

Chemical Geminal Charge Transfer, Vibronic Degeneracy Effects, and Doping Excitons in Superconductivity

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A quantum chemical view of charge transfer related to the Jahn–Teller effect involving two-electron functions (geminals) is compared with BCS theory, the Cooper pair, and Bipolaron theory. For different isotope effects, we have proposed a Renner–Teller mechanism for cyclic crystals (instead of linear molecules) and a Jahn–Teller effect for degenerate vibronic states (instead of degenerate electronic states alone). To illustrate examples of special doping structure in superconductors, we consider $(\text{YBa}_2\text{Cu}_3\text{O}_{7-0.25})_4$ and $(\text{Nd}_{2-0.125}\text{Ce}_{0.125}\text{CuO}_{4-0.625})_{2 \times 4}$ and employ exciton-like Covalon states to render an improved description of the superconductive mechanism. © 1997 Academic Press

I. INTRODUCTION

For an improved description of superconductivity, we propose special structures and effects for the superconductors. These improvements include the consideration of additional degeneracies beyond those previously used in models of charge transfer (1–4) and the use of geminals (two-electron wave functions) in lieu of one-electron molecular orbitals. The geminal model is compared with, and goes beyond, the Cooper pair (5) and the BCS theory (6) of superconductivity. Moreover, we emphasize the inclusion of additional vibrational degeneracies, besides the electronic degeneracy in the spectroscopy of the Jahn–Teller effect (7–9). We also propose a new aspect of the Renner–Teller effect (10) arising from our use of cyclic crystals instead of linear molecules. These new Jahn–Teller and Renner–Teller effects, as well as our consideration of special structures for superconductors, will extend the interaction of the structural sites beyond the nearest-neighbor model, which is related to the simple antisymmetric vibration of nearest neighbors. This extension represents an improvement over the displaced-oscillator (nearest-neighbor) interaction in the Bipolaron theory (11) of superconductivity.

II. CONDUCTIVITY OF CHARGE TRANSFER

We introduce the special consideration of charge transfer as a viable mechanism for conductivity. It will serve as a suitable starting point to be modified and extended to describe superconductivity.

As early as 1960, Bader (12) considered the charge transfer due to the mixing of $(\pi_u)^4 = \psi_0^e(1\Sigma_g^+)$ with $(\pi_u)^3\pi_g = \psi_1^e(1\Sigma_u^+)$ via a vibronic transition with one quantum χ^1 of the vibrational mode $Q_{\Sigma_u^+}$ ($\rightarrow \leftarrow \rightarrow$).

$$\begin{aligned} \psi_0^e(1\Sigma_g^+) &\Rightarrow \psi_0^e(1\Sigma_g^+)\chi^1(Q_{\Sigma_u^+}) \\ &+ \frac{\langle \psi_1^e(1\Sigma_u^+)\chi^0(Q_{\Sigma_u^+}) | Q_{\Sigma_u^+} \partial H / \partial Q_{\Sigma_u^+} | \psi_0^e(1\Sigma_g^+)\chi^1(Q_{\Sigma_u^+}) \rangle}{E(1\Sigma_g^+) + \hbar\omega_{\Sigma_u^+} - E(1\Sigma_u^+)} \\ &\times \psi_1^e(1\Sigma_u^+)\chi^0(Q_{\Sigma_u^+}). \end{aligned} \quad [1]$$

The $\psi_0^e(1\Sigma_g^+)$ state has four electrons in π_u and the $\psi_1^e(1\Sigma_u^+)$ state has three electrons in π_u and one electron in π_g . The difference between them may be approximated as one electron π_u state versus one electron π_g state. If there are three linearly arranged atoms in the π state, we may consider one atom a at the left with an atomic orbital π_{al} , another identical second atom a at the right with an atomic orbital π_{ar} , and the third atom b in the middle with a different coefficient B and with the atomic orbital $B\pi_{bm}$. The molecular orbital of the π_u state is $\pi_u \sim \pi_{al} + B\pi_{bm} + \pi_{ar}$. Its charge structure with the vibration Q is $\pi_u Q_{\Sigma_u^+} \sim \pi_u Q \sim +\rightarrow \leftarrow + \rightarrow$. The molecular orbital of the π_g state is $\pi_g \sim \pi_{al} - \pi_{ar}$. Its charge structure without vibration is $\pi_g \sim + \bullet -$. Here \bullet stands for no electron and $+$ and $-$ designate the upper and lower π electrons, respectively.

The change in charge density due to the mixing in Eq. [1] may be approximately visualized as

$$\begin{aligned}
\pi_u^4 Q + \left\langle \frac{\partial H}{\partial Q} Q \right\rangle \pi_u^3 \pi_g &\approx \pi_u Q + \left\langle \frac{\partial H}{\partial Q} Q \right\rangle \pi_g \\
&\approx (\pi_{al} + B\pi_{bm} + \pi_{ar}) Q + \left\langle \frac{\partial H}{\partial Q} Q \right\rangle (\pi_{al} - \pi_{ar}) \\
&\sim (+ \rightarrow \leftarrow + \rightarrow) + \left\langle \frac{\partial H}{\partial Q} Q \right\rangle (+ \bullet -) \\
&\approx (+ \rightarrow \leftarrow + \bullet \rightarrow).
\end{aligned} \tag{2}$$

The above conductivity due to vibronic charge transfer is a single-electron molecular orbital consideration, but superconductivity in a solid-state infinite crystal, which can be regarded as a cyclic crystal system, is mainly considered as arising from the paired double-electron treatment with momentum $k = 0$ in BCS theory (6).

Instead of coupling the electrons in a Cooper pair (5, 13) for low- T_c superconductors, below we shall correlate their motion by invoking (two-electron) geminal states, along with their different vibronic transitions, and compare the result with the charge-transfer mechanism and BCS theory.

III. THE GEMINAL MODEL

For a two-electron (e_1, e_2) vibronic interaction we propose the quantum-chemical view of the cyclization of the Bloch sum of geminal-type electronic states (ψ^e) and vibrations (Q) for atomic orbitals and displacements, respectively, in a nearest-neighbor approximation at an interatomic distance of a :

$$\begin{aligned}
\psi_\Lambda^e(1, 2) = \psi_\Lambda(1, 2) &= \frac{1}{\sqrt{2N+2}} \sum_{n=0}^{2N+1} e^{\frac{2\pi i \Lambda n}{2N+2}} \phi_{n, n+1}(1, 2) \\
&= \frac{1}{\sqrt{2N+2}} \sum_{n=0}^{2N+1} e^{ikna} \phi_{n, n+1}(1, 2) = \psi_k(1, 2),
\end{aligned} \tag{3}$$

$$\begin{aligned}
\phi_{n, n+1}(1, 2) &= \frac{1}{2} [\phi_n(1) \phi_{n+1}(2) + \phi_n(2) \phi_{n+1}(1)] \\
&\times (\alpha_1 \beta_2 - \beta_1 \alpha_2).
\end{aligned} \tag{4}$$

These electronic states are different from the Cooper pairs of BCS theory, whose electrons have opposing momenta, $\pm \hbar k$, viz.,

$$\begin{aligned}
\psi(1, 2) &= \dots + a_k \phi_{k\alpha}(1) \phi_{-k\beta}(2) + a_{k-q} \phi_{k-q, \alpha}(1) \phi_{-k+q, \beta}(2) \\
&+ \dots
\end{aligned}$$

We also include cyclic vibrations for their use in vibronic transitions, i.e.,

$$Q_\lambda = \frac{1}{\sqrt{2N+2}} \sum_{n=0}^{2N+1} e^{\frac{2\pi i \Lambda n}{2N+2}} \xi_{n, n+1} \tag{5}$$

$$\begin{aligned}
&= \frac{1}{\sqrt{2N+2}} \sum_{n=0}^{2N+1} e^{iqna} \xi_{n, n+1} = Q_q \\
\xi_{n, n+1} &= \xi_n - \xi_{n+1}.
\end{aligned} \tag{6}$$

Because $2\pi\hbar\Lambda/(2N+2)a = 2\pi(r \times p)_z/2\pi r = \hbar k$ is the momentum p of the electron pair, as in BCS theory, we choose ($k - k = 0$) so that the ground state of the electron pair is represented by the spin geminal $\psi_0(1, 2)$.

In analogy to Eq. [1] the charge transfer may be described by vibronic transitions from the ground state, i.e.,

$$\begin{aligned}
\psi(1, 2) &= \psi_0(1, 2) \chi^0(Q_{-\Lambda}) \\
&+ \frac{\langle \psi_\Lambda(1, 2) \chi^1(Q_{-\Lambda}) | Q_{-\Lambda} \partial H / \partial Q_{-\Lambda} | \psi_0(1, 2) \chi^0(Q_{-\Lambda}) \rangle}{E_0 - E_\Lambda - \hbar\omega_{-\Lambda}} \\
&\times \psi_\Lambda(1, 2) \chi^1(Q_{-\Lambda}).
\end{aligned} \tag{7}$$

For a system of $2N + 2$ electrons the ground state of the total system is

$$\begin{aligned}
\psi(1, 2, 3, \dots, 2N+2) &= \left(\frac{1}{(2!)^{N+1} (N+1)! (2N+2)!} \right)^{1/2} \\
&\times \sum_{\mu=1}^{(2N+2)!} \delta_\mu P_\mu \psi(1, 2) \psi(3, 4) \dots \psi(2N+1, 2N+2).
\end{aligned} \tag{8}$$

The normalization constant $(N+1)!$ is due to the equivalence of the $(N+1)$ geminal permutations. The normalization factor $(2!)^{N+1}$ arises from each of the $(N+1)$ geminals which already contain $2!$ permutations (cf. Eq. [4]). The vibronic energy of the geminals is a little different from that given in the following section.

IV. COMPARISON OF THE SECOND-ORDER JAHN-TELLER ENERGY WITH THE LIMITED ANALOGS OF THE BCS AND BIPOLARON THEORIES

The energy expressions arising from these quantum chemical vibronic interactions may be compared with those of the electron-phonon of the BCS theory of Cooper pairs (13). In the latter formulation α^+ and α are electron creation and annihilation operators, while a_q^+ and a_q denote phonon creation and annihilation operators. For a first-order per-

turbation,

$$H' = iD \sum_{k,q} (\alpha_{k+q}^+ \alpha_k a_q - \alpha_{k-q}^+ \alpha_k a_q^+), \quad [9]$$

one makes use of the contact-transformation operator,

$$S' = iD \sum_{k,q} \left(\frac{\alpha_{k+q}^+ \alpha_k a_q}{E_k - E_{k+q} + \hbar\omega_q} - \frac{\alpha_{k-q}^+ \alpha_k a_q^+}{E_k - E_{k-q} - \hbar\omega_q} \right), \quad [10]$$

to deduce the diagonal part of the second-order electron–electron interaction

$$\begin{aligned} H'' &= \frac{1}{2} [H' S - S H']_{\text{diag}} \\ &\approx D^2 \sum_{k,q} \frac{\hbar\omega_q}{(E_k - E_{k-q})^2 - (\hbar\omega_q)^2} \alpha_{-k+q}^+ \alpha_{-k} \alpha_{k-q}^+ \alpha_k. \end{aligned} \quad [11]$$

To arrive at this result it is necessary to recall that BCS theory considers the phonon system to be in the ground (or zero) vibrational state. Hence, upon integrating over the phonon states, Eq. [11] results because only operators of the type $a_q a_q^+$ are nonzero in the zero vibrational state.

Parallel relations may be obtained from the quantum chemical perturbational treatment of vibronic interactions, in which the zero-order Hamiltonian is assumed to be the sum of the nuclear kinetic energy and the electronic Hamiltonian. Perturbations are obtained by expanding the electronic Hamiltonian in a Taylor series involving the vibrational modes. The equations corresponding to the above BCS relations emerge when the first-order perturbation is taken to be those terms that are linear in the vibrational mode. In turn, they may be cast in terms of the creation/annihilation operators. When this is done, the expectation values of the operators are evaluated and it is found that the nonvanishing matrix elements that contribute to the expectation values have the form

$$\begin{aligned} \langle H' \rangle &\cong \langle \psi_{k+q}^e \chi^0(Q_q) | Q_q \partial H / \partial Q_q | \psi_k^e \chi^1(Q_q) \rangle \\ &\quad - \langle \psi_{k-q}^e \chi^1(Q_q) | Q_q \partial H / \partial Q_q | \psi_k^e \chi^0(Q_q) \rangle \end{aligned} \quad [12]$$

and

$$\begin{aligned} \langle H'' \rangle &\cong \frac{1}{2} \left[\frac{|\langle \psi_{k-q}^e \chi^1(Q_q) | Q_q \partial H / \partial Q_q | \psi_k^e \chi^0(Q_q) \rangle|^2}{E_k - E_{k-q} - \hbar\omega_q} \right. \\ &\quad \left. - \frac{|\langle \psi_{-k+q}^e \chi^0(Q_q) | Q_q \partial H / \partial Q_q | \psi_{-k}^e \chi^1(Q_q) \rangle|^2}{E_{-k} - E_{-k+q} - \hbar\omega_q} \right]. \end{aligned} \quad [13]$$

Comparison of Eqs. [9] and [12] shows that the vibronic integrals occurring in the latter equation have been assigned a common value, D , in BCS theory. Further illustration of

this correspondence of D and the vibronic integrals is given by the example of an electron–phonon interaction involving the degenerate electron-pair states, $E_k = E_{-k}$, and the vibrational mode $q = 2k$. Since the first-order contact transformation diagonalizes the Hamiltonian to first order, there are no first-order corrections to the energy. Furthermore, the second-order contributions arise from only the diagonal part of the second-order corrections, which is why we have displayed only that part. Hence, for this case

$$E = E^{(0)} + \langle H'' \rangle = E^{(0)} + E^{(2)}, \quad [14]$$

where

$$\begin{aligned} E^{(2)} &= \langle H''_{\text{diag}} \rangle = - \frac{D^2}{\hbar\omega_{2k}} \\ &= - \frac{|\langle \psi_{-k}^e \chi^1(Q_{2k}) | Q_{2k} \partial H / \partial Q_{2k} | \psi_k^e \chi^0(Q_{2k}) \rangle|^2}{\hbar\omega_{2k}} \\ &= - \frac{|\langle \psi_{-k}^e | \partial H / \partial Q_{2k} | \psi_k^e \rangle|^2}{2m\omega_{2k}^2} = - \frac{|\langle \partial H / \partial Q_{2k} \rangle|^2}{2f}. \end{aligned} \quad [15]$$

Here we have used

$$|\langle \chi^1(Q) | Q | \chi^0(Q) \rangle|^2 = \left(\sqrt{\frac{1}{2\beta}} \right)^2 = \left(\sqrt{\frac{\hbar}{2m\omega}} \right)^2 = \frac{\hbar}{2\sqrt{mf}}, \quad [16]$$

where $\omega = \sqrt{f/m}$ and $\beta = \sqrt{mf}/\hbar = m\omega/\hbar$.

This example is equivalent to the Jahn–Teller result for a double-well potential arising from a perturbed harmonic oscillator potential with force constant f , viz.,

$$E_{\pm} = E^0 + \frac{1}{2} f Q^2 \pm \langle \partial H / \partial Q \rangle Q. \quad [17]$$

The harmonic oscillator potential is of second degree in Q and has a diagonal contribution, while the last term is the perturbing potential and is linear in Q .

For the minima, the potential satisfies

$$(\partial E_{\pm} / \partial Q)_0 = 0 = f Q_0 \pm \langle \partial H / \partial Q \rangle_0, \quad [18]$$

so that

$$Q_0^{\pm} = \mp \langle \partial H / \partial Q \rangle_0 / f$$

and

$$\begin{aligned} E_{\min} &= E^0 + \frac{1}{2} f (Q_0^{\pm})^2 \pm \langle \partial H / \partial Q \rangle_0 Q_0^{\pm} \\ &= E^0 - \frac{|\langle \partial H / \partial Q \rangle_0|^2}{2f} = E^0 - \Delta E. \end{aligned} \quad [19]$$

The quantity $\Delta E = |\langle \partial H / \partial Q \rangle_0|^2 / 2f$ is related to the high- T_c superconductivity gap of Bipolaron theory (11) for

which $\langle \partial H / \partial Q \rangle$ is an exchange integral between two nearest-neighbor atoms separated by a distance a . In that theory the first-order Hamiltonian H' and the second-order energy are

$$H' = \sum_k \sum_q (\gamma_q + 2\delta_q \cos ka) \sqrt{\frac{\hbar}{2m\omega_q}} (\hat{a}_q + a_q) \hat{\alpha}_{k\alpha}^\dagger \hat{\alpha}_{k\beta}^\dagger \alpha_{k\alpha} \alpha_{k\beta} \quad [20]$$

and

$$\begin{aligned} E^{(2)} &= -\frac{\langle H' \rangle^2}{\hbar\omega} \approx -\frac{\langle \partial H / \partial Q \rangle^2 \langle Q \rangle^2}{\hbar\omega} \\ &\approx -\frac{\langle \gamma + 2\delta \cos ka \rangle^2 \langle \sqrt{\hbar/2m\omega} \rangle^2}{\hbar\omega} \\ &= -\frac{|\langle \gamma + 2\delta \cos ka \rangle|^2}{2m\omega^2} = -\frac{|\langle \gamma + 2\delta \cos ka \rangle|^2}{2f} \\ &= -\Delta = -\frac{k_B T_c}{2}, \end{aligned} \quad [21]$$

respectively. The exchange integral is evaluated by

$$\begin{aligned} &\frac{1}{N} \left\langle \sum_{n=0}^{N-1} e^{ikna} \psi_n^e \left| \frac{\partial H}{\partial Q} \right| \sum_{n'=0}^{N-1} e^{ikn'a} \psi_{n'}^e \right\rangle \\ &= \frac{1}{N} \sum_{n=0}^{N-1} \langle \psi_n^e | \frac{\partial H}{\partial Q} | \psi_n^e \rangle \\ &\quad + \frac{1}{N} \sum_{n=0}^{N-1} \left[e^{-ikna} e^{ik(n+1)a} \langle \psi_n^e | \frac{\partial H}{\partial Q} | \psi_{n+1}^e \rangle \right. \\ &\quad \left. + e^{-ikna} e^{ik(n-1)a} \langle \psi_n^e | \frac{\partial H}{\partial Q} | \psi_{n-1}^e \rangle \right] \\ &= \gamma + \delta (e^{ika} + e^{-ika}) = \gamma + 2\delta \cos ka. \end{aligned} \quad [22]$$

The nearest-neighbor effect is essentially due to $\cos ka$. In doped superconductors there may be contributions from

more distant neighbors such as $\cos 2ka$, $\cos 3ka$, etc. The interatomic distance, a , may also be different due to doping. Thus the Jahn–Teller effect for the interaction between two degenerate electronic states (giving rise to a double-well potential whose minima are at equal depth) is also comparable to the interaction of two equivalent (degenerate) neighboring atoms. Nevertheless, our aim is to emphasize the two-electron geminal treatment for the case of a cyclic crystal. Furthermore, we want to go beyond the second-order energy of the BCS and Bipolaron theories.

V. ILLUSTRATION OF THE GEMINAL MODEL: A POSSIBLE SPECIAL JAHN–TELLER EFFECT FOR C_4H_4

One of the reasons for basing our model on the cyclic geminal state may be illustrated with the simple case of the C_4H_4 cyclic “crystal.” The one-electron LCAO-MO for four π $a_{2u}^2 e_g^2 b_{1u}^0$ will not give rise to a degenerate irreducible representation of D_{4h} symmetry, because the product of the electron-pair in the HOMO is $e_g(3) \times e_g(4) = a_{1g}(3,4) + a_{2g}(3,4) + b_{1g}(3,4) + b_{2g}(3,4)$. However, it may be pointed out that the product of the electron pair occupying the HOMO of a cyclic “crystal” of D_{6h} symmetry is $e_{1g}(3) \times e_{1g}(4) = a_{1g}(3,4) + a_{2g}(3,4) + e_{2g}(3,4)$, thereby giving rise to the doubly degenerate $e_{2g}(3,4)$ pair function, with $e_{2g(x^2-y^2)}(3,4)$ and $e_{2g(xy^2)}(3,4)$ being degenerate. In this latter case, our degenerate cyclic geminals, $\psi_1(3,4)$ and $\psi_{-1}(3,4)$, correspond to the real pair function $e_g(3,4)$ having degenerate components $e_{gxz}(3,4)$ and $e_{gyz}(3,4)$. Moreover, cyclic geminals will have degeneracy in all cases.

For the example of C_4H_4 of D_{4h} symmetry (Fig. 1), the cyclic geminals based on the complex irreducible representation Λ in Eq. [3] are $\psi_\Lambda = \psi_0, \psi_{\pm 1}, \psi_2$. In real form, they are $a_{2uz} = \psi_z, e_{gxz} = \psi_x, e_{gyz} = \psi_y$, and $b_{2u(x^2-y^2)z} = \psi_{(x^2-y^2)z}$. The vibrational states are $Q_\lambda = Q_0, Q_\pm, Q_2$, or in real form, $Q_{a_{1g}} = Q_0, Q_{e_{gx}} = Q_x, Q_{e_{gy}} = Q_y$, and $Q_{b_{1g}} = Q_{x^2-y^2}$ or $Q_{b_{2g}} = Q_{xy}$.

With this example, the Jahn–Teller effect yields a second-order energy in complex and real states,

$$\begin{aligned} E^{(2)} &= -\frac{|\langle \psi_1(3,4) \chi^1(Q_2) | Q_2 \partial H / \partial Q_2 | \psi_{-1}(3,4) \chi^0(Q_2) \rangle|^2}{\hbar\omega_2} \\ &\approx -\frac{1}{2} \left[\frac{|\langle \psi_x(3,4) \chi^1(Q_{x^2-y^2}) | Q_{x^2-y^2} \partial H / \partial Q_{x^2-y^2} | \psi_x(3,4) \chi^0(Q_{x^2-y^2}) \rangle|^2}{\hbar\omega_{x^2-y^2}} \right. \\ &\quad \left. + \frac{|\langle \psi_y(3,4) \chi^1(Q_{x^2-y^2}) | Q_{x^2-y^2} \partial H / \partial Q_{x^2-y^2} | \psi_y(3,4) \chi^0(Q_{x^2-y^2}) \rangle|^2}{\hbar\omega_{x^2-y^2}} \right] \\ &\approx -\frac{\langle \frac{\partial H}{\partial Q} \rangle^2 (\sqrt{\hbar/2m\omega})^2}{\hbar\omega} = -\frac{\left| \left\langle \frac{\partial H}{\partial Q} \right\rangle \right|^2}{2m\omega^2} = -\frac{\left| \left\langle \frac{\partial H}{\partial Q} \right\rangle \right|^2}{2f} \\ &= \Delta E \propto m^{-\alpha}, \end{aligned} \quad [23]$$

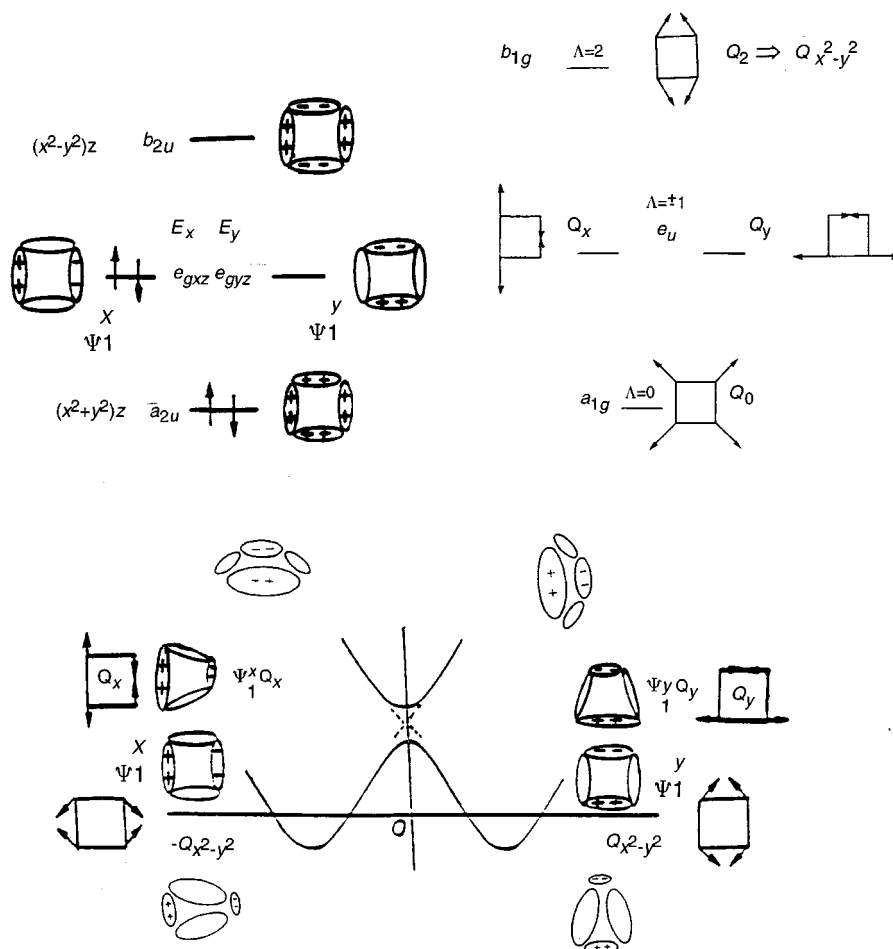


FIG. 1. New Jahn-Teller effect, not only for degenerate electronic geminal states (ψ_1^x and ψ_1^y), but also for degenerate vibronic states [$\psi_1^x \chi(Q_x)$ and $\psi_1^y \chi(Q_y)$].

in which $\alpha = 0$ (meaning no isotope effect for the second-order energy). This is similar to the results of both Kittel (cf. Eq. [15]) and the Bipolaron theory (cf. Eq. [21]).

VI. A NEW RENNER-TELLER EFFECT FOR CYCLIC CRYSTALS WITH THE GEMINAL MODEL

Next we would like to consider cases for superconductors in which: (i) vibronic interactions may arise from corrections other than the second-order energy, (ii) more than purely electronic degeneracy is involved, and (iii) nonzero isotope effects may occur. The first-order energy involving the degeneracy of both the electronic and vibrational states is well known in the Renner-Teller effect for linear molecules. Nevertheless, we will propose this Renner-Teller mechanism for cyclic crystals.

For a molecule lying along the z axis the degenerate one-electron states are $(\psi_1, \psi_{-1}) \approx (\pi_x, \pi_y)$ and (d_{xz}, d_{yz}) , etc., and $(\psi_2, \psi_{-2}) \approx (d_{x^2-y^2}, d_{xy})$, etc., where the pseudo-angular momenta $\Lambda = \pm 1, \pm 2$ are along z . The degener-

ate vibrational modes are $(Q_1, Q_{-1}) \approx (Q_x, Q_y)$ with $[\chi^s(Q_1), \chi^s(Q_{-1})] \approx [\chi^s(Q_x), \chi^s(Q_y)]$ having a vibrational quantum number $s = 0, 1, 2, \dots$. In a molecule there is no vibronic interaction for a vibrational mode Q_λ with $\lambda \geq \pm 2$. A simple example of the Renner-Teller first-order energy, according to Pople and Longuet-Higgins (10), is

$$E^{(1)} = \langle \psi_1^e \chi^1(Q_{-1}) | Fr^2 \cos 2(\phi_e - \phi_v) | \psi_{-1}^e \chi^1(Q_1) \rangle, \quad [24]$$

where ϕ_e and ϕ_v are the azimuthal angles of electrons (e) and vibrations (v). The perturbation operator could arise from

$$H' = \frac{1}{2} \frac{\partial^2 H}{\partial Q_{-1}^2} Q_{-1}^2 + \frac{1}{2} \frac{\partial^2 H}{\partial Q_1^2} Q_1^2 \Rightarrow \frac{1}{2} Fr^2 (e^{2i(\phi_e - \phi_v)} + e^{-2i(\phi_e - \phi_v)}). \quad [25]$$

Because our cyclic crystal can exhibit vibrational modes with pseudo-angular momenta (Eq. [5]) $\Lambda = 0, \pm 1, \pm 2, \dots$ along the z axis, we propose a new Renner–Teller effect involving the vibronic states $\psi_{\pm\Lambda}\chi^1(Q_{\mp\Lambda})$ with Λ lying beyond the ± 1 found in molecules. As Eqs. [24] and [25] indicate, the first-order energy is

$$E^{(1)} = \frac{1}{2} \langle \psi_{\Lambda}(1,2)\chi^1(Q_{-\Lambda}) | \frac{\partial^2 H}{\partial Q_{\Lambda}^2} Q_{\Lambda}^2 + \frac{\partial^2 H}{\partial Q_{-\Lambda}^2} Q_{-\Lambda}^2 \rangle \times | \psi_{-\Lambda}(1,2)\chi^1(Q_{\Lambda}) \rangle. \quad [26]$$

As a simple illustration, the first-order Renner–Teller energy for the previous case of cyclic C_4H_4 is for the topmost electrons,

$$\begin{aligned} E^{(1)} &= \frac{1}{2} \langle \psi_1(3,4)\chi^1(Q_{-1}) | \frac{\partial^2 H}{\partial Q_1^2} Q_1^2 + \frac{\partial^2 H}{\partial Q_{-1}^2} Q_{-1}^2 \rangle \\ &\quad \times | \psi_{-1}(3,4)\chi^1(Q_1) \rangle \\ &\approx \langle \psi_x(3,4)\chi^1(Q_x)\chi^0(Q_y) | \frac{\partial^2 H}{\partial Q_x \partial Q_y} Q_x Q_y \rangle \\ &\quad \times | \psi_y(3,4)\chi^0(Q_x)\chi^1(Q_y) \rangle \\ &= \left\langle \frac{\partial^2 H}{\partial Q_x \partial Q_y} \right\rangle \sqrt{\frac{\hbar}{2m_x\omega_x}} \sqrt{\frac{\hbar}{2m_y\omega_y}} \\ &\approx \left\langle \frac{\partial^2 H}{\partial Q_x \partial Q_y} \right\rangle \frac{\hbar}{2m_1\omega_1} = \left\langle \frac{\partial^2 H}{\partial Q_x \partial Q_y} \right\rangle \frac{\hbar}{2\sqrt{m_1 f}} \\ &\propto m_1^{-\alpha} = m_1^{-1/2}. \end{aligned} \quad [27]$$

This isotope effect with $\alpha = 1/2$ is different from that of the second-order energy with $\alpha = 0$ (Eq. [23]).

VII. A NEW JAHN–TELLER EFFECT FROM DEGENERATE VIBRONIC STATES

Going beyond the Jahn–Teller effect for degenerate electronic states, we propose a new Jahn–Teller effect that involves degenerate vibronic states in the Renner–Teller case (Fig. 1)

$$\begin{aligned} E^{(2)} &= - | \langle \psi_x(3,4)\chi^1(Q_x)\chi^0(Q_y)\chi^1(Q_{x^2-y^2}) | \frac{1}{3!} \frac{\partial^3 H}{\partial Q_x \partial Q_y \partial Q_{x^2-y^2}} \rangle \rangle \\ &\quad \times Q_x Q_y Q_{x^2-y^2} | \psi_y(3,4)\chi^0(Q_x)\chi^1(Q_y)\chi^0(Q_{x^2-y^2}) \rangle |^2 / \hbar\omega_{x^2-y^2} \\ &= - \left| \langle \psi_x(3,4) | \frac{1}{3!} \frac{\partial^3 H}{\partial Q_x \partial Q_y \partial Q_{x^2-y^2}} | \psi_y(3,4) \rangle \right|^2 \\ &\quad \times \left(\sqrt{\frac{\hbar}{2m_x\omega_x}} \sqrt{\frac{\hbar}{2m_y\omega_y}} \sqrt{\frac{\hbar}{2m_{x^2-y^2}\omega_{x^2-y^2}}} \right)^2 / \hbar\omega_{x^2-y^2} \end{aligned} \quad [28]$$

$$\begin{aligned} &= - \left| \left\langle \frac{1}{3!} \frac{\partial^3 H}{\partial Q_x \partial Q_y \partial Q_{x^2-y^2}} \right\rangle \right|^2 \frac{\hbar^2}{(2m_1\omega_1)^2 2m_2\omega_2^2} \\ &= - \left| \left\langle \frac{1}{3!} \frac{\partial^3 H}{\partial Q_x \partial Q_y \partial Q_{x^2-y^2}} \right\rangle \right|^2 \frac{\hbar^2}{4m_1 f_1 2f_2} \propto m_1^{-\alpha} = m_1^{-1}, \end{aligned}$$

where the isotope effect is different from the usual Jahn–Teller result of $\alpha = 0$ (Eq. [23]). The possibility of electronic matrix elements of ψ_x and ψ_y for the Jahn–Teller effect is due to the symmetry relationship

$$x \times y \times (x^2 - y^2) \approx b_{2g} \times b_{1g} = a_{2g} \approx xy - yx,$$

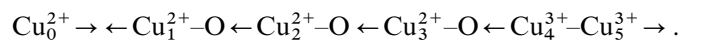
where a_{2g} is symmetric with respect to the operations of the cyclic group C_4 . This simple illustration of cyclic C_4H_4 that uses the uppermost vibration $Q_2 \sim Q_{x^2-y^2}$ amounts to an antisymmetric vibration between nearest neighbors that affects the electronic motion. It is very similar to the case of displaced equivalent oscillators that are related to the Bi-polaron motion between nearest neighbors.

VIII. VIBRONIC INTERACTIONS BETWEEN DISTANT NEIGHBORS

For superconductors that are doped at sites of distant neighbors, we will consider different vibrational modes to allow for different lengths of charge transfer (14). Moreover, we will consider the effect of electronic tunneling (14).

As an example, consider the case in which six linearly arranged atoms (15) have vibrational compressions and extensions at different places (say, between 0–1 and 4–5), e.g., $0 \rightarrow \leftarrow 1 \leftarrow 2 \leftarrow 3 \leftarrow 4 \rightarrow 5 \rightarrow [v_4(\sigma_u^+)]$. This vibration is quite different from the nearest-neighbor case between 2–3 and 3–4, i.e., $\leftarrow 0 \leftarrow 1 \rightarrow \leftarrow 3 \rightarrow 4 \rightarrow 5 \rightarrow [v_2(\sigma_g^+)]$. In fact, the nearest-neighbor case is more similar to the Jahn–Teller (vibronic) interaction (7–9, 16) with the degenerate vibration $C=C-C$ and $C-C=C$, due to $C \rightarrow \leftarrow C$ $C \rightarrow$ and $\leftarrow C$ $C \rightarrow \leftarrow C$, respectively.

As a more concrete example of the use of a vibrational mode of the type $v_4(\sigma_u^+)$, we consider the doped superconductor $(YBa_2Cu_3O_{7-0.25})_4 = Y_4Ba_8Cu_{12}O_{28-1}$, in which one oxygen along the copper-oxide line, $Cu_1-O-Cu_2-O-Cu_3-O-Cu_4-Cu_5$, has been lost, namely that between Cu_4-O-Cu_5 and Cu_4-Cu_5 (cf. Fig. 2). Although other possibilities, such as O^{2-} to O^- , may occur, for illustrative purposes, we consider the electrically neutral species $Y_4^3+Ba_8^2+Cu_{10}^2+Cu_2^3+O_{27}^{2-}$, in which $Cu^{2+}(3d^9)$ has one antibonding electron and the dopant $Cu^{3+}(3d^8)$ has one electron hole. Then, as indicated in Fig. 3, according to our simple hypothetical vibrational mode, for a doped copper-oxide line containing six copper atoms, we have



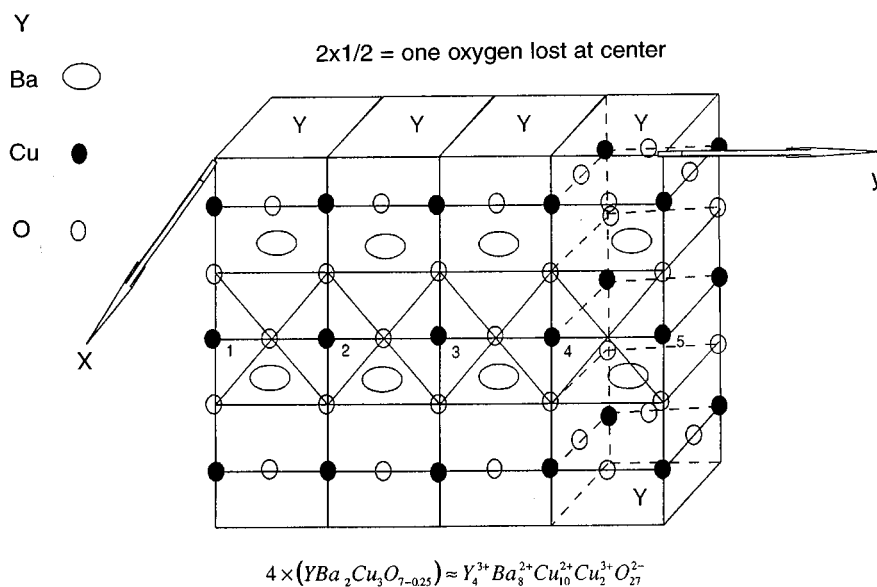
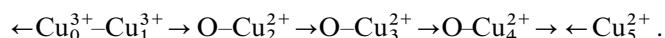


FIG. 2. Hypothetical doped state of $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ with a large emphasized cell built with four unit cells and with a loss of oxygen near the two coppers at the middle of the right unit cell (between #4 and #5 of Cu). In addition to the increase of positive charge of the copper from Cu^{2+} to Cu^{3+} , we can also consider the decrease of the negative charge of the oxygen that will yield the neutral species $\text{Y}_4^{3+}\text{Ba}_8^{2+}\text{Cu}_{10}^{2+}\text{O}_{25}^{2-}\text{O}_2^-$.

The next doped copper-oxide line is



In this simple model we may state qualitatively that the loss of the oxygen (negative charge) will cause the highly posit-

ively charged atoms of Cu^{3+} ($3d^8$) to move away from each other via this vibration. Another thing to be considered is the speed of electron tunneling along a doped line versus the time of the vibrational movement. In this regard it is of interest to know how many doped species can be traversed

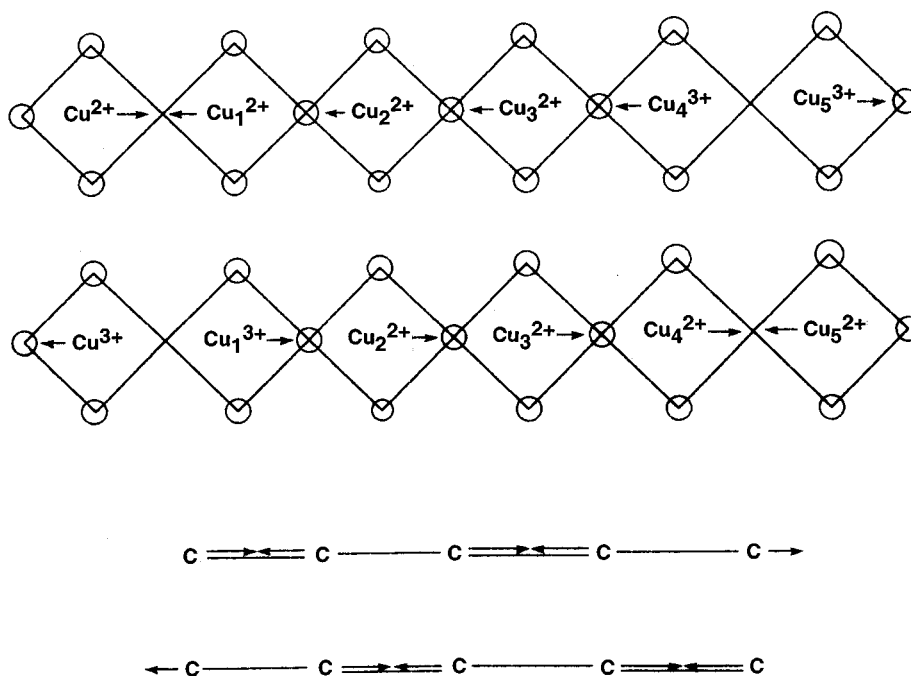


FIG. 3. The position with the loss of the negative charge of the oxygen will favor the lower positive charge of the copper (Cu^{2+} , $3d^9$) and will disfavor the higher positive charge of the nearby copper (Cu^{3+} , $3d^8$). The conduction change of the copper holes from two Cu^{3+} to two Cu^{2+} is illustrated by a (hypothetically simplified) vibration for the large emphasized cell similar to $\nu_4(\sigma_u^+)$ with contraction and expansion differing by four neighbors. It is not the same as the antisymmetric vibration for the conjugated carbon π -bond movement to the nearest neighbor.

by the tunneling mechanism before the vibrational motion reverses and stops the electron's forward movement.

IX. VIBRONIC EFFECTS IN DOPED STRUCTURES WITH THE COVALON MODEL

In addition to the geminals constructed from a symmetry-adapted linear combination of pair functions (cf. Eq. [3]), we next examine the running-wave model of excitons (17, 18), which we have previously considered as Covalons (19–21). Again, instead of the nearest-neighbor movement of the excitons (denoted by an asterisk), such as $C=C^*=C-C=C$ to $C=C-C=C^*=C$, we look at the motion of the distant neighbors, basing our model on the doping distance.

For the doped superconductor $(Nd_{2-0.125}Ce_{0.125}CuO_{4-0.0625})_{2 \times 4} = Nd_{15}CeCu_8O_{31.5}$, we consider the loss of one oxygen between two doping Cu atoms (e.g., Cu–O–Cu to Cu–Cu). In the resulting Cu–Cu bond we also consider the special existence of one Ce^{4+} along the bond (cf. Fig. 4). To maintain charge neutrality in this example, we assign the following oxidation states, $Nd_{15}^{3+}Ce^{4+}Cu_6^{2+}Cu_2^+O_{31.5}^{2-}$. Because $Cu^+(3d^{10})$ has two antibonding electrons among the topmost dsp^2 hybrid, we consider the four antibonding electrons of Cu^+-Cu^+ to be an exciton or Covalon (indicated by an asterisk) near the site of the doping Ce^{4+} , as well as that of three displaced

oxygens. This copper-oxide line is different from its nearest neighbor (Fig. 5). For it we may propose the hypothetical vibration (for six copper atoms), $Cu_{n-1}^+ \leftarrow Cu_n^+ - O \leftarrow Cu_{n+1}^{2+} - O \leftarrow Cu_{n+2}^{2+} - O \leftarrow Cu_{n+3}^{+*} - Cu_{n+4}^{+*} \rightarrow$ and for its immediate overlapping neighbor lying to the left, $\leftarrow Cu_{n-5}^{+*} - Cu_{n-4}^{+*} \rightarrow O - Cu_{n-3}^{2+} \rightarrow O - Cu_{n-2}^{2+} \rightarrow O - Cu_{n-1}^+ \rightarrow \leftarrow Cu_n^+$. This means that the electronic bonding in the right set (first case) is different from that of the left set (second case). In the right set the qualitatively different bonding (indicated by Δ) that occurs for $n+1$, $n+2$ and $n+3$, $n+4$, may be represented by

$$\psi_{n+1, n+4}^*(1, 2, \dots, 6) = \phi_{n+1, n+2}^\Delta(1, 2) \phi_{n+3, n+4}^{*\Delta}(3, 4, 5, 6), \quad [29]$$

where for the first two Cu^{2+} atoms

$$\phi_{n+1, n+2}^\Delta(1, 2) = \frac{1}{2} [\phi_{n+1}(1) \phi_{n+2}(2) + \phi_{n+1}(2) \phi_{n+2}(1)] (\alpha_1 \beta_2 - \beta_1 \alpha_2), \quad [30a]$$

and for the next two Cu^{+*} atoms,

$$\phi_{n+3, n+4}^{*\Delta}(3, 4, 5, 6) = |\phi_{n+3}^*(3) \overline{\phi_{n+3}^*(4)} \overline{\phi_{n+4}^*(5)} \overline{\phi_{n+4}^*(6)}|. \quad [30b]$$

The orbitals ϕ and ϕ^* do not stand for the copper atoms alone. Both represent the local copper oxide; however, ϕ^* also includes the metallic doping. This means that there are less antibonding electrons (only two) in the regular copper oxides ($n+1$, $n+2$) than there are in the Cu^+ copper oxides. The latter have less oxygen and an *excited* Ce^{4+} in place of Nd^{3+} .

The left set (containing Cu_{n-3}^{2+} , Cu_{n-2}^{2+} , Cu_{n-1}^+ , Cu_n^+) accommodates other electrons

$$\psi_{n-3, n}(7, 8, \dots, 12) = \phi_{n-3, n-2}(11, 12) \phi_{n-1, n}(7, 8, 9, 10), \quad [31]$$

where for the two Cu^{2+} atoms

$$\phi_{n-3, n-2}(11, 12) = \frac{1}{2} [\phi_{n-3}(11) \phi_{n-2}(12) + \phi_{n-3}(12) \phi_{n-2}(11)] (\alpha_{11} \beta_{12} - \beta_{11} \alpha_{12}), \quad [32a]$$

and for the two Cu^+ atoms,

$$\phi_{n-1, n}(7, 8, 9, 10) = |\phi_{n-1}(7) \overline{\phi_{n-1}(8)} \overline{\phi_n(9)} \overline{\phi_n(10)}|. \quad [32b]$$

Aside from the number of antibonding electrons involved in the bonding in these monovalent ($4e^-$'s) and divalent ($2e^-$'s) species, a difference arises because of the fact that during the course of our hypothetical vibration, the

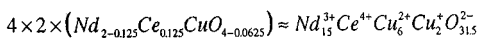
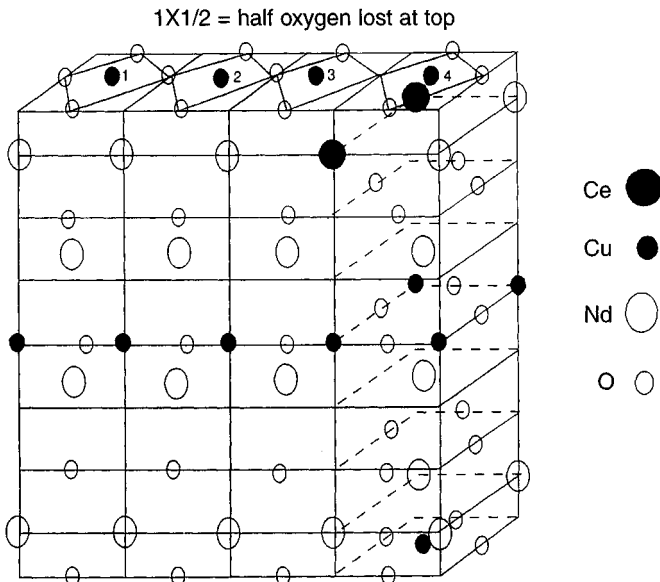


FIG. 4. Hypothetical doped state of $Nd_{2-x}Ce_xCuO_{4-y}$ with a large emphasized cell built with four unit cells and with a loss of oxygen near the two coppers at the top of the right unit cell (between #3 and #4 of Cu).

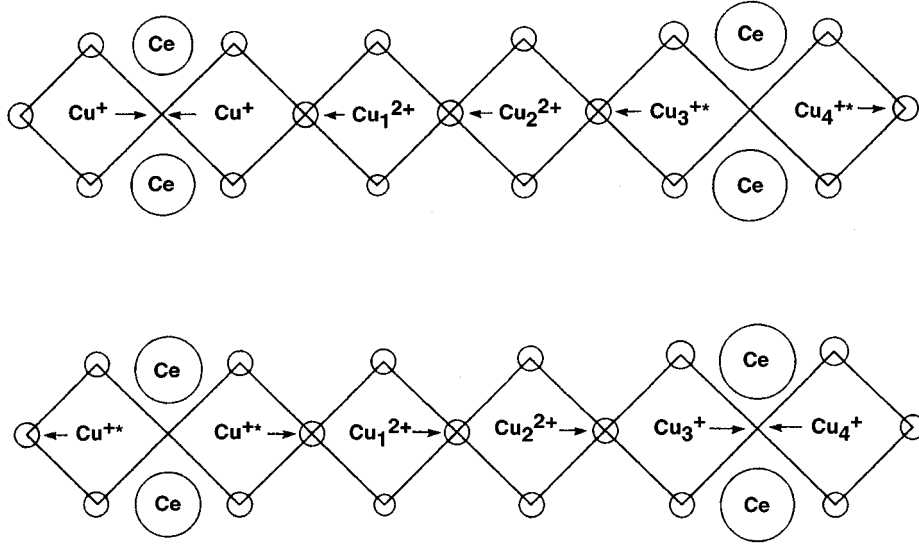


FIG. 5. The conduction change of electrons due to different electron charge density between the lower state (near Cu^+) and excited state (near Cu^{+*}) of the doped area (with Ce replacement of Nd) again illustrated by a hypothetically simplified vibration related to $v_4(\sigma_+^+)$ of six atoms. The change is toward the fourth neighbor because of the large (multiple) cell due to the doping structure.

$\text{Cu}^{+*}-\text{Cu}^{+*}$ bond is expansive while the Cu^+-Cu^+ bond is compressive. The energetic difference between ψ^* and ψ is the main concern of the theories of *exciton* and *Covalon* states. The above expressions reflect just one possible position for oxygen loss and for the placement of Cu^+ and Ce^{4+} . Other possibilities of bonding and placements need to be considered, especially for other doped superconductors.

For the case of $6N$ electrons, $4N/4 = N$ doping sets, and $4N$ copper atoms [Fig. 5 illustrates one and a half doping sets where the one set (1, 2, 3, 4) is similar to $n + 1, n + 2, n + 3, n + 4$], a *covalon*-type Bloch sum is proposed, viz.,

$$\begin{aligned} \psi_\Lambda(1, 2, \dots, 6N) = \mathcal{A} \frac{1}{\sqrt{N}} \sum_{n=0, 4, 8, \dots}^{4N-4} e^{\frac{2\pi i \Lambda n}{4N}} \psi_{n+1, n+4}^* \\ \times \prod_{k=0, 4}^{n-4} \psi_{k+1, k+4} \prod_{m=n+4, n+8, \dots}^{4N-4} \psi_{m+1, m+4}, \end{aligned} \quad [33]$$

in which the electron antisymmetrization operator is

$$\mathcal{A} = [(2!)^N (4!)^N (6N)!]^{-1/2} \sum_{\mu=1}^{(6N)!} \delta_\mu P_\mu, \quad [34]$$

and $\Lambda = 0, 1, 2, \dots, N - 1$. Equations [29–34] represent a qualitative description for the bonding of electrons from the point of view of the covalon model. In forthcoming work the details of the electron bonding in copper oxides and their doped counterparts will be considered in the calculation of the electronic and vibrational states of different superconductors.

For a simple illustration of the Covalon states of a cyclic structure with $N = 3$, $6N = 18e^-$'s, $4N = 12$ copper atoms, and $\Lambda = 0, 1, 2$, we consider

$$\begin{aligned} \psi_1(1, 2, \dots, 18) = [(2!)^3 (4!)^3 (18)!]^{-1/2} \sum_{\mu=1}^{18!} \delta_\mu P_\mu \\ \times \frac{1}{\sqrt{3}} [\psi_{1,4}^* \psi_{5,8} \psi_{9,12} + e^{\frac{2\pi i}{3}} \psi_{1,4} \psi_{5,8}^* \psi_{9,12} \\ + e^{\frac{4\pi i}{3}} \psi_{1,4} \psi_{5,8} \psi_{9,12}^*], \end{aligned} \quad [35]$$

$$\psi_2(1, 2, \dots, 18) = \psi_{-1}(1, 2, \dots, 18), \quad [36]$$

$$\begin{aligned} \psi_0(1, 2, \dots, 18) = [(2!)^3 (4!)^3 (18)!]^{-1/2} \sum_{\mu=1}^{18!} \delta_\mu P_\mu \\ \times \frac{1}{\sqrt{3}} [\psi_{1,4}^* \psi_{5,8} \psi_{9,12} + \psi_{1,4} \psi_{5,8}^* \psi_{9,12} + \psi_{1,4} \psi_{5,8} \psi_{9,12}^*], \end{aligned} \quad [37]$$

The two structures associated with ψ_1 and ψ_0 show the different charge densities of the excited electronic states. The motion of the various positions in the vibronic transitions is similar to that of the charge transfer problem mentioned by Bader (12), in Eq. [1], i.e.,

$$\begin{aligned} \psi = \psi_0 \chi^1(Q_1) \\ + \frac{\langle \psi_1 \chi^0(Q_1) | Q_1 \partial H / Q_1 | \psi_0 \chi^1(Q_1) \rangle}{E_0 + \hbar\omega_1 - E_1} \psi_1 \chi^0(Q_1). \end{aligned} \quad [38]$$

To compare this with BCS theory, in which the overall momentum of the electron pair is $p = \hbar(k - k) = 0$ in order to satisfy the London equation, we choose the related condition $\Lambda - \Lambda = 0$ for the electronic and vibrational interaction together, i.e.,

$$\begin{aligned} \psi(1, 2, \dots, 6N) &= \psi_0(1, 2, \dots, 6N)\chi^0(Q_{-\Lambda}) \\ &+ \sum_{\Lambda} \frac{\langle \psi_{\Lambda}\chi^1(Q_{-\Lambda}) | Q_{-\Lambda} \partial H / Q_{-\Lambda} | \psi_0\chi^0(Q_{-\Lambda}) \rangle}{E_0 - E_{\Lambda} - \hbar\omega_{-\Lambda}} \quad [39] \\ &\times \psi_{\Lambda}(1, 2, \dots, 6N)\chi^1(Q_{-\Lambda}). \end{aligned}$$

This vibronic state, $\psi_{\Lambda}(1, 2, \dots, 6N)\chi^1(Q_{-\Lambda})$, can also include our special Renner–Teller effect (Eqs. [24]–[27]) as well as our special Jahn–Teller effect (cf. Eq. [28]) involving vibronic degeneracy having special isotope effects. These ideas may be used to open new avenues for considering doping situations in superconductors.

X. CONCLUSIONS

We have extended the Jahn–Teller and Renner–Teller effects, as well as the charge-transfer mechanism, to provide improved descriptions of superconductivity. They are different from Bipolaron theory (11), Davydov’s Bisoliton theory (22), Anderson’s Resonating Valence Bond theory (23), and the soliton model of polyacetylene by Su *et al.* (24). For example, for the structural effects of superconduction, we consider the special case of distant-neighbor interactions and vibrations other than the totally antisymmetric vibration of nearest neighbors. Furthermore, the adoption of a cyclic structure for the crystal is different from a local Jahn–Teller effect with, say D_{4h} symmetry (25), and from other local vibronic interactions in unit cells (26, 27). Also our considerations of doped and high- T_c structures are different (28–32). These considerations, based on notions of chemical structure, will yield different properties of high- T_c superconductors than those derived from more physically based models (33–38).

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