiplets and renormalizing the \( \Gamma_8 \) CF states accordingly, as \( \rho_a(J) = [\Gamma_8] \rho_a(J_{eff}) [\Gamma_8] \), where \( [\Gamma_8] \) is the CF GS \( \Gamma_8 \) basis, with WF written as columns in the order of \( M = J_{eff}, \ldots, J_{eff} \). The physical \( J = 9/2 \) moments are then calculated in the standard way, \( \langle O \rangle_{K}^{Q} \rangle_a = \text{Tr} \left[ \rho_a(J)O \rangle_{K}^{Q} \right].

Calculations of dynamical susceptibility. In order to calculate the dynamical magnetic susceptibility \( \chi_{\alpha\beta}(\mathbf{q}, E) \) we implemented a general RPA approach (see, e.g., Ref. [54]). Namely, the general susceptibility matrix in the \( J_{eff} \) space reads

\[
\chi(\mathbf{q}, E) = [I - \chi_0(E)\hat{V}_a]^{-1} \chi_0(E),
\]

where \( \chi_0(E) \) is the local bare susceptibility, \( \hat{V}_a \) is the Fourier transform of SEI matrices \( \hat{V}_{a,\mathbf{R}} \), the bar .. designate a matrix in combined \( [a,\mu] \) indices, where \( a \) label inequivalent sublattices, \( \mu = [K, Q] \) labels multipole.

The local susceptibility \( \chi_{0a}(E) \) for the inequivalent site \( a \) is calculated from the MF eigenvalues \( E^a \) and eigenstates \( \Psi^{a} \):

\[
\chi_{0a}^{\mu \nu}(E) = \sum_{AB} \frac{\langle \Psi^{a}_{\mu} | O_{\alpha} | \Psi^{B}_{\nu} \rangle \langle \Psi^{B}_{\nu} | O_{\alpha} | \Psi^{a}_{\mu} \rangle}{E_{B}^{a} - E_{A}^{a} - E} \left[ p_{A}^{\alpha} - p_{B}^{\alpha} \right],
\]

where \( A(B) \) labels four eigenvalues and eigenstates of the MF Hamiltonian \( \hat{H}_{MF}^a \) on the site \( a \), \( p_{A(B)}^{\alpha} \) is the corresponding Boltzmann weight.

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

DATA AVAILABILITY

The data that support the findings of this study are available from the corresponding author on reasonable request.

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AUTHOR CONTRIBUTIONS

L.V.P. carried out the ab initio calculations and INS spectra simulations. S. K. carried out the order parameters’ analysis. Both authors contributed equally to solving the mean-field equations, analysis of the results and writing of the manuscript.

COMPETING INTERESTS

The authors declare no competing interests.
Supplementary information for
Structure of the hidden order and multipolar exchange springs in NpO₂
by L. V Pourovskii and S. Khmelevskyi

SUPPLEMENTARY TABLE I: CF wavefunctions and CF splitting (in meV) of the \( ^4I_{9/2} \) ground-state multiplet of Np \( f^3 \) calculated by DFT+HI for paramagnetic NpO₂. The states are written as the expansion \( \sum a(J,M) |J;M⟩ \) in pure angular momentum eigenstates \( |J;M⟩ \) of Np \( f^3 \). All contributions with \( a^2(J,M) > 0.005 \) are shown. The CF wavefunctions belonging the ground state \( \Gamma_8 \) quadruplet, the first excited CF \( \Gamma_8 \) quadruplet, and the second excited \( \Gamma_6 \) doublet are separated by horizontal lines. Notice the contributions into the CF wavefunctions due to the excited \( J = 11/2 \) and \( J = 13/2 \) atomic multiplets. For the ground state \( \Gamma_8 \) quadruplet the corresponding \( \mu_{eff} \) quantum numbers in the \( J_{eff} = 3/2 \) basis are shown. The change of phase of the \( \mu_{eff} = +3/2 \) CF wave function with respect to the \( \mu_{eff} = -3/2 \) one is necessary to account for the time-reversal symmetry of \( J_{eff} \).

| \( E - E_{GS} \) | \( \mu_{eff} \) | Eigenstates in \( |J,M⟩ \) basis |
|------|------|------------------|
| 0 | -3/2 | \( +0.667|9/2; -9/2⟩ - 0.594|9/2; -1/2⟩ + 0.221|9/2; +7/2⟩ + 0.144|11/2; -1/2⟩ - 0.074|13/2; -1/2⟩ |
| 0 | -1/2 | \( +0.769|9/2; -5/2⟩ + 0.504|9/2; +3/2⟩ + 0.128|11/2; +11/2⟩ + 0.082|11/2; +3/2⟩ |
| 0 | +1/2 | \( +0.769|9/2; +5/2⟩ + 0.504|9/2; -3/2⟩ - 0.128|11/2; -11/2⟩ - 0.082|11/2; -3/2⟩ |
| 0 | +3/2 | \( -0.667|9/2; +9/2⟩ + 0.594|9/2; +1/2⟩ - 0.221|9/2; -7/2⟩ + 0.144|11/2; +1/2⟩ + 0.074|13/2; +1/2⟩ |
| 68 | \( +0.849|9/2; -7/2⟩ - 0.261|9/2; +9/2⟩ + 0.226|11/2; +1/2⟩ + 0.093|11/2; -7/2⟩ |
| 68 | \( +0.728|9/2; -3/2⟩ - 0.509|9/2; +5/2⟩ - 0.200|11/2; -11/2⟩ - 0.107|11/2; +5/2⟩ - 0.089|11/2; -3/2⟩ |
| 68 | \( +0.728|9/2; +3/2⟩ - 0.509|9/2; -5/2⟩ + 0.200|11/2; +11/2⟩ + 0.107|11/2; -5/2⟩ + 0.089|11/2; +3/2⟩ |
| 68 | \( +0.849|9/2; +7/2⟩ - 0.261|9/2; -9/2⟩ - 0.226|11/2; -1/2⟩ - 0.093|11/2; +7/2⟩ |
| 307 | \( +0.639|9/2; -1/2⟩ + 0.512|9/2; -9/2⟩ - 0.175|11/2; +7/2⟩ + 0.171|9/2; +7/2⟩ - 0.078|11/2; -9/2⟩ |
| 307 | \( +0.639|9/2; +1/2⟩ + 0.512|9/2; +9/2⟩ + 0.175|11/2; -7/2⟩ + 0.171|9/2; -7/2⟩ + 0.078|11/2; +9/2⟩ |

Supplementary References

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SUPPLEMENTARY TABLE II: Superexchange interaction matrix $V_{KK'}^Q$ in the $J_{eff}$ space calculated by the FT-HI method for the nearest-neighbour Np-Np bond, in meV. The local coordinate frame with the bond along $z$ axis and $y$ along the cubic [100] direction is assumed. The order of $K$ and $Q$ is indicated in the first two columns. All matrix elements with the magnitude above 0.01 meV are shown.

|   | -1  | -0.65 |        | -0.15 | -0.60 | 0.07 | 0.95 | -0.41 | 0.52 | -0.44 | 0.08 | -0.08 | -0.30 | -0.68 |
|---|-----|-------|--------|-------|-------|------|------|-------|------|-------|------|-------|-------|-------|
| 1 | 0   | -0.47 | 1.62   |       |       |      |      |       |      |       |      |       |       |       |
|   | -2  |       | -0.04  |       |       |      |      |       |      |       |      |       |       |       |
|   | -1  |       | -0.13  |       |       |      |      |       |      |       |      |       |       |       |
| 2 | 0   | -0.289| 0.289  | -0.289| -0.289|      |      |       |      |       |      |       |       |       |
|   | 1   |       | -0.9 | -0.13 | 0.14 |      |      |       |      |       |      |       |       |       |
|   | 2   |       | -0.24 | 0.14  | 0.19 |      |      |       |      |       |      |       |       |       |
|   | 3   | 0.95  | 0.08  |       | 0.59 | -1.47| 0.18 |       |      |       |      |       |       |       |
|   | 1   | -0.41 | -0.08 |       | 0.18 | 0.59 | -0.05|       |      |       |      |       |       |       |
|   | 2   | 0.52  | -0.30 |       |      | 0.40 | 0.21 | 0.03  | -0.08|       |      |       |       |       |
|   | 3   | -0.44 | -0.68 |       |      | -0.47| 0.27 | -0.08 | 0.57 |       |      |       |       |       |

SUPPLEMENTARY TABLE III: $J_{eff} = 3/2$ dipolar and multipolar moments (order parameters) $\langle O_K^Q(J_{eff}) \rangle_R$ in the ordered phase of NpO$_2$, obtained by mean-field solution of the ab initio SE Hamiltonian (2). $R$ runs over all four inequivalent sublattices of the ordered phase. The definition of the tensors $O_K^Q(J_{eff})$ is given by eq. 10 in Santini et al.$^8$; the octupole tensors can be transformed into the symmetry-adapted ones for the cubic group using the transformation of Shiina et al.$^1$ All non-zero $\langle O_K^Q(J_{eff}) \rangle_R$ are listed. Note the planar, dipole order as well as the 3k quadrupole order.

|   | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| K | Q | | | | | | | | | | | | |
| dipole | | | | | | | | | | | | | |
| -1 | -0.158 | +0.158 | -0.158 | +0.158 | | | | | | | | | |
| +1 | -0.474 | -0.158 | +0.474 | +0.158 | | | | | | | | | |
| quadrupole | | | | | | | | | | | | | |
| -2 | -0.289 | +0.289 | +0.289 | -0.289 | | | | | | | | | |
| -1 | +0.289 | +0.289 | -0.289 | -0.289 | | | | | | | | | |
| +2 | +0.289 | -0.289 | +0.289 | -0.289 | | | | | | | | | |
| octupole | | | | | | | | | | | | | |
| -3 | -0.250 | +0.250 | -0.250 | +0.250 | | | | | | | | | |
| -2 | +0.204 | -0.204 | +0.204 | -0.204 | | | | | | | | | |
| -1 | +0.195 | -0.195 | +0.195 | -0.194 | | | | | | | | | |
| +1 | -0.065 | -0.452 | +0.065 | +0.452 | | | | | | | | | |
| +2 | +0.204 | -0.204 | -0.204 | +0.204 | | | | | | | | | |
| +3 | -0.250 | +0.250 | +0.250 | -0.250 | | | | | | | | | |
SUPPLEMENTARY FIGURE 1: **Multipolar order in the $J_{\text{eff}} = 3/2$ space.** This is a visualization of the NpO$_2$ order (Supplementary Table III) in the $J_{\text{eff}} = 3/2$ space of the $\Gamma_8$ crystal-field ground-state quartet of Np $f^3$. The primary order in the $J_{\text{eff}}$ space combines odd (pseudo-) dipole (a) and octupole (c) moments, which are coupled by super-exchange interactions. Pseudo-quadrupolar order (b) is a “slave” secondary order parameter. Different colors designates four nonequivalent ordered sublattices on the underlying fcc Np sublattice; O sites are not shown. For the dipoles we use the usual (vector) representation, whereas the higher multipoles are shown by their absolute-value isosurfaces, and the negative (positive) sign is indicated by black (other) color, respectively. The dipole order in (a) is projected along the [010] direction to highlight its planar nature and difference in the magnitude of $\langle O_T^x(J_{\text{eff}}) \rangle_R$ between the sublattices.
SUPPLEMENTARY TABLE IV: Physical \((J = \frac{9}{2})\) dipolar and multipolar moments (order parameters) \(\langle O_K^Q(J) \rangle_R\) in the ordered phase of NpO\(_2\), obtained by upfolding the \(J_{\text{eff}} = 3/2\) moments (Supplementary Table III above) as described in Methods. All non-zero \(\langle O_K^Q(J) \rangle_R\) are listed.

| K | Q | \([0,0,0]\) | \([\frac{1}{2}, \frac{1}{2}, 0]\) | \([\frac{1}{2}, 0, \frac{1}{2}]\) | \([0, \frac{1}{2}, \frac{1}{2}]\) |
|---|---|---|---|---|---|
| quadrupole | -2 | +0.06 | +0.06 | -0.06 | -0.06 |
| | -1 | -0.06 | +0.06 | +0.06 | -0.06 |
| | +1 | +0.06 | -0.06 | +0.06 | -0.06 |
| octupole | -3 | +0.02 | -0.02 | +0.02 | -0.02 |
| | -1 | -0.03 | +0.03 | -0.03 | +0.03 |
| | +1 | -0.03 | +0.03 | +0.03 | -0.03 |
| | +2 | +0.03 | +0.03 | -0.03 | -0.03 |
| | +3 | -0.02 | +0.02 | +0.02 | -0.02 |
| hexadecapole | -3 | -0.14 | +0.14 | +0.14 | -0.14 |
| | -2 | +0.14 | +0.14 | -0.14 | -0.14 |
| | -1 | +0.05 | -0.05 | -0.05 | +0.05 |
| | +1 | -0.05 | +0.05 | -0.05 | +0.05 |
| | +3 | -0.14 | +0.14 | -0.14 | +0.14 |
| triakontadiople | -5 | -0.19 | +0.19 | -0.19 | +0.19 |
| | -3 | +0.08 | -0.08 | +0.08 | -0.08 |
| | -1 | +0.18 | -0.18 | +0.18 | -0.18 |
| | +1 | +0.18 | -0.18 | +0.18 | -0.18 |
| | +2 | +0.28 | +0.28 | -0.28 | -0.28 |
| | +3 | -0.08 | +0.08 | +0.08 | -0.08 |
| | +5 | -0.19 | +0.19 | +0.19 | -0.19 |
| 6 | -6 | +0.01 | +0.01 | -0.01 | -0.01 |
| | -5 | +0.02 | +0.02 | +0.02 | -0.02 |
| | -3 | +0.01 | -0.01 | -0.01 | +0.01 |
| | -2 | +0.03 | +0.03 | -0.03 | -0.03 |
| | -1 | -0.02 | +0.02 | +0.02 | -0.02 |
| | +1 | +0.02 | -0.02 | +0.02 | -0.02 |
| | +3 | +0.01 | -0.01 | +0.01 | -0.01 |
| | +5 | +0.02 | -0.02 | +0.02 | -0.02 |
| 7 | -7 | +0.08 | -0.08 | +0.08 | -0.08 |
| | -5 | -0.05 | +0.05 | -0.05 | +0.05 |
| | -3 | +0.04 | -0.04 | +0.04 | -0.04 |
| | -1 | -0.11 | +0.11 | -0.11 | +0.11 |
| | +1 | -0.11 | +0.11 | +0.11 | -0.11 |
| | +2 | +0.11 | +0.11 | -0.11 | -0.11 |
| | +3 | -0.04 | +0.04 | +0.04 | -0.04 |
| | +5 | -0.05 | +0.05 | +0.05 | -0.05 |
| | +6 | +0.11 | +0.11 | -0.11 | -0.11 |
| | +7 | -0.08 | +0.08 | +0.08 | -0.08 |