Calculated g-factors of 5d double perovskites Ba$_2$NaOsO$_6$ and Ba$_2$YOsO$_6$

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Using Wannier functions to represent the density functional results we calculate the hybridization corrections to the orbital momentum operator in the Os 5d shell of the Mott insulators Ba$_2$NaOsO$_6$ and Ba$_2$YOsO$_6$. The g-factors are obtained by evaluating the spin and orbital momentum operators in the atomic ground states of the Os ion. While the hybridization corrections play a minor role in the $d^1$ ion of Ba$_2$YOsO$_6$, with a dominant spin moment, they are instrumental for the observation of the nonzero g-factor of the $d^1$ ions of Ba$_2$NaOsO$_6$. In addition, we analyze the exchange interactions in Ba$_2$YOsO$_6$ and find them to be consistent with the reported magnetic structure.

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I. INTRODUCTION

The high-temperature paramagnetic moment is one of the basic characteristics of magnetic materials which is often used to draw conclusions about the underlying atomic multiplets. In Mott insulators the charge fluctuations are quenched and the low-energy physics is usually governed by a single atomic multiplet. Its symmetry properties (degeneracy), captured by the pseudospin description, are determined by the gross features of the ligand field and do not depend on the material details. The size of the local magnetic moment, encoded in the g-factor, is affected by hybridization with ligands which modifies the shape of the local orbitals. This is particularly important for heavier $d^1$ ions in strong cubic crystal fields. The spin-orbit interaction (SOI) selects the $J_{eff} = \frac{1}{2}$ quadruplet to be the ground state. For purely $d$ orbitals the spin and orbital contributions to the magnetic moment within the $J_{eff} = \frac{1}{2}$ subspace exactly cancel each other, leading to $g = 0$ [1]. The magnetic response of such an ion can therefore arise only due to mixing with higher-lying multiplets or a hybridization correction to the g-factor. Ba$_2$NaOsO$_6$ is a rare example of a $d^1$ insulator with cubic symmetry.

In this article, we present a numerical calculation of g-factors based on the Wannier orbitals and diagonalization of the atomic problem. It is applied to two 5d double-perovskite insulators Ba$_2$NaOsO$_6$ (BNOO) and Ba$_2$YOsO$_6$ (BYOO) that have attracted some interest recently [2–4].

II. NUMERICAL APPROACH

A. Electronic structure calculations

First, we carried out ab initio calculations within the the generalized gradient approximation [5] to the density functional theory using the full-potential code WIEN2k [6,7]. We studied three compounds: the cubic perovskite SrVO$_3$ (SVO) as a simple model system to debug our codes and two cubic double perovskites BNOO and BYOO as the actual goals of the present work. The following lattice parameters were used: $a = 3.8425$ Å for SVO [8] and $a = 8.2870$ (8.5341) Å with an oxygen internal parameter $x = 0.2272$ (0.2350) for BNOO (BYOO) [9,10]. The SOI was included for the 5d systems of BNOO and BYOO, while it was not included for the 3d system SVO.

The WIEN2k bases were characterized by $R_{mt} K_{max} = 7$ and muffin-tin spheres with radii in atomic units: Sr (2.5), V (1.91), and O (1.70) for SVO; Ba (2.5), Y (2.18), Os (2.03), and O (1.66) for BYOO; Ba (2.5), Na (2.15), Os (1.96), and O (1.61) for BNOO.

B. Evaluation of angular and spin momenta

While spin magnetization is straightforward to calculate, orbital magnetization is a more complicated problem. Ceresoli et al. [11] provided a general basis-independent expression for the orbital magnetization of a noninteracting insulator in terms of Wannier functions (WFs), which resolved the problem that orbital currents cannot, in general, be assigned to a particular atomic site. The Mott insulating nature of the studied materials simplifies our task considerably. We assume that the orbital current density is localized in regions around the active (Os) atoms separated by regions where it vanishes. Working in the basis of atom-centered Wannier functions we can express the orbital magnetization as a sum of individual atomic contributions.

The WFs [12,13] with the $|d_{xy}, \uparrow\rangle$, $|d_{yz}, \uparrow\rangle$, $|d_{zx}, \uparrow\rangle$, $|d_{xy}, \downarrow\rangle$, $|d_{yz}, \downarrow\rangle$, and $|d_{zx}, \downarrow\rangle$ symmetries spanning the isolated $t_{2g}$ manifold were obtained using the WANNIER90 [14] and WIEN2WANNIER [15] codes. (See Fig. 1). Without SOI these WFs are well defined by their symmetry properties. With SOI this in general is not the case due to mixing of the spin species. However, since the effect of SOI is predominantly localized on the 5d ion, it is possible to construct the WFs which are, to a high accuracy, eigenstates of the spin $S_z$ operator. The on-site one-particle Hamiltonian in this $t_{2g}$ Wannier basis has the textbook form.
and the one-particle orbital $t$ each terms because of the WF parity. These data are nearly identical for order $l$.

We have used an $8 \times 8 \times 8 \times 8$ mesh for SVO and a $4 \times 4 \times 4 \times 4$ mesh for BNOO and BYOO, which ensured that the WFs were spatially well separated from their aliases. The normalized WFs $\psi_{\alpha}(r)$ were expanded in spherical harmonics inside a sphere of a radius $4a$ ($\sqrt{2}a$) around the V (Os) atom for SVO (BNOO, BYOO),

$$\psi_{\alpha}(r) = \sum_{l,m} c_{lm}^{\alpha}(r)Y_{lm}(\hat{r}).$$

To this end we have employed a dense spherical mesh of $100 \times 60 \times 120$ and $400 \times 180 \times 360$ of $(r, \theta, \phi)$ points for SVO and BNOO/BYOO, respectively. The maximum values of $l$ for this expansion were $l_{\text{max}} = 16$ for SVO and 30 for BNOO and BYOO, which were sufficient to capture 99% of the WF. (See Fig. 2.)

The spherical harmonic representation allows straightforward evaluation of the angular momentum matrix elements in the $t_{2g}$ subspace $I_{\alpha\beta}$,

$$I_{\alpha\beta} = \langle \psi_{\alpha} | \hat{l}_{\alpha\beta} | \psi_{\beta} \rangle = \sum_{l,m} (c_{lm}^{\alpha}|c_{lm}^{\beta}),$$

$$I_{\alpha\beta} = \sum_{l,m} \sqrt{l(l+1)} - m(m+1)(c_{lm+1}^{\alpha}|c_{lm}^{\beta}),$$

$$I_{\alpha\beta} = \frac{I_{\alpha\beta}^{+} + (I_{\alpha\beta}^{-})}{2}, \quad I_{\alpha\beta} = \frac{I_{\alpha\beta}^{-} - (I_{\alpha\beta}^{+})}{2i}.$$  (2)

![FIG. 2. Convergence of the weight of the Wannier function ($|\psi|^2$) and the one-particle orbital $g$-factor ($g_t$) with the spherical harmonic order $l$ for BNOO. Note that there is no contribution of the odd $l$ terms because of the WF parity. These data are nearly identical for each $t_{2g}$ orbital of BNOO and BYOO.](image)

Here, $(f_1|f_2)$ stands for the radial integral $(f_1|r^2f_2)$. For the cubic site symmetry, $I$ has the same form as for pure $d$ orbitals ($I_k$). The higher harmonics in the site expansion of WFs introduces a multiplicative correction factor $I = g_{\text{eff}}$. The physical origin of $g$ is the hybridization with ligands. Using the matrix elements of Eq. (2) we can write the orbital momentum operator in the $t_{2g}$ subspace,

$$\hat{I} = \sum_{m,n} I_{mn}c_{m}^{\dagger}c_{n},$$  (3)

with $m \equiv k\alpha$ being the spin/orbital indices. There is no hybridization screening of the spin moment and thus the spin momentum operator has the standard form

$$\hat{s} = \frac{1}{2} \sum_{k,\alpha,\beta} \sigma_{\alpha\beta} c_{k\alpha}^\dagger c_{k\beta}.$$  (4)

As the final step, we diagonalize the on-site Hamiltonian including the on-site Coulomb interaction and SOI. We denote the matrix elements of the orbital $\hat{I}$ and spin $\hat{s}$ momenta within the ground-state multiplet with a capital $L$ and $S$, respectively. Comparing the magnetic moment elements $M = \mu_{\text{eff}}(2S + L)$ to the ground-state pseudospin operator $J$, we obtain the $g$-factor and the effective paramagnetic moment $\mu_{\text{eff}}$.

### III. RESULTS AND DISCUSSION

#### A. Test case: SrVO$_3$

To test our implementation of Eq. (2) we have chosen a simple system without SOI. Since SrVO$_3$ is a metal, we do not assign a physical significance to this result. We merely want to show that $I$ has the expected form. Evaluating Eq. (2) yields

$$I_x = i \begin{pmatrix} 0.0000 & 0.0000 & -0.7955 \\ 0.7955 & 0.0000 & 0.0000 \\ 0.0000 & 0.0000 & 0.0000 \end{pmatrix},$$  (5)

$$I_y = i \begin{pmatrix} 0.0000 & 0.7955 & 0.0000 \\ -0.7955 & 0.0000 & 0.0000 \\ 0.0000 & 0.0000 & 0.0000 \end{pmatrix},$$  (6)

$$I_z = i \begin{pmatrix} 0.0000 & 0.0000 & 0.0000 \\ 0.0000 & 0.0000 & 0.7956 \\ 0.0000 & -0.7956 & 0.0000 \end{pmatrix},$$  (7)

which amounts to $\gamma = 0.7956$.

#### B. $d^3$ case: Ba$_2$YOsO$_6$

The structural and magnetic properties of BYOO were recently investigated by Kermarrec et al. [9], who reported a frustrated A-type antiferromagnet (AFM) with the Néel temperature $T_N \approx 69$ K, Curie-Weiss temperature $\Theta = 717$ K, and the effective paramagnetic moment $\mu_{\text{eff}} = 3.91 \mu_B$ close to the spin-only value of $3.87 \mu_B$.

Using the above procedure we have obtained $\gamma = 0.587$ for Wannier functions built from the subspace spanning the Os $5d$ bands ($d$-only model). Next, we have used the on-site part of the tight-binding Hamiltonian (including SOI) augmented with the atomiclike Coulomb interaction, parametrized with $U = 1.8$ eV and $J = 0.4$ eV [16], and diagonalized it. The
fourfold degenerate ground state can be represented as a \( J = \frac{3}{2} \) pseudospin. Calculating the matrix elements of the magnetic moment \( \mathbf{M} = \mu_B (2 \mathbf{S} + \mathbf{L}) \) in the ground-state multiplet, we arrive at a \( g \)-factor of 1.89, leading to \( \mu_{\text{eff}} = 3.66 \mu_B \). The matrix elements of \( \mathbf{S}_z \) and \( \mathbf{L}_z \) are shown in the Appendix. This shows that even a relatively strong SOI leads to only a small correction in the case of a half-filled 5d (\( t_{2g} \)) shell and that the local moment is dominated by the spin component [17]. Interestingly, under special circumstances the small corrections may play an important role. Such is the case of the ferrimagnet \( \text{Sr}_2\text{CrOsO}_6 \). Without SOI the band-structure calculations [18,19] show a complete compensation of the spin moments of Cr and Os and only the uncompensated orbital moments arising due to SOI give rise to a net magnetization.

Next, we have calculated the effective interaction between the \( J = \frac{3}{2} \) pseudospins on the nearest-neighbor (NN) and next-nearest-neighbor (NNN) bonds. The spin-orbit entangled atomic states, in general, lead to an anisotropic exchange with transformation [22] (\( \chi^2/U \) expansion) and expanded in spherical tensors. Consistent with the dominant spin nature of the pseudospins, we find that the isotropic dipole-dipole exchange dominates by more than an order of magnitude. A small anisotropy was found between \( J_\parallel = 2.96 \text{ meV} \) and \( J_\perp = 3.13 \text{ meV} \), the interaction of components in and out of the cubic plane for a given NN bond. The NNN interactions are about 30 times weaker than the NN ones. The dominant NN AFM interaction is consistent with the \( A \)-type ordering. We also point out the exchange anisotropy favors the ordered moments to lie in the ferromagnetic (FM) planes. However, the observed anisotropy is rather small to draw solid conclusions without detailed calculations, which are beyond the scope of the present study. The estimated Curie-Weiss temperature \( \Theta = 12.3 J_{\text{NN}} \approx 420 \text{ K} \) is somewhat smaller than the experimental value. Both the theoretical and experimental values contain uncertainties. On the theoretical side it is the value of the on-site Coulomb interaction \( U \) and the limitations of the perturbative expansion. On the experimental side it is in particular the temperature range of the study which is substantially below the experimental \( \Theta \), as pointed by authors of Ref. [9].

C. \( d^1 \) case: Ba\( _2 \)NaOsO\( _6 \)

BNOO is an unusual example of a \( d^1 \) Mott insulator. It exhibits a FM polarization below 10 K [2,23]. The crystal and magnetic structures are still under debate. Specific heat measurements indicate that only \( \ln 2 \) entropy is released above the transition temperature, which contradicts the fourfold degenerate \( J = \frac{3}{2} \) ground state in cubic site symmetry. The structural measurements, nevertheless, indicate that a potential noncubic distortion must be rather small. In the following, we address the question of the origin of the high-temperature paramagnetic response and the size of the \( g \)-factor. This is motivated by an observation that the magnetic moment \( \mathbf{M} = \mu_B (2 \mathbf{S} + \mathbf{L}) \) has only zero matrix elements within the groundstate \( J = \frac{3}{2} \) multiplet of the \( d^1 \) system [1]. In other words, in the \( J = \frac{3}{2} \) quadruplet the spin and orbital contributions to the magnetic moment exactly compensate each other. This conclusion remains valid also in the case of weak noncubic perturbations as long as the mixing with excited \( J = \frac{3}{2} \) states can be neglected. The likely explanation for the paramagnetic moment is the fact that the local orbitals (Wannier functions) do not have an exact \( d \) symmetry, but contain also higher harmonics which rescale the orbital momentum by \( \gamma \).

The \( d-d \) electron-electron interaction is not effective in the \( d^1 \) case and thus we only need to consider the SOI. The relationship between \( g \) and \( \gamma \) in the \( J = \frac{3}{2} \) ground state is given by \( g = \frac{3}{2} (1 - \gamma) \). Our calculations yield \( \gamma = 0.536 \), leading to \( g = 0.31 \) and \( \mu_{\text{eff}} \approx 0.60 \mu_B \). The calculated matrix elements \( I \) as well as \( \mathbf{S}_z \) and \( \mathbf{L}_z \) are shown in the Appendix. This value compares well to the experimentally reported values of 0.596--0.647 [23] and 0.677 [10].

Another contribution to the paramagnetic response is the van Vleck susceptibility arising from field-induced mixing of the excited states. Since this contribution is temperature independent, it is experimentally easy to distinguish from the Curie-Weiss response of local moments. A straightforward calculation in the present atomic treatment yields a van Vleck susceptibility of \( \chi_v(\text{emu/mol}) \approx 3.232 \times 10^{-5}/\Delta \text{(eV)} \), which is inversely proportional to the spin-orbit splitting \( \Delta \approx 0.49 \text{ eV} \) of the \( t_{2g} \) shell. The resulting number compares well to the temperature-independent contribution to the susceptibility (\( 3 \times 10^{-3}-1.8 \times 10^{-4} \text{ emu/mol} \)) reported in Ref. [23].

IV. CONCLUSIONS

We have presented a first principles calculation of the \( g \)-factors of 5d ions in selected double-perovskite Mott insulators. The calculated effective paramagnetic moments \( \mu_{\text{eff}} \) compare well to their experimental counterparts obtained from Curie-Weiss fits to the high-temperature susceptibility. We find that even in the case of 5d electrons with relatively strong SOI the half-filled shell \( d^1 \) configuration is dominated by the first Hund’s rule and the local moments have a predominantly spin character. In the \( d^1 \) configuration the spin and orbital contributions to \( \mu_{\text{eff}} \) cancel each other for orbitals with a pure \( d \) character. The admixture of higher harmonics to the \( d \)-like Wannier functions due to the hybridization with ligands partially lifts this exact cancellation and gives rise to the small \( \mu_{\text{eff}} \) observed in experiments.

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APPENDIX

The matrix elements of the orbital momentum operator \( \hat{\mathbf{I}} \) in the 5d shell of Os in BNOO in the basis of \{\( |dx_y, \uparrow\rangle, |dx_y, \downarrow\rangle, |dz_x, \uparrow\rangle, |dz_x, \downarrow\rangle, |dz_y, \uparrow\rangle, |dz_y, \downarrow\rangle \} \) WFs are calculated.
Due to the SOI, the spin projection and \( t_{2g} \) character are only approximately conserved. This gives rise to the additional matrix elements. These are, nevertheless, more than an order of magnitude smaller than the dominant terms, and are not considered in the evaluation of the \( g \)-factor. The results for BYOO show a similar picture.

The matrix elements of the spin and orbital momentum operator are in the \( J = \frac{3}{2} \) ground state of BYOO (\( d^3 \)). The basis functions are indexed by \( J_z = \frac{3}{2}, \frac{1}{2}, -\frac{1}{2}, -\frac{3}{2} \).

\begin{align*}
S_z &= \begin{pmatrix}
1.442 & 0.000 & 0.000 & 0.000 \\
0.000 & 0.481 & 0.000 & 0.000 \\
0.000 & 0.000 & -0.481 & 0.000 \\
0.000 & 0.000 & 0.000 & -1.442
\end{pmatrix}, \\
L_z &= 0.587 \times \begin{pmatrix}
-0.058 & 0.000 & 0.000 & 0.000 \\
0.000 & -0.019 & 0.000 & 0.000 \\
0.000 & 0.000 & 0.019 & 0.000 \\
0.000 & 0.000 & 0.000 & 0.058
\end{pmatrix}.
\end{align*}

The matrix elements of the spin and orbital momentum operator are in the \( J = \frac{3}{2} \) ground state of BNOO (\( d^1 \)). The basis functions are indexed by \( J_z = \frac{3}{2}, \frac{1}{2}, -\frac{1}{2}, -\frac{3}{2} \). Note that when \( e_g-t_{2g} \) mixing can be neglected (this case), the basis functions are completely specified by symmetry.

\begin{align*}
S_z &= \begin{pmatrix}
\frac{1}{2} & 0 & 0 & 0 \\
0 & \frac{1}{2} & 0 & 0 \\
0 & 0 & -\frac{1}{2} & 0 \\
0 & 0 & 0 & -\frac{1}{2}
\end{pmatrix}, \\
L_z &= 0.536 \times \begin{pmatrix}
-1 & 0 & 0 & 0 \\
0 & -\frac{1}{3} & 0 & 0 \\
0 & 0 & \frac{1}{3} & 0 \\
0 & 0 & 0 & 1
\end{pmatrix}.
\end{align*}

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