Symmetry, Spin-Orbit Interactions, and Spin Anisotropies

T. Yildirim,[1] A. B. Harris,[1] O. Entin-Wohlman,[2] and Amnon Aharony[2]

[1]*Department of Physics, University of Pennsylvania, Philadelphia, Pennsylvania 19104-6396*

[2]*School of Physics and Astronomy, Raymond and Beverly Sackler Faculty of Exact Sciences, Tel Aviv University, Tel Aviv 69978, Israel*

(Received 1 April 1994)

The origins of anisotropy in the effective spin Hamiltonian, describing the ground manifold of Hubbard models with spin-orbit interactions, are critically discussed. For tetragonal symmetry, we show exactly that spin anisotropy can arise only if one includes *both* spin-orbit and Coulomb exchange interactions. For lower symmetries, additional anisotropies arise from terms which were hitherto neglected. Our analytic results are supported by numerical solutions for single bond clusters. These results can explain the easy plane anisotropy in the antiferromagnetic cuprates.

PACS numbers: 75.30.Et, 71.70.Ej, 75.30.Gw

A long standing problem concerns the mechanism whereby spin-orbit interactions give rise to magnetic anisotropies in magnetic insulators. This problem has attracted renewed interest following the discovery of high temperature superconductivity in the doped cuprates [1] and consequent interest in the magnetism of the undoped or lightly doped cuprate insulators. Many properties of such insulators with one hole per site are described by a spin-1/2 Heisenberg antiferromagnet Hamiltonian, with small spin anisotropies [2], $\mathcal{H}_M = \sum_{(i,j)} \mathcal{H}_M(i,j)$ with

$$\mathcal{H}_M(i,j) = \sum_{\mu\nu} J_{\mu\nu}(i,j)\, S_\mu(i)\, S_\nu(j), \qquad (1)$$

where μ and ν label Cartesian components and (i,j) denotes a pair of spins. For the cuprates, we shall mainly consider nearest neighbor (nn) spins in the CuO_2 plane. We refer to the case when $J_{\mu,\nu}(i,j) = J(i,j)\,\delta_{\mu,\nu}$ as isotropic exchange. After Anderson [3] used the superexchange formalism to derive the isotropic terms, Moriya [4] showed that adding spin-orbit (SO) interactions generates anisotropy (and even antisymmetric exchange terms), for sufficiently low lattice symmetry. The recent work on the cuprates required a more systematic study of the relations between lattice symmetry and the spin anisotropies: while Moriya's calculation was extended to yield the antisymmetric exchange in orthorhombic La_2CuO_4 [5–9], which disappears when the orthorhombic distortion vanishes, these calculations did not yield the easy plane anisotropy which is observed to have similar magnitudes in both the orthorhombic and tetragonal cuprates isostructural to La_2CuO_4 [10].

When each site has tetragonal symmetry, then $\mathcal{H}_M$ must have the form

$$\mathcal{H}_M = \sum_{\langle ij\rangle} (J_\parallel S_i^\parallel S_j^\parallel + J_\perp S_i^\perp S_j^\perp + J_z S_i^z S_j^z), \qquad (2)$$

where $\parallel$ and $\perp$ denote components (in the plane) parallel and perpendicular to the bond $\langle ij\rangle$ and z the component perpendicular to the plane. Recently [11], the observed easy plane anisotropies $\Delta J = (J_\parallel + J_\perp)/2 - J_z$ were attributed to Coulomb exchange interactions. However, no systematic discussion was given to show whether or not these results were either model dependent or sensitive to the approximation used. In this Letter we discuss the role of lattice symmetry in determining the various magnetic anisotropies. Specifically, we show exactly that for tetragonal site symmetry the spin Hamiltonian is isotropic *unless* one includes *both* spin-orbit *and* exchange interactions. When both are included, we calculate the J_μ's of Eq. (2) and obtain values for ΔJ which are consistent with experiments. We further mention spin anisotropies at lower lattice symmetries, which arise from terms not included by previous authors.

We start by describing hopping of holes in a Cu d band with the following generic model,

$$\begin{aligned}\mathcal{H} = & \sum_{i,\alpha,\sigma} E_{i\alpha} d^\dagger_{i\alpha\sigma} d_{i\alpha\sigma} \\ & + \sum_{i,\alpha,\beta,\sigma,\sigma'} \lambda [w_i(\alpha,\beta)_{\sigma,\sigma'} d^\dagger_{i\alpha\sigma} d_{i\beta\sigma'} + \text{H.c.}] \\ & + \sum_{\alpha,\beta,\sigma,i<j} t_{i\alpha,j\beta} (d^\dagger_{i\alpha\sigma} d_{j\beta\sigma} + d^\dagger_{j\beta\sigma} d_{i\alpha\sigma}) \\ & + \frac{1}{2} \sum_{i,\alpha,\alpha',\sigma,s} U_{i\alpha,i\alpha'} d^\dagger_{i\alpha\sigma} d^\dagger_{i\alpha' s} d_{i\alpha s} d_{i\alpha\sigma} \\ & + \frac{1}{2} \sum_{i,\alpha\neq\alpha',\sigma,s} K_{i\alpha,i\alpha'} d^\dagger_{i\alpha\sigma} d^\dagger_{i\alpha' s} d_{i\alpha' s} d_{i\alpha'\sigma}. \qquad (3)\end{aligned}$$

Here $d^\dagger_{i\alpha\sigma}$ creates a $3d$ hole on the ith copper ion in the αth spatial orbital with z component of spin σ. The second term arises from the SO interaction, $\lambda \mathbf{l}\cdot\mathbf{s}$ for each hole, and $w_i(\alpha,\beta)_{\sigma,\sigma'} = \sum_\mu L^\mu_{\alpha,\beta}[\sigma_\mu]_{\sigma,\sigma'}/2$, where $L^\mu_{\alpha,\beta}$ is an orbital angular momentum matrix element and $[\sigma_\mu]$ is the Pauli matrix. $\mathcal{H}$ includes Coulomb (**U**) and what we will refer to as Coulomb exchange (**K**) interactions between electrons on the same site [12].

To second order in the hopping **t**, Moriya's superexchange results follow from the simpler Hamiltonian

$$\mathcal{H} = \sum_{\substack{\sigma,\sigma' \\ i<j}} \tilde{t}_{i\sigma,j\sigma'} \tilde{d}^\dagger_{i0\sigma} \tilde{d}_{j0\sigma'} + \frac{1}{2} \sum_{i,\sigma,s} U \tilde{d}^\dagger_{i0\sigma} \tilde{d}^\dagger_{i0s} \tilde{d}_{i0s} \tilde{d}_{i0\sigma}, \qquad (4)$$

where $\tilde{d}^{\dagger}_{i0\sigma}$ creates a hole in the renormalized ground state (with energy zero), which contains contributions from the original excited states through SO matrix elements, and where $\tilde{t}$ may contain spin flip terms (for low symmetry). Perturbation expansion in powers of $\tilde{t}/U$ eliminates the states with two holes on the same ion, and the resulting 4 lowest energy states are then described by the single-bond Hamiltonian as in Eq. (1). This procedure has been the basis for many recent extensions [5–9] of Moriya's work. In particular, starting from Eq. (4), Shekhtman *et al.* [6] discovered a new hidden symmetry, which implied that the single bond $\mathcal{H}_M(i,j)$ is isotropic. However, one should note that with general **U**, **K**, and **t**, Eq. (4) is not equivalent to Eq. (3) above. In particular, since Eq. (4) does not contain hopping among renormalized excited states, its results at high order in $\tilde{t}/U$ differ from those which follow Eq. (3). Other differences are discussed below. Therefore, the hidden symmetry of Ref. [6] does not persist. Had it persisted, it would have precluded any easy plane anisotropy in the tetragonal cuprates.

We now prove our strongest result, concerning tetragonal symmetry based on the full Hamiltonian (3). When $\mathbf{K} = 0$, we prove that the spin Hamiltonian representing the ground manifold is isotropic, regardless of the details of the matrix **U**. For tetragonal d states (as appropriate for the Cu ions), the spatial orbitals $|\alpha\rangle$ are fixed to be $|0\rangle \sim x^2 - y^2$, $|1\rangle \sim 3z^2 - r^2$, $|x\rangle \sim yz$, $|y\rangle \sim xz$, and $|z\rangle \sim xy$, with single ion energies $E_0 = 0$, E_1, $E_x = E_y$, and E_z, and axes chosen as in Fig. 1.

Diagonalization of the SO terms in spin space is achieved using the following pseudospin operators:

$$c^{\dagger}_{i\alpha\mu} = \sum_{\eta} [\sigma_{\alpha}]_{\mu,\eta} d^{\dagger}_{i\alpha\eta}, \tag{5}$$

for $\alpha = x, y, z$ and $c^{\dagger}_{i\alpha\mu} = d^{\dagger}_{i\alpha\mu}$ for $\alpha = 0, 1$. Using this labeling and writing $L^{\mu}_{\alpha,\beta}$ explicitly for the above d states, one finds that the SO interaction is independent of the pseudospin μ. Thus when $\mathbf{K} = 0$, $\mathcal{H}$ becomes

$$\mathcal{H} = \sum_{i,\alpha,\mu} E_{i\alpha} c^{\dagger}_{i\alpha\mu} c_{i\alpha\mu} + \lambda \sum_{i,\alpha,\beta,\mu} W_i(\alpha,\beta) c^{\dagger}_{i\alpha\mu} c_{i\beta\mu} + \sum_{\alpha,\beta,\mu,i<j} t_{i\alpha,j\beta} (c^{\dagger}_{i\alpha\mu} c_{j\beta\mu} + c^{\dagger}_{j\beta\mu} c_{i\alpha\mu}) + \frac{1}{2} \sum_{i,\alpha,\alpha',\mu,\mu'} U_{i\alpha,i\alpha'} c^{\dagger}_{i\alpha\mu} c^{\dagger}_{i\alpha'\mu'} c_{i\alpha'\mu'} c_{i\alpha\mu}, \tag{6}$$

where W contains combinations of the w's. For a nn bond in tetragonal symmetry, $t_{i\alpha,j\beta} = \bar{t}_{\alpha,\beta}$ only connects states of the same symmetry, i.e., it is diagonal except for $\bar{t}_{1,0} = \bar{t}_{0,1}$. Consequently, the transformation to pseudospin does not change the form of the hopping term. We see that $\mathcal{H}$ is a function of the quantities $\sum_{\mu} c^{\dagger}_{i\alpha\mu} c_{j\beta\mu}$, which are rotationally invariant in pseudospin space. Therefore $\mathcal{H}$ is also rotationally invariant in the same space. Since spin and pseudospin are identical in the ground state $|0\rangle$ of all sites, $\mathcal{H}_M$ will be rotationally invariant in the unrotated spin space. In particular, the initially fourfold degenerate ground state of a pair of nn ions will split into a singlet and a triplet, and $\mathcal{H}_M(i,j)$ will be isotropic [13]. Note that this proof applies to all orders in perturbation theory in both t and λ. It thus represents a decisive advance in our understanding of the spin symmetry.

In fact, an essential assumption for our proof was that there be no hopping between states with different symmetries (which would imply hopping between different values of μ). Although this assumption clearly applies for nn hopping in tetragonal symmetry, it may break down for further neighbor hopping. We therefore restrict the following discussions to nn hopping. For that case, there will be no anisotropy without *both* exchange and SO interactions. With only the former the eigenstates of a single atom with two holes have total real spin 1 or 0. With no exchange but with SO interactions, these eigenstates have total pseudospin 1 or 0. In both cases, our numerical evaluation of the energy levels gave singlets and triplets as this argument requires. When both interactions are present, the degeneracies are removed, and $\mathcal{H}_M$ becomes anisotropic. To obtain the anisotropy analytically we carried out a calculation treating hopping, SO, and exchange interactions as perturbations. For tetragonal symmetry we found the leading contribution to anisotropic exchange to be of order $t^2\lambda^2 K$. Our result has the form of Eq. (2) with $J_{\mu} = J_0 + j_{\mu}$, where μ assumes the values $x = \|$, $y = \perp$, and z, and

$$j_{\mu} = -2\lambda^2 \left\{ \frac{|L^{\mu}_{0,\mu}|^2 \bar{t}^2_{0,1} K_{1,\mu}}{(E_{\mu} + E_1 + U_{1,\mu})^2} \left[\frac{1}{E_{\mu}} + \frac{1}{E_1 + U_{0,1}} \right]^2 + \frac{K_{0,\mu}}{(E_{\mu} + U_{0,\mu})^2} \left| \frac{(\bar{t}_{\mu,\mu} - \bar{t}_{0,0}) L^{\mu}_{0,\mu}}{E_{\mu}} + \frac{\bar{t}_{0,1} L^{\mu}_{1,\mu}}{E_1 + U_{0,1}} \right|^2 \right\}, \tag{7}$$

where the index i has been dropped from E, U, and K.

We checked this calculation against results (shown in Fig. 2) obtained from exact diagonalization for the four

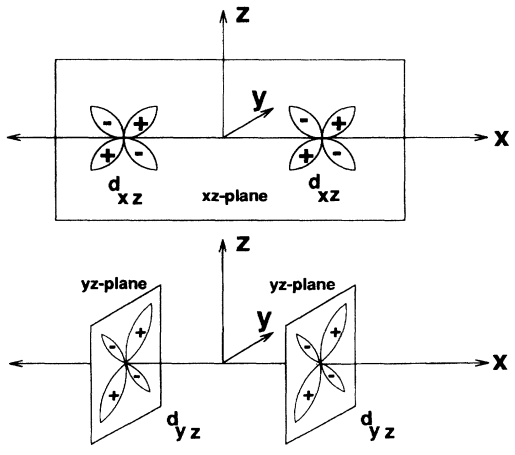

FIG. 1. Schematic view of d_{xz} and d_{yz} of two nn Cu ions on the x axis. While d_{xz} orbitals are in the same plane, those of d_{yz} orbitals are in parallel planes. Hence $\bar{t}_{x,x} \neq \bar{t}_{y,y}$.

lowest levels out of the 190 possible two-hole states for a cluster of 2 nn sites. In particular, by varying the parameters t, λ, and K, we verified the analytic result of Eq. (7) that $j_\mu \sim \lambda^2 t^2 K$. One sees that the perturbative results remain good approximations up to $t = 1$, $K = 1$, and $\lambda = 0.1$ eV. Note that within tetragonal symmetry we do recover the expected full anisotropy for a single bond, under which $J_\parallel$, $J_\perp$, and J_z are all different.

Will these results persist for the tetragonal cuprates, which also contain oxygens? Including all the $2p$ states on the oxygen ion, a pair of holes on the cluster Cu-O-Cu can have 325 states. We diagonalized the resulting Hamiltonian matrix numerically and confirmed isotropic exchange for $\mathbf{K} = 0$. To show this analytically, one introduces pseudospin on the oxygen $2p$ level just as in Eq. (5), where for an oxygen site on a bond along the x axis $|0\rangle$, $|y\rangle$, and $|z\rangle$ denote p_x, p_z, and p_y orbitals, respectively. Then, for $\mathbf{K} = 0$, one again obtains a Hamiltonian of the form of Eq. (6), leading to a rotationally invariant $\mathcal{H}_M$. When we include the exchange interactions, the leading contribution to the anisotropy is of order $t^4\lambda^2 K$. In fact, if one assumes no Coulomb exchange on the oxygens, then the analytic expressions of the perturbation theory at this order can be obtained from those given in Eq. (7) by redefining the effective hoppings

$$\bar{t}_{0,0} = t^2_{0,p_x}/E_{p_x}, \qquad \bar{t}_{0,1} = t_{o,p_x} t_{p_x,1}/E_{p_x}, \qquad \bar{t}_{x,x} = 0,$$
$$\bar{t}_{y,y} = t^2_{y,p_z}/E_{p_z}, \qquad \bar{t}_{z,z} = t^2_{z,p_y}/E_{p_y}. \tag{8}$$

In our numerical estimates in Fig. 2 and below, we took $t_{0,p_x} = -\sqrt{3}\, t_{1,p_x} = \frac{\sqrt{3}}{2}(pd\sigma)$ and $t_{y,p_z} = t_{z,p_y} = pd\pi \approx -\frac{1}{2}(pd\sigma)$, where $pd\sigma \approx 1.5$ eV and $E_{p_x} = E_{p_y} = E_{p_z} = 3.25$ eV [14]. We also checked that the j_μ, shown in Fig. 2, agree within ~10% with those obtained from the full 325 state Hamiltonian for the Cu-O-Cu cluster.

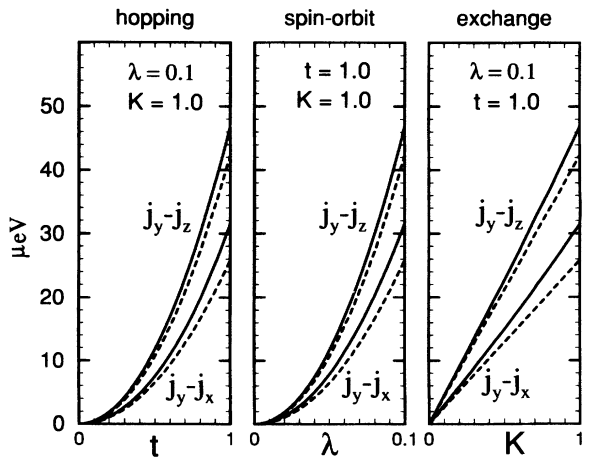

FIG. 2. A comparison of perturbation results in Eq. (7) (dotted line) with the exact diagonalization results (solid line). We took $E_1 = E_\mu \approx 1.8$ eV and estimated $\bar{t}_{\alpha,\beta}$ from Eq. (8) and after. In the left and right panel $\bar{t}_{\alpha,\beta}$ and $K_{\alpha,\beta}$ are replaced by $t\bar{t}_{\alpha,\beta}$ and $KK_{\alpha,\beta}$, respectively. $U_{\alpha,\beta}$ and $K_{\alpha,\beta}$ are given in Table I of Ref. [14]. The values of λ (in eV), t, and K are given in the panels.

We now compare these anisotropies with experiments, taking the experimental value [10], $J_{\rm av} \equiv (J_z + J_\perp + J_\parallel)/3 = 130$ meV for the isotropic part of the exchange. The out-of-plane anisotropy $\alpha_{XY} = \Delta J/J_{\rm av}$ is positive (see Fig. 2) and therefore the spins order in that plane. Our parameters ($K = 1$, $t = 1$, and $\lambda = 0.1$eV) yield $\Delta J = 0.03$ meV and $\alpha_{XY} \approx 2.3 \times 10^{-4}$, and thus the out-of-plane gap $\hbar\omega_{\rm out} = 4SJ_{\rm av}\sqrt{2\alpha_{XY}} = 5.6$ meV. Taking account of quantum fluctuations would increase this value [10], perhaps by the order of 15%, but in any event it is in reasonable agreement with the experimental [10] value 5 meV, particularly in view of the uncertainty in the parameters we used. Given Eq. (7) for single bonds, the classical ground state of Eq. (2) is rotationally invariant in the basal plane. Thus, in the absence of spin wave fluctuations, the in-plane gap is zero. However, this invariance is broken by the dependence of the spin-wave energies on the angle θ between the staggered magnetization and the crystal x axis [15,16]. The quantum zero-point energy of the spin waves was found [15] to select [17] a ground state with $\theta = 0$ or $\theta = \pi/2$, in agreement with some observed structures [15].

Although our analytic and numerical results for the anisotropies are in close agreement with each other, the use of perturbation theory to estimate the *isotropic* exchange, $J_{\rm av}$, is less satisfactory, as also observed by others [18]. For the generic model, perturbation theory is reliable because t/U is small. In contrast, when one adds the oxygens, the parameter t/E_p is sufficiently large to lead to disagreements between the lowest order perturbation results and those from the exact diagonalization of the 325 state Cu-O-Cu cluster. These disagreements arose due to terms which are of higher order in t/E_p. However, these terms contribute little to the anisotropies. Similar difficulties with perturbation theory were encountered by Eskes and Jefferson [18], who reproduced the experimental $J_{\rm av}$ by invoking hopping (of magnitude t_{pp}) between nn oxygen ions. To study the effect of t_{pp} on the exchange anisotropy, consider a Cu-O-Cu-O cluster, where the 2 oxygens are nn (on 2 perpendicular bonds). Within such a cluster, one would obtain an effective symmetry breaking hopping $\bar{t}_{0z}$ of order $t_{0,p_x} t_{pp} t_{z,p_y}/E_{p_x}E_{p_y}$. However, when summed over symmetry related clusters, such effective hoppings which break tetragonal symmetry (e.g., $\bar{t}_{0z}$) must vanish. Nevertheless, small contributions of higher order in t_{pp} may exist, which may not be represented by effective hoppings as in Eq. (8). In any case, we trust that the main contributions to the anisotropy comes from $\mathbf{K}$, as estimated above.

We now turn to the lower symmetry cases using the generic model of Eq. (3). For our numerical studies, we arbitrarily replaced the crystal field orbitals of each atom by an independent unitary transformation applied to those for tetragonal symmetry, thus obtaining new eigenstates of a two-site cluster having no special symmetry. We

then studied the energy splittings as functions of t and λ. In this low symmetry case, we found a complete removal of degeneracy, even when $\mathbf{K} = 0$. For the special case studied in Refs. [5,7–9], when $U_{\alpha,\beta} = U$ and $\mathbf{K} = 0$, these calculations show that the anisotropy first appears at order $t^6\lambda^2$. (This dependence on t can be understood analytically [16].) Thus the equivalence between Eqs. (4) and (3), and therefore also the hidden symmetry found in Ref. [6], break down at this high order.

More generally, when $U_{\alpha,\beta} = U + \Delta U_{\alpha,\beta}$ depends on its indices, both our numerical and analytical results show that the degeneracy is broken at order $t^2\lambda^2\Delta U$ even when $K = 0$. The importance of keeping track of different $U_{\alpha,\beta}$'s was not apparent in Moriya's paper, which had only one parameter U. Nor was this point addressed in later papers. We have generalized Moriya's results in this respect, and up to order $t^2\lambda^2\Delta U/U^2$ or $t^2\lambda^2 K/U^2$ we find the single bond spin Hamiltonian as

$$\mathcal{H}_M = J\mathbf{S}_1 \cdot \mathbf{S}_2 + \mathbf{D} \cdot (\mathbf{S}_1 \times \mathbf{S}_2) + \mathbf{S}_1 M \mathbf{S}_2 - \tfrac{1}{2}\,\mathrm{tr}(M)\mathbf{S}_1 \cdot \mathbf{S}_2, \qquad (9)$$

where explicit expressions for J, $\mathbf{D}$, and the tensor M are given in Ref. [16]. Here we emphasize the difference between our results and those found in Refs. [6,7], based on Eq. (4). The hidden symmetry in Eq. (4) implied that the tensor M can be written as $\mathbf{D} \otimes \mathbf{D}/2J$ and allowed the transformation of $\mathcal{H}_M$ to a rotationally invariant form. This is no longer true when one uses the full Eq. (3), with nonzero $\Delta U_{\alpha,\beta}$ and K.

Adding oxygens between copper atoms yields two intermediate channels at order t^4: one in which two holes are on the same copper site and one in which two holes are on the same oxygen site. The first channel can be represented by the expressions obtained from the generic model by redefining hopping integrals, as done in Eq. (8). This yields expressions which are similar to Eq. (9), requiring nonzero ΔU or K to yield anisotropy at order $\bar{t}^2$. The second channel does not have such analogies. This channel was not important for the tetragonal case without Coulomb exchange on the oxygen, because in that case this channel does not contribute to Eq. (7). In the general case, if the on-site Coulomb repulsion on the oxygen is not very large, then this channel may generate anistropy even when $\Delta U = K = 0$ [19].

In summary, we list our main conclusions

(1) For tetragonal site symmetry, without Coulomb exchange, the effective spin Hamiltonian is isotropic at any order in the parameters t and λ. Inclusion of exchange breaks this degeneracy at order $t^2\lambda^2 K$ for our generic model and at order $t^4\lambda^2 K$ for the cuprate system with an oxygen between the copper atoms.

(2) Equation (7) yields an out of plane spin anisotropy which may explain the related spin wave gap observed [10] in many cuprates (both tetragonal and orthorhombic).

(3) For sufficiently low symmetry and without exchange interactions, the rotational invariance of the single bond Hamiltonian is broken at order $t^6\lambda^2$ for $U_{\alpha,\beta} = U$. Thus, results obtained from Eq. (4), including the hidden symmetry discovered by Shekhtman *et al.* [6] are not valid at such high orders.

(4) For arbitrary $U_{\alpha,\beta}$ and K and sufficiently low symmetry, the single bond Hamiltonian is not rotationally invariant even at order $t^2\lambda^2$, in contrast to the case $U_{\alpha,\beta} = U$ and $K = 0$.

We acknowledge stimulating discussions with R. J. Birgeneau and M. A. Kastner. Work at the University of Pennsylvania was partly supported by the National Science Foundation MRL Program under Grant No. DMR-91-22784 and at Tel Aviv by the U.S.-Israel Binational Science Foundation.

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[12] One also has such interactions between electrons on different sites. For $\lambda \neq 0$, such "direct exchange" (DE) terms [3,4] generate anisotropy in $\mathcal{H}_M$ even without hopping (i.e., for $\mathbf{t} = 0$). In the cuprates nn copper ions are separated by an oxygen ion which tends to inhibit such DE interactions. Since our numerical work indicates that the DE effects can be subsumed in on-site Coulomb exchange when $\mathbf{t} \neq 0$, we do not consider them further.
[13] When this manifold is split into a singlet and a triplet, then it is possible to rotate coordinates (possibly differently) on the two sites so that in terms of the *rotated* spins, $\mathbf{S}'$, one has the isotropic form $\mathcal{H}_M = J\mathbf{S}'(i) \cdot \mathbf{S}'(j)$. The necessary rotation can be deduced by studying the triplet eigenfunctions. A further splitting of the triplet energy implies anisotropy. In our numerical work we used these splittings to deduce the values of the anisotropies.
[14] The parameters for $\mathbf{U} = (\mathbf{U}^t + \mathbf{U}^s)/2$, $\mathbf{K} = (\mathbf{U}^s - \mathbf{U}^t)/2$ (t and s stand for triplet and singlet), and Eq. (8) are those given by H. Eskes *et al.*, Phys. Rev. B **44**, 9656 (1991). λ is the same as used in Refs. [5–9,11].
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