

APPLICATION OF RENNER-TELLER AND JAHN-TELLER EFFECT TO HIGH T_c SUPERCONDUCTIVITY THEORY WITH LCG-MG AND COVALON MODELS

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For combination and extension of physical and chemical approaches, instead of the BCS Theory in momentum space for low T_c superconductors, we propose the position-space theory for high T_c superconductors using quantum chemistry of molecular *geminal* orbital and valence-bond states. Our spectroscopy related vibronic *geminals* and vibronic 'Covalons' will serve as Boson-state quasi-particles. With emphasis on equal-minima double-well potential, besides the Jahn-Teller effect we consider the Renner-Teller effect because of the *geminals* and cyclic crystal boundary. It will have "first-order" vibronic degenerate perturbation in addition to the second-order perturbation energies of BCS and Bipolaron theories.

* YNC is in honor of Prof. István Kovács whose distinguished works on spectroscopy were highly appreciated when YNC was a post doctor in 1962 at the late Prof. Robert Mulliken's Laboratory of Molecular Structure and Spectra. He and fellow chemists were also very impressed by Prof. Kovács's book entitled "Rotational Structure in the Spectra of Diatomic Molecules". YNC is grateful for Prof. Kovács' inspirations that encourage him to continue works on the theory of molecular structure and spectroscopy.

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1. Introduction and comparison of degenerate perturbation of Renner–Teller effect with BCS and Bipolaron theory

The BCS theory [1–6] for low temperature superconductors such as Nb_3Sn deals mainly with essentially free electron pairs of opposite spins and opposite momenta in momentum space. It makes use of electron–phonon interaction to lower the energy of the ground state to create the superconductivity gap and to construct the Boson state of the Cooper pair quasi-particle consisting of two electrons. All of the (anti-parallel) spin paired electrons can occupy the same Boson state quasi-particle, and there will be no collision between paired electrons belonging to the same Cooper pair state. Because vibrations are already included in the electron–phonon interaction of the Cooper pair state, further vibrational prevention of electron conductivity no longer exists. The electron–phonon interaction of paired electrons in the Cooper pair involves second-order perturbation for the mixing of different electron momenta through vibrational running waves with appropriate momenta. There will be an average long-range order and coherence effect. The total zero momentum of the Cooper pair (of two electrons one with $+k$ and one with $-k$) produces the London Equation for the current density (J) dependent only on the electromagnetic vector potential A . This then leads to the penetration depth to reach the Meissner Effect of perfect diamagnetism. We shall make use of some of the wisdom of the above theory for low T_c and propose new approaches for the theory of high T_c . For the high T_c superconducting copper oxides [7–17] which are close to tight-binding molecular crystals with covalent bonds, we propose to consider the quantum chemical position-space treatment of the movement of spin-paired bonding (or antibonding) electrons (or holes) affected by ‘first-order’ degenerate vibronic interaction of the Renner–Teller and Jahn–Teller perturbation besides the usual second-order perturbation.

(1) As an alternative to the linear combination of atomic orbitals to form molecular orbitals (LCAO-MO) and to form electronic bands, we propose the linear combination of (bonding/antibonding) *two-electron geminals* to form molecular (bonding/antibonding) geminals: LCG-MG. This differs from BCS theory which starts essentially free *one-electron* states in momentum space.

(2) As an extension of chemical valence bond theory and Resonating Valence Bond (RVB) theory of Anderson [18], we propose the linear combination of covalent electron bonds in a ‘Covalon’ model that involves detailed chemical structural effects on conjugate (or alternating) covalent bonds [19]. And we include the vibrational effect on deformations (changes in the lengths of unit cells and/or structural bond lengths). This is also different from the Bipolaron theory [9] which deals with more ionic crystals.

(3) As an addition to the electronic effects we include vibronic interaction. But, instead of the usual linear combination of individual atomic movements, we consider the linear combination of individual bond vibrations (or unit cell vibrations) to match our proposed linear combination of binding geminals and covalent bonds.

(4) As a complement to Peierls distortion [20] we propose the consideration

of the Renner–Teller splitting of the doubly degenerate *vibronic states* and the Jahn–Teller splitting of doubly degenerate *electronic states* by *negative* as well as *positive* vibrations resulting in equal-minimum double-well potential as the ground state. Such deformation is still different from the Bisoliton theory [21, 22] that deals with acoustic vibrations.

The Renner–Teller Effect in spectroscopy deals with (equal to and more than triatomic) linear molecules (along axis z) with cylindrical ($C_{\infty v}$ or $D_{\infty h}$) symmetry which has cylindrical electronic state $\psi_{\Lambda}^e \approx \exp(i\Lambda\phi_e)$ with cyclic electronic angular momentum $\Lambda = 0, 1, 2, 3 \dots = \Sigma, \Pi, \Delta, \Phi \dots$ with angle ϕ_e . It also has cyclic vibrational angular momentum $\lambda = 0, 1 = \Sigma^+, \Pi$. The non-zero vibrational angular momentum of doubly degenerate vibrations results from the linear combination of bending vibrations along x and y perpendicular to the linear molecular axis z , i.e.

$$Q_{\pm\pi} = Q_{\pm 1} = Q_x \pm iQ_y = e^{\pm i\phi_v}.$$

A linear crystal with N atoms of cyclic boundary condition is similar to the cylindrical symmetry (of the x, y axes of linear molecules along z axis). The crystal's electronic and phonon states around the cyclic boundary also have pseudo angular momentum comparable with the true angular momentum of linear molecules. For example, the normal phonon mode of the crystal vibration with pseudo-angular momentum λ is:

$$q_{\lambda} = Q_{\lambda} = \frac{1}{\sqrt{N}} \sum_{n=0}^{N-1} e^{2\pi i \lambda n} \xi_n = \frac{1}{\sqrt{N}} \sum_n e^{ikna} \xi_n, \quad (1)$$

where ξ_n is the local atom n 's movement. The linear molecule with π electronic state and $\nu(\pi) (= Q_{\pi} = Q_{\pm})$ normal mode will have two degenerate *vibronic states* such as $\psi_1^e \chi^1(Q_{-1})$ and $\psi_{-1}^e \chi^1(Q_1)$ where $\chi^n(Q)$ stands for the vibrational state with n quanta. These will have mixing interaction of Renner–Teller Effect [23, 24]. It will be perturbed by a simply shown operator of Pople and Longuet-Higgins [25]

$$H' = fr^2(e^{2i(\phi_e - \phi_v)} + e^{-2i(\phi_e - \phi_v)})/2 = fr^2 \cos 2(\phi_e - \phi_v) \quad (2a)$$

which we will rewrite as

$$H' = \frac{1}{2} \frac{\partial^2 H}{\partial Q_{-1}^2} Q_{-1}^2 + \frac{1}{2} \frac{\partial^2 H}{\partial Q_1^2} Q_1^2 \quad (2b)$$

for degenerate perturbation mixing matrix element

$$\left\langle \Psi_1^e \chi^1(Q_{-1}) \left| \frac{1}{2} \frac{\partial^2 H}{\partial Q_{-1}^2} Q_{-1}^2 \right| \psi_{-1}^e \chi^1(Q_1) \right\rangle \neq 0. \quad (3)$$

$$= (2!)^{-1/2} \{ a_k [\Psi_k(1)\Psi_{-k}(2) + \Psi_k(2)\Psi_{-k}(1)] + a_{k+q} [\Psi_{k+q}(1)\Psi_{-k-q}(2) + \Psi_{k+q}(2)\Psi_{-k-q}(1)] + \dots \} \frac{(\alpha_1\beta_2 - \beta_1\alpha_2)}{\sqrt{2}}. \quad (4)$$

The mixing coefficient is related to phonon (q) addition and subtraction from electronic momentum and the ψ_k and ψ_{k+q} states are *not degenerate* and will result in second-order perturbation energy in the Hamiltonian with creation C^+ and annihilation C one-electron operators: (where $k' = -k$ for zero total momentum)

$$H'' = \frac{1}{2} D^2 \sum_{qkk'} C_{k'+q}^+ C_k C_{k-q}^+ C_k \left[\frac{1}{(E_k - E_{k-q} - \omega_q)} - \frac{1}{(E_{k'} - E_{k'+q} + \omega_q)} \right], \quad (5)$$

which is related to the second-order vibronic interaction $|\langle (\partial H / \partial q) q \rangle|^2 / \Delta E$. The Herzberg–Teller expansion for first-order vibronic interaction $(\partial H / \partial q) q$ is related to the BCS theory of first-order perturbation operator $H' = i \sum_q D_q C_{k+q}^+ C_k (a_{q-}^+ a_{-q}^+)$ which deals with *non-degenerate* electronic states, $k \neq k + q$.

But, because we choose two-electron molecular geminal orbitals (Fig. 1) instead of one-electron molecular orbitals we will have $\psi_{-\Lambda}^e(1, 2) \chi^1(\mathbf{Q}_{-\Lambda})$ which is degenerate with $\psi_{-\Lambda}^e(1, 2) \chi^1(\mathbf{Q}_{\Lambda})$. This yields degenerate perturbation matrix element similar to Renner–Teller effect with double-well potential

$$H'_{\mp\Lambda^e, \pm\Lambda^e} = \left\langle \Psi_{-\Lambda}^e(12) \chi^1(Q_{\Lambda}) \left| \frac{1}{2} \frac{\partial^2 H}{\partial Q_{\Lambda}^2} Q_{\Lambda}^2 \right| \Psi_{\Lambda}^e(12) \chi^1(Q_{-\Lambda}) \right\rangle, \quad (6)$$

$$E = E^0 \pm H_{\mp\Lambda^e, \pm\Lambda^e}.$$

This is beyond the second-order interaction of the BCS theory as well as Bipolaron theory (see below). Because of the infinite crystal with cyclic boundary condition, there will be much more vibrational pseudo-angular momenta $\Lambda = 0, 1, 2, 3, \dots$, beyond the limited $\Lambda = 0, \nu(\Sigma^+)$ and $\Lambda = 1, \nu(\pi)$ ($= Q_{\pi} = Q_{\pm 1}$) vibrations of a linear molecule.

The simple Hamiltonian we use is the Herzberg–Teller expansion of vibronic interaction

$$H = H_0(r_e Q^0) + \sum_{\lambda} \left(\frac{\partial H}{\partial Q_{\lambda}} \right)_0 Q_{\lambda} + \frac{1}{2} \sum_{\lambda} \sum_{\lambda'} \left(\frac{\partial^2 H}{\partial Q_{\lambda} \partial Q_{\lambda'}} \right) Q_{\lambda} Q_{\lambda'} + \dots \quad (7)$$

We emphasize the use of such vibronic interaction for Renner–Teller splitting (and Jahn–Teller splitting) of degenerate states similar to first-order perturbation and with double-well potential.

To compare the bipolaron treatment [9] with ours, we will visualize the *small* bipolaron treatment as follows:

$$H = \sum_{\Lambda} \left(\alpha + 2\beta \cos \frac{2\pi\Lambda}{N} \right) b_{\Lambda}^+ b_{\Lambda} + \sum_{\lambda} \hbar\omega_{\lambda} a_{\lambda}^+ a_{\lambda} + \sum_{\Lambda} \sum_{\lambda} \left(\gamma_{\lambda} + 2\delta_{\lambda} \cos \frac{2\pi\Lambda}{N} \right) \left(\frac{\hbar}{2m\omega_{\lambda}} \right)^{1/2} (a_{\lambda} + a_{\lambda}^+) b_{\Lambda}^+ b_{\Lambda}, \quad (8)$$

where b_Λ^\dagger and b_Λ are creation and annihilation operators for the electronic wavefunctions

$$\Psi_\Lambda = \frac{1}{\sqrt{N}} \sum_{n=0}^{N-1} \exp(2\pi i \Lambda n / N) \phi_n, \quad (9)$$

where ϕ_n may be the linear combination of two ions that attract two electrons (bipolarons). Therefore for pairs of electrons $b^\dagger = C_\alpha^\dagger C_\beta^\dagger$ and $b = C_\beta C_\alpha$ where C^\dagger and C are creation and annihilation for one electron only. Also

$$\alpha = \langle \phi_n | H_0(r_e Q^0) | \phi_n \rangle; \quad \beta = \langle \phi_{n+1} | H_0(r_e Q^0) | \phi_n \rangle. \quad (10)$$

a_λ^\dagger and a_λ are the creation and annihilation of vibrational wavefunction $\chi^\nu(\mathbf{Q}_\lambda)$ with ν number of quanta for the normal mode vibration \mathbf{Q}_λ . The vibration related terms are approximated

$$\begin{aligned} \gamma_\lambda &= \left\langle \phi_n \left| \left(\frac{\partial H}{\partial Q_\lambda} \right) \right| \phi_n \right\rangle; \quad \delta_\lambda = \left\langle \phi_{n\pm 1} \left| \left(\frac{\partial H}{\partial Q_\lambda} \right) \right| \phi_n \right\rangle, \\ \left(\frac{\hbar}{2m\omega_\lambda} \right)^{1/2} &= \langle \chi^0(Q_\lambda) | Q_\lambda | \chi^1(Q_\lambda) \rangle = \langle \chi^1(Q_\lambda) | Q_\lambda | \chi^0(Q_\lambda) \rangle, \end{aligned} \quad (11)$$

where \mathbf{Q}_λ is defined in Eq. (1). Here the matrix element between ϕ_{n+1} and ϕ_n is the interaction between displaced neighboring ions. Our first-order Jahn-Teller vibronic interaction may also be extended to the interaction between two degenerate displaced oscillators and $\delta_\lambda (\hbar/2m\omega_\lambda)^{1/2}$ is related to the D_q of BCS theory $H' = i \sum_{kq} D_q C_{k+q}^\dagger C_k (a_q - a_{-q}^\dagger)$ which, however, deals with electronic momentum k and vibrational momentum q . The bipolaron theory deals, however, with local sites n and nearest neighbor ions $n \pm 1$. Such bipolaron although treats pseudo-angular momentum Λ related to momentum k , yet it does not emphasize zero momentum we choose $\psi_0(1, 2)$ and mixtures with zero momentum to satisfy the London equation. In general this kind of bipolaron physical treatment we can simplify to

$$H = E_\Lambda b_\Lambda^\dagger b_\Lambda + \sum_\lambda \hbar\omega_\lambda a_\lambda^\dagger a_\lambda + \sum_\lambda D_\lambda b_\Lambda^\dagger b_\Lambda (a_\lambda + a_\lambda^\dagger). \quad (12)$$

The usual diagonalization by canonical transformation, we will consider as

$$S = b_\Lambda^\dagger b_\Lambda \sum_\lambda \frac{D_\lambda}{\hbar\omega_\lambda} (a_\lambda^\dagger - a_\lambda), \quad (13a)$$

that yields

$$\bar{H} = e^S H e^{-S} = E_\Lambda b_\Lambda^\dagger b_\Lambda + \sum_\lambda \hbar\omega_\lambda a_\lambda^\dagger a_\lambda - \sum_\lambda \frac{b_\Lambda^\dagger b_\Lambda D_\lambda^2}{\hbar\omega_\lambda} = H^0 - H^{(2)}. \quad (13b)$$

This shows only the “second-order” vibronic interaction ($\Delta E_\lambda = \hbar\omega_\lambda$)

$$H^{(2)} = \sum_{\lambda} \frac{\left| \langle \Psi\chi^0(Q_\lambda) | \frac{\partial H}{\partial Q_\lambda} Q_\lambda | \Psi\chi^1(Q_\lambda) \rangle \right|^2}{\Delta E_\lambda}. \quad (13c)$$

However, in our treatment we want to emphasize the possibility of degenerate first-order Renner–Teller and Jahn–Teller vibronic interactions that lead to double-well potential. This is because of the degeneracy of $\Psi_{\pm\Lambda}$ electronic states mix with degenerate $Q_{\mp\Lambda}$ vibrational states to agree with $\Lambda = 0$ state with zero momentum to satisfy the London equation.

2. The proposed model of linear combination of geminals to form molecular geminals (LCG-MG) and the proposed model of “Covalons”

To show the linear combination of (bonding) geminals we consider the $2N + 2$ hypothetical bonds between $2N + 3$ “atoms” with a total of $2N + 2$ higher energy mobile electrons from the conjugate double, triple or quadruple [26] (π and/or δ) bonds or antibonds. These are the electrons besides the lower energy non-moving σ -bonding electrons. The consideration of higher energy electrons is still different from the BCS theory of top Fermi level electrons. Our Bloch sum running wave with linear combination of *geminals* to form molecular geminals (LCG-MG) is as follows:

$$\begin{aligned} \Psi_\Lambda(1, 2) &= \frac{1}{\sqrt{2N+2}} \sum_{n=0}^{2N+1} e^{2\pi i \Lambda n / (2N+2)} \phi_{n, n+1}(1, 2) \\ &= \frac{1}{\sqrt{2N+2}} \sum_n e^{ikna} \phi_{n, n+1}(1, 2) = \Psi_k(1, 2). \end{aligned} \quad (14a)$$

This is different from the usual *one-electron* Bloch sum of nearly free electron waves. Our bonding (or antibonding) geminal is

$$\phi_{n, n+1}(1, 2) = \frac{1}{2} [\phi_n(1)\phi_{n+1}(2) + \phi_n(2)\phi_{n+1}(1)] (\alpha_1\beta_2 - \beta_1\alpha_2) \quad (14b)$$

and $\Lambda (= 0, 1, 2, \dots, 2N + 1 = 0, \pm 1, \pm 2, \dots, \pm N, N + 1)$ is the pseudo-angular momentum for cyclic boundary condition (of circumference $2\pi R = (2N + 2)a$) related to momentum $p (= \hbar k)$ as follows:

$$k\hbar = \frac{2\pi\Lambda\hbar}{(2N+2)a} = \frac{2\pi\Lambda\hbar}{2\pi R} = \frac{2\pi(R \times P)_z}{2\pi R} = \frac{RP}{R} = P. \quad (14c)$$

The (antiparallel) spin pairing of two electrons in a bond (or antibonding) in $\phi_{n,n+1}(1, 2)$ may be replaced by the two paired antibonding electrons (or antibonding holes) of the unit cell of four (CuO_2). In such a unit cell two $\text{Cu}^{+2}(3d^9)$ will give two antibonding $3d_{x^2-y^2}$ electrons and two $\text{Cu}^{+3}(3d^8)$ will give zero antibonding electrons or two antibonding holes. The energy of such a LCG-MG of a given Λ is

$$E_\Lambda = E_k = \alpha + 2\beta \cos \frac{2\pi\Lambda}{2N+2} = \alpha + 2\beta \cos(ka), \quad (15a)$$

where α is the Coulomb energy and β is the resonance integral between nearest neighbor geminals (neglecting next nearest neighbor and beyond)

$$\beta = \langle \phi_{n,n+1}(1, 2) | H | \phi_{n+1,n+2}(1, 2) \rangle. \quad (15b)$$

Taking $\psi_0(1, 2)$ with $\Lambda = 0$ as the basis, the quasi-particle for the ground state containing vibronic interaction [27] with LCG-MG of $\Lambda \neq 0$ is called a *vibronic geminal* as follows [28]:

$$\begin{aligned} \Psi_{gr}(1, 2) = \Psi_0(1, 2) + \sum_{\Lambda} \frac{\langle \Psi_{\Lambda}(1, 2) \chi^1(Q_{-\Lambda}) \left| \frac{\partial H}{\partial Q_{-\Lambda}} Q_{-\Lambda} \right| \Psi_0(1, 2) \chi^0(Q_{-\Lambda}) \rangle}{E_0 - E_{\Lambda} - E_{-\Lambda}^Q} \\ + \Psi_{\Lambda}(1, 2) \chi^1(Q_{-\Lambda}). \end{aligned} \quad (16)$$

In addition, at high $\Lambda \neq 0$, there are also vibronic geminals which are degenerate

$$\begin{aligned} \Psi_{+\Lambda^e}(1, 2) = \Psi_{\Lambda}(1, 2) \chi^1(Q_{-\Lambda}) + \frac{\langle \Psi_0(1, 2) \left| \frac{\partial H}{\partial Q_{\Lambda}} Q_{\Lambda} \right| \Psi_{\Lambda}(1, 2) \chi^1(Q_{-\Lambda}) \rangle}{E_{\Lambda} + E_{\Lambda}^Q - E_0} \psi_0(1, 2) \\ + \sum_{\Lambda'} \frac{\langle \Psi_{\Lambda'}(1, 2) \chi^1(Q_{-\Lambda'}) \left| \frac{\partial^2 H}{\partial Q_{\Lambda'} \partial Q_{\Lambda}} Q_{\Lambda'} Q_{\Lambda} \right| \Psi_{\Lambda}(1, 2) \chi^1(Q_{-\Lambda}) \rangle}{E_{\Lambda} + E_{-\Lambda}^Q - E_{\Lambda'} - E_{-\Lambda'}^Q} \Psi_{\Lambda'}(1, 2) \chi^1(Q_{-\Lambda'}), \end{aligned}$$

$$\begin{aligned} \Psi_{-\Lambda^e}(1, 2) = \Psi_{-\Lambda}(1, 2) \chi^1(Q_{\Lambda}) + \frac{\langle \Psi_0(1, 2) \left| \frac{\partial H}{\partial Q_{-\Lambda}} Q_{-\Lambda} \right| \Psi_{-\Lambda}(1, 2) \chi^1(Q_{\Lambda}) \rangle}{E_{-\Lambda} + E_{\Lambda}^Q - E_0} \Psi_0(1, 2) \\ + \sum_{\Lambda'} \frac{\langle \Psi_{-\Lambda'}(1, 2) \chi^1(Q_{\Lambda'}) \left| \frac{\partial^2 H}{\partial Q_{-\Lambda'} \partial Q_{-\Lambda}} Q_{-\Lambda'} Q_{-\Lambda} \right| \Psi_{-\Lambda}(1, 2) \chi^1(Q_{\Lambda}) \rangle}{E_{-\Lambda} + E_{\Lambda}^Q - E_{-\Lambda'} - E_{\Lambda'}^Q} \Psi_{-\Lambda'}(1, 2) \chi^1(Q_{\Lambda'}). \end{aligned} \quad (17a)$$

This kind of vibronic degeneracy is responsible for Renner-Teller effect with matrix element similar to Eq. (6)

$$H_{+\Lambda^e, -\Lambda^e} = \left\langle \Psi_{+\Lambda^e}(1, 2) \left| \frac{1}{2} \frac{\partial^2 H}{\partial Q_{-\Lambda}^2} Q_{-\Lambda}^2 + \dots \right| \Psi_{-\Lambda^e}(1, 2) \right\rangle. \quad (17b)$$

The vibronic interaction is comparable to the electron-phonon interaction. The vibrational running wave (Q) is taken to be the Bloch sum of the vibration of local bonds ($\xi_{n+1} - \xi_n$) instead of the motion of individual atom (ξ_n) so as to be comparable with the electronic running wave of bonds in LCG-MG

$$Q_\Lambda = \frac{1}{\sqrt{2N+2}} \sum_{n=0}^{2N+1} \exp\left(\frac{2\pi i \Lambda n}{2N+2}\right) q_{n,n+1}; \quad q_{n,n+1} = \xi_{n+1} - \xi_n. \quad (18)$$

Such local bond vibration may be the unit cell vibrations of quadrupole (CuO_2) structures. Such vibrational shortening or lengthening of bonds are related to the bonding/antibonding due to the presence or absence of electrons or holes. Because the vibronically mixed LCG-MG quasi-particle (vibronic geminal) is a Boson state, it can accommodate any number of paired electrons. The total wavefunction for $2N+2$ electrons will be as follows

$$\Psi(1, 2, 3, \dots, 2N+2) = A \Psi(1, 2) \Psi(3, 4) \dots \Psi(2N+1, 2N+2), \quad (19a)$$

where the normalization constant and antisymmetrizer is

$$A = \left[(2!)^{(2N+2)/2} \left(\frac{2N+2}{2} \right)! (2N+2)! \right]^{-1/2} \sum_{\nu=1}^{(2N+2)!} \delta_\nu P_\nu. \quad (19b)$$

The choice of zero total angular momentum and linear crystal momentum ($\Lambda - \Lambda = 0$, $\hbar k = 0$) is comparable to the choice of $+k$ and $-k$ for each of the two electrons respectively in the Cooper pair. It leads to the London equation that requires momentum $P = 0$

$$\left(\frac{c}{4\pi} \nabla \times B = \right) J = -n_s e \frac{1}{m} (p + \frac{e}{c} A) = -\frac{n_s e^2}{mc} A = -\frac{c}{4\pi \lambda^2} A, \quad (20a)$$

$$\frac{c}{4\pi} \nabla \times \nabla B = -\frac{c}{4\pi} \nabla^2 B = -\frac{c}{4\pi \lambda^2} \nabla \times A; \quad \nabla^2 B = \frac{1}{\lambda^2} B, \quad (20b)$$

where λ is the penetration depth to reach the Meissner effect of perfect diamagnetism. The energy of the quasi-particle of LCG-MG (Eq. (16)) is in general as follows

$$E_{gr} = E_0 + \sum_{\Lambda} \left[\frac{\left\langle \frac{\partial H}{\partial Q_{-\Lambda}} Q_{-\Lambda} \right\rangle}{\Delta E} \right]^2 E_{\Lambda} + \dots \quad (21a)$$

In addition there will be the second-order Jahn-Teller effect [30, 31] interaction energy

$$\begin{aligned} E_{gr}^{(2)} &= - \frac{\left| \left\langle \frac{\partial H}{\partial Q_{-\Lambda}} Q_{-\Lambda} \right\rangle \right|^2}{\Delta E} \\ &= - \frac{\left| \langle \Psi_{\Lambda}(1, 2) \chi^1(Q_{-\Lambda}) \left| \frac{\partial H}{\partial Q_{-\Lambda}} Q_{-\Lambda} \right| \Psi_0(1, 2) \chi^0(Q_{-\Lambda}) \rangle \right|^2}{E_{\Lambda} + E_{-\Lambda}^Q - E_0}. \end{aligned} \quad (21b)$$

As an extension and special molecular structures we could also consider first-order Jahn-Teller splitting of the degenerate $\Psi_{\pm\Lambda}(1, 2)$ states by degenerate $Q_{\pm 2\Lambda}$ vibrations

$$E^{(2)} = - \frac{\left| \langle \Psi_{\pm\Lambda}(1, 2) \chi^1(Q_{\pm 2\Lambda}) \left| \frac{\partial H}{\partial Q_{\pm 2\Lambda}} Q_{\pm 2\Lambda} \right| \Psi_{\pm\Lambda}(1, 2) \chi^0(Q_{\pm 2\Lambda}) \rangle \right|^2}{\hbar\omega_{2\Lambda}} \quad (21c)$$

This may be compared with the tunneling interaction of displaced oscillators with equal electronic energy and potential. Aside from the Jahn-Teller effect due to the first-order Herzberg-Teller expansion $(\partial H/\partial Q)Q$, there should also be a first-order energy due to the second-order Herzberg-Teller expansion for the special case of doubly degenerate $\pm\lambda$ vibrations and non-zero $\Lambda \pm \lambda$ total pseudo angular momentum.

$$E^{(1)} = \left\langle \Psi_{\Lambda}(1, 2) \chi^1(Q_{\lambda}) \chi^0(Q_{-\lambda}) \left| \frac{\partial^2 H}{\partial Q_{\lambda} \partial Q_{-\lambda}} Q_{\lambda} Q_{-\lambda} \right| \Psi_{\Lambda}(1, 2) \chi^0(Q_{\lambda}) \chi^1(Q_{-\lambda}) \right\rangle \quad (21d)$$

This is different from the London equation requirement of zero ($= \Lambda - \Lambda$) total pseudo angular momentum with operator $1/2(\partial^2 H/\partial Q_{\pm\Lambda}^2)Q_{\pm\Lambda}^2$ in Renner-Teller effect (Eqs (6) and (17)). The linear combination of the degenerate complex $+\Lambda$ and $-\Lambda$ states can yield states with bonding/antibonding electron geminals at conjugate resonant positions or at left versus right positions. Instead of the simple splitting of degeneracy by vibration as in Peierls distortion, we shall consider the detailed lowering of, for example, the 'right' position e.g. $C - C = C$ state by the *positive* antisymmetric vibration $\leftarrow C C \rightarrow \leftarrow C$ (and the simultaneous raising of the left state $C = C - C$). Similarly the equal level of lowering of the 'left' position state $C = C - C$ by the *negative* anti-symmetric vibration $C \rightarrow \leftarrow C C \rightarrow$ (and the simultaneous raising of the right state e.g. $C - C = C$). This is similar to the Jahn-Teller effect [27, 30, 31]. It results in a double-well potential with two equal minima: one at the positive equilibrium (vibrational) position ($+Q_0$) and one at the negative (vibrational) equilibrium position ($-Q_0$). This will be illustrated in Section 3 and Fig. 2. Such a double-well potential resembles intervalent charge transfer [32]. We believe such a double-well potential will always exist. For example, whenever a pair of bonding electrons moves into a core σ bond it will tend to shorten the bond to one of the double potential minimum positions. There will be a cooperative action when the speed of the tunneling movement matches the velocity of vibration [33, 34]. When the zero point vibration of the ground state is raised up to vibrational level at the *top* of the double-well potential barrier the antisymmetric vibration coordinate becomes zero. The difference between left and right bonding length disappears and there will be complete delocalization of the bonding electrons. As a result the quasi-particle of (antiparallel) spin-paired two electron geminals may disintegrate. This is because there will no longer be any localization of bonding/antibonding electron pairs. An illustration of this vibronic geminal model is given in Section 3 and Fig. 2 that also shows the gap.

The above LCG-MG treatment is an alternative to the LCAO-MO. Next we shall consider the extension of valence bond theory. We shall propose a Covalon

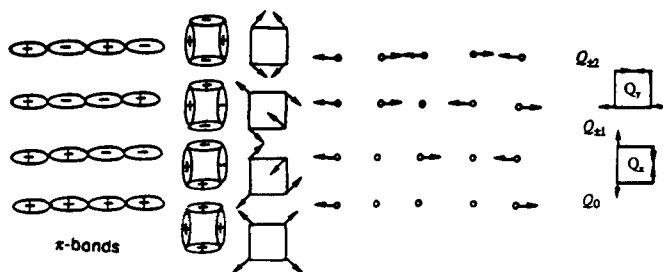


Fig. 2a. Linear combination of four (π) bonding geminals and linear combination of vibrations of four bonds (Q) in $C_0 - C_1 - C_2 - C_3 - C_4$ in the extension from a simple cyclic case to a linear case. Both + and - signs of the coefficients indicate the (π) bonding amplitude phases. Only when the two neighboring π -bonds have opposite phases (+ versus -) and a node, there will be anti(π -)bonding between the two bonds. No + or - sign means no coefficient or no bonding

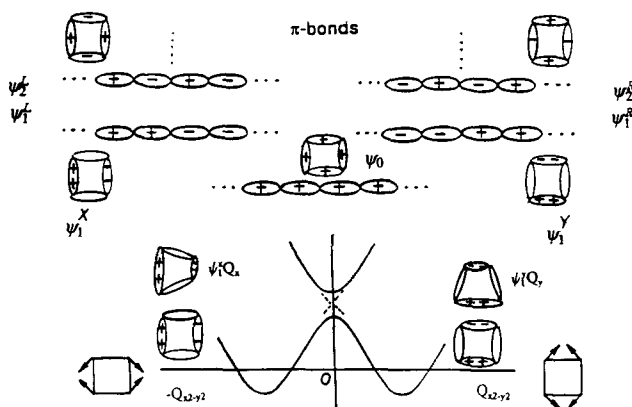


Fig. 2b. When the above linear combinations of bonding geminals, ψ_A , are extended from a small cyclic case to an infinite cyclic boundary condition of infinite linear chains, there will be degeneracy of $\pm\Lambda \neq 0$. For example, the degeneracy of ψ_1^L and ψ_1^R is similar to the linear combination of $(++)$ at $k = 2\pi\Lambda/(Na) = \pi/a$ with $\Lambda = N/2$ resulting in $(++)(-)(-)(++)(-)$. The splitting of electronic ψ_1^x and ψ_1^y (which come from the linear combination of the degenerate states of Fig. 2a) is based on the first-order Jahn-Teller effect. It results in a double-well potential. Similarly, the Renner-Teller splitting of vibronic states $\psi_1\chi^1(Q_{-1})$ and $\psi_{-1}\chi^1(Q_1)$ by operator $1/2(\partial^2 H/\partial Q_{\pm 1}^2)Q_{\pm 1}^2$ is shown by the real vibronic states $\psi_x\chi^1(Q_x)$ and $\psi_y\chi^1(Q_y)$ by real vibrations because $Q_{\pm 1}^2 \approx (x \pm iy)^2 \approx (x^2 - y^2) \pm 2i(xy)$ is related to $Q_{x^2-y^2}$

model [33, 34] that involves the dumping of (antiparallel) spin-paired electrons to crowd around conjugate valence bonds (e.g. the hypothetical $C=C^*=C-C=C$ of C_5H_7 in the illustration of Section 4) and to push the bonds away in cooperation with vibration. The crowded bonds at position s , ϕ_s^* are taken to be the basis of the Covalon. Their movement as a running wave is similar to the movement of Excitons [35, 36]. Again we consider the hypothetical case of $2N+2$ "bonds" between $2N+3$ "atoms" with a total of two more π electrons than the $2N+2$ 'mobile' π electrons in the previous LCG-MG treatment. This means the mobile $2N+4$ π electrons occupy totally $N+2$ (alternating) conjugate resonance bonds. The Bloch sum of the linear combination of the different localized crowded bonds is as follows [28]:

$$\begin{aligned}\Psi_{\Lambda}(1, 2, \dots, 2N+3, 2N+4) &= A \frac{1}{\sqrt{2N+3}} \sum_{s=0}^{2N+2} \exp\left(\frac{2\pi i \Lambda s}{2N+3}\right) \Psi_s^* \\ &= A \frac{1}{\sqrt{2N+3}} \sum_s \exp(iksa') \Psi_s^*,\end{aligned}\quad (22a)$$

where the normalization constant and antisymmetrizer is

$$A = \frac{1}{\sqrt{4!(2!)^N(2N+4)!}} \sum_{\mu=1}^{(2N+4)!} \delta_{\mu} P_{\mu} \quad (22b)$$

and

$$\Psi_s^* \stackrel{S=\text{odd}}{=} \psi_s^* \prod_{n=0,2,\dots}^{s-3} \phi_{n,n+1} \prod_{m=s+2,s+4,\dots}^{2N+1} \phi_{m,m+1}, \quad (22c)$$

$$\Psi_s^* \stackrel{S=\text{even}}{=} \phi_s^* \prod_{n=1,3,\dots}^{s-3} \phi_{n,n+1} \prod_{m=s+2,s+4,\dots}^{2N+2} \phi_{m,m+1}. \quad (22d)$$

The two crowded bonds with four electrons (1,2,3,4) are

$$\begin{aligned}\phi_s^* &= \frac{1}{2\sqrt{4!}} \sum_{\mu=1}^{4!} \delta_{\mu} P_{\mu} \phi_{s-1}(1) \phi_s(2) \phi_s^*(3) \phi_{s+1}(4) \\ &\quad \times (\alpha_1 \beta_2 \alpha_3 \beta_4 + \beta_1 \alpha_2 \beta_3 \alpha_4 - \alpha_1 \beta_2 \beta_3 \alpha_4 - \beta_1 \alpha_2 \alpha_3 \beta_4)\end{aligned}\quad (23a)$$

and the (resonant or conjugate) bond with two (i and j) of the higher energy mobile π electrons is

$$\phi_{n,n+1} = \frac{1}{2} [\phi_n(i) \phi_{n+1}(j) + \phi_n(j) \phi_{n+1}(i)] (\alpha_i \beta_j - \beta_i \alpha_j). \quad (23b)$$

The general energy for such a Covalon state is

$$E_{\Lambda} = E_k = \alpha + 2\beta'' \cos 2 \frac{2\pi \Lambda}{2N+3} = \alpha + 2\beta'' \cos 2ka', \quad (23c)$$

where β'' is the resonance integral between two alternating resonant crowded bonds ($A = A^* = A$) that have their "atomic" centers (A^*) different by two atomic units. This is similar to $A = A^* = A - A = A$ versus $A = A - A = A^* = A$

$$\beta'' = \langle \phi_s^* | H | \phi_{s\pm 2}^* \rangle. \quad (23d)$$

The resonant integral between crowded bonds that differ by one 'atomic' unit will involve too many differently placed conjugate bonds and will be smaller and is neglected. This means $A = A^* = A - A = A - A$ versus $A - A = A^* = A - A = A$

$$\beta' = \langle \phi_s^* | H | \phi_{s\pm 1}^* \rangle \sim 0. \quad (23e)$$

The so-called 'bonds' can be replaced by the paired bonding/antibonding electrons/holes of a given unit cell. The so-called neighboring 'atoms' similarly can be replaced by the neighboring unit cells.

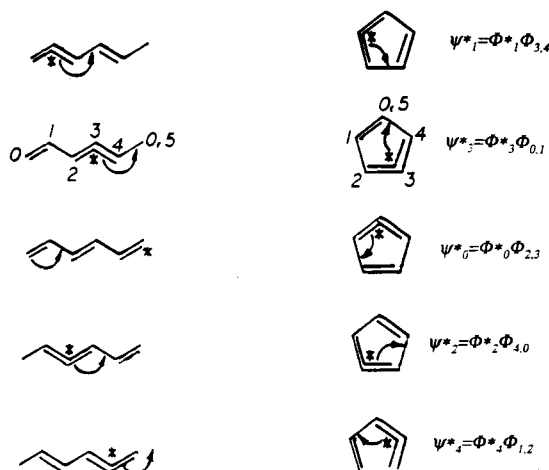


Fig. 3a. The illustration of Covalons using a hypothetical example similar to cyclic $C_5H_5^-$ with six π -electrons. It is translated into a corresponding linear case similar to $C_5H_7^-$ also with cyclic boundary condition

To include vibronic interaction, we use again the same running-wave vibration of bonds (Eq. 18) to match with our treatment of 'bonds'. To satisfy the London equation, again we choose $\Lambda = 0$ as the basis to mix with other $\Lambda \neq 0$ states through vibronic interaction by $Q_{-\Lambda}$:

$$\Psi(1, 2, \dots, 2N + 3, 2N + 4) = \Psi_0(1, 2, \dots, 2N + 3, 2N + 4) \quad (24)$$

$$+ \sum_{\Lambda} \frac{\langle \Psi_{\Lambda} \chi^1(Q_{-\Lambda}) | \frac{\partial H}{\partial Q_{-\Lambda}} Q_{-\Lambda} | \Psi_0 \chi^0(Q_{-\Lambda}) \rangle}{E_0 - E_{\Lambda} - E_{-\Lambda}^Q} \Psi_{\Lambda}(1, 2, \dots, 2N + 3, 2N + 4) \chi^1(Q_{-\Lambda}).$$

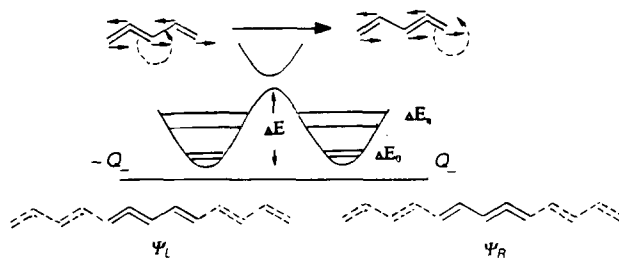


Fig. 3b. The movement of paired electrons in a Covalon model in cooperation with the anti-symmetric vibration. The degeneracy of left and right side of Covalon state before and after pair electron transfer. The splitting of degeneracy results in double-well potential. The splitting ΔE_0 of neighboring equal vibrations at zero quanta is smaller than ΔE_n of n quanta. The raise to the top of the potential barrier ΔE with delocalization and disintegration of the local Boson pairs is related to the gap

In addition, at high $\Lambda \neq 0$, there will also be Covalon states that are degenerate and will yield Renner-Teller effect. In addition, there will also be the second-order Jahn-Teller vibronic interaction energy and first-order Jahn-Teller splitting by antisymmetric vibration of the degeneracy of the two conjugate resonant Covalon bonding states of $+\Lambda$ and $-\Lambda$. We will consider for example, the left-handed vibrational contraction (say $+Q_\lambda$) that will lower the energy of the left bonding state (and raise the right bonding state). Similarly, we will also consider the opposite (say $-Q_\lambda$) right-handed vibrational contraction that will lower the right bonding state (and raise the left bonding state). For example the positive vibration $\leftarrow A A A \rightarrow A \leftarrow A$ favors $A = A - A = A = A$ and the negative vibration $A \rightarrow A \leftarrow A A A \rightarrow$ favors $A = A = A - A = A$. As a result there will be an equal minimum double-well potential state, which we will consider as the ground state with zero-point vibration. There will also be a cooperative effect if the movement of Covalon bonds coincides with the frequency of the anti-symmetric vibration. When this zero-point vibration is raised to the top of the double-well potential barrier at $Q = 0$, the difference between left-versus right conjugate bonding will disappear and the Covalon quasi-particle state is disintegrated. This difference between the potential minimum and the barrier top is considered to be the energy gap. An illustrative example of the Covalon model is shown in Section 4 and Fig. 3.

3. Illustrative example of vibronic interaction and double-well potential for linear combination of geminals to form molecular geminals (LCG-MG)

To illustrate the vibronic interaction and double-well potential for LCG-MG, consider the hypothetical case of $C_5H_5^+$ (or linear $C_5H_7^+$) with cyclic boundary conditions and four π bonding (higher energy) electrons besides the "core" σ bonding electrons. For simplicity, first consider the reduction to a linear case where there are only 4 bonds. The four possible linear combinations of these four bonds and the linear combinations of the vibrations of these four π bonds in $C_0-C_1-C_2-C_3-C_4$ (Fig. 2a) are as follows (see Eqs (14) and (18)) (cyclic boundary condition assumed)

$$\Psi_\Lambda(1, 2) = \frac{1}{\sqrt{4}} \sum_{n=0}^3 e^{2\pi i \Lambda n/4} \phi_{n,n+1}(1, 2), \quad (25a)$$

$$Q_\Lambda = \frac{1}{\sqrt{4}} \sum_{n=0}^3 e^{2\pi i \Lambda n/4} q_{n,n+1}. \quad (25b)$$

Because the LCG-MG can be extended to infinity and the cyclic boundary condition is applied, there will be $+\Lambda$ and $-\Lambda$ double degeneracy for all of the molecular geminals of $\Lambda \neq 0$ (Fig. 2b). We shall name the two degenerate geminals as $\psi_\Lambda^L(1, 2)$ and $\psi_\Lambda^R(1, 2)$ instead of the sine function versus cosine function from the linear combination of $\psi_{+\Lambda}(1, 2)$ and $\psi_{-\Lambda}(1, 2)$.

$$\Psi_1(\text{cosine}) = \frac{1}{\sqrt{2}} [\Psi_1(1, 2) + \Psi_{-1}(1, 2)] = \frac{1}{\sqrt{2}} [\phi_{0,1}(1, 2) - \phi_{2,3}(1, 2)] = \Psi_1^x, \quad (26a)$$

$$\Psi_1(\text{sine}) = \frac{1}{i\sqrt{2}} [\Psi_1(1, 2) - \Psi_{-1}(1, 2)] = \frac{1}{\sqrt{2}} [\phi_{1,2}(1, 2) - \phi_{3,4}(1, 2)] = \Psi_1^y, \quad (26b)$$

$$\Psi_1^L = [\dots + \phi_{0,1}(1, 2) + \phi_{1,2}(1, 2) - \phi_{2,3}(1, 2) - \phi_{3,4}(1, 2) + \dots], \quad (26c)$$

$$\Psi_1^R = [\dots - \phi_{0,1}(1, 2) - \phi_{1,2}(1, 2) + \phi_{2,3}(1, 2) + \phi_{3,4}(1, 2) + \dots]. \quad (26d)$$

The vibronic interaction due to $Q_{-\Lambda}$ that gives rise to a paired two-electron quasi-particle $\Psi(1, 2)$ is as follows:

$$\Psi(1, 2) = \Psi_0(1, 2) + \sum_{\Lambda=1}^2 \frac{\langle \Psi_\Lambda^{L,R}(1, 2) \chi^1(Q_{-\Lambda}) \left| \frac{\partial H}{\partial Q_{-\Lambda}} Q_{-\Lambda} \right| \Psi_0(1, 2) \chi^0(Q_{-\Lambda}) \rangle}{E_0 - E_\Lambda - E_{-\Lambda}^Q} \times \Psi_\Lambda^{L,R} \chi^1(Q_{-\Lambda}), \quad (27)$$

where the $\psi_\Lambda \chi^1(Q_{-\Lambda})$ and $\psi_{-\Lambda} \chi^1(Q_\Lambda)$ are the degenerate vibronic states that will have 'first-order' degenerate Renner-Teller interaction energy by operator $1/2(\partial^2 H / \partial Q_{\pm\Lambda}^2) Q_{\pm\Lambda}^2$. The combination of $\Lambda = \pm 1$ π -electronic state with $\lambda = \pm 1$ π -vibrational state will give four states with two sets of degeneracies Σ , Σ and Δ_+ ,

Δ or Σ^+ , Σ^- and Δ^+ , Δ^- . Figure 2 illustrates the real (not complex) vibronic states in terms of x and y products. Because it is a Boson state, we can put all other pairs of electrons into this quasi-particle to yield the state of the whole system

$$\begin{aligned}\Psi(1234) &= [(2!)^2 2!4!]^{-1/2} \sum_{\nu=1}^4 \delta_{\nu} P_{\nu} \Psi(1, 2)\Psi(3, 4) \\ &= 3^{-1/2} [\Psi(1, 2)\Psi(3, 4) - \Psi(1, 3)\Psi(2, 4) - \Psi(1, 4)\Psi(3, 2)].\end{aligned}\quad (28)$$

The splitting of the two degenerate (L & R) electronic-geminal states by $Q_{\pm\Lambda}$ vibration is similar to Peierls distortion. As an extension of Peierls distortion, we consider not only the raising of Ψ_L (and lowering of Ψ_R) by a positive vibration but also the raising of Ψ_R (and lowering of Ψ_L) by a negative vibration (Fig. 2). We also consider the interaction of Ψ_L and Ψ_R of the whole system resulting in two equal-minimum double-well potentials. The figures are just qualitative illustrations, the detailed numerical vibronic perturbation will be based on detailed and real vibrational coordinates of the similar symmetry.

So far we have considered only four electrons. If we dump in more electrons to add up to six electrons in, for example, the cyclic $C_5H_5^-$ (or linear $C_5H_7^-$), the conjugate bonding style will be different and there will be more crowding of bonds (and more excitation to different atomic orbitals to satisfy Pauli's exclusion principle). But the total state based on the occupation of Boson quasi-particle is similar to Eq. (28) (for a definitive D state)

$$\begin{aligned}\Psi_D(123456) &= [(2!)^3 3!6!]^{-1/2} \sum_{\nu=1}^6 \delta_{\nu} P_{\nu} \Psi_D(1, 2)\Psi_D(3, 4)\Psi_D(5, 6) \\ &= 15^{-1/2} \{ [\Psi_D(1, 2)\Psi_D(3, 4) - \Psi_D(1, 3)\Psi_D(2, 4) - \Psi_D(1, 4)\Psi_D(3, 2)]\Psi_D(5, 6) \\ &\quad - [\Psi_D(1, 2)\Psi_D(3, 5) - \Psi_D(1, 3)\Psi_D(2, 5) - \Psi_D(1, 5)\Psi_D(3, 2)]\Psi_D(4, 6) \\ &\quad - [\Psi_D(1, 2)\Psi_D(5, 4) - \Psi_D(1, 5)\Psi_D(2, 4) - \Psi_D(1, 4)\Psi_D(5, 2)]\Psi_D(3, 6) \\ &\quad - [\Psi_D(1, 5)\Psi_D(3, 4) - \Psi_D(1, 3)\Psi_D(5, 4) - \Psi_D(1, 4)\Psi_D(3, 5)]\Psi_D(2, 6) \\ &\quad - [\Psi_D(5, 2)\Psi_D(3, 4) - \Psi_D(5, 3)\Psi_D(2, 4) - \Psi_D(5, 4)\Psi_D(3, 2)]\Psi_D(1, 6) \}.\end{aligned}\quad (29)$$

4. Illustrative example of the "Covalon" model for the effect on the movement of covalent electron pairs

Consider the hypothetical special case of cyclic $C_5H_5^-$ with six π electrons. It can be translated into a linear case similar to $C_5H_7^-$ but also with cyclic boundary condition to imitate the infinite linear crystal chain (Fig. 3a). The 'Covalon' [33,

34] running wave consists of Bloch sums as follows (see the general case of Eq. 22)

$$\begin{aligned}\Psi_{\lambda}(123456) &= A \frac{1}{\sqrt{5}} \left\{ \exp \frac{2\pi i \lambda 0}{5} \Phi_0^* \Phi_{2,3} + \exp \frac{2\pi i \lambda \cdot 1}{5} \Phi_1^* \Phi_{3,4} \right. \\ &\quad \left. + \exp \frac{2\pi i \lambda \cdot 2}{5} \Phi_2^* \Phi_{4,0} + \exp \frac{2\pi i \lambda \cdot 3}{5} \Phi_3^* \Phi_{0,1} + \exp \frac{2\pi i \lambda \cdot 4}{5} \Phi_4^* \Phi_{1,2} \right\} \\ &= A \frac{1}{\sqrt{5}} \sum_{s=0}^4 \exp \frac{2\pi i \lambda \cdot s}{5} \Psi_s^*,\end{aligned}\quad (30a)$$

where the normalization constant and antisymmetrizer are

$$A = [4!2!6!]^{-1/2} \sum_{\nu=1}^{6!} \delta_{\nu} P_{\nu} \quad (30b)$$

and for example

$$\begin{aligned}\Phi_2^* &= \frac{1}{2} [4!]^{-1/2} \sum_{\nu=1}^{4!} \delta_{\nu} P_{\nu} \phi_1(1) \phi_2(2) \phi_2^*(3) \phi_3(4) \\ &\quad \times (\alpha_1 \beta_2 \alpha_3 \beta_4 + \beta_1 \alpha_2 \beta_3 \alpha_4 - \alpha_1 \beta_2 \beta_3 \alpha_4 - \beta_1 \alpha_2 \alpha_3 \beta_4),\end{aligned}\quad (31a)$$

$$\Phi_{4,0} = \frac{1}{2} [\phi_4(5) \phi_0(6) + \phi_4(6) \phi_0(5)] (\alpha_5 \beta_6 - \beta_5 \alpha_6); \quad \psi_2^* = \Phi_2^* \Phi_{4,0}. \quad (31b)$$

This does not yet contain any vibronic interaction. But qualitatively, the antisymmetric vibration will help the dumped-in extra pair of electrons to push the other (double π -bonding) electrons to move along the chain. The structures at left and right before and after the movement are doubly degenerate and can be split to produce a double-well potential by this antisymmetric vibration (Fig. 3b).

To be more quantitative we shall derive the five Covalon states with $\Lambda = 0, \pm 1, \pm 2$. Instead of complex wavefunctions with complex exponential coefficients, we take linear combinations to get sine and cosine as coefficients. In order to visualize the positional change of 'bond' movements we further take the linear combination of the sine and cosine wavefunctions to get degenerate ($\pm \Lambda$) left versus right bonding states (similar to Eq. (26)).

Because these Covalon states involve bonds, we will again consider the vibronic mixing with vibrations of bonds (Eq. (18)). We shall take the ground state running wave with $\Lambda = 0$ to be the basic state to combine with Covalons with $\Lambda \neq 0$ through vibronic mixing:

$$\begin{aligned}\Psi(123456) &= \Psi_0(123456) \\ &\quad + \sum_{\Lambda=1}^2 \frac{\langle \Psi_{\Lambda}^{L,R} \chi^1(Q_{-\Lambda}) \left| \frac{\partial H}{\partial Q_{-\Lambda}} Q_{-\Lambda} \right| \Psi_0 \chi^0(Q_{-\Lambda}) \rangle}{E_0 - E_{\Lambda} - E_{-\Lambda}^Q} \Psi_{\Lambda}^{L,R}(123456) \chi^1(Q_{-\Lambda}).\end{aligned}\quad (32)$$

5. Discussion

The above treatments deal mainly with the principles of the proposed models. The actual application to (copper-oxide) high T_c superconductors and numerical calculations remain to be done. For example in LCG-MG, the two-electron geminal, instead of being a Heitler–London type valence bond, may involve two electrons in the antibonding molecular orbital of the copper oxide superconductor, e.g. $6A_g^*$ of the quadrupole CuO_2 . As a result Eq. (14b) may become

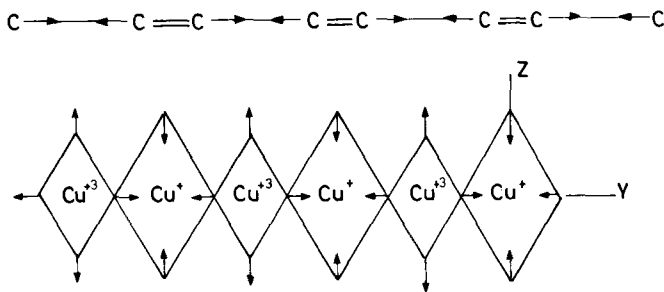


Fig. 4. Comparison of the cooperative charge transfer in a linear conjugate carbon chain and a linear Cu–O chain. The antisymmetric breathing vibration of CuO_4 will cooperate with the transfer of two antibonding electrons from Cu^+ to Cu^{3+} . The expanding vibration favors the entrance of the antibonding electrons of Cu–O. In the case of the carbon chain the contracting vibration favors the entrance of the bonding π -electrons

$$\phi_{n,n+1}(1,2) = \frac{1}{\sqrt{2}} 6A_g^*(1)6A_g^*(2)(\alpha_1\beta_2 - \beta_1\alpha_2). \quad (33)$$

Similarly, while we have taken the linear combination of the vibration of bonds (Eq. (18)), for application to copper-oxide superconductors, we may translate the local bond vibration into the CuO_2 vibration in a unit cell of the lattice (Fig. 4). This vibration is related to the movement of the antibonding electrons, similar to the movement of π electrons in resonant conjugate π bonds (Fig. 4). The crystal vibrations for the movement from local bonds to neighbors are different from the local structure Jahn–Teller effects considered by Johnson et al [37, 38]. Their work involves the splitting of the local degeneracy electronic e_g state of D_{4h} symmetry of CuO_2 unit cell by $\nu(b_{2g})$ and $\nu(b_{3g})$ local vibrations. While we have emphasized in Covalon theory the movement of crowded bond to nearest neighbors in regular conjugate π -bonding structures, different anti-symmetric vibrations and different resonance structures may favor different lengths of movement. The probability of coherence length for movement to longer distance will of course depend on the

resonant integral between the structures with different π -bond positions. Such pairwise electron/hole transfer has some similarity with the intervalent charge transfer [39–42] between two molecules, but has many differences such as long range order, vibronic interaction with infinite crystals, and electron-correlation of many body system, etc. The latter are considered in our proposed LCG-MG and Covalon models. The tunneling of two-electron pair quasi-particles through the double potential barrier reaching other potential wells at different lengths may also be related to the Josephson effect [29].

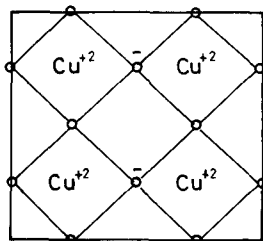


Fig. 5. The conduction plane of the crystal with quadruple unit cell with two holes on one of the quadruple CuO_2 and no hole in the neighboring quadruple CuO_2 . Such alternating on and off of double holes is similar to the (alternating) conjugate resonance of double bonds with two π -electrons

The review [16] of the doped structure in cuprate superconductors shows that high T_c occurs at about 0.2 holes per 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 four copper atoms. To have two holes to simulate the Cooper Pairs (of two electrons), we propose an idealized quadruple cluster cell structure (Fig. 5). For example if we start with a basic quadruple 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 charges 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 $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$ ($x = 0.006-0.2$). The O^- ion is a symbolic designation of a hole within the CuO_2 layer. In the quadruple cell with 32 oxygens, if we place the holes on the top or bottom CuO_2 layer, then it will be the conducting layer with alternating zero hole and two holes per four copper atoms (Fig. 5). We shall use this structure for the application of our principles to high T_c superconductors. It is perhaps not a simple coincidence that such a quadruple cluster cell [43] 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 [44] $(\text{Nd}^{+3})_{15}(\text{Ce}^{+4})(\text{Cu}^{+2})_6(\text{Cu}^{+1})_2(\text{O}^{-2})_{31.5}$ 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 [43], 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.

Because each of the $3d^9$ configuration of Cu^{+2} has one $3d_{x^2-y^2}$ electron, in principle [45] four Cu^{+2} with four spins can have a total spin angular momentum of $S = 2, 1$ and 0 . One must also consider the magneton property and Meissner Effect. In the switch from ferromagnetic to antiferromagnetic spin waves, the artificial change of parallel to antiparallel spins (or change of signs from J to $-J$) in the same artificial approximate Hamiltonian $H = -2J \sum_n S_n \cdot S_{n+1}$ does not necessarily speak for the true dynamics and does not imply any basic mechanism. This is because the change from parallel spin $S = 2$ (or $S = 1$) to antiparallel spin $S = 0$ may require a second-rank tensor operator of small spin-spin magnetic (dipole-dipole) interaction (or small first-order spin-orbit operator for $\Delta S = 1$) [3, 46] which is totally symmetric in a given point group. From the viewpoint of chemical structure, we ask what point group symmetry of the superconducting lattice will let the $S = 2$ (or $S = 1$) and $S = 0$ structures have the same symmetry [47] and will be connected by these small interaction operators.

The quadruple CuO_2 lattice with four 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 [48]) and because of the presence of holes the quadruple CuO_2 lattice may descend into the subgroup D_{2h} symmetry. If there is a $\mathbf{Q}(B_{1g})$ 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 for the quadruple CuO_2 . In the latter, both the $S = 2$ and $S = 1$, can have the same A_g symmetry as $S = 0$. This is illustrated in Table I [30, 47].

Table I

	$S = 2$	$S = 1$	$S = 0$
D_{2h}	$2A_g + B_{1g} + B_{2g} + B_{3g}$	$B_{1g} + B_{2g} + B_{3g}$	A_g
C_{2h}	$3A_g + 2B_g$	$A_g + 2B_g$	A_g

We shall consider the (antisymmetric) linear combination of such a $\mathbf{Q}(B_{1g})$ type vibration for its coupling with LCG-MG and with Covalons. The investigation of such details and variations in actual application and the comparison with newest developments [49] are now in progress.

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References

1. J. Bardeen, L. N. Cooper and J. R. Schrieffer, *Phys. Rev.*, **106**, 162, 1957; **108**, 1175, 1957.
2. G. Rickayzen, *Theory of Superconductivity*, Interscience, New York, 1965.
3. M. Tinkham, *Introduction to Superconductivity*, R. F. Krieger, Malabar, Florida, 1975.
4. A. C. Rose-Innes and E. H. Rhoderick, *Introduction to Superconductivity*, Pergamon, Oxford, 1978.
5. J. R. Schrieffer, *Theory of Superconductivity*, Addison-Wesley, New York, 1983.
6. C. Kittel, *Quantum Theory of Solids*, John Wiley, New York, 1963.
7. J. G. Bednorz, K. A. Mueller, *Z. Phys. B. Condens. Matter*, **64**, 189, 1986.
8. C. P. Poole, Jr., T. Datta, H. A. Farach, *Copper Oxide Superconductors*, John Wiley, New York, 1988.
9. A. S. Alexandrov and J. Ranninger, *Phys. Rev.*, **B23**, 1796 (1981); A. S. Alexandrov, *Phys. Rev.*, **B38**, 925, 1988; A. S. Alexandrov, J. Ranninger and S. Robozkiewicz, *Phys. Rev.*, **B33**, 4526, 1986.
10. J. C. Phillips, *Physics of High Tc Superconductors*, Academic Press, New York, 1989.
11. J. W. Lynn, ed., *High Temperature Superconductors*, Springer-Verlag, New York, 1990.
12. M.-H. Whangbo, M. Evain, M. A. Beno, U. Geiser, J. M. Williams, *Inorg. Chem.*, **26**, 2566, 1987; **26**, 1829, 1987.
13. C. N. R. Rao and B. Raveau, *Accounts Chem. Res.*, **22**, 106, 1989.
14. R. J. Cava, *Science*, **247**, 656, 1990.
15. R. J. Birgeneau, *Am. J. Phys.*, **58**, 28, 1990.
16. M.-H. Whangbo and C. C. Torardi, *Accounts Chem. Res.*, **24**, 127, 1991.
17. G. Burns, *High Temperature Superconductivity*, Academic Press, New York, 1992.
18. P. W. Anderson, *Science*, **235**, 1196, 1987; P. W. Anderson, G. Baskaran, Z. Zou and T. Hsu, *Phys. Rev. Letters*, **36**, 2790, 1987.
19. R. Hoffmann, *Solids and Surfaces: A Chemist's View of Bonding in Extended Structures*, VCH Publisher, New York, 1988.
20. S. L. Altmann, *Band Theory of Solids: An Introduction from the Point of View of Symmetry*, Clarendon Press, Oxford, 1991.
21. A. S. Davydov, *Phys. Stat. Sol. (b)*, **146**, 619, 1988; *Phys. Reports*, **190**, 191, 1990.
22. A. S. Davydov and V. N. Ermakov, *Phys. Stat. Sol. (b)*, **148**, 305, 1988.
23. I. Kovács, *Rotational Structure in the Spectra of Diatomic Molecules*, Akadémiai Kiadó, Hungarian Academy of Sciences, Budapest, 1969.
24. G. Herzberg and E. Teller, *Z. Phys. Chem.*, **B21**, 419, 1933; R. Renner, *Z. Physik*, **92**, 172, 1934.
25. J. A. Pople and H. C. Longuet-Higgins, *Mol. Phys.*, **1**, 372, 1958.
26. Y. N. Chiu and F. E. Wang, *Inorg. Chem.*, **21**, 4264, 1982; *J. Solid State Chem.*, **45**, 353, 1982.
27. Y. N. Chiu, *J. Chem. Phys.*, **64**, 2997, 1976; Y. N. Chiu, B. Friedrich, W. Maring, G. Niedner, M. Noll and J. P. Toennies, *J. Chem. Phys.*, **88**, 6814, 1988.
28. Y. N. Chiu, *J. Chin. Chem. Soc.*, **39**, 361, 1992; *Eur. J. Solid State Inorg. Chem.*, **t30**, 1119, 1993.
29. N. W. Aschcroft and N. D. Mermin, *Solid State Physics*, W. B. Saunders Co., Philadelphia, 1976.
30. G. Herzberg, *Electronic Spectra and Electronic Structure of Polyatomic Molecules*, D. Van Nostrand Co., Princeton, N. J. 1966.
31. Y. N. Chiu, *J. Phys. Chem.*, **88**, 5820, 1984.
32. Y. N. Chiu, *J. Phys. Chem.*, **80**, 992, 1976; **92**, 4352, 1988.
33. Y. N. Chiu and F. E. Wang, *Chem. Phys.*, **18**, 301, 1976.
34. F. E. Wang and Y. N. Chiu, *Chem. Phys.*, **12**, 225, 1976.
35. D. P. Craig and S. A. Walmsley, *Excitons in Molecular Crystals*, W. A. Benjamin, New York, 1968.
36. R. M. Hochstrasser, *Ann. Rev. Phys. Chem.*, **17**, 457, 1966.

37. D. P. Clougherty, K. H. Johnson and M. E. McHenry, *Physica, C*, 162-164, 1475, 1989.
38. K. H. Johnson, D. P. Clougherty and M. E. McHenry, *Mod. Phys. Letters*, 3, 1367, 1989; *High-Temperature Superconductivity*, eds J. Ashkenazi et al., Plenum Press, New York, 1991, p. 341.
39. R. S. Mulliken and W. B. Person, *Molecular Complexes*, Wiley, New York, 1969.
40. N. S. Hush, *Prog. Inorg. Chem.*, 8, 391, 1967; K. Y. Wong, P. N. Schatz and S. B. Piepho, *J. Am. Chem. Soc.*, 101, 2793, 1979.
41. R. A. Marcus and N. Sutin, *Biochim. et Biophys. Acta*, 811, 265, 1985.
42. H. Taube, *Electron Transfer Reactions of Complex Ions in Solution*, Academic Press, New York, 1970.
43. Y. N. Chiu, *J. Chin. Chem. Soc.*, 36, 487, 1989.
44. Y. Tokura, H. Takagi, S. Uchida, *Nature*, 337, 345, 1989.
45. Y. N. Chiu, *J. Chem. Phys.*, 56, 4882, 1972.
46. Y. N. Chiu, *Phys. Rev.*, A20, 32, 1979 and references cited therein.
47. Y. N. Chiu and Meiling Gong, *Chem. Phys.*, 145, 397, 1990.
48. M. Stavola, D. M. Krol, W. Weber, S. A. Sunshine, A. Jayaraman, G. A. Kouroukis, R. J. Cava and E. A. Rietman, *Phys. Rev.*, B36, 850, 1987.
49. H. Kamimura, M. Eto, S. Matsuno and H. Ushio, *Comments on Cond Mat. Phys.*, 15, 303, 1992.