

First-Principles Periodic Calculation of Four-Body Spin Terms in High- T_c Cuprate Superconductors

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A general mapping between the energy of pertinent magnetic solutions and the diagonal terms of the spin Hamiltonian in a local representation provides the first general framework to extract accurate values for the many body terms of extended spin Hamiltonians from periodic first-principle calculations. Estimates of these terms for La_2CuO_4 , the paradigm of high- T_c superconductor parent compounds, and for the SrCu_2O_3 ladder compound are reported. For La_2CuO_4 , present results support experimental evidence by Toader *et al.* [Phys. Rev. Lett. **94**, 197202 (2005)]. For SrCu_2O_3 even larger four-body spin amplitudes are found together with $J_l/J_r = 1$ and non-negligible ferromagnetic interladder exchange.

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The strong antiferromagnetic interactions observed in lamellar cuprates are fundamental ingredients of the high- T_c (HTC) superconductivity microscopic mechanism [1,2]. Magnetic interactions arise from the particular crystal and electronic structure of these cuprates with Cu^{2+} ions arranged in edge sharing Cu_4O_4 plaquettes. The electronic ground state involves a single $d_{x^2-y^2}$ -type hole in each $\text{Cu}(3d)$ shell leading to a network of effective spin $S = 1/2$ particles. Nevertheless, these systems are strongly correlated in nature, making standard band theory techniques unable to accurately describe either their valence or low energy spectrum [3,4].

The low energy spectrum and collective properties of these compounds are assumed to be governed by a Heisenberg Hamiltonian as in the first term of Eq. (1) accounting for the magnetic coupling J_{ij} between nearest-neighbor (NN) centers i and j only. This is in agreement with the widely accepted general picture for HTC superconductivity involving a “Heisenberg sea” where holes are introduced by doping the perfect structures. However, to fully understand the magnetic excitations and the infrared and neutron scattering spectra of 2D [5–11] and spin ladder cuprates [12,13], it has been necessary to extend the spin Hamiltonian as in Eq. (1),

$$\hat{H} = \sum_{i,j} J_{ij} \left(\hat{\mathbf{S}}_i \cdot \hat{\mathbf{S}}_j - \frac{1}{4} \right) + \sum_{i,j,k,l} J_{\text{ring}} \left[(\hat{\mathbf{S}}_i \cdot \hat{\mathbf{S}}_j)(\hat{\mathbf{S}}_k \cdot \hat{\mathbf{S}}_l) + (\hat{\mathbf{S}}_i \cdot \hat{\mathbf{S}}_l)(\hat{\mathbf{S}}_j \cdot \hat{\mathbf{S}}_k) - (\hat{\mathbf{S}}_i \cdot \hat{\mathbf{S}}_k)(\hat{\mathbf{S}}_j \cdot \hat{\mathbf{S}}_l) - \frac{1}{16} \right] + \dots, \quad (1)$$

with other two-body exchange constants J_{ij} [hereafter referred as J for NN interactions in square lattices and J_d for next-nearest-neighbor (NNN) interactions], four-body cyclic terms J_{ring} , and higher order terms. The largest coupling is expected to be precisely J as found for almost all existing HTC superconductor cuprates parent com-

pounds. Nevertheless, NNN interactions may be non-negligible or even of the same order of magnitude as in the case of the $S = 1/2$ CuGeO_3 system [14,15]. Likewise, J_{ring} terms may be important in Cu_4O_4 plaquettes since they are originated by the electrons cyclic circulation around the ring with a clear analogy to π conjugated systems [16]. Similar four-body terms are crucial to describe the ground state properties of ^3He [17].

Although there is a general agreement about the role of J_{ring} in determining the properties of cuprates [9–12], only very recently Toader *et al.* [18] provided definitive evidence of its existence in La_2CuO_4 . They suggest $J_{\text{ring}} \approx 0.5J$, comparable to the pairing energies, and propose that the resulting circulating currents could have an important role in the mechanism of superconductivity. Notwithstanding, previous estimates of J_{ring} for 2D and spin ladder cuprates, obtained from either indirect measurements or numerical simulations with an extended Heisenberg model, propose substantially smaller amplitudes with $J_{\text{ring}} \sim 0.30J$ [7,9,10,12,19]. The J_{ring} terms as evaluated by Toader *et al.* rely on NN and NNN coupling constants of $J = 111.8$ meV and $J_d = -11.4$ meV, respectively, extracted from one of the various fittings of the magnon spectrum [10]. However, it is important to point out that (i) this value for J is smaller than another experimental estimate of 135 ± 6 meV obtained with a nearest-neighbor Heisenberg Hamiltonian [20] and (ii) the ferromagnetic nature of J_d contradicts theoretical predictions [21] and measurements on materials with similar exchange paths [22]. For the SrCu_2O_3 ladder compound the recent Raman response experiments by Schmidt *et al.* propose $J_r = 140$ meV, $J_{\text{ring}}/J_r = 0.2$, and $J_l/J_r = 1.5$ [23].

Clearly, a bottom-up accurate and independent determination of all important terms in the spin Hamiltonian in Eq. (1) for La_2CuO_4 —or any other similar system—is

highly desirable. For various cuprates, unrestricted Hartree-Fock (HF) cluster model predictions for J are in agreement with those resulting from equivalent periodic calculations, thus validating the finite models [24]. Subsequent configuration interaction (CI) calculations on embedded cluster models lead to results which are in very good agreement with available experimental data [25]. Cluster models were also used to extract J_d and J_{ring} in 2D and spin ladder cuprates [26–28]. For the J_{ring}/J ratio, CI calculations predict values in the 0.11–0.22 range. However, the embedded cluster derived J_{ring} values are difficult to validate since (i) convergence check with respect to the cluster model size requires exceedingly large calculations and (ii) a general procedure to validate the cluster results for J_{ring} from periodic calculations is still lacking. Martin and Illas [29] suggested that hybrid density functional (DF) theory could provide a convenient framework for the description of the local magnetic interaction in systems with localized spins. This can be equally applicable to periodic or cluster models, and a suitable choice of the hybrid exchange-correlation potential permits one to reproduce the experimental J values [4,30]. Up to date, this procedure has been restricted to the determination of two-body terms (J and J_d) only. In this Letter, we present a general procedure which enables the *simultaneous* and *independent* calculation of essentially all parameters defining the spin Hamiltonian of Eq. (1) from periodic DF calculations.

The generalization comes from a careful analysis of the procedure used to extract J in cluster and periodic models [24,31]. For a system with two localized $S = 1/2$ spins, the Heisenberg Hamiltonian [Eq. (1)] has two spin eigenfunctions—a singlet (S) and a triplet (T)—with energies $-J$ and 0, respectively [32], and hence $E(S) - E(T) = -J$. Using pure spin electronic *ab initio* CI wave functions to describe the corresponding electronic states of such a system permits one to establish a direct one-to-one mapping between the energies of the S and T electronic states and to compute J from this energy difference. However, in a band theory framework one is constrained to write the wave function or the electron density by means of a single Slater determinant, and this mapping cannot be used. A way to circumvent the problem is to rely on the expectation energy for the single Slater determinant ferromagnetic ($|FM\rangle$) and antiferromagnetic ($|AFM\rangle$) broken symmetry solutions. For the simple case above, one has $|FM\rangle = |\uparrow\uparrow\rangle$ and $|AFM\rangle = |\uparrow\downarrow\rangle$ or $|\downarrow\uparrow\rangle$. For these “magnetic phases” one can easily show that the expectation energies of the Heisenberg Hamiltonian are $\langle FM|H|FM\rangle = 0$ and $\langle AFM|H|AFM\rangle = -J/2$, but $\langle FM|H|FM\rangle$ and $\langle AFM|H|AFM\rangle$ are precisely $E(AF\!M)$ and $E(F\!M)$ and hence $E(AF\!M) - E(F\!M) = -J/2$. The same solution is obtained by making use of the Ising spin Hamiltonian [32], although one has to assume that the system is equally well described by a Heisenberg or a Ising model Hamiltonian.

The use of expectation values for the FM and various AFM broken symmetry solutions is the clue to extract the *various* parameters of the model Hamiltonian in Eq. (1) using a periodic approach. In fact, in a periodic system one can find self-consistent field (SCF) solutions—either for HF or DF potentials—representing $|FM\rangle = |\uparrow\uparrow\uparrow \cdots \uparrow\rangle$ and various $|AFM(i)\rangle = |\uparrow\downarrow \cdots \downarrow\uparrow\rangle$ phases with different spin alignments along the relevant dimensions. The resulting SCF solutions can be related to a localized valence bond (VB) picture where nondynamical correlation effects are introduced partly through spin polarization [33,34]. A quasidegenerate perturbation theory expansion of the matrix representation of a Hubbard-type Hamiltonian in the neutral VB basis up to fourth order permits one to extract the leading interactions— J , J_d , and J_{ring} —involved in each neutral VB localized spin setting. Using cluster models for La_2CuO_4 and SrCu_2O_3 , Calzado and Malrieu [28] have shown that, apart from J , the dominant terms of Eq. (1) correspond precisely to J_d and J_{ring} . The latter appears at fourth order and implies a cyclic circulation of the electrons around a plaquette; notice that in a plaquette with all spins parallel ($\langle S_z = \pm 2 \rangle$) such a current is impossible. However, for spin settings on the plaquette with $\langle S_z \rangle = 0, \pm 1$ these currents lead to additional off-diagonal and diagonal corrections (see Tables III–VIII in Ref. [28]). This is the kernel of the general mapping procedure proposed here to extract these terms from periodic calculations. This permits one to obtain the terms in Eq. (1) simultaneously, avoiding any possible bias due to the choice of a too limited material model.

The calculated energy of several magnetic solutions (either per formula unit or per Cu atom) can be mapped onto the diagonal part of the matrix representation of Eq. (1) in a localized VB basis set [28]. To obtain J in La_2CuO_4 or $\text{Sr}_2\text{CuO}_2\text{Cl}_2$, two magnetic solutions (FM and AFM) are enough (see Ref. [24]). However, several magnetic phases are needed to extract the relevant J_d and J_{ring} terms. Technically, the main difficulty is to obtain a sufficient number of magnetic SCF solutions so as to construct a large enough set of equations that permits one to extract the numeric values of the relevant terms from appropriate energy differences. The complete set of magnetic solutions together with the full justification and development of the set of equations necessary to carry out the mapping procedure exceeds the length of this Letter and will be reported elsewhere [35]. Relevant magnetic solutions and the corresponding equations for La_2CuO_4 and $\text{Sr}_2\text{CuO}_2\text{Cl}_2$ are given in Table I and Fig. 1. For the SrCu_2O_3 ladder compound ten magnetic solutions have been considered [35]; relative energies are in Table II. Notice that double counting is avoided by considering interactions inside a given cell only.

The next and final point is to carry out suitable estimates of the energy of each relevant magnetic solution. To this end periodic hybrid DF calculations using the Fock-35

TABLE I. Energy expressions per Cu atom relative to FM phase for the magnetic solutions in Fig. 1 and their corresponding values (in meV) for the 2D cuprates.

Phase	Energy expressions	Values in La ₂ CuO ₄	Values in Sr ₂ CuO ₂ Cl ₂
AFM	$-J$	-140.1	-130.8
AFM1	$-(J/2 + J_d/2 + J_{\text{ring}}/8)$	-78.9	-70.1
AFM2	$-(J/2 + J_d)$	-78.8	-68.2
FM	0	0.0	0.0

exchange-correlation potential have been performed as done by Moreira *et al.* for NiO [4]. Crystalline orbitals are built as linear combinations of Bloch functions, which in turn are built from atomic orbitals (AOs) optimized for the crystal environment. The AOs are contracted real solid spherical harmonic Gaussian-type functions. Extended all-electron basis sets have been used to describe the Cu²⁺ and O²⁻ ions in the ionic environment, whereas core pseudopotentials have been used to represent inner electrons of the remaining ions [36]. Strict convergence criteria and a set of 105 points in the irreducible Brillouin zone have been used to ensure a numerical accuracy of 10⁻⁷ hartree per formula unit. Calculations have been carried out using the CRYSTAL03 code [37] and experimental cell parameters.

The amplitudes of J , J_d , and J_{ring} estimated from the energy differences corresponding to equations given in Tables I and II are reported in Table III (see also Fig. 1). For the La₂CuO₄ and Sr₂CuCl₂O₂ 2D systems, the set of equations is determined and the values in Table III are univocal. For the SrCu₂O₃ ladder, a least square procedure has been used to solve the overdetermined set of equations. For the 2D systems, the J values predicted by the Fock-35 potential are close to experiment, as expected from previous work on similar systems [24,28,34], thus further confirming the accuracy of the present approach. Next, we come to the most important result of the present work: the first direct estimate of the amplitude of the J_{ring} terms from *ab initio* periodic calculations. For La₂CuO₄, the outcome of the present periodic approach is in agreement with the only available theoretical results for this compound, although arising from cluster calculations [26–28]. Second, the present estimate of $J_{\text{ring}} \sim 35.8$ meV is in excellent agreement with the indirect evaluations of Coldea *et al.* ($J_{\text{ring}} \sim 38 \pm 8$ meV) [10] and the

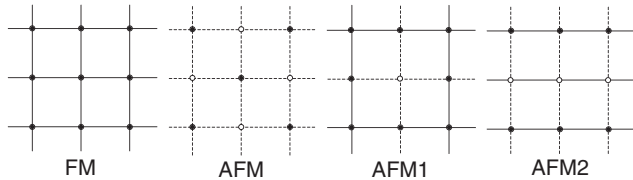


FIG. 1. Schematic representation of the magnetic solutions calculated to extract J , J_d , and J_{ring} in the 2D layered cuprates.

TABLE II. Energy expressions per Cu atom relative to the AFM_{gs} (ground state) phase and the corresponding values (in meV) for the ladder compound.

Phase	Energy expression	Values in SrCu ₂ O ₃
AFM9	$+J_l/6 + J_r/6 - 3J_d/2 - 0.05J_{\text{ring}}$	44.98
AFM8	$+J_l/4 - J_d/4 + J_i/8$	31.92
AFM7	$+J_l/2 - J_d/2 + J_i/4$	67.38
AFM6	$+J_l/2 - J_d/2 - J_i/4$	83.78
AFM5	$+J_l/4 + J_r/8 - J_d/4 - J_i/8 - 0.075J_{\text{ring}}$	57.68
AFM4	$+J_r/4 - J_d/2$	38.87
AFM3	$+J_l/4 + J_r/8 - J_d/4 - 0.075J_{\text{ring}}$	53.43
AFM2	$+J_r/8 - J_d/4$	16.20
AFM1	$+J_l/8 + J_r/16 - J_d/8 - 0.0375J_{\text{ring}}$	26.68
AFM _{gs}	0	0.0

simulations of Mizuno *et al.* ($J_{\text{ring}} \sim 40$ meV) [19]. Notice, however, that the $J_{\text{ring}}/J = 0.25$ ratio predicted here is smaller than that reported by Toader *et al.* [18], which is of 0.5, but in excellent agreement with a more generally accepted ratio $J_{\text{ring}}/J \sim 0.3$ [9,10,19] for this compound. Also, the Fock-35 method predicts an antiferromagnetic $J_d \sim 8.8$ meV, again consistent with the values provided by embedded cluster calculations. Hence, it will be of great interest to repeat the fit in the experiments by Toader *et al.* [18] by using the present estimate of both J and J_d . For Sr₂CuO₂Cl₂, there are no previous values for the amplitude of the four-body exchange terms. Present calculations predict values that are slightly smaller than the corresponding ones in La₂CuO₄ consistent with larger NN and NNN distances in the latter (3.809 vs 3.972 Å for NN and ~ 5.38 vs 5.62 Å for NNN distances). There exists a good agreement between the estimate of the NN interaction ($J \sim 130$ meV) and the experimental value ($J = 125 \pm 6$ meV [38]); the J_d coupling is also predicted to be antiferromagnetic and the J_{ring}/J ratio ~ 0.20 is somewhat smaller than that for La₂CuO₄ but still consistent with previous estimates.

Finally, for the ladder compound the dominant interactions are the couplings across the rungs (J_r) and along the legs (J_l) which are nearly equal in magnitude, i.e., (J_r/J_l) ≈ 1 as expected from the similarity of the Cu-O-Cu exchange paths. On the other hand, J_d is antiferromag-

TABLE III. Two- and four-body exchange amplitudes (in meV) for La₂CuO₄, Sr₂CuO₂Cl₂, and SrCu₂O₃. Experimental values in parenthesis (from Refs. [20,38]).

System	J	J_d	J_{ring}	J_{ring}/J		
La ₂ CuO ₄	140.1(135 ± 6)	8.8	35.8	0.25		
Sr ₂ CuO ₂ Cl ₂	130.0(125 ± 6)	2.8	26.4	0.20		
SrCu ₂ O ₃	J_l	J_r	J_d	J_i	J_{ring}	J_{ring}/J
	153.1	155.6	2.7	-34.2	48.8	0.31

netic as in the 2D cuprates and a non-negligible interladder ferromagnetic exchange is found, $J_i \approx -0.22J_l$. Hence, one should not consider these as noninteracting ladders. Regarding J_{ring} , both its amplitude and the J_{ring}/J_r ratio are larger than for 2D cuprates, but still close to 0.3 in agreement with various experiments [9–12]. In particular, calculated J_r and J_{ring}/J_r are close to those reported by Schmidt *et al.* extracted from Raman response experiments [23], although they ignore J_i and, to justify some differences between ladder and 2D magnetic systems, they propose $J_l/J_r = 1.5$. The present results do not support such large anisotropy between J_l and J_r . Interestingly enough, we found that neglecting J_{ring} results in a larger anisotropy in the fitting. These results strongly suggest revising previous fittings using the present estimates as starting points.

To summarize, the present work proposes a new, general, and unprejudiced scheme to predict the amplitude of the parameters defining a general spin Hamiltonian from DF periodic calculations. The procedure does not need to make assumptions on the relative amplitude of these terms. Instead, it relies on a mapping approach between the energy of pertinent magnetic solutions and the diagonal terms of the spin Hamiltonian in a local representation. Then, the unique possible bias arises from the quality of the exchange-correlation potential. In particular, the present work provides an independent confirmation of the importance of four-body terms in La_2CuO_4 recently evidenced from the experimental work of Toader *et al.* [18] and supplies reliable values for spin Hamiltonian parameters of other key compounds. It is predicted that the importance of four-body terms is likely to be similar for most of the HTC related cuprates and even more important in ladder compounds in agreement with the recent experiments of Schmidt *et al.* [23]. It is also suggested that the fit to neutron scattering data should be revised by considering alternative values for both J and J_d magnetic coupling terms. Finally, the present study adds further evidence that the ferromagnetic interladder exchange introducing spin frustration between legs and the four-body term in the SrCu_2O_3 ladder should not be neglected.

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