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# Direct first principles calculations of $d \rightarrow d$ excitation energies in pure and hole-doped $\text{Sr}_2\text{CuO}_2\text{Cl}_2$

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## Abstract

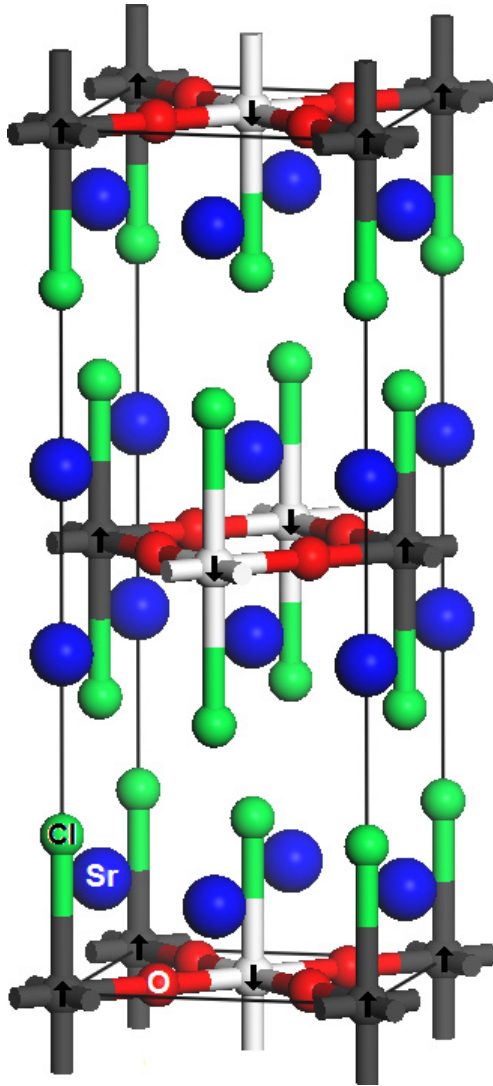
Direct first principles calculations are conducted for the three spin-allowed  $d \rightarrow d$  excitations in pure and hole-doped antiferromagnetic  $\text{Sr}_2\text{CuO}_2\text{Cl}_2$ . The results obtained for the pure system are close to the resonant x-ray Raman spectra reported by Kuiper *et al* (1998 *Phys. Rev. Lett.* **80** 5204), most notably in respect of the  $d_{z^2} \rightarrow d_{x^2-y^2}$  state, which was not observed directly. The energy of 1.53 eV computed for this excitation is in good agreement with the value 1.5 eV deduced from the Raman experiment, and both of these lie well above the energy 0.5 eV suggested previously on the basis of the optical spectrum (Perkins *et al* 1993 *Phys. Rev. Lett.* **71** 1621). The associated spin-flip energy of approximately 0.2 eV proposed by Kuiper *et al* is shown to be entirely consistent with the observed Néel temperature and with first principles calculations, and further, that it corresponds to the flip of an unpaired  $d_{x^2-y^2}$  spin in the ground state rather than a  $d_{z^2}$  spin in the excited state. The two  $t_{2g} \rightarrow e_g$  excitation energies in the current UHF calculations differ by approximately 0.25 eV from the Raman values, an amount ascribed to the difference in pair correlation energies. In addition, hybrid functional calculations incorporating varying contents of exact exchange are found to offer no systematic improvement. The presence of a nearest neighbour hole in the most stable O(p) configuration is shown to have no significant effect upon either the order or the stability of the  $d \rightarrow d$  states, with changes in excitation energy of 0.1–0.2 eV. A comparison with previous cluster calculations indicates that the latter do not capture fully the effect of the surrounding lattice on these highly local excitations. The generality of the direct approach to excitations is further established by calculations of the energies of three nearest neighbour charge-transfer states, which are placed in the range from 5.3 to 5.6 eV, as compared with values around 5 eV predicted previously (Tanaka and Kotani 1993 *J. Phys. Soc. Japan* **62** 464). The  $d \rightarrow d$  and charge-transfer excitations produce extensive renormalization of the valence levels that lead to substantial reductions in energy from the rigid-band estimates based on the ground state eigenvalue spectrum.

## 1. Introduction

A knowledge of elementary excitations has been a time-honoured quest in solid state physics. Whether as an end in itself, or for their possible involvement in other, more complex phenomena, a detailed understanding of these processes is

generally accepted as constituting an important component of our understanding of the electronic structure of specific systems. Following earlier studies of the optical spectra of  $\text{Sr}_2\text{CuO}_2\text{Cl}_2$  (structure shown in figure 1) by Perkins *et al* [1], in which it was surmised that the  $d_{z^2} \rightarrow d_{x^2-y^2}$  excitation occurred at  $\sim 0.5$  eV, with possible implications for the mechanism of superconductivity in the doped system, Kuiper *et al* [2] reported the resonant x-ray Raman spectra, from which they assigned directly the  $d_{xy} \rightarrow d_{x^2-y^2}$  and degenerate

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**Figure 1.** The magnetic unit cell of  $\text{Sr}_2\text{CuO}_2\text{Cl}_2$ . Black, white, red, green and blue spheres represent  $\text{Cu}(\uparrow)$ ,  $\text{Cu}(\downarrow)$ , O, Cl and Sr atoms respectively. The spins of the Cu atoms are shown as arrows.

(This figure is in colour only in the electronic version)

$d_{yz} \rightarrow d_{x^2-y^2}$  and  $d_{xz} \rightarrow d_{x^2-y^2}$  transitions at 1.35 eV and 1.7–1.8 eV respectively and inferred a value of 1.5 eV for the  $d_{z^2} \rightarrow d_{x^2-y^2}$  transition. Using theoretical arguments they showed the latter to be accompanied by a spin-flip which increased the energy by 0.2 eV, thereby denying its direct assignment from the x-ray Raman spectra. While the case made by the latter authors [2] for the last of these assignments well above the previous suggestion [1] appears to be both robust and convincing, independent support of this view, or otherwise, would be useful. Furthermore, while it is reasonable to assume that the  $d \rightarrow d$  excitonic properties of pure  $\text{Sr}_2\text{CuO}_2\text{Cl}_2$  remain essentially unchanged in the hole-doped (superconducting) system, this may not be precisely the case, so that the possible involvement of the  $d_{z^2} \rightarrow d_{x^2-y^2}$  excitation in the superconducting mechanism is not completely resolved. Accordingly, in this article we report, for the first time, direct first principles calculations of the Cu  $d \rightarrow d$  excitations in pure and hole-doped  $\text{Sr}_2\text{CuO}_2\text{Cl}_2$ , which, we believe, both

clarifies the position with regard to the energy of the  $d_{z^2} \rightarrow d_{x^2-y^2}$  excited state in this model high  $T_c$  cuprate and also contributes, more generally, to an understanding of electronic excitation process in strongly ionic systems. A formal basis for our approach to these highly atomic excitations is contained within Kanamori–Brandow analyses of the local d-electron configurations, which show these to be quite different in the ground and excited states, therein necessitating their separate evaluation.

In previous studies of NiO [3, 4], it has been shown that direct first principles, spin-polarized, periodic Hartree–Fock (UHF) calculations of the ground and variationally minimized excited states based on localized, Gaussian orbitals [5] give a qualitatively correct description of both the one- and two-electron Ni  $d \rightarrow d$  excitations in the bulk and, perhaps more significantly, their modification at the (001) surface. In particular, a surface shift of  $\sim 50\%$  was predicted for the  $(t_{2g}^6 e_g^2) \rightarrow (t_{2g}^5 e_g^3)$  ( ${}^3A_{2g} \rightarrow {}^3T_{2g}$ ) excitation and that the two-electron excitation,  $(t_{2g}^6 e_g^2) \rightarrow (t_{2g}^4 e_g^4)$  ( ${}^3A_{2g} \rightarrow {}^3T_{1g}$ ), occurs at lower energy than the one-electron excitation,  $(t_{2g}^6 e_g^2) \rightarrow (t_{2g}^5 e_g^3)$  ( ${}^3A_{2g} \rightarrow {}^3T_{1g}$ ), in the bulk and at the (001) surface, all in excellent agreement with experiment [4]. Similar, direct UHF calculations [6] of Cu  $d \rightarrow d$  excitations in the quasi-one-dimensional, spin-1/2 Heisenberg antiferromagnet,  $\text{Sr}_2\text{CuO}_3$ , in which the local symmetry at Cu is  $D_{4h}$ , as it is in  $\text{Sr}_2\text{CuO}_2\text{Cl}_2$ , found these to lie in the range 1.26–2.20 eV, which is comparable to the resonant Raman energies reported in [2]. Here the  $d_{z^2} \rightarrow d_{x^2-y^2}$  energy was predicted to be 2.20 eV, but as far as we are aware, this system remains unstudied experimentally in that respect. More recently [7], we have obtained  $d \rightarrow d$  excitation energies for NiO within Becke–LYP hybrid exchange–correlation functionals, and found no significant improvement on the UHF energies. Furthermore, it was observed that the stability limits of the excited states occurred between 30% and 40% exact exchange, precluding any estimates of the pure DFT excitation energies.

Direct first principles, periodic calculations of bulk  $d \rightarrow d$  excitations, however, have been a minority pursuit, with more extensive studies based on embedded clusters of the type  $(\text{NiO}_6)^{10-}$ , including calculations based on the multi-reference CEPA [8] and CASSCF/CASPT2 [9, 10] methods. Such approaches go beyond the UHF theory in that they include large fractions of the electron correlation, which must contribute to excitation energies to an extent that depends upon the system and transitions under study. Clusters of this size, however, cannot be expected to capture all of the effects manifesting in the extended lattice, including long-range magnetic order and the presence of neighbouring defects. Importantly, such comparisons as have been made in the case of NiO [4], show that the accuracy of high level cluster calculations compared with experiment is no better than that of periodic UHF calculations. This suggests that, in these systems at least, the contributions to the excitation energies due to the extended lattice are comparable in magnitude to those from electron correlation.

**Table 1.** Sr<sub>2</sub>CuO<sub>2</sub>Cl<sub>2</sub> AF ground and excited state UHF atomic charges,  $q_\alpha$  ( $e$ ), d-orbital populations,  $n_\alpha$  and Cu spin moments,  $n_s$  ( $\mu_B$ ).

State	$q_{Sr}$	$q_{Cu}$	$q_O$	$q_{Cl}$	$n_{xy}$	$n_{xz/yz}$	$n_{z^2}$	$n_{x^2-y^2}$	$n_s$
Ground	2.03	1.83	1.92	1.03	2.00	2.00	1.99	1.01	0.92
$d_{xy} \rightarrow d_{x^2-y^2}$	2.03	1.89	1.93	1.03	1.02	2.00	2.00	2.03	0.98
$d_{z^2} \rightarrow d_{x^2-y^2}$	2.03	1.89	1.93	1.03	2.00	2.00	1.02	2.03	0.98
$d_{xz}/d_{yz} \rightarrow d_{x^2-y^2}$	2.03	1.90	1.93	1.03	2.00	1.02	2.01	2.03	0.99

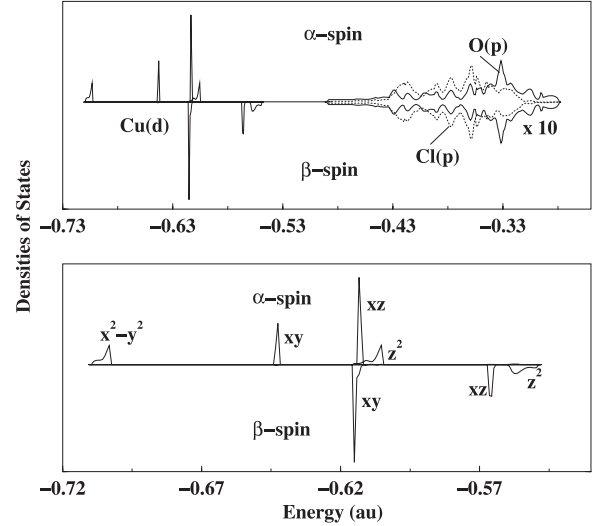
## 2. Computational methods

The computational conditions adopted in our CRYSTAL98 code [5] calculations are similar to those used previously [3, 4, 6, 7], including truncation thresholds for Coulomb overlap and penetration, and exchange overlap and two pseudo-overlap integrals of  $10^{-7}$ ,  $10^{-7}$ ,  $10^{-7}$ ,  $10^{-7}$  and  $10^{-14}$  respectively [5], Monkhorst–Pack reciprocal space sampling with a shrinking factor of 8, and a total energy convergence of  $10^{-6}$  Hartree. Our calculations refer to the experimental  $I4/mmm$  structure of Sr<sub>2</sub>CuO<sub>2</sub>Cl<sub>2</sub> [11, 12], and we note in particular that the interatomic distances adopted in the current study are identical to those used in the earlier correlated cluster calculations [19], permitting a direct comparison of excitation energies. The atomic Gaussian functions comprising the Sr, Cu and O basis sets are those used previously for Sr<sub>2</sub>CuO<sub>3</sub> [6], with the addition of an optimized 1s(8), 2sp(6), 3sp(3), 4sp(1), 5sp(1) set for Cl, where the values in parentheses denote the number of primitive functions included in the shell. As on previous occasions [3, 4, 6, 7], our approach to local defects is based on the use of periodic supercells of varying size, from which the energies and properties of isolated defects can be extracted. We emphasize again that the energies of the d  $\rightarrow$  d and charge transfer excitations are obtained directly from the differences in total energies of the individual, variationally minimized ground and excited states. This procedure has been widely used in the context of molecular calculations, where it would usually be termed a ‘ $\Delta$ (SCF)’ approach, but we note that it has rarely been applied in the solid state. The representation of the degenerate  $d_{yz} \rightarrow d_{x^2-y^2}$  and  $d_{xz} \rightarrow d_{x^2-y^2}$  transitions requires that the lattice symmetry be reduced. The accuracy of the CRYSTAL98 code is such that the energies of the  $d_{xy} \rightarrow d_{x^2-y^2}$  and  $d_{z^2} \rightarrow d_{x^2-y^2}$  transitions remain unchanged within this broken symmetry. No further symmetrization of the excitations has been applied.

## 3. Results

### 3.1. Excitations in the neutral lattice

UHF calculations predict the ground state of Sr<sub>2</sub>CuO<sub>2</sub>Cl<sub>2</sub> to be a highly ionic,  $d^9$  antiferromagnetic (AF) insulator in which the singly occupied  $d_{x^2-y^2}$  orbital lies in the CuO<sub>2</sub> planes and is oriented along the Cu–O bonds. The hypothetical ferromagnetic (FM) spin arrangement, which is also insulating in contrast with the results of previous LMTO [13] and FLMTO [14] calculations, is 26.5 meV per formula unit higher in energy. Atomic charges, d-orbital populations and local Cu spin moments, calculated by the Mulliken prescription, are collected in table 1, where the overall ionic character



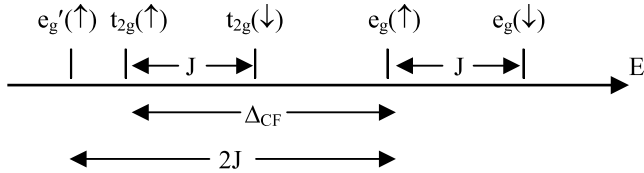
**Figure 2.** Upper panel: AF ground state Cu(d), O(p) and Cl(p) valence band densities of states of Sr<sub>2</sub>CuO<sub>2</sub>Cl<sub>2</sub>. Lower panel: expanded Cu(d) densities of states.

and highly atomic nature of the d manifold are both evident, in agreement with recent UHF calculations by Moreira and Dovesi [15]. Atom projected valence band densities of states, shown in the upper panel of figure 2, confirm the strong ionicity in Sr<sub>2</sub>CuO<sub>2</sub>Cl<sub>2</sub> revealing overlapping O(p) and Cl(p) bands spread over  $\sim 6.5$  eV from the Fermi level, with the Cl(p) upper edge shifted by  $\sim 1$  eV. The Cu(d) bands, which range from  $\sim -8$  eV to  $\sim -12$  eV, are each extremely narrow, in keeping with their highly atomic character. The conduction band edge is predominated by  $d_{x^2-y^2}$  states, so that the band gap of  $\sim 15$  eV is essentially of p  $\rightarrow$  d character, in keeping with the Zaanen–Sawatzky–Allen (ZSA) classification of the first row transition metal chalcogenides [16]. Once again, this contrasts with previous LMTO calculations [13, 14], which find Sr<sub>2</sub>CuO<sub>2</sub>Cl<sub>2</sub> to be a Mott–Hubbard system. The lower panel of figure 2 shows the projected densities of states of the Cu d levels where their juxtaposition indicates clear orbital polarization linked to strong on-site Coulomb ( $U$ ,  $U'$ ) and exchange ( $J$ ) interactions. Now a Kanamori–Brandow [17] analysis of a  $d^9[(t_{2g})^6(e_g)^2(e'_g)^1]$  configuration in the more symmetric O<sub>h</sub> crystal field indicates that the energies of the individual d levels depend on the relative magnitudes of the crystal field splitting  $\Delta_{CF}$  and the average on-site exchange energy,  $J$ . Specifically, for  $2J > \Delta_{CF} > J$ , the filled d-level

**Table 2.** Variations,  $\delta E$  (eV), relative to the fully excited lattice of single  $d \rightarrow d$  excitation energies in supercells containing  $NSr_2CuO_2Cl_2$  formula units.

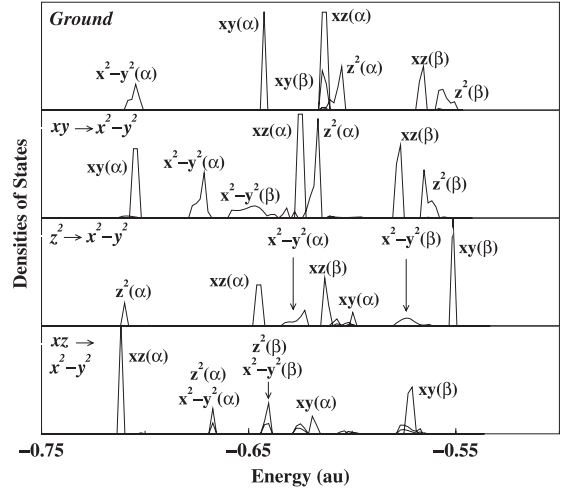
Supercell	$N$	$\delta E_{xy \rightarrow x^2-y^2}$	$\delta E_{z^2 \rightarrow x^2-y^2}$	$\delta E_{xz/yz \rightarrow x^2-y^2}$
2 Cu in plane	2	+0.002	-0.013	-0.008
2 Cu in plane 2 in plane above	4	0.000	-0.018	-0.010
8 Cu in plane	8	0.000	-0.018	-0.010
4 Cu in plane 4 in plane above	8	0.000	-0.017	-0.010

spectrum is of the form



This is broadly similar to the calculated spectrum shown in figure 2, with  $e'_g \equiv d_{x^2-y^2}$  and  $e_g \equiv d_{z^2}$ , but modified by the reduced  $D_{4h}$  symmetry of Cu in  $Sr_2CuO_2Cl_2$ , so that the  $e'_g(\uparrow) - e_g(\uparrow)$  separation is  $(U-U')$  and the splitting of the doubly occupied  $d_{xy}$ ,  $d_{xz}/d_{yz}$  and  $d_{z^2}$  bands are 0.7, 1.2 and 1.4 eV respectively and not all equal. It is immediately clear that in the  $d_{z^2} \rightarrow d_{x^2-y^2}$  excited state, for example, the  $e'_g$  and  $e_g$  levels are inverted, thus ruling out the possibility of any type of rigid-band prediction of the spin-allowed  $d \rightarrow d$  excitations from the ground state eigenvalues. This would put the excited states in the order  $d_{z^2} \rightarrow d_{x^2-y^2} < d_{xz}/d_{yz} \rightarrow d_{x^2-y^2} < d_{xy} \rightarrow d_{x^2-y^2}$ , which is exactly the reverse of the observed order, with energies of  $\sim 25$  eV, which is more than an order of magnitude greater than the experimental (and directly calculated) values. Furthermore, the  $d \rightarrow d$  states would be predicted to be higher in energy than the charge-transfer states, which Tanaka and Kotani [18] have estimated to be in the region of 5 eV.

Similar calculations to those for the ground state, employing identical computational conditions, find the three spin-allowed  $d \rightarrow d$  excited states in the AF alignment to be variationally stable, i.e. local minima, by direct minimization of the total energies, as reported previously for NiO [3, 4, 7] and  $Sr_2CuO_3$  [6]. As shown in table 1, the ionicity of these states is practically identical to that of the ground state, with conservation of the total d population and local spin moment. Changes in the individual d-orbital populations, which are within 2% of  $\pm 1$ , are characteristic of highly local atomic transitions corresponding to fully localized Frenkel excitons. Direct total energy differences between the AF ground and excited states lead to UHF energies of 1.10, 1.53 and 1.57 eV for the  $d_{xy} \rightarrow d_{x^2-y^2}$ ,  $d_{z^2} \rightarrow d_{x^2-y^2}$  and  $d_{xz}/d_{yz} \rightarrow d_{x^2-y^2}$  excitations respectively, which, as presaged from the Kanamori–Brandow analysis of the ground state, indicates strong renormalization of the electronic configuration in the excited state. As a check on the effect of defect–defect interactions in our supercell approach, we have compared the energies of single excitations in supercells of varying size with those of the fully excited lattice. The results collected in table 2 indicate that the excitations are highly local, with energies that vary by less than 0.02 eV across the range of



**Figure 3.** Comparison of AF ground and  $d \rightarrow d$  excited state Cu(d) densities of states.

concentrations. We note that these energy differences lie well below the experimental accuracy [2].

If we now make the reasonable assumptions that whereas the leading correction to the  $e_g \rightarrow e'_g$  excitation energy, namely the difference between the  $(d_{z^2})^2$  and  $(d_{x^2-y^2})^2$  pair correlation energies, can be neglected by comparison with that to the two  $t_{2g} \rightarrow e_g$  excitations, which involve differences between  $(d_{x^2-y^2})^2$ , and  $(d_{xy})^2$  and  $(d_{xy})^2/(d_{yz})^2$  pair correlation energies, and that the corrections to the two  $t_{2g} \rightarrow e_g$  excitations are identical, we arrive at an empirical correlation correction of 0.25 eV for the latter, leading to values of 1.35, 1.53 and 1.82 eV for the energies of the three  $d \rightarrow d$  excited states of  $Sr_2CuO_2Cl_2$ . Thus our calculations fully support the conclusion of Kuiper *et al* [2] that the energy of the  $d_{z^2} \rightarrow d_{x^2-y^2}$  excited state is close to 1.5 eV and not in the mid-infrared at  $\sim 0.5$  eV, as suggested previously [1]. Figure 3 shows the projected densities of valence band states for the three excitations compared with the ground state, from which the origin of the strong renormalization is evident. In addition to the largely uniform relaxation of the O(p) and Cl(p) states, there is extensive reorganization of the Cu d manifold driven by the changes in the on-site Coulomb and exchange interactions, which UHF calculations treat exactly, and it is these adjustments, notably those of the local d states, that lead to the substantial reductions in energy from the rigid band values. Figure 3 also shows that while the excited state d-level structures differ quite clearly from that of ground state, the effects of orbital occupancy and crystal field asymmetry are



**Table 3.** Comparison of the energies (eV) of the three spin-allowed  $d \rightarrow d$  excited states in  $\text{Sr}_2\text{CuO}_2\text{Cl}_2$  from first principles periodic and cluster calculations [19].

Excitation	Periodic UHF	Corrected <sup>a</sup>		Raman [2]
		periodic UHF	Correlated cluster [19]	
$d_{xy} \rightarrow d_{x^2-y^2}$	1.10	1.35	1.23	1.35
$d_{z^2} \rightarrow d_{x^2-y^2}$	1.53	1.53	1.18	1.5
$d_{xz}/d_{yz} \rightarrow d_{x^2-y^2}$	1.57	1.82	1.50	1.7–1.8

<sup>a</sup> Correlation correction to UHF value fitted to experiment.

**Table 4.** Predicted energies (eV) of the spin-allowed  $d \rightarrow d$  excited states in  $\text{Sr}_2\text{CuO}_3$ .

Excitation	Corrected <sup>a</sup>	
	periodic UHF	Correlated cluster [14]
$d_{xy} \rightarrow d_{x^2-y^2}$	1.51	1.08
$d_{yz} \rightarrow d_{x^2-y^2}$	2.12	1.53
$d_{xz} \rightarrow d_{x^2-y^2}$	2.18	1.67
$d_{z^2} \rightarrow d_{x^2-y^2}$	2.20	2.11

<sup>a</sup> Correlation correction to UHF value fitted to experiment.

the same. For all three excited states the singly occupied band is lowest in energy and there is unequal spin-splitting of the four doubly occupied bands in each case. Thus our calculations show quite clearly why the ground state eigenvalue spectrum cannot be taken to provide even a crude predictive guide to the  $d \rightarrow d$  spectra.

As was previously the case for NiO [4], it is instructive to compare our results with the correlated cluster calculations reported by de Graaf and Broer [19] for the insight this offers into the influence of the extended surrounding lattice, even for such highly local excitations. We note that the meaningfulness of this comparison rests upon the reasonable convergence of the present and previous calculations with respect to basis set size and other numerical parameters. These authors found energies of 1.23, 1.18 and 1.50 eV for the  $d_{xy} \rightarrow d_{x^2-y^2}$ ,  $d_{z^2} \rightarrow d_{x^2-y^2}$  and  $d_{xz}/d_{yz} \rightarrow d_{x^2-y^2}$  respectively, which are incorrect with respect to the order of the excited states and too low by 0.12–0.3 eV, although, importantly, they do support the view that the  $d_{z^2} \rightarrow d_{x^2-y^2}$  excitation is not in the mid-infrared region. Table 3 shows that the clusters used by de Graaf and Broer [19], which enable the inclusion of a substantial fraction of the correlation energy, underestimate the effect of the extended surrounding lattice by roughly as much as our empirically deduced correlation energy. While the magnitude of this underestimate might be considered to be small, it can result in a qualitatively different picture of the low energy spectrum from that derived from periodic calculations. In the case of  $\text{Sr}_2\text{CuO}_3$ , for example, for which the periodic UHF  $d \rightarrow d$  excitation energies have been reported previously [6], the inclusion of the correlation corrections deduced here suggests that the  $d \rightarrow d$  excitations all lie above the insulating gap of  $\sim 1.5$  eV reported by Maiti *et al* [20], whereas cluster calculations [19] suggest that the  $d_{xy} \rightarrow d_{x^2-y^2}$  excitation lies below the absorption edge, as indicated in table 4.

**Table 5.** Variations,  $\delta E$  (eV), relative to the UHF values in the  $d_{xy} \rightarrow d_{x^2-y^2}$ ,  $d_{z^2} \rightarrow d_{x^2-y^2}$  and  $d_{xz}/d_{yz} \rightarrow d_{x^2-y^2}$  excitation energies for Becke–LYP hybrid functionals incorporating varying proportions,  $F_0$  (%), of exact exchange.

$F_0$	$\delta E_{xy} \rightarrow x^2 - y^2$	$\delta E_{z^2} \rightarrow x^2 - y^2$	$\delta E_{xz/yz} \rightarrow x^2 - y^2$
100	+0.010	+0.009	+0.001
90	+0.044	+0.039	+0.035
80	+0.085	+0.076	+0.076
70	+0.135	+0.123	+0.126
60	+0.197	+0.183	+0.189
50	+0.272	+0.258	+0.264
40	+0.361	+0.350	+0.350
30	+0.457	+0.452	+0.432

Both for completeness and in view of the current interest in HF–DFT hybrid functionals, we have carried out identical calculations to those reported above with Becke–LYP hybrid Hamiltonians incorporating variable amounts of exact exchange [21]. Our results are contained in table 5, from which a number of points emerge. First there is a more-or-less uniform and monotonic increase in the three excitation energies from the UHF values as the amount of exact exchange is reduced to  $\sim 30\%$ , which appears to be the stability limit of the excited states. A similar limit was found for the  $d \rightarrow d$  excited states in NiO [7]. In the range 50%–60% exact exchange, the increases in excitation energy are close to the 0.25 eV correction suggested earlier for the  $t_{2g} \rightarrow e_g$  excitations in the UHF method, and ascribed to the difference between the  $t_{2g}$  and  $e_g$  pair correlation energies. However, these improvements are at the expense of the  $z^2 \rightarrow x^2 - y^2$  energy, which moves steadily further from the estimated experimental value of 1.5 eV as the exact exchange content falls. Thus, overall, the use of hybrid functionals would appear to offer little systematic improvement over UHF calculations, as reported previously for NiO [7].

### 3.2. Spin-flip energy

In their assignment of the  $d_{z^2} \rightarrow d_{x^2-y^2}$  excitation, which is not observed directly in the x-ray Raman spectra, a crucial step in the argument invoked by Kuiper *et al* [2] is that the excitation is accompanied by a local spin-flip which increases the energy by  $\sim 0.2$  eV to a value close to that observed for  $d_{xz}/d_{yz} \rightarrow d_{x^2-y^2}$ , thereby denying its direct observation. To address the origin and magnitude of this spin-flip energy, we invoke a simple Ising model to describe the magnetism. For a spin Hamiltonian of the form,

$$H_{\text{spin}} = \frac{J}{2} \sum_{ij}^{\text{nn}} \sigma_i \sigma_j,$$

in which the summation runs over nearest neighbour (nn) Cu atoms,  $\sigma_i$  and  $\sigma_j$  are spin variables with values of  $\pm 1$  and  $J$  is the superexchange coupling between nn spins, the mean field disorder temperature is given by  $2J/k_B$ . Simple scaling by the known, geometry-specific factor 0.56 to account for the effect of fluctuations [22] leads to a Néel temperature,  $T_N$ , of  $\sim 1.12J/k_B$ . Now Vaknin *et al* [12] have reported

**Table 6.** Energies (eV) of the three spin-allowed  $d \rightarrow d$  excited states nearest neighbour to  $\pi_{\parallel}$ ,  $\pi_{\perp}$  and  $\sigma$  O(p) holes in AF  $\text{Sr}_2\text{CuO}_2\text{Cl}_2$  compared with the defect free values.

Excitation	$p(\uparrow)-d(\downarrow)$			$p(\uparrow)-d(\uparrow)$			Defect free <sup>a</sup>
	$\pi_{\parallel}$	$\pi_{\perp}$	$\sigma$	$\pi_{\parallel}$	$\pi_{\perp}$	$\sigma$	
$d_{xy} \rightarrow d_{x^2-y^2}$	1.31	1.30	1.24	1.39	1.33	0.86	1.35
$d_{z^2} \rightarrow d_{x^2-y^2}$	1.31	1.39	1.44	1.36	1.41	0.76	1.53
$d_{xz}/d_{yz} \rightarrow d_{x^2-y^2}$	1.62	1.64	1.47	1.66	1.68	1.07	1.82

<sup>a</sup> Correlation correction to UHF value fitted to experiment.

$T_N$  for  $\text{Sr}_2\text{CuO}_2\text{Cl}_2$  to lie in the range 251–310 K, from which we deduce values of  $\sim 19$  to  $\sim 24$  meV for  $J$  in the AF ground state, or more specifically, for the superexchange between two Cu  $d_{x^2-y^2}$  spins. The energy required to flip a single spin in the AF alignment is obtained from  $H_{\text{spin}}$  as  $8J$ , amounting to  $\sim 0.15$  to  $\sim 0.19$  eV based on the values for  $J$  deduced from the Néel temperature. Even allowing for the approximate nature of our deduction, we believe our estimate is supportive of the value proposed by Kuiper *et al* [2]. This suggests that the increase in energy of  $\sim 0.2$  eV for the  $d_{z^2} \rightarrow d_{x^2-y^2}$  excitation in the resonant x-ray Raman spectra of  $\text{Sr}_2\text{CuO}_2\text{Cl}_2$  is due essentially to the flip of a  $d_{x^2-y^2}$  spin in the AF ground state rather than a  $d_{z^2}$  spin in the excited state. UHF calculations lend further support to this interpretation, for while the directly calculated ground state spin-flip energy of 0.05 eV would appear to be too low by a factor of four, the energy to flip a  $d_{z^2}$  spin in the excited state is predicted to be  $\sim 0.002$  eV, which is much lower still. We note that Moreira and Dovesi have reported a similar underestimate of the UHF coupling constants [15]. However, Moreira *et al* [23] have shown that the replacement of the exact (UHF) exchange by a hybrid of 35% exact and 65% functional exchange, including correlation, leads to marked improvements on UHF superexchange constants in NiO. Following their prescription, but retaining all the other computational conditions used in our UHF calculations, we find a value of 32.73 meV for  $J$ , corresponding to a ground state spin-flip energy of 0.26 eV, which again confirms the value proposed by Kuiper *et al* [2].

### 3.3. Excitations in the hole-doped lattice

Turning now to hole-doped  $\text{Sr}_2\text{CuO}_2\text{Cl}_2$ , we adopt the same approach to that used previously for other magnetic oxides [24, 25], including  $\text{Sr}_2\text{CuO}_3$  [6], wherein variationally minimized states are sought for singly ionized supercells in which the Coulomb singularity has been removed by inclusion of a uniform charge-compensating background [26]. This has no effect upon either charge or spin distributions nor, importantly here, upon the total energy differences separating distinct states of the system bearing the same net charge. Operating under identical computational conditions to those for the ground and  $d \rightarrow d$  excited states, we find the lowest energy free hole to be essentially of O(p) character (i.e.  $\sim d^9\bar{L}$ ), in accord with the ground state densities of states, with the lowest energy state  $\pi$ -polarized in the  $\text{CuO}_2$  planes ( $\pi_{\parallel}$ ) and with  $\sim 84\%$  of the charge density and  $\sim 98\%$  of the spin density localized at a single O site. We have also found two excited O(p) states with  $\pi_{\perp}$  and  $\sigma$  polarizations, 0.2

and 0.9 eV respectively higher in energy. These results are adequately converged with respect to isolation of the holes: similar calculations in the largest supercell of table 2 yield relative energies for  $\pi_{\perp}$  and  $\sigma$  states that differ only marginally from those given above. The charge and spin densities of the  $\pi_{\perp}$  state are very similar to those of the  $\pi_{\parallel}$  state, but are more dispersed in the high energy  $\sigma$  state, though still essentially localized. Apart from the changes in the charge and spin densities at the hole site, all other atomic charges, d-orbital populations and local Cu spin moments remain within 2% of the (neutral) ground state values. As before, a naive rigid-band prediction of the spin-allowed  $d \rightarrow d$  excitations nearest neighbour to the hole site put these in the order  $d_{z^2} \rightarrow d_{x^2-y^2} < d_{xz}/d_{yz} \rightarrow d_{x^2-y^2} < d_{xy} \rightarrow d_{x^2-y^2}$ . We have also obtained variationally stable Cl(p) and Cu(d) holes, at energies 2.3 and 4.6 eV respectively above the O( $p\pi_{\parallel}$ ) state, but have not pursued their influence, if any, on the  $d \rightarrow d$  excited states.

Once again UHF calculations employing identical computational conditions find the three spin-allowed  $d \rightarrow d$  excitations nearest neighbour to the O(p) hole to be variationally stable by minimization of the total energy for all three polarizations of the hole in configurations in which the unpaired spin at the hole site is both ferromagnetic  $\{p(\uparrow)-d(\uparrow)\}$  and antiferromagnetic  $\{p(\uparrow)-d(\downarrow)\}$  to the excited state spin. The energies of these excited states with the inclusion of a correlation correction of 0.25 eV for the two  $t_{2g} \rightarrow e_g$  excited states are given in table 6. While the presence of an O(p) hole in all three polarizations and in both local spin alignments reduces the energies of the  $d \rightarrow d$  states, for the two low energy O( $p\pi$ ) holes the reduction is predicted to be in the region of 0.1–0.2 eV, with no evidence for the  $d_{z^2} \rightarrow d_{x^2-y^2}$  state in the region of 0.5 eV. There is a marked reduction for the O( $p\sigma$ ) hole, but the high relative energy of this state, at  $\sim 0.9$  eV, might reasonably be taken to preclude any role it might play in the low temperature properties of  $\text{Sr}_2\text{CuO}_2\text{Cl}_2$ . An analysis of the atomic charges, d-orbital populations and densities of states reveals  $d \rightarrow d$  states whose electronic distributions are changed little from those in the absence of a nearest neighbour hole, with very similar reorganization of the  $t_{2g}$  and  $e_g$  levels.

### 3.4. Charge transfer excitations

Finally, to put our results into context, both from the point of view of the low energy excited states of  $\text{Sr}_2\text{CuO}_2\text{Cl}_2$ , and the more general methodological question as to the wider utility of direct excited state calculations, we have calculated the energies of the nearest neighbour (nn)  $p\pi_{\parallel} \rightarrow d_{x^2-y^2}$ ,  $p\pi_{\perp} \rightarrow d_{x^2-y^2}$  and  $p\sigma \rightarrow d_{x^2-y^2}$  charge-transfer (CT)

states, in which the unpaired oxygen spin is oriented either parallel or antiparallel to the transferred electron spin. We note that a rigid-band estimate based on the ground state densities of states places these states around 15 eV. Once again, a Kanamori–Brandow analysis is instructive, for, quite apart from any changes to the O(p) states at the hole site, the  $d^{10}$  configuration at the acceptor site now assumes the ideal, spin-independent splitting of the  $t_{2g}$  and  $e_g$  states by  $\Delta_{CF}$ , quite unlike that for the  $d^9$  ground state, so that any recourse to a rigid-band estimate is totally inappropriate. Under identical computational conditions to those for the ground and  $d \rightarrow d$  states, direct UHF calculations find energies of (5.249, 5.274), (5.572, 5.598) and (5.545, 5.284) eV respectively for the ( $\uparrow\uparrow$ ,  $\uparrow\downarrow$ ) charge-transfer states, which compare with values of around 5 eV predicted by Tanaka and Kotani [18] based on a parametrized impurity Anderson model. Similarly, we have calculated the nearest off-site  $Cu(d_{z^2}) \rightarrow Cu(d_{x^2-y^2})$  charge transfer energy, which we find to be 9.4 eV. These energies calculated from direct total energy differences neglect the dipole–dipole interaction between supercells so that they are *upper bounds* to the UHF value of the isolated excitation. As in the case of the  $d \rightarrow d$  excited states, the leading correction to the UHF energies are the difference between the  $(p\pi_{\parallel})^2/(p\pi_{\perp})^2$  and  $(d_{x^2-y^2})^2$  pair correlation energies, but it is unlikely that these amount to more than a few tenths of an eV, at most. The incorporation of the band widths, as obtained from the densities of states plots, leads to an estimate for the absorption edge in the region of 2 eV, which is close to the observed value [27]. Mulliken analyses suggest that in these nn ct states  $\sim 70\%$  of net electron charge density is localized at the acceptor (Cu) site and  $\sim 76\%$  of net hole charge density at the nn (O) donor site with  $\sim 88\%$  of the transfer net spin density localized at the two sites. Changes to the surrounding atomic charges and orbital populations amount to less than 2% of the ground state values, so that these nn CT states are also predicted to be Frenkel excitonic in nature. As expected, we find extensive reorganization of the valence levels both at the donor and acceptor sites, which are responsible for substantial relaxations from the rigid band energies.

#### 4. Conclusions

In conclusion, we have shown in this paper that a direct SCF approach to the three spin-allowed  $d \rightarrow d$  excited states in  $Sr_2CuO_2Cl_2$  leads to energies in good agreement with the resonant x-ray Raman spectra of the  $d_{xy} \rightarrow d_{x^2-y^2}$  and  $d_{xz} \rightarrow d_{x^2-y^2}$  excitations observed by Kuiper *et al* [2] and in full support of their conclusion that the energy of the  $d_{z^2} \rightarrow d_{x^2-y^2}$  state, which they did not observe directly, is 1.5 eV rather than 0.5 eV as had been suggested previously [1]. The difference between the UHF and experimental  $d_{xy} \rightarrow d_{x^2-y^2}$  energies, which can be ascribed largely to the difference between  $(d_{x^2-y^2})^2$  and  $(d_{xy})^2$  pair correlation, is 0.25 eV, a value which is very close to the corresponding difference in NiO [4] and might reasonably represent a useful general estimate of the correlation correction to UHF  $t_{2g} \rightarrow e_g$  energies for other late first-row transition metal ions in octahedral and near-octahedral crystal fields. Assuming this correction applies

to the  $d_{xz} \rightarrow d_{x^2-y^2}$  excitation and that the  $(d_{z^2})^2$  and  $(d_{x^2-y^2})^2$  pair correlation energies are similar so that there is essentially no correction to the UHF  $d_{z^2} \rightarrow d_{x^2-y^2}$  excitation energy, we arrive at values of 1.35, 1.53 and 1.82 eV for the  $d_{xy} \rightarrow d_{x^2-y^2}$ ,  $d_{z^2} \rightarrow d_{x^2-y^2}$  and  $d_{xz} \rightarrow d_{x^2-y^2}$  states respectively, compared with values of 1.35, 1.5 and 1.7–1.8 eV reported by Kuiper *et al* [2]. The variations in excitation energy with supercell size indicate that interactions between excitations can safely be neglected in this system, with nearest neighbour interactions estimated to be less than 0.02 eV. Crucial to the assignment of the  $d_{z^2} \rightarrow d_{x^2-y^2}$  energy is the associated spin-flip energy of  $\sim 0.2$  eV, which we have shown to be entirely consistent with the experimental Néel temperature and hybrid functional calculations. Similar calculations in the presence of a nearest neighbour O(p) hole, find changes to the excited state energies of no more than 0.1–0.2 eV, thereby removing any lingering possibility that the  $d_{z^2} \rightarrow d_{x^2-y^2}$  state might be involved in the mechanism of high- $T_c$  superconductivity. With regard to three, more general points, first, our calculations highlight the extent to which even highly atomic excitations involve extensive reorganization of open-shell levels in particular, leading to a substantial lowering of UHF rigid band energies. It follows from this that comparisons of the ground state eigenvalues with experimental spectra are an ill-founded guide as to the quality of the UHF ground state. Whether this is also true for more general Kohn–Sham descriptions is a matter we are currently examining. Second, our calculations show that inter-site transitions, such as charge-transfer excitations are also amenable to a direct SCF approach, leading to excitation energies that are comparable in accuracy to those for on-site transitions and in apparent agreement with previous estimates. Third, the completely consistent theoretical description of  $d \rightarrow d$  excitations in such systems appears to be beyond present density-based estimates of the electron correlation for periodic systems, and must await more accurate developments.

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