

Microscopic origin of temperature-dependent magnetism in spin-orbit-coupled transition metal compounds

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A few 4d and 5d transition metal compounds with various electron fillings were recently found to exhibit magnetic susceptibilities χ and magnetic moments that deviate from the well-established Kotani model. This model has been considered for decades to be the canonical expression for describing the temperature dependence of magnetism in systems with nonnegligible spin-orbit coupling effects. In this paper, we uncover the origin of such discrepancies and determine the applicability and limitations of the Kotani model by calculating the temperature dependence of the magnetic moments of a series of 4d (Ru-based) and 5d (W-based) systems at different electron fillings. For this purpose, we perform exact diagonalization of *ab initio*-derived relativistic multiorbital Hubbard models on finite clusters and compute their magnetic susceptibilities. Comparison with experimentally measured magnetic properties indicates that contributions such as a temperature-independent χ_0 background, crystal field effects, Coulomb and Hund's couplings, and intersite interactions—not included in the Kotani model—are especially crucial for correctly describing the temperature dependence of χ and magnetic moments at various electron fillings in these systems. Based on our results, we propose a generalized approach beyond the Kotani model to accurately describe their magnetism.

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Introduction. The magnetism in spin-orbit-coupled transition-metal-based compounds has been at the focus of intensive studies in recent years, not only because of their relevance to such phenomena as frustrated magnetism [1–5], Kitaev spin liquid phases [6–16], fractionalized excitations [3,4,17–19], or multipolar physics [20–24], but also for their role in, for instance, 4d and 5d hybrid halides, which are being discussed as relevant materials for optoelectronic purposes [25–29]. Owing to the presence of spin-orbit coupling, the usual Curie-Weiss formula for explaining the temperature-dependent susceptibility in these systems does not apply. To overcome this problem, Kotani [30] proposed a temperature-dependent expression for magnetic moments [see Fig. 1(a)], which successfully explains the behavior of the magnetic susceptibility in systems consisting of 4d and 5d transition metal ions in an octahedral environment of ligands where the octahedra are almost isolated or weakly coupled. Some examples are ruthenium halides with

perovskite-related structures such as A_2RuX_6 ($A = K, Cs, Rb$; $X = Cl, Br$) [31–35], and a few cases of Ru-based hybrid halides [36,37]. In some other examples, however, including Ru-based hybrid halides $M_2NaRuCl_6$ ($M = CH_3NH_3$) $M_3Ru_2Br_9$, and vacancy-ordered double perovskites A_2WCl_6 ($A = Cs, Rb, M$) [38–40], the temperature-dependent magnetic susceptibility deviates strongly from the Kotani prediction, challenging this well-established model for spin-orbit-coupled transition-metal complexes. The question is therefore: Why does the Kotani formula describe quite accurately the temperature dependence of the magnetic susceptibility and magnetic moments in some spin-orbit-coupled systems but not in others?

In the present paper we uncover the origin of this discrepancy. Specifically, we resolve (i) the role of electronic fillings shown in Fig. 1(b), (ii) the sensitivity of the magnetic moment components to the crystal-field distortions, (iii) the role of Hund's coupling J_H , specially in d^2 systems, (iv) the role of $t_{2g} - e_g$ crystal fields [41], and (v) the role of inter-site hoppings. For this purpose, we investigate the magnetic behavior of a few representative systems including $M_2NaRuCl_6(d^5)$, $M_3Ru_2Br_9(d^5)$, $Cs_2RuCl_6(d^4)$, and $A_2WCl_6(d^2)$ by performing exact diagonalization of *ab initio*-derived relativistic multiorbital Hubbard models on finite clusters, computing their magnetic susceptibilities, and extracting general rules for the validity range of the Kotani model. Finally, for systems consisting of dimers or clusters of octahedra with strong

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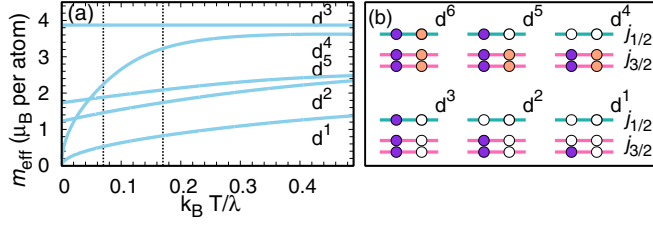


FIG. 1. (a) Kotani plot of m_{eff} for various fillings of t_{2g} orbitals. The dotted vertical lines at $k_B T / \lambda \sim 0.07$ and 0.17 indicate $T = 300$ K when 0.37 eV ($5d$) and $\lambda = 0.15$ eV ($4d$) respectively. (b) Schematic ground-state diagrams for each filling in the relativistic $j_{1/2}$ and $j_{3/2}$ basis.

intersite hoppings, such as $\text{M}_3\text{Ru}_2\text{Br}_9$, the Kotani model is not suitable, and similar mechanisms have been suggested in the past for describing their temperature-dependent magnetic moments [42–44]. For completeness, we also investigate a representative case of dimer system.

Methods. To analyze the systems' magnetism, we consider the improved Curie-Weiss expression for the diagonal components of the susceptibility [45],

$$\chi^\alpha(T) \approx \chi_0^\alpha + \frac{N_A [m_{\text{eff}}^\alpha(T)]^2}{3k_B(T - \Theta^\alpha)}, \quad (1)$$

where α , T , and χ_0^α indicate the field direction, temperature, and temperature-independent background contributions, respectively. N_A , k_B , and Θ^α are Avogadro, Boltzmann, and Weiss constants, respectively. m_{eff} denotes the effective magnetic moment. In systems with weak intersite interactions, the experimentally measured susceptibility is usually mapped to a magnetic moment

$$\tilde{m}_{\text{eff}}^\alpha(T) \approx \sqrt{\frac{3k_B T}{N_A}} \chi^\alpha(T). \quad (2)$$

Here, we denote $\tilde{m}_{\text{eff}}^\alpha(T) = m_{\text{eff}}^\alpha(T)$ only when inter-site hoppings, χ_0 , and Θ^α are set to zero. In our microscopic approach, we use Eq. (2) [43,45] to obtain the magnetic moments where the susceptibility is calculated from

$$\chi^\alpha(T) = \chi_0 + N_A k_B T \left(\frac{1}{Z} \frac{\partial^2 Z}{\partial h_\alpha \partial h_\alpha} \right). \quad (3)$$

h is the external magnetic field and Z is the partition function $Z = \sum_n e^{-E_n/k_B T}$ with E_n being the eigenenergies obtained from exact diagonalization on finite clusters of the Hamiltonian including the kinetic hopping term, crystal-field splitting, spin-orbit coupling, and Coulomb interaction (see the Supplemental Material [46]). The corresponding parameters are hopping parameters $\mathbf{t}$, crystal-field parameters Δ , spin-orbit coupling parameter λ , Coulomb repulsion U , and Hund's coupling J_H . $\mathbf{t}$ and Δ were extracted using the Wannier function projection formalism [47–49] from the electronic structure of density functional theory with the full-potential linearized augmented plane wave basis (LAPW) [50] (see the SM [46]).

Results. The dominant crystal field information and hopping parameters (summarized in Table I) are discussed here and the details are in the SM [46]. Due to the octahedral environment, the transition-metal d states split into e_g and

TABLE I. Largest hopping parameters in meV extracted from DFT calculations for d^5 ($\text{M}_2\text{NaRuCl}_6$, $\text{M}_3\text{Ru}_2\text{Br}_9$), d^4 (Cs_2RuCl_6) and d^2 (Cs_2WCl_6) systems.

$\text{M}_2\text{NaRuCl}_6$	$\text{M}_3\text{Ru}_2\text{Br}_9$	Cs_2RuCl_6	Cs_2WCl_6
−39.1	−338.6	−38.4	−46.6

t_{2g} states. We first consider the t_{2g} -only model widely used in these systems. We start with a d^5 system $\text{M}_2\text{NaRuCl}_6$, which crystallizes in the space group $P\bar{3}m$ and contains chains of face-sharing RuCl_6 and NaCl_6 octahedra along c [Fig. 2(a)]. To explain the experimentally observed effective magnetic moment for $\text{M}_2\text{NaRuCl}_6$ [29], which deviates from the ideal Kotani model [30], we apply the method described above to single-site, two-site and three-site Ru clusters. We used $U = 2.49$ eV and $J_H = 0.4$ eV following the cRPA values of $\alpha\text{-RuCl}_3$ [51]. The results for $\tilde{m}_{\text{eff}}$ are shown in Fig. 3(a). $\tilde{m}_{\text{eff}} = m_{\text{eff}}$ for the one-site case while $\tilde{m}_{\text{eff}} \neq m_{\text{eff}}$ for the few-sites case with nonzero $\mathbf{t}$ and χ_0 . We observe that the experimental results [29] show lower values of the effective magnetic moment compared to the ideal Kotani behavior ($\lambda = 0.075$ eV), and the slopes at low and high temperatures do not fit either. Increasing the value of λ to 0.15 eV, which is comparable to values for other Ru-based systems like $\alpha\text{-RuCl}_3$, reduces the slope of the calculated magnetic moment toward the experimental slope. Including the effect of the trigonal crystal-field distortion $\Delta = -0.01$ eV does not affect the average magnetic moment, but strongly affects the direction-dependent magnetic moments (see the SM [46]).

Including the contribution of all hopping parameters in the two-site and three-site calculation ($\mathbf{t} = \mathbf{t}_{\text{DFT}}$) introduces a sharp reduction of the susceptibility at low temperatures [Fig. 3(a), right panel]. The experimentally measured susceptibility also includes a temperature-independent weak contribution χ_0 , originating from core diamagnetism and Van-Vleck paramagnetism [52,53]. With $\chi_0 = -6 \times 10^{-4}$ emu/mol the effective magnetic moment becomes flat over a temperature range 30–300 K, closely matching the experimental magnetic moment. We conclude that the deviation of the experimental magnetic moment from the Kotani plot in d^5 system can be attributed to both (i) a temperature-independent χ_0 and (ii) intersite interactions. Results for two-site and three-site clusters are very close so we consider only two-site clusters in the following cases.

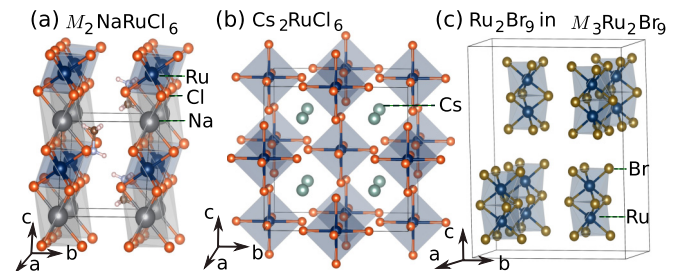


FIG. 2. Crystal structure of (a) $\text{M}_2\text{NaRuCl}_6$ (b) Cs_2RuCl_6 and (c) Ru_2Br_9 face-shared bioctahedral dimer in $\text{M}_3\text{Ru}_2\text{Br}_9$.

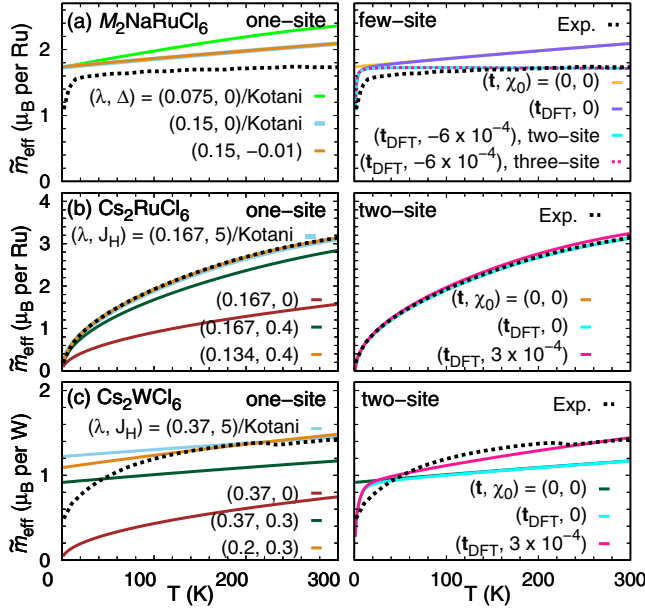


FIG. 3. Temperature dependence of the average magnetic moments for (a) $M_2NaRuCl_6$ (d^5), (b) Cs_2RuCl_6 (d^4), and (c) Cs_2WCl_6 (d^2) from one-site, two-site, and three-sites cluster calculations with various spin-orbit coupling λ , trigonal crystal-fields Δ , Hund's couplings J_H , and hopping parameters t in eV as well as χ_0 in emu per mol.

We now proceed with the d^4 case. The $4d$ -based hybrid vacancy-ordered double perovskite Cs_2RuCl_6 crystallizes in the $Fm\bar{3}m$ space group and consists of isolated $RuCl_6$ octahedra [see Fig. 2(b)]. The largest hopping parameter is -38.4 meV. The results are displayed in Fig. 3(b). The Kotani plot can be reproduced by considering large unphysical J_H (around 5 eV) with $\lambda = 0.167$ eV, or, alternatively choosing $\lambda = 0.134$ eV, $J_H = 0.4$ eV. In fact, various combinations of J_H and λ can reproduce the experimental observations. We also performed two-site cluster calculations with $J_H = 0.4$ eV and find that including χ_0 and hopping parameters modifies only slightly the results. We note that the temperature-dependent magnetic moments need to be considered to reproduce the experimental susceptibility. This property resolves the existence for magnetism in d^4 systems with moderate values of intersite hoppings such as Ba_2YIrO_6 [54–61].

In contrast to d^4 systems, d^2 systems, such as Cs_2WCl_6 , with similar crystal structures to Cs_2RuCl_6 by replacing Ru with W, display a different behavior. We use $U = 1.7$ eV following values previously used for Ir-based systems [62]. The results are shown in Fig. 3(c). The Kotani plot with $\lambda \sim 0.37$ eV [40] can only reproduce the slope of the experimental data by considering large unphysical J_H (around 5 eV) where the triplet state is then the ground state in Kotani's perturbation theory. For $J_H = 0$, the ground state is the singlet state with zero magnetic moment at 0 K. In $5d$ systems, usual values of J_H are around 0.3 eV [62], and the ground state is a mixture of triplet and singlet states. The magnetic moment is therefore between the above two limits. When decreasing λ to 0.2 eV, the contribution of the triplet states becomes

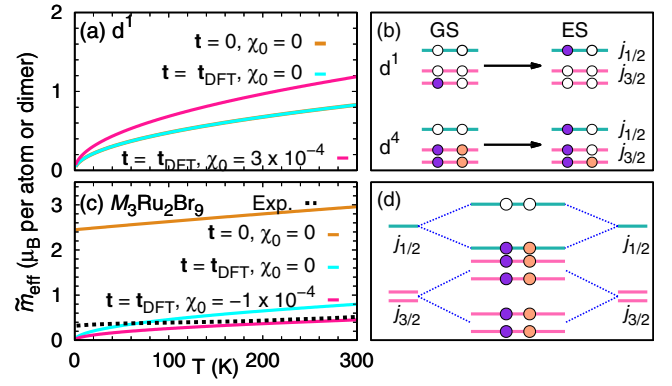


FIG. 4. The average magnetic moments for (a) d^1 system and (c) dimer system $M_3Ru_2Br_9$ with two-site cluster calculations. Schematic diagrams of (b) ground states and first excited states for d^1 and d^4 systems, as well as (d) the ground state of the dimer system $M_3Ru_2Br_9$.

larger, leading to larger magnitudes of the magnetic moments. The two tuning parameters for the magnetic moments are therefore Hund's and spin-orbit coupling strengths. However, different from the d^4 case, the Kotani plot cannot reproduce the experimental data with a combination of λ when assuming physically reasonable values of $J_H = 0.3$ eV. For two-site clusters, the magnitude of the effective magnetic moment is sharply reduced at low temperatures when $t = t_{\text{DFT}}$. Including a positive χ_0 brings a downturn in the magnetic moments, close to the experiment. Our method also reproduces the experimental observations for other d^2 systems (see the SM [46]). We conclude that in d^2 systems, besides the contributions of χ_0 and intersite interactions, as in the d^5 systems, the Hund's coupling plays an important role in reproducing the experimental magnetic moments. Finally, for d^1 systems, inclusion of t_{DFT} , does not significantly affect $\bar{m}_{\text{eff}}$, while adding a nonzero χ_0 significantly changes the slope [see Fig. 4(a)].

Analyzing the previous results, we observe several facts. Already at the level of the Kotani model, the dependence of $\bar{m}_{\text{eff}}$ on the electron filling is rather remarkable, as shown in Fig. 1(a). For t_{2g} states with spin-orbit coupling, the ground state is more conveniently described in terms of the doublet $j_{1/2}$ and quadruplet $j_{3/2}$ [Fig. 1(b)]. Different from the atomic relativistic basis j for p orbitals with $L_p = 1$, here $j_{1/2}$ and $j_{3/2}$ correspond to $L_{\text{eff}} = -L_p$. With an electron filling of d^5 , $m_{\text{eff}} = 1.73 \mu_B$ at 0 K which corresponds to one hole in the relativistic $j_{1/2}$ basis, while with an electron filling of d^2 , $m_{\text{eff}} = 1.22 \mu_B$ at 0 K corresponds to a triplet state (in reality there is a reduction of this value owing to mixing with a singlet state). For these two cases, inclusion of small intersite hoppings significantly reduces $\bar{m}_{\text{eff}}$ at low temperatures, as demonstrated above.

In contrast, at electron fillings of d^1 and d^4 , intersite hoppings seem to not affect the effective magnetic moments. At these fillings, the Kotani model predicts $m_{\text{eff}} = 0$ at 0 K. These two cases are affected differently by χ_0 . For d^4 systems, the effective magnetic moment changes sharply at values below $k_B T / \lambda \sim 0.2$ and is less influenced by other interactions while the curves for d^1 (and also all other fillings) have a smaller slope and are more sensitive to the consideration of further

interactions. This could be explained by analyzing the role of the excited states [see Fig. 4(b)]. In d^1 , there are only two energy levels, the quadruple degenerate ground state $j_{3/2}$ and the doubly degenerate excited state $j_{1/2}$ (magnetic moment $1.73 \mu_B$), the energy difference is $3\lambda/2 \sim 0.22$ eV ($\lambda = 0.15$ eV). At high temperatures, the spin and orbital degrees of freedom are not coupled, therefore the total magnetic moment is $\sqrt{l(l+1) + 4s(s+1)} = \sqrt{5}$ ($s = \frac{1}{2}$, $l = 1$). The magnetic moment changes slowly from 0 to values around $\sqrt{5}$. In d^4 , the energy difference of the ground state and first excited state is $-\frac{1}{2}(5J_H - \sqrt{25J_H^2 + 10J_H\lambda + 9\lambda^2}) \sim 0.096$ eV ($\lambda \sim 0.15$ eV, $J_H \sim 0.4$ eV). There are more available energy levels and the highest magnetic moment at high temperatures is $\sqrt{10}$ ($s = 1$, $l = 1$). Therefore, the magnetic moment increases dramatically from 0 to $\sqrt{10}$ in a small temperature region. For d^3 systems, the effective magnetic moment is constant in the Kotani's plot [see Fig. 1(a)] because the orbital moment is quenched. However, with increasing spin-orbit coupling, in the j_{eff} basis, the total magnetic moment decreases at lower temperatures. This reduction has been observed experimentally in NaOsO₃ [63] and SrTcO₃ [64], and theoretically investigated in Ref. [65].

All systems considered so far have weak intersite hoppings below 65 meV. In what follows, we consider d^5 M₃Ru₂Br₉, which is formed by Ru₂Br₉ dimers comprising two face-sharing RuBr₆ octahedra [see Fig. 2(c)]. The largest nearest-neighbor intradimer hopping is -338.6 meV. To explain the experimental observed effective magnetic moment, which shows a dramatically low, temperature-independent moment compared to the predicted Kotani behavior, we calculate the temperature-dependent magnetic moments using two-site clusters shown in Fig. 4(c). Including the intradimer hopping parameters, the strong binding splits the single site relativistic $j_{1/2}$ and $j_{3/2}$ basis to form molecular bonding and antibonding energy levels [see Fig. 4(d)]. The ten electrons and two holes form a singlet $j_{\text{dim}} = 0$ state, similar to the case of Ba₃CeIr₂O₉ [66], leading to a significant reduction of the magnetic moments as shown in Fig. 4(c). Unlike the experiment, the magnetic moments approach zero at 0 K. These deviations have been suggested to originate from the intra- versus interdimer interactions in d^4 systems Ba₃ZnIr₂O₉ [67], Ba₃CdIr₂O₉ [68], and Ba₃MgIr₂O₉ [56]. In our case, interdimer interactions and possible impurity effects are not included in our calculations. On the other hand, we find that for the cases where intersite hoppings are strongly anisotropic, the suppression of the effective magnetic moment is not so dramatic (see the SM [46]).

From the above results, we observe that in a t_{2g} -only model, the magnetic moments for single site are determined by (i) the ground state at 0 K and (ii) the energy of the excited states. We now discuss whether these two features can be affected by including the e_g orbitals in the calculation as suggested in Refs. [41,69], as well as metal-ligand covalent effects as suggested in Refs. [70–74]. The results are displayed in Fig. 5 for various fillings (d^1 , d^2 , d^4 , and d^5) with t_{2g} - e_g crystal fields around 3 eV. The metal-ligand covalent effects are included by considering a multiplicative correction factor 0.643 of the orbital momentum operator as described in [70].

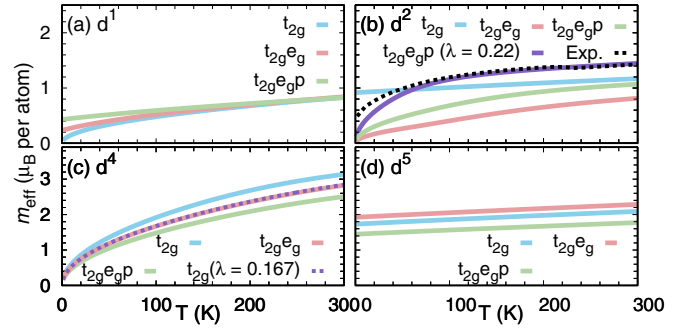


FIG. 5. Temperature dependence of the average magnetic moment for (a) d^1 , (b) d^2 , (c) d^4 , and (d) d^5 including t_{2g} , e_g , and p orbitals. Hund's coupling for $4d$ systems (d^4) is 0.4 eV while for $5d$ systems (d^2 and d^5) is 0.3 eV. The t_{2g} - e_g crystal field is around 3 eV.

For d^1 systems [Fig. 5(a)], we find that consideration of e_g states induces a nonzero magnetic moment at 0 K of the order of $0.2 \mu_B$, similar to the experimental values [75,76]. In our calculations, the small magnetic moments originate from nonzero $j_{1/2}$ states arising from matrix elements between e_g and t_{2g} states. For d^2 systems [Fig. 5(b)], as in Cs₂WCl₆, the presence of the $t_{2g} - e_g$ gap when considering all d orbitals in the calculation, strongly reduces the magnetic moment at 0 K (red curve). The energy difference between doublet and triplet is 0.03 eV. Consideration of p orbitals could reduce the energy of the first excited state and increase the magnetic moment (green curve). Using a slightly reduced spin-orbit coupling 0.22 eV (DFT extracted value 0.27 eV), the magnetic moment increases dramatically, similar to the experimental observations. Unlike Ref. [41], where only the Kanamori model and the first excited state energy gap were used to calculate the susceptibility, our model includes full Coulomb interaction matrices with all Slater parameters as well as all excited states. For d^4 and d^5 fillings, inclusion of e_g states changes minimally the temperature dependence of the magnetic moments. Consideration of p orbitals have similar effects as e_g orbitals.

Conclusions. Summarizing, we investigated the magnetic behavior of a few representative systems including M₂NaRuCl₆(d^5), M₃Ru₂Br₉(d^5), Cs₂RuCl₆(d^4), and A₂WCl₆(d^2) by performing exact diagonalization of *ab initio* derived relativistic multiorbital Hubbard models on finite clusters. We computed their magnetic susceptibilities and extracted general rules for the validity range of the Kotani model. We find that the slope of the effective magnetic moment is crucially dependent on the ground- and excited-state configurations at the various electronic fillings. In the single-site description, crystal-field distortions, spin-orbit coupling, Hund's coupling, t_{2g} - e_g orbitals, and χ_0 , all contribute to the temperature dependence of the effective magnetic moment in a delicate balance, depending on the electronic filling. While the Kotani model contains contribution of spin-orbit coupling and Hund's coupling, often nonphysical values need to be considered to find agreement with experiment. Furthermore, for systems with strong intradimer interactions, such as M₃Ru₂Br₉, m_{eff} is strongly reduced owing to metal-metal bonding.

Our findings resolve the discrepancies between experimental observations and theoretical descriptions of magnetic susceptibilities and effective magnetic moments in spin-orbit-coupled transition metal complexes, and provide a more accurate way to understand magnetism in these systems.

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- [1] B. Normand, Frontiers in frustrated magnetism, *Contemp. Phys.* **50**, 533 (2009).
 - [2] L. Balents, Spin liquids in frustrated magnets, *Nature (London)* **464**, 199 (2010).
 - [3] Y. Zhou, K. Kanoda, and T.-K. Ng, Quantum spin liquid states, *Rev. Mod. Phys.* **89**, 025003 (2017).
 - [4] L. Savary and L. Balents, Quantum spin liquids: A review, *Rep. Prog. Phys.* **80**, 016502 (2017).
 - [5] C. Broholm, R. J. Cava, S. A. Kivelson, D. G. Nocera, M. R. Norman, and T. Senthil, Quantum spin liquids, *Science* **367**, eaay0668 (2020).
 - [6] A. Kitaev, Anyons in an exactly solved model and beyond, *Ann. Phys. (NY)* **321**, 2 (2006).
 - [7] G. Jackeli and G. Khaliullin, Mott insulators in the strong spin-orbit coupling limit: From Heisenberg to a quantum compass and Kitaev models, *Phys. Rev. Lett.* **102**, 017205 (2009).
 - [8] J. Chaloupka, G. Jackeli, and G. Khaliullin, Zigzag magnetic order in the iridium oxide Na_2IrO_3 , *Phys. Rev. Lett.* **110**, 097204 (2013).
 - [9] W. Witczak-Krempa, G. Chen, Y. B. Kim, and L. Balents, Correlated quantum phenomena in the strong spin-orbit regime, *Annu. Rev. Condens. Matter Phys.* **5**, 57 (2014).
 - [10] J. G. Rau, E. K.-H. Lee, and H.-Y. Kee, Spin-orbit physics giving rise to novel phases in correlated systems: Iridates and related materials, *Annu. Rev. Condens. Matter Phys.* **7**, 195 (2016).
 - [11] R. Schaffer, E. K.-H. Lee, B.-J. Yang, and Y. B. Kim, Recent progress on correlated electron systems with strong spin-orbit coupling, *Rep. Prog. Phys.* **79**, 094504 (2016).
 - [12] S. M. Winter, A. A. Tsirlin, M. Daghofer, J. van den Brink, Y. Singh, P. Gegenwart, and R. Valentí, Models and materials for generalized Kitaev magnetism, *J. Phys.: Condens. Matter* **29**, 493002 (2017).
 - [13] G. Cao and P. Schlottmann, The challenge of spin-orbit-tuned ground states in iridates: A key issues review, *Rep. Prog. Phys.* **81**, 042502 (2018).
 - [14] D. A. S. Kaib, S. M. Winter, and R. Valentí, Kitaev honeycomb models in magnetic fields: Dynamical response and dual models, *Phys. Rev. B* **100**, 144445 (2019).
 - [15] H. Takagi, T. Takayama, G. Jackeli, G. Khaliullin, and S. E. Nagler, Concept and realization of Kitaev quantum spin liquids, *Nat. Rev. Phys.* **1**, 264 (2019).
 - [16] S. Trebst and C. Hickey, Kitaev materials, *Phys. Rep.* **950**, 1 (2022).
 - [17] M. Hermanns, I. Kimchi, and J. Knolle, Physics of the Kitaev model: Fractionalization, dynamic correlations, and material connections, *Annu. Rev. Condens. Matter Phys.* **9**, 17 (2018).
 - [18] L. E. Chern and Y. B. Kim, Magnetic order with fractionalized excitations in pyrochlore magnets with strong spin-orbit coupling, *Sci. Rep.* **9**, 10974.
 - [19] J. Knolle, D. L. Kovrizhin, J. T. Chalker, and R. Moessner, Dynamics of fractionalization in quantum spin liquids, *Phys. Rev. B* **92**, 115127 (2015).
 - [20] G. Chen, R. Pereira, and L. Balents, Exotic phases induced by strong spin-orbit coupling in ordered double perovskites, *Phys. Rev. B* **82**, 174440 (2010).
 - [21] A. S. Erickson, S. Misra, G. J. Miller, R. R. Gupta, Z. Schlesinger, W. A. Harrison, J. M. Kim, and I. R. Fisher, Ferromagnetism in the Mott insulator $\text{Ba}_2\text{NaOsO}_6$, *Phys. Rev. Lett.* **99**, 016404 (2007).
 - [22] L. Lu, M. Song, W. Liu, A. P. Reyes, P. Kuhns, H. O. Lee, I. R. Fisher, and V. F. Mitrović, Magnetism and local symmetry breaking in a Mott insulator with strong spin orbit interactions, *Nat. Commun.* **8**, 14407 (2017).
 - [23] D. Hirai, H. Sagayama, S. Gao, H. Ohsumi, G. Chen, T.-h. Arima, and Z. Hiroi, Detection of multipolar orders in the spin-orbit-coupled $5d$ Mott insulator $\text{Ba}_2\text{MgReO}_6$, *Phys. Rev. Res.* **2**, 022063(R) (2020).
 - [24] F. I. Frontini, G. H. J. Johnstone, N. Iwahara, P. Bhattacharyya, N. A. Bogdanov, L. Hozoi, M. H. Upton, D. M. Casa, D. Hirai, and Y.-J. Kim, Spin-orbit-lattice entangled state in A_2MgReO_6 ($\text{A} = \text{Ca}, \text{Sr}, \text{Ba}$) revealed by resonant inelastic x-ray scattering, *Phys. Rev. Lett.* **133**, 036501 (2024).
 - [25] A. Kojima, K. Teshima, Y. Shirai, and T. Miyasaka, Organometal halide perovskites as visible-light sensitizers for photovoltaic cells, *J. Am. Chem. Soc.* **131**, 6050 (2009).
 - [26] M. A. Green, A. Ho-Baillie, and H. J. Snaith, The emergence of perovskite solar cells, *Nat. Photonics* **8**, 506 (2014).
 - [27] J. Burschka, N. Pellet, S.-J. Moon, R. Humphry-Baker, P. Gao, M. K. Nazeeruddin, and M. Grätzel, Sequential deposition as a route to high-performance perovskite-sensitized solar cells, *Nature (London)* **499**, 316 (2013).
 - [28] J.-H. Im, I.-H. Jang, N. Pellet, M. Grätzel, and N.-G. Park, Growth of $\text{CH}_3\text{NH}_3\text{PbI}_3$ cuboids with controlled size for high-efficiency perovskite solar cells, *Nat. Nanotechnol.* **9**, 927 (2014).
 - [29] P. Vishnoi, J. L. Zuo, T. A. Strom, G. Wu, S. D. Wilson, R. Seshadri, and A. K. Cheetham, Structural diversity and

- magnetic properties of hybrid ruthenium halide perovskites and related compounds, *Angew. Chem., Int. Ed.* **59**, 8974 (2020).
- [30] M. Kotani, On the magnetic moment of complex ions. (i), *J. Phys. Soc. Jpn.* **4**, 293 (1949).
- [31] R. B. Johannesen and G. A. Candela, Magnetic susceptibilities and dilution effects in low-spin d^4 complexes: Osmium(IV), *Inorg. Chem.* **2**, 67 (1963).
- [32] A. Earnshaw, B. N. Figgis, J. Lewis, and R. D. Peacock, The magnetic properties of some d^4 -complexes, *J. Chem. Soc.* 3132 (1961).
- [33] P. Vishnoi, J. L. Zuo, J. A. Cooley, L. Kautzsch, A. Gómez-Torres, J. Murillo, S. Fortier, S. D. Wilson, R. Seshadri, and A. K. Cheetham, Chemical control of spin-orbit coupling and charge transfer in vacancy-ordered ruthenium(IV) halide perovskites, *Angew. Chem., Int. Ed.* **60**, 5184 (2021).
- [34] H. Takahashi, H. Suzuki, J. Bertinshaw, S. Bette, C. Mühle, J. Nuss, R. Dinnebier, A. Yaresko, G. Khaliullin, H. Gretarsson, T. Takayama, H. Takagi, and B. Keimer, Nonmagnetic $J = 0$ state and spin-orbit excitations in K_2RuCl_6 , *Phys. Rev. Lett.* **127**, 227201 (2021).
- [35] N. Iwahara and S. Shikano, Vibronic excitations in resonant inelastic x-ray scattering spectra of K_2RuCl_6 , *Phys. Rev. Res.* **5**, 023051 (2023).
- [36] H. Lu, J. R. Chamorro, C. Wan, and T. M. McQueen, Universal single-ion physics in spin-orbit-coupled d^5 and d^4 ions, *Inorg. Chem.* **57**, 14443 (2018).
- [37] D. Appleby, P. B. Hitchcock, K. R. Seddon, J. E. Turp, J. A. Zora, C. L. Hussey, J. R. Sanders, and T. A. Ryan, Tri- μ -bromo-bis[tribromoruthenate(III)] salts: A synthetic, structural, spectroscopic, and electrochemical study, *J. Chem. Soc., Dalton Trans.* 1879 (1990).
- [38] C. D. Kennedy and R. D. Peacock, Complex chlorides and bromides of quadrivalent tungsten, *J. Chem. Soc.* 3392 (1963).
- [39] Z. Liu, X. Qin, Q. Chen, Q. Chen, Y. Jing, Z. Zhou, Y. S. Zhao, J. Chen, and X. Liu, Highly stable lead-free perovskite single crystals with NIR emission beyond 1100 nm, *Adv. Opt. Mater.* **10**, 2201254 (2022).
- [40] E. E. Morgan, G. T. Kent, A. Zohar, A. O'Dea, G. Wu, A. K. Cheetham, and R. Seshadri, Hybrid and inorganic vacancy-ordered double perovskites A_2WCl_6 , *Chem. Mater.* **35**, 7032 (2023).
- [41] K. Pradhan, A. Paramekanti, and T. Saha-Dasgupta, Multipolar magnetism in $5d^2$ vacancy-ordered halide double perovskites, *Phys. Rev. B* **109**, 184416 (2024).
- [42] S. V. Streltsov and D. I. Khomskii, Covalent bonds against magnetism in transition metal compounds, *Proc. Natl. Acad. Sci. USA* **113**, 10491 (2016).
- [43] Y. Li, A. A. Tsirlin, T. Dey, P. Gegenwart, R. Valentí, and S. M. Winter, Soft and anisotropic local moments in $4d$ and $5d$ mixed-valence M_2O_9 dimers, *Phys. Rev. B* **102**, 235142 (2020).
- [44] T. Petersen, L. Prodan, V. Tsurkan, H. A. Krug von Nidda, I. Kézsmárki, U. K. Rößler, and L. Hozoi, How correlations and spin-orbit coupling work within extended orbitals of transition-metal tetrahedra of $4d/5d$ lacunar spinels, *J. Phys. Chem. Lett.* **13**, 1681 (2022).
- [45] Y. Li, S. M. Winter, D. A. S. Kaib, K. Riedl, and R. Valentí, Modified Curie-Weiss law for J_{eff} magnets, *Phys. Rev. B* **103**, L220408 (2021).
- [46] See Supplemental Material at <http://link.aps.org/supplemental/10.1103/PhysRevResearch.7.L012083> for details on derivation of susceptibility, explicit expressions in the electronic Hamiltonian, hopping parameters and its effects for edge-sharing octahedra, direction-dependent magnetic moments for $d5$ system and average magnetic moments for $d2$ materials.
- [47] M. Aichhorn, L. Pourovskii, V. Vildosola, M. Ferrero, O. Parcollet, T. Miyake, A. Georges, and S. Biermann, Dynamical mean-field theory within an augmented plane-wave framework: Assessing electronic correlations in the iron pnictide $LaFeAsO$, *Phys. Rev. B* **80**, 085101 (2009).
- [48] K. Foyevtsova, H. O. Jeschke, I. I. Mazin, D. I. Khomskii, and R. Valentí, *Ab initio* analysis of the tight-binding parameters and magnetic interactions in Na_2IrO_3 , *Phys. Rev. B* **88**, 035107 (2013).
- [49] J. Ferber, K. Foyevtsova, H. O. Jeschke, and R. Valentí, Unveiling the microscopic nature of correlated organic conductors: The case of κ -(ET) $_2$ $Cu[N(CN)_2]Br_xCl_{1-x}$, *Phys. Rev. B* **89**, 205106 (2014).
- [50] P. Blaha, K. Schwarz, F. Tran, R. Laskowski, G. K. H. Madsen, and L. D. Marks, Wien2k: An APW+lo program for calculating the properties of solids, *J. Chem. Phys.* **152**, 074101 (2020).
- [51] D. A. S. Kaib, K. Riedl, A. Razpopov, Y. Li, S. Backes, I. I. Mazin, and R. Valentí, Electronic and magnetic properties of the RuX_3 ($X = Cl, Br, I$) family: two siblings—and a cousin?, *npj Quantum Mater.* **7**, 75 (2022).
- [52] A. Nag and S. Ray, Misjudging frustrations in spin liquids from oversimplified use of Curie-Weiss law, *J. Magn. Magn. Mater.* **424**, 93 (2017).
- [53] H. B. Bebb and A. Gold, Multiphoton ionization of hydrogen and rare-gas atoms, *Phys. Rev.* **143**, 1 (1966).
- [54] F. Hammerath, R. Sarkar, S. Kamusella, C. Baines, H.-H. Klauss, T. Dey, A. Maljuk, S. Gaß, A. U. B. Wolter, H.-J. Grafe, S. Wurmehl, and B. Büchner, Diluted paramagnetic impurities in nonmagnetic Ba_2YIrO_6 , *Phys. Rev. B* **96**, 165108 (2017).
- [55] Q. Chen, C. Svoboda, Q. Zheng, B. C. Sales, D. G. Mandrus, H. D. Zhou, J.-S. Zhou, D. McComb, M. Randeria, N. Trivedi, and J.-Q. Yan, Magnetism out of antisite disorder in the $j = 0$ compound Ba_2YIrO_6 , *Phys. Rev. B* **96**, 144423 (2017).
- [56] A. Nag, S. Bhowal, F. Bert, A. D. Hillier, M. Itoh, I. Carlomagno, C. Meneghini, T. Sarkar, R. Mathieu, I. Dasgupta, and S. Ray, $Ba_3MlIr_2O_9$ hexagonal perovskites in the light of spin-orbit coupling and local structural distortions, *Phys. Rev. B* **97**, 064408 (2018).
- [57] J. Terzic, H. Zheng, F. Ye, H. D. Zhao, P. Schlottmann, L. E. De Long, S. J. Yuan, and G. Cao, Evidence for a low-temperature magnetic ground state in double-perovskite iridates with Ir^{5+} ($5d^4$) ions, *Phys. Rev. B* **96**, 064436 (2017).
- [58] S. Fuchs, T. Dey, G. Aslan-Cansever, A. Maljuk, S. Wurmehl, B. Büchner, and V. Kataev, Unraveling the nature of magnetism of the $5d^4$ double perovskite Ba_2YIrO_6 , *Phys. Rev. Lett.* **120**, 237204 (2018).
- [59] H. Schnait, D. Bauernfeind, T. Saha-Dasgupta, and M. Aichhorn, Small moments without long-range magnetic ordering in the zero-temperature ground state of the double perovskite iridate Ba_2YIrO_6 , *Phys. Rev. B* **106**, 035132 (2022).
- [60] S. Bhowal and I. Dasgupta, Spin-orbit effects in pentavalent iridates: Models and materials, *J. Phys.: Condens. Matter.* **33**, 453001 (2021).
- [61] A. A. Aczel, Q. Chen, J. P. Clancy, C. dela Cruz, D. Reig-i Plessis, G. J. MacDougall, C. J. Pollock, M. H. Upton, T. J. Williams, N. LaManna, J. P. Carlo, J. Beare, G. M. Luke, and

- H. D. Zhou, Spin-orbit coupling controlled ground states in the double perovskite iridates $A_2B\text{IrO}_6$ ($A = \text{Ba, Sr}$; $B = \text{Lu, Sc}$), *Phys. Rev. Mater.* **6**, 094409 (2022).
- [62] S. M. Winter, Y. Li, H. O. Jeschke, and R. Valentí, Challenges in design of Kitaev materials: Magnetic interactions from competing energy scales, *Phys. Rev. B* **93**, 214431 (2016).
- [63] Y. G. Shi, Y. F. Guo, S. Yu, M. Arai, A. A. Belik, A. Sato, K. Yamaura, E. Takayama-Muromachi, H. F. Tian, H. X. Yang, J. Q. Li, T. Varga, J. F. Mitchell, and S. Okamoto, Continuous metal-insulator transition of the antiferromagnetic perovskite NaOsO_3 , *Phys. Rev. B* **80**, 161104(R) (2009).
- [64] E. E. Rodriguez, F. Poineau, A. Llobet, B. J. Kennedy, M. Avdeev, G. J. Thorogood, M. L. Carter, R. Seshadri, D. J. Singh, and A. K. Cheetham, High temperature magnetic ordering in the $4d$ perovskite SrTcO_3 , *Phys. Rev. Lett.* **106**, 067201 (2011).
- [65] H. Matsuura and K. Miyake, Effect of spin-orbit interaction on $(4d)3-$ and $(5d)3-$ -based transition-metal oxides, *J. Phys. Soc. Jpn.* **82**, 073703 (2013).
- [66] A. Revelli, M. M. Sala, G. Monaco, P. Becker, L. Bohatý, M. Hermanns, T. C. Koethe, T. Fröhlich, P. Warzanowski, T. Lorenz, S. V. Streltsov, P. H. M. van Loosdrecht, D. I. Khomskii, J. van den Brink, and M. Grüninger, Resonant inelastic x-ray incarnation of Young's double-slit experiment, *Sci. Adv.* **5**, eaav4020 (2019).
- [67] A. Nag, S. Middey, S. Bhowal, S. K. Panda, R. Mathieu, J. C. Orain, F. Bert, P. Mendels, P. G. Freeman, M. Mansson, H. M. Ronnow, M. Telling, P. K. Biswas, D. Sheptyakov, S. D. Kaushik, V. Siruguri, C. Meneghini, D. D. Sarma, I. Dasgupta, and S. Ray, Origin of the spin-orbital liquid state in a nearly $j = 0$ iridate $\text{Ba}_3\text{ZnIr}_2\text{O}_9$, *Phys. Rev. Lett.* **116**, 097205 (2016).
- [68] M. S. Khan, A. Bandyopadhyay, A. Nag, V. Kumar, A. V. Mahajan, and S. Ray, Magnetic ground state of the distorted $6H$ perovskite $\text{Ba}_3\text{CdIr}_2\text{O}_9$, *Phys. Rev. B* **100**, 064423 (2019).
- [69] G. L. Stamokostas and G. A. Fiete, Mixing of $t_{2g} - e_g$ orbitals in $4d$ and $5d$ transition metal oxides, *Phys. Rev. B* **97**, 085150 (2018).
- [70] K.-H. Ahn, K. Pajskr, K.-W. Lee, and J. Kuneš, Calculated g -factors of $5d$ double perovskites $\text{Ba}_2\text{NaOsO}_6$ and Ba_2YOsO_6 , *Phys. Rev. B* **95**, 064416 (2017).
- [71] N. Iwahara, V. Vieru, and L. F. Chibotaru, Spin-orbital-lattice entangled states in cubic d^1 double perovskites, *Phys. Rev. B* **98**, 075138 (2018).
- [72] S. Gangopadhyay and W. E. Pickett, Interplay between spin-orbit coupling and strong correlation effects: Comparison of the three osmate double perovskites Ba_2AOsO_6 ($A = \text{Na, Ca, Y}$), *Phys. Rev. B* **93**, 155126 (2016).
- [73] S. V. Streltsov, Magnetic moment suppression in $\text{Ba}_3\text{CoRu}_2\text{O}_9$: Hybridization effect, *Phys. Rev. B* **88**, 024429 (2013).
- [74] L. Xu, N. A. Bogdanov, A. Princep, P. Fulde, J. van den Brink, and L. Hozoi, Covalency and vibronic couplings make a non-magnetic $j=3/2$ ion magnetic, *npj Quantum Mater.* **1**, 16029 (2016).
- [75] H. Ishikawa, T. Takayama, R. K. Kremer, J. Nuss, R. Dinnebier, K. Kitagawa, K. Ishii, and H. Takagi, Ordering of hidden multipoles in spin-orbit entangled $5d^1$ Ta chlorides, *Phys. Rev. B* **100**, 045142 (2019).
- [76] V. da Cruz Pinha Barbosa, J. Xiong, P. M. Tran, M. A. McGuire, J. Yan, M. T. Warren, R. V. Aguilar, W. Zhang, M. Randeria, N. Trivedi, D. Haskel, and P. M. Woodward, The impact of structural distortions on the magnetism of double perovskites containing $5d1$ transition-metal ions, *Chem. Mater.* **34**, 1098 (2022).