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Quantum structural approach to high-T_c superconductivity theory: Herzberg-Teller, Renner-Teller, Jahn-Teller effects and intervalent geminal charge transfer

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We use quantum molecular structure and spectroscopic thoughts of various possible vibronic interactions for the position space of two-electron geminal orbitals with Bloch sums. Our geminals have different degeneracy from one-electron molecular orbitals and are different from the momentum space of BCS free electrons. Based on Herzberg-Teller expansions, our consideration of the aspect of the Renner-Teller effect for cyclic boundary crystals (instead of the usual linear molecules) involves first-order vibronic interaction with isotope effects different from the second-order electron-phonon energy of BCS theory, bipolaron theory, etc. Our consideration of the Jahn-Teller effect with equal-minimum double-well potential leads to the intervalent charge transfer between two degenerate vibrationally affected electronic structures. Our considerations of different style vibrations other than the antisymmetric vibration for the nearest neighbor (e.g., displaced oscillator, etc.) may possibly be related to the case of special chemical structures with special doping and special coherence length. Our simple structural illustrations of such different vibronic Renner-Teller, Jahn-Teller effects and intervalent charge transfer (of $La_{2-x}Sr_xCuO_4$ and $YBa_2Cu_3O_{7-x}$) may promote some possible thoughts of quantum chemical structures compared and mixed with the physical treatments of special high-T_c superconductors. [S0163-1829(97)05809-8]

I. INTRODUCTION

Instead of free electrons for the Cooper pair[1] of BCS theory[2] for low-T_c superconductors as well as correlation effects,[3] we emphasize the quantum chemical structural aspects of (two-electron) geminals Eqs. (2) and (3). Instead of Peierls' single solid-state potential distortion, we emphasize positive and negative vibration in spectroscopy's Jahn-Teller effect[4–6] which gives rise to right and left equal (double-well) potential minima [Eq. (9), Figs. 2(c), 3, 4)]. Instead of the (nearest-neighbor) displaced-oscillator interaction in bipolaron theory[7,8] [Eq. (26)], we emphasize unique vibrations for doped systems that will have no (simple) antisymmetry vibration for the movement to nearest neighbors (Fig. 5, Sec. V), this is similar to going *beyond* the conjugate double-bond charge transfer to the nearest neighboring (single) bond. Instead of Van Vleck's method[9] and canonical transformation[9–12] to yield second-order $H^{(2)}$ electron-phonon interaction energy for the (double-well) potential [Eqs. (7), (10), and (12)], we propose a (first-order) crystal Renner-Teller (vibronic) effect[4] [Eqs. (14), (15), (39), Figs. 2(c) and 3] that will give different isotope effects for different doping high-T_c superconductors. Instead of the *free-electron zero momentum space* ($k-k=0$) for high-T_c superconductivity,[13] we study position space of the structural electron/hole pairs with *vibronic zero pseudoangular momentum* ($\Lambda-\Lambda=0$) for the cyclic boundary condition over the finite crystal structure [Eqs. (3) and (25)]. Aside from the conductivity principles,[14] we study the role of charge-transfer effects.[15–18] We also propose special states (Sec. III) for excitons and consider their excited charge transfer by nonantisymmetric vibration [Eq. (38), Fig. 5]. Our approaches differ from other past considerations[19–21] as well as recent discussions.[22,23]

II. LINEAR COMBINATION OF BONDING GEMINALS AND VIBRONIC MOLECULAR BONDING GEMINALS (LCBG-MBG)

While the BCS theory[2] of Cooper pairs[1] uses (opposite) momentum $\hbar k$ for each free electron,

$$\psi(1,2)=\cdots+a_k\phi_{k\alpha}(1)\phi_{-k\beta}(2)+a_{k-q}\phi_{k-q,\alpha}(1)\phi_{-k+q,\beta}(2)+\cdots\ , \qquad (1)$$

we consider pseudoangular momentum (Λ) for the (two-electron) bonding geminal of periodic Bloch structures. As an illustration, consider the hypothetical large linear conjugate bonding molecular structure with cyclic boundary condition $C_{2N+3}H^{+}_{2N+5}$. The $C{=}C$ double π bonding structure with two-electron geminal may be replaced by the CuO_2 structure of high-T_c superconductors. The linear combination of bonding geminals (LCBG) to yield molecular bonding geminals (MBG) as a Bloch sum of the cyclic boundary condition, with $\Lambda=0,1,2,\ldots 2N+1$:

$$\psi_\Lambda(1,2)=\frac{1}{\sqrt{2N+2}}\sum_{n=0}^{2N+1}e^{2\pi\imath\Lambda n/(2N+2)}\phi_{n,n+1}(1,2)=\frac{1}{\sqrt{2N+2}}\sum_{n=0}^{2N+1}e^{\imath kna}\phi_{n,n+1}(1,2)=\psi_k(1,2), \qquad (2)$$

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where $\hbar k = 2\pi\hbar\Lambda/(2N+2)a$ is the momentum and the bonding geminal is $\phi_{n,n+1}(1,2) = 1/2[\phi_n(1)\phi_{n+1}(2) + \phi_n(2)\phi_{n+1}(1)](\alpha_1\beta_2 - \beta_1\alpha_2)$ where aside from the π orbital ϕ may be $s,p,d,\ldots$ atomic electron/hole orbital depending on the different cases of superconductor structures. For zero momentum $(k-k=k-q-k+q=0)$ to satisfy the London equation and for vibronic interaction mixing to compare with Cooper pairs Eq. (1), we choose overall $\Lambda-\Lambda=0$:

$$\psi(1,2) = \psi_0(1,2) + \sum_{\Lambda} \frac{\langle \psi_\Lambda(1,2)\chi^1(Q_{-\Lambda})|(\partial H/\partial Q_{-\Lambda})Q_{-\Lambda}|\psi_0(1,2)\chi^0(Q_{-\Lambda})\rangle}{E_0 - E_\Lambda - \hbar\omega_{-\Lambda}}\, \psi_\Lambda(1,2)\chi^1(Q_{-\Lambda})$$

$$\psi(1234\ldots 2N+2) = \left(\frac{1}{(2!)^{N+1}(N+1)!(2N+2)!}\right)^{1/2} \sum_{\mu=1}^{(2N+2)!} \delta_\mu P_\mu \psi(1,2)\psi(3,4)\cdots\psi(2N+1,2N+2). \tag{3}$$

The $(2N+2)!$ permutations of P_μ have antisymmetry signs δ_μ. The P_μ also contains the permutation movement of $(N+1)$ sets of geminals $[\psi(n,n+1)]$. Because the geminals are similar therefore they need the removal $[(N+1)!]^{-1/2}$. The P_μ also contains the double permutation of the two electrons (2!) of $(N+1)$ sets of geminals. Because the double permutation was also done in the geminals, therefore they need the removal $[(2!)^{N+1}]^{-1/2}$. In Eq. (3), χ^0 and χ^1 stand for zero and one *vibrational* quantum number of the eigenfunctions, and the vibrational mode Q_Λ is taken to be the linear combination of $q_{n,n+1} = \xi_n - \xi_{n+1}$ similar to the linear combination of bonding geminals [Eq. (2)]. The choice of the best Λ among the summation of all Λ's may depend on structures and doping. It will be illustrated in Sec. V. Our second-order vibronic energy is

$$E^{(2)} = \frac{|\langle \psi_\Lambda(1,2)|(\partial H/\partial Q_{-\Lambda})|\psi_0(1,2)\rangle|^2 |\langle \chi^1(Q_{-\Lambda})|Q_{-\Lambda}|\chi^0(Q_{-\Lambda})\rangle|^2}{E_0 - E_\Lambda - \hbar\omega_{-\Lambda}}. \tag{4}$$

It may be compared with Davydov's[11] second-order Hamiltonian energy after canonical transformation

$$\hat{H} = e^{-iS} H e^{iS} = e^{-iS}(H_0 + H_{\text{int}})e^{iS} = H_0 + \hat{H}_2,$$

$$\hat{H}_1 = H_{\text{int}} + i[H_0, S] = 0,$$

$$\hat{H}_2 = \frac{i}{2}[H_{\text{int}}S - SH_{\text{int}}],$$

$$H_{\text{int}} = \sum_{kq} [iD_q \alpha^+_{k-q}\alpha_k a_q - iD^+_q \alpha^+_k \alpha_{k-q} a^+_q], \tag{5}$$

where for one electron, α is the annihilation operator and α^+ is the creation operator. The movements of α_k and α_{k-q} are shown in Fig. 1. The transformation operator is

$$S = \sum_{k,q}\left[\frac{D_q \alpha^+_{k-q}\alpha_k a_q}{E_k + \hbar\omega_q - E_{k-q}} - \frac{D_q \alpha^+_k \alpha_{k-q} a^+_q}{E_{k-q} - E_k - \hbar\omega_q}\right] \tag{6}$$

and only $\langle \Pi_q x^0(Q_q)|a_q a^+_q|\Pi_q x^0(Q_q)\rangle = 1$ but $a_q a_{q'}$, $a^+_q a^+_{q'}$, and $a^+_q a_{q'}$, etc., yield zero:

$$\begin{aligned}\langle \Pi_q x^0(Q_q)|\hat{H}_2|\Pi_q x^0(Q_q)\rangle &= \langle O_{\text{phonon}}|\hat{H}_2|O_{\text{phonon}}\rangle \\ &= \sum_{k,q} \frac{D_q D^+_q \alpha^+_{k-q}\alpha_k \alpha^+_k \alpha^+_{k-q}}{E_{k-q} - E_k - \hbar\omega_q} \Rightarrow D^2 \sum_{kq} \frac{\alpha^+_{k-q}\alpha_k \alpha^+_k \alpha_{k-q}}{E_{k-q} - E_k - \hbar\omega_q} \overset{q=2k}{\Rightarrow} E^{(2)} = -\frac{D^2}{\hbar\omega_q},\end{aligned} \tag{7}$$

where $q=2k$ yields zero momentum for one electron k and another electron $-k$ [Fig. 1(a)]. $E_{k-q} - E_k = E_{-k} - E_k = 0$ and $D_q D^+_q \Rightarrow D^2$. However this case has an approximation of the same $D = \langle(\partial H/\partial Q)Q\rangle$ for all different k and q instead of

$$
\begin{aligned}
E^{(2)}&=\sum_{k,q}\frac{\langle\psi_{k-q}\chi^{0}(Q_q)|(\partial H/\partial Q_q)Q_q|\psi_k\chi^{1}(Q_q)\rangle\langle\psi_k\chi^{1}(Q_q)|(\partial H/\partial Q_q)Q_q|\psi_{k-q}\chi^{0}(Q_q)\rangle}{E_{k-q}-E_k-\hbar\omega_q}\\
&=\sum_{k,q}\left|\left\langle\psi_{k-q}\right|\frac{\partial H}{\partial Q_q}\left|\psi_k\right\rangle\right|^2|\langle\chi^{1}(Q_q)|Q_q|\chi^{0}(Q_q)\rangle|^2\frac{\langle\psi_{k-q}|\alpha^{+}_{k-q}\alpha_k|\psi_k\rangle\langle\psi_k|\alpha^{+}_{k}\alpha_{k-q}|\psi_{k-q}\rangle}{E_{k-q}-E_k-\hbar\omega_q}\\
&\overset{q=2k}{=}-\frac{|\langle\psi_k\chi^{1}(Q_q)|(\partial H/\partial Q_q)Q_q|\psi_{-k}\chi^{0}(Q_q)\rangle|^2}{\hbar\omega_q}.
\end{aligned}
\tag{8}
$$

This is because $\langle\psi_k|\alpha^{+}_{k}\alpha_{k-q}|\psi_{k-q}\rangle=1$ and $\langle\psi_{k-q}|\alpha^{+}_{k-q}\alpha_k|\psi_k\rangle=1$ where α is the annihilation and α^{+} is the creation operator for *one* electron. Our emphasis will be to search for a unique pseudoangular momentum $[\psi_\Lambda(1,2)\approx\psi_k(1,2)]$ of the bonding geminals interacting with unique vibrational modes Q_Λ. We also want to emphasize the Jahn-Teller effect with degenerate electronic geminal states $(\psi_\Lambda,\psi_{-\Lambda})$ leading to double-well potential. The perturbed electronic part is

$$
\begin{aligned}
&\psi_{\pm\Lambda}(12)_{\text{perturbed}}\chi^{1}(Q_{\mp\Lambda})\\
&=\left[\psi_{\pm\Lambda}(12)+\frac{\langle\psi_{\mp\Lambda}(12)\chi^{1}(Q_{\pm2\Lambda})|(\partial H/\partial Q_{\pm2\Lambda})Q_{\pm2\Lambda}|\psi_{\pm\Lambda}(12)\chi^{0}(Q_{\pm2\Lambda})}{E_{\pm\Lambda}-E_{\mp\Lambda}-\hbar\omega_{\pm2\Lambda}}\,\psi_{\mp\Lambda}(12)\chi^{1}(Q_{\pm2\Lambda})\right]\chi^{1}(Q_{\mp\Lambda}).
\end{aligned}
$$

The second-order energy is

$$
\begin{aligned}
E^{(2)}&=\frac{|\langle\psi_\Lambda(1,2)|(\partial H/\partial Q_{-2\Lambda})|\psi_{-\Lambda}(1,2)\rangle|^2|\langle\chi^{1}(Q_{-2\Lambda})|Q_{-2\Lambda}|\chi^{0}(Q_{-2\Lambda})\rangle|^2}{E_{-\Lambda}-E_{\Lambda}-\hbar\omega_{-2\Lambda}}\\
&=\frac{|\langle\psi_\Lambda(1,2)|(\partial H/\partial Q_{-2\Lambda})|\psi_{-\Lambda}(1,2)\rangle|^2|\langle1|Q_{-2\Lambda}|0\rangle|^2}{-\hbar\omega_{-2\Lambda}}\\
&=-\frac{|\langle\psi_\Lambda(1,2)|(\partial H/\partial Q_{-2\Lambda})|\psi_{-\Lambda}(1,2)\rangle|^2}{2m\omega^{2}_{-2\Lambda}}.
\end{aligned}
\tag{9}
$$

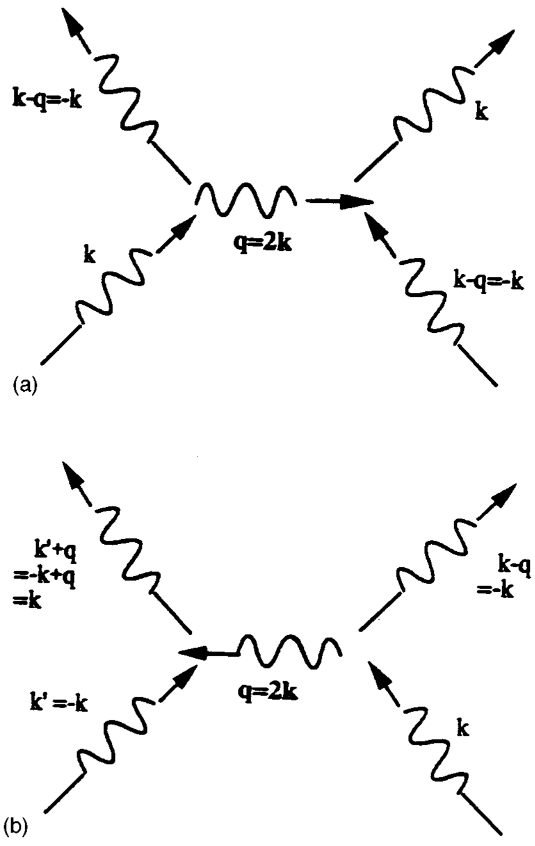

FIG. 1. (a) The electron-phonon interaction states that lead to second-order vibronic interaction energy related to Eq. (7). (b) Related to Eq. (10).

Our simple illustration for the above will be the geminal state of cyclic C_4H_4 [Sec. V, Fig. 2(a)] with degenerate real wave functions ψ^{x}_{1} and ψ^{y}_{1} [Eq. (29), Fig. 2(a)] under the vibration of $\nu(Q_{x^2-y^2})$ [Fig. 2(c)]. This is because $|\langle1|Q|0\rangle|^2=1/2\mathrm{B}=\hbar/2m\omega$. Such a second-order lowering energy is the vibronic binding energy related to the gap of superconductivity from bipolaron theory.[7] Our Jahn-Teller result may be reached by Davydov's case [Eq. (7)] with $q=2k$ similar to our $Q_{\pm2\Lambda}$ and $E_{k-q}-E_k=E_{-k}-E_k=0$. It also may be compared with the nondegenerate second-order energy operator for the Cooper pair [Eq. (1)] in Kittel's book[10] with canonical transformation $H=e^{-S}He^{S}=H_0+1/2[H',S]=H_0+H''$ where $H'=iD\Sigma_{kq}\alpha^{+}_{k+q}\alpha_k(a_q-a^{+}_{-q})$, and

$$
S=\sum_{k,q}\left[\frac{iD_q\alpha^{+}_{k+q}\alpha_k a_q}{E_k+\hbar\omega_q-E_{k+q}}-\frac{iD_q\alpha^{+}_{k-q}\alpha_k a^{+}_{q}}{E_k-E_{k-q}-\hbar\omega_q}\right].
$$

When we set $k'=-k$ and also set $q=2k$, similar to our $Q_{\pm2\Lambda}$,

$$
\begin{aligned}
H''&=D^2\sum_{q}\sum_{kk'}\frac{\hbar\omega_q}{(E_k-E_{k-q})^2-(\hbar\omega_q)^2}\alpha^{+}_{k'+q}\alpha_{k'}\alpha^{+}_{k-q}\alpha_k\\
&\overset{q=2k}{=}\frac{D^2}{-\hbar\omega_{2k}}\alpha^{+}_{k}\alpha_{-k}\alpha^{+}_{-k}\alpha_k\Rightarrow-\frac{D^2}{\hbar\omega_{2k}}=E^{(2)}.
\end{aligned}
\tag{10}
$$

Both Eqs. (7) and (10) are illustrated by Fig. 1. Both solid-state equations (7) and (10) are limited second-order vibronic energy with zero isotope effect (for $\alpha=0$ in $m^{-\alpha}$ without mass m) because Eq. (9) shows that $\omega=\sqrt{f/m}$ and

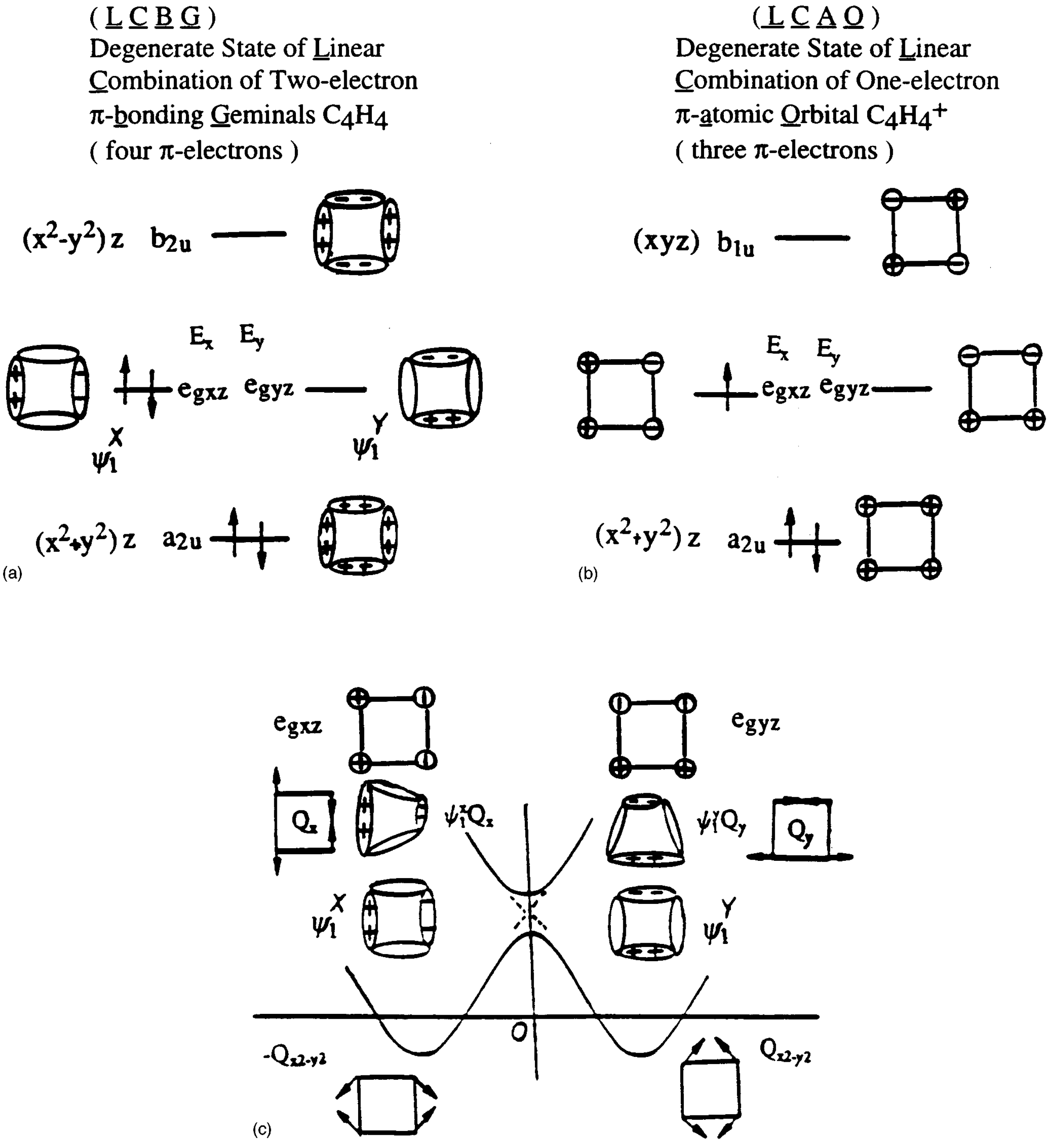

FIG. 2. (a), (b) Comparison of the degeneracy of two-electron geminal state (linear combination of bonding geminals-molecular geminals LCBG-MG) and one-electron LCAO-MO state. If there are four electrons in LCAO-MO, the degenerate states that can compare with the geminal states are $(a_{2u}e^2_{gxz}e_{gyz}, a_{2u}e_{gxz}e^2_{gyz})$ or $(a^2_{2u}e_{gxz}b_{1u}, a^2_{2u}e_{gyz}b_{1u})$, but $(a^2_{2u}e^2_{g})$ has no degeneracy in LCAO-MO. (c) The Jahn-Teller effect of the degenerate *electronic* geminal state (Ψ^x_1, Ψ^y_1) and *electronic* LCAO-MO state (e_{gxz}, e_{gyz}) and their extension to second-order vibronic energy and double-well potential. Also the comparison with the related vibrational effect on the degenerate electronic-vibrational (Renner-Teller vibronic) state $(\Psi^x_1 Q_x, \Psi^y_1 Q_y)$ or $(\Psi_1 Q_{-1}, \Psi_{-1} Q_1)$ [see Eq. (14)].

$$\langle D\rangle = \left\langle \psi_\Lambda \chi^1(Q) \left| \frac{\partial H}{\partial Q}\, Q \right| \psi_{-\Lambda}\chi^{(0)}(Q) \right\rangle = \left\langle \psi_\Lambda \left| \frac{\partial H}{\partial Q} \right| \psi_{-\Lambda} \right\rangle \left(\frac{\hbar}{2m\omega} \right)^{1/2} \tag{11}$$

and

$$E^{(2)} = -\frac{D^2}{\hbar\omega} = -\frac{|\langle \psi_\Lambda | \partial H/\partial Q | \psi_{-\Lambda}\rangle|^2}{2m\omega^2} = -\frac{|\langle \psi_\Lambda | \partial H/\partial Q | \psi_{-\Lambda}\rangle|^2}{2f} \approx m^{-0} = m^{-\alpha}. \tag{12}$$

We propose from Eq. (3) the possibility of first-order energy similar to the Renner-Teller effect of linear molecules with cylindrical electronic states (e.g., π-electronic state with $\Lambda=\pm 1$ and bending vibration, e.g., $Q_x \pm iQ_y = Q_{\pm 1}$). The linear molecules have $\nu(\Sigma^{\pm})$ and $\nu(\Pi_{\pm})$ vibrations of $\Lambda=\pm 1$ only, although they have electronic states of arbitrary $\Lambda=\Sigma,\Pi,\Delta,\Phi\ldots$ etc. Their advanced vibrational angular momentum $l=\pm n\mp 2S$ depends only on the distribution of the total number of quanta (n) into $\pm\Lambda=\pm 1$ (with $n-S$) and $\mp\Lambda=\mp 1$ (with S). But our Renner-Teller effect of cyclic boundary crystals will have $\nu(\Lambda)$ vibrations with many possible Λ's other than 0 and ± 1 and with possible electronic geminal states with Λ up to the geminal size (say $2N+2$) of the crystal, $\Lambda=0,1,2,\ldots(2N+1)$.

Instead of the equation related to Pople and Longuet-Higgins,[24]

$$\Delta E^{(1)}=\langle \psi_{\pi+}\chi^1(Q_{-1})|fr^2 \cos 2(\phi_e-\phi_v)|\psi_{\pi-}\chi^1(Q_{+1})\rangle, \tag{13}$$

where ϕ_e and ϕ_v are the azimuths of electrons and vibrations. We propose the first-order energy of $E=H_{aa}\pm H_{ab}=E_0\pm\Delta E^{(1)}$ which stands for degeneracy of *vibronic states (not pure degeneracy of electronic states only)*. The choice of such vibronic states with a special Λ can depend on the Fermi level or doping structure.

$$\Delta E^{(1)}=\frac{1}{2}\left\langle \psi_{\Lambda}(1,2)\chi^1(Q_{-\Lambda})\right. \\ \left.\times\left|\frac{\partial^2 H}{\partial Q_{-\Lambda}^2}Q_{-\Lambda}^2\right|\psi_{-\Lambda}(1,2)\chi^1(Q_{\Lambda})\right\rangle. \tag{14}$$

Our simple illustration (Sec. V) will be cyclic crystal C_4H_4 with degenerate real vibronic wave functions $\psi_1^x\theta_x$ and $\psi_1^y\theta_y$ [Fig. 2(b)] under the perturbation Hamiltonian of $(1/2)(\partial^2 H/\partial\theta_x\partial\theta_y)\theta_x\theta_y$. This is because the cyclic boundary condition of a linear infinite crystal will also have a cylindrical electronic running-wave state with pseudoangular momentum Λ in ψ_Λ as well as cylindric vibrational states also with pseudoangular momentum Λ in Q_Λ. It has a different isotope effect ($m^{-\alpha}$) from second order, for example,

$$\langle 1|Q^2|1\rangle=\langle 1|Q|0\rangle\langle 0|Q|1\rangle+\langle 1|Q|2\rangle\langle 2|Q|1\rangle=\frac{1}{2\beta}+\frac{2}{2\beta} \\ =\frac{3}{2\beta}=\frac{3\hbar}{2m\omega}=\frac{3\hbar}{2\sqrt{mf}}\approx m^{-1/2}=m^{-\alpha};\quad \alpha=\frac{1}{2}. \tag{15}$$

Our use of the higher-power perturbation Hamiltonian $(1/2)(\partial^2 H/\partial Q^2)Q^2$ is part of the Herzberg-Teller expansion for vibronic interaction:

$$H=H_0+\sum_q \frac{\partial H}{\partial Q_q}Q_q+\frac{1}{2!}\sum_q\sum_{q'}\frac{\partial^2 H}{\partial Q_q\partial Q_{q'}}Q_qQ_{q'} \\ +\frac{1}{3!}\sum_q\sum_{q'}\sum_{q''}\frac{\partial^3 H}{\partial Q_q\partial Q_{q'}\partial Q_{q''}}Q_qQ_{q'}Q_{q''}+\cdots. \tag{16}$$

This higher-power approach is not considered by the quantum approach[25] of electron (r)-phonon (Q_q) interaction for atomic displacement (ξ_l) from fixed local lattice position l

$$H'=\sum_{kk'}\langle k|V(r-l-\xi_l)|k'\rangle C_k^+C_{k'}=\sum_{kk'}\left(\int dre^{-ik\cdot r}\frac{1}{\sqrt{N}}\sum_q e^{iq\cdot(r-l-\xi_l)}V_qe^{ik'\cdot r}\right)C_k^+C_{k'} \\ =\sum_{kk'}e^{i(k'-k)\cdot(l+\xi_l)}V_{k'-k}C_k^+C_{k'}=\sum_{kk'}\left[e^{i(k'-k)\cdot l}+i(k'-k)\frac{1}{\sqrt{N}}\sum_q e^{i(k'-k)\cdot l}e^{iql}Q_q\right]V_{k'k}C_k^+C_{k'}. \tag{17}$$

This is because $q=k-k'$ in the integration over dr and because of the *limited* expansion

$$e^{i(k'-k)\xi_l}=1+i(k'-k)\xi_l+\cdots \\ =1+i(k'-k)\frac{1}{\sqrt{N}}\sum_q e^{iq\cdot l}Q_q+\cdots, \tag{18}$$

which yields a first-order electron-phonon perturbation similar only to $(\partial H/\partial Q)Q$ of the Herzberg-Teller expansion and similar to Davydov's H_{int} [Eq. (7)] and Kittel's H' [Eq. (10)]. This expansion upon canonical transformation gives only second-order electron-phonon interaction energy like Eqs. (7) and (10). We consider the relative importance of first-order vs second-order vibronic interaction for special electronic geminal states and special vibrational modes (e.g., nearest-neighbor antisymmetric mode vs next-to-nearest-neighbor modes) for different high-T_c superconductors with different dopings. As a simplified illustration of our proposed Renner-Teller effect for cyclic linear crystals, consider the case of cyclic C_4H_4 geminal states with four π electrons $4e^-$ (linear combination of bonding geminals to molecular bonding geminals LCBG-MBG). It is not the linear combination of atomic orbitals-molecular orbitals (LCAO-MO) state [consider $4e^-$ instead of $3e^-$ in Fig. 2(a)] which has no such degenerate vibronic interaction because *each electron has a symmetry state*. Therefore, aside from $a_{2u}(1)a_{2u}(2)$, the remaining two electrons in (E_x,E_y) yield nondegenerate states of $A_{1g}[E_x(3)E_x(4)+E_y(3)E_y(4)]$, $A_{2g}[E_x(3)E_y(4)-E_y(3)E_x(4)]$, $B_{2g}[E_x(3)E_y(4)+E_y(3)E_x(4)]$, and $B_{1g}[E_x(3)E_x(4)-E_y(3)E_y(4)]$. For geminal states (LCBG-MBG), there must be *two electrons* to have a *symmetry state*. Therefore, aside from $a_{2u}(12)$, there will be degeneracy of $E_x(3,4)$ and $E_y(3,4)$ or $E_1(3,4)$ and $E_{-1}(3,4)$. It is similar to $C_4H_4^+$ with three π electrons in LCAO-MO and with degeneracy of $E_x(3)$ and $E_y(3)$. The double-well potential and the first- and second-order vibronic interactions are shown in Fig. 2, where $Q_{-1}^2=(Q_x^2-Q_y^2)-i(Q_xQ_y+Q_yQ_x)$ leads to a similar first power interaction.

III. SPECIAL EXCITON THEORY OF RUNNING WAVES OF PAIRED-ELECTRON PRODUCTS WITH THE VIBRONIC INTERACTION

The quantum theory of solids[10] deals with the approximation of the product of ''*pair*'' free electrons in different momenta k,[10]

$$\phi_0(1234\ldots)=\prod_k (U_k+V_k\alpha_k^+\alpha_{-k}^+)|\text{vac}\rangle, \tag{19}$$

where U_k and V_k are constant coefficients for the special electron pairs. But we would rather use chemical structure bases to determine these electron-pair coefficients. We emphasize the product of structural geminal electrons reacting with appropriate vibrational modes. As an illustration consider the hypothetical $C_{2N+3}H_{2N+5}^-$ with $(2N+4)e^-$ and with the cyclic boundary condition. The special state ϕ_s^* we propose is comparable to excitons.[26] But it may stand for specially doped orbitals in high-T_c superconductors. For the case of nearest-neighbor conjugate bonds

$$\psi_\Lambda(1234\ldots 2N+4)=\mathcal{A}\left(\frac{1}{2N+3}\right)^{1/2}\sum_{s=0}^{2N+2} e^{2\pi i\Lambda_s/(2N+3)}\psi_s^*, \tag{20}$$

$$\psi_s^*=\phi_s^*\prod_{n=0,2,4,\ldots}^{s-3}\phi_{n,n+1}\prod_{m=s+2,s+4,\ldots}^{2N+1}\phi_{m,m+1}; \quad s=\text{odd}, \tag{21}$$

$$\psi_s^*=\phi_s^*\prod_{n=1,3,5,\ldots}^{s-3}\phi_{n,n+1}\prod_{m=s+2,s+4,\ldots}^{2N+2}\phi_{m,m+1}; \quad s=\text{even}, \tag{22}$$

$$\phi_s^*=\frac{1}{2\sqrt{4!}}\sum_{\mu=1}^{4!}\delta_\mu P_\mu\phi_{s-1}(i)\phi_s(j)\phi_{s*}(k)\phi_{s+1}(l)$$
$$\times(\alpha_i\beta_j\alpha_k\beta_l+\beta_i\alpha_j\beta_k\alpha_l-\alpha_i\beta_j\beta_k\alpha_l-\beta_i\alpha_j\alpha_k\beta_l), \tag{23}$$

$$\mathcal{A}=\left(\frac{1}{4!(2!)^{2N/2}(2N+4)!}\right)^{1/2}\sum_{\mu=1}^{(2N+4)!}\delta_\mu P_\mu, \tag{24}$$

where $\mathcal{A}$ stands for antisymmetrization, and δ_μ stands for the even or odd factor of the permutation P_μ.

It contains the double permutation of two electrons 2! of $(2N/2)$ geminals. Therefore it needs the removal $[(2!)^{2N/2}]^{-1/2}$. It also contains the double permutation of the special state ϕ_s^* with four electrons. Therefore it needs the removal $(4!)^{-1/2}$. For zero momentum and double-well potential due to Jahn-Teller vibronic interaction between ψ_Λ and $\psi_{-\Lambda}$ we also consider states similar to Eq. (3)

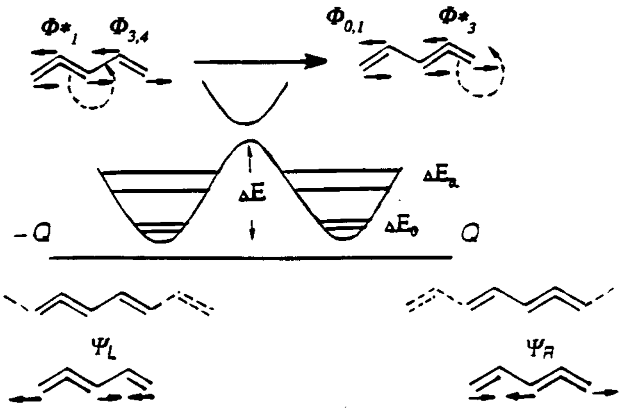

FIG. 3. Start with five atoms $(0,1,2,3,4=2N+3)$ and six π electrons $(1,2,3,4,5,6=2N+4)$ [Eqs. (20)–(23)]. The (nearest-neighbor) antisymmetric vibration (top) causes double-well potential of the degenerate special states under the Jahn-Teller effect. The other vibration (bottom) may also have Jahn-Teller (and Peierls) distortion. There can also be Renner-Teller effect for Ψ_Λ $(1,2,3,4\ldots 2N+4)\chi^1(Q_{-\Lambda})$ and $\Psi_{-\Lambda}$ $(1,2,3,4\ldots 2N+4)\chi^1(Q_\Lambda)$. The relative importance of the different vibration, different special bonding and different Renner-Teller effect depend on the details of chemical structure. Such a difference will also yield a different double-well potential barrier related to the superconductivity energy gap ΔE.

$$\psi(1234\ldots 2N+4)$$
$$=\psi_0(1234\ldots 2N+4)$$
$$+\sum_\Lambda\frac{\langle\psi_\Lambda\chi^1(Q_{-\Lambda})|(\partial H/\partial Q_{-\Lambda})Q_{-\Lambda}|\psi_0\chi^0(Q_{-\Lambda})\rangle}{E_0-E_\Lambda-\hbar\omega_{-\Lambda}}$$
$$\times\psi_\Lambda(1234\ldots 2N+4)\chi^1(Q_{-\Lambda}). \tag{25}$$

There can also be a Renner-Teller effect between $\psi_\Lambda(1234\ldots 2N+4)\chi^1(Q_{-\Lambda})$ and $\psi_{-\Lambda}(1234\ldots 2N+4)\chi^1(Q_\Lambda)$. This Jahn-Teller effect case is illustrated in Fig. 3. It is a special case for nearest-neighbor conjugate bonds. Therefore it makes use of nearest-neighbor antisymmetric vibrations. Different high-T_c structures with different electron/hole pair distributions will require different vibrations for double-well potential and tunneling motion (between the two double-well potential bases).

IV. APPLICATION TO HIGH-T_c COPPER OXIDE SUPERCONDUCTORS

We have been emphasizing the alternate conjugate geminal structures and the double charge transfer movement under the effect of antisymmetric vibrations with double-well potential. We propose that the superconducting geminals similar to Cooper pairs exist at the bottom of the double-well potential minima. But, at the top of the double-well potential barrier where the vibration (Q) is zero, the extension/contraction of superconducting geminals, and the boson state of antibonding/bonding of holes/electrons no longer exists. Therefore we consider the double-well potential barrier to be the superconducting gap. Our second-order energy [Eqs. (9), (12)] of the Jahn-Teller effect is comparable with the energy gap of the bipolaron theory for high-T_c superconducting[7] which deals with the action of displaced nearest-neighboring oscillators, e.g., the first-order vibronic interaction is similar to[27]

$$H' = \sum_{\Lambda} \sum_{\lambda} \left(\gamma_\lambda + 2\delta_\lambda \cos \frac{2\pi\Lambda}{N} \right) \left(\frac{\hbar}{2m\omega_\lambda} \right)^{1/2} \times (a_\lambda + a_\lambda^+) b_\Lambda^+ b_\Lambda , \qquad (26)$$

where $\gamma_\lambda = \langle \phi_n | \partial H / \partial Q_\lambda | \phi_n \rangle$, $\delta_\lambda = \langle \phi_{n\pm 1} | \partial H / \partial Q_\lambda | \phi_n \rangle$, $b_\Lambda^+ = \alpha_{\Lambda\alpha}^+ \alpha_{\Lambda\beta}^+$, and $b_\Lambda = \alpha_{\Lambda\beta}\alpha_{\Lambda\alpha}$. It is related to

$$\langle H' \rangle = \sum_{\Lambda} \sum_{\lambda} \left\langle \Psi_\Lambda \chi^1(Q_\lambda) \left| \frac{\partial H}{\partial Q_\lambda} \Omega_\lambda \right| \Psi_\Lambda \chi^0(Q_\lambda) \right\rangle ,$$

$$\Psi_\Lambda = \frac{1}{\sqrt{N}} \sum_{n=0}^{N-1} e^{2\pi i \Lambda n/N} \phi_n = \frac{1}{\sqrt{N}} \sum_{n=0}^{N-1} e^{ikna} \phi_n , \qquad (27)$$

$$\langle \chi^1(Q_\lambda) | Q_\lambda | \chi^0(Q_\lambda) \rangle = \frac{1}{\sqrt{2\beta}} = \left(\frac{\hbar}{2m\omega_\lambda} \right)^{1/2} .$$

In $H = H^0 + H'$, upon canonical transformation[27] it yields only the second-order Hamiltonian and energy as follows, which is comparable with Eqs. (7) and (10). It is related to

$$E^{(2)} \Rightarrow \frac{|\langle D \rangle|^2}{E_{n\pm1} - E_n - \hbar\omega_\lambda} = \frac{|\langle (\partial H/\partial Q_\lambda) Q_\lambda \rangle|^2}{E_{n\pm1} - E_n - \hbar\omega_\lambda}, \quad E_{n\pm1} - E_n = 0,$$

$$H^{(2)} = -\sum_{\Lambda} \sum_{\lambda} \frac{D_\lambda^2 b_\Lambda^+ b_\Lambda}{\hbar\omega_\lambda}, \qquad (28)$$

$$\langle H^{(2)} \rangle = -\frac{D^2}{\hbar\omega_\lambda} = -\sum_{\lambda} \frac{|\langle \partial H/\partial Q_\lambda \rangle|^2}{2m\omega_\lambda^2} = -\sum_{\lambda} \frac{\langle \partial H/\partial Q_\lambda \rangle^2}{2f} \approx m^{-0} = m^{-\alpha}; \quad \alpha = 0.$$

Therefore it has zero isotope effect also.

We have gone beyond the second order and study the Renner-Teller *first-order effect*. Furthermore we also want to demonstrate the alternative conjugation of geminal bonding/antibonding in high-T_c superconductors in comparison with low-T_c superconductors. There have been recent studies[28–31] of isotope effects and transitions of La_2CuO_4. As an example consider the special doping of the $(La_{1.875}Sr_{0.125}CuO_4)_2$ unit cell which we multiply by four to extend to a quadruple unit cell $La_{15}SrCu_8O_{32}$. For neutrality we could either illustrate it as the change from Cu_8^{+2} to $Cu_7^{+2}Cu^{+3}$ or from O_{32}^{-2} to $O_{31}^{-2}O^-$. The truth, of course, is the local CuO_2 electron orbital distribution. But for simple illustration we consider the O^- hole either *equally distributed* among all quadruple unit cells similar to the delocalized equally distributed π-bonding electrons under no vibration $\mathrm{C}\overset{\cdot}{—}\mathrm{C}\overset{\cdot}{—}\mathrm{C}\overset{\cdot}{—}\mathrm{C}\overset{\cdot}{—}\mathrm{C}$, or *unequally distributed* with geminal holes on one quadruple unit cell and not on neighboring quadruple unit cell similar to the conjugate bonding C═C—C═C—C, (Fig. 4). With short-long bonds due to vibrational contractions/extensions, such geminal structures can be applied to the linear combination of bonding/antibonding geminal theory (of Sec. II) and the special exciton theory (of Sec. III). The emphasis will be to investigate our proposed first-order Renner-Teller effect besides the second-order effect of BCS theory and bipolaron theory, etc., which a special situation under doping will have more mixing of first- and second-order energy, remains to be investigated. In addition, the location of the doper Sr in our quadruple unit cell must also be related to the short-long bondings of electron/hole geminals in CuO_2. With emphasis on the chemical spectroscopy of the Renner-Teller and Jahn-Teller effect and on chemical structures, we can also consider different vibrations for different electron/hole geminals and dopers. As an example C═C—C═C—C uses vibration ←CC→←CC→←C for double-well potential transfer to C—C═C—C═C. But C═C═C—C═C may use a different ←CCC→C←C vibration to yield C═C—C═C═C. Such a difference will be related to conductivity, energy gap, and isotope effects, etc. The case of $YBa_2Cu_3O_{7-x}$ will also be compared in the next section. Our approach has some aspects different from other works.[32–36]

V. SIMPLIFIED ILLUSTRATIONS OF CHEMICAL STRUCTURAL AND CHARGE-TRANSFER APPROACH

For the linear combination of bonding π *geminals* of the hypothetical $C_{2N+3}H_{2N+5}^+$ [Eq. (2)] with $N=1$, the case is $C_5H_7^+$ with major structure $C_{(0)}-C_{(1)}-C_{(2)}-C_{(3)}-C_{(4)}$. With the cyclic boundary condition then $C_{(4)}$ is equal to $C_{(0)}$ and the case is similar to the cyclic C_4H_4 with D_{4h} symmetry and with four bonds where the π *geminal* (say electrons No. 1 and No. 2) can lie in (Fig. 2), i.e., LCBG-MBG of the two-electron geminal case defined in Eq. (2) plus the vibrational mode Q_Λ:

$$\psi_\Lambda(12) = \frac{1}{\sqrt{4}} \sum_{n=0}^{3} e^{2\pi i \Lambda n/4} \phi_{n,n+1}(12),$$

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

$$\psi_1^x(12) = \frac{1}{\sqrt{2}} [\psi_1(12) + \psi_{-1}(12)] = \frac{1}{\sqrt{2}} [\phi_{01}(12) - \phi_{23}(12)], \qquad (29)$$

$$\psi_1^y(12) = \frac{1}{i\sqrt{2}} [\psi_1(12) - \psi_{-1}(12)] = \frac{1}{\sqrt{2}} [\phi_{12}(12) - \phi_{30}(12)]. \qquad (30)$$

These are similar to four sets of quadruple CuO_2cells  with alternating double O^- holes [Fig. 4(a)] between differ-

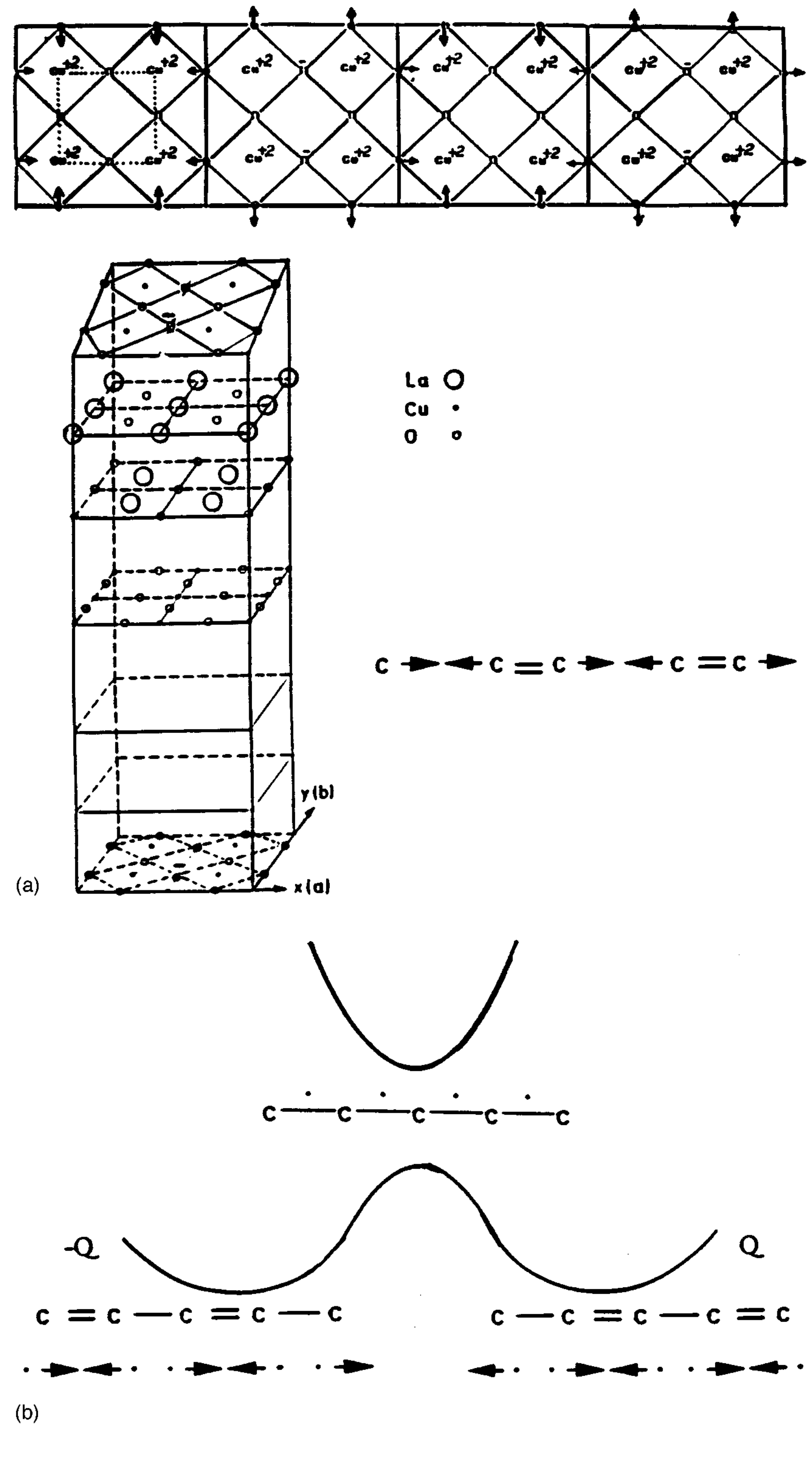

FIG. 4. (a) Start with $(La_2CuO_4)_{2\times4}$. The illustration of a doped quadruple unit cell $(La_{1.875}Sr_{0.125}CuO_4)_{2\times4}=La_{15}^{+3}Sr^{+2}Cu_8^{+2}{}_8O_{31}^{=}O^{-}$ with one O^- ($1\times1/2$=half on the top $(CuO_2)_4$ layer and $1\times1/2$=half on the bottom layer). When every quadruple unit has the same number of O^-, this is comparable with the $C\overset{\cdot}{-}C\overset{\cdot}{-}C\overset{\cdot}{-}C\overset{\cdot}{-}C$ with equal distribution of the delocalized (single) π electron. Illustration of four top layers of $(CuO_2)_4$ of $4(La_2CuO_4)_{2\times4}$ with alternating zero O^- and two O^- [$2\times1/2$=one on the top $(CuO_2)_4$ layer shown, $2\times1/2$=one on the bottom $(CuO_2)_4$ layer not shown]. Such alternation $2O^-=2O^-\times1/2+2O^-\times1/2$ with *two* sets are comparable with the case of C—C═C—C═C with alternating conjugate (*two*) π-electron bonding. (b) Simplified illustration of the antisymmetric vibrational Jahn-Teller effect with intervalent charge transfer of degenerate alternating conjugate double-electron bonding structures. The double-well potential barrier ΔE_c is considered to be related to the energy gap for the superconducting double-electron pairs C═C—C═C—C being raised and disintegrated into $C\overset{\cdot}{-}C\overset{\cdot}{-}C\overset{\cdot}{-}C\overset{\cdot}{-}C$.

ent cells, e.g., $\psi_1^x = \boxed{=}\boxed{-}\boxed{=}\boxed{-}$ and $\psi_1^y = \boxed{-}\boxed{=}\boxed{-}\boxed{=}$. They are affected by the antisymmetric vibration $Q_2 \leftarrow 0 \; 1 \rightarrow \leftarrow 2 \; 3 \rightarrow \leftarrow 4$ for the Jahn-Teller effect (Fig. 4). It is similar to intervalent charge transfer.

For D_{4h} symmetry the molecular bonding π-*geminal* states ψ_0 is a_{2u}, $\psi_{\pm 1}$ is (e_{gxz}, e_{gyz}) or expressed as (E_x, E_y), and ψ_2 (identical as ψ_{-2}) is $b_{2u}(x^2-y^2)z$. For the (planar) vibrational states Q_0 is $a_{1g}, Q_{\pm 1}$ is (e_{ux}, e_{uy}), and Q_2 (identical to Q_{-2}) is $b_{1g}(x^2-y^2)$ [or $b_{2g}(xy)$]. We may consider only the high level ψ_{+1} or ψ_{-1} (compare with the Fermi level of *one-electron* LCAO-MO) of two electrons [No. 3 and No. 4 aside from the lowest level with two electrons No. 1 and No. 2 $a_{2u}(1,2)$]. The Jahn-Teller vibronic perturbation[4–6,37,38] leading to double-well potential of the degenerate $\psi_1(3,4)$ and $\psi_{-1}(3,4)$ high electronic levels with zero vibronic pseudoangular momentum is as follows:

$$\psi_{\pm 1}(34)_{\text{pertubed}}\chi^1(Q_{\mp 1}) = \Bigg(\psi_{\pm 1}(34)\chi^0(Q_{\pm 2}) + \frac{\langle \psi_{\mp 1}(34)\chi^1(Q_{\pm 2}) | (\partial H/\partial Q_{\pm 2}) Q_{\pm 2} | \psi_{\pm 1}(34)\chi^0(Q_{\pm 2}) \rangle}{E_{\pm 1} - E_{\mp 1} - \hbar\omega_{\pm 2}} \psi_{\mp 1}(34)\chi^1(Q_{\pm 2}) \Bigg) \chi^1(Q_{\mp 1}). \tag{31}$$

This perturbation is similar to the splitting in Fig. 2 of ψ_1^x and ψ_1^y by $Q_{x^2-y^2}$. If there is a *structural alternative* Jahn-Teller mixing by a *different (higher power, with two vibrational quanta) vibration* it will give a second-order energy of a different isotope effect:

$$\psi_{\pm 1}(34)\chi^0(Q_{\pm 1}) + \frac{1}{2} \frac{\langle \psi_{\pm 1}(34)\chi^2(Q_{\pm 1}) | (\partial^2 H/\partial Q_{\pm 1}^2) Q_{\pm 1}^2 | \psi_{\pm 1}(34)\chi^0(Q_{\pm 1}) \rangle}{E_{\pm 1} - E_{\mp 1} - 2\hbar\omega_{\pm 1}} \psi_{\mp 1}(34)\chi^2(Q_{\pm 1})$$

$$E^{(2)} = -\frac{|\langle \partial^2 H/\partial Q_{\pm 1}^2 \rangle|^2 |\langle 2|Q_{\pm 1}^2|0\rangle|^2}{4\hbar\omega_{\pm 1}} = -\frac{|\langle \partial^2 H/\partial Q_{\pm 1}^2 \rangle|^2 \hbar}{8m^2\omega_{\pm 1}^3} \approx -\frac{1}{\sqrt{m}} \Rightarrow m^{-1/2} = m^{-\alpha}; \quad \alpha = \frac{1}{2},$$

$$\langle 2|Q^2|0\rangle = \langle 2|Q|1\rangle\langle 1|Q|0\rangle = \sqrt{\frac{2}{2\beta}} \sqrt{\frac{1}{2\beta}} = \frac{\sqrt{2}\hbar}{2m\omega}. \tag{32}$$

There is also the Renner-Teller vibronic interaction [Eqs. (14) and (15)] which has isotope effect similar to the above.

$$\Delta E^{(1)} = \frac{1}{2} \left\langle \psi_{+1}(34)\chi^1(Q_{-1}) \left| \frac{\partial^2 H}{\partial Q_{-1}^2} Q_{-1}^2 \right| \psi_{-1}(34)\chi^1(Q_1) \right\rangle.$$

This is the case of the vibronic interaction of mainly two electrons (No. 3 and No. 4) without the other two electrons (No. 1 and No. 2). But, for the low-energy quasiparticle boson state with zero vibronic pseudoangular momentum, we will have

$$\psi(12) = \psi_0(12) + \frac{\langle \psi_{\pm 1}(12)\chi^1(Q_{\mp 1}) | (\partial H/\partial Q_{\mp 1}) Q_{\mp 1} | \psi_0(12)\chi^0(Q_{\mp 1}) \rangle}{E_0 - E_{\pm 1} - \hbar\omega_{\mp 1}} \psi_{\pm 1}(12)_{\text{pertubed}}\chi^1(Q_{\mp 1}) + \frac{\langle \psi_2(12)\chi^1(Q_{-2}) | (\partial H/\partial Q_{-2}) Q_{-2} | \psi_0(12)\chi^0(Q_{-2}) \rangle}{E_0 - E_2 - \hbar\omega_{-2}} \psi_2(12)\chi^1(Q_{-2}). \tag{33}$$

It will have similar vibronic interactions as the upper level case of electrons No. 3 and No. 4. But the unique case of the nondegenerate $\psi_2(12)\chi^1(Q_{-2})$ at the *end* of the top may be related to the unique doping structure's limit value of the cyclic boundary condition. If the boundary is large, there may be other values of $\Lambda \gg 1$ and the $\psi_{\pm\Lambda}(12)\chi^1(Q_{\mp\Lambda})$ is related to an interaction with a different vibrational mode such as $Q_{\pm\Lambda}^2$. Also $\langle \psi_{\pm\Lambda}(12)\chi^1(Q_{\pm 2\Lambda}) | (\partial H/\partial Q_{\pm 2\Lambda}) Q_{\pm 2\Lambda} | \psi_{\mp\Lambda}(12)\chi^0(Q_{\pm 2\Lambda}) \rangle$ has a Jahn-Teller effect for $Q_{\pm 2\Lambda}$ beyond $Q_{\pm 2}$. By putting all electrons in the *same* quasiparticle boson state of vibronic linear combination of geminals, there should be no electronic and vibrational resistance of high-T_c superconductivity:

$$\psi(1234) = \left(\frac{1}{(2!)^2 2! 4!} \right)^{1/2} \sum_{\mu=1}^{4!} \delta_\mu P_\mu \psi(12)\psi(34) = \left(\frac{1}{3} \right)^{1/2} [\psi(12)\psi(34) - \psi(13)\psi(24) - \psi(14)\psi(32)]. \tag{34}$$

This will have Jahn-Teller and Renner-Teller vibronic effects on all (four) electrons. Our detailed chemical considerations of the first- and second-order vibronic interaction of running waves are different from the recent treatment by the perturbation Hamiltonian of Kresin and co-workers[33,39]

$$H_T=g_1\sum_{ij}\alpha_i^+\alpha_j(a_i^++a_i)+g_2\sum_{ij}\alpha_i^+\alpha_j(a_i^++a_i)^2, \tag{35}$$

which deals with the creation (α^+) and annihilation (α) of localized single electrons as well as the creation (a^+) and annihilation (a) of local movements of atoms. Our first-/second-order chemical considerations are also different from the bipolaron[7] theory's second-order energy and Davydov's bisoliton theory,[40] Anderson's[41] resonating valence bond theory, high-T_c superconductivity,[42,43] and also Su, Schrieffer, and Heeger's soliton of polyacetylene[44] as well as other considerations.[45–47] Instead of the product of two-electron quasiparticle bosons [Eq. (34)], an alternative way to arrive at the whole set of electrons is our Bloch sum running wave of products of conjugate bonds and the special ϕ_s^* [Eq. (20), Sec. III] related to excitons.[48]

As a simplified illustration of Sec. III, consider the hypothetical case of $C_9H_{11}^-$ with ten π electrons, $C_{(0)}—C_{(1)}—C_{(2)}—C_{(3)}\cdots C_{(7)}—C_{(8)}$. With the cyclic boundary condition the $C_{(8)}$ is identical to $C_{(0)}$ and the case is similar to cyclic $C_8H_8^=$. It is different from the $C_5H_5^-$ simple case.[49] Our cyclic structure has emphasis aside from the local Jahn-Teller effect with D_{4h} structure[50] and aside from other (local) unit-cell vibronic interactions.[51,52] There are eight bonding positions for the placement of one excited special ϕ_s^* with four π electrons [Eq. (23)] and for the additional placement of three more π-bonding pairs ϕ_{ij} [Eq. (21) and (22)], e.g., $\psi_1'=\phi_1^*\phi_{34}\phi_{56}\phi_{70}$ with a structure like $C_0{=}C_1^*{=}C_2—C_3{=}C_4—C_5{=}C_6—C_7{=}C_0$. The linear combination of the special structures (and of vibrations q) as running waves are as follows:

$$\begin{aligned}\psi_\Lambda(1234\ldots9{,}10)&=\left(\frac{1}{4!(2!)^3 10!}\right)^{1/2}\sum_{\mu=1}^{10!}\\&\quad\times\delta_\mu P_\mu\left(\frac{1}{8}\right)^{1/2}\sum_{s=0}^{7}e^{2\pi i\Lambda s/8}\psi_s^*\\&=\mathcal{A}\left(\frac{1}{8}\right)^{1/2}\sum_{s=0}^{7}e^{2\pi i\Lambda s/8}\psi_s^*,\\Q_\Lambda&=\frac{1}{\sqrt{8}}\sum_{n=0}^{7}e^{2\pi i\Lambda n/8}q_{n,n+1}.\end{aligned}\tag{36}$$

Because of the small cyclic structure, for the unique and different structures of each ψ_s^* we choose to use a different example from before and let

$$\psi_s^*=\phi_s^*\phi_{s+2,s+3}\phi_{s+4,s+5}\phi_{s+6,s+7}.$$

When $s+m=8,9,10,11,12,13,14,15$ they are the same as 0,1,2,3,4,5,6,7. The antisymmetric special linear combinations as well as the antisymmetric vibration are for $\Lambda=4$. With antisymmetric vibration ($Q_\Lambda=Q_4$), the degenerate special state for the Jahn-Teller effect is $\psi_{\pm2}(1234\ldots,9,10)$. Such a case of antisymmetric vibration has been illustrated for LCBG-MBG of C_4H_4 related to the charge-transfer[53] movement of the $(\mathrm{La}_{1.875}\mathrm{Sr}_{0.125}\mathrm{CuO}_4)_{2\times4}$. We will consider a different, not antisymmetric vibration (not $\Lambda=4$ but $\Lambda=\pm2$ for $C_8H_8^=$) reacting with a different degenerate electronic part $\psi_{\pm1}(1234\ldots9{,}10)$ for the Jahn-Teller effect. Such different considerations will be related to different doping and different high-T_c structures.[54–57] It will be related to the charge-transfer movement of a hypothetical quadruple cell of the doped $(\mathrm{YBa}_2\mathrm{Cu}_3\mathrm{O}_{7-0.25})_4$, i.e., $\mathrm{Y}_4^{+3}\mathrm{Ba}_8^{+2}\mathrm{Cu}_{12}^{+2}\mathrm{O}_{25}^{=}\mathrm{O}_2^{-}$ with two oxygen holes O^- or two Cu^{+3} in $\mathrm{Y}_4^{+3}\mathrm{Ba}_8^{+2}\mathrm{Cu}_{10}^{+2}\mathrm{Cu}_2^{+3}\mathrm{O}_{27}^{=}$. The real degenerate special wave functions we will consider are ($\psi_\Lambda=\psi_\pm$)

$$\begin{aligned}\frac{1}{\sqrt{2}}(\psi_1+\psi_{-1})(1234\ldots9{,}10)&=\mathcal{A}\,\frac{1}{2}\left[\psi_0^*+\frac{1}{\sqrt{2}}\psi_1^*-\frac{1}{\sqrt{2}}\psi_3^*\right.\\&\quad\left.-\psi_4^*-\frac{1}{\sqrt{2}}\psi_5^*+\frac{1}{\sqrt{2}}\psi_7^*\right],\\\frac{1}{i\sqrt{2}}(\psi_1-\psi_{-1})(1234\ldots9{,}10)&=\mathcal{A}\,\frac{1}{2}\left[\frac{1}{\sqrt{2}}\psi_1^*+\psi_2^*\right.\\&\quad\left.+\frac{1}{\sqrt{2}}\psi_3^*-\frac{1}{\sqrt{2}}\psi_5^*-\psi_6^*-\frac{1}{\sqrt{2}}\psi_7^*\right].\end{aligned}\tag{37}$$

The addition of the special structures is illustrated in the cyclic $C_8H_8^=$ with multiple positive (+) and negative (−) probability amplitudes in Fig. 5. The real vibrational state we consider for the Jahn-Teller effect of the above is $1/i\sqrt{2}(Q_2-Q_{-2})$.

$$\begin{aligned}\frac{1}{i\sqrt{2}}(Q_2-Q_{-2})&=\frac{1}{2}[q_{12}-q_{34}+q_{56}-q_{70}],\\\frac{1}{\sqrt{2}}(Q_2+Q_{-2})&=\frac{1}{2}[q_{01}-q_{23}+q_{45}-q_{67}].\end{aligned}\tag{38}$$

The vibration of $-(1/i\sqrt{2})(Q_2-Q_{-2})$ is ←0 ←1 2→ 3→←4←5 6→7→←0. It will also have a Jahn-Teller effect on the special (cyclic) structures [of the linear chains of quadruple cells $4\times(\mathrm{Y}_4^{+3}\mathrm{Ba}_8^{+2}\mathrm{Cu}_{12}^{+2}\mathrm{O}_{25}^{=}\mathrm{O}_2^{-})$] with oxygen O^- holes (h) or $4\times(\mathrm{Y}_4^{+3}\mathrm{Ba}_8^{+2}\mathrm{Cu}_{10}^{+2}\mathrm{Cu}_2^{+3}\mathrm{O}_{27}^{=}]$ with copper [bonding (Cu^h)]. In Fig. 5 we consider only four Cu^h (of Cu^{+3}) inside the eight coppers with vibration changes the cyclic structure (Cu_0 is the same as Cu_8) which resembles $1/i\sqrt{2}(\psi_1-\psi_{-1})$, $\mathrm{Cu}_0\mathrm{OCu}_1^h—\mathrm{Cu}_2^h\mathrm{OCu}_3—\mathrm{Cu}_4\mathrm{OCu}_5^h—\mathrm{Cu}_6^h\mathrm{OCu}_7—\mathrm{Cu}_0$ into another cyclic structure which resembles $1/\sqrt{2}(\psi_1+\psi_{-1})$, $\mathrm{Cu}_0^h\mathrm{OCu}_1—\mathrm{Cu}_2\mathrm{OCu}_3^h—\mathrm{Cu}_4^h\mathrm{OCu}_5—\mathrm{Cu}_6\mathrm{OCu}_7^h—\mathrm{Cu}_0^h$. Aside from the Jahn-Teller effect, there should also be more (first-order) Renner-Teller effects than the C_4H_4 case[57] as the LCBG-MBG of Sec. II [Eq. (14)]. Namely, aside from the $\psi_{\pm1}\chi^1(Q_{\mp1})$ Renner-Teller effect there is also the Renner-Teller effect of

$$\frac{1}{2}\left\langle\psi_2(1234\ldots9{,}10)\chi^1(Q_{-2})\right.\left|\frac{\partial^2H}{\partial Q_{-2}^2}Q_{-2}^2\right|\left.\psi_{-2}(1234\ldots9{,}10)\chi^1(Q_2)\right\rangle. \tag{39}$$

There could also be the importance of the structural difference to be compared with high-T_c superconductivity properties.[58–65] The extra loss of oxygens in Fig. 5(a) may have been transferred from the neighbor or may have come

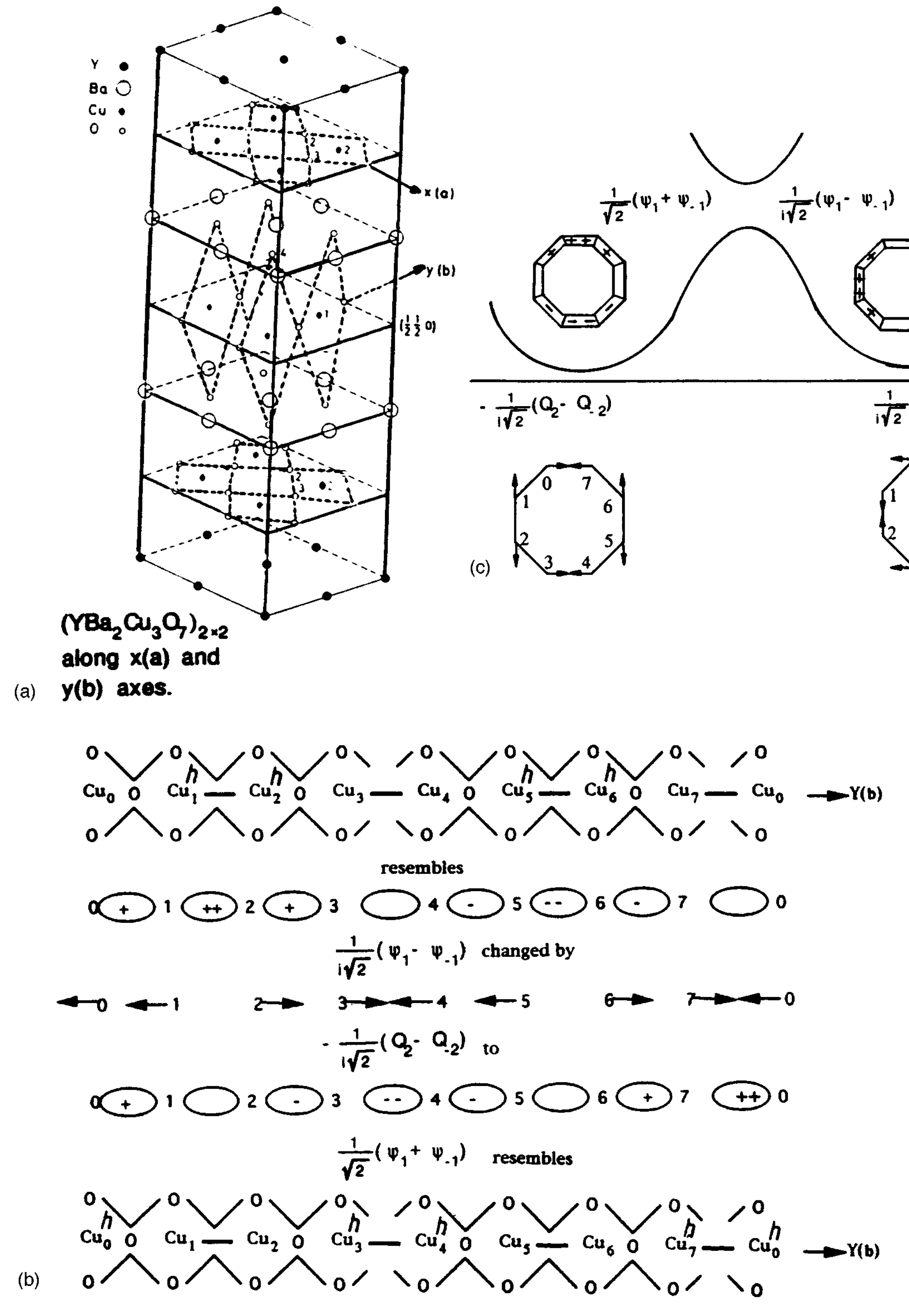

FIG. 5. (a) Illustration of a (square) quadrupole unit cell $(YBa_2Cu_3O_7)_{2\times2}$ along $x(a)$ and $y(b)$ axes. (b) The hypothetical CuO_2 linear chain with eight Cu along at the middle center and front line of $y(b)$ out of the four doped cells, $4(YBa_2Cu_3O_{7-0.25})_{2\times2}$, of (a). We consider all of the four $[4\times(-0.25)\times2\times2]$ lost oxygens, each lost oxygen is inside the two coppers: Cu-Cu in the front line of $y(b)$. Besides the eight oxygen O^- holes of $Y_{16}^{+3}Ba_{32}^{+2}Cu_{48}^{+2}O_{100}^{=}O_8^{-}$, we consider the alternative eight copper Cu^{+3} bonding (stand as Cu^h) of $Y_{16}^{+3}Ba_{32}^{+2}Cu_{40}^{+2}Cu_8^{+3}O_{108}^{=}$. Part of the four Cu^h, because of the high positive Cu^{+3} situation, would like to be away in the back line of $y(b)$ to interact with the true oxygen $O^{=}$ with more negatives than O^-. We consider only the other four Cu^h to interact with two of the loss of oxygens, e.g., Cu^h-Cu^h and another Cu^h-Cu^h. We also consider the need of vibrations to move the positive Cu^h away from the loss oxygen with zero negative. The eight copper (4 Cu^h+4Cu) are labeled as 0,1,2 . . . 7 (with the showing of an additional zero 0 as the eight number of the cyclic case instead of the linear situation): $Cu_0OCu_1^h$—$Cu_2^hOCu_3$—$Cu_4OCu_5^h-Cu_6^hOCu_7$—Cu_0. The multiple + and − signs stand for the relative real probability amplitudes of the special geminal electron pairs, Eq. (37). The vibration $(Q_\Lambda=Q_{\pm2})$ for the Jahn-teller perturbation to yield double-well potential is shown by arrows →. It causes the movement from one degenerate state $(1/i\sqrt{2})(\Psi_1-\Psi_{-1})$ to another degenerate state $(1/\sqrt{2})(\Psi_1+\Psi_{-1})$ [Eq. (37)] as shown in (c). (c) The cyclic structure of eight coppers with the Jahn-Teller effect of two degenerate states under the vibration $(1/i\sqrt{2})(Q_2-Q_{-2})$.

from a different doping $(YBa_2Cu_3O_{7-0.5})_4$. The Cu-Cu *bond* picture is to illustrate the vacuum due to the loss of oxygen in between the two coppers. For eight Cu's, if we consider hypothetically 16 Cu-O and lengths, the total length is $16 \times 1.9 = 30.4$ Å which happens to be not too far from the coherence lengths.

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