Superexchange interactions between spin-orbit-coupled $j \approx 1/2$ ions
in oxides with face-sharing ligand octahedra

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Using ab initio wave-function-based calculations, we provide valuable insights with regard to the magnetic exchange in 5d and 4d oxides with face-sharing ligand octahedra, BaIrO$_3$ and BaRhO$_3$. Surprisingly strong antiferromagnetic Heisenberg interactions as large as 400 meV are computed for idealized iridate structures with 90° Ir-O-Ir bond angles and in the range of 125 meV for angles of 80° as measured experimentally in BaIrO$_3$. These estimates exceed the values derived so far for corner-sharing and edge-sharing systems and motivate more detailed experimental investigations of quantum magnets with extended 5d/4d orbitals and networks of face-sharing ligand cages. The strong electron-lattice couplings evidenced by our calculations suggest rich phase diagrams as function of strain and pressure, a research direction with much potential for materials of this type.

INTRODUCTION

The interest in the preparation and characterization of 5d oxides and halides goes back to the 1950’s but some of the major implications of having a strong spin-orbit coupling (SOC), at least for certain 5d$^0$ electron configurations, have been only recently realized. The work of Kim et al. on the square-lattice 5d$^5$ iridate Sr$_2$IrO$_4$ [1, 2], for example, led to the concept of a spin-orbit driven (Mott-like) insulator while Jackeli and Khaliullin [3] brought to the forefront of oxide research the honeycomb 5d$^5$ iridates, as possible hosts for Kitaev physics [4] and novel magnetic ground states and excitations [5]. Both types of these iridate structures – square and honeycomb lattices – have been the topic of extensive investigations in recent years. The honeycomb compounds display edge-sharing ligand octahedra and advanced electronic-structure calculations indicate that the Kitaev exchange is indeed the largest inter-site magnetic coupling [6, 7]. Remarkably large anisotropic interactions were also found for corner-sharing ligand cages in Sr$_2$IrO$_4$, in that case of Dyzaloshinskii-Moriya type, with strengths in the range of 10–15 meV [3, 8].

In contrast to the cases of corner- and edge-sharing coordination, little is known with respect to the magnitude of the effective coupling constants for adjacent octahedra connected through a O$_3$ facet. Representative materials of the latter type are the canted antiferromagnet BaIrO$_3$ [9–14], the putative spin-liquid Ba$_3$Ir$_2$O$_9$ [15], the spin-gapped system Ba$_3$BiIr$_2$O$_9$ [16], BaRhO$_3$ [17], and BaCoO$_3$ [18]. Here we provide ab initio results with regard to the strength of facet-mediated superexchange for IrO$_6$ (RhO$_6$) octahedra as found in the 5d (4d) $t_{2g}$ system BaIrO$_3$ (BaRhO$_3$). We predict remarkably large antiferromagnetic (AFM) Heisenberg interactions in the range of 100 meV for Ir-O-Ir angles of about 80° as found experimentally in BaIrO$_3$ [17]. Moreover, for bond angles $\gtrsim$85° the Heisenberg $J$ even exceeds 200 meV in our simulations. So strong AFM superexchange has been found so far only in one-dimensional corner-sharing cuprates [19, 20].

Our findings point to a picture of unusually large, AFM couplings within the face-sharing octahedral units of BaIrO$_3$. The strong dependence on bond angles of the effective magnetic interactions further resonates with available experimental data on BaIrO$_3$ [10, 13, 21–23] and Ba$_3$BiIr$_2$O$_9$ [16], that indicate subtle interplay between the electronic and lattice degrees of freedom.

MATERIAL MODEL

BaIrO$_3$ features a distorted hexagonal structure with both face-sharing and corner-sharing IrO$_6$ octahedra [24]. Those connected by one single ligand form honeycomb-like planes; the linkage of adjacent honeycomb layers is ensured by interlayer Ir ions located such that blocks of three face-sharing octahedra are formed along the c axis, see Fig. 1(a). Since for any pair of nearest-neighbor (NN) octahedra the actual point-group symmetry is very low, we focus in our study on an idealized material model displaying $D_{3h}$ symmetry: [Ir$_2$O$_6$]$^{10–}$ units as depicted in Fig. 1(b) around which we additionally considered, for keeping overall charge neutrality, three Ba sites within the plane of the median O$_3$ facet and two extra Ba ions along the z axis. Although this material model is somewhat oversimplified, it should rather well describe the essential short-range electron interactions, as confirmed by similar investigations of edge-sharing 5d$^0$ compounds [7].

One feature of 5d transition-metal (TM) ions is that their valence orbitals are much more diffuse as compared to first-series TM species. The ligand field is therefore more effectively felt and for instance the Ir$^{4+}$ ions tend to adopt low-spin $t_{2g}^5$ configurations. The more extended nature of the 5d functions further gives rise to large intersite hoppings and large superexchange, as in e.g. Sr$_2$IrO$_4$ [3, 8] and CaIrO$_3$ [25]. Under strong octahedral crystal fields (CFs) and spin-orbit interactions, with one single unpaired electron ($S=1/2$) in the $t_{2g}$ manifold (orbital angular momentum $L=1$), the $5d^5$ ($4d^5$) valence electron configuration of Ir$^{4+}$ (Rh$^{4+}$) in BaIrO$_3$.
The eigenstates of such a two-site system are the singlet \( |\Psi_S\rangle \) and the three triplet components \( |\Psi_T\rangle = \frac{1}{\sqrt{2}} \left( |\uparrow\uparrow\rangle + |\downarrow\downarrow\rangle \right) \). The corresponding eigenvalues are

\[
E_S = -\frac{3}{4} \bar{J}, \quad E_1 = \frac{1}{4} \bar{J} - \frac{1}{2} \bar{\Gamma}, \quad E_2 = \frac{1}{4} \bar{J} + \bar{\Gamma}, \quad E_3 = \frac{3}{4} \bar{J} - \frac{1}{2} \bar{\Gamma}.
\]

Expression (1) can be then simplified to

\[
\mathcal{H}_{ij} = \bar{J} \hat{S}_i \cdot \hat{S}_j + \bar{\Gamma} \hat{S}_i^z \hat{S}_j^z;
\]

where \( \bar{J} \equiv J + \bar{\Gamma} \) and \( \bar{\Gamma} \equiv -3\bar{\Gamma} \).

The first step in the actual QC calculations is defining a relevant set of Slater determinants in the prior complete-active-space self-consistent-field (CASSCF) treatment [27]. For two \( \text{Ir}_6 \) octahedra, an optimal choice is having five electrons and three \( t_{2g} \) orbitals at each of the two magnetically active Ir (Rh) sites. The self-consistent-field optimization was carried out for an average of the lowest nine singlet and lowest nine triplet states associated with this manifold. Subsequent multireference configuration-interaction (MRCI) computations were performed for each spin multiplicity, either singlet or triplet, as nine-root calculations. All these states entered the spin-orbit treatment [28], in both CASSCF and MRCI. Within the group of 36 spin-orbit eigenvectors associated with the \( t_{2g}^1 - t_{2g}^1 \) manifold, the lowest-lying four “magnetic” states are separated by a significant energy gap from the other 32 states. The latter correspond to on-site \( j \approx 3/2 \) to \( j \approx 1/2 \) transitions, and are therefore left aside in the actual mapping procedure. In other words, given the strong SOC and large \( j \approx 3/2 \) to \( j \approx 1/2 \) excitation energies, the initial 36×36 problem can be smoothly mapped onto a 4×4 construction as defined by the effective Hamiltonian (1).

All computations were carried out with the MOLPRO quantum-chemistry software [29]. In the MRCI treatment, single and double excitations from the six Ir (Rh) \( t_{2g} \) orbitals and from the 2p shells of the bridging O ligand sites were taken into account. The Pipek-Mezey localization module [30] available in MOLPRO was employed for separating the metal 5d (4d) and O 2p valence orbitals into different groups. To derive the magnitude of direct exchange, we additionally performed calculations in which the active space is again defined by ten electrons and six orbitals but intersite \( t_{2g} - t_{2g} \) excitations are forbidden by restricting to maximum five the number of electrons per TM site. We refer to these results as rAS (restricted active space, maximum one hole per site).

**[Ir\(_5\)O\(_{16}\)] unit**

Effective magnetic couplings for Ir\(_2\)O\(_9\) fragments of two face-sharing IrO\(_6\) octahedra are listed in Table I, for an Ir-Ir interatomic distance \( d_0 = 2.63 \) Å and ligand coordinates that provide Ir-O-Ir angles \( \theta_0 = 80^\circ \). These structural parameters, obtained by averaging the bond lengths and bond angles in the experimentally determined lattice configuration of BaIrO\(_3\) [17], correspond to slightly elongated octahedra. For cubic (undistorted) octahedra, \( \theta_c = 70.52^\circ \).

Results at three different levels of approximation are shown: spin-orbit rAS (rAS+SOC), CASSCF (CAS+SOC), and MRCI (CI+SOC). The rAS data account for only direct \( d-d \) exchange. For \( d_0 = 2.63 \) Å and \( \theta_0 = 80^\circ \), the rAS \( J \) is \(-14.9 \) meV while the anisotropic \( \bar{\Gamma} \) is \(-0.7 \) meV when including SOC. The magnitude of the ferromagnetic (FM) rAS
result. By accounting for correlation effects, the symmetric
123.3 meV, about 70% larger as compared to the CAS+SOC
electrons. In the CASSCF approximation, only
slightly larger as compared with the AFM rAS
coupling constants at different levels of approximation, for
three values without SOC by
rAS, CAS, and CI are −1.2, 27.4, and 35.4 meV, respectively.
TABLE I. Energy splittings for the lowest four spin-orbit states of
two face-sharing NN IrO$_6$ octahedra and the corresponding effective
coupling constants for variable Ir-O-Ir bond angles while keeping the overall
D$_{3h}$ point-group symmetry. We performed additional calculations for dis-
torted geometries with all ligands pushed closer to (or farther from)
the Ir-Ir axis, which therefore yields larger (or smaller)
Ir-O-Ir bond angles while keeping the overall D$_{3h}$ point-group
symmetry. The resulting MRCI+SOC results (meV). The NN Ir-Ir distance is
2.63 Å. The Ir-O-Ir angle is listed for each geometry; distances between
Ir-Ir and the bridging O’s, d(Ir-O), are provided within brackets.
TABLE II. Energy splittings for the lowest four spin-orbit states and
the corresponding effective coupling constants for variable Ir-O-Ir
angle, MRCI+SOC results (meV). The NN Ir-Ir distance is d$_0$=2.63 Å. The Ir-O-Ir angle $\theta$ is listed for each geometry; distances between
Ir and the bridging O’s, d(Ir-O), are provided within brackets.

$J$ is similar to that computed in square-lattice 3$d^9$ Cu oxides
[31–34] and in the corner-sharing iridate Ba$_2$IrO$_4$ [35]. The
anisotropic $\bar{\Gamma}$ is also FM at the rAS level and its magnitude is
slightly larger as compared with the AFM rAS $\bar{\Gamma}$ of the corner-
sharing iridate Ba$_2$IrO$_4$ [35]. By CASSCF and MRCI, the
singlet $\Psi_S$ becomes the ground state, well below the “triplet”
components $\Psi_1$, $\Psi_2$, and $\Psi_3$. This indicates that the isotropic
Heisenberg exchange $\bar{J}$ ($\bar{J}>0$) defines now the largest energy
scale. In the CASSCF approximation, only $t_{2g}^{-2}t_{2g}^{-2}$ intese excitations are accounted for, i.e., $t_{2g}^{-2}t_{2g}^{-2}$ configurations. The
$\bar{J}$ value extracted by CAS+SOC, 72 meV, is twice as large as compared, e.g., to the CASSCF $\bar{J}$’s in layered 3$d^9$ cuprates
[31–34] and in the corner-sharing iridate Ba$_2$IrO$_4$ [35]. In the
configuration-interaction treatment, which includes TM $t_{2g}$ to
$e_g$ and charge-transfer O 2$p$ to Ir 5$d$ excitations as well, $\bar{J}$ is
123.3 meV, about 70% larger as compared to the CAS+SOC result. By accounting for correlation effects, the symmetric
anisotropic coupling $\bar{\Gamma}$ is also significantly enlarged, from
−0.7 meV by rAS+SOC to 6.3 meV by spin-orbit MRCI.

In the case of face-sharing ligand octahedra, the TM ions
often form dimers, trimers, or chains [17]. This type of low-
dimensional packing usually results in sizable distortions of
the ligand cages. It is known that the effective spin interactions
are strongly dependent on structural details such as bond
angles [36–39] and bond lengths [40]. For better insight into the
dependence of the NN magnetic couplings on such structural
parameters, we performed additional calculations for dis-
torted geometries with all ligands pushed closer to (or farther from)
the Ir-Ir axis, which therefore yields larger (or smaller)
Ir-O-Ir bond angles while keeping the overall D$_{3h}$ point-group
symmetry. The resulting MRCI+SOC data are provided in Ta-
ble II. The overall trends for the magnetic couplings $\bar{J}$ and $\bar{\Gamma}$
are illustrated graphically in Fig. 2(a). It is seen that the angle
dependence for both $\bar{J}$ and $\bar{\Gamma}$ can be rather well reproduced
FIG. 2. Dependence on structural details of the NN effective magnetic couplings for Ir$_2$O$_9$ and Rh$_2$O$_9$ fragments of face-sharing octahedra, spin-orbit MRCI results. (a, c) Variations as function of the Ir-O-Ir bond angle $\theta$ and Rh-O-Rh bond angle $\theta'$ when fixing the Ir-Ir distance to $d_0 = 2.63 \text{ Å}$ and the Rh-Rh distance to $d'_0 = 2.58 \text{ Å}$. Ligands are radially displaced in planes perpendicular to the $z$ axis. Curves were drawn as a guide to the eye; a simple fit is not possible for $\Gamma$ in the case of $4d$ magnetic sites. (b, d) Variations as function of the TM-TM interatomic distance when keeping unchanged the positions of the ligands. The latter are at distances of $r_0 = 1.57 \text{ Å}$ (Ir$_2$O$_9$) and $r'_0 = 1.54 \text{ Å}$ (Rh$_2$O$_9$) from the $z$ axis.

with parabolic curves. The Heisenberg $\bar{J}$ displays a steep increase with larger angle, i.e., from 58 meV at 70.5° to 417 meV at 90°. On the other hand, the anisotropic coupling $\bar{\Gamma}$ shows a rapid decrease, from a remarkably large value of 30 meV at 70.5° to 2 meV at 90°.

We further analyzed the dependence on the Ir-Ir interatomic distance $d$(Ir-Ir) of the magnetic interactions. In this set of calculations, the distance between the O ligands and the $z$ axis (along the Ir-Ir bond) was fixed to 1.57 Å, while $d$(Ir-Ir) was either increased or reduced by up to 5% with respect to the reference Ir-Ir separation $d_0 = 2.63 \text{ Å}$. As shown in Fig. 2(b) (see also Appendix B, Table A2), both $\bar{J}$ and $\bar{\Gamma}$ have again pronounced parabolic dependence on $d$(Ir-Ir). In contrast to the variations as function of angle displayed in Fig. 2(a), here $\bar{J}$ and $\bar{\Gamma}$ follow the same trend. More specifically, both $\bar{J}$ and $\bar{\Gamma}$ rapidly increase with decreasing $d$(Ir-Ir).

We also performed calculations in which the six O ligands not shared by the Ir ions were displaced as well along the $z$ axis, such that each Ir site remains in the center of the respective octahedron. We found that the differences between the $\bar{J}$ values obtained from these computations and the corresponding $\bar{J}$'s in Fig. 2(b) are rather small, not more than 15%.

The face-sharing linkage and additional distortions applied to the two-octahedra clusters split the $t_{2g}$ levels into $a_{1g}$ and $e_g^\pi$ components. For all Ir$_2$O$_9$ units considered here, we find that the $a_{1g}$ sublevels lie at lower energy and that the $t_{2g}$ hole has $e_g^\pi$ character without accounting for SOC. The $a_{1g}$ orbitals belonging to NN sites have substantial direct overlap [see Fig 3(a)], much larger than in the case of $e_g^\pi$ orbitals [see Fig 3(b)]. The rather small AFM Heisenberg $\bar{J}$ derived from the calculations without SOC (see caption of Table I) is therefore the result of (relatively) weak direct exchange involving the higher-lying $e_g^\pi$ states. By accounting for spin-orbit interactions, however, the Heisenberg $\bar{J}$ is enhanced to impressive values that are up to three times larger than the results obtained without SOC (72 vs 27 meV at the CASSCF level, 123 vs 35 meV by MRCI, see Table I). This strong increase of the Heisenberg $\bar{J}$ is the consequence of mixing $a_{1g}$ character to the spin-orbit ground-state wave-function.

In order to make a informative comparison between 5$d$ and 4$d$ oxides, we also performed calculations for the effective magnetic couplings on [Rh$_2$O$_9$] fragments consisting of two
face-sharing RhO$_3$ octahedra, with a Rh-Rh interatomic distance $d'_0 = 2.58$ Å and Rh-O-Rh bond angles $\theta'_0 = 80^\circ$. As for the material model of face-sharing 5$d^5$ octahedra, the structural parameters of the Rh$_2$O$_3$ cluster were chosen according to the average bond lengths and bond angles of the BaRhO$_3$ compound. We used in this regard the crystallographic data reported in Ref. [17]. QC results are presented in Table III. Interestingly, the $\bar{J}$ value obtained by spin-orbit rAS is the same as for the Ir$_2$O$_3$ cluster (Table I). However, the $\bar{J}$'s obtained by CAS+SOC and CI+SOC are significantly smaller as compared with those in Table I. Still, $\bar{J}$ remains much larger than the magnetic couplings in the edge-sharing 4$d^5$ compounds Li$_2$RhO$_3$ and $\alpha$-RuCl$_3$ [37, 38].

Energy splittings within the group of the four low-lying 4$d$−4$d$ states and the resulting effective coupling constants for different Rh-O-Rh angles are listed in Table IV. Furthermore, the dependence of $\bar{J}$ and $\bar{\Gamma}$ on the Rh-O-Rh bond angles and on the Rh-Rh interatomic distances are illustrated in Fig. 2(c) and Fig. 2(d), respectively (for more details see Appendix B, Table A3 and Table A4). As indicated in Fig. 2(c), $\bar{J}$ displays nearly linear behavior with variable angle, increasing from 1.5 meV at 70.5$^\circ$ to 164 meV at 90$^\circ$. $\bar{\Gamma}$ changes sign from FM coupling close to 75$^\circ$, with a minimum of $-6$ meV at 85$^\circ$, and then changes back to AFM values for larger angles. On the other hand, with variable $d$(Rh-Rh) [Fig. 2(d)], $\bar{\Gamma}$ is always FM, with a minimum of $-2.8$ meV at 2.56 Å, and $\bar{J}$ features a similar trend as for Ir sites in Fig. 2(b).

**DISCUSSION**

We analyze in more detail in this section the relative values of the different contributions to intersite exchange, i.e., direct $t_{2g}^{-}\bar{t}_{2g}$ exchange, $t_{2g}^{-}\bar{t}_{2g}$ electron/hole hopping, and indirect hopping via the bridging oxygens. In first place, it is clear that a systematically small portion of FM potential exchange to the overall $\bar{J}$ is here of secondary importance. The contribution coming from direct hopping can be straightforwardly estimated from the CASSCF $\bar{J}$ since only intersite Mo($t_{2g}^{-}\bar{t}_{2g}$) superexchange excitation processes ($t_{2g}^{-}\bar{t}_{2g}$,$t_{2g}^{-}\bar{t}_{2g}$) polar configurations) are taken into account at the CASSCF level. In the CI treatment, superexchange paths including the bridging-ligand 2$p$ and TM $e_g$ orbitals are also added on top of direct hopping, providing a more comprising description of intersite exchange mechanisms. In the case of BaIrO$_3$, for instance, when the Ir-O-Ir bond angle is 80$^\circ$, the exchange calculated at the CASSCF level (without SOC), $\bar{J} = 27.4$ meV, is already 77% of the CI result, 35.4 meV (see Table I). While this fraction is significantly reduced if the Ir-O-Ir bond angle is modified towards 90$^\circ$ (see Table A1), indicating that the $d$−$p$+$d$ superexchange contribution starts to rise as a result of shorter Ir-O bonds, the data computed for 80$^\circ$ bond angles show that, given the large direct-hopping integrals, the direct AFM $d$−$d$ superexchange may surpass the $d$−$p$+$d$ superexchange. The two mechanisms should be considered in any case on equal footing for high-quality estimates. In the context of recent discussions on the role of the various types of intersite exchange [41, 42], our QC data provide a more quantitative picture on the different contributions.

Given the facet-sharing geometry, the direct $d$−$d$ electron/hole hopping between $a_{1g}$ orbitals is considerable. This hopping interferes with the indirect hopping via the bridging-oxygen O$_3$ group, providing a total transfer integral $t$. Since the exchange coupling $\bar{J}$ is mainly controlled by the square of $t$ ($\bar{J} \sim \bar{t}^2/U$, where $U$ is the on-site Coulomb repulsion),

**TABLE III.** Energy splittings for the lowest four spin-orbit states of two face-sharing NN RhO$_3$ octahedra and the corresponding effective coupling constants at different levels of approximation, for $d'_0 = 2.58$ Å and $\theta'_0 = 80^\circ$ (all in meV). The $\bar{J}$ values without SOC by rAS, CAS, and CI are $-0.9$, 19.0, and 29.4 meV, respectively.

| $\bar{J}$, $\bar{\Gamma}$ | rAS+SOC | CAS+SOC | CI+SOC |
|--------------------------|---------|---------|---------|
| $\psi_0 = (|\uparrow\downarrow\rangle - |\downarrow\uparrow\rangle)/\sqrt{2}$ | 16.0 | 0.0 | 0.0 |
| $\psi_1 = (|\uparrow\downarrow\rangle - |\downarrow\uparrow\rangle)/\sqrt{2}$ | 0.0 | 25.4 | 54.0 |
| $\psi_2 = (|\uparrow\downarrow\rangle + |\downarrow\uparrow\rangle)/\sqrt{2}$ | 0.0 | 25.4 | 54.0 |
| $\psi_2 = (|\uparrow\downarrow\rangle + |\downarrow\uparrow\rangle)/\sqrt{2}$ | 1.1 | 26.5 | 55.5 |

**TABLE IV.** Energy splittings and the corresponding effective coupling constants for variable Rh-O-Rh angle, MRCI+SOC results (meV). The NN Rh-Rh distance is 2.58 Å. The Rh-O-Rh angle $\theta'$ is listed for each geometry; distances between Rh and the bridging O’s, $d$(Rh-O), are provided within brackets.

| $\theta'$ | $\psi_0$ | $\psi_1$ | $\psi_2$ | $\psi_2$ |
|-----------|-----------|-----------|-----------|-----------|
| 70.5$^\circ$ (2.23Å) | 75$^\circ$ (2.12Å) | 80$^\circ$ (2.04Å) | 85$^\circ$ (1.91Å) | 90$^\circ$ (1.82Å) |
| $\bar{J}$, $\bar{\Gamma}$ | 1.5, 4.4 | 152.0, -0.4 | 555.5, -2.8 | 1378.4, -4.3 | 1640.0, 18.8 |

**FIG. 3.** Natural orbitals of $a_{1g}$ (a) and $e'_g$ (b) type for a Ir$_2$O$_3$ fragment of face-sharing octahedra, as obtained by CASSCF calculations. The former have strong $\sigma$-type overlap.
a large $J$ value of up to $\approx400$ meV (see Table A1 and A2) is not surprising. Both the direct ($\sim t^{dd}$) and indirect ($\sim t^{ddp}$) transfer processes can occur through the $e^{\pi}_g$ and $a_{1g}$ channels independently. As discussed in Appendix A, the total transfer integral $t$ can be then decomposed as $t = w_e t_e + w_{a} t_{a}$, where $t_{e,a} = t^{dd}_{c,a} + t^{dpd}_{c,a}$. The corresponding channel weights, $w_e$ and $w_a$, are controlled by the ratio $\Delta_t/\lambda$, with $\lambda$ being the spin-orbit coupling, 0.47 eV for Ir and 0.15 eV for Rh [43]; the dependence of the trigonal splitting $\Delta_t$ on bond angles is illustrated in Table V. The different terms entering the total transfer integral $t$ are expected to be behave differently when varying the geometry of the M-O$_3$-M structure. The large direct overlap between two NN $a_{1g}$ orbitals suggests that the direct hopping $t^{dd}_{a}$ contributes significantly to $t_{a}$, as evidenced in Fig. 3. In contrast, the $e^{\pi}_g$ orbitals are tilted with respect to the $z$ axis, thus giving rise to weaker direct overlap and more significant $d-p-d$ couplings (see Fig. 3(b)), i.e., a more important role of $t^{dpd}_{c}$ in $t_e$. It is the interplay between these processes, $d-d$ and $d-p-d$ superexchange, that is mainly responsible for the strong variations as function of bond angles and bond lengths. From a wider perspective, it is clear that the equilibrium geometrical configuration and the associated $J$ value depend on interactions and degrees of freedom that also involve the extended crystalline surroundings. An interesting aspect to be considered is inter-site couplings within the entire M$_3$O$_{12}$ block of three face-sharing octahedra along the $c$ axis (see Fig.1(a)). One question concerns the possibility of cooperative M–M dimerization as driving force for the charge density wave observed in BaIrO$_3$ [10]. Two-site bond formation on three-center units with a spin 1/2 at each magnetic site and long-range ordering of these ‘dimers’ has been earlier proposed in the quasi-1D system NaV$_2$O$_5$ [44, 45].

To summarize, we employ quantum chemistry methods to provide valuable insights on the effective magnetic interactions in 5$d$ and 4$d$ oxides with face-sharing oxygen octahedra, BaIrO$_3$ and BaRhO$_3$. The same methodology has previously been used to derive magnetic coupling constants in good agreement with experimental estimates in the perovskite iridate CaIrO$_3$ [25, 46], in square-lattice Ba$_2$IrO$_4$ [35] and Sr$_2$IrO$_4$ [8], and in pyrochlore iridates [39]. The large AFM Heisenberg interactions computed here for face-sharing octa-

TABLE V. Angle dependence of the trigonal CF splitting $\Delta_t$ (eV) obtained from MRCI calculations for Ir$_2$O$_3$ and Rh$_2$O$_3$ fragments of face-sharing octahedra. The $a_{1g}$ level is for all angles the lowest in energy.

| $\theta/\theta'$ | $\Delta^b_t$ | $\Delta^R_{t}$ |
|------------------|--------------|---------------|
| 70.5             | $-0.86$      | $-0.69$       |
| 75               | $-0.89$      | $-0.67$       |
| 80               | $-0.71$      | $-0.53$       |
| 85               | $-0.43$      | $-0.29$       |
| 90               | $-0.20$      | $-0.10$       |

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Appendix A: Effective spin model

To put in perspective the general trends obtained in the QC calculations for the isotropic exchange coupling $J$, an effective two-site model is analyzed here. Two different mechanisms are considered: (a) direct $t_{2g} - t_{2g}$ hopping $\sim t_{dd}$ and (b) indirect processes via the bridging oxygens, $\sim t_{dpd}$. The three bridging oxygens within the median $xy$ mirror plane are denoted as $O_{n}$, with $n \in \{1, 2, 3\}$. For each metal ion at sites $I = A, B$, the trigonal CF term $H_{CF,t}$ splits the $t_{2g}$ orbital states into a two- and an one-dimensional subspace with basis states $|e_{12}\rangle, |e_{21}\rangle$ and $|a_{i}\rangle$, respectively [48]. In what follows, these hole states are denoted as $|\phi_{\mu}\rangle$, with $\mu = 1, 2$ for $|e_{12}\rangle$, $\mu = 3$ for $|a\rangle$, and the creation (annihilation) operator $\phi_{\mu,\sigma}^{\dagger}$ ($\phi_{\mu,\sigma}$), where the spin variable $\sigma = \pm 1/2$ is added. Restricted to this low-energy orbital space, a single hole is described by the effective orbital angular momentum operator $L = 1$ [48] in the spin-orbit term $H_{SO} = \sum_{L} \mathbf{L}_{I} \mathbf{S}_{I}$; here, $\mathbf{S}$ is the spin-1/2 operator and $\lambda > 0$. Altogether, relevant intra-atomic interactions are collected in the effective Hamiltonian $H_{at} = H_{CF,t} + H_{SO} + H_{U}$, where

$$H_{CF,t} + H_{SO} = \frac{\Delta_{t}}{3} \sum_{\mu, \sigma} \sum_{l} (\delta_{\mu 1} + \delta_{\mu 2} - 2\delta_{\mu 3}) \phi_{\mu,\sigma}^{\dagger} \phi_{\mu,\sigma} + \lambda \sum_{\mu, \sigma} \sum_{l} \mathbf{L}_{l} \mathbf{L}_{l}^{\dagger} \cdot |S_{l}\rangle |S_{l}\rangle \phi_{\mu,\sigma}^{\dagger} \phi_{\mu,\sigma}. \quad (A1)$$

Here, $[\mathbf{L}_{l} | \phi_{\mu,\sigma}^{\dagger} \mathbf{L}_{l} | \phi_{\mu,\sigma}]$ while $\Delta_{t}$ is the trigonal CF splitting between $|e_{12}\rangle$ and $|a\rangle$ `local' states. As stated in the main text, without SOC the calculated hole ground state of Ir$^{4+}$/Rh$^{3+}$ ions is of $e$-orbital character, which means $\Delta_{t} < 0$. The term $H_{U}$ includes the leading on-site Coulomb interaction

$$H_{U} = \frac{U}{2} \sum_{\mu, \sigma} \sum_{l, l^{'}} n_{\mu,\sigma} n_{l,\sigma}, \quad (A2)$$

where $n_{\mu,\sigma} = \phi_{\mu,\sigma}^{\dagger} \phi_{\mu,\sigma}$. The approximation of assuming the Coulomb $U$ in the above expression to be independent of the orbital indices $\mu$ and $\sigma$ simplifies the calculation of the isotropic exchange $J$ but excludes obtaining an estimate for the weaker anisotropic exchange $\Gamma$.

Within the one-hole sector and in the cubic limit $\Delta_{t} \rightarrow 0$, $H_{at}$ is reduced to $H_{SO}$. As well known [48], the `original' six $L = 1$ atomic states $|L_{z} = 0, \pm 1/2; \sigma = \pm 1/2\rangle$ are split by $H_{SO}$ into the Kramers doublets $|j = 1/2; m = \pm 1/2\rangle$ and the quartet $|j = 3/2; m = \pm 1/2, \pm 3/2\rangle$, whose eigenvalues are $-\lambda$ and $\lambda/2$, respectively; here, the site index $l$ is omitted for brevity. When lowering the CF symmetry to six $H_{J}$ the Coulomb calculations for the isotropic exchange coupling and the quartet mechanisms are considered: ($\frac{1}{48}$).<br>

In Eq. (A3) the term $k = 1$ only, which reads with the replacement $m \rightarrow s$ as

$$\begin{align*}
|a_{i}; \sigma = \pm 1/2\rangle & \rightarrow \mp \cos \gamma |\psi_{1}(s = \pm 1/2\rangle), \\
|e_{11}; \sigma = \pm 1/2\rangle & \rightarrow \frac{1}{\sqrt{2}} \sin \gamma |\psi_{1}(s = \pm 1/2\rangle), \\
|e_{22}; \sigma = \pm 1/2\rangle & \rightarrow \pm \frac{i}{\sqrt{2}} \sin \gamma |\psi_{1}(s = \mp 1/2\rangle),
\end{align*} \quad (A4)$$

where $\cos \gamma = (c_{1} - \sqrt{2}c_{2})/\sqrt{3}$ and $\sin \gamma = (\sqrt{2}c_{1} + c_{2})/\sqrt{3}$. In the following, the creation (annihilation) of state $|\psi_{1}(s)\rangle$ is associated with the operator $\psi_{1,\mu,s}^{\dagger}$ ($\psi_{1,\mu,s}$). Projected onto the pseudospin-1/2 subspace, the Coulomb interaction $H_{U}$ takes the Hubbard-like form $H_{U} = U \sum_{l} n_{l,\mu} n_{l,\mu}$. Actually, the unitary transformation (A3) yields $\sum_{\mu, \sigma} n_{\mu,\sigma} = \sum_{k, m} n_{kl,m}$, where only the term $l = k$ is kept.

In case of face-sharing octahedra, the relatively short $M_{A} - M_{B}$ distance dictates inclusion of the direct $t_{2g} - t_{2g}$ hopping term

$$H_{dd}^{dd} = \sum_{\mu, \sigma} t_{dd}^{\mu} \phi_{\mu,\sigma}^{\dagger} \phi_{\mu,\sigma, B, \sigma} + H.C., \quad (A5)$$

where $t_{dd}^{\mu} = \sum_{s} (\psi_{1,\mu,\sigma}^{\dagger} \psi_{1,\mu,\sigma}) \phi_{\mu,\sigma, B, \sigma} + H.C.$, (A6)
group. A detailed analysis shows that in the low-energy subspace the indirect hopping term $H_{hop}$ has the same structure as $H_{hop}^{dd}$, Eq. (A6), with the replacement $t^{dd} \rightarrow t^{dpd} = t^{dpd} \sin^2 \gamma + t^{dpd} \cos^2 \gamma$. The hopping integrals $t^{dpd}_{e,a}$ due to second-order processes that occur through intermediate ligand-hole states in the $ee$- and $aa$-channel, respectively, can be expressed in factorized form as $t^{dpd}_{e,a} \approx \left[ (t^{dp})_e / \Delta_{C,T} \right] F_{e,a}(\theta)$. Here, $t^{dp}$ and $\Delta_{C,T}$ define the characteristic $p - d$ hopping and charge-transfer energy scales. While the factor $F_{e,a}(\theta)$ is strongly dependent on the angle $\theta$, the parameter $t^{dp}$ is most sensitive to the metal-oxygen distance $d_{MO}$. According to [49], $t^{dp} \sim d_{MO}^{-\gamma/2}$. Transitions of first-order ($\sim t^{dd}$) and second-order type ($\sim t^{dpd}$) contribute in each sector independently to give the total transfer integral $t = t_e \sin^2 \gamma + t_a \cos^2 \gamma$, where $t_e,a = t^{dd}_{e,a} + t^{dpd}_{e,a}$. The resultant hopping Hamiltonian $H_{hop}$ takes the same form as in Eq. (A6), but with the replacement $t^{dd} \rightarrow t$. The weight factors of the $e$- and $a$- channels are $w_e = \sin^2 \gamma$ and $w_a = \cos^2 \gamma$, respectively. As discussed above, these factors are controlled by the ratio $\Delta_\gamma / \gamma$.

It is seen that the generic Hamiltonian $H = H_{at} + H_{hop}$ derived above takes the form of an effective 'single-orbital' Hubbard model operating in the pseudospin-1/2 subspace of NN metal ions. It can be treated perturbatively in the strong correlation regime $t/U \ll 1$, meaning that excited polar states with two holes on the same metal ion are well separated from the low-energy magnetic excitations. In this regime, one immediately obtains as second-order estimate for the isotropic exchange $J = 4t^2 / U$.

### Appendix B: Intersite magnetic couplings

All computations were performed with the MOLPRO quantum chemistry package [29]. Energy-consistent relativistic pseudopotentials were used for the Ir [50] and Rh [51] ions. For the Ir/Rh sites, the valence orbitals were described by basis sets of triple-zeta quality supplemented with two $f$ polarization functions [50, 51]. For the ligand O’s bridging the two magnetically active Ir (Rh) ions, quintuple-zeta valence basis sets and four $d$ polarization functions were applied [52]. The other O’s were modeled by triple-zeta valence basis sets [52]. The five Ba ions were modeled by Ba$^{2+}$ ‘total-ion’ pseudopotentials (TIP’s) supplemented with a single $s$ function [53]. We used interatomic distances as derived by E. Stitzer et al. [17].

The mapping of the ab initio quantum chemistry data onto the effective spin model defined by (1) implies the lowest four spin-orbit states associated with the different possible couplings of two NN pseudospins-1/2. In order to safely identify the singlet and triplet components [8], we also consider the Zeeman coupling

$$\hat{H}^Z = \sum_{l=A,B} \mu_B (L_l + g_e S_l) \cdot H, \tag{A7}$$

where $L_l$ and $S_l$ are angular-momentum and spin operators at a given Ir/Rh site, while $g_e$ and $\mu_B$ stand for the free-electron Landé factor and Bohr magneton, respectively. Each of the resulting matrix element computed at the quantum chemistry level is assimilated to the corresponding matrix element of the effective spin Hamiltonian. This one-to-one correspondence between ab initio and effective-model matrix elements enable a clear assignment of each magnetically active spin-orbit CASSCF/MRCI state and determination of all couplings constants [8]. Effective coupling constants at the rAS+SOC, CAS+SOC, and CI+SOC levels are listed in Table A1. Table A2, Table A3, and Table A4, complementary to tables and figures in the main text.
TABLE A2. Energy splittings for the lowest four spin-orbit states of two face-sharing NN IrO₆ octahedra and the corresponding effective coupling constants obtained from rAS+SOC, CAS+SOC, and MRCI+SOC calculations. The relative distances from the O ligands to the z-axis were fixed to 1.57 Å. The data are presented as complementary to those in Fig. 2(b) (all values in meV).

| d(Ir-Ir) | rAS+SOC | CAS+SOC | MRCI+SOC |
|---------|---------|---------|----------|
| 2.50Å:  |         |         |          |
| Ψ₅      | 22.0    | 0.0     | 0.0      |
| Ψ₂      | 0.5     | 188.6   | 329.7    |
| Ψ₁      | 0.0     | 198.1   | 345.0    |
| Ψ₃      | 0.0     | 198.1   | 345.0    |
| J, Γ    | -21.5, -0.93 | 188.6, 18.9 | 329.7, 30.5 |
| 2.56Å:  |         |         |          |
| Ψ₅      | 18.3    | 0.0     | 0.0      |
| Ψ₂      | 0.4     | 106.7   | 187.2    |
| Ψ₁      | 0.0     | 111.2   | 194.3    |
| Ψ₃      | 0.0     | 111.2   | 194.3    |
| J, Γ    | -17.9, -0.8 | 106.7, 8.9 | 187.2, 14.2 |
| 2.63Å:  |         |         |          |
| Ψ₅      | 15.2    | 0.0     | 0.0      |
| Ψ₂      | 0.4     | 72.0    | 123.3    |
| Ψ₁      | 0.0     | 74.0    | 126.5    |
| Ψ₃      | 0.0     | 74.0    | 126.5    |
| J, Γ    | -14.9, -0.7 | 72.0, 4.1  | 123.3, 6.3 |
| 2.69Å:  |         |         |          |
| Ψ₅      | 12.6    | 0.0     | 0.0      |
| Ψ₂      | 0.3     | 54.7    | 90.5     |
| Ψ₁      | 0.0     | 55.5    | 91.7     |
| Ψ₃      | 0.0     | 55.5    | 91.7     |
| J, Γ    | -12.4, -0.54 | 54.7, 1.7  | 90.5, 2.2 |
| 2.76Å:  |         |         |          |
| Ψ₅      | 10.4    | 0.0     | 0.0      |
| Ψ₂      | 0.2     | 44.5    | 72.1     |
| Ψ₁      | 0.0     | 44.8    | 72.4     |
| Ψ₃      | 0.0     | 44.8    | 72.4     |
| J, Γ    | -10.3, -0.4 | 44.5, 0.6  | 72.1, 0.5 |

TABLE A3. Energy splittings for the lowest four spin-orbit states of two face-sharing NN RhO₆ octahedra and the corresponding effective coupling constants obtained from rAS+SOC, CAS+SOC, and MRCI+SOC calculations. For each geometry the Rh-Rh distance was fixed to 2.58 Å. Distances between the Rh sites and the bridging O’s, d(Rh-O), are provided within brackets. The data are presented as complementary to those in Table IV (all values in meV).

| θ, d(Rh-O) | rAS+SOC | CAS+SOC+SOC | MRCI+SOC |
|------------|---------|-------------|----------|
| 70.5° (2.23Å): |        |             |          |
| Ψ₅        | 10.4    | 6.5         | 0.0      |
| Ψ₂        | 0.0     | 1.0         | 3.7      |
| Ψ₁        | 0.0     | 1.0         | 3.7      |
| Ψ₃        | 0.6     | 0.0         | 1.5      |
| J, Γ      | -9.9, -1.1 | -6.5, 2.0  | 1.5, 4.4 |
| 75° (2.12Å): |        |             |          |
| Ψ₅        | 13.3    | 0.0         | 0.0      |
| Ψ₂        | 0.0     | 0.1         | 15.0     |
| Ψ₁        | 0.0     | 0.1         | 15.0     |
| Ψ₃        | 0.8     | 0.4         | 15.2     |
| J, Γ      | -12.5, -1.7 | 0.4, -0.6  | 15.2, -0.4 |
| 80° (2.06Å): |        |             |          |
| Ψ₅        | 16.0    | 0.0         | 0.0      |
| Ψ₂        | 0.0     | 25.4        | 54.0     |
| Ψ₁        | 0.0     | 25.4        | 54.0     |
| Ψ₃        | 1.1     | 26.5        | 55.5     |
| J, Γ      | -14.9, -2.3 | 26.5, -2.2 | 55.5, -2.8 |
| 85° (1.91Å): |        |             |          |
| Ψ₅        | 17.7    | 0.0         | 0.0      |
| Ψ₂        | 0.0     | 82.4        | 135.7    |
| Ψ₁        | 0.0     | 82.4        | 135.7    |
| Ψ₃        | 1.3     | 84.0        | 137.8    |
| J, Γ      | -16.4, -2.6 | 84.0, -3.2 | 137.8, -4.3 |
| 90° (1.82Å): |        |             |          |
| Ψ₅        | 16.5    | 0.0         | 0.0      |
| Ψ₂        | 0.0     | 165.4       | 173.4    |
| Ψ₁        | 0.0     | 165.4       | 173.4    |
| Ψ₃        | 0.9     | 190.5       | 164.0    |
| J, Γ      | -15.6, -1.8 | 190.5, -50.2 | 164.0, 18.8 |
TABLE A4. Energy splittings for the lowest four spin-orbit states of two face-sharing NN RhO₆ octahedra and the corresponding effective coupling constants obtained from rAS+SOC, CAS+SOC, and MRCI+SOC calculations. The relative distances from the O ligands to the z axis are fixed to 1.54 Å. The data are presented as complementary to those in Fig. 2(d) (all values in meV).

| d(Rh-Rh) | rAS+SOC | CASSCF+SOC | MRCI+SOC |
|----------|---------|------------|----------|
| 2.45 Å:  |         |            |          |
| Ψ₅       | 22.0    | 0.0        | 0.0      |
| Ψ₃       | 0.0     | 49.5       | 157.6    |
| Ψ₁       | 0.0     | 49.5       | 157.6    |
| Ψ₂       | 1.6     | 50.0       | 158.1    |
| \(\bar{J}, \bar{\Gamma}\) | -20.4, -3.2 | 50.0, -1.1 | 158.1, -1.1 |
| 2.51 Å:  |         |            |          |
| Ψ₅       | 18.8    | 0.0        | 0.0      |
| Ψ₃       | 0.0     | 30.1       | 73.2     |
| Ψ₁       | 0.0     | 30.1       | 73.2     |
| Ψ₂       | 1.4     | 31.1       | 74.5     |
| \(\bar{J}, \bar{\Gamma}\) | -17.5, -2.7 | 31.1, -2.1 | 74.5, -2.5 |
| 2.58 Å:  |         |            |          |
| Ψ₅       | 16.0    | 0.0        | 0.0      |
| Ψ₃       | 0.0     | 25.4       | 54.0     |
| Ψ₁       | 0.0     | 25.4       | 54.0     |
| Ψ₂       | 1.1     | 26.5       | 55.5     |
| \(\bar{J}, \bar{\Gamma}\) | -14.9, -2.3 | 26.5, -2.2 | 55.5, -2.8 |
| 2.64 Å:  |         |            |          |
| Ψ₅       | 13.6    | 0.0        | 0.0      |
| Ψ₃       | 0.0     | 23.8       | 47.0     |
| Ψ₁       | 0.0     | 23.8       | 47.0     |
| Ψ₂       | 1.0     | 24.7       | 48.3     |
| \(\bar{J}, \bar{\Gamma}\) | -12.6, -1.9 | 24.7, -2.0 | 48.3, -2.6 |
| 2.71 Å:  |         |            |          |
| Ψ₅       | 11.5    | 0.0        | 0.0      |
| Ψ₃       | 0.0     | 22.6       | 42.6     |
| Ψ₁       | 0.0     | 22.6       | 42.6     |
| Ψ₂       | 0.8     | 23.5       | 43.7     |
| \(\bar{J}, \bar{\Gamma}\) | -10.7, -1.6 | 25.5, -1.7 | 43.7, -2.2 |
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