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Importance of Static Correlation in the Band Structure of High-Temperature Superconductors

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Recently we presented a new band structure for $La_{2-x}Sr_xCuO_4$ and other high-temperature superconductors in which a second narrow band was seen to cross the primary band at the Fermi level. The existence of this second Fermi level band is in complete disagreement with the commonly accepted LDA band structure. Yet it provided a crucial piece of physics which led to an explanation for superconductivity and other unusual phenomena in these materials. In this work, we present details as to the nature of the failure of conventional methods in deriving the band structure of the cuprates. In particular, we use a number of chemical analogues to describe the problem of static correlation in the band structure calculations and show how this can be corrected with the predictable outcome of a Fermi level band crossing.

Introduction

Since their discovery more than a dozen years ago,[1] the cuprate high-temperature superconductors have proven to be among the most unusual and intriguing materials devised this century. While their most obvious and important characteristic is that they superconduct at temperatures far in excess of the commonly accepted upper limit for conventional BCS superconductors, various experimental probes of their superconducting and normal state properties have revealed anomalous behavior of a much more general nature. The NMR,[2] angle-resolved photoemission (ARPES),[3] neutron scattering,[4] Josephson tunneling,[5] and IR[6] have all characterized these materials as extremely exotic.

The materials can generally be described as having two-dimensional CuO_2 sheets sandwiched between other metal oxide sheets which serve as charge reservoirs.[7] In the case of $La_{2-x}Sr_xCuO_4$, the prototypical high-temperature superconductor, the environment around each Cu is a distorted octahedron with the apical O's, which belong to the La/Sr/O planes, further from the Cu center than the in-plane O's. When the material is undoped, $x = 0$, the charge on the La is formally $+3$, the charge on each O is formally -2, and the charge on the Cu is formally $+2$. The Cu(II) is expected to be in its open-shell d^9 configuration, with the La and O ions in closed shell. This leads to the existence of a "half-filled band" from simple electron counting arguments. Upon doping, substitution of La(III) with Sr(II), Cu(III) ions are formally created as more electrons are removed from that "half-filled band". Superconductivity is observed over the very narrow doping range of approximately $x = 0.10-0.25$, with the optimal doping ($T_c = 39$ K) at $x = 0.15$.[8]

From early LDA band structure calculations it was generally concluded that the materials were indeed very two-dimensional.[9] A Fermi surface arose from a single half-filled band composed of the antibonding arrangement of the Cu $d_{x^2-y^2}$ and O p_σ orbitals in the signature CuO_2 planes, confirming simple expectations. However, this band structure poses a great problem for physicists since there is virtually nothing remarkable about it that would suggest some sort of exotic supercondicting properties. This has led to the development of a rather odd attitude toward these LDA calculations. It is clearly agreed that they are missing some crucial physics. Beyond that, the overwhelming collection of unusual data which characterizes these materials has led physicists to agree only that this missing physics must be deeply complicated. Somehow, in spite of these deficiencies, the qualtitative picture of the LDA band structure has effectively become conventional wisdom.

Yet, Tahir-Kheli and Perry[10,11] recently offered a new theory of high-temperature superconductivity which is remarkably simple and explains substantially more than all previous theories. We showed that much of the confusion about these materials stems from incorrect assumptions about their band structure. The LDA band structure calculations are based on the mean-field approximation, which is known to breakdown in the limit of weakly interacting particles. Such is the case for the cuprates, for which it has been well accepted that many-body effects (or dynamic correlation) are important. Correlation has been introduced in some models to correct the problem, but to our knowledge this has always been done in a limited way, applying the correction only to the three bands produced by the Cu $d_{x^2-y^2}$ and two O p_σ orbitals.[12] These three band Hubbard models, which are often reduced to one-band Hubbard models, ignore the effect that correlation has on the other bands in the material since it is widely assumed that they are irrelevant. Yet we have argued that this underlying assumption that the single particle band structure is qualitatively correct is in fact false and such a limited approach to the incorporation of correlation actually misses the most important consequence: that the relative energy of the half-filled band changes with respect to the full bands. This is due to the improper description of *static* correlation in the LDA band structure. In our model, where the correlation correction is applied more universally, the effect is so dramatic that a second band appears at the Fermi level. This is shown in Figure 1. This new band structure still has the approximately half-filled 2-D Cu $d_{x^2-y^2}$/O p_σ band, but a second 3-D Cu d_{z^2}/O′ p_z band is seen at the Fermi level as well, such that electrons are removed from both bands upon doping. Significantly, we identified a symmetry-allowed Fermi level crossing of the two bands which we showed was the crucial element in understanding the physics of these materials. This band crossing allows for the formation of a new type of interband Cooper pair,

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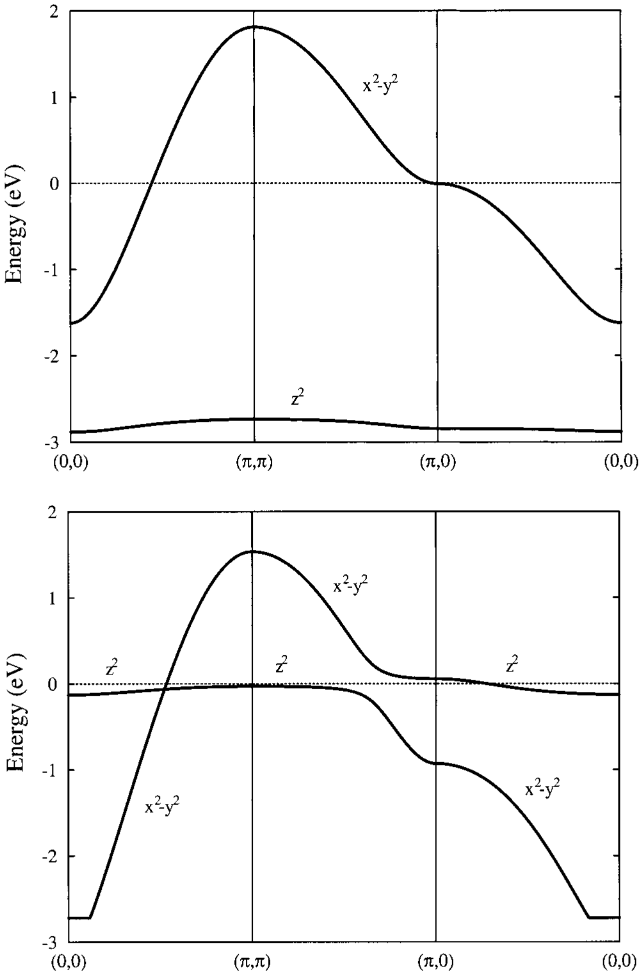

Figure 1. (a, top) Calculated 2-D band structure for optimally doped $La_{1.85}Sr_{0.15}CuO_4$ using our Hubbard model and retaining the mean-field approximation. (b, bottom) Calculated 2-D band structure using our Hubbard model and including static correlation. The two bands are seen to cross along the (0, 0) − (π, π) direction very near the Fermi level. Note: other bands are not shown for clarity.

representing a simple twist on the conventional BCS theory of superconductivty. Moreover, the wealth of experimental data which demonstrates more general anomalous behavior can easily be explained by this unusual band structure, and in a number of cases has already been quantitatively reproduced.[10,11,13,14]

In this work, we present arguments as to the nature of the correlation problem in conventional LDA calculations and why correcting this problem intuitively leads to the new band structure. We develop these arguments from a chemist's perspective using a number of familiar molecular systems to illustrate various aspects of the correlation problem. In particular, the chemistry of H_2, benzene, and the Cu ion dimer will be discussed, leading up to a discussion of the band structure for $La_{2-x}Sr_xCuO_4$.

The Problem with H_2 Dissociation

To understand the basic problem with the LDA band structure calculations of the cuprates, it is only necessary to consider the fundamental problem of dissociation consistency in single configuration based methods.[15] In Figure 2 we show the dissociation curves for H_2 as calculated at the Hartree−Fock (HF) and the B3LYP[16] density functional (DFT) levels using both a restricted spin and symmetry approach and an unrestricted spin and symmetry approach. For both methods (and the case is the same for other DFT functionals), the restricted approach leads to dissociation to an excited state description of two H atoms. The unrestricted approach leads to proper dissociation. This behavior is well understood and represents the primary motivation behind the development of methods such as generalized valence bond (GVB).[17]

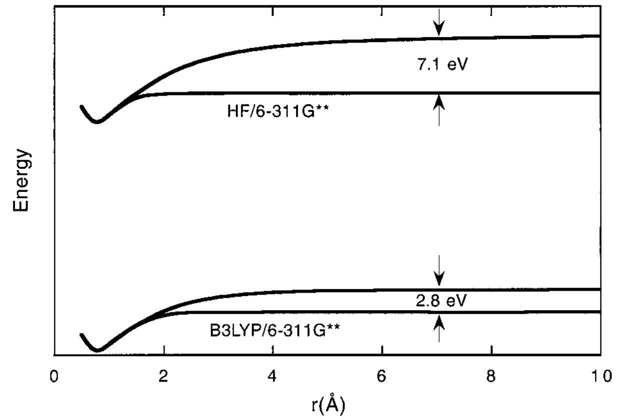

Figure 2. Calculated dissociation curves for H_2 at the HF (top) and B3LYP (bottom) levels using both a spin and symmetry restricted approach and a spin- and symmetry-unrestricted approach. For both computational levels the restricted approach is seen to dissociate to an incorrect higher limit.

The problem with the restricted approach is that two electrons are forced to occupy the same orbital (the σ_g orbital in the case of H_2). This is a fine approximation near the equilibrium bond length, and indeed both the restricted and unrestricted approaches lead to the same state in this region. However, upon dissociation, forcing two electrons to occupy the same orbital is clearly not appropriate since the local representation of this can be seen to be 50% covalent (the correct dissociation limit) and 50% ionic (an excited state). Explicitly, that is

$$\Psi_g = (\sigma_g)^2$$

$$= {}^1/_2(1s(H1) + 1s(H2))^2$$

$$= {}^1/_2((1s(H1))^2 + (1s(H2))^2 + (1s(H1))^1(1s(H2))^1 + (1s(H2))^1(1s(H1))^1)$$

$$= (1/\sqrt{2})(\Psi(\text{ionic}) + \Psi(\text{covalent}))$$

For the HF wave function, the energy of this state is

$$E_g(r{=}\infty) = 2E_{1s} + {}^1/_2 J_{1s,1s}$$

where E_{1s} is the ground state energy of an H atom and $J_{1s,1s}$ is the self-Coulomb energy associated with the H 1s orbital. The situation is similar for DFT where the exchange and correlation functionals will cancel some but not all of the self-Coulomb term. As a result the error for HF (7.1 eV) is seen to be larger than that for B3LYP (2.8 eV), but the error for B3LYP and other DFT functionals is nevertheless nonzero.

The unrestricted approach overcomes the problem of the self-Coulomb energy by breaking spin and symmetry and localizing the α spin electron on one H atom and the β spin electron on the other. As a result, there is dissociation to the proper Ψ(covalent) limit. Alternatively, a method which introduces static correlation, such as GVB (or more generally CASSCF), overcomes this problem without breaking spin by describing the bond with two configurations as

$$\Psi_{\mathrm{GVB}} = c_1(\sigma_g)^2 - c_2(\sigma_u)^2$$

where $c_1^2 + c_2^2 = 1$. The energy upon dissociation is

$$E_{\mathrm{GVB}}(r{=}\infty) = c_1^{\,2}E_g(r{=}\infty) + c_2^{\,2}E_u(r{=}\infty) - c_1c_2J_{1s,1s}$$

Clearly since $E_g = E_u$ upon dissociation, the optimal set of coefficients is $c_1 = c_2 = 1/\sqrt{2}$. Hence the GVB wave function dissociates properly to

$$E_{\mathrm{GVB}}(r{=}\infty) = 2E(1s)$$

While this is all very familiar, the point is that it is pertinent to the electronic structure of high-temperature superconductors. In these materials the Cu(II) d^9 spins of the half-filled band are separated by 3.8 Å. At this separation, a breakdown in the mean-field approximation is expected, resulting in a substantial overestimate of the self-Coulomb term. Recognition of this has been the motivation behind calculations in which the La_2CuO_4 unit cell has been doubled to allow for spin polarization.[18,19] In these calculations, α and β spins localize to alternating sites in the undoped material, thus removing the self-Coulomb term associated with the half-filled band much like the unrestricted spin and symmetry calculations remove the self-Coulomb term from dissociated H_2. The work of Svane[18] is particularly important in this regard since it also accounts for the fact that the self-Coulomb term and the self-exchange and correlation terms do not completely cancel. As a solution, he applies a self-interaction correction (SIC) to those orbitals that can be well localized. While in context this is correct, and to some extent his calculations are in agreement with ours, as we show next, correlation of delocalized orbitals is important, too.

Static Correlation in Benzene

A more complicated example of static correlation is the case of aromatic benzene. At the HF level, there are three orbitals having the symmetries A_{2u} and E_{1g} under the D_{6h} point group which represent the delocalized form of the three benzene π orbitals. Yet the six atomic p_π orbitals which form these three molecular orbitals have only a moderate overlap with each other. This leads to an overestimate of the self-Coulomb term associated with the bonds which requires correlation of the type just described. The easiest way to introduce such correlation is through the GVB approach in which symmetry is broken and the three delocalized HF π orbitals are localized to three π bonds corresponding to one of the two resonating Kekulé structures. Similarly, the three corresponding π antibonding orbitals are localized and the GVB wave function becomes

$$\Psi_{\mathrm{GVB}} = (c_1(\pi_g(1))^2 - c_2(\pi_u(1))^2)(c_1(\pi_g(2))^2 - c_2(\pi_u(2))^2)(c_1(\pi_g(3))^2 - c_2(\pi_u(3))^2)$$

The energy of the GVB wave function is 1.12 eV lower than that of the HF wave function using a 6-311G** basis set.[20] This represents a lowering of 0.37 eV per bond, which can be directly related to a reduction in the self-Coulomb term associated with each bond.

Additional correlation to account for spin polarization of the bonds can be introduced through the RCI wave function which adds the single excitation configuration $c_3(\pi_g)^1(\pi_u)^1$ for each bond in the above equation for Ψ_{GVB} while also relaxing some inherent constraints on the GVB coefficients. This correlation effectively allows α and β spins to separate and lowers the total energy by another 0.30 eV.

Resonance can then be included by allowing all excitations between the bonds (i.e., all excitations of the six electrons within the space of the six GVB orbitals). This GVBCI wave function lowers the total energy by another 0.53 eV. Significantly, this GVBCI wave function is also strictly equivalent to the commonly used CASSCF wave function. The two are related by a simple transformation from the localized space (GVBCI) to the delocalized space (CASSCF). The very existence of this transformation implies that the correlation which exists in the GVBCI also exists in the CASSCF. Since it is clear that the most important correlation in the GVBCI is that which reduces the self-Coulomb energy of the π bonds, the same must be true of the CASSCF, although it is much less transparent. In other words, the correlation which reduces the self-Coulomb energy is independent of whether the orbitals are localized or delocalized.

The presence of this same type of correlation in systems that are delocalized is often overlooked. In the case of the superconductors, methods that depend on the localization of orbitals in order to reduce the self-Coulomb energy[18] are in fact biased toward such well localized states since they miss the fact that the energy can be similarly lowered by application of such correlation to states that cannot be well localized. This is not to say that undoped La_2CuO_4 does not in fact have well-localized spins, since the undoped material is clearly an antiferromagnet. But upon doping, when orbitals can no longer be easily localized, this type of correlation should not be expected to just disappear. By our argument here, reduction of the self-Coulomb energy should be considered for both localized and delocalized orbitals in evaluating the band structure. The consequences of this are addressed in the next section.

The Problem with Separated Cu Ions

The ground state of Cu(I) is known to be ^1S d^{10}, the ground state of Cu(II) is known to be ^2D d^9, and the ground state of Cu(III) is known to be ^3F d^8.[21] While it is the case that there is only one possible d^{10} configuration for Cu(I), and the five possible d^9 configurations for Cu(II) are degenerate, for Cu(III) the 10 different possible triplet d^8 configurations lead to different mixtures of the ^3F and higher energy ^3P states. Only the two configurations in which one hole is in the d_σ orbital and the other is in a d_δ orbital lead to a pure ^3F state in a single reference description.

Using a triple-ζ contraction of Hay and Wadt's ECP basis set,[22] we calculate a second ionization potential (the difference between Cu(I) and Cu(II)) to be 17.54 eV at the HF level and 20.65 eV at the B3LYP level in comparison to the experimental value of 20.29 eV. Similarly, we calculate a third ionization potential (the difference between Cu(II) and Cu(III)) to be 34.32 eV at the HF level and 37.06 eV at the B3LYP level in comparison to the experimental value of 36.83 eV. Clearly, B3LYP is a suitable method for studying the Cu ions.

Yet we find that when two Cu ions are low spin coupled and separated by a long distance, these methods have difficulty. As with H_2, an unrestricted spin and symmetry approach will properly describe the two ions, but attempting to use a restricted spin and symmetry approach fails. The nature of this failure is quite revealing, however, in how it relates to the band structure of the high-temperature superconductors.

Results of calculations on various Cu ion dimers are given in Table 1. As can be seen, the energy of the Cu(I) + Cu(I) dimer where both ions are d^{10} is correct. The energy of the Cu(I) + Cu(II) dimer where each ion is an average of d^9 and d^{10} is also correct. However, the energy of the singlet state of Cu-

TABLE 1: Calculated Energetics for the Cu Ion Dimer (in eV)[a]

dimer	HF(calc)	HF(exact)	B3LYP(calc)	B3LYP(exact)
Cu(I/^{1}S) + Cu(I/^{1}S)	0.00	0.00	0.00	0.00
Cu(I/^{1}S) + Cu(II/^{2}D)	17.54	17.54	20.65	20.65
Cu(II/^{2}D) + Cu(II/^{2}D)	49.50	35.08	45.60	41.30
Cu(II/^{2}D) + Cu(III/^{1}G)	56.15	56.15	61.57	61.57
Cu(II/^{2}D) + Cu(III/^{3}F)	67.53	51.86	62.74	57.71

[a] HF(calc) and B3LYP(calc) are computed under a spin- and symmetry-restricted formalism. HF(exact) and B3LYP(exact) represent the correct values for two noninteracting ions.

(II) + Cu(II) is high by 14.42 eV at the HF level and high by 4.30 eV at the B3LYP level. This state has the following orbital occupations

$$\mathrm{Cu(II)} + \mathrm{Cu(II)} = (xy_g)^2(xy_u)^2(xz_g)^2(xz_u)^2(yz_g)^2(yz_u)^2(z^2_g)^2(z^2_u)^2(x^2 - y^2_g)^2(x^2 - y^2_u)^0$$

As shown for H_2 and benzene, the error in the Cu(II) + Cu(II) energy can be unambiguously attributed to the lack of static correlation in the half-filled $d_{x^2-y^2}$ pair of orbitals which leads to this copper dimer being described as 50% Cu(II) + Cu(II) and 50% Cu(I) + Cu(III). This state can be correctly described by the GVB or CASSCF method or by breaking symmetry and spin in an unrestricted approach. Alternatively, changing the spin to triplet and singly occupying each of the two $d_{x^2-y^2}$ orbitals will lead to the correct ground state.

This Cu(II) + Cu(II) model by itself offers a good argument for what might be wrong with conventional LDA band structure calculations of the cuprate superconductors. Doubling the unit cell to allow breaking of symmetry and spin with localization of the α and β spins on alternating copper sites may be one logical solution for understanding the undoped material. Alternatively, introducing more rigorous correlation with a Hubbard model of the isolated Cu $d_{x^2-y^2}$/O p_σ band may be another logical solution. However, when our model is taken one step further to consider Cu(II) + Cu(III), the most important aspect of the lack of static correlation in the half-filled band can be seen, and this point has received little attention until now.

When one more electron is removed from the $d_{x^2-y^2}$ pair of orbitals to form Cu(II) + Cu(III), the doublet state is again described *correctly* even though it corresponds to an excited state configuration of Cu(III). The state is actually ^{2}D Cu(II) + ^{1}G Cu(III), where the ^{1}G d^8 configuration of Cu(III) corresponds to having the $d_{x^2-y^2}$ orbital empty. We calculate the $^3\mathrm{F} \rightarrow {}^1\mathrm{G}$ excitation energy to be 4.29 eV at the HF level and 3.86 eV at the B3LYP level. However, when an electron is instead removed from the d_{z^2} pair of orbitals, which should lead to a ground state description of ^{2}D Cu(II) + ^{3}F Cu(III), the doublet coupling of the two ions is *too high* in energy by 15.67 eV at the HF level and 5.03 eV at the B3LYP level. Even correcting the improper exchange interaction between the d_{z^2} and $d_{x^2-y^2}$ electrons in this configuration, the HF energy is still 14.95 eV too high, and the B3LYP energy is still 4.48 eV too high.

The difference between these two states of Cu(II) + Cu(III) can be understood in that removing an electron from the $d_{x^2-y^2}$ orbitals removes the problem with static correlation whereas removing an electron from the d_{z^2} orbitals does not. In the former case, there is only one electron remaining in the $d_{x^2-y^2}$ orbitals and it is shared equally between the two ions. In the latter case, there are still two electrons in the $d_{x^2-y^2}$ orbitals and without proper correlation the self-Coulomb energy will remain too high. In the end, this means that in starting with a half-filled set of $d_{x^2-y^2}$ orbitals in Cu(II) + Cu(II) there is an improper bias of 14.42 eV at the HF level and 4.30 eV at the B3LYP level *toward* removing an additional electron from $d_{x^2-y^2}$. However, there is actually a bias of 0.53 eV at the HF level and 0.18 eV at the B3LYP level *against* removing an electron from d_{z^2}. In other words, the lack of correlation in the $d_{x^2-y^2}$ orbitals raises the energy of'those particular orbitals with respect to all the other orbitals.

The three models discussed here (H_2, benzene, and the Cu ion dimer) suggest that static correlation needs to be considered in the band structure of the cuprate superconductors, that it needs to be applied to all orbitals regardless of whether or not they can be well localized, and that the primary result will surely be to lower the energy of the entire half-filled band with respect to the other filled bands.

Importance of Static Correlation in the Band Structure of High-Temperature Superconductors

We have chosen to study the band structure of optimally doped $La_{2-x}Sr_xCuO_4$ with a Hubbard model which uses parameters derived from DFT calculations on a CuO_6 cluster. The details of the cluster calculations and the procedure for extracting the Hubbard parameters are given explicitly in Perry and Tahir-Kheli.[11] All parameters necessary to describe the Cu $d_{x^2-y^2}$/O p_σ and Cu d_{z^2}/O′ p_z bands were derived. These parameters include orbital energies, Coulomb and exchange energies, and orbital couplings. Our original set of parameters, which were published in that work, came from BLYP/6-31+G* calculations (using an ECP on the Cu). We have since derived parameters from B3LYP/6-311+G* calculations and found the resulting 2-D band structure (detailed below) to be qualitatively the same as that obtained with the earlier parameter set. However, we have also included a 3-D coupling in this new band structure and as a result we can now calculate such experimental observables as the NMR Cu and O spin relaxation rates,[13] the ARPES Fermi surface, the neutron scattering, and the mid-IR absorption[14] with near-quantitative accuracy, something that has not been done with any other band structure.

The validity of the general approach can be tested by calculating the Hubbard model band structure within the mean-field approximation. The calculation must be done iteratively until self-consistency is achieved because the orbital energies depend on the Coulomb and exchange field which depends on the orbital occupations which depend on the orbital energies. The first step is to calculate the orbital energies as a function of the orbital occupations. Under the mean-field approximation, this is

$$E_i = E_i^0 - \sum_j (2 - N_j)(J_{i,j} - {}^1/_2 K_{i,j})$$

where E_i^0 are the calculated orbital energies when all valence bands are full (formally La(III), Sr(II), Cu(I), and O(−II)), N_j are the atomic orbital occupations, $J_{i,j}$ are the Coulomb terms between orbitals, and $K_{i,j}$ are the exchange terms. Details of how the long-range Coulomb field is handled are given in the cited ref 11. Once the orbital energies are determined, a Hubbard matrix is constructed at every **k** vector on a grid covering the first Brillouin zone, the eigenvectors and eigenvalues of each matrix are determined corresponding to the orbitals and orbital energies at each **k** point, the Fermi level is adjusted such that the correct number of orbitals are occupied for the particular doping level, the atomic orbital occupations are then determined, and the process is repeated. It should be noted that in our model $J_{i,i} = K_{i,i}$ such that when an orbital is half-occupied its energy is $E_i = E_i^0 - {}^1/_2 J_{i,i}$.

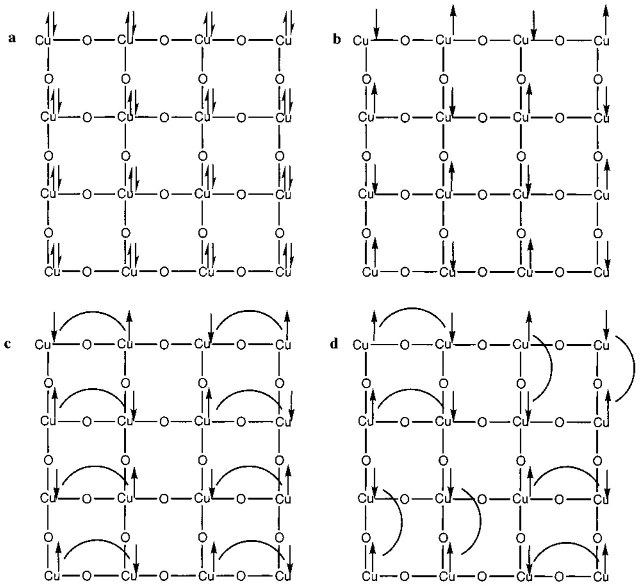

Figure 3. (a) Schematic description of Cu spin couplings under the mean-field approximation. Each Cu site is 50% α spin and 50% β spin. (b) Schematic description of the antiferromagnetic state where alternating Cu sites are either α spin or β spin. (c and d) Two schematic descriptions of the paramagnetic state where a given Cu site may be spin paired with any of the four adjacent Cu sites.

As shown in Figure 1a, using the mean-field approximation to determine orbital energies as above and constraining the model to a 2-D description of the material leads to a band structure which is nearly quantitatively identical to those published using conventional LDA band structure techniques.[9] A single Cu $d_{x^2-y^2}$/O p_σ band which is widely dispersing is seen to cross the Fermi level. A second Cu d_{z^2}/O′ p_z band is seen to be several electronvolts lower in energy. This good agreement effectively validates the procedure.

It is interesting to note, however, that the bottom of the d_{z^2} band is several electronvolts below the bottom of the $d_{x^2-y^2}$ band even though at $\mathbf{k} = (0,0)$ the $d_{x^2-y^2}$ orbital represents a nonbonding combination of the Cu orbitals, having no O p_σ character at all, while the d_{z^2} orbital has significant antibonding O′ p_z character. Ligand field theory would suggest that the d_{z^2} band should be higher in energy than the $d_{x^2-y^2}$ band at this $\mathbf{k}$ point unless the d_{z^2} atomic orbital is itself significantly more stable than the $d_{x^2-y^2}$ atomic orbital. This is indeed the case, but it cannot be explained by differences in the intrinsic E_i^0 atomic orbital energies for d_{z^2} and $d_{x^2-y^2}$ since this difference is only 0.13 eV. The stabilization of the d_{z^2} band with respect to the $d_{x^2-y^2}$ band is seen only upon removal of electrons from the $d_{x^2-y^2}$ band. This is counterintuitive and exactly the opposite behavior should be expected from such basic principles as Hund's rule. It is a direct result though of the improper accounting of the self-Coulomb energy in the mean-field approximation for this strongly correlated system. This behavior is completely analogous to that seen for the Cu ion dimer discussed above. Thus, we expect that correlation that would reduce the self-Coulomb term of partially occupied orbitals would lower the energy of the Cu $d_{x^2-y^2}$ orbital with respect to the Cu d_{z^2} orbital.

Introducing static correlation to the band structure in a rigorous way is an extremely difficult problem. However, the effect of this correlation on the self-Coulomb term in the mean-field equation can easily be approximated. This is best seen by considering Figure 3 and thinking about what the self-Coulomb energy should be when a particular atomic orbital is half-filled.

Figure 3 depicts a localized description of the Cu $d_{x^2-y^2}$/O p_σ band. Such localization can be exact only when the band is half-filled. The localization can still be approximately correct with the addition or removal of electrons if the ensuing delocalized states are viewed as arising from the resonance of localized states. Figure 3a shows the mean-field spin coupling in the CuO_2 plane while Figure 3b shows an antiferromagnetic spin coupling which is relevant when the material is undoped. Upon doping, this antiferromagnetic order is destroyed and a correlated paramagnetic spin coupling such as that depicted in Figure 3c,d is expected.

In the mean-field picture, when the Cu $d_{x^2-y^2}$ orbital is half-occupied, the local spin is 50% α and 50% β leading to a self-Coulomb term which is $^1/_2J$. However, in both the antiferromagnetic and correlated paramagnetic pictures when the Cu $d_{x^2-y^2}$ orbital is half-occupied, a resonance exists between states that have a local spin in that orbital that is purely α or purely β. This picture is fundamentally different from that of the mean-field approximation and leads to a self-Coulomb term which is $0J$. From the arguments used to make the connection between the GVBCI and CASSCF descriptions of benzene, the same can be said of the Cu d_{z^2} and O′ p_z orbitals even though localization of these orbitals is not as straightforward. That is, delocalized states must be viewed as arising from the resonance of very low symmetry localized states. So for the Cu $d_{x^2-y^2}$ and d_{z^2} orbitals and the O′ p_z orbital, the correlation corrected mean-field equation becomes

$$E_i = E_i^0 - (2 - N_i)J_{ii} - \sum_{j\neq i}(2 - N_j)(J_{ij} - {}^1/_2K_{ij}), \quad N_i > 1$$

$$E_i = E_i^0 - J_{ii} - \sum_{j\neq i}(2 - N_j)(J_{ij} - {}^1/_2K_{ij}), \quad N_i \leq 1$$

Upon examination, it can easily be seen that if an orbital is half-occupied or less, the full self-Coulomb term will be removed from E_i^0.

The situation is a little less clearcut for the O p_σ orbitals. In the antiferromagnetic picture of Figure 3b, α or β spin is localized to alternating Cu sites, but as a result each O site is then 50% α and 50% β. Thus, the self-Coulomb term is expected to be $^1/_2J$ for the half-occupied orbital as it is under the mean-field approximation. In the correlated paramagnetic picture of Figure 3c,d, for the one O atom that lies between two spin-paired Cu atoms, the self-Coulomb term also turns out to be $^1/_2J$. However, for the three other O atoms surrounding any particular Cu site, the self-Coulomb term is expected to be $^1/_4J$. This is because the uncorrelated spins between the two Cu atoms lead to spin on the O which is 25% pure α, 25% pure β, and 50% half-α/half-β. The latter term leads to the $^1/_4J$ Coulomb repulsion. On average then, when the O p_σ orbital is half-occupied, the self-Coulomb term is $^3/_4 \times {}^1/_4J + {}^1/_4 \times {}^1/_2J = {}^5/_{16}J$. The correlation corrected mean-field equation for this orbital then becomes

$$E_i = E_i^0 - \frac{11}{16}(2 - N_i)J_{ii} - \sum_{j\neq i}(2 - N_j)(J_{ij} - {}^1/_2K_{ij}), \quad N_i > 1$$

$$E_i = E_i^0 - \left(\frac{5}{16}(2 - N_i) + \frac{3}{8}\right)J_{ii} - \sum_{j\neq i}(2 - N_j)(J_{ij} - {}^1/_2K_{ij}), \quad N_i \leq 1$$

This latter set of equations is clearly approximate and may vary substantially from that obtained from the exact wave function,

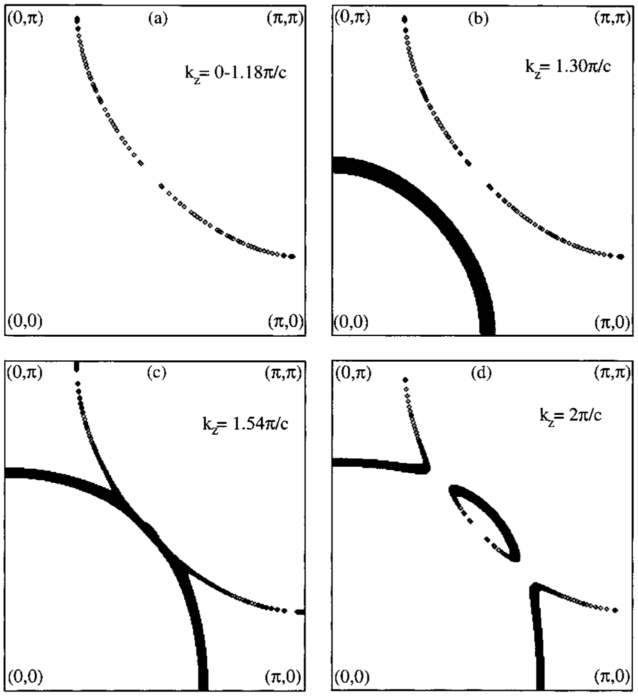

Figure 4. 3-D Fermi surface for optimally doped $La_{1.85}Sr_{0.15}CuO_4$. Cross sections of this Fermi surface are given at (a) $k_z = 0$, (b) $k_z = 1.3(\pi/c)$, (c) $k_z = 1.54(\pi/c)$, and (d) $k_z = 2(\pi/c)$. Electrons begin to come out of the second band at $k_z = 1.54(\pi/c)$, allowing the formation of interband Cooper pairs in the vicinity of the band crossing.

which is of course unknown. So we should note that we have generated band structures with a variety of values for the extent of the self-Coulomb term removed from the O p_σ E_i^0 atomic orbital energies to test the importance of this term. For values ranging from $^1/_2J$ removed at half-occupancy to a full J removed, no qualitative difference in the band structure was observed. We thus feel that the choice of $^{11}/_{16}J$ removed from the orbital energy for O p_σ at half-occupany is reasonable.

The results of including this static correlation in the Hubbard model can be seen in Figure 1b. Here we present the two-dimensional band structure obtained with the newer B3LYP/6-311+G* parameters. As occurs with the older BLYP/6-31+G* band structure, the Cu $d_{x^2-y^2}$/O p_σ band is seen to be stabilized with respect to the Cu d_{z^2}/O′ p_z band. The change is so dramatic that the second band is seen now to lie just below the Fermi level at optimal doping, a rather robust effect. As we pointed out in our first published work on this subject, a symmetry allowed crossing of the two bands is observed very near the Fermi level.[11] For this newer set of parameters, it is just 0.024 eV below the Fermi level. The existence of such a crossing provides the unique opportunity for a new type of Cooper pair to form. In conventional BCS superconductors, pairs of electrons near the Fermi level form an attractive coupling when one of the electrons is in state **k** and the other is in state −**k**. With the existence of a Fermi level band crossing, such an attractive coupling (can be formed between electrons in states **k** and −**k** where each of the electrons belongs to a *different* band. This new and simple twist on the conventional theory immediately provides an explanation for the *d*-wave gap observed in the Josephson tunneling[5,10] and ARPES.[3,14a]

While our early work resorted to empirical modifications to the Hubbard model to a achieve a band crossing at exactly the Fermi level, recently we found that the introduction of a small 3-D coupling on the order of 0.05−0.15 eV between O′ p_z orbitals of neighboring planes was enough to produce a Fermi level band crossing.[14c] This is shown in Figure 4. The crossing occurs in a limited area of the 3-D Brillouin zone, but this is all that is necessary for the formation of interband Cooper pairs. We should mention that several researchers have previously noted z^2 character near the Fermi level in spin-polarized band structure calculations on undoped La_2CuO_4,[18,19] so this new band structure should not come as a complete surprise even though it is radically different from the band structure that has gained common acceptance. To our knowledge though, no one has ever noted the band crossing before, and it is this that leads directly to the unusual physics of high-temperature superconductivity.

Conclusions

We have shown that the conventional LDA band structure calculations for $La_{2-x}Sr_xCuO_4$ and other high-temperature superconductors have failed due to an underestimation of the static correlation. This same failure affects molecular systems such as H_2, benzene, and the Cu ion dimer in a well-understood way. We have corrected the problem within the framework of a Hubbard model by altering the accounting associated with the self-Coulomb term. The result was a radically different band structure in which a second Cu d_{z^2}/O′ p_z band was seen to cross the primary Cu $d_{x^2-y^2}$/O p_σ band at the Fermi level. The observation of this band crossing led to a new interband pairing theory for the mechanism of superconductivity in these materials.

Finally, we must stress that not only does the new band structure and interband pairing theory explain the origin of *d*-wave superconductivity in these materials, it also explains the origin of the high T_c as resulting from unusual behavior in the dielectric constant stemming from the band crossing.[14b] It also quantitatively explains the anomolous behavior of the NMR Cu and O spin relaxation rates as simply the result of rapidly changing orbital character near the Fermi level.[13] It explains the ARPES pseudogap as originating from the very narrowly dispersing Cu d_{z^2} band.[14a] It further explains the incommensurate peaks of the neutron scattering and the mid-IR absorption.[14d] None of the physics associated with understanding these experiments is particularly difficult when this new band structure is used. In contrast, the physics that has been proposed by various sources in reference to the conventional band structure to explain any one of the above-mentioned experiments has always been deeply complex and limited in its predictive capability. We suggest that nature usually prefers the simpler solution.

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