

## Vibronic pairwise charge transfer in copper-oxide sheets: A possible approach to high temperature superconductivity theory

Ying-Nan Chiu<sup>1</sup>, Samuel H. Brown<sup>2</sup>, Neal Sondergaard<sup>2</sup>, Frederick E. Wang<sup>3</sup>

<sup>1</sup> Center for Molecular Dynamics and Energy Transfer, Department of Chemistry, The Catholic University of America, Washington, DC 20064 USA

<sup>2</sup> Naval Surface Warfare Center, Carderock Division, Annapolis, MD 21402 USA

<sup>3</sup> Innovative Technology International Inc. 10747-3 Tucker Street, Beltsville, MD 20705 USA

Received 22 April 1993/Accepted August 16, 1994

**Summary.** To accommodate the number of holes and fractional number of atoms in doped high  $T_c$  superconductors, and to produce a periodic structure with given symmetry, we postulate a quadruple cell with four copper atoms on the  $\text{CuO}_2$  layer. The quadruple cell structure has  $D_{2h}$  symmetry which can be distorted to  $C_{2h}$  geometry under  $B_{1g}$  vibration. Such a structure allows the interconversion of different spin angular momenta into paired spins similar to Cooper pairs. It also provides vibronic interactions that lower the energy of the ground state. For electron (hole) pairing, we construct the running wave Bloch sums consisting of linear combination of bonding/antibonding geminals (instead of one-electron atomic orbitals) in these quadruple cells. For “bond” movement we construct the Bloch sums consisting of linear combination of “Covalon” waves in quadruple cells related to the movement of conjugate (alternating) bonds. In both cases the pair-wise charge (hole/electron) transfer is coupled with antisymmetric vibrations under a double-well potential related to Peierls distortion. The vibronic mixing of different running bonds with different antisymmetric vibrations at various distances, accounts for the different long-range order of charge transfer. Our formulations represent an alternative view of BCS theory, Bisoliton theory and Resonating Valence Bond theory by using a quantum chemical, position-space approach to a more tight binding situation.

**Key words:** High  $T_c$  superconductivity – Molecular geminals – Charge transfer – Vibronic interaction – Renner–Teller effect – Jahn–Teller effect – Herzberg–Teller expansion

### 1. Introduction: Non-stoichiometry and quadruple cell structure of superconducting cuprates

High  $T_c$  copper oxide superconductors involve compounds with complicated molecular structures [1–4]. The theory of Bardeen, Cooper and Schrieffer (BCS) [5–9] has been successful in explaining a numbers of properties of low  $T_c$  superconductors (such as the  $A_3B$   $\beta$ -tungsten alloys). The BCS theory's general formulation in momentum space does not deal with the detailed non-stoichiometric molecular structure of the compounds which should be studied by quantum chemical

formations in position space. Many standard numerical methods for calculation of electron-phonon interaction of the BCS theory are available and have been applied to the high  $T_c$  compounds [10, 11]. Detailed quantum mechanical studies of the chemical structure in position space of such doped inorganic complexes may lead to an understanding of the molecular structure, band structure, lattice potentials, hole density, bond valence sum etc. [12, 13], which may simply give the overt correlation of such phenomena as hole density versus  $T_c$ . These molecular studies may not necessarily reveal the fundamental, intrinsic principles of the dynamics and mechanisms for high- $T_c$  superconductivity. Superconductivity also involves spin-pairing, attractive electron correlation through electron-phonon interaction, cooperative effects, long-range order, coherence and superconductivity gaps for the superconducting ground state etc. most of which were treated by the BCS theory. We intend to combine and consolidate the ideas from detailed quantum molecular studies of high  $T_c$  compounds in position space with the ideas of the momentum space in BCS theory and with the ideas of other theories such as Bisoliton theory and Resonating Valence Bond Theory (RVB). The purpose is to postulate different new approaches for determining the dynamical mechanisms for high  $T_c$  superconductivity. These involve mainly applying quantum mechanical symmetry principles to the molecular structure and dynamics of the high  $T_c$  compounds. Detailed numerical calculations will be performed in later works.

A review [13] of the structure property correlation in cuprate superconductors shows that high  $T_c$  occurs at about 0.2 holes per  $\text{CuO}_2$  unit. This means one hole per five copper atoms. For the sake of symmetry in periodic structures of solids, we shall consider the case of one hole per about four copper atoms. To have two holes to simulate the Cooper pairs (of two electrons), we propose an idealized quadruple cluster cell structure with eight copper atoms (Fig. 1). For example if we start with a basic perovskite like structure  $(\text{La}_4\text{Cu}_2\text{O}_8)_4$ , after doping, in order to satisfy electrical neutrality, we may have the atomic charge arranged as follows:  $(\text{La}^{+3})_{15}(\text{Sr}^{+2})(\text{Cu}^{+2})_8(\text{O}^{-2})_{31}(\text{O}^-)_1$ . This amounts to non-stoichiometric fractions  $\text{La}_{1.875}\text{Sr}_{0.125}\text{CuO}_4$  which is not inconsistent with the experimental superconductor  $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$  ( $x = 0.06-0.2$ ). The O-ion (instead of the  $\text{O}^-$  ion) is a symbolic designation of a hole within the  $\text{CuO}_2$  layer. In the quadruple cell with 32 oxygens, if we place the holes on the top or bottom  $\text{CuO}_2$  layer, then it will be the conducting layer with two holes per four copper atoms (Fig. 2). We shall use this structure to formulate the principles of high  $T_c$  superconductors and to visualize its relationship to low  $T_c$  superconductors. It is perhaps not a simple coincidence that such a quadruple cluster cell [14] with the right number of conducting holes/electrons can also be postulated for the hole superconductor, 123 compound  $(\text{YBa}_2\text{Cu}_3\text{O}_{6.75})_4$  and the electron superconductor [15]  $(\text{Nd}^{+3})_{15}(\text{Ce}^{+4})(\text{Cu}^{+2})_6(\text{Cu}^{+1})_2(\text{O}^{-2})_{31.5}$  which amounts to  $\text{Nd}_{1.875}\text{Ce}_{0.125}\text{CuO}_{3.9375}$  (comparable to the experimentally proven superconductor  $\text{Nd}_{1.85}\text{Ce}_{0.15}\text{CuO}_{3.93}$ ). In all of these cases, the quadruple cells help to resolve the fractional atomic ratios of non-stoichiometry to produce paired holes and electrons [14], and to yield a periodic series of quadruple cells with alternating short versus long bonds that will produce double-well potentials similar to those of intervalent (double) charge transfers.

To visualize the pairing of holes (or electrons), we consider the molecular orbitals of the  $\text{CuO}_2$  lattice (Fig. 3) coming from the top layer of the quadruple cell (Fig. 1). Although the two symbolic O-holes may be on the  $P\pi$  orbital of oxygen [16], the band structure studies [13, 17] generally fill up the lower  $P\pi$  orbitals and assign the holes to the antibonding  $\sigma^*$  orbitals involving the  $3d_{x^2-y^2}$  bands of

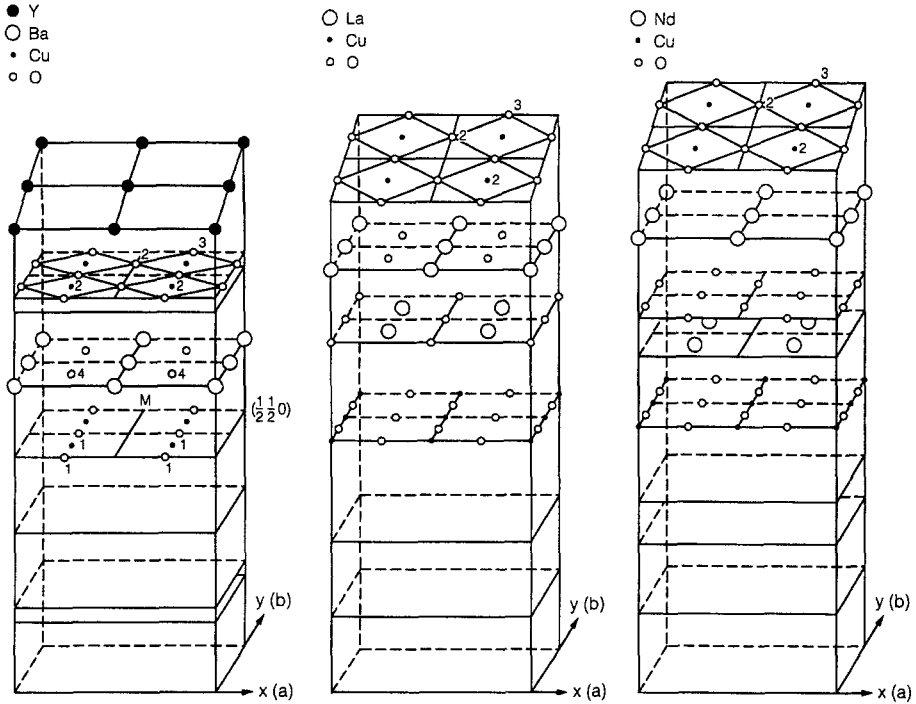


Fig. 1. The three postulated quadruple cells  $(YBa_2Cu_3O_7)_4$ ,  $(La_2CuO_4)_8$ ,  $(Nd_2CuO_4)_8$ . The distribution of oxygen vacancies,  $O^-$  and mixed-valent Cu-ions will be visualized based on this. Drawings are schematic. Atoms on the symmetric (by reflection) lower part are omitted

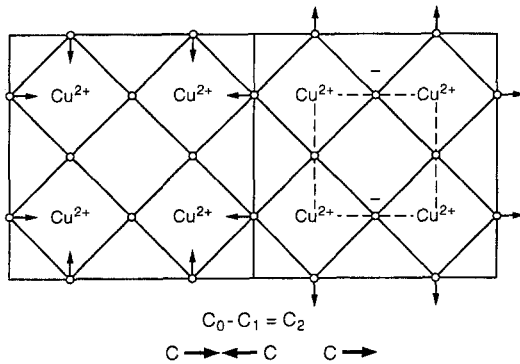
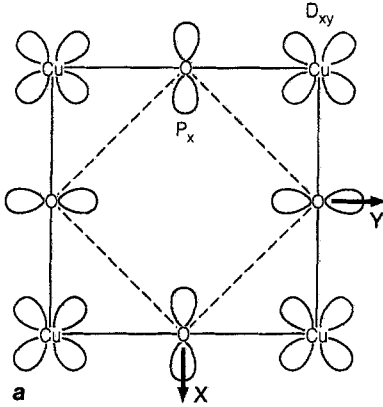


Fig. 2. Qualitative illustration of the movement of two holes between four copper complexes, similar to the movement of two  $\pi$  electrons among two alternating nearest neighbor C-C bonds and the cooperation with "anti-symmetric" vibration. Although not explicitly shown, the bonding environments involving the holes around the Cu complexes should be different (and alternating). The two  $O^-$  (instead of  $O=$  which is drawn as  $O$ ) is the symbolic representation of two antibonding holes, namely two fewer antibonding electrons in the antibonding  $\sigma^*$  orbitals consisted of oxygen  $sp$  hybrid and copper  $3d_{x^2-y^2}$ ,  $4s$ ,  $4p_x$ ,  $4p_y$  ( $dsp^2$ ). Since the  $\sigma^*$  orbital is a linear combination of oxygen and copper orbitals the holes are also shared by oxygen and copper and may be transferred even to oxygen  $p_x$  orbitals



**a**  $D_{2h}$  (vs  $D_{4h}$ ) symmetry antibonding  $\sigma^*$  orbitals between  $dsp^2$  of copper and sp of oxygen

	( $D_{2h}$ )	( $D_{4h}$ )
	— $5B_{1g}^*$	$B_{1g}$
$6B_{2u}^*$ —	— $6B_{3u}^*$	$E_u$
	— $7A_g^*$	$A_{1g}$
	— $4B_{1g}^*$	$B_{1g}$
$5B_{2u}^*$ —	— $5B_{3u}^*$	$E_u$
	— $6A_g^*$	$A_{1g}$

mainly oxygen (O) in-plane  $p_x=p_z$  of oxygens on top and bottom horizontal lines and  $p_y$  of oxygens on half way of vertical lines (Fig.3a)

	$5A_g^*$ —	
$4B_{2u}^*$ —		$4B_{3u}^*$ —
	$4A_g^*$ —	

**Fig. 3a.** The tetragonal arrangement of  $CuO_2$  plane. The  $D_{4h}$  symmetry may be distorted to  $D_{2h}$  through second-order Jahn–Teller effect. **b** The molecular orbitals of planar  $CuO_2$  lattice. The orbitals are designated by the irreducible representation of  $D_{2h}$  symmetry. The  $B_{2u}$  and  $B_{3u}$  are not degenerate unless the symmetry is  $D_{4h}$ . The 24 molecular orbitals are formed from eight oxygen sp hybrid orbitals plus four oxygen  $p_\pi$  orbitals plus four copper  $d_{xy} = d_x$ , orbitals plus eight (out of 16) copper  $dp^2$   $\sigma$  orbitals. There are 16 electrons from the Cu–O  $\sigma$  bonds, plus eight lone pair d electrons on  $d_{xy} = d_x$ , plus four lone d electrons on antibonding orbitals (for  $Cu^{+2} 3d^9$ ) plus eight lone-pair electrons on the four oxygen  $p_\pi$  orbital of O = (or two single electrons for the two  $O^-$  which is equal to two holes of Fig. 2 in these two oxygen  $p_\pi$  orbitals. These holes may also be transferred to the  $dsp^2$  antibonding  $\sigma^*$  orbitals, or mainly the  $d_{x^2-y^2}$  antibonding orbitals)

copper (e.g. bands from the  $5A_g^*$ ,  $5B_{2u}^*$ ,  $5B_{3u}^*$  or  $4B_{1g}^*$  antibonding  $\sigma^*$  molecular orbitals). Of course, molecular orbital considerations and the band structure studies are just some of the various artificial and approximate ways to interpret the truth of nature. This is because the (one-electron) molecular orbital does not

involve electron–electron correlation and *electronic* orbital and band theories do not involve the effect of molecular vibrations which is relevant and important when the movement of electrons (holes) affect the molecular structure. For example consider conjugate  $\pi$  bonds that may stay at one set of  $\sigma$  bond locations (say the left side set) or at another set of neighboring  $\sigma$  bond position (say the right side set). These two sets of (resonant) conjugate  $\pi$ -electron structures are doubly degenerate. The contracting vibration (say at left-side set bonds) favors the presence of  $\pi$ -bonds (at the left-side set also) and lowers the energy to a minimum on this left-side set similar to Peierls distortion. But, in addition to this (one-side) Peierls distortion, the opposite contracting vibration (at right-side bonds) will favor the other set of conjugate  $\pi$ -bonds (at the right-side setting) and lower the energy to the other minimum which is of the same height as the previous minimum. This is the reason for the double-minimum double-well potential which we will emphasize for the movement of the conjugate  $\pi$ -electrons from left to right and vice versa. Therefore we will consider vibronic perturbation interaction that will involve the relevant antisymmetric vibration (that has opposite contraction/expansion between neighboring bonds) and configuration mixing (that improves electron correlation) due to this perturbation.

So far we have just been asserting a molecular orbital picture and assuming delocalization of the electrons of the four copper atoms and oxygen atoms. The purpose is just to pay attention to the molecular electronic structure of a more tight binding “molecular” crystal in high  $T_c$  superconductor which is different from the nearly free electron (even with a modified reduced mass) of BCS theory for the atomic crystals.

Existing theories appear to be more concentrated on the equilibrium ground-state structure. For example, because numerical band calculations give oxygen  $P\pi$  bonds of lower energy, it is then assumed that the electrons will pile up and pair up at such lower levels. As a result the major holes will be at the antibonding  $\sigma^*$  orbitals consisted of oxygen  $sp$  hybrid and copper  $3d_{x^2-y^2}$ ,  $4s$ ,  $4p_x$ ,  $4p_y$ . Merely such equilibrium ground-state structure does not provide information as to how the other excited configurations arise due to vibronic interaction, what causes the difference of the spin multiplicity of the excited states and how the electric field perturbation affect the states during conductivity. Similarly, in the switch from ferromagnetic to antiferromagnetic spin waves, the artificial change in the approximate Heisenberg Hamiltonian [6]  $H = -2J\sum_n \mathbf{S}_n \cdot \mathbf{S}_{n+1}$  does not necessarily speak for the true dynamics or imply any basic mechanism. For example the change may involve the sign of the exchange integral  $J$  or alternatively the change may give rise to opposite (instead of identical) signs of the spins at even versus odd positions in  $H = -2J\sum_n \mathbf{S}_{2n} \cdot \mathbf{S}_{2n+1}$  where  $S_{2n}^z = S_{2n+1}^z \cong S = -S_{2n+1}^z$  in the equation of spin motion due to magnetic torque  $\hbar d\mathbf{S}_{2n+1}/dt = -(g\beta_0/\hbar)(\mathbf{S}_{2n+1} \times \mathbf{B}_{2n+1}) = 2J\mathbf{S}_{2n+1} \times (\mathbf{S}_{2n+1} + \mathbf{S}_{2n})$ . There is no dynamical mechanism given for the switch from parallel to antiparallel spins. Similarly, for Meissner effect of superconductors, even though there is London equation  $\nabla = 1/\lambda^2$ ,  $B$  where the London penetration depth  $\lambda$  determines the location of  $B = 0$ , yet there appears to be no clear molecular structural mechanism for the magnetic susceptibility of  $\chi = M/H = -1$  (or  $-1/(4\pi)$ ). Therefore, we like to consider some mechanistic aspects of spin multiplicity change aside from the simple pairing of spins as in BCS theory and we like to consider position space representation of molecular structural wavefunctions for the high  $T_c$  superconductors.

In a tetragonal environment each of the  $3d^9$  configuration of  $\text{Cu}^{+2}$  has one lone  $3d_{x^2-y^2}$  electron. In principle [18, 19] four  $\text{Cu}^{+2}$  with four spins can have a total

spin angular momentum of  $S = 2, 1$  and  $0$ . A question may be asked about the mechanism of formation of the Cooper pairs apart from the energy lowering. For the four  $3d_{x^2-y^2}$  lone electrons (or two lone electrons, if there are two holes), the change from parallel spin  $S = 2$  (or  $S = 1$ ) to antiparallel spin  $S = 0$  may require a second-rank tensor operator to small spin-spin magnetic (dipole-dipole) interaction (or small first-order spin-orbit operator for  $\Delta S = 1$ ) [20, 21] which is totally symmetric in a given point group. From the view point of chemical structure, we ask under what point group symmetry of the superconducting lattice will be  $S = 2$  (or  $S = 1$ ) and  $S = 0$  structures have the same symmetry [22] and can be connected by these small interaction operators.

In BCS theory [5, 9], the attractive electron correlation is due to the second order electron-phonon perturbation Hamiltonian  $H'' = 1/2D^2 \sum_{qkk'} C_{k'+q}^+ C_{k'} C_{k-q}^+ C_k (1/(E_k - E_{k-q} - W_q) - 1/(E_{k'} - E_{k'+q} + W_q)) = -V \sum_{kk'} C_{k'+q}^+ C_{k'} C_{k-q}^+ C_k$ . Because of the neighboring product of electron creation ( $C^+$ ) and annihilation ( $C$ ) operators of opposite momenta  $\pm k'$  and  $+k$  and because the total electron wavefunction in a Slater determinant  $\psi = |\dots \phi_k \phi_{-k} \dots|$  also contains neighboring product of one-electron orbitals of opposite momenta  $\phi_k$  and  $\phi_{-k}$ , the permutation of  $\phi_{-k}$  to the front to be operated by the annihilation operator  $C_{-k}$  will yield a sign change for the total wavefunction that is different from the sign change of the later permutation of the neighboring  $\phi_k$  to the front to be operated by  $C_k$ . The overall change in the sign of the total wavefunction will be cancelled by the subsequent similar sign change due to the creation of two neighboring one-electron wavefunctions  $\phi_{k'}$  and  $\phi_{-k'}$  by  $C_{k'}^+$  and  $C_{-k'}^+$ . Therefore, in the electron-phonon scattering only when two electrons of opposite momenta ( $k, -k$ ) are simultaneously annihilated and two electron of (a different set) of opposite momenta ( $k', -k'$ ) are simultaneously created will the (transition) matrix element of  $\langle H'' \rangle$  maintain a negative value for gap lowering of energy. The electron pair ( $k$  and  $-k$ ) must have opposite spins so that there will be no "exchange" integral that yields a negative sign and a positive  $\langle H'' \rangle$  matrix element. This is similar to the spin-paired two-electron chemical bond situation. And the change of  $k$  to  $k'$  is similar to the change of bonding electron orbital due to configuration mixing. That is why we want to explore the bonding structure of high  $T_c$  superconductor in a chemists' view of position space instead of momentum space. Since the electrons with opposite momentum will have higher probability density, we should study how well can the momentum space treatment of low  $T_c$  superconductors be replaced by a position space description of paired electrons in high  $T_c$  superconductors.

The above second-order electron-phonon perturbation Hamiltonian  $H''$  results from the first-order Hamiltonian  $H' = i \sum_q D_q C_{k+q}^+ C_k (a_q - a_{-q}^+)$  which contains phonon creation ( $a_{-q}^+$ ) and annihilation ( $a_q$ ) operators and which resembles the Herzberg-Teller expansion of first-order vibronic interaction  $(\partial H / \partial Q) Q$ . That is why we also will translate the electron-phonon interaction into a vibronic interaction related to Jahn-Teller effect [23, 24] in position space and ask how it will lower the energy to yield the superconducting gap which we relate to the splitting of degenerate vibronic levels in a double-well potential.

Our Jahn-Teller splitting is related to the degenerate perturbation with *first-order resonance* integral between two degenerate vibronic states as

$$\frac{1}{2} \left\langle \psi_{\Lambda}(1, 2) \chi^0(Q_{\Lambda}) \chi^1(Q_{-\Lambda}) \left| \frac{\partial^2 H}{\partial Q_{-\Lambda}^2} Q_{-\Lambda}^2 \right| \psi_{-\Lambda}(1, 2) \chi^1(Q_{\Lambda}) \chi^0(Q_{\Lambda}) \right\rangle.$$

This is different from an example of the detailed second-order perturbation of BCS theory such as

$$\frac{1}{2} D^2 C_{-k+\lambda}^+ C_{-k} C_{k-\lambda}^+ C_k \left( \frac{1}{E_k - w_\lambda - E_{k-\lambda}} - \frac{1}{E_{-k} + w_\lambda - E_{-k+\lambda}} \right),$$

where the  $D^2/\Delta E$  may be compared with our quantum chemical view of second-order perturbation energy

$$E^{(2)} =$$

$$\frac{\left\langle \phi_{k-\lambda}(1) \phi_{-k+\lambda}(2) \chi^1(Q_\lambda) \chi^1(Q_{-\lambda}) \left| \frac{\partial^2 H}{\partial Q_\lambda \partial Q_{-\lambda}} Q_\lambda Q_{-\lambda} \right| \phi_k(1) \phi_{-k}(2) \chi^0(Q_\lambda) \chi^0(Q_{-\lambda}) \right\rangle^2}{\Delta E}.$$

But the  $\phi(i)$  with  $i = 1, 2$  of BCS theory are one-electron wavefunctions which differ from our two-electron geminals  $\psi_{\pm\Lambda}$  (1, 2). Our use of Herzberg-Teller expansion

$$H = H_0(r_e Q^0) + \sum_\lambda \left( \frac{\partial H}{\partial Q_\lambda} \right)_0 Q_\lambda + \frac{1}{2!} \sum_\lambda \sum_{\lambda'} \left( \frac{\partial^2 H}{\partial Q_\lambda \partial Q_{\lambda'}} \right)_0 Q_\lambda Q_{\lambda'} + \dots$$

and our use of the two-electron geminal approach of degenerate perturbation is also different from Bipolaron theory [25–27]. We choose to visualize the Hamiltonian of Bipolaron as follows

$$\begin{aligned} H &= \sum_A \left( \alpha + 2\beta \cos \frac{2\pi A}{N} \right) b_A^\dagger b_A + \sum_\lambda \hbar \omega_\lambda a_\lambda^\dagger a_\lambda + \\ &+ \sum_A \sum_\lambda \left( \gamma_\lambda + 2\delta_\lambda \cos \frac{2\pi A}{N} \right) \sqrt{\frac{\hbar}{2m\omega_\lambda}} (a_\lambda^\dagger + a_\lambda) b_A^\dagger b_A \\ &= \sum_A \varepsilon_A b_A^\dagger b_A + \sum_\lambda \hbar \omega_\lambda a_\lambda^\dagger a_\lambda + \sum_A \sum_\lambda D_\lambda (a_\lambda^\dagger + a_\lambda) b_A^\dagger b_A, \end{aligned}$$

where  $b^+$  and  $b$  stand for electronic and  $a^+$  and  $a$  for vibrational creation and annihilation operators.

$$\begin{aligned} \alpha &= \langle (\phi_n | H_0 | \phi_n) \rangle; \quad \beta = \langle \phi_{n\pm 1} | H_0 | \phi_n \rangle; \\ \gamma_\lambda &= \langle \phi_n | (\partial H / \partial Q_\lambda)_0 | \phi_n \rangle; \quad \delta_\lambda = \langle \phi_{n\pm 1} | (\partial H / \partial Q_\lambda)_0 | \phi_n \rangle, \\ (\hbar / (2m\omega_\lambda))^{1/2} &= \langle \chi^0(Q_\lambda) | Q_\lambda | \chi^1(Q_\lambda) \rangle = \langle \chi^1(Q_\lambda) | Q_\lambda | \chi^0(Q_\lambda) \rangle. \end{aligned}$$

The linear combination of the  $\phi_n$  at local states will have the wavefunction

$$\Psi_A = \frac{1}{\sqrt{N}} \sum_{\Lambda=0}^{N-1} \exp(2\pi i \Lambda n / N) \phi_n.$$

The  $\phi_n$  further stands for the linear combination of two local ions that attracted two electrons (bipolaron). Hence  $b_A^\dagger = C_{A\alpha}^+ C_{A\beta}^+$  and  $b_A = C_{A\beta} C_{A\alpha}$  where  $c^+$  and  $c$  stand for *one-electron* creation and annihilation operators. Bipolaron theory deals with local ionic site  $n$  interacting with nearest-neighbor ions at  $n \pm 1$  which have equivalent but displaced oscillators. Yet, such treatment appears to have not emphasized the zero momentum we choose (e.g.  $\Lambda - \Lambda = 0$  in

$\Psi(1, 2) = \psi_A(1, 2)\chi^1(Q_{-A})$  and is different from the two-electron geminal quasi-particle Boson state. We consider for the antisymmetrized ( $A$ ) complete state  $\Psi(123456 \dots) = A\Psi(1, 2)\Psi(3, 4)\Psi(5, 6) \dots$ . Upon diagonalization by canonical transformation with

$$S = \sum_A b_A^\dagger b_A \sum_\lambda \frac{D_\lambda}{\hbar\omega_\lambda} (a_\lambda^\dagger - a_\lambda),$$

the Bipolaron Hamiltonian is

$$\bar{H} = e^S H e^{-S} = \sum_A \varepsilon_A b_A^\dagger b_A + \sum_A \hbar\omega_\lambda a_\lambda^\dagger a_\lambda - \sum_{A\lambda} \frac{b_A^\dagger b_A D_\lambda^2}{\hbar\omega_\lambda} = H^0 - H^{(2)}.$$

This again is similar to BCS theory to have a second-order perturbation  $H^{(2)}$  which also does not have our *first-order* degenerate perturbation (Renner–Teller).

We will study how vibronic interactions will be related to movement of a pair of electrons as Bosons. We also look for the origin of the long range-order and for the structure that contributes to high  $T_c$ . We shall depart from existing numerical band calculations approach without correlations and without vibronic interactions. We shall also depart from existing BCS mathematical approach in momentum space to go into a quantum chemical approach in position space in order to understand the structure and bonding principles. Although the approach may not be perfect, it at least offers an alternative based on the fundamental principles for a different superconductor theory of high  $T_c$ .

## 2. Spin pairing and vibronic interaction in high $T_c$ cuprates

In Fig. 3a, the quadruple  $\text{CuO}_2$  lattice with four  $\text{Cu}^{++}$  atoms can in principle have  $D_{4h}$  tetragonal symmetry. But, because the superconductor is of orthorhombic symmetry (for example the 1, 2, 3 cuprate [28]) and because of the presence of holes we have adopted the subgroup  $D_{2h}$  symmetry. We use this symmetry to designate the molecular orbitals. It is different from the  $D_{4h}$  symmetry of one set of copper oxide (e.g.  $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$ ) local structure [26, 27]. If we assume the energy dictates the distribution of electrons to the lowest level, then the configuration for the  $^1A_g$  ground state will be  $(4B_{3u})^2(5A_g^*)^2(6A_g^+)^2[5B_{2u}^*]^0$  or  $(5B_{3u}^*)^0$  with the “two holes” on the  $d_{x^2-y^2}$  orbitals (the  $\sigma^*$  antibonding molecular orbitals  $5B_{2u}^*$  or  $5B_{3u}^*$  that have the mixing with the oxygen  $sp$  hybrid orbitals). The next higher configuration will have two holes on the  $5A_g$  oxygen  $p_{\pi x}$  orbitals (which interacts with the  $d_{xy}$  orbital) and will have the configuration  $(4B_{3u})^2(5A_g)^0(6A_g^*)^2[(5B_{2u}^*)^2$  or  $(5B_{3u}^*)^2]$ . The repulsive electron correlation ( $+e^2/r_{ij}$ ) will require the mixing of all of these possible configurations of the same symmetry. Therefore, the holes or electrons in the bonds formed by these molecular orbitals will spread over the four  $\text{CuO}_2$  in the quadruple cell layer. Such spreading turns out to be quite justifiable in high  $T_c$  cuprate superconductors, because the copper  $3d$  orbital and oxygen  $2p$  orbital have quite close valence orbital ionization potentials (14.0 eV versus 14.8 eV) and the holes/electrons see almost no potential barrier in their movement. But if they are spread out, the question is how will they pair up with opposite spins when they move from one quadruple  $\text{CuO}_2$  lattice to a neighboring lattice in superconduction. In fact, if one is to consider the magnetic structure, the four lone  $3d_{x^2-y^2}$  electrons in four copper atom are conventionally considered to be *localized* and no special mechanism is given for them to change from parallel to antiparallel



in the spin wave treatment. On the other hand, if there is  $Q(B_{1g})$  vibration which correlates to the  $A_g$  symmetry of  $C_{2h}$  subgroup, then it will involve the descent from the higher symmetry  $D_{2h}$  structure to the  $C_{2h}$  structure. In the latter, both the  $S = 2$  and  $S = 1$ , can have the same  $A_g$  symmetry as  $S = 0$ , this is illustrated in the Table 1 [22, 23].

This geometrical transformation and descent in symmetry can be achieved by the  $B_{1g}$  vibration of  $D_{2h}$  (from  $E_u$  in  $D_{4h}$ ). Note that among the subgroups of  $D_{4h}$  and  $D_{2h}$  only in  $C_{2h}$ , not in  $C_{2v}$ , can all  $S = 2, 1$  and  $0$  have the common  $A_g$  symmetry and can commingle and interconvert via the spin-spin and spin-orbit interactions that have  $A_g$  symmetry. If, during the onset of superconductivity, the  $B_{1g}$  vibration is activated, which reduces the distorted structure to  $C_{2h}$  symmetry, then the conversion to  $S = 0$  Boson-state should be no problem from the microscopic point of view for a quadruple planar cell. This  $Q(B_{1g})$  vibration can be included by analogy with the two-cell. This  $Q(B_{1g})$  vibration can be induced by analogy with the two-electron scattering through electron-phonon interaction of the BCS theory. For example we can take the configuration interaction with a doubly excited-state  ${}^1B_{1g} = 5B_{2u}^*5B_{3u}^*$  coming from the excitation of  $(6A_g^*)^2$ . This  ${}^1B_{1g}$  state will stabilize or lower the energy of the ground  $A_g$  state by the second-order Jahn-Teller effect,

$$E^{(2)} = \frac{\left\langle {}^1B_{1g} \chi^1(B_{1g}) \left| \frac{\partial H}{\partial Q(B_{1g})} Q(B_{1g}) \right| A_g \chi^0(B_{1g}) \right\rangle^2}{E({}^1A_g) - E({}^1B_{1g}) - E_q(B_{1g})} < 0. \quad (1)$$

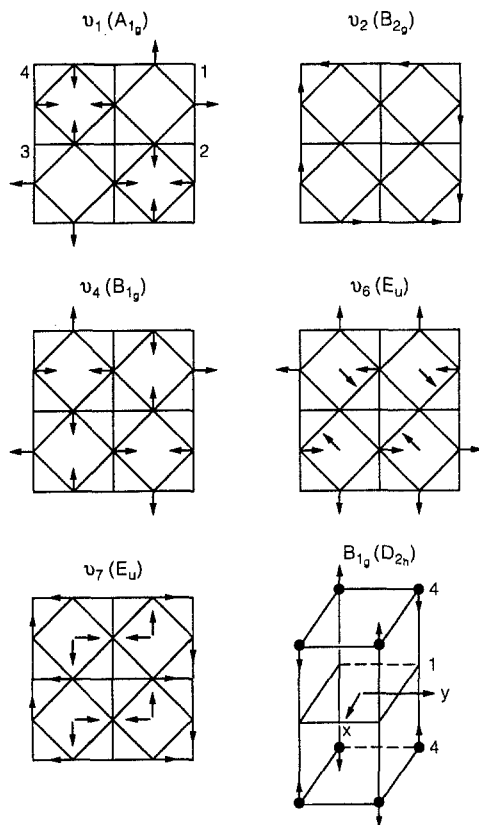
If the excitation is from the oxygen  $(5A_g)^2$ , then this vibronic mixing will create probability for two holes on the in-plane  $p_\pi$  orbital of oxygen which may be the  $p_x$  orbital not pointing at copper. The excitation can also come from the Cu-O  $\sigma$  bonding orbital  $(2A_g)^2$ . In that case the two holes will be essentially on the  $sp$  hybrid bond of oxygen.

In case of no holes there are four single  $3d_{x^2-y^2}$  electrons of four copper atoms which can be in the configuration of  $(6A_g^*)^2(5B_{2u}^*)(5B_{3u}^*)$  of  $D_{2h}$  symmetry. In case of four small polaron situation the four unpaired electrons will be localized in the four polarized copper atom position. It is still different from the four unpaired electron in the four different configuration  $(6A_g^*)(5B_{2u}^*)(5B_{3u}^*)(4B_{1g}^*)$ .

In this way the attractive (energy lowering) "electron correlation" due to vibronic interaction also affects the electrons or holes in the  $\text{CuO}_2$  quadruple cell in the same way as the repulsive ( $e^2/r_{ij}$ ) electron correlation. And, because of the singlet ground state, the vibronic interaction, which is spin-independent, requires all of the mixing excited states to be singlets ( $S = 0$  with antiparallel spins) similar to the singlet Bosons of Cooper pairs. The  $B_{1g}$  vibration coming from the cooperative vibration of four (neighboring)  $\text{CuO}_4$  ( $D_{4h}$ ) structures are shown in Fig. 4.

Table 1

	$S = 2$	$S = 1$	$S = 0$
$D_{4h}$	$A_{1g} + B_{1g} + B_{2g} + E_g$	$A_{2g} + E_g$	$A_{1g}$
$D_{2h}$	$2A_g + B_{1g} + B_{2g} + B_{3g}$	$B_{1g} + B_{2g} + B_{3g}$	$A_g$
$C_{2v}$	$2A_1 + A_2 + B_1 + B_2$	$A_2 + B_1 + B_2$	$A_1$
$C_{2h}$	$3A_g + 2B_g$	$A_g + 2B_g$	$A_g$



**Fig. 4.** Schematic representation of the cooperative vibration of four planar  $MX_4$  molecules, each of  $D_{4h}$  symmetry. We take only in plane vibrations and only those combinations that will descend into (or contain)  $B_{1g}$  of  $D_{2h}$  symmetry for  $(MX_4)_4$  and will subsequently descend into  $A_g$  of  $C_{2h}$  symmetry for  $(MX_4)_4$  and will subsequently descend into  $A_g$  of  $C_{2h}$  symmetry for  $(MX_4)_4$ . There are four linear combination for each vibration of  $MX_4$  ( $D_{4h}$ ), counting the  $MX_4$  unit clockwise, the linear combination for  $v_1(A_{1g})$  is  $1 - 2 + 3 - 4$ . This combination yields two sets of different sites, but does not involve small between-chain movement of the bridge oxygen. The linear combination for  $v_2(B_{2g})$  is  $1 + 2 + 3 + 4$ . The linear combination for  $v_4(B_{1g})$  is  $1 - 2 + 3 - 4$ . This latter does not create different sites. The linear combination for  $v_6(E_u)$  is  $1 - 2 - 3 + 4$ . The linear combination for  $v_7(E_u)$  is  $-1 - 2 + 3 + 4$ . The last two combinations are not irreducible representations of  $D_{2h}$ , but contain  $B_{1g}$  (and  $A_g$ ). The cancelling opposite vibrations are omitted. The reinforcing coincident vibrations are indicated by larger arrows. The out-of-plane  $B_{1g}$  ( $D_{2h}$ ) vibrations are for the apical oxygens of  $(YBa_2Cu_3O_{6.75})_4$ .

Our second-order vibronic treatment is different from Johnson *et al.*'s [29, 30] Jahn-Teller splitting of the degenerate  $e_g$  of  $D_{4h}$  symmetry (into  $b_{2g}$  and  $b_{3g}$ ) of the oxygen-oxygen  $O(p_z\pi)-O(p_z\pi)$  bonding in one set of copper oxide. Such *first-order vibronic interaction* will lead to the combinational pairing of the two separate electrons in  $e_g$  (presumably from the triplet  ${}^3A_{2g}$  of  $e_g^2$  configuration to the singlet  ${}^1A_{1g}$  of  $b_{2g}b_{3g}^0$  or  $b_{2g}^0b_{3g}^2$ ). One of the Jahn-Teller vibration,  $b_{1g}$  or  $b_{2g}$  of  $D_{4h}$  symmetry (depending on the assignment of the  $D_{2h}$  principle axis,  $C'_2$  or  $C''_2$ ) will distort and discent the  $D_{4h}$  symmetry to  $D_{2h}$  ( $A_g$ ) symmetry.

But in any case these vibronic interactions are still limited to the *local* structures. That is why in the next section we want to consider the movement of the

holes/electrons from one local structure to another neighboring structure due to the vibronic interaction of a (linear) crystal structure with (double-degeneracy due to) cyclic boundary condition and with double-well potential. It is a Jahn–Teller first-order interaction due to the (anti-symmetric) normal mode of crystal (phonon) vibration. Because the movement of holes/electrons cooperates with such anti-symmetric vibration, therefore the conductivity will not be resisted by the vibration.

Furthermore because of the pairing of electrons, that is why we propose the structure of *two electrons/holes* molecular *geminal* orbitals to replace the conventional (*one-electron*) molecular orbitals. In addition we also consider the valence-bond treatment by proposing two-electron “Covalons” in crystals.

### 3. Pairwise charge transfer and double well potential of two-electron/hole geminals

While the  $B_{1g}$  vibration will lower the energy of the ground state and will provide the mechanism for conversion of spin states into pairing singlets within the quadruple cell, it determines nothing about the movement of the paired electron holes away from this quadruple cell and about the long-range order and coherence of superconductors. The movement of the paired electron/holes will also be facilitated by the equal energy of the Cu( $3d$ ) and O( $2p$ ) orbitals. But, for a hole conductor we must start with finding where the holes are located, which implies a place with fewer  $\sigma^*$  anti-bonding electrons between  $d_{x^2-y^2}$  of Cu (and the  $sp$  hybrid of oxygen). Therefore, it means shorter CuO bond distances in the  $\text{CuO}_2$  quadruple cell compared with the neighboring cell. The symbolic nature of the alternative short-long bonds between nearest neighbors are similar to the alternating double-single bonds in conjugated hydrocarbons [31] or in the low  $T_c$  superconductor  $A_3B$ . This superconductor with chain integrity of  $A$ , for example  $A = \text{Nb}$ , has alternating triple-double bonds [32]. Such movement of bonding electrons (or antibonding holes) from  $\xi_L - \xi_R = Q_- < 0$  for a shorter bond length at left ( $\xi_L$ ) to a neighboring longer bond length at right ( $\xi_R$ ) will alter the bond length difference that becomes  $\xi_L - \xi_R = Q_- > 0$ . The movement amounts to a double well potential as a function of  $Q_-$  (Fig. 5), an anti-symmetric vibration. Such a double-well potential should also be present when a bonding Cooper electron pair moves from one inter-atomic region to another.

The alternating double bond in Fig. 5 which we use to imitate the contracted/expanded quadruple cells, may be considered to have come from the instantaneous potential well due to antisymmetric vibrations cooperating with electron redistribution. In the limited case of two sets of bonds with three atoms  $C_0-C_1=C_2$  one at the left  $\phi_L$  ( $C_0=C_1-C_2$ ) and one at the right  $\phi_R$  ( $C_0-C_1=C_2$ ) (Fig. 5), the wavefunction can be represented as a linear combination of these bonds as follows:

$$\begin{aligned}\psi_A &= \frac{1}{\sqrt{2}} \sum_{n=0}^1 \exp(2\pi i \Lambda n/2) \cdot \phi_n, \\ \psi_0 &= \frac{1}{\sqrt{2}}(\phi_0 + \phi_1) = \frac{1}{\sqrt{2}}(\phi_L + \phi_R) = \psi_+, \\ \psi_1 &= \frac{1}{\sqrt{2}}(\phi_0 - \phi_1) = \frac{1}{\sqrt{2}}(\phi_L - \phi_R) = \psi_-, \end{aligned} \quad (2)$$

where  $\phi_0$ ,  $\phi_L$  stand for  $C=C-C$  and  $\phi_1$ ,  $\phi_R$  stand for  $C-C=C$ .

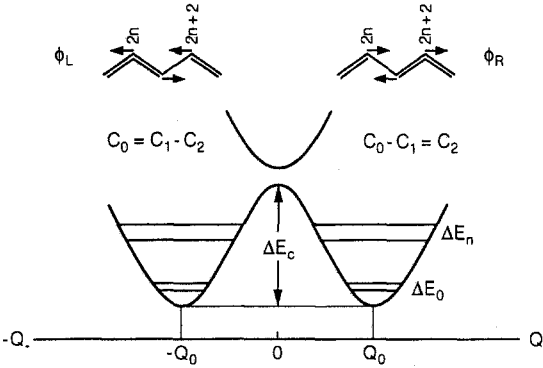


Fig. 5. The double oscillator model for the cooperation between an antisymmetry vibration and bond movement.

$$Q = r_{2n, 2n+1} - r_{2n+1, 2n+2} = \xi_L - \xi_R = Q_-$$

The double well potential barrier is related to the superconductivity gap. This is because at the top of the barrier with no vibration ( $Q_- = 0$ ) there is no electron/hole pairing under ( $\pm Q_-$ ) anti-symmetric vibration. The second-order energy barrier

$$\Delta E_c = - \left| \left\langle \frac{\partial H}{\partial Q} \right\rangle \right|^2 / 2m\omega^2$$

is comparable to Bipolaron theory's gap

The antisymmetric vibration can also be obtained as linear combination of left bond ( $\xi_L$ ) and right bond ( $\xi_R$ ) vibrations with  $A = 1$

$$\begin{aligned} Q_1 &= \frac{1}{\sqrt{2}} \sum_{n=0}^1 \exp(2\pi i n/2) \cdot \xi_n, \\ &= \frac{1}{\sqrt{2}} (\xi_0 - \xi_1) = \frac{1}{\sqrt{2}} (\xi_L - \xi_R) = Q_-, \end{aligned} \tag{3}$$

where  $\xi_L = \xi_0 = q_1 - q_0$  and  $\xi_R = \xi_1 = q_2 - q_1$  and  $q_i$  is the motion of atom  $i$  in  $C_0 \rightarrow C_1 \rightarrow C_2 \rightarrow$ . By symmetry selection rule we can mix the wavefunctions with different electronic  $A$ 's by vibronic perturbation of appropriate vibrational  $A$  as follows ( $\Delta A = 1$ )

$$\begin{aligned} \psi &= \psi_0 + a_1 \psi_1 = \psi + \chi^0(Q_-) + a_1 \psi_-, \\ a_1 &= \frac{\left\langle \psi - \chi^1(Q_-) \left| \frac{\partial H}{\partial Q_-} \right| \psi + \chi^0(Q_-) \right\rangle}{E_+ - E_- - E_Q} \chi^1(Q_-). \end{aligned} \tag{4}$$

In the limiting case the vibronic mixing may give  $1/\sqrt{2}(\psi_+ + \psi_-) = \phi_L$  that leaves the bonding electrons at left or may give  $1/\sqrt{2}(\psi_+ - \psi_-) = \phi_R$  that leaves the bonding electrons at right. Because the left and right bonds are doubly degenerate, similar to Peierls distortion, the anti-symmetric vibration will lower one and raise the other. We want to emphasize not just vibration but the positive versus negative vibration,  $\pm Q_-$ . The former (positive vibration  $\leftarrow C_0 \ C_1 \rightarrow \leftarrow C_2$ ) favors and

lowers the right side bond energy ( $C_0-C_1=C_2$ ) and the latter (negative vibration  $C_0 \rightarrow \leftarrow C_1 C_2 \rightarrow$ ) favors and lowers the left side bond energy ( $C_0=C_1-C_2$ ). The result is the double-minimum, double-well potential (Fig. 5).

This will paraphrase the antisymmetric vibration of neighboring quadruple  $\text{CuO}_2$  cells (Fig. 2). In Fig. (2) the presence of two O-(instead of  $\text{O}^-$  which is simply drawn as O) is the symbolic representation of the presence of two antibonding holes in the quadruple cell, i.e. two less electrons in the  $\sigma^*$  antibonding orbitals between the oxygen  $sp$  hybrid orbitals and the copper  $3d_{x^2-y^2}$ ,  $4s$ ,  $4p_x$ ,  $4p_y$  ( $dsp^2$ ) orbitals. For four  $\text{Cu}^{++}$  ( $3d^9$ ) there are usually four antibonding electrons in the antibonding orbitals (for example  $(6A_g^*)^2(5B_{2u}^*)^2$ ). In this case the Cu-O bonds will be longer and looser because of more antibonding. But when two antibonding electrons are gone (namely when there are only two, instead of four antibonding electrons, for example  $(6A_g^*)^2(5B_{2u}^*)^0$ ). This means the presence of two antibonding holes. In this case the Cu-O bonds will be shorter and firmer because of less antibonding. Therefore, the contraction (to shorter bonds) invites the antibonding holes to move in and extension (to long bonds) pushes the antibonding holes away. This is also because shorter bonds make the antibonding orbital energy higher and *disfavor the presence of antibonding electrons with high energy but favors the presence of antibonding holes* and vice versa for the longer bonds. To generalize this to a solid-state system with  $N$  quadruple cells we take  $\phi_n(1, 2)$  to be the two electron/two-hole antibonding/bonding geminal orbital of the  $n$ th cell and  $\xi_n$  to be the contraction/expansion breathing-type vibration of the  $n$ th quadruple cell (Figs. 2 and 4), and construct Bloch sum linear combination as follows:

$$\psi_\Lambda(1, 2) = \frac{1}{\sqrt{N}} \sum_{n=0}^{N-1} \exp(2\pi i \Lambda n/N) \cdot \phi_n(1, 2) = \frac{1}{\sqrt{N}} \sum_{n=0}^{N-1} \exp(i k n a) \cdot \phi_n(1, 2), \quad (5a)$$

$$Q_\Lambda = \frac{1}{\sqrt{N}} \sum_{n=0}^{N-1} \exp(2\pi i \Lambda n/N) \cdot \xi_n = \frac{1}{\sqrt{N}} \sum_{n=0}^{N-1} \exp(i k n a) \cdot \xi_n, \quad (5b)$$

where  $\hbar k$  is the crystal momentum related to the quasi-angular momentum  $\hbar \Lambda = (R \times P)_z$  as follows:

$$\hbar k = \frac{2\pi \hbar \Lambda}{Na} = \frac{2\pi (R \times P)_z}{2\pi R} = P. \quad (6)$$

The movement of two antibonding holes is related (though opposite) to the movement of two antibonding (say  $(5B_{2u}^*)^2$ ) electrons. For the latter case we can represent the two-electron *geminal* orbital as follows

$$\phi_n(12) = \frac{1}{\sqrt{2}} 5B_{2u}^{*n}(1) 5B_{2u}^{*n}(2) (\alpha_1 \beta_2 - \beta_1 \alpha_2).$$

We consider the superconducting vibronic two-electron geminal ground state as follows:

$$\Psi(1, 2) = \psi_0(1, 2) + \sum_{\Lambda} \frac{\left\langle \psi_\Lambda \chi^\Lambda(Q_{-\Lambda}) \left| \frac{\partial H}{\partial Q_{-\Lambda}} \right| Q_{-\Lambda} \right| \psi_0 \chi^0(Q_{-\Lambda}) \right\rangle}{E_0 - E_\Lambda - E_{Q_{-\Lambda}}} \psi_\Lambda(1, 2) \chi^\Lambda(Q_{-\Lambda}). \quad (7a)$$

In the limiting case, the interaction of

$$\psi_0(1, 2) = \psi_0 = \frac{1}{\sqrt{N}}(\phi_0 + \phi_1 + \phi_2 - \phi_3 + \dots)$$

and

$$\psi_{N/2}(1, 2) = \psi_{N/2} = \frac{1}{\sqrt{N}}(\phi_0 - \phi_1 + \phi_2 - \phi_3 + \dots) \quad (7b)$$

is due to the nearest-neighbor antisymmetric vibration

$$Q_{N/2} = \frac{1}{\sqrt{N}}(\xi_0 - \xi_1 + \xi_2 - \xi_3 + \dots),$$

which favors the motion of the geminals in the limit at

$$\frac{1}{\sqrt{2}}(\psi_0 + \psi_{N/2}) = \frac{\sqrt{2}}{\sqrt{N}}(\phi_0 + \phi_2 + \phi_4 + \dots)$$

to

$$\frac{1}{\sqrt{2}}(\psi_0 - \psi_{N/2}) = \frac{\sqrt{2}}{\sqrt{N}}(\phi_1 + \phi_3 + \phi_5 + \dots). \quad (7c)$$

Different vibrations and different interaction will give different long-range order of movement and different coherence length. In addition if we consider two sets of vibronic interaction, we can start with the first set of degenerate vibronic states  $\psi_A(1, 2)\chi^1(Q_{-A})$  and  $\psi_{-A}(1, 2)\chi^1(Q_A)$  which will be splitted by first-order special Renner–Teller effect (the second instead of the first Herzberg–Teller expansion) as follows:

$$\frac{1}{2} \left\langle \psi_A(1, 2)\chi^1(Q_{-A}) \left| \frac{\partial^2 H}{\partial Q_{-A}^2} Q_{-A}^2 \right| \psi_{-A}(1, 2)\chi^1(Q_A) \right\rangle. \quad (7d)$$

This two-electron geminal state with vibronic perturbation mixing is a quasi-particle that resembles Cooper pair state with electron–phonon interaction. But, instead of two electrons with opposite  $k$ 's, we choose a (two-electron) geminal with zero  $k$  (and zero  $A$ ) or zero momentum. This will also satisfy the London equation [33, 34] of  $j = -ne(P + e/cA)/m = -(ne^2/mc)A = -c/(4\pi\lambda^2)A$ . Our approach for the high  $T_c$  superconductor is closer to the tight-binding treatment (with local charges and local bonds) in solids. It is meant to be different from the conventional treatment of low  $T_c$  superconductor. The conventional treatment uses almost “free” electrons moving in uniformly smeared charge environment of solids. The corresponding total wavefunction for many (say  $N/2$ ) electron pairs will result from antisymmetrization ( $N!$  permutation  $P_\mu$  with, antisymmetry sign  $\delta_\mu$ ) and correction for the redundancy of  $N/2$  two-electron Boson states.

$$\Psi(1, 2, \dots, N) = \left( (2!)^{N/2} \left( \frac{N}{2} \right)! N! \right)^{-1/2} \sum_{\mu=1}^{N!} \delta_\mu P_\mu \Psi(1, 2) \Psi(3, 4) \dots \Psi(N-1, N). \quad (8)$$

For the movement of paired holes or electrons over periodic structure we shall consider the similar movement of bonds as paired electrons in electron conductivity. In order to compare with physicists' Bisoliton theory [35, 36] and resonanting

valence bond theory of superconductivity, we shall formulate the running wave of valence bonds with (linear or quasi-angular) momentum to be related to the wave vector. In particular, we shall consider the movement of a pair of excited perturbed (e.g. due to external applied electric field) electrons in a “Covalon” picture [31, 32] which we proposed in 1976 to stand for the cooperative pairwise charge transfer of “neighboring” covalent bonds interacting cooperatively with the antisymmetric vibration which creates double-well potential. The perturbed pair is taken to be at the place where two double bonds are crowded around one atom (with \*) (Fig. 6). The exciton-like “Covalon” [31, 32] wavefunction is elaborated exactly in detail as follows for a system with  $2N + 3$  atoms and  $2N + 4$  electrons. Again we use conjugate carbon  $\pi$ -electron bonds to imitate the alternating contracted/expanded bonds of quadruple cells. The linear combination is similar to the Bloch sum (for excitons, etc.):

$$\Psi_A(r_1 r_2 \cdots r_{2N+4}) = A \left\{ \sum_{n=1}^{N+1} e^{\frac{2\pi i A(2n)}{2N+3}} \Psi^*(2n) + \sum_{n=0}^{N+1} e^{\frac{2\pi i A(2n+1)}{2N+3}} \Psi^*(2n+1) \right\} / \sqrt{2N+3}, \quad (9a)$$

where

$$\Psi^*(2n) = \Phi^*(2n) \prod_{k=0}^{n-2} \Phi(2k+1, 2k+2) \prod_{m=n+1}^{N+1} \Phi(2m, 2m+1),$$

$$\Psi^*(2n+1) = \Phi^*(2n+1) \prod_{k=0}^{n-1} \Phi(2k, 2k+1) \prod_{m=n+1}^N \Phi(2m+1, 2m+2),$$

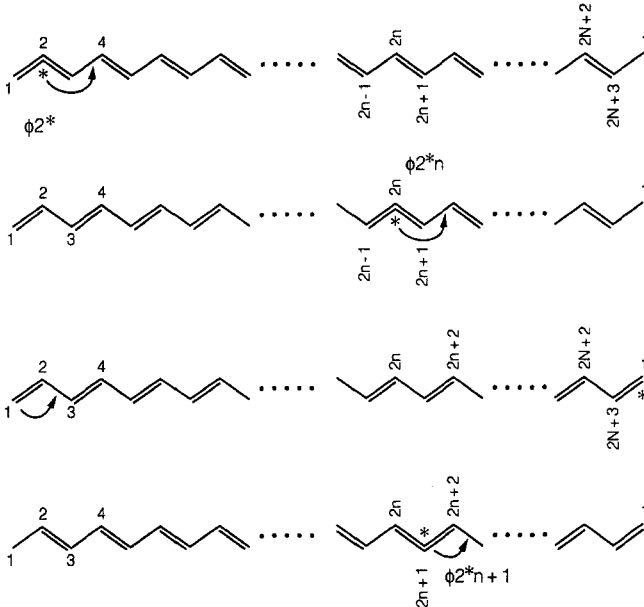


Fig. 6. Movement of a pair of excited (\*) electrons (a  $\pi$  bond) along a conjugate linear system. Cyclic boundary condition is adopted

and where

$$A = (4!(2!)^N(2N + 4)!)^{-1/2} \sum_{\mu=1}^{(2N+4)!} \delta_{\mu} P_{\mu} \quad (9b)$$

and the two bonding  $\pi$ -electrons are

$$\begin{aligned} \Phi(2k, 2k + 1) = & 1/2[\phi_{2k}(2k + 1)\phi_{2k+1}(2k + 2) + \phi_{2k}(2k + 2)\phi_{2k+1}(2k + 1)] \\ & \times (\alpha_{2k+1}\beta_{2k+2} - \beta_{2k+1}\alpha_{2k+2}) \end{aligned} \quad (9c)$$

and the two excited  $\pi$ -bonds are

$$\Phi^*(p) = \frac{1}{2}(4!)^{-1/2} \sum_{v=1}^{4!} \delta_v P_v \phi_{p-1} \phi_p \phi_p^* \phi_{p+1} (\alpha\beta\alpha\beta + \beta\alpha\beta\alpha - \alpha\beta\beta\alpha - \beta\alpha\alpha\beta). \quad (9d)$$

$A$  is the quasi-angular momentum if we use cyclic boundary conditions for connecting the two ends of the chain. In this cyclic case the No.  $2N + 4$  atom is the same as the No. 1 atom and No.  $2N + 3$  atom is the same as the No. 0 atom. This formulation is for the movement of two spin-paired (excited or activated by external electric potential) electrons in a conjugate  $\pi$  bond. The movement is similar to exciton propagation [37–40] with momentum  $k\hbar = 2\pi A\hbar / (2N + 3)r = A\hbar/R$ , where  $R$  is the radius of the circle. The resonance integral [41]  $U$  between the two neighboring excited pairs will give the interaction energy for the movement across the double well potential [31, 32] of an anti-symmetric vibration (Fig. 5).

$$U = \langle \Phi^*(2n) | H | \Phi^*(2n + 2) \rangle. \quad (10)$$

Such an antisymmetric vibration ( $Q$ ) will cooperate with the bond movement across the nearest-neighbors. This is because the stretching vibration on the left creates longer bond distances and higher  $\pi$ -bond energies thus discouraging the paired  $\pi$  electron from staying at this particular site. At the same time the contracting vibration on the right creates a shorter bond distance and lower energy due to more nuclear attraction which favors the  $\pi$ -electron pair to move over here to form a double bond. Such energy lowering of the doubly degenerate (resonant) nearest-neighbor conjugate  $\pi$ -bonds is of course similar to Peierls' distortion. Such electron–vibration coupling is weaker than electron-resonance and will preserve left-right identity. As a result the lower potential energy curve has a double minimum (at left and right) and a potential barrier  $V$  in between. If the individual vibration at the left or right has force constant  $f$ , the barrier without left-right coupling will be  $1/2fQ_0^2$ . The coupling matrix element  $U$  will lower the barrier, but the stabilization energy  $|U|^2/2fQ_0^2$  at the minimum will deepen the barrier [36] giving the expression

$$V = \frac{1}{2}fQ_0^2 - |U|^2 + \frac{|U|}{2fQ_0^2} = \Delta E_c. \quad (11)$$

In the 1976 paper of Chiu and Wang [31], this kind of barrier for pairwise charge transfer from  $C=C-C$  to  $C-C=C$  was estimated to be  $\Delta E_c = 0.20 \times 10^{-13}$  erg  $\approx 145^\circ$  K. This early estimate turns out to be comparable to the current high  $T_c$  number when the barrier is considered to be the superconductivity gap.



If the classical frequency of left/right vibrational energy levels is  $\nu_0$ , the splitting  $\Delta E_0$  of the two degenerate left/right vibrational energy levels  $E_0$  will be larger for smaller  $V$ ,

$$\Delta E_0 = E_0^- - E_0^+ = \frac{h\nu_0/\pi}{\exp\left(\frac{2}{\hbar} \int_0^{Q_0} [2\mu(V - E_0)]^{1/2} dQ\right)}. \quad (12)$$

Such splitting to create a lower energy level may also be compared with the formation of the superconductivity gap due to electron-phonon interaction. The time for tunneling [42, 43] for this case  $t_0$  is inversely proportional to the splitting energy  $\Delta E_0$ ,  $t_0 = \hbar/2\Delta E_0$ . There will be a cooperative effect if the electron tunneling time matches the period of vibration with a given vibrational quanta. If the two degenerate vibrational states at the two sides are higher in energy level  $E_n$ , the splitting of these two degenerate levels will result in large energy level difference (Fig. 5) and faster time (smaller  $t_n = \hbar/2\Delta E_0$ ) for tunneling. Such raising of the vibrational level may be due to the raise of temperature or the application of external electric field. Even though there is a faster moment of the higher (degenerate) vibrational levels, but the (paired) electron (hole) density at these higher vibrational levels are less localized and less motion from one local side to another side. Eventually, when the higher vibrational level reaches the top of the barrier of double-well potential, the electron (hole) density is delocalized evenly on both sides with the disintegration of the pairing of charges. Therefore, there is no pairwise charge conductivity as well as no vibrational tunneling (of localized vibrations). For high  $T_c$  superconductors with existing bonds in quadruple  $\text{CuO}_2$  structure (Fig. 2) the force constant is large and the system is more resistant to thermal perturbation to raise it above the zero-point energy level. For lower  $T_c$  superconductors the force constant, coming essentially from the instantaneous potential curve due to second-order electron-phonon interaction, is small and therefore will be more susceptible to thermal perturbation which breaks down the phonon-coupled Cooper pairs.

The double-well potential for the movement of electrons (or holes) across the nearest-neighbor will require near-neighbor antisymmetric vibration. For  $N'$  (= even) atoms this antisymmetric vibration correspond to  $\Lambda = N'/2$  in Eq. (5b). This will mix the ‘‘Covalon’’ running wave with mixing coefficient as follows [44]:

$$a_\Lambda = a_{N'/2} = \frac{\left\langle \psi_{N'/2} \chi^1(Q_\Lambda) \left| \frac{\partial H}{\partial Q_\Lambda} \right| \psi_0 \chi^0(Q_\Lambda) \right\rangle}{E_0 - E_{N'/2} - E_{Q_\Lambda}}. \quad (13)$$

To have longer-range order and coherence for the movement of bonds we will need antisymmetric vibrations with bonds further away. For example  $\Lambda = N'/4$  will correspond to next-to-nearest-neighbor antisymmetric vibration and  $\Lambda = N'/8$  will correspond to next-to-next nearest-neighbor antisymmetric vibration, etc. Each will have a double well potential that correspond to the movement of bonds (Fig. 5) further and further away. In addition to the alternating conjugate double bonding structure, there are also other (valence bond) resonance structures that may be considered along with different antisymmetric vibrations. The vibronic mixing to parallel the two-electron Cooper pair will consist of the sum over ( $\Lambda$  of) all of the vibronic perturbation mixing of the Covalon running waves.

$$\Psi(r_1 r_2 \cdots r_{2N+4}) = \Psi_0(r_1 r_2 \cdots r_{2N+4}) + \sum_{\Lambda} a_\Lambda \Psi_\Lambda(r_1 r_2 \cdots r_{2N+4}). \quad (14)$$

The  $a_A$ 's are expected to be smaller for larger separation of the bonds because of the smaller resonance integrals (Eq. (10)). The movement of the excited electron pair in  $\Phi^*$  (Fig. 6a, b) is very similar to the wave propagation of Bisolitons [35, 36]. The double bonds on the left of  $\Phi^*$  is slanted one way while the double bonds on the right of  $\Phi^*$  is slanted in another way. This is like taking the crowded double bond  $\Phi^*$  as the "wall" or as the "kink". Because our approach involves linear combination of different valence bonding structures, it represents a different resonant valence bond theory from that of Anderson [45, 46] which does not specify exactly the molecular bonding structure. This also represents a different vibronic interactions in terms of position space. It differs from vibronic mixing (electron-phonon interaction) of two (spin  $\uparrow\downarrow$  paired) electrons with opposite momentum  $k$  with another set of opposite momentum  $k'$  in a Boson state of BCS theory:

$$\psi(r_1 r_2) = \sum_k a_k \psi_k(1)\uparrow\psi_{-k}(2)\downarrow. \quad (15)$$

This BCS theory has the overall antisymmetric ( $A$ ) ground state:

$$\psi(r_1 r_2 \cdots r_{2N+4}) = A \psi(r_1 r_2) \psi(r_3 r_4) \cdots \psi(r_{2N+3} r_{2N+4}), \quad (16)$$

which differs from our Covalon state for the movement of bonding electrons (Eqs. (9) and (14)).

#### 4. Summary and discussions of further work

Based on non-stoichiometry of doping and the presence of holes (and electrons) we have proposed a periodic structure with quadruple  $\text{CuO}_2$  layer (Fig. 1) and have used this to formulate a position space approach of understanding the dynamics and mechanism of high  $T_c$  superconductors. This involves the mechanism of pairing of spins due to vibronic distortion of the structure, the pairwise charge transfer and its cooperation with antisymmetric vibration with a double well potential. It also involves the long-range order and coherence due to antisymmetric vibration at large separation corresponding to the charge transfer between these widely separated valence bonds.

Our approach represent a different view of resonance valence bond theory, a different position-space approach to the BCS principle of (free) electron-phonon interaction and a different structural view from Bisoliton movement and a new view of double-well potential in pairwise charge transfer to tight binding molecular crystals which may account for high  $T_c$  superconductivity [2, 3, 57, 48]. Based on our formulation, the types of numerical calculations that can be performed are as follows:

1. Calculation of the vibronic mixing coefficients (Eqs. (4) and (13)) and determination of when the coefficients diminish at how far away of the bond transfer and at how distant (instead of the nearest neighbor vibration) the cooperative antisymmetric vibration. This will lead to a determination of the coherence range.
2. Calculate the resonance integral (Eq. (10)), the potential barrier (Eq. (11)) as well as the vibrational frequency for the double-well potential. Compare the double well for high  $T_c$  compounds versus low  $T_c$  compounds.
3. Calculate the vibronic lowering of energy (Eqs. (1), (4) and (13)) for the ground state superconducting gap.

4. Find the splitting of the double well and its contribution to the energy gap and find the tunneling probability.
5. Search for other periodic structures (Fig. 2), similar to finding different resonance valence bonding structures of Eq. (9a). These numerical calculations are now in progress.

## References

1. Bednorz JG, Mueller KA (1986) *Z Phys* B64:189
2. Poole Jr CP, Datta T, Farach HA (1988) *Copper oxide superconductors*. Wiley, New York
3. Phillips JC (1989) *Physics of high  $T_c$  superconductors*. Academic Press, New York
4. Rao CNR, Raveau B (1989) *Account Chem Res* 22:106
5. Bardeen J, Cooper LN, Schrieffer JR (1957) *Phys Rev* 106:162; 108:1175
6. Kittel C (1963) *Quantum theory of solids*. Wiley, New York
7. Rose-Innes AC, Rhoderick EH (1978) *Introduction to superconductivity*. Pergamon, Oxford
8. Tinkham M (1975) *Introduction to superconductivity*. R. F. Krieger, Malabar, Florida
9. Schrieffer JR (1983) *Theory of superconductivity*. Addison-Wesley, New York
10. Cohen RE, Pickett WE, Krakauer H (1989) *Phys Rev Lett* 62:831 (1990) 64:2575
11. Hybertsen MS, Stechel EB, Schluter M, Jennison DR (1990) *Phys Rev* B41:11068
12. Cava RJ (1990) *Science* 247:656
13. Whangbo M-H, Torardi CC (1991) *Accounts Chem Res* 24:127
14. Chiu YN (1989) *J Chin Chem Soc* 36:487; (1989); (1993) *European J Solid State Inorg Chem* T30:1119
15. Tokura Y, Takagi H, Uchida S (1989) *Nature* 337:345
16. Birgeneau RJ (1990) *Am J Phys* 58:28
17. Whangbo M-H, Evain M, Beno MA, Geiser U, Williams JM (1987) *Inorg Chem* 26:2566; 26:1829
18. Chiu YN (1972) *J Chem Phys* 56:4882
19. Brodsky MB (1991) *MRS Bulletin* P31
20. Tinkham M (1964) *Group theory and quantum mechanics*. McGraw-Hill, New York.
21. Chiu YN (1979) *Phys Rev* A20:32 and references cited therein
22. Chiu YN, Meiling Gong (1990) *Chem Phys* 145:397
23. Herzberg G (1966) *Electronic spectra and electronic structure of polyatomic molecules*. D. Van Nostrand, Princeton, NJ
24. Chiu YN (1984) *J Phys Chem* 88:5820
25. Alexandrov AS, Ranninger J (1981) *Phys Rev* B23:1796
26. Alexandrov AS, Ranninger J, Robaszkiewicz S (1986) *Phys Rev* B33:4526
27. Alexandrov AS (1988) *Phys Rev* B38:925
28. Stavola M, Krol DM, Weber W, Sunshine SA, Jayarama A, Kouroukis GA, Cava RJ, Rietman EA (1987) *Phys Rev* B36:850
29. Clougherty DP, Johnson KH, McHenry ME (1989) *Physica C* 162-164:1475
30. Johnson KH, Clougherty DP, McHenry ME (1989) *Modern Phys Lett* 3:1367 (1991); In: Ashkenazi et al. (eds) *High-temperature superconductivity*. Plenum Press, New York, p 341
31. Wang FE, Chiu YN (1976) *Chem Phys* 12:225; YN Chiu, FE Wang (1976) *Chem Phys* 18:301
32. Chiu YN, Wang FE (1982) *J Solid State Chem* 45:353; (1982) *Inorg Chem* 21:4264
33. Hook JR, Hall HE (1991) *Solid state physics*. Wiley New York
34. Christman JR (1988) *Fundamentals of solid state physics*. Wiley, New York
35. Davydov AS (1988) *Phys Stat Sol (b)* 146:619; (1990) *Phys Reports* 190:191
36. Davydov AS, Ermakov VN (1988) *Phys Stat Sol (b)* 148:305
37. Craig DP, Walmsley SA (1968) *Excitons in molecular crystals*. Benjamin, New York
38. Hochstrasser RM (1966) *Ann Rev Phys Chem*. 17:457
39. Robinson GW (1970) *Ann Rev Phys Chem* 21:429
40. Davydov AS (1962) *Theory of molecular excitons*. McGraw-Hill, New York
41. Chiu YN (1976) *J Phys Chem* 80:992
42. Bell RP (1980) *The tunnel effect in chemistry*. Chapman and Hall, London

43. Marcus RA, Sutin N (1985) *Biochimica et Biophysica Acta* 811:265
44. Chiu YN (1976) *J Chem Phys* 64:2997; Chiu YN, Friedrich B, Maring W, Niedner G, Noll M, Toennies JP (1988) *J Chem Phys* 88:6814
45. Anderson PW (1987) *Science* 235:1196
46. Anderson PW, Baskaran G, Zou Z, Hsu T (1987) *Phys Rev Lett* 38:2790
47. Lynn JW (ed) (1990) *High temperature superconductors*. Springer, New York
48. Burns G (1982) *High temperature superconductivity*. Academic Press, New York