

**Antiferromagnetic band structure of  $\text{La}_2\text{CuO}_4$ : Becke-3–Lee-Yang-Parr calculations**Jason K. Perry,<sup>1,2</sup> Jamil Tahir-Kheli,<sup>1,2</sup> and William A. Goddard III<sup>2</sup><sup>1</sup>*First Principles Research, Inc., 8391 Beverly Boulevard, Suite No. 171, Los Angeles, California 90048*<sup>2</sup>*Materials and Molecular Simulation Center, Beckman Institute, California Institute of Technology, Pasadena, California 91125*

(Received 7 July 2000; revised manuscript received 12 December 2000; published 19 March 2001)

Using the Becke-3–Lee-Yang-Parr (B3LYP) functional, we have performed band-structure calculations on the high-temperature superconductor parent compound,  $\text{La}_2\text{CuO}_4$ . Under the restricted spin formalism ( $\rho_\uparrow = \rho_\downarrow$ ), B3LYP band structure agrees well with the standard local-density approximation (LDA) band structure. It is metallic with a single Cu  $x^2-y^2/O p_\sigma$  band crossing the Fermi level. Under the unrestricted spin formalism ( $\rho_\uparrow \neq \rho_\downarrow$ ), the B3LYP band structure has a spin-polarized antiferromagnetic solution with a band gap of 2.0 eV, agreeing well with experiment. This state is 0.52 eV (per formula unit) lower than that calculated under the restricted spin formalism. The apparent high energy of the spin-restricted state is attributed to an overestimate of on-site Coulomb repulsion, which is corrected in the unrestricted spin calculations. The stabilization of the total energy with spin polarization arises primarily from the stabilization of the  $x^2-y^2$  band, such that the character of the eigenstates at the top of the valence band in the antiferromagnetic state becomes a strong mixture of Cu  $x^2-y^2/O p_\sigma$  and Cu  $z^2/O' p_z$ . Since the Hohenberg-Kohn theorem requires the spin-restricted and spin-unrestricted calculations to give identical ground-state energies and total spatial densities for the exact functionals, this large disparity in energy reflects the inadequacy of current functionals for describing the cuprates. This calls into question the use of band structures based on current restricted spin-density functionals (including LDA) as a basis for single-band theories of superconductivity in these materials.

DOI: 10.1103/PhysRevB.63.144510

PACS number(s): 74.25.Jb, 71.15.Mb

**INTRODUCTION**

Almost immediately following the discovery of the superconducting cuprates (e.g.,  $\text{La}_{2-x}\text{Ba}_x\text{CuO}_4$  in 1986), several research groups characterized the band structures with density-functional theory (DFT).<sup>1-3</sup> Using the standard local-density approximation (LDA), the resulting band structures consistently showed the Fermi-level behavior of these materials to be characterized by a single metallic two-dimensional (2D) band, comprised of Cu  $x^2-y^2/O p_\sigma$  hybrid orbitals (from here on called the  $x^2-y^2$  band). All other occupied bands were buried 0.5 eV or more below the Fermi level. While the basic orbital picture appeared to agree with some experimental data, the absence of antiferromagnetic (AF) order in the band structure of the undoped parent compound (e.g.,  $\text{La}_2\text{CuO}_4$ ) was cause for concern. In time, the inability of this band structure to explain an increasingly diverse range of normal-state phenomena of the doped materials led many to conclude that Fermi-liquid theory is not applicable. Indeed, no major theories based solely on this conventional band structure have survived. Still, the LDA band structure is widely viewed as a reasonable starting point for superconductivity theories, and experimental data are routinely compared to these calculations.

In the early 1990s, a number of groups succeeded in computing an alternative AF band structure for undoped  $\text{La}_2\text{CuO}_4$  within the DFT formalism. Using a pseudopotential approach, Shiraishi *et al.*<sup>4</sup> achieved a spin-polarized solution where  $\uparrow$  and  $\downarrow$  spins reside on different Cu sites of a doubled unit cell. This opened up a band gap of 0.6 eV between occupied and unoccupied bands [the measured gap is 2.0 eV (Ref. 5)]. Other groups attempted to correct certain known flaws in the LDA functional. Most notably, Svane<sup>6</sup> applied a

self-interaction correction local-spin-density (SIC-LSD) approach, in which the residual Coulomb interaction an electron improperly “sees” with itself is removed from the LSD functional. Spin localization was achieved with this method and an AF band structure was found with an indirect band gap of 1.04 eV. Temmerman, Szotek, and Winter<sup>7</sup> later found similar results using an alternative SIC-LSD approach. They reported an improved band gap of 2.1 eV. Czyzyk and Sawatzky<sup>8</sup> took yet another approach, embedding a Hubbard Hamiltonian into the local-spin-density approximation (LSDA+*U*). They also achieved an AF state with a band gap of 1.65 eV.

A common characteristic of all these calculations was a significant change in orbital character near the top of the valence band as compared to the standard LDA band structure. All of the above authors noted a large increase in either the apical oxygen ( $O'$ ) or Cu  $z^2$  density of states. While these results suggested the single-band ( $x^2-y^2$ ) picture of the LDA may not be an adequate starting point for the doping range of superconductivity, it was not immediately apparent that a more complicated band picture was consistent with the experimental data either. Unresolved was the difficult question of how to describe the doped state of the superconductor, which appears to produce a Fermi surface in the Brillouin zone of the single unit cell.<sup>9</sup> Removing electrons from a rigid band structure may be appropriate with the standard metallic state, but this procedure is less clear when starting from the undoped spin-polarized insulating band structure in the reduced Brillouin zone (doubled unit cell). Thus, the LDA band structure has remained the de facto standard in the field to this day.

In this work, we revisit the DFT band structure using the Becke-3–Lee-Yang-Parr (B3LYP) functional.<sup>10</sup> The superi-

ority of this hybrid functional, which includes a contribution of the exact Hartree-Fock exchange, has been well documented for molecular systems. Notably, Martin and Illas<sup>11</sup> showed the utility of such hybrid functionals in dramatically improving the calculation of the coupling constant  $J$  from cluster models of  $\text{La}_2\text{CuO}_4$ . Unfortunately, the method is still little used to determine band structures, partly because of the expense of such computations. We show here that spin-unrestricted B3LYP (U-B3LYP) leads to an AF band structure in agreement with the SIC-LSD and LSDA+ $U$  results cited above. This assuages doubts about that work and confirms the  $\text{Cu } z^2/\text{O}' p_z$  character at the Fermi level. Most importantly, this AF state is found to be 0.52 eV per formula unit more stable than the state calculated from the spin-restricted (R-B3LYP) functional. Considering the Hohenberg-Kohn theorem<sup>12</sup> requires the exact spin-restricted and spin-unrestricted functionals to yield identical total spatial densities ( $\rho_\uparrow + \rho_\downarrow$ ) and total energies, this discrepancy indicates a serious flaw in current functionals (B3LYP and LDA). Therefore, use of the LDA band structure to justify single-band models of superconductivity in the cuprates is highly questionable.

## RESULTS AND DISCUSSION

Calculations were performed using CRYSTAL98,<sup>13</sup> which employs an atomic Gaussian-type orbital basis set. For O, the standard 8-411G basis set with a  $D$  polarization exponent of 0.65 was used.<sup>14</sup> For Cu and La, the Hay-Wadt<sup>15</sup> effective core potentials (ECP's) were used. These ECP's treat explicitly the outer core ( $3s$  and  $3p$  for Cu,  $5s$  and  $5p$  for La) and valence electrons. The basis sets used with these ECP's were modified from the original basis sets of Hay and Wadt, since some functions are too diffuse for calculations on crystals. For Cu, the two diffuse  $S$  exponents were replaced by a single exponent optimized to 0.30 from LDA calculations on  $\text{La}_2\text{CuO}_4$ . The two Cu diffuse  $P$  exponents were replaced by a single exponent optimized to 0.20. The basis set was contracted to ( $3s3p3d$ ) based on atomic Cu(II) calculations. For La, the two diffuse  $S$  exponents were replaced with a single exponent optimized to 0.10. The two diffuse  $P$  exponents and the diffuse  $D$  exponent were removed without replacement. The basis set was contracted to ( $3s2p1d$ ) based on atomic La(III) and La(II) calculations. Overall, the quality of the basis set is superior to that used by Su *et al.*<sup>16</sup> in their CRYSTAL95 Hartree-Fock (HF) study of  $\text{La}_2\text{CuO}_4$ . Several alternative basis sets were tested, all leading to similar results. The tetragonal  $\text{La}_2\text{CuO}_4$  crystal structure was taken from Hazen.<sup>17</sup>

Figure 1 presents the results of our LDA and R-B3LYP calculations with restricted spin and tetragonal symmetry. The LDA band structure is in excellent agreement with previous plane-wave calculations<sup>1-3</sup> and there is little difference with the R-B3LYP band-structure result. As expected for restricted-spin calculations, both methods produce Pauli paramagnetic (PM) band structures. In each, the only band crossing the Fermi level is the highly 2D  $x^2-y^2$  band. The next band ( $z^2$ ) is approximately 1 eV below the Fermi level.

The lack of antiferromagnetic order in these band struc-

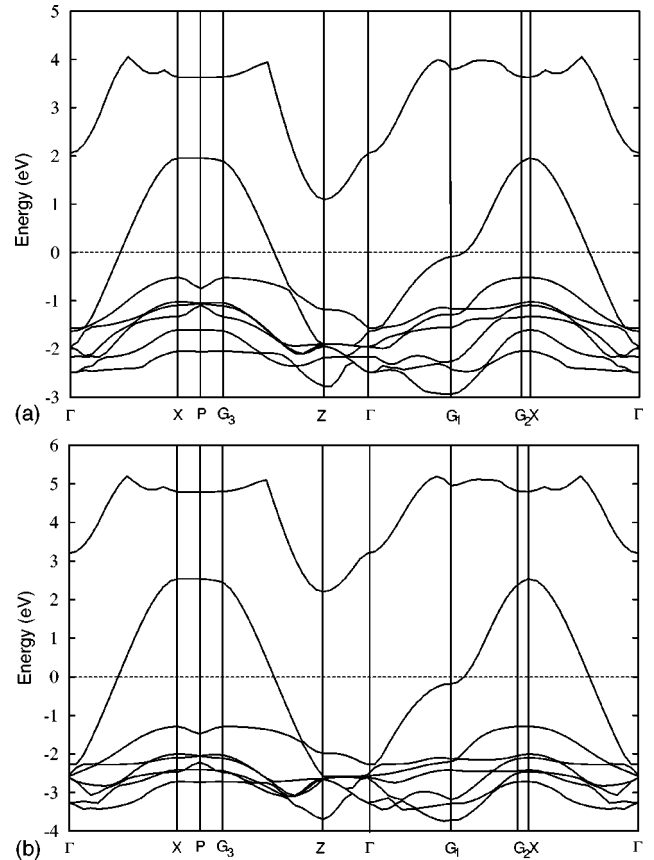


FIG. 1. Band dispersions of  $\text{La}_2\text{CuO}_4$  plotted along symmetry lines of the tetragonal Brillouin zone (see Ref. 1) from restricted spin (a) LDA and (b) R-B3LYP calculations. Results are in good agreement with the LDA computations of Refs. 1-3.

tures limits their usefulness for analyzing properties of the undoped material. On the other hand, such PM band structures may be entirely appropriate for understanding the nature of the doped state. Indeed, the LDA and R-B3LYP band structures seem to be consistent with some experimental data such as the angle-resolved photoemission spectroscopy (ARPES) Fermi surface,<sup>9</sup> but they remain incompatible with many other experiments. An analysis of the density of states shows the nature of the intrinsic undoped hole (lowest unoccupied states totaling 1 hole per formula unit) is 48%  $\text{Cu } x^2-y^2$  and 47%  $\text{O } p_\sigma$ . While we have not explicitly carried out computations on the doped state ( $x=0.15$ ), we can estimate the nature of the doped hole (highest occupied states totaling 0.15 electron) is 47%  $\text{Cu } x^2-y^2$ , 38%  $\text{O } p_\sigma$ , 6%  $\text{O}' p_z$ , and 5%  $\text{Cu } z^2$ . The relatively small amount of  $\text{O}'$  and  $z^2$  character in these orbitals is in keeping with most models for superconductivity in the cuprates. However, x-ray absorption studies (XAS) support a total  $z^2$  hole contribution of 5% to 20% and a similar range for  $\text{O}' p_z$ .<sup>18</sup> Details such as the ARPES pseudogap,<sup>19</sup> the anomalous background signal,<sup>20</sup> and other probes of the normal-state properties such as NMR,<sup>21</sup> resistivity,<sup>22</sup> and neutron scattering<sup>23</sup> also appear to have no explanation using this conventional band structure.

We find that a different state emerges under the unre-

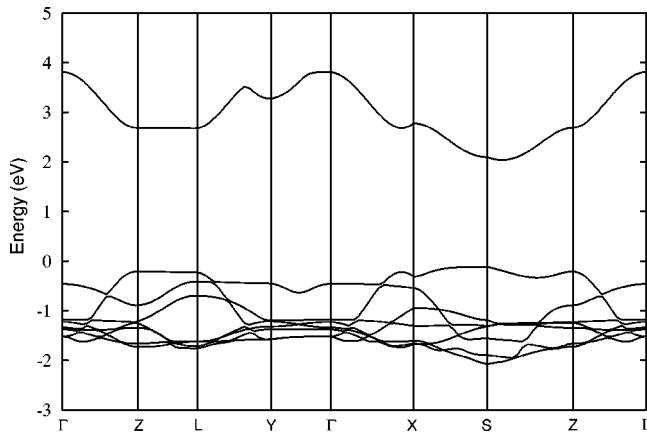


FIG. 2. Band dispersion plotted along symmetry lines of the orthorhombic Brillouin zone (see Ref. 8) from the unrestricted spin U-B3LYP calculation of  $\text{La}_2\text{CuO}_4$ . Results are in good agreement with the SIC-LSD and LSDA+ $U$  computations of Refs. 6–8.

stricted spin (U-B3LYP) implementation of this functional. Using an orthorhombic unit cell, the resulting band structure from these calculations is shown in Fig. 2. The combination of a spin functional and a doubled unit cell allows for a possible spin-polarized solution. Indeed, we find an apparent AF state with a gap of 2.0 eV. The band dispersion is in excellent agreement with previously published DFT band structures for this AF state,<sup>6–8</sup> and the computed gap agrees with the measured gap.<sup>5</sup> Furthermore, a U-B3LYP calculation of the FM state, which has a pure  $\uparrow$  spin per formula unit under tetragonal symmetry, is found to be 0.18 eV higher in energy. This compares favorably (noting caveats<sup>16</sup>) with the experimental  $J$  value of 0.13 eV.<sup>24</sup>

A principal advantage of this new U-B3LYP AF band structure is that it follows unambiguously using a well-established functional. No additional empirical corrections were necessary. Furthermore, while no comparison of the relative stabilities of the LDA state and the SIC-LSD (or LSDA+ $U$ ) state has been previously reported, such a comparison is rather straightforward with our calculations. Significantly, the U-B3LYP AF ground state and FM excited state are found to be 0.52 and 0.34 eV per  $\text{La}_2\text{CuO}_4$  formula unit more stable than the R-B3LYP state. This represents a rather dramatic failure on the part of the spin-restricted functional. Clearly the U-B3LYP calculation leads to a superior representation of the ground state of  $\text{La}_2\text{CuO}_4$ .

To better understand the significance of this 0.52-eV energy difference, one must consider the theoretical foundation of DFT. The Hohenberg-Kohn theorem<sup>10</sup> proves the existence of two functionals  $F_{\text{HK}}[\rho]$  and  $F_{\text{HK}}[\rho_{\uparrow}, \rho_{\downarrow}]$  where the first is a functional of the total density  $\rho = \rho_{\uparrow} + \rho_{\downarrow}$  and the second is a functional of the two spin densities  $\rho_{\uparrow}$  and  $\rho_{\downarrow}$ . For a spin-independent potential, the first functional will lead to the exact ground-state energy and total spatial density,  $\rho = \rho_{\uparrow} + \rho_{\downarrow}$ . For spin-dependent spatial potentials, the use of the second functional will lead to the ground-state energy and spin densities  $\rho_{\uparrow}$  and  $\rho_{\downarrow}$ . In addition,  $F_{\text{HK}}[\rho_{\uparrow}, \rho_{\downarrow}]$  can be used for the special case of a spin-independent potential

where it must obtain the same ground-state energy and total density  $\rho$  as  $F_{\text{HK}}[\rho]$ .

The Kohn-Sham orbitals arising from energy minimization for  $\text{La}_2\text{CuO}_4$  will be of restricted (doubly occupied) Hartree-Fock type for  $F_{\text{HK}}[\rho]$  with  $\rho(r) = 2\sum_{\text{occ}}|\phi_i(r)|^2$  and of unrestricted Hartree-Fock type for  $F_{\text{HK}}[\rho_{\uparrow}, \rho_{\downarrow}]$  where the  $\uparrow$ -spin orbitals may be different from the  $\downarrow$ -spin orbitals. Both minimizations should lead to exactly the same energy and ground-state total density  $\rho$ . If the R-B3LYP functional were close to  $F_{\text{HK}}[\rho]$  and the U-B3LYP functional were close to  $F_{\text{HK}}[\rho_{\uparrow}, \rho_{\downarrow}]$ , then the energies of the two calculations for  $\text{La}_2\text{CuO}_4$  should also be close.

Our computed 0.52-eV energy difference leads us to conclude that at least one of the two functionals is not close to the exact functional. Since the U-B3LYP band structure is an excellent description of the AF state, we are led to question the quality of the R-B3LYP functional.

It is well known in fact that spin-density-functional approximations to  $F_{\text{HK}}[\rho_{\uparrow}, \rho_{\downarrow}]$  are superior to total density approximations to  $F_{\text{HK}}[\rho]$  since it is much easier to empirically design functionals to correct for the exchange coupling of like spins when  $\rho$  is separated into  $\rho_{\uparrow}$  and  $\rho_{\downarrow}$ . In the restricted spin functionals, R-B3LYP and LDA, the improper treatment of exchange in strongly correlated systems leads to an overestimate of on-site Coulomb repulsion.

A classic example of the problems that occur with these functionals is the dissociation of  $\text{H}_2$ . At equilibrium distances, the molecule is well described both by closed-shell LDA and by B3LYP functionals. However, at the dissociation limit both functionals lead to an energy calculated to be higher than two H atoms due to the ionic components ( $\text{H}^+ + \text{H}^-$ ). With current functionals, to properly describe dissociation requires calculation of either the triplet state or the symmetry-broken unrestricted ‘‘singlet’’ spin state, either of which leads to net formation of magnetic moments on each H atom. This difference between the spin-restricted and -unrestricted functionals should not be considered a failure of density-functional theory. Instead, it is a failure of the empirical spin restricted functionals that have been developed so far.

By analogy to  $\text{H}_2$ , the FM state of undoped  $\text{La}_2\text{CuO}_4$  (where each site has a pure  $\uparrow$  spin) and the AF state (where each site has either a pure  $\uparrow$  or a pure  $\downarrow$  spin) are well described by the spin-unrestricted U-B3LYP functional. Using the spin-restricted formalism where each site is 50%  $\uparrow$  and 50%  $\downarrow$  (R-B3LYP) leads not only to an overestimate (0.52 eV per formula unit) of the total energy but also to an incorrect band structure. In particular, the  $x^2 - y^2$  band is elevated relative to the other bands as a result of the improper on-site Coulomb repulsion associated with the  $\text{Cu}x^2 - y^2/\text{O}p_{\sigma}$  orbital. Removing this repulsion through the localization of spins in either the FM or AF states stabilizes the  $x^2 - y^2$  band, resulting in an increase in  $z^2$  character near the top of the valence band.

As compared to the R-B3LYP state, the added stability of the U-B3LYP total energy by 0.52 eV is associated with an approximately 1-eV stabilization of the  $x^2 - y^2$  band with respect to the other bands. This is most noticeable in the nature of the doped hole. We characterize the U-B3LYP un-

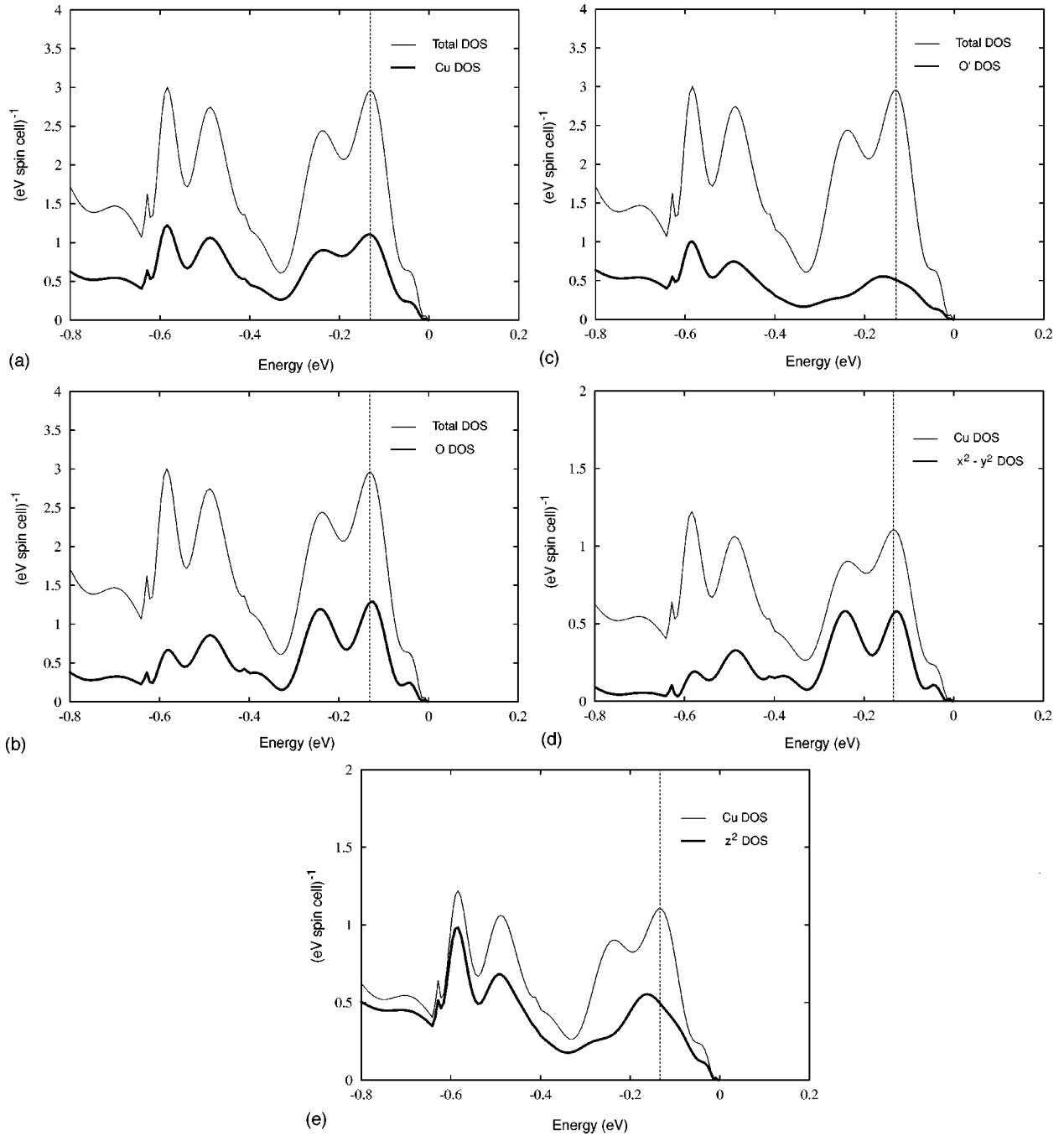


FIG. 3. Detail of the density of states from the unrestricted spin U-B3LYP AF calculation of  $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$  ( $x=0$ ). The Fermi level is positioned to a doping level of  $x=0.15$ . (a) Projected Cu density of states (DOS) vs total DOS. (b) Projected O DOS vs total DOS. (c) Projected O' DOS vs total DOS. (d) Projected Cu  $x^2-y^2$  DOS vs total Cu DOS. (e) Projected Cu  $z^2$  DOS vs total Cu DOS.

doped hole as 56% Cu  $x^2-y^2$  and 38% O  $p_\sigma$ , a picture not substantially different from the R-B3LYP calculation. The ratio of Cu  $x^2-y^2$ /O  $p_\sigma$  character is somewhat larger in the U-B3LYP state, but qualitatively both calculations agree that the undoped hole states are nearly purely derived from these two orbitals. The picture changes substantially upon considering the nature of the doped holes. Figure 3 presents a detail of the density of states in the vicinity of the Fermi level for the  $x=0.15$  doped state, assuming a rigid-band model. The nature of the doped hole is characterized as 17% Cu  $x^2$

$-y^2$ , 40% O  $p_\sigma$ , 21% O'  $p_z$ , and 19% Cu  $z^2$ . This is summarized in Table I. The significant increase in the Cu  $z^2$  and O'  $p_z$  character of the doped hole as compared to the R-B3LYP results is comparable to that noted in previous AF band structure calculations.<sup>4,6-8</sup> While doubts about the quality of the previous band structures undermined the significance of these findings, the cumulative weight of these results now strongly favors the scenario where  $z^2$  holes are formed upon doping.

While the U-B3LYP band structure may be a good repre-

TABLE I. Orbital character of intrinsic undoped holes (totaling 1 hole), doped holes (totaling 0.15 hole), and total holes at optimal doping (totaling 1.15 holes). Results are shown for both the restricted-spin R-B3LYP state and unrestricted spin U-B3LYP AF state.

Orbital	B3LYP			U-B3LYP		
	Undoped	Doped	Total	Undoped	Doped	Total
Cu $x^2-y^2$	48%	47%	48%	56%	17%	51%
O $p_\sigma$	47%	38%	46%	38%	40%	38%
O' $p_z$	1%	6%	2%	1%	21%	4%
Cu $z^2$	1%	5%	2%	0%	19%	3%

sensation of the AF ground state of undoped  $\text{La}_2\text{CuO}_4$ , we should not lose sight of the fact that ultimately a spin-restricted (total-density) functional should be equally successful. Indeed, a proper PM band structure is more useful in understanding the role of doping in superconductivity. In our view, such a band structure has yet to be achieved with DFT, leading many to conclude that Fermi-liquid theory has failed for these materials. The simpler answer might just be that LDA has failed. The calculations presented here demonstrate the shortcomings of these methods and suggest possible solutions. We might postulate the existence of a modified R-B3LYP functional that gives exactly the same total density and total energy as the U-B3LYP functional. The PM band structure associated with this new functional may be substantially different from the one we have calculated here. Elsewhere, we have already incorporated such a correction into a simple tight-binding model for the doped superconductor.<sup>25</sup> By effectively introducing a local magnetic moment at each Cu site within a PM model of optimally doped  $\text{La}_{1.85}\text{Sr}_{0.15}\text{CuO}_4$ , we showed that the  $x^2-y^2$  band is significantly stabilized relative to the other bands. This brings the

narrow  $z^2$  band to the Fermi level. The resulting band structure has a unique crossing between the 2D-like  $x^2-y^2$  band and the 1D-like  $z^2$  band. This reflects a dramatic first-order correction to the standard band structure. Indeed, this model has already been used to interpret the ARPES pseudogap and anomalous background,<sup>26</sup> the NMR Cu and O relaxations and Knight shifts,<sup>27</sup> the Hall effect, and Josephson tunneling.<sup>28</sup>

## CONCLUSIONS

In summary, we have presented the results of R-B3LYP and U-B3LYP band-structure calculations on  $\text{La}_2\text{CuO}_4$ . The R-B3LYP results are in good agreement with previous LDA calculations and the U-B3LYP results are in good agreement with previous SIC-LSD calculations (among others). The large discrepancy in energy between the two states (0.52 eV per formula unit) is attributed to an improper overestimate of on-site Coulomb repulsion within the spin-restricted calculations. The automatic correction of this error within the U-B3LYP AF state leads to the stabilization of the  $x^2-y^2$  band relative to the other occupied bands. As a result, the  $z^2$  band is then brought to the top of the valence band and contributes significantly to the doped hole states. These results cast significant doubt on the continued use of LDA band structures as the starting point for theories of superconductivity in these materials.

## ACKNOWLEDGMENTS

We wish to acknowledge helpful discussions with Dr. Francesco Faglioni and Dr. Eugene Heifets. This work was partially supported by the Materials and Process Simulation Center (MSC) at Caltech, which is supported by grants from DOE-ASCI, ARO/DURIP, ARO/MURI, 3M, Beckman Institute, Seiko-Epson, Dow, Avery-Dennison, Kellogg, and Asahi Chemical.

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