Effects of the structural distortion on the electronic band structure of NaOsO$_3$ studied within density functional theory and a three-orbital model

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(Dated: October 27, 2017)

Effects of the structural distortion associated with the OsO$_6$ octahedral rotation and tilting on the electronic band structure for the $5d^3$ compound NaOsO$_3$ are investigated using the density functional theory (DFT) and within a three-orbital model. Comparison of the essential features of the DFT band structures with the three-orbital model for both the undistorted (cubic) and distorted (orthorhombic) structures provides insight into the orbital and directional asymmetry in the electron hopping terms resulting from the structural distortion. The orbital mixing terms obtained in the transformed hopping Hamiltonian resulting from the octahedral rotations are shown to account for the fine features in the DFT band structure. Study of staggered magnetization indicates weak coupling behavior, suggesting relevance of Slater mechanism in the magnetic transition.
I. INTRODUCTION

The strongly spin-orbit coupled $5d^3$ osmium compounds NaOsO$_3$ and Cd$_2$Os$_2$O$_7$ exhibit several novel electronic and magnetic properties. These include G-type antiferromagnetic (AFM) structure for NaOsO$_3$ with spins oriented along the $c$ axis, significantly reduced magnetic moment ($\sim 1\mu_B$) as measured from neutron scattering and ascribed to itinerant-electron behavior due to hybridization between Os $5d$ and O $2p$ orbitals, continuous metal-insulator transition (MIT) that coincides with the AFM transition ($T_N = T_{\text{MIT}} = 410$ K) as seen in neutron and x-ray scattering, and large spin wave energy gap of 58 meV as seen in resonant inelastic X-ray scattering (RIXS) measurements indicating strong magnetic anisotropy. Large spin wave gap has also been observed in the frustrated type I AFM ground state of the double perovskites Ba$_2$YOsO$_6$, Sr$_2$ScOsO$_6$, Ca$_3$LiOsO$_6$ in neutron scattering and RIXS studies of the magnetic excitation spectrum, highlighting the importance of spin-orbit coupling (SOC) induced anisotropy despite the nominally orbitally-quenched ions in the $5d^3$ and $4d^3$ systems.

First-principle calculations have been carried out to investigate the electronic and magnetic properties of the orthorhombic perovskite NaOsO$_3$, related osmium based perovskites AOsO$_3$ ($A=$Ca,Sr,Ba), and double perovskites Ca$_2$CoOsO$_6$ and Ca$_2$NiOsO$_6$. Density functional theory (DFT) calculations have shown that the magnetic moment is strongly reduced from $3\mu_B$ in the localized-spin picture to nearly $1\mu_B$ (essentially unchanged by SOC) due to itineracy resulting from the strong hybridization of the $t_{2g}$ orbitals with the oxygen $2p$ orbitals, which is significantly affected by the structural distortion. Furthermore, from total energy calculations for different spin orientations with SOC included, the easy axis was determined as $\langle 001 \rangle$ as also observed by Calder et al. with large energy cost for orientation along the $\langle 010 \rangle$ axis and very small energy difference between orientations along the nearly symmetrical $a$ and $c$ axes.

A moderate $U$ value $\sim 1$-$2$ eV has been considered in earlier DFT studies for producing the insulating state with a G-type AFM order. For the distorted structure with SOC, an indirect band gap is seen to open only at a critical interaction strength $U_c \approx 2$ eV. Below $U_c$, the indirect band gap becomes negative due to lowering of the bottom of the conduction band. Similarly, metallic band structure is obtained for the undistorted structure. Optimal value of $U \sim 0.5$ eV has been estimated based on the low temperature optical gap of 0.1
These studies suggest that NaOsO$_3$ is a weakly correlated system in which Coulomb interaction and structural distortion effects on electron hopping and band structure are comparable.

A recent RIXS study of the electronic and magnetic excitations in NaOsO$_3$ shows that while local electronic excitations do not change appreciably through the MIT, the low energy magnetic excitations present in the insulating state become weakened and damped through the MIT$^{12}$ presumably due to self doping. Such continuous progression towards the itinerant limit through MIT is suggested to provide physical insight into the nature of the MIT beyond the relativistic Mott or pure Slater type insulators.

Besides the Mott-Hubbard and Slater pictures, the “spin-driven Lifshitz transition” mechanism proposed recently$^{10}$ is relevant for systems with small electron correlation and large hybridization. This mechanism, which relies on the small indirect band gap in the AFM state in the presence of strong SOC, with the bottom of the upper band descending below the Fermi energy on increasing temperature accompanied with progressively growing small electron pocket, can account not only for the continuous metal-insulator transition but also the concomitant magnetic transition, with low transition temperature despite the large magnetic anisotropy energy. Although weak correlation effects are central to the Slater scenario for both NaOsO$_3$ and Cd$_2$Os$_2$O$_7$ which exhibit continuous MIT concomitant with three dimensional AFM ordering, magnetic interactions and excitations in both compounds have been studied only within the localized spin picture. A minimal three-orbital-model description of the electronic band structure within the $t_{2g}$ sector for the sodium osmate compound NaOsO$_3$ and a microscopic understanding of the large magneto-crystalline anisotropy within such a minimal model have not been investigated so far.

In this paper, we will therefore investigate the electronic band structure within a minimal three-orbital model, specifically aimed at identifying the orbital and directional asymmetry introduced in the electron hopping parameters due to the OsO$_6$ octahedral rotation and tilting. Moderate bandwidth reduction due to the octahedral rotations has been noted as an important contributing factor to the gapped AFM state. In this paper, we will show that this bandwidth reduction is slightly orbitally and directionally asymmetric, which is expected to play a crucial role in the expression of the SOC-induced magnetic anisotropy in this compound.

The structure of this paper is as follows. DFT investigation of the electronic band struc-
ture for NaOsO$_3$ is presented in Sec. II, including discussion of the density of states (DOS) for Os, AFM ordering and reduced magnetic moment, and effect of octahedral rotations on the band structure. In Sec. III, the electronic band structure and staggered magnetization are studied within a minimal three-orbital model and compared with DFT results for both the undistorted (cubic) and distorted (orthorhombic) structures. In the last part of this section we will highlight the orbital and directional asymmetry in the hopping terms resulting from the cubic symmetry breaking, followed by conclusions in Sec. IV.

II. DENSITY FUNCTIONAL ELECTRONIC STRUCTURE

Crystal structure of NaOsO$_3$ is orthorhombic with space group $P_{nma}$ (62) consisting of four formula units per unit cell. The experimental lattice constants are $a=5.384$ Å, $c=5.328$ Å and $b=7.58$ Å. The unit cell is approximately $\sqrt{2}a_0 \times \sqrt{2}a_0$ in the $ac$ plane and doubled ($2a_0$) perpendicular to the plane, where $a_0$ is the nearest-neighbor Os-Os distance in the plane. In the plane, the Os octahedra tilt by 12.48°, which is a rotation about the $a$ axis, followed by a second rotation of 8.74° about the $b$ axis as discussed in the Appendix. Along the $b$ axis, a doubling of the unit cell occurs due to the out-of-phase tilting of adjacent Os octahedra. The Wyckoff’s positions according to the site symmetry are: Na(4c), Os(4b), O(4c), and O(8d).

The full-potential linearized muffin-tin orbital (LMTO) method$^{14–16}$ was used to calculate the electronic band structure within the local spin density approximation (LSDA)$^{17}$ for the exchange and correlation functional including the Hubbard $U$ and SOC (LSDA+SO+U), with SOC=0.4eV and $U=2eV$. The experimental lattice parameters were used throughout the calculations. The unshifted $k$-space mesh $8 \times 8 \times 6$ was used for the Brillouin-zone integration.

Fig. 1 shows the calculated total and partial DOS for a single Os atom within the LSDA+SO+U method. The orbital resolved PDOS shows that states near the Fermi level are mainly $t_{2g}$-like, as seen in Fig. 1 (c).

The calculated magnetic moment is shown in Table III (Sec. III). The magnetic moments are calculated by integrating the spin density within the muffin-tin sphere. In the absence of Coulomb repulsion, electrons are not fully spin polarized and the magnetic moment is therefore relatively small (0.66 $\mu_B$). With the inclusion of SOC, it is further reduced due...
FIG. 1: (Color Online) Density of states (DOS) for NaOsO$_3$ as obtained with the LSDA+SO+U method. Different panels show (a) total DOS in black (red) for spin ↑ (↓) per unit cell, (b) partial density of states (PDOS) of the $e_g$ states, and (c) exchange splitting in the $t_{2g}$ manifold for a single Os atom.

to spin mixing. Finally, when Coulomb interaction is included, the magnetic moment is enhanced, as expected, since the Coulomb term favors spin polarization in order to reduce the Coulomb energy. The calculated moment of 0.96 $\mu_B$ is in reasonable agreement with the experimental value of 1.0 $\mu_B$. Note that the calculated value can vary slightly depending on the size of the muffin-tin radius chosen.

The calculated spin density contours in the $ac$ plane for the electron states in the conduction bands are shown in Fig. 2. Each contour represents mainly the $d_{xy}$ part of the $t_{2g}$ orbitals, since the other two orbitals ($d_{xz}, d_{yz}$) have negligible contribution on this plane. The figure clearly shows the G-type AFM ordering.
FIG. 2: (Color Online) Contour plot of the spin density difference ($\rho^\uparrow - \rho^\downarrow$) on the $ac$ plane calculated for the electron states within 0.2 eV of the conduction band minimum, computed with the LSDA+SO+U method. The magnetic moment presented in Table III correspond to the net moment within the muffin-tin spheres indicated by the circles. Arrows indicate the net spins on the Os sites, indicating the AFM structure.

Band structures were calculated for both the real crystal structure and the undistorted (cubic) structure (without rotations) for the same G-type AFM configuration. We find a net energy gain of about 264 meV (per formula unit) for the distorted structure over the undistorted structure, consistent with previous works. The calculated DFT bands with and without structural distortion are shown in Figs. 4 and 5 in Sec. III. Band energies are shown along high symmetry directions in the Brillouin zone, defined with respect to the crystal axes. The momenta $k_x, k_y, k_z$ are in units of $a^{-1}, c^{-1},$ and $b^{-1},$ respectively, for the distorted structure.

The octahedral rotations modify the electron hopping parameters as discussed in the Appendix. As seen from the band structure plots [Figs. 4 and 5], we indeed find that octahedral rotations have important effects on the DFT bands. For instance, the band dispersion and the band width are significantly modified in the distorted structure. In fact, the bands near the Fermi energy become narrower and flatter in the distorted structure resulting in an insulating gap of $\sim 0.1$ eV. The positions of the conduction band minimum and the valence band maximum also shift. For example, there are multiple valence band maxima away from the $\Gamma$ point where the maximum lies for the undistorted structure. These modifications are discussed in the next section within a three-orbital model.
III. THREE-ORBITAL MODEL AND ELECTRONIC BAND STRUCTURE

The electronic and magnetic behaviour of the 5\textsuperscript{d}\textsuperscript{3} compound NaOsO\textsubscript{3} involve a complex interplay between SOC, structural distortion, magnetic ordering, Hund’s rule coupling, and weak correlation effect. While strong SOC would favor spin-orbital entangled states energetically separated into the \( J = 1/2 \) doublet and \( J = 3/2 \) quartet, strong Hund’s rule coupling would favor the spin-disentangled, high-spin nominally \( S = 3/2 \) state in the system with three electrons per Os ion. In the high-spin state, Hund’s rule coupling would also effectively enhance the local exchange field, supporting the weak correlation term in the formation of the AFM state in this half-filled system. The enhanced local exchange field would energetically separate the spin up and down states, thus self consistently suppressing the SOC.

In order to obtain a detailed microscopic understanding of the electronic and magnetic properties including magnetic anisotropy and large spin wave gap induced by spin orbit coupling in this half-filled AFM insulating system, it will be helpful to start with a simplified model for the electronic band structure. In this section, we will therefore consider a minimal three-orbital model involving the \( yz, xz, xy \) 5\textsuperscript{d} orbitals constituting the \( t_{2g} \) sector, aimed at reproducing the essential features of the DFT calculation discussed in the previous section.

A. Non-magnetic state

We start with the free part of the Hamiltonian including the local spin-orbit coupling and the band terms represented in the three-orbital basis \((yz\sigma, xz\sigma, xy\sigma)\)\textsuperscript{18}:

\[
\mathcal{H}_{SO} + \mathcal{H}_{\text{band}} = \sum_{k\sigma} \psi_{k\sigma}^\dagger \begin{pmatrix} \mathcal{E}_{yz}^{k} & i\sigma \frac{\lambda}{2} & -\sigma \frac{\lambda}{2} \\ -i\sigma \frac{\lambda}{2} & \mathcal{E}_{xz}^{k} & i\frac{\lambda}{2} \\ -\sigma \frac{\lambda}{2} & -i\frac{\lambda}{2} & \mathcal{E}_{xy}^{k} \end{pmatrix} \psi_{k\sigma} 
\]

(1)

where \( \mathcal{E}_{\mu}^{k} \) are the band energies for the three orbitals \( \mu = yz, xz, xy \), defined with respect to a common spin-orbital coordinate system. In the following it will be convenient to distinguish between the band energy contributions from hopping terms connecting opposite sublattices \( (\epsilon_{k}^{\mu}) \) and same sublattice \( (\epsilon_{k}^{\mu}) \). In addition to the orbital-diagonal band terms above, hopping terms involving orbital mixing will be considered below. For simplicity, we have considered
the two-sublattice case for illustration, which can be easily extended to the realistic four-
sublattice basis considered in the band structure study.

**B. AFM state and staggered field**

Including the symmetry-breaking staggered fields $-s\sigma.\Delta_\mu$ for the three orbitals $\mu = yz, xz, xy$, where $s = \pm 1$ for the two sublattices A/B, the staggered-field contribution:

$$\mathcal{H}_{sf} = \sum_{k\sigma s} s\sigma \psi_{k\sigma s}^\dagger \begin{pmatrix} -\Delta_{yz}^z & 0 & 0 \\ 0 & -\Delta_{xz}^z & 0 \\ 0 & 0 & +\Delta_{xy}^z \end{pmatrix} \psi_{k\sigma s}$$

for ordering in the $z$ direction. For general ordering direction with components $\Delta_\mu = (\Delta_{x\mu}, \Delta_{y\mu}, \Delta_{z\mu})$ for orbital $\mu$, the spin-space representation of the staggered field contribution:

$$\mathcal{H}_{sf} = \sum_{k\sigma s\mu} \psi_{k\sigma s\mu}^\dagger (-s\sigma.\Delta_\mu)_{\sigma\sigma'} \psi_{k\sigma' s\mu} = \sum_{k\sigma s\mu} s\sigma \psi_{k\sigma s\mu}^\dagger \begin{pmatrix} -\Delta_{\mu\mu}^z & -\Delta_{\mu\mu}^x + i\Delta_{\mu\mu}^y \\ -\Delta_{\mu\mu}^x - i\Delta_{\mu\mu}^y & \Delta_{\mu\mu}^z \end{pmatrix} \psi_{k\sigma' s\mu}$$

Combining the SO, band, and staggered field terms, the total Hamiltonian is given below in the composite three-orbital, two-sublattice basis, showing the hopping terms connecting same and opposite sublattices, and the staggered field contribution (for $z$ direction ordering). Also included are the hopping terms involving orbital mixing between $yz, xz$ and $xy$ orbitals due to the structural distortion resulting from the octahedral rotation and tilting. Involving nearest-neighbor (NN) hopping, these orbital mixing terms are placed in the sublattice-off-diagonal ($s\bar{s}$) part of the Hamiltonian:

$$\mathcal{H}_{SO} + \mathcal{H}_{band} + \mathcal{H}_{sf} = \sum_{k\sigma s} \psi_{k\sigma s}^\dagger \begin{pmatrix} \epsilon_{yz}^k & i\sigma^\frac{\lambda}{2} & -\sigma^\frac{\lambda}{2} \\ -i\sigma^\frac{\lambda}{2} & \epsilon_{xz}^k & \epsilon_{xy}^k \\ -\sigma^\frac{\lambda}{2} & -i\lambda^\frac{\lambda}{2} & \epsilon_{xy}^k \end{pmatrix} - s\sigma \begin{pmatrix} \Delta_{yz}^z & 0 & 0 \\ 0 & \Delta_{xz}^z & 0 \\ 0 & 0 & -\Delta_{xy}^z \end{pmatrix} \psi_{k\sigma s}$$

$$+ \sum_{k\sigma s} \psi_{k\sigma s}^\dagger \begin{pmatrix} \epsilon_{y\bar{z}}^k & \epsilon_{y|z\bar{z}}^k & \epsilon_{y|z\bar{z}}^k \\ -\epsilon_{y|z\bar{z}}^k & \epsilon_{z\bar{x}|z}^k & \epsilon_{z\bar{x}|z}^k \\ -\epsilon_{z\bar{x}|z}^k & -\epsilon_{x\bar{z}|x}^k & \epsilon_{x\bar{z}|x}^k \end{pmatrix} \psi_{k\sigma\bar{s}}$$

The staggered fields $\Delta_\mu$ are self-consistently determined from:

$$2\Delta_\mu = U_\mu m_\mu + J_H \sum_{\nu \neq \mu} m_\nu$$

(5)
in terms of the staggered magnetizations \( m_\mu = (m_\mu^x, m_\mu^y, m_\mu^z) \) for the three orbitals \( \mu \). The above staggered fields arise from the Hartree-Fock (HF) approximation of the electron correlation terms: \( \sum_{ij} U_\mu n_{i\mu\uparrow} n_{i\mu\downarrow} - 2J_H \sum_{i,\mu \neq \nu} S_{i\mu} S_{i\nu} \) in the AFM state. For ordering in the \( z \) direction (\( \Delta_\mu = \Delta \hat{z} \)), the staggered magnetizations are evaluated from the spin-dependent electronic densities \( n_{\mu\sigma} \) obtained by summing over the occupied states:

\[
m^{\hat{z}}_\mu(\Delta) = \frac{1}{N} \sum_{kl} |\phi_{kl\mu}^\uparrow|^2 - |\phi_{kl\mu}^\downarrow|^2 A(\Delta).
\]

where \( l \) is the branch label and \( N \) is the total number of \( k \) states. In practice, it is easier to consider a given \( \Delta \) and self-consistently determine the interaction strength \( U_\mu \) from Eq. 5.

We will also consider the energy resolved staggered magnetization \( \delta m = (1/3N_k) \sum_{kl} (n_{kl\mu\uparrow} - n_{kl\mu\downarrow}) \) averaged over the three orbitals, where \( \sum_k' \) indicates that band energies \( E_{kl\mu}^\sigma \) lie in a narrow energy range \( E \pm \delta E/2 \) of width \( \delta E \).

For straight Os-O-Os bonds (undistorted structure), all hopping terms between NN Os ions are orbital-diagonal with no orbital mixing. Due to twisting of Os-O-Os bonds associated with rotation and tilting of the OsO\(_6\) octahedra in NaOsO\(_3\), local cubic axis of OsO\(_6\) octahedra are alternatively rotated, giving rise to mixing between orbitals.

It is instructive to start with the atomic limit and consider how the SOC-split energy levels (the \( J=1/2 \) doublet and \( J=3/2 \) quartet) evolve with increasing local exchange field \( \Delta \) (assumed identical for all three orbitals for simplicity). While SOC tends to entangle the states with respect to orbital and spin, the exchange field tends to energetically disentangle
the spin up and down states for all orbitals. The resulting competition is shown in Fig. 3(a). The states which evolve linearly in energy with increasing $\Delta$ are the $J = 3/2$ sector states ($|yz, \sigma \rangle + |xz, \sigma \rangle)/\sqrt{2}$ with no spin mixing. Effect of this disentanglement is also evident from the growth of the local moment with staggered field $\Delta$ as shown in Fig. 3(b).

C. Tight-binding model for NaOsO$_3$

This orthorhombic-structure compound has four Os atoms per unit cell. This is because while neighboring OsO$_6$ octahedra within the $a - c$ plane undergo staggered rotation with respect to $b$ axis by angle $\sim 9^\circ$, the octahedral rotations are same for $b$-direction neighbors, which does not conform with the staggered (G-type) magnetic order. The OsO$_6$ octahedra also undergo staggered tilting by angle $\sim 12^\circ$ about the $a$ axis.

For the undistorted (cubic) case, we will consider identical hopping terms for all three orbitals and for equivalent directions corresponding to the cubic symmetry. Here $t_1$ ($\pi$ overlap), $t_2$ ($\sigma$ overlap), and $t_3$ ($\pi$ overlap) are the first, second, and third neighbor hopping terms, respectively. Furthermore, $t_{1\delta}$ is the first neighbor hopping term corresponding to the $\delta$ overlap, again for all three orbitals. An energy offset $\epsilon_{xy}$ for the $xy$ orbital relative to the degenerate $yz/xz$ orbitals has been included to allow for any signature of tetragonal splitting. The various band dispersion terms in Eq. (4) are given by:

\begin{align*}
\epsilon_{k}^{xy} &= -4t_1 \cos (k_x/2) \cos (k_y/2) - 2t_{1\delta} \cos k_z \\
\epsilon_{k}^{y'y'} &= -2t_2 (\cos k_x + \cos k_y) - 4t_3 \cos k_x \cos k_y + \epsilon_{xy} \\
\epsilon_{k}^{yz} &= -2[t_1 \cos \{(k_x - k_y)/2\} + t_1 \cos k_z + t_{1\delta} \cos \{(k_x + k_y)/2\}] \\
\epsilon_{k}^{y'z'} &= -4t_2 \cos \{(k_x - k_y)/2\} \cos k_z - 2t_3 [\cos(k_x - k_y) + \cos(2k_z)] \\
\epsilon_{k}^{xz} &= -2[t_1 \cos \{(k_x + k_y)/2\} + t_1 \cos k_z + t_{1\delta} \cos \{(k_x - k_y)/2\}] \\
\epsilon_{k}^{z'x'} &= -4t_2 \cos \{(k_x + k_y)/2\} \cos k_z - 2t_3 [\cos(k_x + k_y) + \cos(2k_z)] \\
\epsilon_{k}^{yz|xy} &= -4t_{m1} \cos (k_x/2) \cos (k_y/2) \\
\epsilon_{k}^{y|xy} &= +2t_{m2} [\cos \{(k_x + k_y)/2\} + 2 \cos \{(k_x - k_y)/2\} + \cos k_z] \\
\epsilon_{k}^{z|xy} &= -2t_{m2} [2 \cos \{(k_x + k_y)/2\} + \cos \{(k_x - k_y)/2\} + \cos k_z] 
\end{align*}

(7)

The $k$-space directions correspond to the crystal axes, whereas the $t_{2g}$ sector orbitals ($xz, yz, xy$) and the spin space directions are defined with respect to the OsO$_6$ octahedra
TABLE I: Hopping parameter values in the three-orbital-model for the undistorted structure in terms of the energy scale unit $|t_1|$.

| $t_1$ | $t_2$ | $t_3$ | $t_{\text{1s}}$ | $t_{m1}$ | $t_{m2}$ | $\epsilon_{xy}$ |
|-------|-------|-------|----------------|----------|----------|------------|
| -1.0  | 0.3   | 0     | 0              | 0        | 0        | 0          |

with coordinate axes along the Os–O directions as in Fig. 8 of Appendix. Here $k_x$ and $k_y$ are in unit of $(\sqrt{2}a_0)^{-1}$ while $k_z$ is in unit of $(2a_0)^{-1}$ corresponding to the $\sqrt{2}a_0 \times \sqrt{2}a_0 \times 2a_0$ unit cell.

Mixing between $xz$ and $yz$ orbitals and between $xy$ and $xz, yz$ orbitals is represented by the first neighbor hopping terms $t_{m1}$ and $t_{m2}$, respectively. The orbital mixing hopping terms are related to the OsO$_6$ octahedral rotation and tilting angles through $t_{m1} = V_x \theta_r = t_1 \theta_r$ and $t_{m2} = V_x \theta_t/\sqrt{2} = t_1 \theta_t/\sqrt{2}$ in the small angle approximation. This follows from the transformation of the hopping Hamiltonian matrix in the rotated basis, as shown in Eq. A.8 of the Appendix. The orbital mixing hopping terms have the usual antisymmetry properties: $\left[\epsilon_{yz}^{|x_z|s_{x}}^{|x_z|s_{x}}\right]_{ss'} = -\left[\epsilon_{xz}^{|x_z|y_{z}}^{|x_z|y_{z}}\right]_{ss'} = \left[\epsilon_{yz}^{|x_z|y_{z}}^{|x_z|y_{z}}\right]_{ss}$ etc. For the undistorted structure, we will set the orbital mixing terms to zero.

Figure 4 shows the calculated band structures for the undistorted case as obtained from DFT calculation without SOC (a) and with SOC (b), and correspondingly from the three-orbital model (c,d). To reproduce the essential features of the DFT band structure, we have taken hopping-parameter values as listed in Table I, staggered field $\Delta = 0.7$, and SOC = 0.8, with energy scale $|t_1| = 500$ meV ($\Delta = 0.35$ eV and SOC = 0.4 eV). The separation into two groups of three bands above and three below the Fermi energy corresponds to the scenario where Hund’s rule coupling dominates over spin-orbit coupling in the atomic limit. For no SOC, the upper band minima are degenerate at $X, Y, T$, but the minimum at $T$ becomes lower when SOC is included. As seen from Fig. 4(d), strong SOC-induced splitting of the energy bands (e.g., around $\Gamma$) results in negative indirect band gap. The electronic band structure calculated from the three-orbital model [Fig. 4(c,d)] is broadly consistent with DFT results [Fig. 4(a,b)].

For the distorted structure, we will allow for orbital and directional asymmetry in the hopping terms corresponding to the cubic symmetry breaking. In the following, $t^{(\mu)}_{n(s)}$ and $t^{(\mu)}_{n(d)}$ refer to the $n$th neighbor hopping term for orbital $\mu$ connecting sites in the same ($s$)
FIG. 4: Electronic band structures in the AFM state obtained for the undistorted structure from DFT calculation (a,b), and from the three-orbital model (c,d), without (a,c) and with (b,d) SOC. The momentum-space path considered is: $\Gamma(0,0,0) \rightarrow X(\pi,0,0) \rightarrow S(\pi,\pi,0) \rightarrow Y(0,\pi,0) \rightarrow \Gamma(0,0,0) \rightarrow Z(0,0,\pi) \rightarrow T(0,\pi,\pi) \rightarrow R(\pi,\pi,\pi)$.

and different (d) $xy$ planes, respectively. The $xy$ planes here are identified with respect to the octahedral rotation axis (taken as $z$). Due to the lifting of the cubic symmetry in the distorted case, and the resulting four-sublattice structure (A,B and $A',B'$ in alternating $xy$ planes) of the Os lattice, first neighbors in the same $xy$ plane involve AB / $A'B'$, whereas second neighbors involve AA / BB / $A'A'$ / $B'B'$. However, first neighbors in different $xy$ planes involve $AB' / A'B$, whereas second neighbors involve $AA' / BB'$.

It should be noted that for the $xy$ orbital, both first and second neighbor hopping terms connect sites in the same layer only. Similarly, for the $xz, yz$ orbitals, the second neighbor hopping terms connect sites in different layers only. However, the first neighbor hopping terms for the $xz, yz$ orbitals connect sites in both same and different layers. Therefore, in
FIG. 5: Electronic band structures in the AFM state of NaOsO$_3$ obtained from (a) DFT calculation and (b) the three-orbital model, both with SOC and structural distortion.

the following, we will consider $t_{1(s)}^{(xy)} \neq t_{1(d)}^{(xz)} = t_{2(s)}^{(xy)} \neq t_{2(d)}^{(xz)} = t_{2(d)}^{(yz)}$ etc.

Figure 5 shows the electronic band structures for the distorted case from DFT calculation and from the three-orbital model. In order to reproduce essential features and the overall energy scale of the DFT band structure, we have taken hopping-parameter values as listed in Table II, staggered field $\Delta = 0.9$, and SOC $= 1.0$, with energy scale $|t_{1(s)}^{(xy)}| = 400$ meV ($\Delta = 0.36$ eV and SOC $= 0.4$ eV). The octahedral distortion effect has been incorporated in our three-orbital model by introducing both orbital and directional asymmetries in hopping parameters, as discussed above.

The DFT bands clearly show that the valence band peak at $\Gamma$ (undistorted structure) shifts to finite momentum (distorted structure). This is accompanied with significant band narrowing near the top of the valence band [Figure 5]. We show here that these features can be reproduced by introducing first neighbor hopping asymmetry in the $z$ direction. Consider the band dispersion term for the $xz$ and $yz$ orbitals: $\varepsilon_{k}^{(\alpha)} = -2[t_{1(s)}^{(x)} \cos(k_{x}/2) + t_{1(d)}^{(x)} \cos k_{z}]$ along the $\Gamma \rightarrow X$ direction, where $k_{z} = \pi$ for the upper branch of the valence band near the $\Gamma$ point. Since this term contributes to the AFM state energy as: $-\sqrt{(\Delta^2 + \varepsilon_{k}^{(x)}^2)}$, the valence band peak near $\Gamma$ corresponds to $\varepsilon_{k}^{(x)} = 0$. Now, for $t_{1(s)}^{(x)} = t_{1(d)}^{(x)}$ (cubic symmetry), the peak occurs at $k_{x} = 0$ (Gamma point), as seen for the undistorted structure [Fig. 4]. However, $t_{1(d)}^{(x)} < t_{1(s)}^{(x)}$ for the peak to occur at finite $k_{x}$, as seen for the distorted structure [Fig. 5]. So the band structure for the distorted case clearly indicates a first neighbor hopping asymmetry for the $xz$ and $yz$ orbitals, with a reduced out-of-plane hopping.

The essential features distinguishing the distorted structure are: (i) overall energy scale
TABLE II: Hopping parameter values in the three-orbital-model for the distorted structure. The energy scale unit is $|t_{1(s)}^{(x,y)}|$ and $\alpha = xz, yz$.

| $t_{1(s)}^{(x,y)}$ | $t_{1(d)}^{(x,y)}$ | $t_{1(d)}^{(s)}$ | $t_{1(s)}^{(x,y)}$ | $t_{2(s)}^{(x,y)}$ | $t_{2(d)}^{(x,y)}$ | $t_{m1}$ | $t_{m2}$ | $\epsilon_{xy}$ |
|-------------------|-------------------|-------------------|-------------------|-------------------|-------------------|--------|--------|--------|
| -1.0              | -1.0              | -0.6              | -0.1              | -0.2              | 0.3               | 0.2    | 0.3    | 0.25   | 0      |

FIG. 6: Variation of (a) staggered magnetization with $U$ and (b) energy resolved staggered magnetisation with energy in the three-orbital model. SOC and hopping parameter values correspond to Fig. 4 (d) for the undistorted case.

reduction (from 500 meV to 400 meV), (ii) negative curvature at $\Gamma$ (resulting from $t_{1(s)}^{(x,y)} < t_{1(d)}^{(x,y)}$, $t_{2(d)}^{(x,y)} < t_{2(s)}^{(x,y)}$, orbital mixing), and (iii) the fine band splitting due to the orbital mixing term $t_{m2}$ (between $xy$ and $xz, yz$ orbitals). These modifications in the hopping parameters for the distorted structure correspond to effective bandwidth reduction for the $xz, yz$ orbitals compared to that for the $xy$ orbital.

Some other fine features can be further improved by incorporating additional terms in the three band model. For example, the energy of the lower branch at $S$ can be pulled down by including negative 2nd neighbor hopping $\tilde{t}_2$ ($\pi - \delta$ overlap) and positive 3rd neighbor hopping $t_3$ ($\pi$ overlap). The $S - Y$ versus $S - X$ asymmetry (conduction band) as seen in DFT calculation is obtained by including hopping asymmetry corresponding to $c < a$.

In order to determine the $U$ values corresponding to Figs. 4 and 5 for the band structure within the three-orbital model, we have also evaluated the staggered magnetization in the AFM state from Eq. 6. The $k$ sum over the three-dimensional Brillouin zone was performed using a $20 \times 20 \times 20$ mesh. For the undistorted case, Fig. 6 shows a strong variation of $m_\mu$. 


in the physically relevant $U$ range near $\Delta/|t_1| = 0.7$ as in Fig. 4(d), highlighting the weak correlation in NaOsO$_3$.

As indicated by the arrow in Fig. 6, we obtain $m_{\mu} \approx 0.48$ (for all three orbitals), yielding $m_{\text{total}} = \sum_{\mu} m_{\mu} \approx 1.4$. This is somewhat larger than our DFT result (Sec. II) and the experimental value of about 1 $\mu_B$ due to neglect of the strong Os – O hybridization which reduces the electron density on Os in the $t_{2g}$ sector. From Eq. 5 and assuming $J_H = U/4$, the self-consistently determined value $U \approx 1$ eV is within the estimated range for osmates. For the distorted structure (Fig. 5), we obtain $m_{xz} = m_{yz} \approx 0.54$ and $m_{xy} \approx 0.50$ for the staggered magnetizations and again $U \approx 1$ eV. This small orbital disparity is consistent with our finding of an effective bandwidth narrowing for the $xz, yz$ orbitals relative to the $xy$ orbital from our electronic band structure investigation.

Comparison of the magnetic moment values as obtained from the different methods used in our work is shown in Table III. The moment value in the atomic limit is obtained from Fig. 3(b) with $2\Delta \approx U$ and $\Delta/\lambda \sim 1$, corresponding to the physically relevant parameters. The large moment reduction in the band limit compared to the atomic limit highlights the highly itinerant character of the system.

TABLE III: Comparison of the magnetic moment values (in $\mu_B$) calculated within DFT and the three-orbital model.

| Method                | LSDA | +SO | +SO+U | Exp |
|-----------------------|------|-----|-------|-----|
| DFT                   | 0.66 | 0.22| 0.96  | 1   |
| Three-orbital model   | -    | -   | 1.4   | -   |
| Atomic limit          | -    | -   | 2.5   | -   |
terms for the distorted structure. The essential modifications required in the tight binding model include reduced $t_{1(d)}^{(\alpha)}$ and $t_{2(d)}^{(\alpha)}$ for $\alpha = xz, yz$ orbitals compared to the corresponding hopping terms $|t_{1(s)}^{(xy)}|$ and $t_{2(s)}^{(xy)}$ for the $xy$ orbital. These modifications in the hopping terms effectively amount to orbital bandwidth asymmetry, which is consistent with the slightly greater magnitude of the staggered magnetization for the $xz, yz$ orbitals compared to that for the $xy$ orbital in our three-orbital model.

As seen from Fig. 5, the distortion-induced bandwidth narrowing results in a marginally insulating system. Further reduction in $\Delta$ due to temperature will lead to formation of small electron (hole) pockets at the T (Γ) points, resulting in a continuous MI transition and magnetic transition due to the low DOS at the Fermi energy. This spin driven Lifshitz transition scenario has been recently proposed for the NaOsO$_3$ compound, where the continuous metal-insulator transition is suggested to be associated with a progressive change in the Fermi surface topology.$^{10}$

IV. CONCLUSIONS

The band structure of NaOsO$_3$ was investigated using density-functional methods. The calculated magnetic moment per Os atom is in good agreement with the experimental value. Our results show that NaOsO$_3$ is an AFM band insulator with a small gap ($\sim 0.1$ eV) consistent with experiments. Octahedral rotations have a significant effect on the band structure. While a negative indirect band gap is obtained for the undistorted structure, a small band gap opens up for the distorted structure with the octahedral rotations, along with significant bandwidth reduction and flattening of certain bands near the Fermi energy.

Essential features of the DFT band structure for both the undistorted and distorted structures were reproduced within a minimal three-orbital model with only the first- and second-neighbor hopping terms. Orbital and directional asymmetry in the electron hopping terms associated with the cubic symmetry breaking resulting from the structural distortion was clearly indicated in the band structure comparison. Orbitally asymmetric bandwidth reduction induced by structural distortion should be important for a microscopic understanding of the SOC-induced magneto-crystalline anisotropy in this compound.

The band structure comparison showed that some minute and robust features in the DFT band structure such as the fine band splitting and the conduction band features in the X-S-Y
momentum range can be ascribed to orbital mixing arising from the octahedral rotation and tilting. The required magnitudes of the orbital mixing terms are in good agreement with the analysis of the Hamiltonian matrix transformation induced by rotation and tilting.

The behaviour of staggered magnetization with interaction strength $U$ in the three-orbital model provides confirmation of weak coupling behavior, suggesting relevance of the Slater mechanism in the magnetic transition. Nearly 50% additional contribution to the staggered field is provided by the Hund’s coupling term, highlighting its importance in stabilizing the barely insulating AFM state in NaOsO$_3$, along with the bandwidth narrowing due to structural distortion.

Appendix: Transformation of the d electron tight-binding hopping matrix elements for osmates under rotation and tilting

In this Appendix, we provide the expressions for the tight-binding (TB) hopping integrals between the d orbitals located on two Os atoms. The atoms denoted by A and B are separated by a distance vector with direction cosines ($l$, $m$, and $n$) (Fig. 7), and the local coordinate axes (with respect to which the orbital lobes are defined) are rotated with respect to the crystalline axes. The local axes point towards the O atoms on the OsO$_6$ octahedra.

FIG. 7: Two neighboring Os sites, with the angles describing the octahedral rotation with respect to the crystalline axes. Direction cosines are denoted by $l$, $m$, and $n$.

In the osmates, the octahedra are more or less undistorted, but they are rotated with respect to the crystalline axes. The rotation can be described as a tilt and a rotation, which vary from site to site as indicated in Fig. 8. The local octahedral axes are obtained by first rotating the crystalline axes counterclockwise by the angle $\theta_t$ about the diagonal direction indicated by $a$ (this is referred to as tilting), followed by a rotation of $\theta_r$ about the $\hat{z}$ axis. These axes are fixed for every Os atom as are the magnitudes of the angles $\theta_t$ and $\theta_r$. 

FIG. 8: Tilt and rotation of the octahedra at the Os sites in NaOsO₃ (*left*). The two signs on each site indicate the sense of the tilt and the rotation, counter clockwise (+) or clockwise (−). The full rotation is described by the tilt $\theta_t$ (rotation about the $a$ axis), followed by the rotation $\theta_r$ (with respect to octahedral $\hat{z}$ axis). Octahedral orientations on the $ac$ plane (*right*); signs indicate the location of oxygen atoms above (+) or below (−) the $xy$ plane.

$\theta_r$ (both about $11^\circ$ for NaOsO₃), but the rotations and tilts are either counterclockwise (+) or clockwise (−) as indicated by the pair of signs next to each Os atom in Fig. (8). For example the ‘−+’ next to the Os atom at the origin means that the tilt and rotation angles there are given by ($-\theta_t$ and $+\theta_r$).

We follow the standard convention that the function contours are rotated and the coordinate axes (or the basis vectors) always stay fixed (active rotation).

Any rotation can be expressed in terms of the Euler angles, $\alpha$, $\beta$, and $\gamma$, for which we follow Rose’s definition. The sequence of the three rotations are: first rotate by $\gamma$ about the $z$ axis, then by $\beta$ about $y$, and finally by $\alpha$ about $z$ again, all in the original fixed coordinate system. The same transformation may be obtained by rotating in the reverse order about the intermediate axes, viz., first $\alpha$ about the original $z$ axis, then by $\beta$ about the intermediate axis $y'$, and finally by $\gamma$ about $z''$. Clearly, if $R_x(\theta)$ rotates the function by $\theta$ about $x$ axis, then the net effect of the rotation is given by the matrix $R(\alpha, \beta, \gamma) \equiv R_z(\theta)R_y(\beta)R_z(\gamma)$ (or, equivalently by $R_{x'\prime}(\gamma)R_{y'\prime}(\beta)R_z(\alpha)$, which is easier to visualize).

For the osmates, the final rotation matrix may also be generated by the sequence of the tilt and the rotation, viz., $R(\alpha, \beta, \gamma) = R_z(\theta_r)R_a(\theta_t)$. All angles vary from one Os atom to
another, as indicated in Fig. [8], and they are related by the expressions: \( \alpha = -45^\circ + \theta_r, \beta = \theta_t, \) and \( \gamma = 45^\circ. \)

Rotations don’t mix functions with different angular momenta \( L \), and therefore the d orbitals (\( L = 2 \)) transform among one another, the transformation determined by a site-dependent \( 5 \times 5 \) rotation matrix. We denote the unrotated orbitals as \( |\alpha\rangle \) (\( xy, yz, zx, x^2 - y^2, \) and \( z^2 - 1 \), in that order), rotated orbitals by \( |\alpha'\rangle \) on site A and \( |\alpha''\rangle \) on site B, the corresponding rotation matrices by \( R' \) and \( R'' \), so that \( |\alpha'\rangle = \hat{R}|\alpha\rangle \) and \( |\alpha''\rangle = \hat{R}'|\alpha\rangle \). Then the hopping integrals between the rotated orbitals are given by \( \tilde{H}_{\alpha'\beta''} \equiv \langle \alpha'|\hat{H}|\beta''\rangle = \langle \alpha|R'^T\hat{H}R''|\beta\rangle \), or

\[
\tilde{H} = R'^T\hat{H}R''.
\] (A.1)

**Rotation matrix for the Osmates** – It is convenient to express the total rotation matrices for the d orbitals on each Os site in terms of the two individual rotations, so that

\[ R(\theta_r, \theta_t) = R_z(\theta_r)R_\alpha(\theta_t), \] (A.2)

the two angles being positive or negative depending on the Os site. For pure rotations about \( \hat{z} \), the Euler angles are simply \( (\alpha, \beta, \gamma) = (\theta_r, 0, 0) \), while for pure tilt (rotation about \( \hat{a} \)), they are \( (\alpha, \beta, \gamma) = (-45^\circ, \theta_t, 45^\circ) \). Using these angles and the expression for \( R_2 \) (Eq. A.13), we readily get the results:

\[
R_z(\theta_r) = \begin{pmatrix}
xy & yz & zx & x^2 - y^2 & 3z^2 - r^2 \\
xy & \cos 2\theta_r & 0 & 0 & \sin 2\theta_r & 0 \\
yz & 0 & \cos \theta_r & \sin \theta_r & 0 & 0 \\
xz & 0 & -\sin \theta_r & \cos \theta_r & 0 & 0 \\
x^2 - y^2 & -\sin 2\theta_r & 0 & 0 & \cos 2\theta_r & 0 \\
x^2 - z^2 - r^2 & 0 & 0 & 0 & 0 & 1
\end{pmatrix}.
\] (A.3)

\[
R_\alpha(\theta_t) = \begin{pmatrix}
\frac{1}{2}(1 + \cos^2 \theta_t) & \frac{1}{2\sqrt{2}} \sin \theta_t & \frac{1}{2\sqrt{2}} \sin \theta_t & \frac{1}{2\sqrt{2}} \sin \theta_t & \frac{1}{2\sqrt{2}} \sin \theta_t & 0 & -\frac{1}{2} \sin^2 \theta_t \\
-\frac{1}{2\sqrt{2}} \sin \theta_t & \frac{1}{2}(2\cos^2 \theta_t + \cos \theta_t - 1) & \frac{1}{2} \sin \theta_t & \frac{1}{2} \sin \theta_t & 0 & -\frac{1}{2} \sin \theta_t & \sqrt{\frac{2}{3}} \sin \theta_t \\
\frac{1}{2\sqrt{2}} \sin \theta_t & -\frac{1}{2}(2\cos^2 \theta_t - \cos \theta_t - 1) & \frac{1}{2} \sin \theta_t & \frac{1}{2} \sin \theta_t & 0 & -\frac{1}{2} \sin \theta_t & \sqrt{\frac{2}{3}} \sin \theta_t \\
0 & -\frac{1}{2\sqrt{2}} \sin \theta_t & \frac{1}{2}(2\cos^2 \theta_t + \cos \theta_t - 1) & \frac{1}{2} \sin \theta_t & \frac{1}{2} \sin \theta_t & 0 & \frac{1}{2} \sin \theta_t \\
-\frac{1}{2}\sin^2 \theta_t & \sqrt{\frac{2}{3}} \sin \theta_t & -\frac{1}{2}\sin^2 \theta_t & 0 & \sqrt{\frac{2}{3}} \sin \theta_t & 0 & 1 - \frac{3}{2} \sin^2 \theta_t
\end{pmatrix}.
\] (A.4)
So the combined effect of tilting and rotation is given by the product of these matrices, and keeping terms linear in the angles, we get

\[
R(\theta_r, \theta_t) = \begin{pmatrix}
1 & \frac{1}{\sqrt{2}} \theta_t & -\frac{1}{\sqrt{2}} \theta_t & 2\theta_r & 0 \\
-\frac{1}{\sqrt{2}} \theta_t & 1 & \theta_r & -\frac{1}{\sqrt{2}} \theta_t & -\sqrt{\frac{3}{2}} \theta_t \\
\frac{1}{\sqrt{2}} \theta_t & -\theta_r & 1 & -\frac{1}{\sqrt{2}} \theta_t & \sqrt{\frac{3}{2}} \theta_t \\
-2\theta_r & \frac{1}{\sqrt{2}} \theta_t & \frac{1}{\sqrt{2}} \theta_t & 1 & 0 \\
0 & \sqrt{\frac{3}{2}} \theta_t & -\sqrt{\frac{3}{2}} \theta_t & 0 & 1
\end{pmatrix}. \tag{A.5}
\]

**TB hopping in the rotated basis** – The TB matrix elements between the d orbitals on two different sites may be obtained by a straightforward use of Eqs. (A.1) and (A.2). We illustrate this for the nearest-neighbor hopping from the Os at the origin to the Os located along the + \hat{x}, \hat{y}, or \hat{z} directions, for which the TB matrix elements in the unrotated basis can be obtained from Harrison’s book.\(^{20}\) These are

\[
H_{100} = \begin{pmatrix}
V_\pi & 0 & 0 & 0 & 0 \\
0 & V_\delta & 0 & 0 & 0 \\
0 & 0 & V_\pi & 0 & 0 \\
0 & 0 & 0 & \frac{1}{4} (3V_\sigma + V_\delta) & -\frac{\sqrt{3}}{4} (V_\sigma - V_\delta) \\
0 & 0 & 0 & -\frac{\sqrt{3}}{4} (V_\sigma - V_\delta) & \frac{1}{4} (V_\sigma + 3V_\delta)
\end{pmatrix},
\]

\[
H_{010} = \begin{pmatrix}
V_\pi & 0 & 0 & 0 & 0 \\
0 & V_\pi & 0 & 0 & 0 \\
0 & 0 & V_\delta & 0 & 0 \\
0 & 0 & 0 & \frac{1}{4} (3V_\sigma + V_\delta) & \frac{\sqrt{3}}{4} (V_\sigma - V_\delta) \\
0 & 0 & 0 & \frac{\sqrt{3}}{4} (V_\sigma - V_\delta) & \frac{1}{4} (V_\sigma + 3V_\delta)
\end{pmatrix},
\]

and

\[
H_{001} = \begin{pmatrix}
V_\delta & 0 & 0 & 0 & 0 \\
0 & V_\pi & 0 & 0 & 0 \\
0 & 0 & V_\delta & 0 & 0 \\
0 & 0 & 0 & V_\sigma & 0 \\
0 & 0 & 0 & 0 & V_\sigma
\end{pmatrix}. \tag{A.6}
\]

In the following, we neglect \(V_\delta\), which is much smaller compared to \(V_\sigma\) and \(V_\pi\), but can be included without any problem. The TB hopping matrix in the rotated basis is obtained from

\[
\tilde{H}_{1mn} = R^T(\mathbf{A})H_{1mn}R(\mathbf{B}). \tag{A.7}
\]
Referring to Fig. 8, we have $R(A) = R(\theta_r, -\theta_t)$, while $R(B) = R(-\theta_r, \theta_t)$ for hopping to the B atom located along $\hat{x}$ or $\hat{y}$ and $R(B) = R(\theta_r, \theta_t)$ along $\hat{z}$. Thus, for example, $\tilde{H}_{100} = R(\theta_r, -\theta_t)^T H_{100} R(-\theta_r, \theta_t)$. Using their explicit forms already given, the hopping matrices in the rotated basis are readily calculated. They read

$$
\tilde{H}_{100} = H_{100} + \frac{1}{\sqrt{2}} \begin{pmatrix}
0 & V_x \theta_t & -2\theta_t V_x & -(3V_\sigma + 4V_\pi)\theta_r / \sqrt{2} & \sqrt{3/2}V_\sigma \theta_r \\
-\theta_t V_x & 0 & -\sqrt{2}V_\sigma \theta_r & 0 & 0 \\
2\theta_t V_x & \sqrt{2}V_\sigma \theta_r & 0 & -(3V_\sigma + 2V_\pi)\theta_t / 2 & \sqrt{3}(V_\sigma + 2V_\pi)\theta_t / 2 \\
(3V_\sigma + 4V_\pi)\theta_r / \sqrt{2} & 0 & (3V_\sigma + 2V_\pi)\theta_t / 2 & 0 & 0 \\
-\sqrt{3/2}V_\sigma \theta_r & 0 & -\sqrt{3}(V_\sigma + 2V_\pi)\theta_t / 2 & 0 & 0 \\
\end{pmatrix},
$$

$$
\tilde{H}_{010} = H_{010} + \frac{1}{\sqrt{2}} \begin{pmatrix}
0 & 2\theta_t V_x & -\theta_t V_x & -(3V_\sigma + 4V_\pi)\theta_r / \sqrt{2} & -\sqrt{3/2}V_\sigma \theta_r \\
-2\theta_t V_x & 0 & -\sqrt{2}V_\sigma \theta_r & -(3V_\sigma + 2V_\pi)\theta_t / 2 & -\sqrt{3}(V_\sigma + 2V_\pi)\theta_t / 2 \\
\theta_t V_x & \sqrt{2}V_\sigma \theta_r & 0 & 0 & 0 \\
(3V_\sigma + 4V_\pi)\theta_r / \sqrt{2} & (3V_\sigma + 2V_\pi)\theta_t / 2 & 0 & 0 & 0 \\
\sqrt{3/2}V_\sigma \theta_r & \sqrt{3}(V_\sigma + 2V_\pi)\theta_t / 2 & 0 & 0 & 0 \\
\end{pmatrix},
$$

and

$$
\tilde{H}_{001} = H_{001} + \frac{1}{\sqrt{2}} \begin{pmatrix}
0 & V_x & -V_x & 0 & 0 \\
-V_x & 0 & 0 & V_x & -\sqrt{3}(V_\sigma + V_\pi) \\
V_x & 0 & 0 & -V_x & \sqrt{3}(V_\sigma + V_\pi) \\
0 & V_x & V_x & 0 & 0 \\
0 & \sqrt{3}(V_\sigma + V_\pi) & -\sqrt{3}(V_\sigma + V_\pi) & 0 & 0 \\
\end{pmatrix}. \quad (A.8)
$$

The TB hopping matrices for other pairs of atoms may be similarly calculated.

**TB hopping Integrals** – For ready reference, we provide the TB hopping integrals between two atoms. The TB hopping integrals $H_{i\alpha,j\beta}$ between the d orbitals located on two sites $i$ and $j$ in the orbital basis $\alpha = xy, yz, xz, x^2 - y^2$ and $3z^2 - r^2$ are given by\textsuperscript{20}

$$
H = H_\pi + H_\sigma + H_\delta,
$$

where

$$
H_\pi = V_{\pi} \begin{pmatrix}
(l^2 + m^2 - 4l^2 m^2) & ln(1 - 4m^2) & mn(1 - 4l^2) & 2lm(m^2 - l^2) & -2\sqrt{3}mnw \\
ln(1 - 4m^2) & m^2 + n^2 - m^2 n^2 & ltn(1 - 4n^2) & -mnw_+ & -\sqrt{3}mnw_0 \\
mn(1 - 4l^2) & ltn(1 - 4n^2) & l^2 + n^2 - 4l^2 n^2 & nlw_+ & \sqrt{3}nlw_0 \\
2lm(m^2 - l^2) & -mnw_+ & nlw_+ & l^2 + m^2 - (l^2 - m^2)^2 & \sqrt{3}n^2(m^2 - l^2) \\
-2\sqrt{3}mnw & -\sqrt{3}mnw_0 & \sqrt{3}nlw_0 & \sqrt{3}n^2(l^2 - m^2) & 3n^2(l^2 - m^2) \\
\end{pmatrix},
$$

$$
H_\sigma = V_{\sigma} \begin{pmatrix}
3l^2 m^2 & 3l^2 m^2 & 3l^2 mn & 3\sqrt{3}ml(l^2 - m^2) & \sqrt{3}lm \\
3lm^2 n & 3m^2 n^2 & 3l^2 mn & 3\sqrt{3}mn(l^2 - m^2) & \sqrt{3}mn \\
3l^2 mn & 3ml^2 n & 3l^2 n^2 & 3\sqrt{3}nl(l^2 - m^2) & \sqrt{3}nl \\
3\sqrt{3}ml(l^2 - m^2) & 3\sqrt{3}mn(l^2 - m^2) & 3\sqrt{3}nl(l^2 - m^2) & 3\sqrt{3}l^2(m^2 - l^2) & \sqrt{3}(l^2 - m^2) w \\
\sqrt{3}lm & \sqrt{3}mn & \sqrt{3}nl & \sqrt{3}l^2(m^2 - l^2) & 3\sqrt{3}(l^2 - m^2) w \\
\end{pmatrix},
$$

$$
H_\delta = V_{\delta} \begin{pmatrix}
\sqrt{3}m^2 & \sqrt{3}m^2 & \sqrt{3}mn & 3l^2 m^2 & 3lm^2 \frac{\sqrt{3}}{2} \frac{l^2 - m^2}{w} \\
\sqrt{3}m^2 & \sqrt{3}m^2 & \sqrt{3}mn & 3lm^2 \frac{\sqrt{3}}{2} \frac{l^2 - m^2}{w} & \sqrt{3}mn \\
\sqrt{3}mn & \sqrt{3}mn & \sqrt{3}nl & 3l^2 mn & 3\sqrt{3}nl \frac{\sqrt{3}}{2} \frac{l^2 - m^2}{w} \\
\sqrt{3}ml \frac{\sqrt{3}}{2} \frac{l^2 - m^2}{w} & \sqrt{3}ml \frac{\sqrt{3}}{2} \frac{l^2 - m^2}{w} & \sqrt{3}ml \frac{\sqrt{3}}{2} \frac{l^2 - m^2}{w} & \sqrt{3}ml \frac{\sqrt{3}}{2} \frac{l^2 - m^2}{w} & \sqrt{3}ml \frac{\sqrt{3}}{2} \frac{l^2 - m^2}{w} \\
\end{pmatrix}.
$$
and

\[
H_S = V_3 \begin{pmatrix}
(n^2 + l^2m^2) & ln(m^2 - 1) & mn(l^2 - 1) & 1/2lm(l^2 - m^2) & \sqrt{2}lm(1 + n^2) \\
ln(m^2 - 1) & (l^2 + m^2n^2) & lm(n^2 - 1) & mn[1 + 1/2(l^2 - m^2)] & \sqrt{2}mn(l^2 + m^2) \\
mx(n^2 - 1) & lm(n^2 - 1) & (m^2 + l^2n^2) & -ntu & -\sqrt{2}nt(m^2 + l^2) \\
1/2lm(l^2 - m^2) & mn[1 + 1/2(l^2 - m^2)] & -ntu & n^2 + 1/4(l^2 - m^2)^2 & \sqrt{2}(1 + n^2)(l^2 - m^2) \\
\frac{1}{\sqrt{2}}mn(1 + n^2) & -\sqrt{2}mn(l^2 + m^2) & -\sqrt{2}mn(l^2 + m^2) & \frac{1}{\sqrt{2}}(1 + n^2)(l^2 - m^2) & \frac{1}{\sqrt{2}}(l^2 + m^2)^2
\end{pmatrix} \quad \text{(A.10)}
\]

Here, \(l, m,\) and \(n\) denote the direction cosines of the distance vector \((\vec{r}_j - \vec{r}_i)\) between the atoms, \(u = [1 - 1/2(l^2 - m^2)], \) \(v = [n^2 - 1/2(l^2 + m^2)], \) \(w = [n^2 - 1/2(l^2 + m^2)^2], \) \(w_\pm = [1 \pm 2(l^2 - m^2)], \) and \(w_0 = (l^2 + m^2 - n^2).\)

**Rotation of the \(L = 1\) and \(L = 2\) cubic harmonics in terms of the Euler angles** – The rotation matrix \(R_L\) for \(L = 1\) cubic harmonics \((x, y,\) and \(z)\) or for ordinary vectors is expressed in terms of the Euler angles as

\[
R_1 = \begin{pmatrix}
\cos \alpha \cos \beta \cos \gamma - \sin \alpha \sin \gamma & -\cos \alpha \cos \beta \sin \gamma - \sin \alpha \cos \gamma & \sin \beta \cos \alpha \\
\sin \alpha \cos \beta \cos \gamma + \cos \alpha \sin \gamma & -\sin \alpha \cos \beta \sin \gamma + \cos \alpha \cos \gamma & \sin \alpha \sin \beta \\
-\sin \beta \cos \gamma & \sin \sin \gamma & \cos \beta
\end{pmatrix} \quad \text{(A.11)}
\]

Sometimes it is useful to make a rotation of angle \(\theta\) about a given axis \(\hat{u} = (l, m, n).\) In this case, the rotation matrix is given by

\[
R_1(\theta) = \begin{pmatrix}
\cos \theta + l^2(1 - \cos \theta) & lm(1 - \cos \theta) - n \sin \theta & ln(1 - \cos \theta) + m \sin \theta \\
lm(1 - \cos \theta) + n \sin \theta & \cos \theta + m^2(1 - \cos \theta) & mn(1 - \cos \theta) - l \sin \theta \\
ln(1 - \cos \theta) - m \sin \theta & mn(1 - \cos \theta) + l \sin \theta & \cos \theta + n^2(1 - \cos \theta)
\end{pmatrix} \quad \text{(A.12)}
\]

For the \(L = 2\) cubic harmonics \((xy, yz, xz, x^2 - y^2\) and \(3z^2 - r^2),\) the expression for the rotation matrix \(R_2(\alpha, \beta, \gamma)\) is

\[
R_2 = \frac{1}{2} \begin{pmatrix}
\beta_+^2 \cos(2\alpha + 2\gamma)/2 & \beta_+ \sin \beta \cos(2\alpha + \gamma) & \beta_+ \sin \beta \sin(2\alpha + \gamma) & \beta_+^2 \sin(2\alpha + 2\gamma)/2 & \sqrt{3} \sin^2 \beta \\
-\beta_+^2 \cos(2\alpha - 2\gamma)/2 & +\beta_+ \sin \beta \cos(2\alpha - \gamma) & -\beta_+ \sin \beta \sin(2\alpha - \gamma) & +\beta_+^2 \sin(2\alpha - 2\gamma)/2 & \sin 2\alpha \\
-\beta_- \sin \beta \cos(\alpha + 2\gamma) & -\beta_- \beta_-'' \cos(\alpha + \gamma) & \beta_- \beta_-'' \sin(\alpha + \gamma) & -\beta_- \sin \beta \cos(\alpha + 2\gamma) & \sqrt{3} \sin \gamma \\
-\beta_- \sin \beta \cos(\alpha - 2\gamma) & +\beta_- \beta_-'' \cos(\alpha - \gamma) & -\beta_- \beta_-'' \sin(\alpha - \gamma) & +\beta_- \sin \beta \cos(\alpha - 2\gamma) & \sin 2\beta \\
\beta_- \sin \beta \sin(\alpha + 2\gamma) & -\beta_- \beta_-'' \sin(\alpha + \gamma) & \beta_- \beta_-'' \cos(\alpha + \gamma) & -\beta_- \sin \beta \sin(\alpha + 2\gamma) & \sqrt{3} \cos \gamma \\
+\beta_- \sin(\alpha + 2\gamma) & -\beta_- \beta_-'' \sin(\alpha + \gamma) & \beta_- \beta_-'' \sin(\alpha + \gamma) & +\beta_- \sin \beta \sin(\alpha + 2\gamma) & \sin 2\beta \\
-\beta_- \sin(2\alpha + 2\gamma)/2 & -\beta_- \sin \beta \sin(2\alpha + \gamma) & \beta_- \sin \beta \cos(2\alpha + \gamma) & \beta_-^2 \sin(2\alpha + 2\gamma)/2 & \sqrt{3} \sin^2 \beta \\
+\beta_- \sin(2\alpha - 2\gamma)/2 & -\beta_- \sin \beta \sin(2\alpha - \gamma) & -\beta_- \sin \beta \cos(2\alpha - \gamma) & +\beta_-^2 \sin(2\alpha - 2\gamma)/2 & \sin 2\alpha \\
-\sqrt{3} \sin^2 \beta \sin 2\gamma & \sqrt{3} \sin 2\beta \sin \gamma & -\sqrt{3} \sin 2\beta \cos \gamma & \sqrt{3} \sin^2 \beta \cos 2\gamma & 2 - 3 \sin^2 \beta
\end{pmatrix} \quad \text{(A.13)}
\]

where \(\beta_+ = 1 \pm \cos \beta\) and \(\beta_-'' = 2 \cos \beta \pm 1.\)
Acknowledgement

We thank Zoran S. Popović for helpful discussions and the U.S. Department of Energy, Office of Basic Energy Sciences, Division of Materials Sciences and Engineering (Grant No. DE-FG02-00ER45818) for financial support. Computational resources were provided by the National Energy Research Scientific Computing Center, a user facility also supported by the U.S. Department of Energy.

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