# Modulation of superexchange and covalent binding in metal oxides by current-carrier fluctuations

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A local suppression of covalent copper-oxygen binding by current carriers through intra-atomic correlations leads to an effective electron-phonon coupling, fluctuations in the superexchange integral, and an exciton component of the attraction of holes. An isotope effect and the relaxation of the spins of copper nuclei are discussed.

1. While the relaxation properties of the oxygen nuclear spins in YBaCuO (Ref. 1) are more or less standard from the standpoint of the Bardeen-Cooper-Schrieffer theory, the relaxation of copper nuclei, which has been studied by various groups, exhibits a totally unusual behavior. On the one hand, the high relaxation rates and the nonlinear behavior at $T > T_C$ apparently indicate that (a) the relaxation is associated not with fluctuations of spins in the conduction band but with localized copper spins and (b) the carriers move in the oxygen $p$ subband,[2] which is not hybridized with copper states. On the other hand, the relaxation falls off below $T_c$ in the way it would if the coherence factor were that corresponding to the attenuation of sound. The latter circumstance suggests that the spectral density of low-frequency fluctuations of localized copper spins is closely related to fluctuations in the current-carrier density.

2. To explore this possibility, we consider in more detail the binding of a Cu–O pair in the $CuO_2$ plane, which is to a large degree covalent. The energy advantage in the hybridization of a half-filled $d_{x_2} - y_2$ orbital with a filled $p_\sigma$ state is $t^2/\Delta$, where $\Delta$ is the energy of the transition $(Cu^{2+} - O^{2-}) \rightarrow (Cu^+ - O^-)$. The presence of a current carrier (a hole in a $p_\pi$ orbital) changes the situation radically, although the state $p_\pi$ does not itself form a covalent bond with the $d_{x_2} - y_2$ function. In the first place, the $p$ orbitals are less extended in the $O^-$ state (as in the case of the $F^-$ ion), and the transport integral satisfies $t' < t$. Second, the energy ($\Delta'$) of the transition $(Cu^{2+} - O^-) \rightarrow (Cu^+ - O)$ is greater than $\Delta$, primarily because of the intra-atomic electron-hole attraction $U_{\pi\sigma}\eta_{p_\sigma}n$, where $n = c^+_\pi c_\pi$ is the hole density in the $p_\pi$ orbital. Consequently, the covalent binding in the $Cu^{2+} - O^-$ pair is essentially suppressed, since the relation $(t')^2/\Delta' \ll t^2/\Delta$ holds. This result means that the motion of a hole is accompanied by a local restructuring of the $d$–$p_\sigma$ chemical bond; as we will see below, this restructuring has important implications for both magnetism (a fluctuation in the exchange integral) and superconductivity (a nonstandard mechanism for coupling with the lattice, and an exciton component of the hole attraction).

3. We consider the model Hamiltonian

$$\mathcal{H} = \epsilon_d^0 n_d + \epsilon_p^0 n_{p_i} + t_0(d_{p_i}^+ + p_i^+ d)(1 - n_i) + \tilde{t}_0(d_{p_i}^+ + p_i^+ d) n_i$$

$$+ t_\pi c_i^+ c_j - U_{\pi\sigma} n_{p_j} n_i - U_{\pi d} n_d n_i, \tag{1}$$

where $i$ runs over the oxygen sites; $p = p_\sigma$, $c = p_\pi$, $n_i = c_i^+ c_i$, and $d = d_1, d_2$ refer to half-filled $d_{x, -y_2}$ orbitals in the $Cu_1-O_i-Cu_2$ trio; $t_0 = t_0' - U_{\pi, od}$, where $U_{\pi, od} \propto \sqrt{U_{\pi\sigma} U_{\pi d}} \cdot S_\sigma$ is the Coulomb hybridization; and $S_\sigma$ is the overlap integral. The quantities $U_{\pi\sigma} > U_{\pi d} > U_{\pi, od} > 0$ are Coulomb integrals screened by both bound and free charges. A sum over the spins is to be understood.

4. If the values of the Coulomb parameter $U$ are large in comparison with the energy of the band motion, $t_\pi$, the effect of a carrier on a covalent bond is local and "instantaneous." In this case, excluding the excited states of $Cu^+$, we find that the covalent binding energy in the $Cu_1-O_i-Cu_2$ trio is

$$\mathcal{H}_{cov} = -\epsilon_{cov}(1 - n_i) - \tilde{\epsilon}_{cov} n_i, \quad \epsilon_{cov} = \{t_0^2(R_1) + t_0^2(R_2)\}/(\epsilon_d^0 - \epsilon_p^0),$$

$$\tilde{\epsilon}_{cov} = \{\tilde{t}_0^2(R_1) + \tilde{t}_0^2(R_2)\}/(\epsilon_d^0 - \epsilon_p^0 + U_{\pi\sigma} - U_{\pi d}) \ll \epsilon_{cov}. \tag{2}$$

The strong dependence of the transport integrals on the distance results in an effective coupling of a carrier with the lattice. The value of $\epsilon_{cov}$ is most sensitive to a change in the bond length $R(Cu_1 - Cu_2)$, and there is no coupling with optical vibrations of oxygen in the harmonic approximation:

$$\delta\epsilon_{cov} = -2\epsilon_{cov}\alpha|\delta R|/R, \quad \alpha = (x t_x'/t)_{x=R/2}. \tag{3}$$

Since $t_{pd}(R) \sim R^{-4}$ (Ref. 3), we have $\alpha = 4$. We write $\delta R$ in terms of phonon operators:

$$\mathcal{H}_{p-ph} = -\alpha\epsilon_{cov} \frac{i\sqrt{2}}{\sqrt{S}\rho v_s^2} \sum_{kp} \gamma_k \sqrt{\frac{\omega_k}{2}} (b_k - b_{-k}^+) c_{p+k}^+ c_p,$$

$$\gamma_k = (k_x \sin ak_x + k_y \sin ak_y)/ak^2, \quad a = R/2, \quad \rho = (M_{Cu} + 2M_0)/R^2. \tag{4}$$

Here $v_s$ and $\omega_k$ are the velocity and frequency of an acoustic phonon. Interaction (4) has a very unusual origin: Although the $p_\pi$ holes do not themselves hybridize with $d$ states (so they cannot localize, forming covalent pairs), they completely control the $d-p_\sigma$ coupling through intra-atomic correlations.

The attraction of holes which results from (4) is

$$V_{p-p}^{(1)} = -\frac{3(\alpha\epsilon_{cov})^2}{2\rho v_s^2 a_0^2} \beta(k_F), \tag{5}$$

$$\beta(k_F) = \frac{8}{3\pi a^2} \cdot \frac{1}{2k_F} \int_0^{2k_F} \frac{dk}{k^2} \int_0^\pi d\varphi \cos^2\varphi \sin^2(ak\cos\varphi) = \frac{8}{3} I(y)/y,$$

$$I(y) = \int\limits_0^y dx(1 - J_0(x) + J_2(x))/x^2, \quad y = 2\sqrt{2}\,ak_F,$$

where $a_0$ is the constant of the oxygen sublattice. Potential (5) decreases with increasing hole concentrations: $\beta \approx 1 - (10\pi/27)\langle n\rangle$. If we assume $\epsilon_{cov} \sim 1$ eV, $n = 0.2$, and $v_s = 5 \times 10^5$ cm/s, with a state density per oxygen atom $N = 0.2$ eV$^{-1}$, we find that the contribution of interaction (5) to the parameter $\lambda$ of the BCS theory is $\lambda_{ph}^{(1)} \approx 0.3$. With regard to the ordinary electron-phonon coupling, associated with the modulation of the band width $t_\pi$, its contribution to $\lambda$ apparently has a value $\lambda_{ph}^{(2)} \sim 0.2$–0.3. Optical vibrations of oxygen with a frequency of $\Omega$ probably play the leading role here.

5. The anomalously large values of the superexchange integral in the high-temperature superconducting oxides indicate that the energy of the $d$–$p_\sigma$ transition and the Coulomb parameters are highly screened. If it turns out that the relation $U_{\pi\sigma} \sim \Delta < 4t_\pi$ holds, a broken covalent bond will not adiabatically follow a hole, and retardation effects will result in an exciton component of the attraction. We can demonstrate this point by treating the interaction in (1) as a perturbation of the band motion. Separating out the average-field effects, and transforming the $p_\sigma$ and $d$ operators in order to make a transformation to a "regular" basis—in terms of the bonding operators $b_i^+$, $b_i$ and the antibonding operators $a^+$, $a$ of the states of the Cu$_1$–O$_i$–Cu$_2$ "molecule"—we find from (1)

$$\mathcal{H} = \epsilon_a(n_{a_1} + n_{a_2}) + \epsilon_b n_{b_i} + t_\pi c_i^+ c_j - (U_a \delta n_a + U_b \delta n_{b_i})\delta n_i$$
$$+ V(a_1^+ b_i + a_2^+ b_i + \kappa c)\delta n_i + \frac{1}{2}\epsilon_{cov}(R_1)\delta n_i + \frac{1}{2}\epsilon_{cov}(R_2)\delta n_i. \tag{6}$$

The renormalized parameters are

$$\epsilon_a = \epsilon_d^0 - U_{\pi d}\langle n\rangle + \gamma^2\Delta_0, \quad \epsilon_b = \epsilon_p^0 - U_{\pi\sigma}\langle n\rangle - 2\gamma^2\Delta_0, \quad \gamma = t/\Delta_0 < 1,$$

$$\Delta_0 = \epsilon_d^0 - \epsilon_p^0 + (U_{\pi\sigma} - U_{\pi d})\langle n\rangle, \quad t = t_0 - \delta t_0\langle n\rangle, \quad \delta t_0 = t_0 - \tilde{t}_0, \tag{7}$$

$$\epsilon_{cov} \approx 4\gamma\delta t_0, \quad V = \gamma(U_{\pi\sigma} - U_{\pi d}) + \delta t_0, \quad U_a = \epsilon_{cov}/2, \quad U_b = U_{\pi\sigma} - U_{\pi d} - \epsilon_{cov}.$$

The parameter $V$ determines the coupling of $p_\pi$ holes with an exciton: a transition through molecular orbitals. Evaluating the first nonvanishing diagrams, we find the charge susceptibilities $\chi_{ab} = 4/\Delta_0$, $\chi_{bb} = \chi_{ab}(VN)^2$ and the exciton component of $\lambda$:

$$\lambda_{ex} = \lambda_{ex}^0/(1 - 2\lambda_{ex}^0) \approx \frac{4}{\Delta}V^2N(1 + U^2N^2), \quad \Delta = \Delta_0 - 8V^2N, \quad U = U_b - U_a. \tag{8}$$

At $\lambda_{ex}^0 \gtrsim 0.5$, an exciton and a hole are bound; this case corresponds to the case $U_{\pi\sigma} \gg t_\pi$, which we discussed above. In this case there is of course no exciton component of the attraction of the current carriers, since there is no retardation in the electron response.

In this model, the nature of the exciton is similar to that studied by Varma et al.,[4] but Varma's model,[4] in which the $d$ states are delocalized, apparently does not fit the

situation in the high-temperature superconducting oxides.

If we use the values $t_0 = 1$ eV and $U_{d-d} = 5$ eV, we find from $J_{\text{Cu}-\text{Cu}} = 4t_0^4/\Delta_0^2 U_{d-d} \sim 0.1$ the value $\Delta_0 \sim 3$ eV. Assuming $U_{\pi\sigma} = 3$ eV, $U_{\pi d} = 1$ eV, $U_{\pi, od} = 0.4$ eV, $t'_0 = 0.9$ eV, and $N = 0.2$ eV$^{-1}$ (which seems completely reasonable), we find from (7) $V \approx U \approx 1.1$ eV and $\epsilon_{cov} \approx 0.8$ eV. In this case we have $\lambda_{ex} \approx 0.3$ and $\lambda_{ph}^{(1)} \approx 0.2$. We see from these estimates that values $\lambda_{ex} \sim 0.2\text{-}0.3$ and $\lambda_{ph} = \lambda_{ph}^{(1)} + \lambda_{ph}^{(2)} \sim 0.3\text{-}0.5$ are completely acceptable. The average logarithmic frequency,

$$\overline{\omega} = \omega_{ak}^{\lambda_{ph}^{(1)}/\lambda} \Omega^{\lambda_{ph}^{(2)}/\lambda} \Delta^{\lambda_{ex}/\lambda} \tag{9}$$

then turns out to be nearly an order of magnitude greater than the phonon frequencies; this result, along with $\lambda = \lambda_{ex} + \lambda_{ph} \sim 0.5\text{-}0.6$ and a pseudopotential $\mu^* \sim 0.1\text{-}0.2$, would given us the values of $T_c$ which we need. The isotope effects in terms of copper and oxygen decrease by factors of $\lambda_{ph}^{(1)}/\lambda$ and $\lambda_{ph}^{(2)}/\lambda$, respectively.

6. Returning to the problem of the relaxation of copper nuclei, we note that the breaking of the covalent bond by a current carrier causes the superexchange integral to become a dynamic variable: $J_{\text{Cu}-\text{Cu}}(\tau) \approx J(1 - \langle n \rangle) - J\delta n(\tau)$. It follows that if the copper spins are in the state of a singlet spin density[5] with a pseudogap, then electron transitions will also participate in singlet-triplet transitions which lead to nuclear relaxation. The freezing of the electron transitions below $T_c$ might lead to a sharp decrease in the low-frequency fluctuations of the spins and in the nuclear relaxation rate.

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Translated by Dave Parsons