ABSTRACT: Macroscopic assemblies of interacting spins give rise to a broad spectrum of behaviors determined by the spatial arrangement of the magnetic sites and the electronic interactions between them. Compounds of copper(II), in which each copper carries spin 1/2, exhibit a vast variety of physical properties. For antiferromagnetically coupled spin sites, there are two limiting scenarios: spin chains in which the spins can exhibit a long-range order or a mixture of dimers in which the spins within each pair are entangled but do not interact with the spins from other dimers. In principle, the two types can be distinguished on the basis of experimental observations and modeling using empirically parameterized effective Hamiltonians, but in practice, ambiguity may persist for decades, as is the case for copper oxalate. Here, we use high-level ab initio calculations to establish the validity of the nearest-site Heisenberg model and to predict the interaction strength between the magnetic sites. The computed magnetic susceptibility provides an unambiguous interpretation of magnetic experiments performed over half a century, clearly supporting the infinite spin-chain behavior of solid copper oxalate.

1. INTRODUCTION

Strongly correlated materials exhibit unusual properties, which are exploited in emerging applications such as quantum information science and spintronics. Physical properties depend on the spatial arrangement and the strengths of electronic couplings between the magnetic sites, as illustrated in Figure 1. For example, chains of antiferromagnetically coupled spins exhibit long-range spin correlations and a zero spectral gap at zero magnetic field. In contrast, an assembly of weakly coupled spin pairs has no long-range order and has a gap at zero field. Both cases give rise to a bell-shape magnetic susceptibility curve \( \chi(T) \). In both types of systems, the equilibrium state can be converted to a fully spin-polarized state above the saturation field, roughly equal to the exchange coupling. The differences between the two cases can be seen at low temperatures, for example, spin chains have finite \( \chi(T) \), in contrast to dimers. The spectral gap and long-range order can also be probed by neutron scattering experiments, for example, dynamic structural factors for the spin-chains at zero field start at zero energy and show a characteristic sinusoidal shape, following the spinon dispersion relation \( \epsilon(k) = \pi/2 |J| \sin(k) \), as was illustrated for copper sulfate; whereas the dimers are expected to show flat bands at finite energy. In addition to their technological relevance, spin chains are also fundamentally interesting—for example, they give rise to quantum criticality around the saturation field.

Copper(II) salts can behave both as antiferromagnetic spin chains and as spin-paired dimers. Copper compounds also...
exhibit more complicated types of magnetic interactions, such as magnetic helixes emerging due to the interplay of spin chains and spin frustration,7 zigzag spin chains,8 and alternating spin chains.9–11 When experimental data are limited to finite-temperature magnetic susceptibility, as in the case of copper oxalate, one cannot confidently identify the magnetic structure without first-principles calculations. Here, we report the first fully ab initio determination of the effective Hamiltonian and macroscopic magnetic susceptibility for copper oxalate. The results provide unambiguous interpretation of magnetic experiments performed over half a century and clearly support the infinite spin chain behavior of the solid copper oxalate.

As shown in Figure 1, an infinite chain of spins can be treated with the XXX Heisenberg Hamiltonian

$$H = -J \sum_i S_i S_{i+1}$$

where $S_i$ are the local spins and $J$ is the effective exchange constant. If the effective exchange constant is negative, the system adopts the antiferromagnetic singlet ground state with opposite spin orientation of the adjacent magnetic centers. The case of $S = 1/2$ is one of the few known quantum integrable models. Its exact solution is given by the Bethe ansatz,12 which facilitated the development of solid-state physics and mathematics of integrable systems. The thermodynamic properties of this model are well known and have been used to explain experimental observables of real materials, containing, for instance, copper,7,13 vanadium,14 and magnesium15 magnetic centers. We note that earlier studies often employed the Ising model, which can be described as an approximation to the Heisenberg model in which only the $S_i$ components of the spin operators $S$ are retained; however, such a treatment yields an incorrect state degeneracy pattern in the dimers and noticeably different results for magnetic susceptibility of extended systems.16

An oxalate ligand is a common building block in transition-metal compounds. Despite its simplicity, the magnetic structure of copper oxalate has not been settled. The first measurements of magnetic susceptibility of copper oxalate17,18 were fitted using a dimer model. Another susceptibility measurement19 provided fitting to the Ising spin chain model. These contradictory explanations prompted a question of which model should be used to interpret magnetic susceptibility.16 Jotham16 compared the results of fitting magnetic susceptibilities of several copper salts (including copper oxalate) to the Ising, Heisenberg, and dimer models and explained the limitations of the Ising model, arguing in favor of the dimer model for some salts while emphasizing that for copper oxalates the infinite Heisenberg spin-chain model provides the best description. Later, EPR and EXAFS experiments20,21 also proposed the infinite quantum Heisenberg model. However, even after the determination22 of the crystal structure in 2014, the choice of magnetic model remained open: for example, the dimer model was used to treat magnetic susceptibility in this most recent study.27

Importantly, in all these earlier studies, the validity of the model was assessed solely on its ability to provide a good fit to the experimental data and no attempts to validate these models using first-principles calculations were done. The first such attempt23 was made in 1980 by Girerd, Kahn, and Verdaguer, who carried out calculations for copper oxalate using an empirical extended Hückel model; the results argued in favor of the infinite quantum Heisenberg model. Later computational studies employed more advanced theoretical approaches, yet most of the previous work on copper oxalate complexes was carried out for dinuclear complexes and employed spin-broken density functional theory (DFT).24–27 The only exceptions are ab initio perturbative analysis28 and a spin-flip study.29 The limitations and empirical nature of broken-symmetry DFT are well documented30,31—the results depend on the functional and on the exact form of the projector and are not systematically improvable. Moreover, applications to polyradical systems suffer from additional ambiguity due to the rapidly growing number of broken-symmetry solutions. Hence, first-principles calculations are highly desirable.31

Even when the model is known, the first-principles determination of the effective exchange constant is not trivial. The strongly correlated nature of magnetic systems combined with their large sizes pose a formidable challenge for quantum chemistry. Among ab initio methods, configuration interaction (CI) methods have been used for single-molecule magnets.31–34 Multireference CI and perturbation theory approaches have been applied to bulk magnetic systems.35 Here, we use state-of-the-art wave function methods based on equation-of-motion coupled-cluster (EOM-CC) theory.36 In contrast to popular broken-symmetry DFT, our approach has no empirical or system-dependent parameters and does not rely on unphysical spin-scrambled solutions. We begin with the full-electron treatment of model systems (dimers, trimers, and tetramers) and use the resulting wave functions to build effective Hamiltonians,31,37,38 which afford a coarse-grained description of the electronic structure and allow the extrapolation to infinite systems. This is the first application of the spin-flip EOM-CC method to describe a periodic system, opening a new route in the treatment of periodic strongly correlated systems. Our theoretical results provide unambiguous interpretation of the magnetic measurements19,20 of copper oxalate performed over several decades.

2. THEORY

The EOM-CC36,39–42 parameterizes a manifold of electronic states $\Psi$ as

$$\ket{\Psi} = \sum_i \Phi_i \ket{\Phi_0}$$

where $\Phi_0$ is a reference determinant, $\hat{T}$ is a CC excitation operator describing the correlation of the reference state, and $\hat{R}$ is a general EOM excitation operator. The exact choice of $\hat{R}$ defines the specific EOM-CC model. For example, in EOM-EE-CCSD43 (designed to describe excitation energies), the operator $\hat{R}$ contains $1h1p$ and $2h2p$ excitation operators ($h$ and $p$ denote holes and particles, respectively) and the operator $\hat{T}$ is truncated at the same level. In EOM-IP-CCSD44,45 and EOM-DIP-CCSD46,47 (variants for ionization and double ionization potentials), the operators $\hat{R}$ are of $1h1p$ and $2h3l$ types, respectively. EOM-EA-CCSD48 and EOM-DEA-CCSD48–51 describe attachment of one and two electrons by means of $1p/1h2p$ and $2p/1h3p$ operators. EOM-SF-CCSD52–54 a spin-flip variant of the theory, starts from a high-spin reference state and applies spin-flip excitation operators of the $1k1p/2h2p$ type that change the spin-projection by $\Delta M_s = -1$. The spin-flip ansatz treats important open-shell and closed-shell configurations in a balanced manner (see Figure 2), which is crucial for the quantitative description of the electronic structure of di- and triradical.
species.\textsuperscript{55,56} EOM-DSF-CCSD,\textsuperscript{57} a double spin-flip variant, uses $2h2p$ and $3h3p$ operators; it can tackle systems with four unpaired electrons, but has an $N^6$ cost that limits its applications to small systems. In EOM-CC, amplitudes $\hat{T}$ are computed from either CC or MP2 equations for the reference state. Then, amplitudes $\hat{R}$ are found by the diagonalization of the similarity-transformed Hamiltonian $\hat{H}$ in the corresponding sector of the Fock space

$$\hat{H} = e^{-T} \hat{H} e^{T}$$

(3)

$$\hat{H} \hat{R}_K = E_K \hat{R}_K$$

(4)

$$L_1 \hat{H} = L_1 E_1 \hat{A}$$

(5)

where the left vector $L$ describes the bra-state. Because $\hat{H}$ is not Hermitian, left and right states are not Hermitian conjugates of each other, but can be chosen to form a biorthogonal set.

Bloch’s effective Hamiltonian theory\textsuperscript{38} provides a recipe for a rigorous construction of effective Hamiltonians from ab initio calculations. It introduces a wave operator $\Omega$ that maps the model space to a target space

$$|\Psi_{\mu}'\rangle = \Omega \bar{|\Psi_{\mu}\rangle}$$

(6)

where a set of model states (states expressed in a compact model space) is denoted by $|\Psi_{\mu}\rangle$, and a set of target states (expressed in the full Hilbert space) is denoted by $|\Psi_{\mu}'\rangle$. Effective Hamiltonian acts in the model space and by construction yields exactly the same eigenenergies for the manifold of states it was constructed for as the original Hamiltonian

$$\hat{H} |\Psi_{\mu}'\rangle = E_{\mu} |\Psi_{\mu}'\rangle$$

(7)

$$\hat{H}^{\text{eff}} |\bar{\Psi}_{\mu}\rangle = E_{\mu} |\bar{\Psi}_{\mu}\rangle$$

(8)

There are different recipes for construction of effective Hamiltonians and wave operators. We use Bloch’s\textsuperscript{58} and des Cloizeaux\textsuperscript{59} forms of effective Hamiltonians. Applied to EOM-CC,\textsuperscript{58} they give

$$|\Psi_{\mu}^{R}\rangle = \hat{R}_{\mu} |\Psi_{0}\rangle$$

(9)

where $I$ is the intermediate matrix composed of the overlaps between the target states and the model configurations and $H_{\text{eff}}$ and $H_{\text{eff}}^{-1}$ are the effective Hamiltonians in the Bloch’s and des Cloizeaux’ forms. Bold font denotes matrices, such as $R = (|\Phi_{\mu}\rangle |\Psi_{\mu}^{R}\rangle)_{\mu,\mu'}$—the amplitude vectors, expressed on the basis of model functions.

Our approach to treating strong correlation closely follows the coarse-graining strategy proposed by Mayhall and Head-Gordon.\textsuperscript{30,60} We begin with high-spin reference states (e.g., with 2, 3, and 4 unpaired same-spin electrons for the dimer, trimer, and tetramer model systems, respectively) and carry out single spin-flip calculations. We then use effective Hamiltonian theory\textsuperscript{58} to construct the effective Hamiltonians, whose diagonalization yields the full manifold of electronic states, including those that are not accessible in single spin-flip calculations. Here, we use this approach to construct the effective Hamiltonians for the model systems of the increasing size (dimers, trimers, and tetramers). These calculations allow us to validate the nearest-neighbor Heisenberg Hamiltonian, which we then employ to describe the infinite system and to compute macroscopic susceptibility.

### 3. COMPUTATIONAL DETAILS

Cartesian coordinates were extracted from the crystal unit cell parameters of copper oxalate (CuC$_2$O$_4$) reported in ref 22. The crystal structure is composed of the polymer CuC$_2$O$_4$ (Figure 3). The unit cell was repeated and the CuC$_2$O$_4$ stripes were extracted. Hydrogen atoms were added to the oxygen ends of the chain with the corresponding to oxalic acid bond lengths and angles. The Cartesian coordinates for all structures are given in the Supporting Information.

All calculations were performed with the Q-Chem quantum chemistry package.\textsuperscript{61,62} We used Dunning’s cc-pVDZ and cc-pVTZ basis sets for all atoms.\textsuperscript{63–66} Unrestricted orbitals were used in calculations with open-shell references. To accelerate electronic structure calculations, we used single precision\textsuperscript{67} for CCSD, intermediates, and EOM-SF-CCSD, combined with the libxm library for tensor contractions.\textsuperscript{68}

We used the open-shell frozen natural orbital truncation of the virtual space\textsuperscript{69} with the truncation threshold corresponding to 99% of the total preserved occupation in the virtual space. Core electrons were frozen in all calculations. Triples corrections were computed using (FT) perturbative triples\textsuperscript{70} for EOM-SF-CCSD. In the (FT) calculations for a model dimer, the 40 lowest occupied orbitals were frozen for the dimer fragment. In all other calculations, 36, 51, and 66 lowest occupied orbitals were frozen for the dimer, trimer, and tetramer, respectively.

Calculations of spin—orbit couplings\textsuperscript{71} were performed using EOM-DIP-CCSD wave functions\textsuperscript{72} within the state-interaction approach. We used 10 singlet and 10 triplet
correlation effects, folded in by means of the Bloch wave operator. We then use the Heisenberg Hamiltonian to obtain the states that are not reachable by a single spin-flip, as was pioneered by Mayhall and Head-Gordon for single-molecule magnets.

Note that in these calculations, we constructed the full Heisenberg Hamiltonian (as shown in the pink box in Figure 1), that is, without assuming the nearest-neighbor approximation or constraining all neighboring $J$ to be the same. The analysis of these ab initio constructed effective Hamiltonians clearly reveals antiferromagnetic spin interactions. The off-diagonal elements decay rapidly with the distance between the copper centers, such that only the nearest-neighbor spin couplings are significant. Non-nearest-neighbor couplings are about 1 cm$^{-1}$ or less, which is comparable with the thresholds used in the calculations. To further quantify the impact of neglecting the non-nearest neighbor contributions, we carried out two additional numeric tests. First, we computed eigenvalues of the Heisenberg Hamiltonian in which we zeroed the contributions from non-nearest neighbors and compared them with the eigenvalues of the full Hamiltonian; the results are shown in Table S3 of the Supporting Information. As one can see, the individual eigenvalues change by less than 0.5 cm$^{-1}$ and the effect on the spectral gap is of the same magnitude—for example, the difference between the highest and the lowest eigenstate in the 4-copper Hamiltonian changes by 0.44 cm$^{-1}$ due to the zeroing out non-nearest neighbor elements, which is indeed small compared to the value of the gap (301.07 cm$^{-1}$). Second, we triadiagonalized the full effective Hamiltonian for the 3 and 4 copper centers, so that the effect of the non-nearest neighbor contributions is folded into the remaining matrix elements. The results (Figure S2 in the Supporting Information) show that this operation changes the value of the key matrix element (between the two middle coppers) by only 0.63 cm$^{-1}$. Therefore, we conclude that the nearest-neighbor approximation is indeed fully justified for this system, such that the full Heisenberg Hamiltonian for the fragments can be replaced by the XXX Heisenberg Hamiltonian for the infinite spin chain, eq 1, which we use to extrapolate the Hamiltonian to the limit of the infinite number of copper centers. The effective exchange constants computed for the fragments of increasing sizes (collected in Table S2) show little variation and converge rapidly with respect to the model system size. Hence, for calculations of thermodynamic properties, we use the 1J/1 constant from the middle of the 4-copper fragment ($-178.1$ cm$^{-1}$).

To account for weak correlations beyond EOM-CCSD, we calculated a perturbative triples correction using the (FT) method for a model dimer. Surprisingly, inclusion of triple excitations leads to a more than 20% increase of 1J ($42.7$ cm$^{-1}$), illustrating that weak correlations are important for quantitative results. The direction of the change can be explained by the Pauli repulsion principle. Pauli repulsion, which is already built-in in the wave function at the mean-field level by virtue of using Slater determinants, allows the electrons in the triplet state to avoid each other. The resulting Pauli hole covers the errors due to an incomplete description of the Coulomb hole, which requires electron correlation. Consequently, the correlation effects are always smaller for triplet states$^{53}$ and improving correlation treatment results in stabilizing singlets relative to triplets. Previous calculations of dicopper single-molecule magnets suggested that the cc-pVDZ

4. RESULTS AND DISCUSSION

The crystal structure$^{30}$ of copper oxalate (shown in Figure 3) reveals a regular pattern of copper oxalate chains with a bidentate orientation of the oxalate ligands. We begin with EOM-SF-CCSD/cc-pVDZ calculations for the fragments of increasing length (containing 2, 3, and 4 copper centers, as shown in Figure 3, and capped with hydrogen atoms). We use the resulting energies and wave functions to build effective Hamiltonians$^{31,38}$, which afford a coarse-grained description of the electronic structure.

The effective Heisenberg Hamiltonians for fragments built from these highly accurate EOM-SF-CCSD calculations are shown in the middle panel of Figure 3. Bloch’s and des Cloizeaux’s versions of the effective Hamiltonians are consistent with each other and yield nearly the same values of effective exchange constants $J$, as shown in Table S2 in the Supporting Information. This procedure provides a rigorous mapping between the full-electron description and effective interactions between the magnetic centers. In particular, the resulting effective exchange constant includes not only the contribution from the exchange integral, but also screening and

$$H = -\sum_{i<j} J_{ij} S_i S_j \implies H = -J \sum_i S_i S_{i-1}$$

Figure 3. Top, left: Crystal structure of copper oxalate (Cu$_2$C$_2$O$_4$). Top, right: Fragments with 2, 3, and 4 copper atoms from the crystal. Middle: Localized orbitals defining the open-shell model spaces. Bottom: Des Cloizeaux effective Hamiltonians built from the EOM-SF wave functions in the basis of open-shell determinants. The energies are shifted to produce a zero trace. The numbers in blue show the couplings between the nearest neighbors. The numbers in red show the couplings between distant centers.
basis is nearly sufficient. To account for a basis-set effect beyond cc-pVDZ, we performed EOM-SF-CCSD calculations for the dimer with the cc-pVTZ basis set. These calculations show that this improvement of the basis set reduces the $|J|_1$ value by 8.5 cm$^{-1}$.

To account for spin–orbit interactions, which can split and shift energy levels, we computed spin–orbit couplings (for the model dimer) using the Breit–Pauli Hamiltonian within spin–orbit mean-field approximation and nonrelativistic EOM-CC states. In these calculations, we used the EOM-DIP-CCSD ansatz, which can describe not only the lowest singlet and triplet states (i.e., the Heisenberg states), but the entire manifold of the low-lying states derived from different occupations of copper’s $d$-orbitals. Although these states are relatively far in energy from the lowest singlet/triplet pair (about 1.6 eV above the lowest singlet), they are expected to be important for spin–orbit coupling by virtue of El-Sayed’s rule, which says that states with different orbital occupations give rise to large spin–orbit interactions.

The EOM-DIP-CCSD ansatz, which can handle strong correlation well but underestimate weak correlation and orbital relaxation, overestimates the energy gap relative to EOM-SF-CCSD ($J = -388.6$ cm$^{-1}$ for the dimer). To correct for this limitation, we combined the EOM-SF-CCSD energy gap with EOM-DIP-CCSD spin–orbit couplings to evaluate the effective $|J|$. Table S4 illustrates the convergence of the $J$ constant with respect to the lowest singlet number of interacting states. We observe that both the lowest singlet and the lowest triplet states interact strongly through the spin–orbit operator with higher excited states. This interaction shifts both states, largely canceling the effect of the spin–orbit coupling on the singlet-triplet gap. Nevertheless, the singlet interacts more strongly with the excited states than the triplet does, which results in a substantial (13%) increase of antiferromagnetic $|J|_1$ by 32 cm$^{-1}$. We note that these results indicate that neglect of the spin–orbit interaction in previous studies of dicopper single-molecule magnets might be responsible for the reported systematic discrepancies between the theoretical and computed $J$-values.

Table 1 summarizes the various contributions to the effective $J$ and gives our best estimate of $J = -244$ cm$^{-1}$ = $-30.25$ meV. Compared to other copper spin chains, this value is 33 times higher than that of copper pyrazine and 118 times higher than that of copper sulfate, implying that a much stronger magnetic field (on the order of 400–500 T) would be required to bring this system to the fully polarized spin state and into the quantum criticality regime.

To compare the computed effective exchange constants with the experimental observable, one needs to compute macroscopic magnetic susceptibility $\chi(T)$. In the classical treatment, the quantum Heisenberg Hamiltonian is mapped onto the classical Heisenberg Hamiltonian. The connection between the quantum and classical parameters in the case of $S = 1/2$ is given by

$$J^{\text{quant}}/2 = J^{\text{cl}}$$

$$g^{\text{quant}} = g^{\text{cl}}$$

The analytic solution of the $\chi(T)$ exists for the case of a classical linear spin chain with the nearest-neighbor approximation under the assumption of uniformness, meaning that $J_{\text{eff}}$ and $g$ are the same for all local spins. The solution has the following form

$$\chi(T) = \frac{N_g \chi^{\text{cl}}}{2k_BT}$$

where $N$ is the number of centers, $g^{\text{cl}}$ is a classical electron $g$-factor (we assumed $g^{\text{cl}} = g^{\text{quant}} = 2$), $\mu_B$ is Bohr’s magneton, and $k$ is the Boltzmann constant. This expression predicts a maximum on the susceptibility curve at

$$kT_{\text{max}} \approx 0.2382|J|^{\text{cl}}$$

The analytic expression for quantum susceptibility is not known, but there are Padé approximants fitted to numerical curves with high quality. We used such a curve (fit 1 in Table I in ref 78) for calculation of quantum magnetic susceptibility. The susceptibility curve of a quantum infinite spin chain has a maximum at

$$kT_{\text{max}} \approx 0.640851|J|$$

One can immediately see that for the same value of $J^{\text{quant}}$, the classical model yields $T_{\text{max}}$ which is about 5.4 times lower than that of the quantum model. Conversely, using the classical model to fit the experimental data would yield a 5.4 times larger effective exchange constant.

It is instructive to compare the predictions of the Heisenberg model with the dimer model, which gives the well-known Bleaney–Bowers expression for magnetic susceptibility

$$\chi^{\text{dim}}(T) = \frac{N_g \chi^{\text{cl}}}{kT} \left( 1 + \frac{e^{-J/kT}}{2} \right)$$

The susceptibility of the dimer reaches the maximum at

$$kT_{\text{max}}^{\text{dim}} \approx 0.624|J|$$

Thus, although based on very different physics, the dimer model yields a very similar value of $T_{\text{max}}$, that is, within 3% from the quantum susceptibility derived from the Heisenberg model.

The results of the classical and quantum Heisenberg models and the dimer model are shown in Figure 4. The susceptibility of the classical spin model differs dramatically from the quantum spin model (Figure 4, left), making the classical approximation not satisfactory in the interpretation of the magnetic data. This is expected because the susceptibility of the classical model approaches the susceptibility of the quantum model only for the large spin on each center.
Classical, quantum, and experimental susceptibility curves reach maximum at 42, 225, and 260 K, respectively. The quantum dimer model gives the maximum at 219 K. The difference between the quantum infinite chain and the dimer Heisenberg models in terms of the maximum position of the $\chi(T)$ curve is not large, but the absolute values are vastly different (the dimer model yields absolute values that are about four times higher). Figure 5 shows the comparison between $\chi(T)$ but also the overall shape of the curve much better than the scaled and shifted dimer model.

We also see that the $\chi(T)$ curve is broad and rather flat, which makes it difficult to precisely extract $T_{\text{max}}$ from the noisy experimental data. Hence, the comparison on the basis of the maximum may be misleading, and one should look at the overall shape. Near zero-temperature results would be important to further highlight the discrepancy, but, unfortunately, there are no reliable data, as the study that attempted such measurements clearly shows contamination of the sample.

The right panel of Figure 4 shows the impact of different effects on the overall magnetic susceptibility of the quantum spin chain model. The value of the effective exchange constant from the 4-center fragment results in a susceptibility curve that is far from the experimental one. Inclusion of spin–orbit effects and weak correlation through perturbative triples improves agreement. The impact of the basis set is relatively small but it improves agreement even further. The more effects are included, the closer the agreement with the experiment becomes. This systematic convergence of the computed magnetic susceptibility to the experimental value shows the power of fully ab initio treatment.

Inelastic neutron scattering allows one to probe the manifold of spin states of a magnetic system. The intensity of inelastic neutron scattering is proportional to the dynamic structure factor, given by

$$S^{\sigma\sigma'}(k, \omega) = \sum_i \langle \Psi_i | \delta^{\sigma\sigma'} | \Psi_i \rangle \langle \Psi_i | S_k^\sigma | \Psi_0 \rangle \delta(\omega - \omega_i)$$

where $S_k^\sigma = \frac{1}{N} \sum_{\eta} e^{i k \cdot S_\eta} S_\eta^\sigma$ are the spin operators in the periodic representation, $\Psi_0$ and $\Psi_i$ are the ground and excited states, and $\omega_i$ is the excitation energy of excited state $\Psi_i$. Mixtures of weakly interacting antiferromagnetic dimers would have a sharp intensity peak at the transfer energy matching the singlet–triplet gap. The energy position of the peak does not depend on the momentum transfer $k$. In contrast, extended spin chains show a characteristic dispersion law, where the intensity is large at the distribution of energies and wave vectors. Future neutron scattering experiments for copper oxalate could further confirm the infinite spin-chain...
model and tighten the experimental error bar on the effective exchange constant.

5. CONCLUSIONS

We presented fully ab initio treatment of the infinite spin-chain solid, copper oxalate, based on the EOM-CC theory and effective Hamiltonian approach. The rigorously derived ab initio effective Hamiltonian for copper oxalate corresponds to the infinite Heisenberg spin chain model and validates the nearest-neighbor approximation. This is the first purely theoretical validation of the XXX Heisenberg model for copper oxalate that is based on nonempirical all-electron many-body calculations and not relying on spin-symmetry broken solutions. Our results show that both strong and weak body calculations and not relying on spin-symmetry broken account for all these effects whereas the dependence on the basis set is relatively weak. The spin–orbit interaction introduces a noticeable additional shift that further changes the effective exchange constant. Only after accounting for all these effects does the magnetic susceptibility of the quantum spin model agree well with the experimental values. This is the first application of the EOM-SF-CC method to describe a periodic system, opening a new route in the treatment of strongly correlated periodic systems. These results provide a solid basis for future quantitative modeling of spin chains, including magnetic field effects.

ASSOCIATED CONTENT

Supporting Information
Relevant Cartesian geometries, details of spin–orbit calculations, effective Hamiltonians in Bloch’s and des Cloizeaux’s forms, analysis of the truncation of the non-nearest neighbor interactions, relationship between classical and quantum Heisenberg models (PDF)

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Notes
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REFERENCES

(1) Jungwirth, T.; Marti, X.; Wadley, P.; Wunderlich, J. Antiferromagnetic spintronics. Nat. Nanotechnol. 2016, 11, 231.
(2) Mourigal, M.; Enderle, M.; Klöpperpieper, A.; Caux, J.-S.; Stunault, A.; Rannow, H. M. Fractional spin excitations in the quantum Heisenberg antiferromagnetic chain. Nat. Phys. 2013, 9, 435–441.
(3) Coleman, P.; Schofield, A. J. Quantum criticality. Nature 2005, 433, 226–229.
(4) Breunig, O.; Garst, M.; Klimper, A.; Rohrkamp, J.; Turnbull, M. J.; Lorenz, T. Quantum criticality in the spin-1/2 Heisenberg chain system copper pyrazine dinitrate. Science 2017, 360, 451–465.
(5) Bleaney, B.; Bowers, K. D. Anomalous paramagnetism of copper acetate. Proc. R. Soc. London, Ser. A 1952, 214, 622–636.
(6) Maurice, R.; Sivalingam, K.; Ganyushin, D.; Guihery, N.; de Graaf, C.; Neese, F. Theoretical determination of the zero-field splitting in copper acetate monohydrate. Inorg. Chem. 2011, 50, 6229–6236.
(7) Capogna, L.; Mayr, M.; Horsch, P.; Raichle, M.; Kremer, R. K.; Sofin, M.; Maljuk, A.; Jansen, M.; Keimer, B. Helicoidal magnetic order in the spin-chain compound NACu2O2. Phys. Rev. B: Condens. Matter Mater. Phys. 2005, 71, 140402.
(8) Maeshima, N.; Higawara, M.; Narumi, Y.; Kindo, K.; Kobayashi, T. C.; Okunishi, K. Magnetic properties of S = 1/2 zigzag spin chain compound (N4H4)CuCl4. J. Phys.: Condens. Matter Mater. Phys. 2003, 15, 3607–3618.
(9) Bonner, J. C.; Friedberg, S. A.; Kobayashi, H.; Meier, D. L.; Blöte, H. W. J. Alternating linear-chain antiferromagnetism in copper nitrate Cu(NO3)2.25H2O. Phys. Rev. B: Condens. Matter Mater. Phys. 1983, 27, 245–260.
(10) Herrling, E.; Fischer, G.; Matejcek, S.; Pälwka, B.; Henke, H.; Odenwald, I.; Wendl, W. Structural and magnetic properties of the alternating Heisenberg spin-chain compound dichloro(2,5-dithiolhexanecopper(II). Phys. Rev. B: Condens. Matter Mater. Phys. 2003, 67, 014407.
(11) Willenberg, B.; Ryll, H.; Kiefer, K.; Tennant, D. A.; Groft, F.; Rolfs, K.; Manel, P.; Khalyavin, D.; Rule, K. C.; Wolter, A. U. B.; et al. Luttinger liquid behavior in the alternating spin-chain system copper nitrate. Phys. Rev. B: Condens. Matter Mater. Phys. 2015, 91, 060407.
(12) Bethe, H. Zur Theorie der Metalle. Z. Phys. 1931, 71, 205–226.
(13) Motoyama, N.; Eikaisi, H.; Uchida, S. Magnetic susceptibility of ideal spin 1/2 Heisenberg antiferromagnetic chain systems, Sr2CuO3 and SrCuO2. Phys. Rev. Lett. 1996, 76, 3212–3215.
(14) Johnston, D. C.; Johnson, J. W.; Goshorn, D. P.; Jacobson, A. J. Magnetic susceptibility of (VO)2P2O7: A one-dimensional spin-1/2 Heisenberg antiferromagnet with a ladder spin configuration and a singlet ground state. Phys. Rev. B: Condens. Matter Mater. Phys. 1987, 35, 219–222.
(15) Richards, P. M.; Quinn, R. K.; Morosin, B. Magnetic and structural properties of manganese pyridine linear chain salts. J. Chem. Phys. 1973, 59, 4447–4477.
(16) Jotham, R. W. Criticism of the use of the Ising model to describe linear chains of antiferromagnetically coupled copper(II) ions. J. Chem. Soc., Chem. Commun. 1973, 19, 178–179.
(17) Zelentsov, V. V.; Aminov, T. G. Magnetic susceptibility of cupric oxalate and cupric succinate. Dokl. Akad. Nauk SSSR 1964, 158, 1393–1395.
(18) Figgis, B. N.; Martin, D. J. The magnetic properties and structure of the cupric α, α-dicarboxylates. Inorg. Chem. 1966, 5, 100–104.
(19) Dubicki, L.; Harris, C. M.; Kokot, E.; Martin, R. L. Magnetic studies with copper (II) α-
dicarboxylates and their amine derivatives. Inorg. Chem. 1966, 5, 93–100.
(20) McGregor, K. T.; Soos, Z. G.; Soos, Z. G. Anisotropic exchange and temperature-dependent electron paramagnetic resonance line width in one-dimensional copper(II) complexes. 2. Magnetic properties of copper(II) oxalate-1/3-water. Inorg. Chem. 1976, 15, 2159–2165.
(21) Michalowicz, A.; Girerd, J. J.; Goulon, J. EXAFS [extended x-ray absorption fine structure] determination of the copper oxalate structure. Relation between structure and magnetic properties. Inorg. Chem. 1979, 18, 3004–3010.
(22) Christensen, A. N.; Lebech, B.; Andersen, N. H.; Grivel, J.-C. The crystal structure of paramagnetic copper(II) oxalate (CuC₂O₄): formation and thermal decomposition of randomly stacked anisotropic nano-sized crystallites. Dalton Trans. 2014, 43, 16754–16768.
(23) Girerd, J. J.; Kahn, O.; Verdaguer, M. Orbital reversal in (oxalato)copper(II) linear chains. Inorg. Chem. 1980, 19, 274–276.
(24) Cano, J.; Alemany, P.; Alvarez, S.; Verdaguer, M.; Ruiz, E. Exchange coupling in oxalato-bridged copper(II) binuclear compounds: A density functional study. Chem. Eur. J. 1998, 4, 476–484.
(25) Pal, P.; Konar, S.; El Fallah, M. S.; Das, K.; Bauzá, A.; Frontier, A.; Mukhopadhyay, S. Synthesis, crystal structures, magnetic properties and DFT calculations of nitrate and oxalate complexes with 3,5-dicarboxylates and their amine derivatives. J. Phys. Chem. C 2012, 116, 3985–3996.
(26) Julve, M.; Gleizes, A.; Chamoreau, L. M.; Ruiz, E.; Verdaguer, M. Antibonding interactions in copper(II) μ-oxalato dinuclear complexes: The role of the counterion. Eur. J. Inorg. Chem. 2018, 509–516.
(27) Santana, F. S.; Briganti, M.; Cassaro, R. A.; Totti, F.; Ribeiro, R. J.; Hughes, D. L.; Nunes, G. G.; Reis, D. M. An oxalate-bridged copper(II) complex combining monodentate benzoate, 2,2′-bipyridine and aqua ligands: Synthesis, crystal structure and investigation of magnetic properties. Mol. 2020, 25, 1898.
(28) Chalot, M. F.; Verdaguer, M.; Journaux, Y.; De Loth, P.; Daudey, J. P. Ab initio direct calculation of the singlet-triplet splitting in a μ-oxalato copper(II) binuclear complex. Inorg. Chem. 1984, 23, 3802–3808.
(29) Orms, N.; Krylov, A. I. Singlet-triplet energy gaps and the degree of diradical character in binuclear copper molecular magnets characterized by spin-flip density functional theory. Phys. Chem. Chem. Phys. 2018, 20, 13127–13144.
(30) Mayhall, N. J.; Head-Gordon, M. Computational quantum chemistry for multiple-site Heisenberg spin couplings made simple: Still only one spin-flip required. J. Phys. Chem. Lett. 2015, 6, 1982–1988.
(31) Malrieu, J. P.; Caballol, R.; Calzado, C. J.; de Graaf, C.; Guihéry, N. Magnetic interactions in molecules and highly correlated materials: Physical content, analytical derivation, and rigorous extraction of magnetic Hamiltonians. Chem. Rev. 2013, 114, 429–492.
(32) Calzado, C. J.; Cabredo, J.; Malrieu, J. P.; Caballol, R. Analysis of the magnetic coupling in binuclear complexes. II. Derivation of valence effective hamiltonians from ab initio CI and DFT calculations. J. Chem. Phys. 2002, 116, 3985–4000.
(33) Maurice, R.; Bastardis, R.; Graaf, C. d.; Suaud, N.; Mallah, T.; Guihéry, N. Universal theoretical approach to extract anisotropic spin hamiltonians. J. Chem. Theory Comput. 2009, 5, 2977–2984.
(34) Monari, A.; Maynau, D.; Malrieu, J.-P. Determination of spin Hamiltonians from projected single reference configuration interaction calculations. I. Spin 1/2 systems. J. Chem. Phys. 2010, 133, 044106.
(35) Bogdanov, N. A.; Manni, G. L.; Sharma, S.; Gunnarsson, O.; Alavi, A. New superexchange paths due to breathing-enhanced hopping in corner-sharing cuprates. 2018, arXiv:1803.07026.
(36) Krylov, A. I. Equation-of-motion coupled-cluster methods for open-shell and electronically excited species: The hitchiker’s guide to Fock space. Annu. Rev. Phys. Chem. 2008, 59, 433–462.
(37) de Graaf, C.; Broer, R. Magnetic Interactions in Molecules and Solids; Springer, 2016.
(38) Pokhilo, P.; Krylov, A. I. Effective Hamiltonians derived from equation-of-motion coupled-cluster wave-functions: Theory and application to the Hubbard and Heisenberg Hamiltonians. J. Chem. Phys. 2020, 152, 094108.
(39) Emrich, K. An extension of the coupled-cluster formalism to excited states (I). Nucl. Phys. 1984, 292, 379–396.
(40) Bartlett, R. J. The coupled-cluster revolution. Mol. Phys. 2010, 108, 2905–2920.
(41) Sneskov, K.; Christiansen, O. Excited state coupled cluster methods. Wiley Interdiscip. Rev. Comput. Mol. Sci. 2012, 2, 566–584.
(42) Bartlett, R. J. Coupled-cluster theory and its equation-of-motion extensions. Wiley Interdiscip. Rev. Comput. Mol. Sci. 2012, 2, 126–138.
(43) Stanton, J. F.; Bartlett, R. J. The equation of motion coupled-cluster method. A systematic biorthogonal approach to molecular excitation energies, transition probabilities, and excited state properties. J. Chem. Phys. 1993, 98, 7029–7039.
(44) Stanton, J. F.; Gouss, J. Analytic energy derivatives for ionized states described by the equation-of-motion coupled cluster method. J. Chem. Phys. 1994, 101, 8938–8944.
(45) Pieniazek, P. A.; Bradford, S. E.; Krylov, A. I. Charge localization and Jahn-Teller distortions in the benzene dimer cation. J. Chem. Phys. 2008, 129, 074104.
(46) Sattelmeyer, K. W.; Schaefer, H. F.; Stanton, J. F. Use of 2h and 3h-p like coupled-cluster Tamm-Dancoff approaches for the equilibrium properties of ozone. Chem. Phys. Lett. 2003, 378, 42–46.
(47) Musial, M.; Perera, A.; Bartlett, R. J. Multireference coupled-cluster theory: The easy way. J. Chem. Phys. 2011, 134, 114108.
(48) Nooijen, M.; Bartlett, R. J. Equation of motion coupled cluster method for electron attachment. J. Chem. Phys. 1995, 102, 3629–3647.
(49) Musial, M.; Kucharski, S. A.; Bartlett, R. J. Multireference double electron attachment coupled cluster method with full inclusion of the connected triple excitations: MR-DA-CCSDT. J. Chem. Theory Comput. 2011, 7, 3088–3096.
(50) Volume 9 of A Memorial Festschrift from Theoretical Chemistry Accounts; Perera, A., Molt, R. W., Lotrich, V. F., Bartlett, R. J., Shavitt, I. I., Cramer, C. J., Truhlar, D. G., Eds.; Springer, 2016; p 153.
(51) Guanla, S.; Kjonsetad, E. F.; Stanton, J. J.; Koch, H.; Krylov, A. Equation-of-motion coupled-cluster method with double electron-attaching operators: Theory, implementation, and benchmarks. J. Chem. Phys. 2021, 154, 114115.
(52) Krylov, A. I. Size-consistent wave functions for bond-breaking: The equation-of-motion spin-flip model. Chem. Phys. Lett. 2001, 338, 375–384.
(53) Krylov, A. I. The spin-flip equation-of-motion-coupled-cluster electronic structure method for a description of excited states, bond-breaking, diradicals, and triradicals. Acc. Chem. Res. 2006, 39, 83–91.
(54) Casanova, D.; Krylov, A. I. Spin-flip methods in quantum chemistry. Phys. Chem. Chem. Phys. 2020, 22, 4326–4342.
(55) Slipchenko, L. V.; Krylov, A. I. Singlet-triplet gaps in diradicals. Acc. Chem. Res. 2002, 35, 4326–4342.
(56) Slipchenko, L. V.; Krylov, A. I. Singlet-triplet gaps in diradicals by the spin-flip approach: A benchmark study. J. Chem. Phys. 2002, 117, 4694–4708.
(57) Krylov, A. I. Triradicals. J. Phys. Chem. A 2005, 109, 10638–10645.
(58) Casanova, D.; Krylov, A. I. Spin-flip methods in quantum chemistry. Phys. Chem. Chem. Phys. 2020, 22, 4326–4342.
(59) Des Cloizeaux, J. Extension d’une formule de lagrange a des problemes de valeurs propres. Nucl. Phys. 1960, 20, 321–346.
(60) Mayhall, N. J.; Head-Gordon, M. Computational quantum chemistry for single Heisenberg spin couplings made simple: Just one spin-flip required. J. Chem. Phys. 2014, 134, 134111.
(61) Shao, Y.; Gan, Z.; Epifanovsky, E.; Gilbert, A. T. B.; Wormit, M.; Kussmann, J.; Lange, A. W.; Behn, A.; Deng, J.; Feng, X.; et al. Advances in molecular quantum chemistry contained in the Q-Chem 4 program package. Mol. Phys. 2015, 113, 184–215.

(62) Krylov, A. I.; Gill, P. M. W. Q-Chem: An engine for innovation. Wiley Interdiscip. Rev. Comput. Mol. Sci. 2013, 3, 317–326.

(63) Dunning, T. H., Jr. Gaussian basis sets for use in correlated molecular calculations. I. The atoms boron through neon and hydrogen. J. Chem. Phys. 1989, 90, 1007–1023.

(64) Balabanov, N. B.; Peterson, K. A. Systematically convergent basis sets for transition metals. I. All-electron correlation consistent basis sets for the 3d elements Sc–Zn. J. Chem. Phys. 2005, 123, 064107.

(65) Koput, J.; Peterson, K. A. Ab initio potential energy surface and vibrational–rotational energy levels of X2Σ+ CaOH. J. Phys. Chem. A 2002, 106, 9595–9599.

(66) Wilson, A. K.; Woon, D. E.; Peterson, K. A.; Dunning, T. H. Gaussian basis sets for use in correlated molecular calculations. IX. The atoms gallium through krypton. J. Chem. Phys. 1999, 110, 7667–7676.

(67) Pokhilko, P.; Epifanovsky, E.; Krylov, A. I. Double precision is not needed for many-body calculations: Emergent conventional wisdom. J. Chem. Theory Comput. 2018, 14, 4088–4096.

(68) Kaliman, I. A.; Krylov, A. I. New algorithm for tensor contractions on multi-core CPUs, GPUs, and accelerators enables CCSD and EOM-CCSD calculations with over 1000 basis functions on a single compute node. J. Comput. Chem. 2017, 38, 842–853.

(69) Pokhilko, P.; Izmodenov, D.; Krylov, A. I. Extension of frozen natural orbital approximation to open-shell references: Theory, implementation, and application to single-molecule magnets. J. Chem. Phys. 2020, 152, 034105.

(70) Manohar, P. U.; Krylov, A. I. A non-iterative perturbative triples correction for the spin-flipping and spin-conserving equation-of-motion coupled-cluster methods with single and double substitutions. J. Chem. Phys. 2008, 129, 194105.

(71) Pokhilko, P.; Epifanovsky, E.; Krylov, A. I. General framework for calculating spin–orbit couplings using spinless one-particle density matrices: theory and application to the equation-of-motion coupled-cluster wave functions. J. Chem. Phys. 2019, 151, 034106.

(72) Zhao, H.; Wang, Z.; Guo, M.; Wang, F. Splittings of d⁸ configurations of late-transition metals with EOM-DIP-CCSD and FSCCSD methods. J. Chem. Phys. 2020, 152, 134105.

(73) Boys, S. F. Construction of some molecular orbitals to be approximately invariant for changes from one molecule to another. Rev. Mod. Phys. 1960, 32, 296.

(74) El-Sayed, M. A. Spin–orbit coupling and the radiationless processes in nitrogen heterocycles. J. Chem. Phys. 1963, 38, 2834–2838.

(75) El-Sayed, M. A. Triplet state: Its radiative and non-radiative properties. Acc. Chem. Res. 1968, 1, 8–16.

(76) Pokhilko, P.; Krylov, A. I. Quantitative El-Sayed rules for many-body wavefunctions from spinless transition density matrices. J. Phys. Chem. Lett. 2019, 10, 4857–4862.

(77) Fisher, M. E. Magnetism in one-dimensional systems—the Heisenberg model for infinite spin. Am. J. Phys. 1964, 32, 343–346.

(78) Johnston, D. C.; Kremer, R. K.; Troyer, M.; Wang, X.; Klümpner, A.; Bud’ko, S. L.; Panchula, A. F.; Canfield, P. C. Thermodynamics of spin S = 1/2 antiferromagnetic uniform and alternating-exchange Heisenberg chains. Phys. Rev. B: Condens. Matter Mater. Phys. 2000, 61, 9558–9606.

(79) Xiang, T. Thermodynamics of quantum Heisenberg spin chains. Phys. Rev. B: Condens. Matter Mater. Phys. 1998, 58, 9142–9149.

(80) Furrer, A.; Güdel, H. U. Interference effects in neutron scattering from magnetic clusters. Phys. Rev. Lett. 1977, 39, 657–660.

(81) Zheludev, A.; Shirane, G.; Sasago, Y.; Hase, M.; Uchinokura, K. Dimerized ground state and magnetic excitations in CaCuGe2O6. Phys. Rev. B: Condens. Matter Mater. Phys. 1996, 53, 11642–11646.

(82) Caux, J.-S.; Hagemans, R.; Mallet, J. M. Computation of dynamical correlation functions of Heisenberg chains: the gapless anisotropic regime. J. Stat. Mech. Theor. Exp. 2005, 2005, P09003.

(83) Kohno, M. Dynamically dominant excitations of string solutions in the spin-1/2 antiferromagnetic Heisenberg chain in a magnetic field. Phys. Rev. Lett. 2009, 102, 037203.