The effect of electron correlation on the electronic structure and spin-lattice coupling of the high-\(T_c\) cuprates: quantum Monte Carlo calculations

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We present high fidelity first principles quantum Monte Carlo calculation of La\(_2\)CuO\(_4\), CaCuO\(_2\), and the isolated CuO\(_2\) plane. By increasing the level of accuracy over traditional electronic structure methods, it is possible to reproduce several important material properties from experiment, such as the spin coupling \(J\), the correlated gap, and the magnetic moment on the Cu atoms, without adjustable parameters. We further investigate the spin-lattice coupling in these materials, and find evidence that the cuprates have a strong coupling between spin and lattice, which is affected by the nominally inert interlayer. This result may imply that phonon and magnetism based pairing are not completely independent in these systems.

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The phenomenon of high temperature superconductivity in the copper oxides has been a decades long challenge to fully describe. The phase diagram is very complicated, with structural transitions, magnetic transitions, and metal-insulator transitions occurring in close proximity to one another. There are indications of strong coupling of electrons with some other degree of freedom\[1\] that may be magnetic or structural in origin, and there is a puzzling isotope effect at low doping\[2, 3\] that disappears around optimal doping. These indications of electron-phonon coupling\[4\] are seemingly in contradiction to the strong evidence for a magnetic origin for superconductivity summarized recently in Ref \[5\]. It is thus clear that spin, charge, and lattice degrees of freedom are active in the phase space near the superconducting state, but their precise roles are still controversial.

The interactions between spin and lattice are challenging to probe both experimentally and theoretically. Experimentally, most techniques can only probe one of these degrees of freedom directly, and the magnetic excitations and lattice degrees of freedom are near to one another, making it challenging to disentangle their effects on each other, although there has been notable progress in that area\[6\]. From the theoretical standpoint, accurately describing the electronic structure of the cuprates has been a tremendous challenge because of the strong effects of electron correlation present in these materials. Standard density functionals fail on a qualitative level\[7\], particularly in the insulating undoped system, requiring \textit{a posteriori} corrections\[8\] that rob the method of predictive power. It seems clear that the electron-phonon interactions calculated in DFT are not always reliable\[9, 10\]. It has been proposed that spin and lattice can act cooperatively to enhance superconductivity\[11\], which provides a compelling impetus to completely understand the magneto-structural coupling in the cuprates.

In this article, we present first-principles quantum Monte Carlo (QMC) calculations of several instances of the CuO\(_2\) plane present in the cuprates: the real materials La\(_2\)CuO\(_4\) and CaCuO\(_4\), and a hypothetical unsupported CuO\(_2\)\(^{2-}\) plane. Unlike density functional methods, the QMC calculations explicitly treat electron correlation within these strongly correlated materials, which allows us to make a clear assessment of the importance of this physics to the basic electronic structure. We examine the effect of explicit correlations on the spin-lattice coupling, which is relatively straightforward to evaluate in the QMC methodology, and focus on understanding the difference between the s-wave \(A_{1g}\) and d-wave \(B_{1g}\) oxygen buckling modes. The \(B_{1g}\) symmetry oxygen buckling mode has been studied closely in models\[4\] and experiment\[13-19\]. Experimentally, the

![Graph](image-url)
TABLE I: Validation of the first-principles FN-DMC calculation for La$_2$CuO$_4$. The B$_{1g}$ and A$_{1g}$ modes refer to the oxygen buckling modes in the tetragonal symmetry labeling. The hypothetical A$_{1g}$ mode used for comparison here is not an eigenmode of the dynamical matrix, and thus does not have an experimental value.

| Quantity                  | PBE | PBE0 | FN-DMC | Experiment |
|---------------------------|-----|------|--------|------------|
| J (eV)                    | 0.34| 0.16 | 0.16(13)| 0.14       |
| Mag moment of Cu (Bohr)   | 0.36| 0.69 | 0.6    | 0.6        |
| Quasiparticle gap (eV)    | 0.33| 3.86 | 2.0(3) | 2.2        |
| AFM B$_{1g}$ freq (meV)   | 30  | 30   | 32(1)  | 33(12)     |
| FM B$_{1g}$ freq (meV)    | 24  | 25   | 25(1)  |            |
| AFM A$_{1g}$ freq (meV)   | 42.8| 45.1 | 45(1)  |            |
| FM A$_{1g}$ freq (meV)    | 39.9| 43.7 | 43(1)  |            |

*For consistency, we estimated the PBE J by forcing AFM and FM magnetic orders and taking the energy difference. PBE predicts an unpolarized state at lower energy than the FM state, so the implicit Heisenberg model does not technically apply in that case. PBE0 and FN-DMC do not suffer from this ambiguity.

FIG. 2: Comparison of the electronic structure of CaCuO$_2$ calculated by density functional theory in the PBE approximation to that calculated by fixed-node diffusion Monte Carlo.

B$_{1g}$ mode shifts and broadens on entering the superconducting state, while the closely related A$_{1g}$-symmetry oxygen buckling mode does not. Also, the B$_{2g}$ mode has also been implicated in dispersion kinks in ARPES.\cite{20} However, the closely related A$_{1g}$ mode does not seem to be strongly affected. A straightforward hybrid DFT calculation (Fig 1) shows that the B$_{1g}$ mode has a very large reaction to a change in the magnetic state, which could be an explanation for the shifts in mode; however, as we mentioned before, it is not clear that the DFT calculations are reliable in these materials. We find that in contrast to DFT calculations, state of the art QMC methods can accurately predict many properties of the cuprates, including the gap, magnetic coupling, and phonon frequencies. The A$_{1g}$ and B$_{1g}$ modes are differentiated in a rather prosaic way, through interaction with the interlayer.

We apply fixed-node diffusion Monte Carlo (FN-DMC) as implemented in the QWalk package\cite{21}. We start with one-particle orbitals from a density functional calculation from CRYSTAL2009\cite{22}, using pseudopotentials\cite{23–25}. A Slater determinant is then constructed from the one-particle orbitals and multiplied by a Jastrow correlation factor, which is variance optimized. Finally, the FN-DMC method is performed with the resulting Slater-Jastrow wave function as a guiding function. The general procedure is outlined in Refs \cite{20,25} and enough details to reproduce the results, including basis sets and pseudopotentials, are presented in the supplementary information. We checked that the magnetic energies did not change within error bars for increasing the cell either in the planar direction or in the c-axis direction. We thus believe that, while these results might change in a small quantitative way with larger simulation cells, the overall conclusions will not change. As we shall see later, the effects we are considering are order-of-magnitude in size, so small corrections due to finite size will not change the conclusions.

The results of the FN-DMC procedure in comparison to experiment and two common density functionals are summarized in Table I As one can see from the comparison table, even with the hybrid functional PBE0, the gap is overestimated significantly, while FN-DMC is able to describe the gap and the exchange coupling accurately, without any fitting. As has been noted before\cite{29}, the DFT-calculated frequency of the modes is in fairly good agreement with experiment. Our FN-DMC results are also able to reproduce the phonon frequencies quite accurately. However, in the PBE approximation, the buckling mode of CaCuO$_2$ is unstable\cite{30}. This is not the case in QMC or the hybrid PBE0.

In order to compare the many-body FN-DMC results to the DFT calculations, we evaluate the fluctuations of number operators $n_i^\sigma$ of a spin $\sigma$ and site $i$, on CaCuO$_2$. This operator is formed by, for a given configuration, counting the number of electrons of spin $\sigma$ within the Voronoi polyhedron around a given nucleus. The magnetic moment on an atom is given by $\langle n_i^\sigma - n_i^{-\sigma} \rangle$, for example. The FN-DMC and DFT largely agree on the charges of the atoms: Cu is +1.1, Ca +1.5, and oxygen -1.3. However, the theories differ in the fluctuations of the number of electrons on the atoms. In Fig 2 we report two fluctuation operators. The first is $\langle (n_i^\uparrow - n_i^\downarrow)^2 \rangle$, which represents the fluctuations in number of spin $\uparrow$ electrons. In the atomic limit, this quantity is equal to zero, and for a metallic system, this quantity is large. DFT overestimates this quantity for all atoms by a large amount for all atoms, meaning that it over-delocalizes the wave function.

We also evaluate the $\uparrow$ / $\downarrow$ covariance $\langle (n_i^\uparrow - n_i^\downarrow)(n_i^\downarrow - n_i^\uparrow) \rangle$
FIG. 3: (a) The curvature of the $A_{1g}$ and $B_{1g}$ oxygen buckling phonon modes as a function of the system. (b) The renormalized change in curvature upon entering the ferromagnetic spin ordering. Also shown is a comparison to the hopping model in Eqn [3]. (c) The calculated $J$ in the tetragonal unit cell for each of the three cuprates considered. Note that the isolated plane is significantly changed from the more realistic models, showing the change in $J$ due to the interlayer.

\[
\langle n_1^2 \rangle.
\]

For a system with a strong Hubbard-like term, one expects that this covariance will be strongly negative, while for a non-interacting system, this quantity is zero. As one might expect, the wave function formed from DFT orbitals generally underestimates the absolute value of this covariance. Surprisingly, the oxygen atom has a very strong on-site repulsion that is completely missed by the DFT wave function. One can approximately associate the same-spin variance with the hopping $t$, and the opposite spin covariance with the on-site repulsion $U$. In that association, we find that the DFT wave functions overestimate $t$ and underestimate $U$, particularly on the oxygen atom.

For the purposes of finding the magneto-elastic coupling, we calculate the Heisenberg superexchange parameter $J$ by comparing the electronic state constrained to have all copper moments spin-aligned (FM) to the spin-anti-aligned moments in the checkerboard pattern (AFM). For a given frozen phonon distortion $u$, we calculate the superexchange parameter

\[
J(u) \propto E_{FM}(u) - E_{AFM}(u).
\]

To check the validity of the Heisenberg model, we also calculated the energy of the mixed moment alignment (stripe) state, with aligned moments along the $a$ direction and anti-aligned moments along the $b$ direction. We found that $E_{FM}(u) - E_{AFM}(u) = 2(E_{stripes} - E_{AFM})$ in FN-DMC within error bars and in PBE0, justifying the use of the Heisenberg model. Two oxygen buckling modes are considered: $A_{1g}$ where all oxygen atoms move in phase, and $B_{1g}$, which has a $d$-wave alternating pattern of oxygen displacements. As mentioned above, the $B_{1g}$ mode has been implicated in a number of interesting phenomena in the cuprates. To assess the importance of the interlayer, we consider three different systems: $La_2CuO_4$ with apical oxygen atoms, $CaCuO_2$, which lacks apical oxygen atoms, and the isolated copper-oxide plane $CuO_2^-$. To assess the coupling calculated \textit{ab initio}, we compare to a simple model based on electron hopping. Following Ref [31], the hopping between oxygen and copper is given by

\[
t_{pd} = A_0 d^{\alpha_0} \cos^{\beta_0} \theta,
\]

where $\alpha_0 = 3$ or $3.5$, $\beta_0 = 1$, $d$ is the Cu-O bond length, and $\theta$ is the Cu-O-Cu bond angle. For direct comparison, we will write $d$ and $\theta$ in terms of the symmetric bond length $d_0 \simeq 1.6\,\text{Å}$ and the displacement of the oxygen atoms out of the plane $u$. $d^2 = d_0^2 + u^2$, and for small distortions, one can approximate $\cos \theta \simeq -1 + 2u^2/d_0^2$. Since $J \propto t_{pd}^4$, we obtain

\[
J(u) = J_0 d_0^{4\alpha_0} (d_0^2 + u^2)^{-2\alpha_0} \left( 1 - \frac{2u^2}{d_0^2} \right)^4
\]

where we fixed $J(0) = J_0$. Therefore, the curvature at $u = 0$ is given by $-4J_0(4 + \alpha_0)d_0^{-2}$. We fit the $J(u)$ curves from the FN-DMC data to a quadratic form (except for the $CaCuO_2$ $B_{1g}$ mode, which is highly anharmonic and fitted to a quartic function) to find $J_0$ and $\delta c_1$ in $J(u) = J_0 + \delta c_1 u^2$. In Fig [3], the reduced curvature $\delta c_1/J_0$ is presented, and compared to the hopping model of Eqn [3]. The hopping model seems to be qualitatively quite reasonably correct. However, we note that there is a large difference between the two cuprates, which is due to the different interlayers. The simple hopping model of Eqn [3] predicts that the $A_{1g}$ and $B_{1g}$ modes have the same $J(u)$. Accounting for statistical uncertainties, this is true for the isolated $CuO_2^-$ plane; it may or may not be true for the $CaCuO_2$ material, and it is highly unlikely to be true for the $La_2CuO_4$ cuprate. It thus appears that the interlayer is important for differentiating these two modes in terms of $J(u)$.

The main difference between the spin-phonon coupling of the different cuprate systems is the difference in frequency between the $A_{1g}$ and $B_{1g}$ modes. For a given $J(u) \simeq J_0 + \delta c_1 u^2 + \delta c_2 u^4$, the coupling constant $\gamma$ of a phonon mode to the FM mode with eigenstates $|\bar{n}\rangle$ and frequency $\omega$ is given by

\[
\gamma = \frac{\langle 0 | J(u) | 2 \rangle}{2\omega} = \frac{1}{2\sqrt{2}m\omega^2} \left( \delta c_1 + 3\delta c_2 \right)
\]

(note that we divide by twice the frequency because $J(u)$ is even and thus couples with a double phonon excitation). It therefore turns out that as long as $c_1$ is even roughly
predicted by the hopping model, then the coupling constants are mainly determined by the phonon frequencies. We find that for the modes and materials considered here, the coupling constants are reasonably well-predicted by the hopping model, if the \textit{ab-initio} phonon frequencies are used (Table II).

We thus have a clear reason for why the B$_{1g}$ mode couples more strongly to the magnetism than the A$_{1g}$ mode. The A$_{1g}$ mode simply has a higher frequency for two main reasons: the first is that it interacts more strongly with the interlayer, and second, that the bond angle of the copper for the A$_{1g}$ mode is more unfavorable; the B$_{1g}$ mode creates a tetrahedral arrangement, which is energetically more accessible. This can be seen in the curvatures for different cuprates in Fig 3 and in the spin density plots in Fig 4 in which it is clear that the copper-oxygen bonding and superexchange are both affected by the interlayer, once the phonon mode is activated.

The picture presented here fits well with experimental data. In LCO, the frequency of the B$_{1g}$ mode is changed by 6-8 meV upon changing the magnetic state, which is 18-24\% of the frequency of the mode. This is of a size quite large enough to explain the shift in the B$_{1g}$ mode observed in experiment [33]. The calculated isotope effect on $J$ is negligibly small, which is also observed in experiment [32]. Finally, our results predict the presence of phonon side bands in the magnetic spectrum, which have been observed [33] [34].

In summary, the results presented here are two-fold. The first is that we have demonstrated that the base state of the cuprates can be described accurately with a fully first-principles implementation of quantum Monte Carlo techniques. Since this method has no adjustable parameters, it is predictive and can be used in searches for new exotic materials. The lack of parameters will also be important in future studies, in which we will examine the effect of doping, which involves a delicate metal-insulator transition. In other metal-insulator transitions, such as VO$_2$, it has been observed that the hybrid functionals that happened to perform reasonably well in this work fail dramatically [35], so they cannot be a solution for parameter-free prediction of correlated materials.

The second main result is that the coupling between magnetism and the lattice are quite large. For the B$_{1g}$ mode in LCO, this is close to what one would expect from a simple hopping theory. However, in the A$_{1g}$ mode, the interlayer seems to prevent the magneto-elastic coupling from occurring, mainly by shifting the phonon frequency up, which is likely why experiment observes a shift in the B$_{1g}$ mode but not the A$_{1g}$ mode upon changing the magnetic state. This coupling was present in both the cuprates considered here, but the nature of the coupling is very different between them. This may help explain why the different cuprates have such drastically different $T_c$’s, since it is apparent from these results that the coupling between magnetism and lattice is highly dependent on the supposedly inert interplane layers.

As for the importance of explicit correlation in the undoped cuprates, it seems that once the basic material parameters are set, such as $J$ and the phonon frequencies, a simple hopping model does describe the behavior of the superexchange and the coupling constants with respect to the B$_{1g}$ and A$_{1g}$ modes within a factor of 2. The hybrid DFT methods perform quite reasonably well, with a few striking exceptions such as the potential energy surface of CaCuO$_2$ and a 50\% overestimate of the gap.

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\begin{table}[h]
\begin{tabular}{|c|c|c|}
\hline
& Calculated $\gamma$ & Theory $\gamma$ \\
\hline
LCO B$_{1g}$ & -0.12(1) & -0.14 \\
LCO A$_{1g}$ & -0.03(1) & -0.07 \\
CCO B$_{1g}$ & -1.8(1) & -2.33 \\
CCO A$_{1g}$ & -0.04(1) & -0.17 \\
\hline
\end{tabular}
\caption{The coupling constant $\gamma$ from Eqn 4 for the two realistic cuprates considered in this work. The 'theory' numbers are calculated using $J(u)$ from Eqn 3 and the frequencies from FN-DMC.}
\end{table}

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FIG. 4: A slice through the $ac$ plane of the three cuprates considered in this study. The column marked 'Tetragonal' denotes the undistorted $P4/mmm$ structure, while the $A_{1g}$ and $B_{1g}$ columns denote frozen phonon vibrations with each of those symmetries. Contour lines are logarithmically spaced, with red denoting down spin and blue up spin. The projected position of the atoms are denoted by circles: Cu(yellow), O(red), Ca(magenta), and La(green).
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