New superexchange paths due to breathing-enhanced hopping in corner-sharing cuprates

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We present ab initio calculations of the superexchange antiferromagnetic spin coupling \( J \) for two cuprates, \( \text{Sr}_2\text{CuO}_3 \) and \( \text{La}_2\text{CuO}_4 \). Good agreement with experimental estimates is obtained. We find that \( J \) increases substantially as the distance between Cu and apical O is increased. There is an important synergetic effect of the Coulomb interaction, expanding the Cu 3d orbital when an electron hops into this orbital, and the O-Cu hopping, being increased by this orbital expansion (breathing).

This is a new ingredient in superexchange models. In a model with a fixed basis, breathing effects can be described as a mixing of 3d and 4d orbitals or as a single 3d → 4d excitation.

Cuprates with corner-sharing CuO\(_4\) plaquettes have received much attention due to discoveries of high-temperature superconductivity [1] and exotic states where spin and charge [2] or spin and orbital [3] degrees of freedom are separated. In these systems spins are coupled antiferromagnetically (AF), and it is believed that spin fluctuations play an important role. The strength of the AF coupling can be characterized by the nearest-neighbor (NN) coupling \( J \), which enters in, e.g., the Heisenberg model for undoped systems and the t–J model for doped systems [4]. Experimentally, the magnitude of \( J \) varies strongly between different cuprates, typically in the range 0.12–0.25 eV [3, 5–8].

This variation has been assigned to the dimensionality of the CuO network [9] and to the distance \( d_{\text{CuO}} \) between Cu and apical O [9, 10]. Our \textit{ab initio} calculations show that an increase of \( d_{\text{CuO}} \) leads to substantially larger \( J \). Recent experimental work indeed finds such an increase [11].

The AF coupling in these compounds occurs via superexchange [12, 13]. This involves the (virtual) electron hopping between the Cu 3d and O 2p orbitals. Antiparallel spins on neighboring Cu atoms allow for more hopping possibilities than parallel spins, leading to an AF coupling [14, 15]. While the superexchange is well understood on the model level, the \textit{ab initio} calculation of \( J \) is a major problem. For instance, calculations in a minimum through physically plausible basis set underestimate \( J \) by almost an order of magnitude. This is therefore a long-standing problem in the \textit{ab initio} community [16–19].

We use wavefunction-based methods [20] relying on full configuration interaction quantum Monte Carlo (FCIQMC) [21, 22] and density-matrix renormalization group (DMRG) [23, 24] as underlying solvers and restrict the calculations to the NN \( J \). An exact calculation within our model would involve correlating \( \approx 100 \) electrons among \( \approx 300 \) orbitals, leading to a eigenvalue problem in a Hilbert space of \( 10^{135} \) determinants. Since problems on such a scale are out of reach, we use the method of complete-active-space-self-consistent-field (CASSCF) together with multi-reference perturbation theories to systematically approximate the correlation energy [25]. In the CASSCF(\( n,m \)) approach, a subset \( n \) of the electrons (the active electrons) are fully correlated among an active set of \( m \) orbitals, leading to a highly multi-configurational (CAS) reference wavefunction. The choice of the active space will be discussed shortly, but let us note that although this is still an exponential-scaling problem, it is manageable with the aforementioned techniques as long as \( n \) and \( m \) are not too large. In the SCF step, all orbitals are self-consistently optimised in the field of the multi-determinant wavefunction (WF), to yield the variational minimum. The CAS WF is then augmented using a number of second-order techniques, including n-electron perturbation theory (NEVPT2) [26, 27], multi-reference linearized coupled cluster (MR-LCC2) [27, 28], or multireference configuration interaction with single and double excitations (MR-CISD) [20]; these methods capture the remaining (weak) correlation involving electrons and orbitals outside of the active space. We use these different second order methods as a gauge of their reliability. As the active space is enlarged, the corresponding second-order corrections diminishes. The key question that arises is: what is the “minimal” active space necessary to obtain a qualitatively correct reference wavefunction, sufficient to compute \( J \) reliably? We find that the necessary active space needs to be far larger than previously imagined, including relatively high energy Cu 4d and O 3p orbitals. Exclusion of these states from the active spaces leads a dramatic underestimation of \( J \).

We analyze the reason for the strong dependence of \( J \) on the active space and, in particular, the importance of 4d orbitals. As mentioned above, the superexchange mechanism depends on O-Cu hopping. The Coulomb energy cost \( U_{\text{eff}} \) of this hopping is strongly reduced by an expansion of the Cu 3d orbitals, referred to as breathing [29], when an electron hops into a Cu 3d orbital. This breathing effect at the same time increases the Cu-O ef-
fective hopping integral $t_{\text{eff}}$ [30]. In a similar way the O 2p orbital breathes as the O occupancy is changed. In the superexchange mechanism, $J$ depends on both $U_{\text{eff}}$ and $t_{\text{eff}}$ [15] and the breathing effects therefore strongly influence $J$. In a Hilbert space constructed with orthogonal orbitals, the breathing effect is described by the formation of linear combinations of, e.g., 3d and 4d orbitals, showing up as an increased occupancy of the 4d orbitals.

The breathing effects involve a single 3d → 4d excitation, leading to an expansion of the charge density when an electron is added to the d shell. There are also important double 3d → 4d excitations, which provide radial (in-out) correlations [20]. For a fixed number of d electrons, these correlations lead to a contraction of the charge density, at least if the basis has sufficient flexibility to satisfy the virial theorem. Correlation and breathing compete, making the simultaneous description complicated. Both effects lead to the occupancy of 4d orbitals, but are otherwise very different.

To study the electronic structure of cuprates we employ the embedded cluster model. With this approach accurate high-level calculation is performed for a small representative unit of the solid, while its environment is treated in a more approximate manner [31]. We use clusters that include two CuO$_4$ (CuO$_6$) units, two (ten) neighboring Cu$^{2+}$ ions and all adjacent Sr$^{2+}$ (La$^{3+}$) ions, in total [Cu$_2$O$_2$Sr$_{16}$] and [Cu$_9$O$_{11}$La$_{16}$] for Sr$_2$CuO$_3$ and La$_2$CuO$_4$ respectively. The rest of the solid is modeled by an array of point charges fitted to reproduce the Madelung potential in the cluster region [32–34]. We employed the crystal structures as reported in Refs. [35] and [36]. The value of the NN superexchange parameter can be easily extracted by mapping the energy spectrum of the two-magnetic-site cluster to two-site Heisenberg model. To make this mapping straightforward, the peripheral Cu ions are represented by total-ion potentials with no associated electrons, such that $J$ can be extracted as the energy difference of lowest triplet and singlet states [31]. We use all electron cc-pVDZ and cc-pVTZ basis sets for central Cu and O ions [37, 38], large-core effective potentials for other species [39–41] and utilize several quantum chemistry computational packages [42–46], see supplementary material for more details [15].

We first perform CASSCF calculation with two singly occupied Cu 3d$_{x^2-y^2}$ orbitals in the active-space, CASSCF(2,2) similar to the one-band Hubbard model. Such minimal active-space calculation accounts for the unscreened Anderson superexchange mechanism ($d^9$ – $d^9$ and $d^8$ – $d^{10}$ configurations) and gives a qualitatively correct AF $J$ coupling. The value of the $J$ obtained this way is, however, only $\approx 20\%$ as compare to the experimental data [3, 5–7], see Table I. As it can be seen, the second order corrections nearly double $J$, but are clearly an insufficient treatment. Such uniform behavior of the different dynamical correlation methods suggests that the reference CASSCF calculation is inadequate to qualitatively describe the system, and that the active space has to be enlarged. The only exception is the difference-dedicated configuration interaction (DDCI) method that gives values of $J$ very close to experiment on top of CASSCF(2,2) reference [17, 47]. However, the DDCI is essentially a subspace of the MRCI-SD, and significant differences of $J$ calculated by these two methods imply that the description of electronic structure given by DDCI is far from being complete.

Because an electron hopping from the bridging O $\sigma$-bonding 2p$_y$ orbital to the Cu 3d$_{x^2-y^2}$ plays a crucial role in the superexchange (see, e.g., Ref. 14), this orbital is an obvious candidate to add into the active space. Such CASSCF(4,3) calculation roughly corresponds to an unscreened 3-band Hubbard model. However, the obtained magnetic couplings turn out to be less than 1 meV higher compared to CASSCF(2,2). The reason is that, despite the inclusion of important ligand-hole determinants ($d^9$–$p^5$–$d^{10}$ and $d^{10}$–$p^4$–$d^{10}$), their energy is too high to be effective, as the orbital optimization is primarily driven by the dominant $d^9$–$p^6$–$d^9$ configuration [16, 18, 48]. When we include the effect of further excited determinants at 2nd-order level on top of the CASSCF(4,3) WF, $J$ becomes significantly larger, 105 eV using MR-CISD for the Sr$_2$CuO$_3$ compound. It is still more than two times smaller than the experimental value, indicating that important details are still missing.

To give the WF flexibility for accounting the orbital relaxation in $d^9$–$p^6$–$d^{10}$ and $d^9$–$p^5$–$d^{10}$ determinants, one

| TABLE I: Values of the superexchange parameters $J$ (in meV) obtained with different methods, see the text. |
|------------------------------------------------------|
| Sr$_2$CuO$_3$ | La$_2$CuO$_4$ |
| CASSCF(2,2) | +MR-LCC2 | +MR-CISD | +NEVPT2 | +DDCI | 249 | 253 | 241 | 151 | 145 | 260 | 249 |
| Sr$_2$CuO$_3$ | cc-pVDZ | cc-pVTZ | cc-pVTZ | cc-pVDZ | 37 | 35 | 60 | 52 | 67 | 246 | 253 |
| +MR-LCC2 | 57 | 52 | 45 | 39 | 59 |
| +MR-CISD | 57 | 52 | 60 | 59 |
| +NEVPT2 | 67 | 78 | 67 | 67 |
| +DDCI | 246 | 274 | 246 | 246 |
| CASSCF(4,3) | +MR-LCC2 | +MR-CISD | +NEVPT2 | +CASPT2 | 70 | 151 | 145 | 260 | 70 | 151 | 145 | 260 | 70 | 151 | 145 | 260 |
| Sr$_2$CuO$_3$ | 39 | 38 | 70 | 69 | 70 | 112 | 107 |
| +MR-LCC2 | 151 | 148 | 145 | 143 | 145 | 143 | 143 |
| +MR-CISD | 153 | – | – | – | 153 | – | – |
| +NEVPT2 | 145 | 143 | 145 | 143 | 145 | 143 | 143 |
| +CASPT2 | 260 | 205 | 260 | 205 | 260 | 205 | 205 |
| CASSCF(8,10) | +MR-LCC2 | +MR-CISD | +NEVPT2 | +CASPT2 | 70 | 151 | 145 | 260 | 70 | 151 | 145 | 260 | 70 | 151 | 145 | 260 |
| Sr$_2$CuO$_3$ | 39 | 38 | 70 | 69 | 70 | 112 | 107 |
| +MR-LCC2 | 151 | 148 | 145 | 143 | 145 | 143 | 143 |
| +MR-CISD | 153 | – | – | – | 153 | – | – |
| +NEVPT2 | 145 | 143 | 145 | 143 | 145 | 143 | 143 |
| +CASPT2 | 260 | 205 | 260 | 205 | 260 | 205 | 205 |
| CASSCF(24,26) | +MR-LCC2 | +MR-CISD | +NEVPT2 | +CASPT2 | 125 | 252 | 253 | 256 | 253 | 256 | 256 |
| Sr$_2$CuO$_3$ | 116 | 145 | 262 | 148 | 253 | 145 | 145 |
| +MR-LCC2 | 252 | 256 | 253 | 256 | 253 | 256 | 256 |
| +MR-CISD | 252 | 256 | 253 | 256 | 253 | 256 | 256 |
| +NEVPT2 | 253 | 262 | 253 | 262 | 253 | 262 | 262 |
| +CASPT2 | 253 | 262 | 253 | 262 | 253 | 262 | 262 |

$^a$ Ref. 18, calculations performed with different clusters and basis sets.
The additional many-body contribution from the Cu and FCIQMC as approximate solvers [15, 24, 51]. With perturbation theory [18]. But our calculations give 60 and 80% of the experimental values for the Sr and La cuprates respectively. To get the balanced description of all relevant effects we add all copper 3d and 4d together with the bridging oxygen 2p3 and 3p orbitals, resulting in CASSCF(24,26). This active space yields diagonalization problem in the space of \( \approx 10^{14} \) Slater determinants and is not feasible with conventional diagonalization methods, therefore we have to proceed with DMRG and FCIQMC as approximate solvers [15, 24, 51]. With the additional many-body contribution from the Cu 1s9 and \( \pi \)-bonding O orbitals taken into account in the large CASSCF we find further stabilization of the singlet compared to the triplet. Second order correction on top of the CASSCF(24,26) reference finally brings \( J \) close to the experimental values, see the last block in Table I. Orbitals as optimized in the variational calculation are shown in Figure 1. One can notice that both 3d and 4d orbitals have significant amplitudes at the bridging oxygen p orbitals.

In the standard theory [12, 13] of superexchange, a model of Cu2O is treated, with one nondegenerate orbital on each atom. As discussed above, including only these orbitals in CASSCF(4,3) underestimates \( J \) by almost one order of magnitude. We now discuss why it is necessary to consider the large active space.

In calculations for the singlet and triplet states, the configuration \( d^{10}-p^{6}-d^{9} \) dominates, and correlation effects in this configuration are very important for the total energy. However, the contributions for the singlet and triplet states are similar and therefore not very important for \( J \). In superexchange theory, hopping of electrons between Cu and O plays a crucial role, involving, e.g., \( d^8-d^{10} \) determinants in addition to the nominal \( d^9-d^9 \). There are more configurations of this type available for the singlet than the triplet state. Although these configurations have rather small weights, they are crucial for \( J \). These configurations are indicated in the supplementary material [15].

The on-site Coulomb integral between two 3d electrons is very large (\( \approx 28 \text{ eV} \) [52]), leading to drastically suppressed charge fluctuations in the simplest model. This is the reason the CASSCF(2,2) and CASSCF(4,3) give a very small \( J \). However, by increasing the active space size, this energy cost can be strongly reduced. Crucial effects are the change of the effective radial extent of the 3d orbital (breathing) and rearrangements of the non-3d charge density as the number of 3d electrons varies (screening) [29], which are captured in the CASSCF(24,26) calculation with second-order correction.

In order to disentangle these different effects we performed a series of simpler constrained calculations [15, 53]. We put all hopping integrals from d (3d or 4d) basis functions on the Cu atoms equal to zero. We can then prescribe the total occupancy of d orbitals on each Cu atom. We performed two calculations, one with the configurations \( d^9-d^9 \) and one with \( d^8-d^{10} \). In both cases the system is allowed to fully relax, except that hopping to or from d orbitals is suppressed. We then obtain that the energy for the \( d^9-d^{10} \) state is about 12 eV higher than for \( d^8-d^9 \). This means that \( U \approx 28 \text{ eV} \) has been reduced to \( U_{\text{eff}} \approx 12 \text{ eV} \). According to other estimates, \( U_{\text{eff}} \) is reduced even further (\( \approx 8 \text{ eV} \) [54]).

Figure 2 shows charge differences due to breathing and screening for the \( d^8-d^{10} \) calculation, discussed above. A calculation was first performed for \( d^9-d^9 \), then a d electron was moved from one Cu atom to the.
other keeping all orbitals unchanged. The corresponding densities are denoted \( \rho_{d^8} \) and \( \rho_{d^{10}} \). This \( d^8 - d^{10} \) state was then allowed to relax self-consistently, giving the densities \( \rho_{d^8} \) and \( \rho_{d^{10}} \). The full red curve shows the change in charge density \( \rho_{d^{10}} - \rho_{d^{8}} \), illustrating how charge is moved from the inner part of Cu to the outer part (breathing). The red dashed curve shows a radial integral of the charge density difference. It shows that more charge is removed from the inner part than added to the outer part. Since the number of d-electrons is the same in the two calculations, non-d charge has been moved away from the Cu atom with the \( d^{10} \) configurations as a response to the addition of one d electron (screening). Adding a d electron to a Cu atom then only leads to an increase of the net charge by about half an electron, due to screening, which substantially reduces the energy cost.

As in can be seen in Table I, magnetic coupling in Sr\(_2\)CuO\(_3\) is nearly two times larger than in La\(_2\)CuO\(_4\). In both cases the computation of J is done using only two magnetic centers, therefore this difference should not be attributed to dimensionality of two materials. The other structural difference is the presence of apical oxygen ions in the La\(_2\)CuO\(_4\) that changes the local multiplet splittings, mainly the position of 3d\(_{z^2}\) levels [3, 55–57]. Relative energy of 3d\(_{z^2}\) orbital is believed to be connected to the shape of the Fermi surface and the value of the critical temperature in doped cuprates [58–61].

There are experimental evidences that J also changes depending on the local geometry [8]. However, because experimentally different compounds have to be used, local distortions are accompanied by changes of Cu–O distances and type of adjacent metal ions. Therefore it is instructive to investigate the dependence of J on the distance to apical oxygen ions in La\(_2\)CuO\(_4\) compound with accurate computational method. We varied the apical O’s positions within the cluster keeping the electrostatic potential untouched and compute magnetic couplings using the procedure described above. The results of these calculations are presented in Figure 3. It can be seen that with increase of the distance to apical oxygen the NN J grows. It shows that the growth is faster with more electron correlation is taken into account. One obvious effect that leads to increase of J is the lowering of the 4d\(_{z^2}\) orbital energy and corresponding enhancement the orbital breathing: we observe 13% growth of the occupation of 4d\(_{z^2}\) orbitals upon 0.8 Å displacement of apical oxygens at the CASSCF(24,26) level. Recent experimental results for J in thin films is in good agreement with our calculations [11].

In this letter we presented state-of-the are \textit{ab initio} calculations of the NN magnetic coupling in cuprate compounds. We find that orbital breathing involving Cu 4d orbitals is essential to properly describe magnetism in these materials. We find that a synergistic coupling between orbital breathing and enhanced hopping lead to the observed J. This mechanism also leads to a strong dependence of J on the distance to apical oxygen ions, where a 30% increase of the coupling occurs under 30% elongation of the Cu–O distance. More generally, breathing-enhanced hopping may be expected to play an important role in generating longer range hopping and exchange interactions, beyond nearest neighbors. Significant long range hopping would provide a mechanism to generate frustration on the square lattice, and in the doped cuprates may be relevant in the mechanism leading to superconductivity. These questions are left for a future study.

![FIG. 2: Electron density difference due to orbital relaxation in the d\(^8\) – d\(^{10}\) configuration. (a) In the plane of Cu\(_4\) plaquettes; (b) integrated over a sphere centered on one of the Cu atoms (full curves) as a function of the radius as shown in (a). The results of an additional radial integration are shown by the dashed curves as a function of the upper integration limit.](image1)

![FIG. 3: Dependence of J on the distance to apical oxygens in La\(_2\)CuO\(_4\).](image2)
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SUPPLEMENTARY MATERIAL

DETAILS OF CALCULATIONS

For small CASSCF calculations up to (8,10) active space were done with MOLCAS, MOLPRO and PySCF programs [43–45]. Results by different codes are fully consistent, differences of total energies were not more than $10^{-6}$ Hartree. All NEVPT2 and MR-LCC2 calculations were carried out with IC-MPS-PT and BLOCK programs [23, 27]. MRCl-SD calculations were done with MOLCAS driver [43, 46]. CASPT2 calculations were performed with MOLCAS 8 [43]. DDCI calculations were done with MRCI module of MOLPRO [45]. Large CASSCF(24,26) calculations were carried out with CASSCF module of MOLCAS using NECI as a solver [42, 43, 51] and independently with PySCF using BLOCK as a solver [23, 44].

Data shown in Fig. 2 was obtained in constrained calculations using generalized active space SCF (GASSCF) method as implemented in MOLCAS [43, 53]. We split atomic-like orbitals in three groups: all d orbitals at the first copper ion (15 in cc-pVDZ basis), all d orbitals at the second copper ion (15), and the rest. Any orbital rotation between these groups are forbidden via supersymmetry constrain. With GASSCF we specify two disconnected active spaces, e.g., (8,5) and (10,5) for the first and the second Cu ion respectively. This way we can fix occupation of d orbitals at each site and perform all the possible remaining optimizations.

Clusters used in calculations are shown in Fig. S2 and Fig. S3, both belong to the D_{2h} point group. In calculations with MOLCAS, NECI, COLUMBUS, PySCF, and BLOCK were done within the full point-group symmetry. Irreducible-representation composition of active orbitals reads CAS(2,2): [1a_g, 1b_2u]; CAS(4,3): [1a_g, 2b_2u]; CAS(8,10): [4a_g, 6b_2u]; CAS(24,26): [4a_g, 2b_1g, 2b_2g, 2b_3g, 2a_u, 4b_1u, 6b_2u, 4b_3u]. In our setting the Cu-O-Cu link is along the y direction. Due to technical limitations calculations with MOLPRO were done within the C_1 point group.

All NEVPT2, MR-LCC2, and MRCl calculations were done correlating all Cu d and O p electrons, which is in total 60 and 84 electrons for Sr_2CuO_3 and La_2CuO_4 respectively.

To illustrate better the constrained GASSCF calculations presented in the main text we show in Fig. S1 electron density differences between three states. We start with fully optimized d^9 state, then obtain (d^8 – d^10) state by moving an electron from one Cu site to the other keeping the orbitals untouched, and finally reach the d^8 – d^10 state after orbital relaxation that captures breathing and screening. One should notice that in both latter states multiplet effects at the d^8 site are taken into account by including all determinants that arise by distributing 8 electrons in five d orbitals into the WF expansion. This multiplet effects lead to $\approx 1$ eV reduction of the $U_{eff}$.

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FIG. S1: Electron density differences as obtained from constrained calculations for Sr_2CuO_3.

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All NEVPT2, MR-LCC2, and MRCl calculations were done correlating all Cu d and O p electrons, which is in total 60 and 84 electrons for Sr_2CuO_3 and La_2CuO_4 respectively.

To illustrate better the constrained GASSCF calculations presented in the main text we show in Fig. S1 electron density differences between three states. We start with fully optimized d^9 state, then obtain (d^8 – d^10) state by moving an electron from one Cu site to the other keeping the orbitals untouched, and finally reach the d^8 – d^10 state after orbital relaxation that captures breathing and screening. One should notice that in both latter states multiplet effects at the d^8 site are taken into account by including all determinants that arise by distributing 8 electrons in five d orbitals into the WF expansion. This multiplet effects lead to $\approx 1$ eV reduction of the $U_{eff}$.
Having discussed the breathing effect, we first consider a free atom, setting $t_{11} = t_{12} = t_{21} = t_{22} = 0$ in Eq. 3.4. We put two electrons on one site and write down the wavefunction

$$
|\Phi\rangle = \left[ a_{11} c_{11\uparrow}^\dagger c_{11\downarrow}^\dagger + a_{12} \left( c_{11\uparrow}^\dagger c_{12\downarrow}^\dagger + c_{12\uparrow}^\dagger c_{11\downarrow}^\dagger \right) + a_{22} c_{12\uparrow}^\dagger c_{12\downarrow}^\dagger \right] |\text{vac}\rangle \tag{3.5}
$$

Apart from the last term, we have replaced the 3d orbital by an expanded orbital described by $c_{11\sigma}^\dagger$

$$
c_{11\sigma}^\dagger = \frac{1}{b} \left( \sqrt{a_{11}} c_{11\uparrow}^\dagger + \frac{a_{12}}{\sqrt{a_{11}}} c_{12\uparrow}^\dagger \right), \tag{3.5}
$$

where $b^2 = a_{11} + a_{12}^2/a_{11}$. The coefficients are shown in Table 3.1. The table illustrates that the last term in

**BREATHING IN A Cu$_2$ MODEL**

In this section we discuss breathing in a very simple Cu$_2$ model, with an effecting hopping directly between two Cu atoms rather than via bridging O. We show how the radial extent of the Cu 3d orbital is effectively increased in intermediate states with increased 3d occupancy. This has two important consequences. First, the effective energy cost of increasing the occupancy of 3d level is reduced, since the electrons can avoid each other better[29]. Second, the hopping between the two sites is enhanced, as the Cu 3d orbital expands[30].

In the CASSCF calculations in the main text, a fixed orthogonal basis set is used for all intermediate states. Therefore the breathing effect of a 3d orbital is then described as a mixing of the 3d and 4d orbitals. The system can then effectively expand or contract an effective 3d orbital, depending on the relative sign of the mixing. To illustrate how this happens we consider a Cu$_2$ dimer, including just one 3d and one 4d level on each atom, as indicated in Fig. 3.4. The levels have spin but no orbital degeneracy. We use the Hamiltonian

$$
H = \sum_{\sigma} \left[ \sum_{i=1}^{2} \sum_{j=1}^{2} \varepsilon_{ij} n_{ij\sigma} + \sum_{i=1}^{2} \sum_{j=1}^{2} t_{ij} \left( \phi_{i\sigma}^\dagger \phi_{j\sigma} + \phi_{j\sigma}^\dagger \phi_{i\sigma} \right) \right] + \sum_{i=1}^{2} \left[ U_{11} n_{i\uparrow} n_{i\downarrow} + U_{22} n_{i\uparrow} n_{i\downarrow} + U_{12} \sum_{\sigma\sigma'} n_{i\sigma} n_{i\sigma'} \right]
$$

Here the first index on $c_{ij\sigma}$ refers to the site and the second labels the orbital, i.e., $j = 1(2)$ refers to a 3d (4d) orbital. The hopping between the Cu atoms is described by $t_{12}$. We also include the direct on-site Coulomb integrals $U_{11}, U_{12}$, and $U_{22}$, describing 3d–3d, 3d–4d and 4d–4d interaction, respectively. $K_i$ refers to a Coulomb integral with three equal orbitals and the fourth different:

$$
K_i = e^2 \int d^3 r \int d^3 r' \frac{\phi_i(r)^2 \phi_i(r')}{|r-r'|}. \tag{3.2}
$$

These integrals are crucial for the breathing effect. If, e.g., the 3d orbital on an atom is doubly occupied, the last term in Eq. 3.1 can excite a single electron from the 3d orbital to the 4d orbital. For radial (in-out) correlation it is important to include terms where two 3d electrons are excited to the 4d level. Such terms are neglected here.

For simplicity, we here put $t_{12} = t_{21} = \sqrt{U_{11} U_{22}}$, $U_{12} = \sqrt{U_{11} U_{22}}$ and $K_1/K_2 = \sqrt{U_{11}/U_{22}}$. We have used $\varepsilon_2 - \varepsilon_1 = 24$ eV, $U_{11} = 13$ eV, $U_{22} = 10$ eV, $K_1 = -8$ eV, $t_{11} = -0.5$ eV and $t_{22} = -0.8$ eV.
We now turn to the full Cu$_2$ model. Table SII below shows the singlet-triplet splitting. It illustrates how the inclusion of the integral $K$ strongly increases the splitting, due to breathing effects. To understand the results better, we consider a simpler model within only three determinants for the singlet state.

Table SII: Coefficients of the wave function in Eq. (S3) for the isolated atom.

| $a_{11}$ | $a_{12}$ | $a_{22} - a_{12}^2/a_{11}$ |
|---------|---------|-----------------------------|
| 0.91    | 0.29    | -0.01                       |

Eq. (S3) is indeed very small, and the single-determinant with doubly-occupied extended orbital is an adequate description. The breathing lowers the energy cost of double occupancy and renormalizes the effective $U_{\text{eff}}$.

Dimer

We can now use Löwdin folding, focusing on the upper $2 \times 2$ corner of $(z - H)^{-1}$

\[
(z - H)^{-1} = \begin{pmatrix}
\varepsilon_1 & 2t_{11} & \varepsilon_2 + U_{12} \\
2t_{11} & 2\varepsilon_1 + U_{11} & \sqrt{2}t_{12} \\
\sqrt{2}t_{12} & \sqrt{2}K_1 & \varepsilon_1 + \varepsilon_2 + U_{12}
\end{pmatrix}^{-1}
\]

(S7)

where $\Delta E = \varepsilon_2 - \varepsilon_1 + U_{12}$ and we have introduced the approximation $z \approx 2\varepsilon_1$ at some places. The matrix in Eq. (S7) shows rather clearly that there is an interference between breathing and hopping from the 3d orbital on one site to the 4d orbital on the other site. The effective value of $U$ has now been reduced

\[
U_{11} \rightarrow U_{11}^{\text{eff}} = U_{11} - 2\frac{K_1^2}{\Delta E}
\]

(S8)

and the effective hopping has been increased

\[
t_{11} \rightarrow t_{11}^{\text{eff}} = t_{11} - 2\frac{t_{12}K_1}{\Delta E},
\]

(S9)

since $K_1 < 0$ and $t_{11}$ and $t_{12}$ have the same sign. For the triplet case the basis state (2) does not exist, and these renormalization effects are not present. The singlet-triplet splitting is then

\[
E_T - E_S \approx \frac{4(t_{11} - t_{12}K_1/\Delta E)^2}{U_{11} - 2K_1^2/\Delta E} = 4\left(\frac{t_{11}^{\text{eff}}}{U_{11}^{\text{eff}}}\right)^2.
\]

(S10)

This illustrates the importance of the renormalization of $U_{11}$ and $t_{11}$.

Table SIII: Triplet-singlet splitting without ($K_1 = 0$) and with breathing. All values in eV.

| $K_1$ exact, Eq. (S1) | Eq. (S6) |
|-----------------------|---------|
| 0                     | 0.073   |
| -8                    | 0.176   | 0.167   |

FIG. S4: Schematic representation of the Cu$_2$ dimer with 3d and 4d levels.

We can now use Löwdin folding, focusing on the upper $2 \times 2$ corner of $(z - H)^{-1}$

\[
(z - H)^{-1} = \begin{pmatrix}
\varepsilon_1 & 2t_{11} & \varepsilon_2 + U_{12} \\
2t_{11} & 2\varepsilon_1 + U_{11} & \sqrt{2}t_{12} \\
\sqrt{2}t_{12} & \sqrt{2}K_1 & \varepsilon_1 + \varepsilon_2 + U_{12}
\end{pmatrix}^{-1}
\]

(S7)

where $\Delta E = \varepsilon_2 - \varepsilon_1 + U_{12}$ and we have introduced the approximation $z \approx 2\varepsilon_1$ at some places. The matrix in Eq. (S7) shows rather clearly that there is an interference between breathing and hopping from the 3d orbital on one site to the 4d orbital on the other site. The effective value of $U$ has now been reduced

\[
U_{11} \rightarrow U_{11}^{\text{eff}} = U_{11} - 2\frac{K_1^2}{\Delta E}
\]

(S8)

and the effective hopping has been increased

\[
t_{11} \rightarrow t_{11}^{\text{eff}} = t_{11} - 2\frac{t_{12}K_1}{\Delta E},
\]

(S9)

since $K_1 < 0$ and $t_{11}$ and $t_{12}$ have the same sign. For the triplet case the basis state (2) does not exist, and these renormalization effects are not present. The singlet-triplet splitting is then

\[
E_T - E_S \approx \frac{4(t_{11} - t_{12}K_1/\Delta E)^2}{U_{11} - 2K_1^2/\Delta E} = 4\left(\frac{t_{11}^{\text{eff}}}{U_{11}^{\text{eff}}}\right)^2.
\]

(S10)

This illustrates the importance of the renormalization of $U_{11}$ and $t_{11}$.

Table SIII: Triplet-singlet splitting without ($K_1 = 0$) and with breathing. All values in eV.

| $K_1$ exact, Eq. (S1) | Eq. (S6) |
|-----------------------|---------|
| 0                     | 0.073   |
| -8                    | 0.176   | 0.167   |

FIG. S5: Schematic representation of states in Eq. (S5) for the dimer model.

---

| $K_1$ exact, Eq. (S1) | Eq. (S6) |
|-----------------------|---------|
| 0                     | 0.073   |
| -8                    | 0.176   | 0.167   |
HOPPING FOR Cu$_2$O MODEL

Fig. S6 illustrate hopping possibilities for the singlet and triplet state in a Cu$_2$O model with nondegenerate levels on Cu (3d) and O (2p). For the triplet case the hopping possibilities are severely limited. In this model $J$ is given by

$$J = \frac{4t_{\text{eff}}^2}{(U_{\text{eff}} + \Delta)^2} \left( \frac{t^2}{U_{\text{eff}}} + \frac{t_{\text{eff}}^2}{U_{\text{eff}} + \Delta} \right), \quad (S11)$$

where $U$ is the 3d – 3d Coulomb integral, $t$ is the hopping from Cu 3d to O 2p and $\Delta$ is the energy difference between the Cu 3d orbital and the O 2p orbital. In a model with 4d orbitals on the Cu atoms, $t$ is renormalized to $t_{\text{eff}}$ and $U$ to $U_{\text{eff}}$.

FIG. S6: Schematic representation of the Cu$_2$O model with Cu 3d and O 2p levels. The O atom is the bridging atom. The upper (lower) part of the figure illustrate available configurations for the singlet (triplet) state.