The open access journal at the forefront of physics

# **PAPER • OPEN ACCESS**

# Estimation of biquadratic and bicubic Heisenberg effective couplings from multiorbital Hubbard models

To cite this article: Rahul Soni et al 2022 New J. Phys. 24 073014

View the article online for updates and enhancements.

# You may also like

- The quantum  $J_4 J_4 J_2$  spin-1/2 Heisenberg model: influence of the interchain coupling on the ground-state magnetic ordering in two dimensions R F Bishop, P H Y Li, R Darradi et al.
- The quantum J<sub>1</sub>-J<sub>1</sub>-J<sub>2</sub> spin-1 Heisenberg model: Influence of the interchain coupling on the ground-state magnetic ordering in
- 2D R. F. Bishop, P. H. Y. Li, R. Darradi et al.
- Broken discrete and continuous symmetries in two-dimensional spiral antiferromagnets A Mezio, C N Sposetti, L O Manuel et al.

# **New Journal of Physics**

The open access journal at the forefront of physics

Deutsche Physikalische Gesellschaft **OPG** 

**IOP** Institute of Physics

Published in partnership with: Deutsche Physikalische Gesellschaft and the Institute of Physics

CrossMark

**OPEN ACCESS** 

**RECEIVED** 28 February 2022

**REVISED** 8 June 2022

ACCEPTED FOR PUBLICATION

23 June 2022

PUBLISHED 12 July 2022

Original content from this work may be used under the terms of the Creative Commons Attribution 4.0 licence.

Any further distribution of this work must maintain attribution to the author(s) and the title of the work, journal citation and DOI.



Estimation of biquadratic and bicubic Heisenberg effective couplings from multiorbital Hubbard models

Rahul Soni<sup>1,2,\*</sup>, Nitin Kaushal<sup>2</sup>, Cengiz Şen<sup>3</sup>, Fernando A Reboredo<sup>2</sup>, Adriana Moreo<sup>1,2</sup> and Elbio Dagotto<sup>1,2,\*</sup>

- Department of Physics and Astronomy, The University of Tennessee, Knoxville, TN 37996, United States of America
- <sup>2</sup> Materials Science and Technology Division, Oak Ridge National Laboratory, Oak Ridge, TN 37831, United States of America
  - Department of Physics, Lamar University, Beaumont, TX 77710, United States of America
- \* Authors to whom any correspondence should be addressed.

E-mail: rsoni1@vols.utk.edu and edagotto@utk.edu

Keywords: Heisenberg model, multiorbital Hubbard model, strongly correlated systems, exact diagonalization

# Abstract

PAPER

We studied a multi-orbital Hubbard model at half-filling for two and three orbitals per site on a two-site cluster via full exact diagonalization, in a wide range for the onsite repulsion *U*, from weak to strong coupling, and multiple ratios of the Hund coupling  $J_{\rm H}$  to *U*. The hopping matrix elements among the orbitals were also varied extensively. At intermediate and large *U*, we mapped the results into a Heisenberg model. For two orbitals per site, the mapping is into a S = 1 Heisenberg model where by symmetry both nearest-neighbor  $(\mathbf{S}_i \cdot \mathbf{S}_j)$  and  $(\mathbf{S}_i \cdot \mathbf{S}_j)^2$  are allowed, with respective couplings  $J_1$  and  $J_2$ . For the case of three orbitals per site, the mapping is into a S = 3/2 Heisenberg model with  $(\mathbf{S}_i \cdot \mathbf{S}_j)$ ,  $(\mathbf{S}_i \cdot \mathbf{S}_j)^2$ , and  $(\mathbf{S}_i \cdot \mathbf{S}_j)^3$  terms, and respective couplings  $J_1$ ,  $J_2$ , and  $J_3$ . The strength of these coupling constants in the Heisenberg models depend on the *U*,  $J_{\rm H}$ , and hopping amplitudes of the underlying Hubbard model. Our study provides a first crude estimate to establish bounds on how large the ratios  $J_2/J_1$  and  $J_3/J_1$  can be. We show that those ratios appear rather limited and, as a qualitative guidance, we conclude that  $J_2/J_1$  is less than 0.4 and  $J_3/J_1$  is less than 0.2, establishing bounds on effective models for strongly correlated Hubbard systems. Moreover, the intermediate Hubbard *U* regime was found to be the most promising to enhance  $J_2/J_1$  and  $J_3/J_1$ .

#### 1. Introduction

The study of the one-dimensional spin-one (S = 1) Heisenberg chain by Haldane [1], with only nearest-neighbor spin-spin interactions (called here 'bilinear' interactions), and the prediction, and subsequent confirmation, of a spin liquid gapped ground state with protected edge states, was seminal for the start of the field of topological materials. The Haldane chain has been physically realized in several materials, such as CsNiCl<sub>3</sub> [2], AgVP<sub>2</sub>S<sub>6</sub> [3], NENP [4], and Y<sub>2</sub>BaNiO<sub>5</sub> [5], and recently theory predicted that doping of the fermionic two-orbital Hubbard version of the idealized Haldane chain may lead to hole pairing and eventual superconductivity [6, 7]. Earlier related work employing t - J model approximations also predicted superconductivity with doping although strongly competing with ferromagnetism [8].

While the solution of the Heisenberg S = 1 chain by Haldane was mathematically elegant, simpler intuition was provided later by Affleck–Kennedy–Lieb–Tasaki (AKLT) [9] when they solved exactly an extension of the original bilinear Hamiltonian by adding 'biquadratic' terms. In its exactly solvable point, the magnitude of the ratio biquadratic to bilinear couplings is  $\beta = 1/3$  [9]. At this special point, the model has properties qualitatively similar to those of the Haldane chain, with a unique spin-gapped ground state, exponentially decaying spin–spin correlations, and S = 1/2 spins at the edges when open boundary conditions are used.

Our primary goal is to crudely estimate whether the recently introduced more realistic electronic two-orbital Hubbard model realization of the Haldane chain [6] can, at large and/or intermediate Hubbard

*U* and Hund  $J_{\rm H}$  couplings, reach the biquadratic/bilinear ratio  $\beta = 1/3$  when fermionic versus pure spin Hamiltonian models are compared at low energies. Specifically, here we solve exactly the two-site problem of the fermionic model and represent the lowest energy states using the generalized Heisenberg bilinear–biquadratic model in a vast region of parameter space, including varying the elements of the hopping matrix. Our conclusion is that it is indeed possible to reach the AKLT point by suitably selecting the values of *U* and  $J_{\rm H}$ . On the other hand, for the Bethe-ansatz solvable case we conclude that it would be difficult to reach  $\beta = 1$  using the fermionic system defined in [6]. Our efforts were extended to the three-orbital per site Hubbard models as well, allowing us to estimate crude upper bounds for the biquadratic and bicubic Heisenberg couplings emerging at large Hubbard *U* and low energy.

# 1.1. Previous investigations of S = 1 and S = 3/2 spin models including bilinear-biquadratic-bicubic terms

Interest in spin Heisenberg models with spin higher than 1/2 started years ago with the search for exactly solvable Hamiltonians, in dimension one or more, to uncover disordered spin liquid ground states in antiferromagnets. Of particular interest were valence bond (VB) states, which could serve as toy models for Anderson's ideas using S = 1/2 resonant valence bonds related to high- $T_c$  superconductivity [10]. The AKLT model extended the notion of VB states to spins higher than 1/2 [9], as explained before. For S = 1 adding a biquadratic nearest-neighbor term with coupling  $J_2$  in addition to the standard (bilinear) Heisenberg interaction with coupling  $J_1$ , AKLT found that for  $\beta = J_2/J_1 = 1/3$  (with  $J_1$  and  $J_2$  both positive) the ground state is exactly solvable and indeed made out of valence bonds. This AKLT model is defined as

$$H_{\text{AKLT}} = \sum_{\langle i,j \rangle} \mathbf{S}_i \cdot \mathbf{S}_j + \frac{1}{3} \sum_{\langle i,j \rangle} (\mathbf{S}_i \cdot \mathbf{S}_j)^2.$$
(1)

The same model but for  $|\beta| = J_2/J_1 = 1$  can be solved using the Bethe ansatz [11]. At this special point the ground state is gapless with a power-law decay. This point, with  $J_1 > 0$  and  $J_2 < 0$ , separates the spin liquid gapped phase for  $\beta > -1$  from a dimerized phase for  $\beta < -1$ . Our crude analysis below suggests that the AKLT case  $\beta = 1/3$  could be realized with a two-orbital per site electronic model at intermediate Hubbard *U*, but the ratio  $|\beta| = 1$  is large and may require more general electronic models.

To summarize, the isotropic S = 1 Heisenberg model with a biquadratic term was previously studied. The phase diagram in 1D was obtained via DMRG [12]. These authors verified that for  $\beta = 1/3$  the ground state is indeed a VB state. In addition they obtained the following phases: (i) for  $J_1 > 0$  and  $J_2 = 0$  the system has a non-degenerate disordered ground state with antiferromagnetic spin correlations that decay exponentially indicating a spin gap (i.e. the Haldane state); (ii) at  $\beta = 1/3$  with  $J_1$  and  $J_2$  both positive, the system has the VB ground state with a spin gap (i.e. the AKLT state); (iii)  $|\beta| = 1$  with both  $J_1$  and  $J_2$ positive is the critical point where the Hamiltonian is integrable with a gapless ground state [13].

Moreover, recent efforts by one of the coauthors (ED) and collaborators searched for spin liquids in two dimensions focusing on the SU(3) point where the strength of the bilinear and biquadratic interactions are equal  $\beta = 1$ , and adding further interactions [14, 15]. Spin liquids were unveiled for these spin-only models, a conceptually interesting result. But, from our rough estimation in this publication, it is difficult to establish which electronic fundamental multiorbital model can realize these complex spin models at large U, with the exception of the AKLT state, which appears reachable with the two-orbital per site model studied here. Our investigations provide crude limits based on basic Hubbard models on what range of  $\beta$  is realizable in practice. Our qualitative estimation is that for larger values of  $\beta$  more complex fermionic models will be required.

In addition, it was shown that for certain values of parameters higher spin Heisenberg Hamiltonians in one dimension possess conformal invariance, property that allows an analytical determination of critical exponents [16]. The integrable high-spin Heisenberg models are given by a Hamiltonian with a polynomial form in powers of nearest-neighbor Heisenberg interactions ranging from 1 to 2*S*. This was demonstrated via a mapping into the Wess–Zumino–Witten model at specific values of the Hamiltonian parameters [17, 18]. Various numerical studies of higher spin Heisenberg Hamiltonians were performed to understand whether the higher spin anisotropic Heisenberg Hamiltonians belong to the same universality class as the S = 1/2 isotropic model or, instead, the isotropic integrable higher spin ones [19–21].

It is worth remarking that the bilinear-biquadratic S = 1 Heisenberg model was recently realized within the context of organic materials. Specifically, using on-surface synthesis, S = 1 chains arising from polycyclic aromatic hydrocarbon triangulene building blocks were prepared, with  $\beta = 0.09$  [22]. Moreover, in the same context, recently [23] the mapping of a Hubbard model of four-sites to a S = 1 model was also studied, establishing an interesting connection between our effort and related ones in a different field. Other authors have explored the S = 1 biquadratic model in two dimensions using DMRG in the context of high- $T_c$  superconductors finding nematic phases [14], at robust  $J_2/J_1$ . On the other hand, the isotropic S = 3/2 Heisenberg model has not been as much explored. The isotropic and anisotropic cases were studied to determine if they belong to the same universality class as the S = 1/2 Heisenberg model, which was confirmed using Lanczos and DMRG approaches [9, 19–21].

#### 1.2. Limitations and studies in two dimensions

Spin 1 systems are also realized in two dimensional ruthenates [24], often using three-orbital per site Hubbard models with four electrons in those three orbitals leading to a net S = 1 per site. Rich phase diagrams were reported. But in the ruthenates, S = 1 effective Hamiltonians are rarely employed. Spin 1 systems often appear also within iron superconductors because Fe<sup>2+</sup>, with n = 6 electrons in the 3*d* shell, is the usual iron valence, either in planes or ladders. However, these iron-materials are considered to reside in the intermediate *U* region [25, 26] and, again, they are not often theoretically described via purely spin systems but with multi-orbital electronic models instead [27].

We acknowledge that our study has severe limitations and for this reason it is only qualitative. For example, the addition of a Zeeman magnetic term to the biquadratic S = 1 model was explored using DMRG [28], and a spin nematic phase was observed in a triangular lattice [29]. The addition of single-ion anisotropy to the S = 1 spin Heisenberg model was studied using quantum Monte Carlo and series expansions [30], and for the model with biquadratic term [31] with density matrix renormalization group (DMRG). Adding next-nearest neighbor terms to the S = 1 Heisenberg model with biquadratic coupling was also explored with DMRG [32]. More recently, research on this model focused on entanglement and topological properties [33, 34].

Note that the models studied by other groups described in this paragraph often have either a Zeeman term, single-ion anisotropy, or next-nearest neighbor interactions. Thus, it is too early to make definite statements on whether these models can or cannot be realized with fermionic two-orbital Hubbard models. Consequently, our study should be considered only *qualitative*, but still providing a crude but valuable estimation of how large some extra terms beyond the canonical bilinear interactions can be.

#### 1.3. Multiples in the four sites S = 1 model

Because our study relates to a single bond, we cannot distinguish between square and triangular lattices. Including more than a single bond, terms such as  $(\mathbf{S}_i \cdot \mathbf{S}_j)(\mathbf{S}_i \cdot \mathbf{S}_k)$  with sites (i, j, k) belonging to the same plaquette, also appear in the large *U* expansion rendering the study too complex. Here, we explain the complexity that the mere increase from two to four sites would introduce into the analysis, and intuitively provide the reason why using two sites we can still obtain useful estimations of the biquadratic coupling.

In general, the mixing of two spins  $S_1$  and  $S_2$  produces states with total spin in the range of spin states given by:  $(S_1 + S_2), \ldots, |S_1 - S_2|$ , which can also be represented by the following form:

$$S_1 \otimes S_2 = (S_1 + S_2) \oplus \cdots \oplus |S_1 - S_2|. \tag{2}$$

For the case of a two-site spin-1 system, this leads to  $1 \otimes 1 = 2 \oplus 1 \oplus 0$ , i.e. a total of 9 spin state multiplets: 1 singlet, 3 degenerate states in a triplet, and 5 degenerate states in a quintuplet, represented by 0, 1 and 2 on the right hand site of the equation starting this paragraph.

For a four-sites spin-1 system, the decomposition into multiples can start similarly by using two pairs of two-site spin-1 systems  $1 \otimes 1 = 2 \oplus 1 \oplus 0$ , and then mix them with one other. Moreover, from merely counting states (we have three per *S* = 1) we know the total number of states must be  $9 \times 9 = 81$ . How do they decompose into multiplets? Mathematically,

$$(2 \oplus 1 \oplus 0) \otimes (2 \oplus 1 \oplus 0) = (2 \otimes 2) \oplus (2 \otimes 1) \oplus (2 \otimes 0)$$
$$\oplus (1 \otimes 2) \oplus (1 \otimes 1) \oplus (1 \otimes 0)$$
$$\oplus (0 \otimes 2) \oplus (0 \otimes 1) \oplus (0 \otimes 0), \tag{3}$$

where,

$$\begin{array}{c} (2 \otimes 2) = 4 \oplus 3 \oplus 2 \oplus 1 \oplus 0, \\ (1 \otimes 1) = 2 \oplus 1 \oplus 0, \\ (0 \otimes 0) = 0, \\ (2 \otimes 1) = (1 \otimes 2) = 3 \oplus 2 \oplus 1 \\ (2 \otimes 0) = (0 \otimes 2) = 2 \\ (1 \otimes 0) = (0 \otimes 1) = 1 \end{array} \right\}.$$

$$(4)$$

In summary, we have 3 singlets (one state each), 6 triplets (three states each), 6 quintuplets (five states each), 3 septuplets (7 states each), and 1 nonuplet (9 states each). The total number of multiples is 19.

This large number clearly illustrates how difficult would it be to use a four-site cluster to estimate coupling strengths from the two-orbital Hubbard model. The task of deducing an analytical expression for  $J_2/J_1$  is impossible. Moreover, the relative energy order of these 19 multiples states may start with a singlet and finish with the nonuplet, but, in between, the states surely will be arranged in a complicated manner. In addition, more importantly, a four-site system will require other terms in the effective spin Hamiltonian, as the t/U expansion indicates, such as those involving the four different spins in two dot products. Having these extra terms will *dilute* the importance of the biquadratic term and likely lead to a weaker value of  $J_2/J_1$  than found using only two sites. Thus, we believe in order to crudely estimate the maximum range of the ratio  $J_2/J_1$ , a two-site system is the most practical way to proceed.

# 2. Model and method

#### 2.1. Multi-orbital Hubbard model

For the exact-diagonalization calculations, we work with the multi-orbital Hubbard model mentioned in [6, 7] and described as follows:

$$H_{\rm H} = -\sum_{\langle i,\gamma;j,\gamma'\rangle;\sigma} t_{\gamma\gamma'} \left( c^{\dagger}_{i,\gamma,\sigma} c_{j,\gamma',\sigma} + {\rm h.c.} \right) + U \sum_{i,\gamma} n_{i,\gamma,\uparrow} n_{i,\gamma,\downarrow} + \left( U' - \frac{J_{\rm H}}{2} \right) \sum_{i,\gamma<\gamma'} n_{i,\gamma} n_{i,\gamma'} - 2J_{\rm H} \sum_{i,\gamma<\gamma'} \mathbf{S}_{i,\gamma'} \cdot \mathbf{S}_{i,\gamma'} + J_{\rm H} \sum_{i,\gamma<\gamma'} \left( P^{\dagger}_{i,\gamma} P_{i,\gamma'} + {\rm h.c.} \right),$$
(5)

where  $c_{i,\gamma,\sigma}^{\dagger}(c_{i,\gamma,\sigma})$  creates (annihilates) an electron at site *i*, with orbital  $\gamma$ , and spin projection along the *z*-axis  $\sigma$ . The first term represents the inter- and intra-orbital hopping between only nearest-neighbor sites. General hopping matrices for the two- and three-orbitals per site cases are displayed in equations (6) and (7), respectively, and in our study we allowed for the hoppings to vary over broad ranges to search for the largest ratios of Heisenberg interactions. The second term is the standard onsite Hubbard repulsion *U* between spins  $\uparrow$  and  $\downarrow$  electrons, at the same orbital. The third term contains the onsite inter-orbital repulsion, with the usual relation  $U' = U - 2J_{\rm H}$  due to rotational invariance. The fourth term involves the Hund's coupling  $J_{\rm H}$  that explicitly shows the ferromagnetic character between orbitals. The last term represents the onsite inter-orbital electron-pair hopping  $P_{i,\gamma} = c_{i,\gamma,\uparrow}c_{i,\gamma,\downarrow}$ . All these terms in the Hubbard model are canonical.

The general hopping matrices used here for the exact-diagonalization calculation of two- and three-orbitals per site on the two-site system are:

$$t_{\gamma\gamma'}^{2-\text{orb}} = \begin{pmatrix} t_{11} & t_{12} \\ t_{21} & t_{22} \end{pmatrix},\tag{6}$$

$$t_{\gamma\gamma\gamma'}^{3-\text{orb}} = \begin{pmatrix} t_{11} & t_{12} & t_{13} \\ t_{21} & t_{22} & t_{23} \\ t_{31} & t_{32} & t_{33} \end{pmatrix},$$
(7)

where  $t_{\alpha\beta}$  represents the nearest-neighbor hopping element from orbital  $\alpha$  to orbital  $\beta$ . Due to rotational symmetry of the two-site system,  $t_{\alpha\beta} = t_{\beta\alpha}$ . This reduces the number of hopping elements from  $N_o^2$  to  $N_o(N_o + 1)/2$ , where  $N_o$  is the number of orbitals.

#### 2.2. Heisenberg model with higher order terms

The allowed high-order Heisenberg model for any spin-S system can be written generically as:

$$H_{S} = \sum_{\langle i,j \rangle} \sum_{n=1}^{2S} J_{n} \left( \mathbf{S}_{i} \cdot \mathbf{S}_{j} \right)^{n}.$$
(8)

Using the above equation we can write the general Hamiltonian for S = 1 spin system as:

$$H_1 = \sum_{\langle i,j \rangle} \left[ J_1 \left( \mathbf{S}_i \cdot \mathbf{S}_j \right) + J_2 \left( \mathbf{S}_i \cdot \mathbf{S}_j \right)^2 \right].$$
(9)







hopping parameters are  $t_{22} = t_{11}$  and  $t_{12} = t_{21} = 0$  for this example, namely the unit matrix. To help the readers, the hopping matrix is presented as inset in the plot (the same will be done in all other figures below). The bandwidth for this set of hoppings is  $W = 4t_{11}$ . Here and in all figures below 'bandwidth' is defined with regards to the tight-binding model with the hoppings used here but in the bulk limit.

We diagonalize the Hamiltonian in equation (9) for the two-site system and obtain the following three energy levels:

$$E_{s} = -2J_{1} + 4J_{2}, \quad \text{Singlet } s$$

$$E_{t} = -J_{1} + J_{2}, \quad \text{Triplet } t$$

$$E_{q} = J_{1} + J_{2}, \quad \text{Quintuplet } q$$

$$(10)$$

In figure 1, we illustrate the plot of these energy levels vs  $J_2/J_1$ . For  $J_2/J_1 \le 1/3$ , the ordering of these levels strictly follows the singlet-triplet-quintuplet sequence in increasing order of energies. This is vital as the same sequence appears in the more fundamental two-orbital per site Hubbard model in strong coupling.

Of course, when comparing these energies mentioned in equation (10) with the Hubbard results obtained from exact-diagonalization in the strong coupling regime a constant offset in energies must be included, leading generically to  $E'_a = E_a + E_{off}$  where a = s, t, q and  $E_{off}$  is the offset energy. Based on this information and the energies provided in equation (10) one can exactly derive the ratio  $J_2/J_1$  in terms of the Hubbard energies obtained from exact-diagonalization  $E'_a$ 's as:

$$\frac{J_2}{J_1} = \frac{E'_q - 3E'_t + 2E'_s}{3(E'_q - E'_t)}.$$
(11)

The above equation is used to calculate exactly the values of  $J_2/J_1$  in our two-site two-orbitals per site exact-diagonalization study, in the range where the Hubbard model energies are in the expected singlet–triplet–quintuplet order, starting from the singlet ground state (this assumption tends to break







down only in weak coupling, already outside the range of the Heisenberg model description, as discussed below).

Similarly for S = 3/2 the high-order Heisenberg Hamiltonian reads:

$$H_{\frac{3}{2}} = \sum_{\langle i,j \rangle} \left[ J_1 \left( \mathbf{S}_i \cdot \mathbf{S}_j \right) + J_2 \left( \mathbf{S}_i \cdot \mathbf{S}_j \right)^2 + J_3 \left( \mathbf{S}_i \cdot \mathbf{S}_j \right)^3 \right].$$
(12)

We diagonalize this Hamiltonian in equation (12) for the two-site system and obtain four energy levels:

$$E_{s} = \frac{-15}{64} (16J_{1} - 60J_{2} + 225J_{3}), \text{ Singlet } s$$

$$E_{t} = \frac{-11}{64} (16J_{1} - 44J_{2} + 121J_{3}), \text{ Triplet } t$$

$$E_{q} = \frac{-3}{64} (16J_{1} - 12J_{2} + 9J_{3}), \text{ Quintuplet } q$$

$$E_{v} = \frac{9}{64} (16J_{1} + 36J_{2} + 81J_{3}), \text{ Septuplet } v$$

$$(13)$$

Following the same reasoning as in the case of S = 1, i.e. considering an offset energy, then  $E'_a = E_a + E_{off}$  where a = s, t, q, v, and using the set of equations provided in equation (13) the analytical



**Figure 5.**  $J_2/J_1$  vs  $U/t_{11}$  for a two-site three-orbitals per site system obtained via exact diagonalization, at the ratios  $J_H/U$  shown. The color convention is the same in (a) and (b). The hopping parameters chosen for panel (a) are  $t_{11} = 1.0$ ,  $t_{22} = 0.25$ ,  $t_{33} = 0$ ,  $t_{12} = 0.75$ ,  $t_{23} = 0.25$  and  $t_{13} = 0$ , with bandwidth  $W \approx 5.9t_{11}$  and in (b) are  $t_{11} = 1.0$ ,  $t_{22} = 0.25$ ,  $t_{33} = 0$ ,  $t_{12} = 0.75$ ,  $t_{23} = 0.25$  and  $t_{13} = 0$ , with bandwidth  $W \approx 5.9t_{11}$  and in (b) are  $t_{11} = 1.0$ ,  $t_{22} = 0.25$ ,  $t_{33} = 0$ ,  $t_{12} = 0.75$ ,  $t_{23} = 0.5$  and  $t_{13} = 0$ , with bandwidth  $W \approx 6.05t_{11}$  (for definition of bandwidth see caption of figure 2). The hopping matrices are shown also in each panel (inset). The ratios  $J_3/J_1$  are not shown because they are considerably smaller than  $J_2/J_1$ , as in figure 4.



**Figure 6.** (a)  $J_2/J_1$  and (b)  $J_3/J_1$  vs  $U/t_{11}$  for a two-site three-orbitals per site system obtained via exact diagonalization, at the several  $J_H/U$ 's indicated. Color convention is common to both panels. The hopping parameters chosen for the plot are  $t_{11} = t_{22} = 1.0$ ,  $t_{33} = 0$  and  $t_{\alpha\beta} = 0$  for all  $\alpha \neq \beta$ . The bandwidth for these set of hopping is  $W = 4t_{11}$  (for definition of bandwidth see caption of figure 2).

expression for  $J_2/J_1$  and  $J_3/J_1$  in terms of  $E'_a$ 's for S = 3/2 becomes

$$\frac{J_2}{J_1} = \frac{4}{3} \frac{\left(29E'_v - 85E'_q + 81E'_t - 25E'_s\right)}{\left(81E'_v + 115E'_q - 351E'_t + 155E'_s\right)},\tag{14}$$

and

$$\frac{J_3}{J_1} = \frac{16}{3} \frac{\left(E'_v - 5E'_q + 9E'_t - 5E'_s\right)}{\left(81E'_v + 115E'_a - 351E'_t + 155E'_s\right)}.$$
(15)

Equations (14) and (15) were used for calculating the values of  $J_2/J_1$  and  $J_3/J_1$  in our two-site three-orbitals per site exact-diagonalization study, respectively. Here, we do not include a figure like figure 1 for the case of S = 3/2 because it would require a three-dimensional plot of energy vs  $J_2/J_1$  and  $J_3/J_1$  which would be difficult to visualize. For this reason, we simply have included here the relevant equations that were employed.

# 3. Results

In this section, we will discuss our numerical results via exact-diagonalization for the two-site system. Note that not only U and  $J_{\rm H}$  are varied, but the most time-consuming portion of the calculation arises from the large number of hopping amplitude ratios studied (using  $t_{11}$  as unit of reference). Specifically, we analyzed hundreds of different ratios of Hamiltonian parameters and in all cases mapped the low-energy results into



**Figure 7.**  $J_2/J_1$  vs  $U/t_{11}$  for a two-site three-orbitals per site system using exact diagonalization, at several ratios of  $J_H/U$  (color convention is the same for both panels). The hoppings chosen for panel (a) are  $t_{11} = t_{22} = 1.0$ ,  $t_{33} = 0.125$  and  $t_{\alpha\beta} = 0$  for all  $\alpha \neq \beta$  and for panel (b) are  $t_{11} = t_{22} = 1.0$ ,  $t_{33} = 0.25$  and  $t_{\alpha\beta} = 0$  for all  $\alpha \neq \beta$ . These hoppings are also shown in the insets. The bandwidth for both sets of hopping is  $W = 4t_{11}$  (for definition of bandwidth see caption of figure 2).



**Figure 8.** (a) and (b) Double occupancy (as defined in the vertical label) vs  $U/t_{11}$  for the two-site two-orbitals per site system obtained via exact diagonalization. The Hund coupling is fixed to  $J_H/U = 0.25$  because this number is considered realistic for some materials such as the iron superconductors. The hopping parameters are shown as insets, and match the parameters shown in the section of two-orbitals in the main portion of the text. Results are shown for the first singlet, triplet, and quintuplet states in the spectrum as colored indicated (the last one being ferromagnetic then has zero double occupancy). The results show that at the lower extreme of the range investigated double occupancy is only 0.10, and decreases fast with increasing  $U/t_{11}$ . Thus, charge fluctuations do not play a significant role in most of the important range in our reported results, and in our qualitative conclusions.

the Heisenberg models. On average we run over 30 values of U and 12 values of  $J_{\rm H}/U$ , for each fixed set of hopping amplitudes. This already amounts to 360 runs. For two orbitals per site, we used 36 combinations of  $t_{22}/t_{11}$  and  $t_{12}/t_{11}$  for a total of  $360 \times 36 = 12960$  cases. For three orbitals per site, we used 196 combinations of  $t_{22}/t_{11}$ ,  $t_{33}/t_{11}$ ,  $t_{12}/t_{11}$ ,  $t_{13}/t_{11}$ , and  $t_{23}/t_{11}$  for a total of  $360 \times 196 = 70560$  cases. Crudely, the total number of cases studied is approximately  $4 \times 10^4$ , giving to the readers an idea of how complex these multivariable calculations are. We automatized the fittings, and from the many results we isolated approximately 150 sets of data containing the largest ratios for  $J_2/J_1$  and  $J_3/J_1$ . Those special cases were plotted and visually inspected. From that set, the very small subset displayed in this section is the subset that, in our judgement, best represents cases where the Heisenberg coupling ratios are robust in absolute value, because our primary aim is to establish upper bounds on those quantities. These ratios can be positive or negative.

#### 3.1. Two-site two-orbitals per site

First, we present our two-site two-orbitals per site exact-diagonalization results. All the results below have the same low-energy order: first a singlet (total spin  $S_{\text{Tot}} = 0$ ) for the ground state, then a triplet ( $S_{\text{Tot}} = 1$ ) for the first excited state, and finally a quintuplet ( $S_{\text{Tot}} = 2$ ) for the second excited state.

In both figures 2 and 3 we first performed exact diagonalization of the multi-orbital Hubbard model equation (5). The hopping parameters used is in an inset, for better visualization, and also in the caption.

For each  $J_H/U$ , we identified the range of *U* that gives the ordering: singlet, triplet and quintuplet for the ground-state, first excited-state, and second excited state, respectively. The energies of these respective states were used to calculate  $J_2/J_1$  using equation (11). Note that with reducing  $U/t_{11}$  in the horizontal axis, curves end abruptly. The reason is that the order singlet–triplet–quintuplet is altered at smaller values of  $U/t_{11}$  and the fitting is no longer possible. This occurs both for two and three orbitals, namely for both S = 1 and S = 3/2 spins.

Our main result is that the largest ratio observed (in absolute value) is close to 0.4. For a wide variety of 'less symmetric' hopping amplitudes, namely employing neither the unit matrix or the matrix with all elements equal, we observed that  $|J_2/J_1|$  is smaller than those in figures 2 and 3. Two important details are: (a) the ratios can be both positive and negative and for this reason the two examples shown were chosen. In both cases, positive and negative, the largest magnitudes of the ratios are not too different. (b) As obvious from the figures, the largest ratios are obtained as *U* is reduced from very strong coupling. This makes sense because in the limit where a perturbative expansion in  $t_{11}/U$  is valid,  $J_1$  is the lowest order and  $J_2$  the next leading order. Naturally, their ratio of coefficients scales as  $t_{11}/U$  and  $J_2/J_1$  converges to zero as *U* diverges. *As a consequence, we can firmly conclude that the most promising region to observe the effects of the biquadratic term is U/W \sim 1, <i>i.e. the intermediate coupling regime*. Intuitively, this conclusion appears qualitatively valid independently of the cluster size studied. This region of parameter space often contains a variety of exotic phases because here several tendencies are in close competition leading to 'frustration' effects which are not obvious at the Hamiltonian level.

#### 3.2. Reason for having both signs for the coupling ratios

Regarding the two possible signs of  $J_2/J_1$ , at first sight a negative  $J_2/J_1$  is not unexpected, given the prevalence of minus signs in the math arising from the anticommutation rules of fermions when they move on a two-site cluster with two orbitals. The complexity of the calculations prevents us from providing an intuitive rule based on the two-orbital Hubbard model parameters for when biquadratic couplings are positive or negative. As illustration, we refer readers to reference [35], to be discussed in more detail in section 4, where strong coupling perturbation theory in  $t_{11}/U$  for two sites was reported. The expressions for the higher order terms, such as the biquadratic, contain combinations of positive and negative terms that may lead to positive or negative  $J_2$ . The same comment is valid for the case of three orbitals.

However, fortunately still some simple intuition can be provided. Analyzing the key equation (11), clearly the sign of the ratio  $J_2/J_1$  is controlled by the numerator, because in the range we focus on, the denominator is always positive. Thus, the rule to obtain a positive  $J_2/J_1$  is that  $E'_q - 3E'_t + 2E'_s > 0$ , while for a negative  $J_2/J_1$  the condition must be  $E'_q - 3E'_t + 2E'_s < 0$ . In simpler words, it is the location of the triplet state inside the range of the quintuplet-singlet energy gap that regulates the sign of  $J_2/J_1$ . To put it another way, the closer the triplet is to the singlet ground state energy in comparison to the quintuplet, the higher the chances that  $J_2/J_1$  is positive. The precise location of couplings where the switch in sign occurs certainly will be cluster size dependent, but the conclusion that there is a sign changing location is likely present in all clusters.

#### 3.3. Two-site three-orbitals per site

Here, we present our two-site three-orbitals per site exact diagonalization results. All the results below have the same energy ordering: singlet ( $S_{\text{Tot}} = 0$ ) for the ground state, triplet ( $S_{\text{Tot}} = 1$ ) for the first-excited state, quintuplet ( $S_{\text{Tot}} = 2$ ) for the second-excited state, and septuplet ( $S_{\text{Tot}} = 3$ ) for the third-excited state. The latter originates in the three orbital per site nature of the problem, and it does not appear for two orbitals per site. The extra spin manifold occurs because the total number of electrons in the system is 6 which allows total spins 3, 2, 1, and 0, contrary to a total of four electrons in the previous subsection.

Unlike the two-orbital per site case, here for three orbitals we observe that it is the 'less symmetric' (as mentioned in section 3.1) hopping amplitudes that give large ratios  $|J_2/J_1|$  and  $|J_3/J_1|$ .

Qualitatively, the conclusions of figure 4 resemble those for the two-orbital case: the ratios are the largest as  $U/t_{11}$  decreases from strong coupling. Thus, the intermediate coupling  $U/W \sim 1$  is the most promising to observe sizable values for  $J_2$  and  $J_3$ . Also, the largest values of  $J_2/J_1$  are similar to those of the two-orbital per site case. However, as expected from the strong coupling expansion,  $J_3/J_1$  is an order of magnitude smaller than  $J_2/J_1$  because it requires the next order in the large U expansion to develop, as compared with  $J_2/J_1$ .

Figure 5 illustrates the dependence of the results varying slightly the hopping amplitudes. Focusing on the matrices contained in both panels, the only difference between both cases resides in  $t_{23}$ , which varies by a factor 2. However, this relatively small modification leads to a reduction in approximately a factor two in  $J_2/J_1$ . This sensitivity to small changes in the hoppings is somewhat surprising. Such effect manifest the most at intermediate couplings, while in strong coupling the ratios are less sensitive to small hopping modifications.

In figure 6, we illustrate the case where the hoppings reside only along the diagonal, but one of them, i.e.  $t_{33}$ , is zero. In this case the fits lead to negative values for both  $J_2/J_1$  and  $J_3/J_1$ . The strength is also reduced when compared with figure 5. In figure 7,  $J_2/J_1$  is shown now increasing  $t_{33}$  from zero, as compared with figure 6. Here, as  $t_{33}$  increases the largest value of the  $J_2/J_1$  decreases slowly, indicating that to find the maximum possible value of  $J_2/J_1$  the hopping amplitude  $t_{33}$  must be zero. Similarly, we tune other hopping amplitudes and find the best possible scenario where we achieve the largest value of  $J_2/J_1$  and  $J_3/J_1$ .

### 4. Discussion and conclusions

In our study we focused on a two-site electronic multi-orbital Hubbard model to deduce, crudely due to the size limitation, what range of biquadratic and bicubic Heisenberg couplings are reasonable to expect at intermediate and large values of the Hubbard U. In particular, for two orbitals per site we focused on how large the biquadratic-bilinear ratio strength  $J_2/J_1$  can become. First, we noticed that  $J_2/J_1$  can be of both signs, a robust conclusion that intuitively should be size independent. Then, regarding its magnitude it appears limited to  $\sim 0.4$  or less. This is sufficient for the AKLT model [9] to be realized employing electronic models. It would be interesting to investigate if these associated electronic model-namely selecting suitable Hubbard U, Hund coupling  $J_{\rm H}$ , and hoppings such that  $J_2/J_1 = 1/3$ —will also lead to a valence bond ground state, although likely the said electronic model will not be exactly solvable. On the other hand, we estimate that the exactly solvable case  $J_2/J_1 = 1$  in principle cannot be realized with the electronic model we used. With two orbitals we systematically found that biquadratic and bicubic couplings are smaller than the bilinear coupling by at least a factor 2. For the case of spin S = 3/2, using three orbitals per site, the conclusions are similar: once again  $J_2/J_1$  cannot exceed ~0.4, while  $J_3/J_1$  is even smaller by another factor of approximately 2. It may arise also the doubt on whether charge fluctuations may be so strong that they can invalidate the mapping into a spin-only Hamiltonian. In the appendix we have addressed this matter for two orbitals for simplicity. While at the lowest  $U/t_{11}$  studied the charge double occupancy is 0.1 (already a small number), this number decreases very fast with further increasing the Hubbard coupling, thus justifying the use of an effective spin model to map results of the two-orbital Hubbard model.

Note that the formidable challenge of using four-site clusters involving 19 multiplets is unrealistic (note that for only two sites already a set of 70 560 different couplings were investigated in this effort because the hoppings were also varied over broad ranges). However, we believe that the primary conclusions of our effort are crude but qualitatively robust: (i) the biquadratic coupling cannot be as large as the bilinear, (ii) these couplings arise with the two possible signs, (iii) the best range of U to enhance the biquadratic and bicubic strength is intermediate U.

Our study also suggests that spin-only models mixing bilinear, biquadratic, and bicubic terms that are often studied searching for quantum spin liquids should impose constraints on the parameter space explored. To realize spin liquids using electronic models the most optimal path continues being the addition of hoppings beyond nearest-neighbors to create explicit frustration.

Our qualitative conclusions using a two-site multiorbital Hubbard model are, remarkably, in good agreement with calculations using a two-orbital per site Hubbard model [35], carried out perturbatively at small t/U up to fourth order (first and third order cancel; the second order gives the canonical bilinear Heisenberg model, and the fourth order the biquadratic contribution). Using this fairly different procedure, nevertheless conclusions similar to ours were reached:  $J_2/J_1$  is limited at large U, providing confidence to the results of our calculations. These results, valid at any value of U because they do not rely on perturbation theory, suggest strongly again that *intermediate U is more promising than strong U*. Still, even at intermediate U,  $J_2/J_1$  cannot reach values above 0.4. The methodology proposed in reference [36], adding to the problem an extra orbital residing in a neighboring site, may reduce  $J_1$ , providing a promising path to enhance  $J_2/J_1$  [37]. Our next goal is to investigate the effect of on-site spin–orbit coupling in these two-site multi-orbital Hubbard systems [38] and estimate the range of biquadratic–bilinear Heisenberg couplings in these conditions.

# Acknowledgments

RS, NK, FR, AM, and ED were supported by the US Department of Energy (DOE), Office of Science, Basic Energy Sciences (BES), Materials Sciences and Engineering Division.

# Data availability statement

The data that support the findings of this study are available upon reasonable request from the authors.

# Appendix. Charge fluctuations

Because we are exploring not only the strong coupling region, but also the more promising intermediate  $U/t_{11}$  regime (more promising because in there, the  $J_2/J_1$  and  $J_3/J_1$  are enhanced the most), it is important to consider how robust are the charge fluctuations in such intermediate coupling regime. If charge fluctuations are important, then the mapping into a spin only model is less reliable.

In this appendix, we report the double occupancy,  $\langle n_{\gamma,\uparrow}n_{\gamma,\downarrow}\rangle$  where the orbital index  $\gamma$  could be 1 or 2 (note that the two orbitals give the same results because we do not have a crystal field in the Hamiltonian, to avoid adding even more complexity in the calculations). Results are in figure 8, where we show the double-occupancy expectation value. The maximum value it reaches in the range investigated, which matches the range shown in the main text for two orbitals, is 0.10 and it decreases very fast with increasing  $U/t_{11}$ . We conclude that in most of the region investigated charge fluctuations are actually not important, and thus our methodology is justified.

### **ORCID iDs**

Rahul Soni <sup>(D)</sup> https://orcid.org/0000-0003-1771-4299 Nitin Kaushal <sup>(D)</sup> https://orcid.org/0000-0003-1723-9547

## References

- [1] Haldane F D M 1983 Phys. Rev. Lett. 50 1153
- [2] Tun Z, Buyers W J L, Armstrong R L, Hirakawa K and Briat B 1990 Phys. Rev. B 42 4677
- [3] Mutka H, Payen C, Molinié P, Soubeyroux J L, Colombet P and Taylor A D 1991 Phys. Rev. Lett. 67 497
- [4] Ma S, Broholm C, Reich D H, Sternlieb B J and Erwin R W 1992 Phys. Rev. Lett. 69 3571
- [5] Di Tusa J F, Cheong S-W, Park J-H, Aeppli G, Broholm C and Chen C T 1994 Phys. Rev. Lett. 73 1857
- [6] Patel N D, Kaushal N, Nocera A, Alvarez G and Dagotto E 2020 npj Quantum Mater. 5 27
- [7] Patel N D, Nocera A, Alvarez G, Moreo A and Dagotto E 2017 Phys. Rev. B 96 024520
- [8] Riera J, Hallberg K and Dagotto E 1997 Phys. Rev. Lett. 79 713
- [9] Affleck I, Kennedy T, Lieb E H and Tasaki H 1987 Phys. Rev. Lett. 59 799
- [10] Anderson P W 1987 Science 235 1196
- [11] Takhtajan L A 1982 Phys. Lett. A 87 479
- [12] Schollwöck U, Jolicœur T and Garel T 1996 Phys. Rev. B 53 3304
- [13] Itoi C and Kato M 1997 Phys. Rev. B 55 8295
- [14] Hu W-J, Gong S-S, Lai H-H, Si Q and Dagotto E 2020 Phys. Rev. B 101 014421
- [15] Hu W-J, Lai H-H, Gong S-S, Yu R, Dagotto E and Si Q 2020 Phys. Rev. Res. 2 023359
- [16] Belavin A A, Polyakov A M and Zamolodchikov A B 1984 Nucl. Phys. B 241 333
- [17] Affleck I 1986 Phys. Rev. Lett. 56 746
- [18] Affleck I 1986 Phys. Rev. Lett. 56 2763
- [19] Moreo A 1987 Phys. Rev. B 36 8582
- [20] Alcaraz F C and Moreo A 1992 Phys. Rev. B 46 2896
- [21] Hallberg K, Wang X Q G, Horsch P and Moreo A 1996 Phys. Rev. Lett. 76 4955
- [22] Mishra S et al 2021 Nature 598 287
- [23] Catarina G and Fernández-Rossier J 2021 arXiv:2110.07442
- [24] Hotta T and Dagotto E 2001 Phys. Rev. Lett. 88 017201 and references therein
- [25] Herbrych J, Alvarez G, Moreo A and Dagotto E 2020 Phys. Rev. B 102 115134 and references therein
- [26] Sroda M, Dagotto E and Herbrych J 2021 Phys. Rev. B 104 045128 and references therein
- [27] Zhang Y, Lin L-F, Hu W-J, Moreo A, Dong S and Dagotto E 2020 *Phys. Rev.* B **102** 195117 and references therein. Nickelates often have Ni in an S = 1 state and treatments employing spin models are common, but recent developments for Ni-based superconductivity require a valence +1 for Ni and thus they are not S = 1 systems
- [28] Okunishi K 1999 Phys. Rev. B 60 4043
- [29] Tsunetsugu H and Arikawa M 2006 J. Phys. Soc. Japan 75 083701
- [30] Albuquerque A F, Hamer C J and Oitmaa J 2009 Phys. Rev. B 79 054412
- [31] De Chiara G, Lewenstein M and Sanpera A 2011 Phys. Rev. B 84 054451
- [32] Pixley J H, Shashi A and Nevidomskyy A H 2014 Phys. Rev. B 90 214426
- [33] Thomale R, Rachel S, Bernevig B A and Arovas D P 2015 J. Stat. Mech. P07017
- [34] Jolicoeur T and Golinelli O 2019 C. R. Chim. 22 445
- [35] Tanaka K, Yokoyama Y and Hotta C 2018 J. Phys. Soc. Japan 87 023702
- [36] Mila F and Zhang F C 2000 Eur. Phys. J. B 16 7
- [37] Lin L-F, Zhang Y, Alvarez G, Moreo A and Dagotto E 2021 Phys. Rev. Lett. 127 077204 this is similar in spirit to the recently discovered mechanism to produce a ferromagnetic state under special conditions in a multiorbital system, without the need of using double exchange mechanisms
- [38] Kaushal N, Soni R, Nocera A, Alvarez G and Dagotto E 2020 Phys. Rev. B 101 245147