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Quantum Chemical Formulation of High-T_C Superconductivity

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A detailed understanding of superconductivity in the cuprates is formulated. A cluster model is defined and evaluated by means of the regularized complete active space self-consistent field method. Signatures of local pair-breaking excitations in a low-dispersive oxygen metal band, attenuated by the nearby buffer ions, and nonadiabatically spin-coupled to a disjoint antiferromagnetic band are quantified and proposed to be consistent with the spin−flip signature of high-T_C superconductivity in $YBa_2Cu_3O_{6+x}$. Critical properties of the scenario are (i) hole-clustering instabilities producing local angular (D-wave) *and* radial (S-wave) Cooper instabilities and (ii) nonadiabaticity between local hole cluster states and antiferromagnetism. The cuprates are said to belong to a class of superconductors for which the macroscopic ground state is accessed by means of phase coherent hole cluster resonances. This understanding is illustrated by a real-space BCS-like deduction of the superconducting gap. A microscopic understanding of the order parameter symmetry emerges.

1. Introduction

The discovery of high-T_C superconductivity in the cuprate oxides[1] has uncovered flaws in the basic understanding of charge transport in the oxide materials. Early, a Mott−Hubbard understanding was attempted, based on a $Cu^{2+}-Cu^{3+}$ mixed valence, produced upon doping. It was soon realized that the charge carriers did not switch oxidation states on Cu, rather the holes were seen to end up on the oxygens.[2] An ingenious resolution of the apparent contradiction, which preserves the approximate validity of the single-band Hubbard model was proposed by Zhang and Rice,[3] who introduced the hole into the oxygen $2p_\sigma$ orbitals that mix with the Cu $3d_{x^2-y^2}$ orbitals.

Since first proposed in 1988, the Zhang−Rice singlet understanding has been the main tool for interpretation and modeling of superconductivity in the cuprates, ignoring early independent ab initio quantum chemical calculations on Cu−O chains,[4] which propose the holes enter into quasi-localized $O2p_\pi$ orbitals, orthogonal to the $O2p_\sigma$ and the Cu $3d_{x^2-y^2}$ bands. Coupling between the antiferromagnetically ordered spins in the Cu $3d_{x^2-y^2}$ band and $O2p_\pi$ holes were obtained by exchange interaction. We have found this basic understanding to hold in the case of *hole clusters* in the CuO_2 planes, i.e., where the superconducting condensate is presently believed to be contained, and a rich but still simple local spectroscopy is being unraveled.[5−9] This notion of fluctuating hole clusters implies the binding of charge carriers in generally nonperiodic potentials, which is a complementary scenario to the extended Hubbard Hamiltonian approach of Stechel and Jennison.[10]

Temperature dependent hole distribution between the localized and delocalized states has been proposed previously to explain depletion of mobile holes with lowering of temperature, i.e., from the upper Hubbard band of mainly Cu $3d_{x^2-y^2}$ character into the lower band of mainly $O2p_\sigma$ character. The scenario of the present effort is arrived at if (a) the lower Hubbard band and the $O2p_\pi$ band have similar stabilities and the latter is taken to contain the localized holes, i.e., the $O2p_\sigma$ and $O2p_\pi$ hole states are near-degenerate, (b) at some temperature T^* the Fermi surface becomes "pseudogapped" as the material starts to display hole-clustering inhomogeneities, (c) the entrance into the superconducting state is determined by formations of phase coherent hole cluster resonances, and (d) phase coherence between hole clusters in the $O2p_\pi$ band is achieved by spin fluctuations in the AF Cu $3d_{x^2-y^2}$ band. The scenarios (a−d) will be discussed in detail below, i.e., taking superconductivity to emerge from a pseudogapped Fermi surface normal state, as caused by hole clustering due to lattice instabilities.

Recently, a challenge to the theoretical models of the cuprate high critical temperature superconductors were formulated by Fong et al.[11] and by Mook et al.[12] On the basis of high-quality neutron scattering experiments, magnetic spin−flip resonances at 27, 33, and 40 meV for three different hole dopings in the $YBa_2Cu_3O_{6+x}$ superconductor were determined and found to correlate with the critical temperatures for superconductivity.[11] These resonances disappear above T_C and were consequently interpreted, on the basis of BCS theory, to be associated with a magnetic spin−flip coupling to the quasi-particle pairs production across the superconducting gap below T_C. An apparently linear increase of T_C with magnitude of the magnetic spin−flip resonance was demonstrated. The observation of Fong et al. is consistent with a magnetic superlattice, while Mook et al.[12] report additional magnetic excitations incommensurate with the underlying tetragonal lattice. Hence, strong indicators of possibly general detailed correlation between magnetic and superconductivity properties were observed.

The conventional BCS understanding of superconductivity

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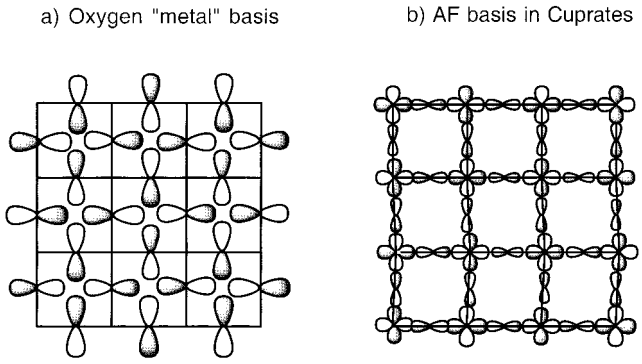

Figure 1. Oxygen "metal" (a) and the AF (b) bands displayed on the atomic basis.

emerges from Cooper's observation that the electron gas in a metal is unstable to electron pairs formation.[13] The origin of this instability is found in the near-degenerate independent particle states at the Fermi surface, and pairing is obtained upon introduction of an infinitesimal effective electron−electron attraction. The original BCS formulation of superconductivity[14] envisaged nonadiabatic coupling between independent electron and phonon degrees of freedom to produce the opening of a gap in the excitation spectrum of the resulting correlated electrons. The strategy of Bogoliubov[15] was to express the correlated many-body ground state in a Fock space algebra, expanding the Fermi surface portion of the correlated electronic ground-state wave function in a plane wave basis and introducing new effective fermions (so-called quasi-particles) by allowing for a mix of electron states and hole states as a means to go beyond the independent particle level of theory. The amount of mixing between electron states and hole states is mainly determined by the effective attractive interaction.

Our strategy to understand superconductivity in the cuprates is to seek the near-degeneracy quality, necessary for the Cooper instability, locally.[5−9] Indeed, the origin of a low-dispersive virtually pure oxygen "metal" band in the CuO_2 plane emerges from the calculations. Hence, both the locality approximation and the Cooper instability condition are satisfied for this band. The oxygen charge carrier band results from the weakly overlapping in-plane $O2p_\pi$ orbitals (Figure 1a). The local symmetry constraints imposed by the crystal structure preserve orthogonality between the $O2p_\pi$ band and the σ-band (Figure 1b). The latter is responsible for the antiferromagnetism exhibited by the undoped material. The effect of introducing holes into the $O2p_\pi$ band is to reduce the antiferromagnetic (AF) coupling in the σ system by adding a ferromagnetic contribution to the net AF interaction, in accord with Hund's rule (cf. Anderson[16]). This suggests that the nonadiabatic electron−phonon coupling in the BCS scenario for low-T_C superconductivity should be replaced, in the case of the high-T_C materials, by the interband spin coupling between the "metallic" π-band and the magnetic in-plane σ-band. The methodology, scenario, and hole cluster characteristics are outlined in sections 2.I−III and discussed further in section 3.

The approach attempted in the present undertaking is to seek the essence of the spin−flip anomaly in a cluster spectroscopy. *But if this anomaly is a signature of superconductivity, i.e., indicative of global phase coherence, how can this property be addressed in a cluster study?* For a local pair-breaking excitation (PBE) to contribute to the global ground-state many-body wave function, this excitation must be absorbed by the material, meaning that a pair resonance has to occur elsewhere. In this scenario the local spectroscopy would reflect (i) the stability of the pairing potential in the $O2p_\pi$ band, (ii) the characteristics of spin excitations in the σ-band, and (iii) nonadiabatic spin coupling between the two disjoint bands, which communicates the PBE information in the charge carrier channel by means of virtual spin excitations in the σ-system. This understanding has spin and space symmetry preserved locally, while the number of pairs would be a macroscopic property. This way, high-T_C superconductivity becomes a ground-state property in the cuprates, which results from resonance-stabilization-driven delocalization of hole pairs. Detailed connection between this understanding and BCS theory is provided in section 2.IV, while section 2.V. discusses how a hole cluster scenario may be employed to interpret experiments.

The connection between the spin−flip excitation and the pairing potential is defined in section 2.VI. The spin−flip anomaly is understood to signify the locality constraints imposed by the fluctuating long-range AF order, known to develop with the opening of the spin gap at temperature T_0. The pseudogap at T^* is associated with hole-clustering fluctuations, resulting from lattice instabilities. Fluctuating or static superstructures of such instabilities are suggested to produce the stripe phase detected by neutron diffraction. Phase coherent hole cluster resonances produce superconductivity at T_C.

2. Physical and Chemical Concepts

Any successful computational scheme, which aims to formulate a mechanism for high-T_C superconductivity based on nonadiabatic coupling between charge carrier and magnetic bands, must be able to account in a balanced way and simultaneously for (i) the spectroscopy of the PBE, (ii) the spectroscopy of the magnetic degree of freedom, and (iii) the inter-band coupling. It can be claimed that this balanced quantitativity becomes a quality in itself, and very much so were it to be responsible for achieving the long-range phase coherence necessary for superconductivity. In conventional superconductivity theory, a normal-state Fermi liquid understanding is adopted and an explicit electron correlation treatment is added a posteriori. In systems where a hole-hopping-driven normal conductivity is envisaged, the essential electron correlation treatment must be taken locally. A consistent realization of these considerations is presented below.

I. Probing Local Electronic Properties by Quantum Chemistry. Ab initio quantum chemistry is a robust, though computationally elaborate, technique to produce quantitative information on molecular structures and spectroscopic properties, which matches the accuracy of most relevant experiments. In an ongoing investigation, we suggest and explore the usefulness of the detailed properties of a quantum chemical cluster model[5−8] in resolving possible origins of the rich, and apparently local, spectroscopy of the high critical temperature superconductors.[17] The complete active space self-consistent field (CASSCF) method,[18,19] augmented with a recently designed effective description of the Coulomb hole,[20−22] is employed. This method describes static correlation by including all near-degenerate independent particle states explicitly in the variational wave function, while dynamic correlation is accounted for by regularization of the Coulombic Green's function. Hence, the Bogoliubov transformation mixing of electron states and hole states is replaced by the variationally determined partial occupations of the "natural orbitals" in configuration interaction (CI) theory.

The simplest cluster model which displays both nearest neighbor and next-nearest neighbor Cu−Cu, Cu−O, and O−O interactions and includes the effects of the buffer ions closest to this CuO_2 plane was designed[5] (Figure 2). The electronic

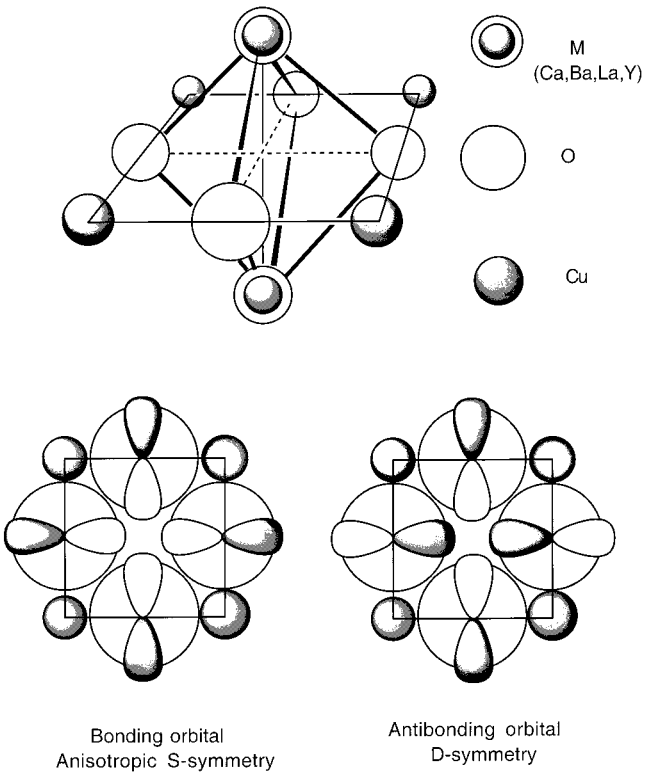

Figure 2. Cluster model for which the ab initio electronic structure calculations were performed and the orbitals of 1S and D symmetries that produce pairing.

structure of this model was chosen to reflect a *maximum* hole-clustering scenario, and the stability of the ground state of the cluster was suggested to relate to the stability of the hole-pairing potential of the superconductor. Local wave function characteristics were determined and quantified,[6−8] suggestive of a two-band scenario, i.e., a pure oxygen metal band in a local "π" symmetry with respect to the Cu−O−Cu "σ" axis side-by-side with the conventional understanding of antiferromagnetism to reside in the space spanned by $Cu3d_{x^2-y^2}-O2p_\sigma-Cu3d_{x^2-y^2}$ orbitals of local σ symmetry.

The computational details are described in ref 7 and only the relevant features will be reiterated here. Hence, we perform standard quantum chemistry calculations on a cluster model, i.e., we minimize the energy for a CASSCF wave function ansatz comprising the four in-plane $O2p_\pi$ orbitals that describe the "metallic" degree of freedom, and the four $Cu3d_{x^2-y^2}$ orbitals that, mixed with the $O2p_\sigma$ orbitals, span the AF degree of freedom, i.e., eight electrons in eight orbitals (cf. Figure 3a,b). The ANO basis sets of Pierloot et al. were used.[23] Atomic basis sets composed of 5s4p3d for Cu^{2+} (Zn^{2+}), 4s3p1d for O^-, and 5s4p for Ca^{2+} were deemed adequate.

II. Quantum Chemistry Scenario. It is implied that the cluster spectroscopy possesses both energy and symmetry information on the hole-pairing interaction and consequently contains the essential elements of the superconducting gap.

How can this be? Suppose the correlated electronic wave function is qualitatively expandable in a basis that factorizes the oxygen "metal" and AF degrees of freedom, $\psi_{metal} \times \psi_{AF}$. While each factor preserves neither spin nor space symmetry, the product does. A PBE exemplifies an excitation in the "metal", which becomes absorbed in the ground-state many-body wave function by a simultaneous excitation in the local AF background (cf. Figure 3). This is the nonadiabatic physics, which replaces the electron−phonon coupling in the BCS scenario. The *local* availability of a magnetic degree of freedom, such that it also displays a fluctuating long-range AF order, would allow for a *local* PBE to become a property of the *global* material ground state by the local magnetic response to the PBE initiating a spin wave in the AF background. The emission and absorption of spin excitations through the AF would in turn produce the required macroscopic phase coherence in pair formation and pair destruction. The charge carriers, thus *coherently* coupled, define the superconducting condensate. The number of such particles is determined by the thermodynamics of the system. It should be noted that since the fluctuating AF background and the charge carriers comprise two disjoint fermionic systems, each displaying Fermi−Dirac statistics, the resulting temperature dependencies of the properties of high-T_C superconductors are expected to be complicated. The development of a coherent description of these is beyond the scope of the present effort. What we do seek to address here are the local energetics and symmetry properties of the crucial intraband and nonadiabatic interband interactions that result from electron correlation. In this context, a cluster can indeed be understood to possess crucial information regarding the superconducting order parameter and the energy gap.

III. Characteristics of a Local Holes Cluster. The hole-pairing physics in the superconductors is associated in refs 5−8 with the formation of a weak four-center peroxy chemical bond, which mixes independent-particle states of anisotropic S and D symmetries (cf. Figures 2 and 3). This is achieved *not* by orbitals rotations, which would be symmetry forbidden, but by allowing for doubly excited independent particle states to contribute to the correlated ground state. The stability of this singlet ground state was monitored using the positions, radii, and charges of the out-of-plane ions. Increasing ionic charge was found to stabilize the hole-pairing potential. Ionic radii of the buffer ions at the 4-fold hollow sites and the distances of these ions to the CuO_2 plane were found to be sensitive parameters for the PBE. This is because Pauli repulsion acts to reduce the strength of the four-center peroxy chemical bond.[5,6] The interference of holes with AF order was quantified and taken to explain the formation of stripe phases in some underdoped cuprate superconductors.[7] Also, the destructive effects on AF of Zn^{2+}, Ni^{2+}, and Mg^{2+} substitutions into the CuO_2 plane were quantified in refs 6 and 7, and thus a direct connection to the common understanding of AF as a crucial component in the basic mechanism of high-T_C superconductivity in the cuprates was made. The sensitivity of AF to orthorhombic−tetragonal distortions was calculated and taken to explain the appearance of superconductivity in the ladder compound $(Ca,Sr)_{14}Cu_{24}O_{41}$ under pressure.[8] The oxygen metal band was proposed to be a common feature of the cuprates and the manganites, but while the antiferromagnetic band is spatially orthogonal to the "metal" band in the cuprates, the half-filled Mn 3d orbitals of t_{2g} symmetry in the manganites are responsible for the ferromagnetic metal to antiferromagnetic insulator transition by mixing with the oxygen "metal" orbitals.[9]

IV. Superconductivity from Holes Cluster Resonances. The simplest direct connection to the BCS theory of superconductivity is achieved by writing down an effective macroscopic real-space wave function ansatz for the charge carrier channel in the form

$$\Psi = \Pi_i[u_i(\mu_i c^\dagger_{i1S\uparrow}c^\dagger_{iD\uparrow} + \nu_i c^\dagger_{i1S\uparrow}c^\dagger_{i2S\uparrow} + \zeta_i c^\dagger_{i2S\uparrow}c^\dagger_{iD\uparrow}) + e^{i\theta}v_i(\alpha_i c^\dagger_{i1S\downarrow}c^\dagger_{i1S\uparrow} + \beta_i c^\dagger_{iD\downarrow}c^\dagger_{i1D\uparrow} + \kappa_i c^\dagger_{i2S\downarrow}c^\dagger_{i2S\uparrow})]|0\rangle \quad (1)$$

i.e., in terms of phase coherent independent hole clusters that

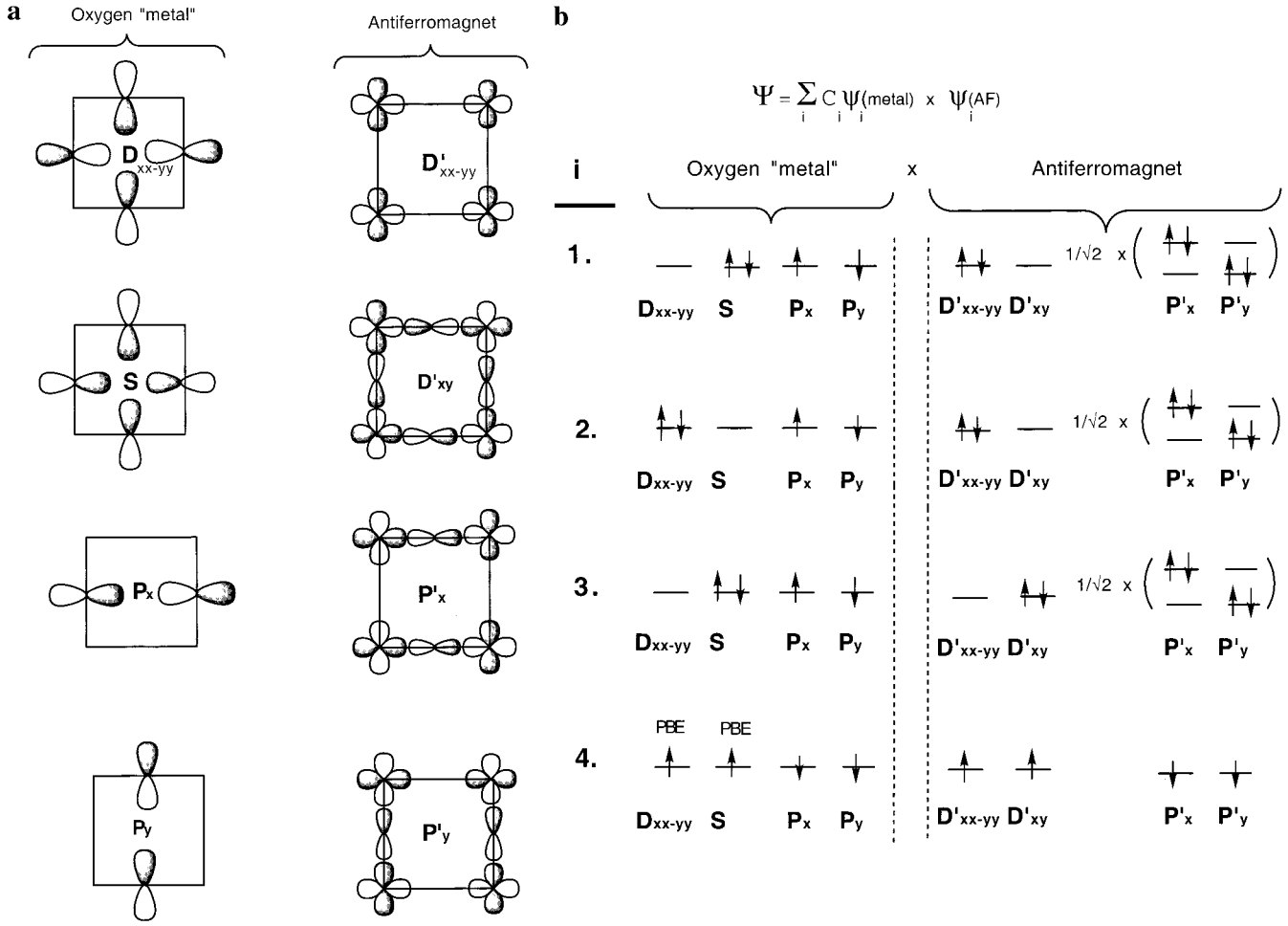

Figure 3. (a) Eight essential molecular orbitals. Left and right columns comprise local representations of charge carrier and antiferromagnetic bands, respectively. (b) Four of the 8-electron independent-particle states (432 states in all) that contribute to the net $^1B_{1g}$-orthorhombic many-body ground state. States 1 and 2 describe the pair state, and states 1 and 3 describe the AF order. State 4 represents the crucial pair-breaking excitations (PBE) into the $D_{x^2-y^2}$ and $D'_{x^2-y^2}$ orbitals, which make it possible for a local PBE to contribute to the many-body ground state.

display amplitudes for pair-broken (u_i) and paired (v_i) states at the sites $\mathbf{r}_i$ and obeys the usual normalization conditions $\mu_i^2 + \nu_i^2 + \zeta_i^2 = 1$, $\alpha_i^2 + \beta_i^2 + \kappa_i^2 = 1$, $u_i^2 + v_i^2 = 1$. It must be carefully noted in (1) how the $S_z = 0$ components of the pair-broken triplet resonances with amplitude u_i *do not* mix with the $S_z = 0$ pair-resonance components. The former components are each spanned in a cross-terms spatial basis (1S × D or 1S × 2S or 2S × D), while the latter resonances employ the same space orbital for both electrons (1S × 1S or 2S × 2S or D × D).

We note that if all u_i amplitudes were zero in (1), this wave function would describe a molecular crystal, i.e., $\Psi = \Pi_i \Phi_i$ where Φ_i are nonoverlapping molecular wave functions. In fact, the cluster size defines the shortest length scale of relevance to superconductivity in the cuprates. The mixing of singlet and triplet states in the charge carrier channel, due to the nonadiabatic coupling with the fluctuating AF background, is the decisive feature for achieving superconductivity. The demonstration of this coupling by means of quantum chemistry calculations is a key element in this presentation. The local cluster orbital of anisotropic S symmetry (1S) is node-less (see Figure 2), 2S has one radial node, and the $D_{x^2-y^2}$ orbital has two angular nodes and no radial node (see Figure 2 again). The wave function (1) thus displays coexistence of the two order parameter symmetries: D (1S × D, and 2S × D) and S (1S × 2S) in the sense that any super-fluid state $|f\rangle$ on the form (1) must display a nonzero expectation value for the pairwise creation and annihilation of pairs belonging to the condensate; i.e., $\langle f|\psi^\dagger(\mathbf{r}')\ \psi(\mathbf{r})|f\rangle \neq 0$ and $\psi(\mathbf{r})$ annihilates a pair at $\mathbf{r}$. Employing the resolution of the identity and requiring that one intermediate state $|i\rangle$ dominates produces

$$\Sigma_a \langle f|\psi^\dagger(\mathbf{r}')|a\rangle\langle a|\psi(\mathbf{r})|f\rangle = \langle f|\psi^\dagger(\mathbf{r}')|i\rangle\langle i|\psi(\mathbf{r})|f\rangle \qquad (2)$$

The order parameter $\Omega(\mathbf{r}) = \langle i|\psi(\mathbf{r})|f\rangle$ becomes the quality that couples states which differ by one super-fluid particle, reflecting the so-called off-diagonal long-range order. The removal of one such object amounts to increases in the u_i and reductions in the v_i amplitudes. Hence, the symmetry property of $\Omega(\mathbf{r})$ becomes directly connected to the symmetry of the local pair-breaking excitation and the underlying crystal structure. The excitation contributions to the u_i amplitude are displayed in Figure 4.

The detailed descriptions of the pair-breaking excitation channels involving the 2S orbital are left for future work. It is expected that these channels become increasingly more important with increased hole doping, i.e., as hole mobility increases and the hole clusters are destabilized. In over-doped samples the S-wave (1S × 2S) and the D-wave (D × 2S) channels are expected to dominate over the purely angular depairing excitation channel of D-symmetry (1S × D), while at low dopings the latter is expected to prevail.

The present study focuses on the (1S × D) D-wave channel at low dopings for illustration. This implies use of the simplified wave function ansatz

$$\Psi = \Pi_i[u_i c^{\dagger}_{iS\uparrow} c^{\dagger}_{iD\uparrow} + e^{i\theta} v_i(\alpha_i c^{\dagger}_{iS\downarrow} c^{\dagger}_{iS\uparrow} + \beta_i c^{\dagger}_{iD\downarrow} c^{\dagger}_{iD\uparrow})]|0\rangle \quad (3)$$

where $\alpha_i^2 + \beta_i^2 = 1$ and $u_i^2 + v_i^2 = 1$. We calculate $\langle E\rangle$ by employing the reduced Hamiltonian

$$H_{red} = \Sigma_{iL\sigma}\epsilon_{iL} c^{\dagger}_{iL\sigma} c_{iL\sigma} + {}^1/_2\Sigma_j(c^{\dagger}_{jD\downarrow} c_{jS\uparrow} - c^{\dagger}_{jS\downarrow} c_{jD\uparrow})\Sigma_i V_{ij}(c^{\dagger}_{iS\uparrow} c_{iD\downarrow} - c^{\dagger}_{iD\uparrow} c_{iS\downarrow}) \quad (4)$$

The summation over angular moment quantum numbers, L, is one fundamental common denominator with the **k**-space independent particle basis, employed in the BCS theory to span the correlated many-body wave function. The energy expression becomes

$$\langle E\rangle = \Sigma_i[u_i^2(\epsilon_{iS} + \epsilon_{iD}) + 2v_i^2(\alpha_i^2\epsilon_{iS} + \beta_i^2\epsilon_{iD})] + \Sigma_i u_i v_i(\alpha_i + \beta_i)\Sigma_j V_{ij} u_j v_j(\alpha_j + \beta_j) \quad (5)$$

Taking $\epsilon_{iD} = \epsilon_{iS} + \gamma_i$ we have

$$\langle E\rangle = \Sigma_i[\epsilon_{iS} + \epsilon_{iD} - \gamma_i v_i^2(\alpha_i^2 - \beta_i^2)] + \Sigma_i u_i v_i(\alpha_i + \beta_i)\Sigma_j V_{ij} u_j v_j(\alpha_j + \beta_j) \quad (6)$$

Minimizing $\langle E\rangle$ with respect to u_i and v_i produces

$$-\gamma_i(\alpha_i^2 - \beta_i^2)d(v_i^2) + 2d(u_i v_i)(\alpha_i + \beta_i)\Sigma_j V_{ij} u_j v_j(\alpha_j + \beta_j) = 0 \quad (7)$$

which can be written

$$-u_i v_i \gamma_i(\alpha_i - \beta_i) - \Delta_i(u_i^2 - v_i^2) = 0 \quad (8)$$

where

$$\Delta_i = -\Sigma_j u_j v_j(\alpha_j + \beta_j)V_{ij} \quad (9)$$

Relating the amplitudes u_i and v_i via E_i according to

$$2u_i^2 = 1 - \gamma_i(\alpha_i - \beta_i)/E_i \quad \text{and} \quad 2v_i^2 = 1 + \gamma_i(\alpha_i - \beta_i)/E_i \quad (10)$$

results in

$$-[E_i^2 - \gamma_i^2(\alpha_i - \beta_i)^2]^{1/2} + \Delta_i = 0 \quad (11)$$

or equivalently

$$E_i^2 = \Delta_i^2 + \gamma_i^2(\alpha_i - \beta_i)^2 \quad (12)$$

Note that Δ takes its largest value E when $\alpha_i = \beta_i$. Introducing (10) into (9), given (11), we get the self-consistent gap equation

$$2\Delta_i = -\Sigma_j \Delta_j(\alpha_j + \beta_j)V_{ij}/E_j \quad (13)$$

Assuming $\Delta_i = \Delta_j = \Delta$, $\alpha_i = \alpha_j = \alpha$, $\beta_i = \beta_j = \beta$, and $\gamma_i = \gamma_j = \gamma$ implies $E_i = E_j = E$ and results in

$$2 = -(\alpha + \beta)E^{-1}\Sigma_j V_{ij} \quad (14)$$

We observe that V_{ij} must be a rapidly decaying function of $|\mathbf{r}_i - \mathbf{r}_j|$ for the electron-like excitation energy E to become of the order of 10−20 meV, i.e., the experimentally observed Δ (cf. eq 12). Minimum T_C is achieved if only nearest neighbors are coupled by V_{ij}. Experimental observations of fluctuating long-range AF order in the doped cuprates have been produced.[16]

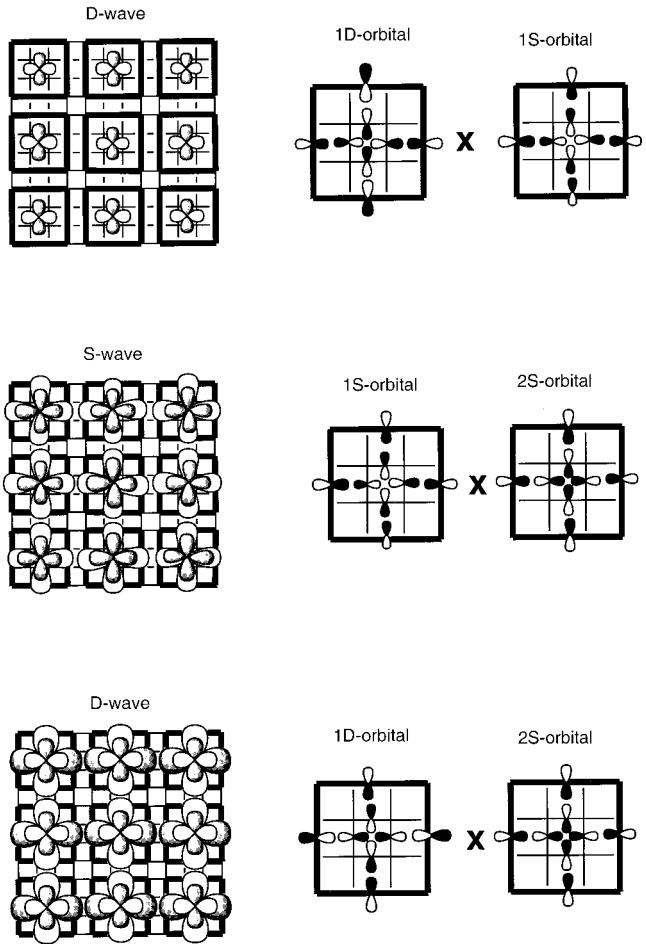

Figure 4. (Left column) contributions to the wave function of excitations for the components $c^{\dagger}_{i1S\uparrow}c^{\dagger}_{iD\uparrow}|0\rangle$, $c^{\dagger}_{i1S\uparrow}c^{\dagger}_{i2S\uparrow}|0\rangle$, and $c^{\dagger}_{i2S\uparrow}c^{\dagger}_{iD\uparrow}|0\rangle$ on a cluster basis. (Right column) the corresponding cluster states expressed on an oxygen atom basis.

These provide one candidate mechanism for achieving phase coherence by coupling nearest neighbors and possibly also beyond. This scenario will be discussed further below.

Assuming nonzero contributions from interactions with the $x \geq 1$ neighbors, and $V_{ij} = -V$ results in

$$E = (x/2)(\alpha + \beta)V \quad (15)$$

By virtue of (12) we obtain

$$\Delta^2 = (x/2)^2(\alpha + \beta)^2V^2 - \gamma^2(\alpha - \beta)^2 \quad (16)$$

Equation 12 trivially implies that at low temperatures there are no electron-like excitations for energies smaller than Δ, and eq 16 relates Δ to the effective attractive interaction V. We observe that $\Delta_{max} = E$, which requires $\alpha = \beta$, and that this is equivalent to γ $(=\epsilon_D - \epsilon_S) = 0$. This comprises the real-space reflection of the Cooper instability. The fact that V couples pair and pair-broken resonances at sites separated by 16 Å implies (a) that the local electronic excitations must display a single-particle spectrum on the energy scale of the medium and (b) that the latter must possess properties that ensure that long-range phase coherence is maintained. In a scenario based on nonadiabaticity between disjoint charge-carrier and AF bands, the consequences of (a) is that E is similar to the spin excitations in the Cu σ band. Hence, the simplest connection between a *localized* real-space understanding of superconductivity and the BCS theory is formulated.

V. Possible Connection to Normal State Properties. *How can a scenario which has the charge carriers occupying quasi-localized oxygen orbitals be reconciled with the rather large and temperature independent Fermi surface seen in angular resolved photoemission spectroscopy (ARPES)?* A possible resolution is found in the temperature dependence of the Hall coefficient R_H, which in turn reflects the mobile hole density n_H. It is found that n_H changes approximately linearly with temperature.[24] An explanation would be that, increasingly, hole transitions from the conducting σ band into the local $O2p_\pi$ cluster states occur with the lowering of temperature. Because ARPES is a nonlocal probe and cannot distinguish between hole occupations in the σ and π bands by symmetry alone, as these are related by a (a/2,b/2,0) translation, the apparent Fermi surface would not be seen to change much with temperature, while the R_H measurements would observe a depletion of charge carriers. Having said this, there is growing experimental evidence of suppression of the ARPES spectral density below the gap, as accompanied by the development of the pseudogapped Fermi surface.[25] Indeed, it is suggested that the pseudogapped Fermi surface is the normal state, from which high-T_C superconductivity evolves. It is gratifying to note that this shift of holes from the AF band(σ), exploiting the $O2p_\pi$ bands to accommodate the hole clusters, can be taken to explain the increased recovery of local AF order with lowering of temperature. This understanding contrasts that of Hybertsen et al.,[26] who demonstrate the efficiency of a single band description in reproducing the single-particle low-energy behavior in the cuprates. It is suggested here that a partial separation of the charge carriers into two liquids occurs with the opening of the pseudogap and that experiment observes signatures of the "σ-liquid" and "π-hole cluster liquid" coexistence in the low-energy spectra at $T < T^*$.

The results of the yttrium Knight shift experiments in $YBa_2Cu_3O_{6+x}$ are considered to be a serious argument against any $O2p_\pi$ hole scenario. The controversy is well represented by the discussion in ref 27. For the purpose of the present investigation, it is sufficient to stress that charge carrier clustering implies majority and minority Y^{3+} surroundings in the case of YBCO. Hole clustering may be taken to imply that a minority of Y^{3+} ions will see the $O2p_\pi$ hole clusters, while the majority of Y^{3+} ions will experience effectively undoped surroundings. If hole-clustering instabilities do indeed reflect the pseudogapped normal state, then increasingly nonequivalent Y^{3+} surroundings are automatically implied as the temperature is lowered. Analysis of data based on such a possibility is encouraged.

VI. Properties That Decide V_{ij}. The key observations in refs 5−7 comprise (a) the formulation of a hole cluster, (b) the buffer metal ion (e.g., La, Ba, Ca, Y)-to-plane distance being an efficient parameter for controlling the stability of the pairing in the interesting energy range (0−60 meV), and (c) the nearest neighbor Cu−O distance controlling the strength of the AF coupling. These structural parameters are used below to span the recently reported detailed data on the spin−flip excitation resonance in the $YBa_2Cu_3O_{6+x}$ materials.

3. Results and Discussion

The objective of the present study is to formulate a scenario for high-T_C superconductivity, by employing ab initio quantum chemistry as the "experimental" probe. The pair-breaking excitation (PBE) energy becomes the energy difference between the $^7B_{1g}$ and the $^9B_{1g}$ cluster states (cf. Figure 3), as controlled by the Ca^{2+}-to-plane distance. Similarly, the measure of the spin−flip excitation is taken to reflect the remaining coupling in the cluster, to which the antiferromagnetic coupling contributes significantly. It becomes the total energy difference between the $^1B_{1g}$ and the $^7B_{1g}$ cluster states (cf. Figure 3 again). The AF coupling is controlled by the Cu−O distance. All calculations are performed in the orthorhombic point group symmetry.

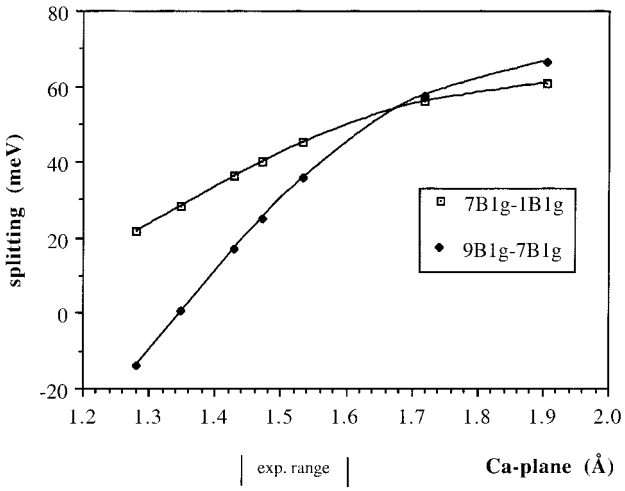

Figure 5. Shallow curve describing the "spin−flip" energetics ($^1B_{1g} - {}^7B_{1g}$). The $^7B_{1g}-{}^9B_{1g}$ curve displays the PBE energy 2δ. Both are determined as a function of Ca^{2+}-to-plane distance.

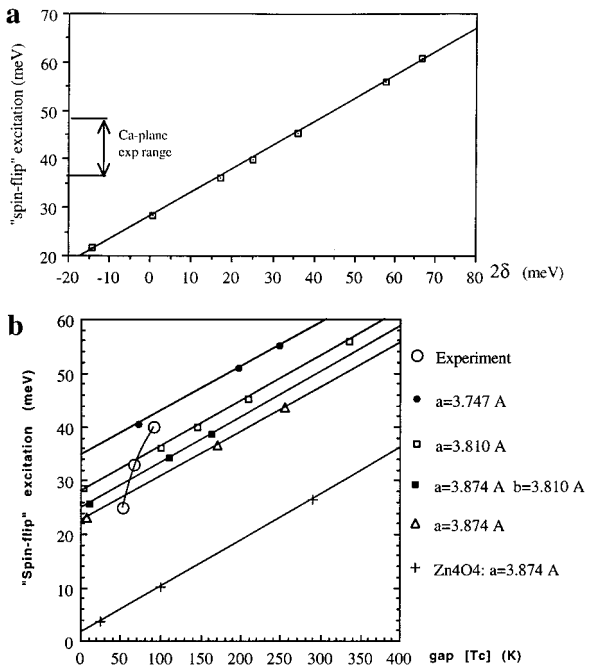

Figure 6. (a) "Spin−flip" energetics plotted against the PBE energy 2δ. (b) Same physics as (a) for various a values, including also one orthorhombic arrangement. The result obtained by replacing Cu^{2+} with Zn^{2+} is displayed, and direct connection to T_C is made by including the experimental values of Fong et al.[11]

The two excitation energies are displayed in Figure 5 as functions of Ca^{2+}-to-plane distance, for $R(Cu-O) = 1.905$ Å. In Figure 6a the spin−flip excitation, that is $\Delta E(^1B_{1g} - {}^7B_{1g})$, is plotted against the PBE, i.e., $2\delta = \Delta E(^7B_{1g} - {}^9B_{1g})$. In Figure 6b, the spin−flip excitation is displayed as a function of δ, expressed in Kelvin, for different Cu−O distances. The results for the nonmagnetic Zn_4O_4 loop are included in Figure 6b for comparison, as are also the experimental values of Fong et al.[11] It is seen from the Zn results that the spin−flip excitation is not solely magnetic but includes a charge carrier quality that originates from the P_x and P_y hole spectroscopy (cf. Figure 3a).

Indeed, a possible interpretation of the results is that the spin−flip correlation with T_C may originate from an improved efficiency of the fluctuating AF background in condensing the holes as four-hole cluster resonances. The corresponding two-hole scenario would produce low-T_C, as discussed in the ladder compound study.[8]

The presented results suggest the existence of structural instabilities, which would produce structural superlattice resonances below T_C. The degree of local compression in the a−b plane, and buffer ion-to-plane distance elongation, would correlate with the concentration of holes.

While it is clear that this cluster model does not take the thermodynamics and the macroscopic nature of the superconducting state directly into account, it can be claimed that it does articulate efficiently a possible interpretation of the spin−flip anomaly (cf. Figure 6b). Thus, it becomes important to stress consistency with our previously presented understanding of a the cuprate superconductor, i.e., in terms of a low-dispersive oxygen "metal" band attenuated by the electrostatic field from and Pauli repulsion interactions with the closest buffer ions. The hole-clustering resonances would provide means for the material to recover some of its native antiferromagnetism, which was destroyed by the hole doping. Indeed, simple inspection of the cluster wave function has the oxygen metal band *disjoint* from the antiferromagnetic band. Were the bands to display the same local symmetry, effects such as those displayed by the manganites would be observed, i.e., the π-"metal" property would be suppressed in order to achieve antiferromagnetic order (ferromagnetic metal to antiferromagnetic insulator transition) as discussed in ref 9. In fact, the reasons for the scarcity of high-T_C superconductors throughout the periodic table are the simultaneous requirements of (a) a low-dispersive "metal" band and (b) antiferromagnetic and metallic properties in occupying disjoint bands. Promising for the future is that both the chemical pairing and pairs delocalization, as communicated by nonadiabatic interband spin coupling between the σ and π bands, appear to be direct consequences of (a) and (b).

As a tool for interpretation, the above scenario provides a particularly simple possible explanation to the observed coupling between the out-of-plane oxygen mode of B_{1g}-tetragonal symmetry and the superconducting gap, as observed by Raman spectroscopy.[28] This has been proposed to indicate an energy gap with nodes, e.g., corresponding to an order parameter of D-wave symmetry. From our calculations we have that the decisive near-degenerate independent particle states, which accommodate the oxygen holes, belong to the A_{1g}-tetragonal (S) and B_{1g}-tetragonal ($D_{x^2-y^2}$) irreducible representations and that the PBE displays $x^2 - y^2$ symmetry (cf. Figure 2). While an order parameter of $x^2 - y^2$ symmetry is easiest to extract from the cluster wave function (cf. section 2), it should be pointed out that there are excitations in the hole cluster other than the PBE that contribute to the cluster ground state, being accessed by "simultaneous" excitations in the magnetic degree of freedom. Particularly, $P_x \times P_y$ contributions could cause the time reversal symmetry breaking, which would be realized by a biased double summation over sites $\mathbf{r}_i$ and $\mathbf{r}_j$ in the reduced Hamiltonian defined by eq 4. Discussions on such an additional order parameter symmetry component are presently found in the literature.[29]

The crucial *common* role of the buffer ions in the immediate vicinity of the CuO_2 planes (La^{3+}, Ba^{2+}, Y^{3+}, Ca^{2+}, etc.) is stressed (see also ref 30). This common role emphasizes the importance of the Raman spectroscopy observations that report strong antiresonance features in the *c*-axis vibration of Ba^{2+}.[28] Such so-called Fano profiles on the phonon peaks are generally understood to indicate coupling to the charge carrier continuum. This scenario connects to that assumed by Monien and Zawadowski[31] to explain the intriguing continuum in the Raman excitation spectrum (cf. ref 28) in terms of inter band excitations between the high-dispersive σ-band and a low-dispersive $O2p_\pi$ band. Demonstration of the sensitivity of the $\sigma-\pi$ excitation energies to the crystal field are made elsewhere.[32] Investigations on pairing-induced suppression of low-energy excitations are in progress.

Hole doping in the planes is likely to result in an increased M^{x+}-to-plane distance, due to reduced screening of Coulomb repulsion through the plane. This effect would in turn act to stabilize the hole-clustering potential by formations of superlattice structures. In fact, in the case of the apical oxygen, diffuse neutron scattering has been analyzed and shown to be consistent with two $Cu_{plane}-O_{apical}$ distances.[33] A similar analysis should detect an anticorrelated M^{x+} superstructure, which would provide useful information for our model, constraining the magnitudes of the possible displacements of these ions. Consistency between this understanding and a joint experimental and computational work on the pressure effect in the mercury cuprates, which particularly addresses the accommodation of the Ba^{2+} ion, is presented elsewhere.[34]

4. Concluding Remarks

Local spectroscopic properties of a recently proposed cluster model of possible relevance to high critical temperature superconductivity in the cuprates have been discussed. A model has been exploited to interpret the experimentally demonstrated correlation between the magnitude of a spin−flip resonance and the critical temperatures for three different hole dopings in $YBa_2Cu_3O_{6+x}$.[11] An understanding based on charge carriers and AF residing in disjoint bands was articulated. Connection to BCS theory was made by introducing the notion of phase coherent independent hole clusters in **r**-space, and the nonlocal pair quality was introduced explicitly into the wave function ansatz. The symmetry of the order parameter and coexistence of different order parameter symmetries, S and D, were discussed in terms of cluster properties. Spin-mediated nonadiabaticity between the charge carrier and AF channels was proposed to allow for nonlocality of the pairs, and phase coherence was understood to result from the hole clusters exchanging virtual AF spin-wave excitations. Thus, the spin−flip anomaly becomes a possible signature of a class of superconductors in which macroscopic phase coherence emerges from microscopic hole-clustering resonances.

The presented understanding has features in common with the resonating valence bond model of Anderson,[35] yet the real-space analogy with BCS theory is claimed to be original. The work contrasts the SO(5) field theory of Zhang,[36] the spin-bag scenario of Schrieffer et al.,[37] and the spin-fluctuation mechanism advocated by Monthoux et al.[38] All three effective models were originally understood within the *single-band* Zhang−Rice scenario. The *SO(5) theory* emerges from a competition between AF and superconductivity, whereas the present understanding emerges from coexistence of pairing in the charge carrier channel and short-range AF fluctuations. Nonadiabaticity between the two degrees of freedom produce macroscopic phase coherence. The *spin-bag scenario* has holes coupled via the AF background, while a hole cluster scenario was realized here. The *spin-fluctuation scenario* again claims crucial connection between AF and superconductivity. Still, the *explicit* understanding presented here, of phase coherent hole cluster reso-

nances in conjunction with charge carriers and magnetic degrees of freedom nonadiabatically coupled while occupying two *disjoint* bands and of the demonstration of how use can be made of wave function based quantum chemistry on cluster models, clearly implies that this effort provides a complementary scenario.

At present, increasingly more experimental observations of electronic and lattice instabilities are made in the cuprate materials. Neutron diffraction data are analyzed in terms of dynamic and static stripe phases,[39] and theories are developed on the basis of these features being of crucial importance to high-T_C superconductivity.[40] In this context, the hole-clustering instability scenario provides a truly microscopic understanding, i.e., on the atomistic length scale, while superstructures of hole cluster resonances may very well produce the physics of the stripe phases. Hence, it is hoped that the present effort will be useful in connecting normal-state properties and superconductivity in the cuprates, possibly via dynamic stripe phases, to the chemical and structural properties of these materials. Work in progress includes further exploration of detailed features of the presented real-space analogue to BCS theory, investigation of connections to mesoscopic properties of the cuprates, and the search for superconductivity in materials yet unknown.

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