Bond-charge repulsion and hole superconductivity in the atomic representation of the CuO_2 plane

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The pairing theory of superconductivity is applied to tightly bound electrons in narrow energy bands that interact via short-range Coulomb interactions. We depart from the model Hamiltonian proposed by Hirsch that emphasizes the role of the bond-charge repulsion for the attractive interaction between holes in the almost-filled $p\pi$ band of the planar O^{2-} anion lattice of the CuO_2 layer. Using the method of Appel and Kohn we cast the pairing theory for the $p\pi$ electrons into the atomic representation and construct the set of vertex equations on the two-dimensional square lattice that determine the transition temperature T_c. A parameter study of T_c is presented that gives a strong increase of T_c with increasing value of the *nearest-neighbor* bond-charge parameter Δt, confirming the results of the theory of Hirsch and Marsiglio. We extend our parameter study to incorporate also both the *next-nearest-neighbor* bond-charge repulsion Δt_3 and the Coulomb interaction V_2. The trends of the previous T_c results remain unchanged: The adverse effect of V_2 is compensated for by the increase of T_c with Δt_3. Analytical evaluation of the unscreened bond-charge matrix elements yields the quantitative values: $\Delta t = 0.806$ eV and $\Delta t_3 = 0.13$ eV, resulting in an *attractive* pairing interaction. The effect of dielectric screening on Δt and Δt_3 is not known at this time and, therefore, it remains an open question whether the bond-charge repulsions by themselves lead to an attraction between holes or mitigate the Coulomb repulsions to the extent that an attractive bosonic exchange can result in high-T_c superconductivity.

I. INTRODUCTION

Since the discovery of high-T_c superconductors, considerable effort has been made to construct a mechanism that replaces the phonon-mediated electron-electron interaction of the BCS theory of superconductivity. Assuming some two-electron pairing mechanism between Fermi-liquid particles also for these superconductors, the central question arises whether or not the Coulomb interaction between the electrons in the CuO_2 layers can by itself lead to superconductivity. The idea that superconductivity may be caused by electron-correlation effects was first proposed by Kohn and Luttinger[1] by using an expansion of Feynman graphs, i.e., perturbation theory, to obtain an attractive interaction between two electrons, basically due to the Friedel charge oscillation that surrounds a given electron. More recently, the strongly repulsive on-site Coulomb interaction U between tightly bound electrons is studied with the Hubbard model by Monte Carlo calculations to look for hints of an instability in the pair-field susceptibility.[2-4] These calculations are also applied to the extended Hubbard model that takes into account the nearest-neighbor Coulomb interaction V. So far, no clear indication is obtained for s-wave superconductivity in the frame of the single-band Hubbard model and the possibility of d-wave pairing—indicated by NMR experiments—remains an open question. For three-band Hubbard models with on-site and nearest-neighbor Coulomb repulsion, it is found that s-wave pairing can be possible.[5,6]

Hirsch[7,8] recently suggested another type of nondiagonal Coulomb interaction to be important for superconductivity, namely, the so-called *bond-charge repulsion,* i.e., the Coulomb interaction between a bond charge and an atomic charge. This repulsion is not yet considered in Monte Carlo calculations. The corresponding Coulomb-matrix element contains at least one bond charge given by $e\phi^*(\mathbf{r}-\mathbf{R}_i)\phi(\mathbf{r}-\mathbf{R}_j)$, $i\neq j$, whereas the density-density matrix elements contain only the atomic-charge densities $e|\phi(\mathbf{r}-\mathbf{R}_i)|^2$, where $\phi(\mathbf{r}-\mathbf{R}_i)$ is a wave function centered at the lattice site $\mathbf{R}_i$. The importance of the bond-charge matrix element was first recognized by Kivelson *et al.*[9] in their theory of the effect of Coulomb interactions on the Peirels instability in polyacetylene. Besides U and V, the authors introduce the matrix element (in their notation, X) given by

$$\Delta t = \int d^3r\, d^3r'\, \phi^*(\mathbf{r}-\mathbf{R}_i)\phi(\mathbf{r}-\mathbf{R}_j) \times V_{ee}(|\mathbf{r}-\mathbf{r}'|)|\phi(\mathbf{r}'-\mathbf{R}_i)|^2 , \quad (1)$$

where i,j are nearest neighbors and V_{ee} is the effective electron-electron (e-e) interaction. The matrix element Δt also plays the key role for the theory of superconductivity developed by Marsiglio and Hirsch for the holes in almost-filled and narrow energy bands.[10,11] The authors depart from a Hamiltonian that includes the bond-charge matrix element Δt besides U and V as the relevant Coulomb interaction.

This paper has a twofold purpose. First, we study the effect of Δt on the superconducting transition temperature T_c by an independent mathematical method developed by Appel and Kohn[12] for the superconductivity of tightly bound electrons in narrow energy bands. This method is formally equivalent to solving the BCS gap equation for T_c, the procedure used by Hirsch and Marsiglio. Our method is, however, ideally suited to take into account at successive stages the effects of on-site, nearest-neighbor, next-nearest-neighbor, and higher-

order Coulomb matrix elements. The same procedure is used for a parameter study of T_c as a function of Δt, U, and V and for investigating the effect of higher-order matrix elements on T_c, such as the next-nearest-neighbor bond-charge repulsion Δt_3.

Second, based on the self-consistent charge X_α method of Grodzicki,[13] we present a detailed discussion of the magnitudes of the bond-charge matrix elements. We address the importance of the instantaneous Coulomb interactions on superconductivity in narrow-band conductors, regardless of specific systems such as high-T_c superconductors. Since our Hamiltonian for the $p\pi$ electrons of the anion O^{2-} lattice *serves as a model* for the study of the Coulomb effects contained in Δt, U, V, and higher-order interactions, our discussion is not based on the conjecture of Marsiglio and Hirsch,[10] according to which superconductivity in the CuO_2 planes is in the first place determined by the holes in the oxygen $p\pi$ bands and that the Cu spin degrees of freedom are unimportant for superconductivity.

II. MODEL HAMILTONIAN

The single-band ("conduction-band") Hamiltonian of Hirsch[7] for the in-plane $p\pi$ electrons has the following form in a two-center approximation:

$$H=-t\sum_{\langle ij\rangle,\sigma}(c_{i\sigma}^{\dagger}c_{j\sigma}+cc_{j\sigma}^{\dagger}c_{i\sigma})+U^{(0)}\sum_i n_{i\uparrow}n_{i\downarrow}+V^{(0)}\sum_{\langle ij\rangle,\sigma\sigma'}n_{i\sigma}n_{j\sigma'}+\Delta t^{(0)}\sum_{\langle ij\rangle,\sigma}(c_{i\sigma}^{\dagger}c_{j\sigma}+c_{j\sigma}^{\dagger}c_{i\sigma})(n_{i,-\sigma}+n_{j,-\sigma})\ . \tag{2}$$

Here $\langle ij\rangle$ implies summation over all the nearest-neighbor pairs. The first term accounts for the hopping between nearest neighbors; t consists of the kinetic energy and the Coulomb potential of the ion cores,

$$t=\left\langle i\left|-\frac{\hbar^2}{2m}\nabla^2-\frac{Ze^2}{|\mathbf{r}-\mathbf{R}_i|}-\frac{Ze^2}{|\mathbf{r}-\mathbf{R}_j|}\right|j\right\rangle\ . \tag{3}$$

The effective charge Z of the oxygen ions at the nearest-neighbor sites i,j is determined by the ion-core charge, the electrons of the valence bands, and the background charge of the Cu^{2+} lattice. Hence the oxygen charge $Z\approx 1$. The electron-electron (e-e) matrix elements $U^{(0)}$, $V^{(0)}$, and $\Delta t^{(0)}$ (which are positive numbers) contain the Coulomb interaction e^2/r. The Coulomb interaction between neighbors of higher order is neglected. The screening by the electrons of the partially filled conduction band is ignored at this point. The pertinent effect of the electrons in the filled valence bands is—within this model—to screen the pseudopotentials of the ion cores which determine the hopping matrix element t.

As a first step toward the use of more realistic parameters, t is renormalized by the classical Coulomb interaction, that is, the Hartree term of the e-e interaction between the conduction electrons. This term must then be subtracted from the original e-e interaction. In a second step, the incorporation of the exchange interaction leads to the Hartree-Fock approximation, $t\rightarrow t_{\mathrm{HF}}$. Correspondingly, the Hartree-Fock terms have to be subtracted from the e-e interaction. This procedure is given by Hubbard[14] and shows how the partition of the Hamiltonian leads to a significant reduction of the original two-electron interaction. The partition can be carried out in two different ways.

(i) With Hubbard's procedure, the hopping matrix element is t_{HF} and the remaining e-e interaction represents the correlation part.

(ii) In the local-density approximation (LDA), the hopping matrix element is evaluated as t_{LDA} and one is left with the effective interactions Δt, U, and V. The Hamiltonian is

$$H=-t_{\mathrm{LDA}}\sum_{\langle ij\rangle,\sigma}(c_{i\sigma}^{\dagger}c_{j\sigma}+c_{j\sigma}^{\dagger}c_{i\sigma})+U\sum_i n_{i\uparrow}n_{i\downarrow}+V\sum_{\langle ij\rangle,\sigma\sigma'}n_{i\sigma}n_{j\sigma'}+\Delta t\sum_{\langle ij\rangle,\sigma}(c_{i\sigma}^{\dagger}c_{j\sigma}+c_{j\sigma}^{\dagger}c_{i\sigma})(n_{i,-\sigma}+n_{j,-\sigma})\ . \tag{4}$$

The hopping matrix element t_{LDA} is obtained by local-density band or cluster calculations.[15] It differs from t_{HF} in replacing the exchange interaction by the Kohn-Sham $\alpha\rho^{1/3}$ potential ($\alpha=\frac{2}{3}$) and including some correlation effects in a local approximation. The on-site Coulomb repulsion U for some atoms can be determined from experimental data,[16,17] unlike the Coulomb parameters V and Δt. The quantities U, V, and Δt are reduced by screening effects as compared with $U^{(0)}$, $V^{(0)}$, and $\Delta t^{(0)}$. The theoretical discussion of Marsiglio and Hirsch[7] departs from the model Hamiltonian defined with the bare interaction $U^{(0)}$, $V^{(0)}$, and $\Delta t^{(0)}$ and with the corresponding hopping matrix elements T_{ij}. However, in his calculations of superconducting parameters such as the transition temperature T_c, he eventually uses screened Coulomb interactions. By comparing (2) and (4), we conclude that the Coulomb interaction V_{ee} contained in the matrix elements U, V, and Δt is screened by the conduction electrons of the partially filled $p\pi$ band. In addition, there is the screening of the e-e interaction by the electrons of the filled valence bands. Within Hirsch's single-band model, the latter can be accounted for by modifying the matrix elements in Eq. (2). We assume from here on that the Coulomb potential V_{ee} contains both of these screenings effects so that the parameters U, V, and Δt of our present parameter study correspond to the numerical values used by Marsiglio and Hirsch. We note that the Hamiltonian [Eq. (4)] is different from the Hubbard Hamiltonian, where t and U are the relevant parameters and where the hole occupation plays an important role, too, because of U.

Of central importance is the matrix element Δt that reduces the hopping frequency between nearest-neighbor sites. As can be seen from the last term of Eq. (2), the hopping of an electron between the two sites is hindered by the presence of another electron at the initial or final site. This corresponds to an effective band narrowing

$$t\rightarrow t_{\mathrm{eff}}=t-\langle n\rangle\Delta t\quad(0\le\langle n\rangle\le 2)\ , \tag{5}$$

where $\langle n\rangle$ is the band filling by electrons. The band is

especially narrow for the case of a nearly occupied electron band, i.e., a nearly empty hole band.

In the hole picture, Hirsch[7] shows how an attraction due to Δt is obtained between two holes with antiparallel spins by applying an electron-hole transformation to the Hamiltonian [Eq. (2)]. Formally, the attraction between holes is due to the asymmetry between electrons and holes that arises in going beyond the rigid-band model. The asymmetry has its origin in both single-particle and correlation effects and is formally evident from the band renormalization [Eq. (5)]. In the Hartree approximation, the value of t is determined by two opposing effects. First, the filling of the conduction band with electrons reduces the attractive Coulomb potentials by virtue of screening effects leading to smaller hopping matrix elements. Second, the reduction in the strength of the attractive potential results in a spreading of the electron wave function, leading to an increase of the hopping matrix element. The second effect dominates the first because it depends on the exponential decay of the overlapping electron wave functions, whereas the first effect is determined by the $1/r$ dependence of the attractive pseudopotential. As a consequence, the width of the electron band should *broaden* in the *Hartree approximation.* In addition, however, there are the *correlation effects* which are known to *narrow* the conduction bands. These effects are the more important the narrower are the original Bloch bands. From experiments it is known that we are dealing with narrow bands in the CuO_2 plane, and therefore the minus sign in Eq. (5) appears justified.

In the hole picture, Eq. (5) becomes

$$t \rightarrow t_{\text{eff}} = t^h + \delta\,\Delta t \quad (0 \le \delta \le 2) , \tag{6}$$

where $t^h = t - 2\,\Delta t$ and δ is the hole occupation. The above discussion shows that Eqs. (5) and (6) must be understood as a phenomenological description of the experimentally observed width of the partially filled hole band. The term $\delta\Delta t$ is the first-order contribution of an expansion of t_{eff} in the Coulomb interaction, valid only in the neighborhood of a nearly empty hole band. The Hamiltonian given by Eq. (4) is our point of departure for the following discussion of the relevant Coulomb effects on T_c.

III. T_c EQUATION

Based on the Hamiltonian [Eq. (4)], the transition temperature T_c is calculated by using the method of Appel and Kohn.[12] Thereby, we can take into account the e-e interaction beyond the on-site Hubbard repulsion U, that is, nearest, next-nearest, and higher-order neighbor interactions. The temperature T_c is determined as the eigenvalue of a matrix equation that in our site representation takes the place of the BCS T_c equation. For the lattice-site matrix (i,j), the equation for the e-e vertex function Γ takes the form,

$$\Gamma(\mathbf{R}_i,\omega) = \frac{1}{\beta} \sum_{\omega',j} \Gamma(\mathbf{R}_j,\omega') K(\mathbf{R}_j,\omega';\mathbf{R}_i,\omega) \tag{7}$$

[Eq. (2.27) of Ref. 12]. The interaction kernel K for two electrons contains the imaginary frequencies $\omega = i\pi\beta^{-1}(2n+1)$ and $\omega' = i\pi\beta^{-1}(2n'+1)$, where $n,n' = 0,\pm1,\pm2,\cdots$,

$$K(\mathbf{R}_j,\omega';\mathbf{R}_i,\omega) = -\sum_k F(\mathbf{R}_k,\omega') I_c(\mathbf{R}_j-\mathbf{R}_k,\omega'-\omega;\mathbf{R}_i,\omega) . \tag{8}$$

Here $F(\mathbf{R}_k,\omega')$ is the anomalous Green's function for an electron pair in the site representation and I_c is the contracted pairing interaction between two electrons, defined below. The propagation of an electron pair between two sites separated by $\mathbf{R}_i$ is given by

$$F(\mathbf{R}_i,\omega) = \frac{1}{N} \sum_{\mathbf{k}} \frac{\exp(i\mathbf{k}\cdot\mathbf{R}_i)}{|\omega|^2 + [\varepsilon(\mathbf{k})-\mu]^2} , \tag{9}$$

where N is the number of lattice sites, $\varepsilon(\mathbf{k})$ is the dispersion of the conduction band, and μ is the Fermi energy; $\mathbf{k}$ is a vector in the first Brillouin zone. The contracted pairing interaction of the kernel K is given by

$$I_c(\mathbf{R}_j,\omega';\mathbf{R}_i,\omega) = \sum_k I(\mathbf{R}_j+\mathbf{R}_k,\mathbf{R}_k,\omega';\mathbf{R}_i,\mathbf{0},\omega) , \tag{10}$$

[Eq. (2.30) of Ref. 12], where I is the four-site interaction between two electrons initially at the sites $\mathbf{R}_j+\mathbf{R}_k$ and $\mathbf{R}_k$ to be scattered to the final sites $\mathbf{R}_i$ and $\mathbf{0}$.

We now proceed to discuss the interaction kernel K in terms of the functions F and I_c, determined by the model Hamiltonian [Eq. (4)]. Our calculation presumes a square lattice of oxygen ions to present the CuO_2 layer. This assumption implies that the holes are in the oxygen $p\pi$ bands of the anion O^{2-} lattice and that the Cu ions merely play the role of providing a positively charged background. For this model, with zero interplane hopping and with the nearest-neighbor matrix element t_{eff} for in-plane hopping, the dispersion of the conduction band is

$$\varepsilon(\mathbf{k}) = -2t_{\text{eff}}(\cos ak_x + \cos ak_y) , \tag{11}$$

where a is the lattice constant. We take $\varepsilon = 4t_{\text{eff}}$ for the occupied electron band, i.e., the empty hole band. Using this dispersion, we can evaluate the pair function F. To this end, the $\mathbf{k}$ summation in Eq. (9) is replaced by an integration over energy shells,

$$F(\mathbf{R}_i,\omega) = \int_{-4t_{\text{eff}}}^{4t_{\text{eff}}} d\varepsilon \frac{N(\mathbf{R}_i,\varepsilon)}{|\omega|^2 + (\varepsilon-\mu)^2} . \tag{12}$$

Here $N(\mathbf{R}_i,\varepsilon)$ is the generalized density of states given by

$$N(\mathbf{R}_i\varepsilon) = \frac{a^2}{4\pi^2} \int_{-\pi/a}^{\pi/a} dk_x \int_{-\pi/a}^{\pi/a} dk_y \cos(\mathbf{k}\cdot\mathbf{R}_i) \times \delta(\varepsilon - \varepsilon(\mathbf{k})) . \tag{13}$$

For $\mathbf{R}_i = 0$, $N(\mathbf{R}_i,\varepsilon)$ is the usual density of states per lattice site and per spin. For $\mathbf{R}_i \neq 0$, some of the generalized density of states functions are as shown in Fig. 1.

The pairing interaction I_c [Eq. (10)] is determined by the instantaneous Coulomb interaction, independent of ω and ω',

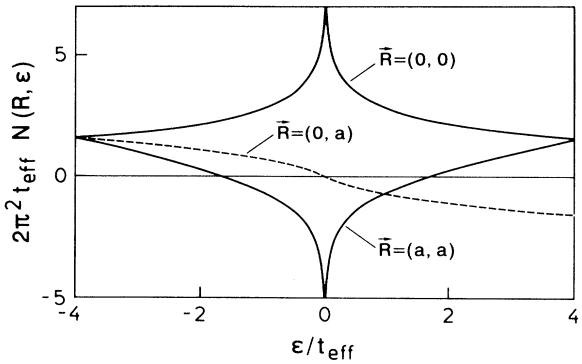

FIG. 1. Generalized density of states $N(\mathbf{R},\varepsilon)$.

$$I(\mathbf{R}_i,\mathbf{R}_j;\mathbf{R}_k,\mathbf{R}_l) = \int d^3r\, d^3r'\, \phi^*(\mathbf{r}-\mathbf{R}_i)\phi^*(\mathbf{r}'-\mathbf{R}_j) \times V_{ee}(|\mathbf{r}-\mathbf{r}'|)\phi(\mathbf{r}-\mathbf{R}_k)\phi(\mathbf{r}'-\mathbf{R}_l)\ . \quad (14)$$

The proper choices of the site combinations (i,j,k,l) lead to the Coulomb matrix elements U, V, and Δt.

The vertex equation (7) now takes a simple form. Because of the instantaneous pairing interaction [Eq. (14)], the pairing kernel K becomes independent of ω. The ω' summation can be carried out to obtain the vertex equation for $\Gamma(\mathbf{R}_i)=\Gamma(\mathbf{R}_i,\omega)$,

$$\Gamma(\mathbf{R}_i)=\frac{1}{\beta}\sum_j K_c(\mathbf{R}_i,\mathbf{R}_j)\Gamma(\mathbf{R}_i)\ , \quad (15)$$

where

$$K_c(\mathbf{R}_i,\mathbf{R}_j)=\sum_{\omega'} K(\mathbf{R}_j,\omega';\mathbf{R}_i,\omega) = -\sum_k I_c(\mathbf{R}_j-\mathbf{R}_k,\mathbf{0},\mathbf{R}_i,\mathbf{0})\sum_{\omega'} F(\mathbf{R}_k,\omega')\ . \quad (16)$$

By writing Eq. (15) as a system of homogeneous equations, T_c is found from the roots of the equation $\det[\beta^{-1}K_c(\mathbf{R}_i,\mathbf{R}_j)-E]=0$, where E is the unit matrix. The detailed procedure is given by Paulsen.[18]

IV. PARAMETER STUDY OF T_c

We solve Eq. (15) numerically to find the effect of the different Coulomb contributions to T_c. To this end, we assume the screened matrix elements U, V, and Δt to be the variables of this parameter study.

For a narrow, almost-filled electron band—corresponding to an almost-empty hole band—the dependence of T_c on the pertinent bond-charge parameter Δt is shown in Fig. 2. The results correspond to different values of the bandwidth, i.e., the hopping matrix element t_{eff}. The band filling is given by $\mu=3.8t_{eff}$. The on-site and nearest-neighbor Coulomb interactions are assumed as $U=5$ eV and $V=2$ eV, respectively. Figure 2 shows a large increase of T_c with Δt.

For a wider band of width 1 eV ($t_{eff}=0.125$ eV), we find a smaller increase of T_c with Δt and we also get a larger minimum value of Δt required for the occurrence of superconductivity, i.e., $T_c>0$. This behavior of T_c, shown in Fig. 2, is in agreement with Marsiglio and Hirsch,[7,10] who predict a strong increase of T_c with the bond-charge parameter Δt provided that the bands are sufficiently narrow. It is seen from Fig. 3 how the minimum Δt necessary for superconductivity becomes smaller when U or V are decreased.

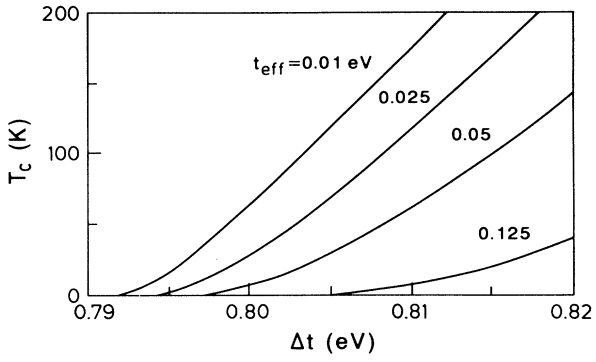

FIG. 2. Transition temperature T_c vs the bond-charge repulsion for four different values of the hopping parameter t_{eff}. The Fermi energy is fixed at $\mu=3.8t_{eff}$, corresponding to an almost-filled electron band with the hole occupation given by $\delta=1-\mu/4t_{eff}=0.05$. The on-site and nearest-neighbor Coulomb parameters are $U=5$ eV and $V=2$ eV, respectively.

The dependence of T_c on the band occupation, i.e., on the Fermi energy μ, is shown in Fig. 4 for $t_{eff}=0.125$ eV, where, however, the renormalization of the bandwidth [Eq. (6)] is ignored.

We also check the condition for the existence of superconductivity given by Eq. (41c) of Ref. 7 in terms of the parameter b defined by the equation in Ref. 19. Using this equation and the condition $b>0$, corresponding to $T_c>0$, we find the minimum value Δt_{min}, which is necessary to get superconductivity with all the other parameters being fixed. In order to control our calculation quantitatively, we compare Hirsch's values for Δt_{min} with the values found from our procedure. The results are given in Fig. 5 as functions of the band occupation. The elec-

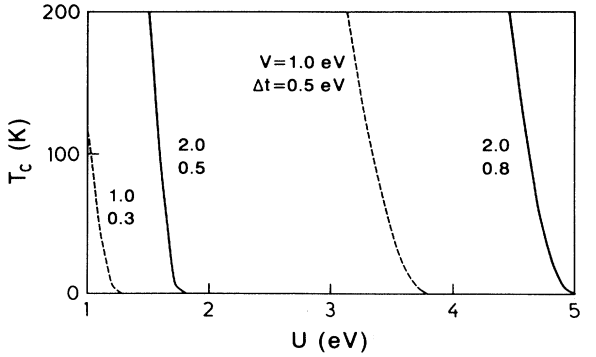

FIG. 3. Transition temperature T_c vs the on-site Coulomb interaction U for different values of Δt and V; $t_{eff}=0.125$ eV, the same μ as in Fig. 2.

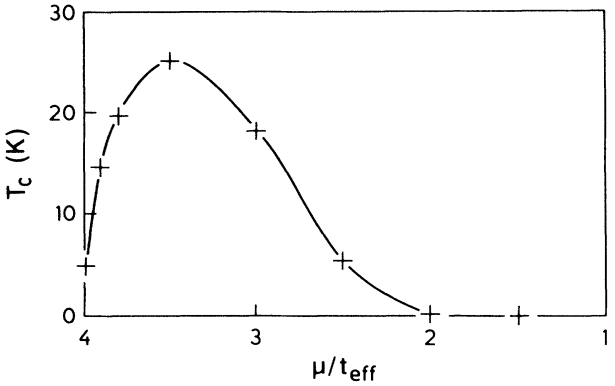

FIG. 4. Transition temperature T_c vs the Fermi energy μ. The value of $\mu=4t_{\rm eff}$ corresponds to an empty hole band; the same Coulomb parameters U,V as in Fig. 2, $t_{\rm eff}=0.125$ eV, $\Delta t=0.815$ eV. The crosses represent the numerical T_c values found from Eq. (15) by using the parameter values above. The line interpolates between the calculated values.

tron (hole) occupation increases to the right (left). For this comparison, we use the density of states at the Fermi energy, whereas Hirsch takes the density of states averaged over the bandwidth. We mention that the values of $\Delta t_{\rm min}$ will decrease if, e.g., the value of U is smaller than 5 eV (see Fig. 3) because a value of 2 eV is found empirically in one case.[17]

V. HIGHER-ORDER COULOMB INTERACTIONS

We proceed beyond the three-parameter study and discuss the question to what extent higher-order Coulomb matrix elements can be important besides U, V, and Δt. As seen from Fig. 6, the next step is to include both the next-nearest-neighbor Coulomb matrix element V_2 and the three-center bond-charge matrix element Δt_3. The two matrix elements are

$$V_2=I(\mathbf{R}_i,\mathbf{R}_j;\mathbf{R}_i,\mathbf{R}_j) \tag{17}$$

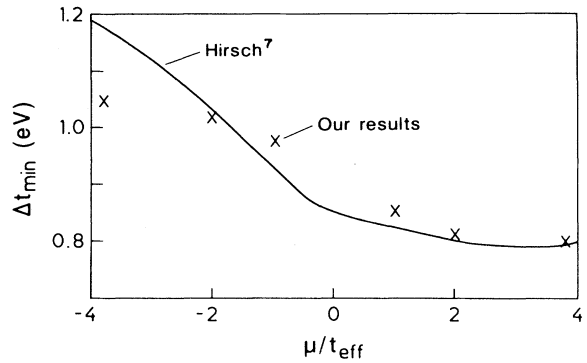

FIG. 5. Minimum value of the bond-charge parameter for which superconductivity can occur, $\Delta t_{\rm min}$, vs $\mu/t_{\rm eff}$. The results of Hirsch (Ref. 7) are compared with our values denoted by $\times$; the same Coulomb parameters U,V as Fig. 2. When band renormalization is taken into account that occurs when the hole concentration increases—i.e., the widening given by Eq. (6)—the dependence of $\Delta t_{\rm min}$ on μ becomes much stronger.

and

$$\Delta t_3=\int d^3r\, d^3r'\, \phi^*(\mathbf{r}-\mathbf{R}_j)\phi(\mathbf{r}-\mathbf{R}_k) \times V_{ee}(|\mathbf{r}-\mathbf{r}'|)|\phi(\mathbf{r}'-\mathbf{R}_i)|^2 . \tag{18}$$

Here i, j, and k denote the three-site configuration shown in Fig. 6(b). The three-center integral Δt_3 is proportional to the overlap matrix S between $\phi^*(\mathbf{r}-\mathbf{R}_j)$ and $\phi(\mathbf{r}-\mathbf{R}_k)$. To be consistent, the hopping matrix element t [Eq. (3)] must be augmented by a corresponding term

$$\left\langle i\left|\sum_{k\neq i,j}\frac{Ze^2}{|\mathbf{r}-\mathbf{R}_k|}\right|j\right\rangle .$$

The dependence of T_c on the Coulomb parameter V_2 is shown in Fig. 7 for the almost-filled band $\mu=3.8t_{\rm eff}$. For the same case and different V_2's, the effect of the bond-charge interaction Δt_3 on T_c is shown in Fig. 8. Whereas Δt_3 has a similar effect as Δt, i.e., an increase of T_c, the density-density interaction V_2 has the expected opposite effect. The value of $V_2=(1/\sqrt{2})V$ would correspond to the distance ratio between next-nearest and nearest neighbors. To account for screening effects, we take somewhat smaller values of V_2 in Fig. 8.

Next, we discuss the relative magnitudes of the bond-

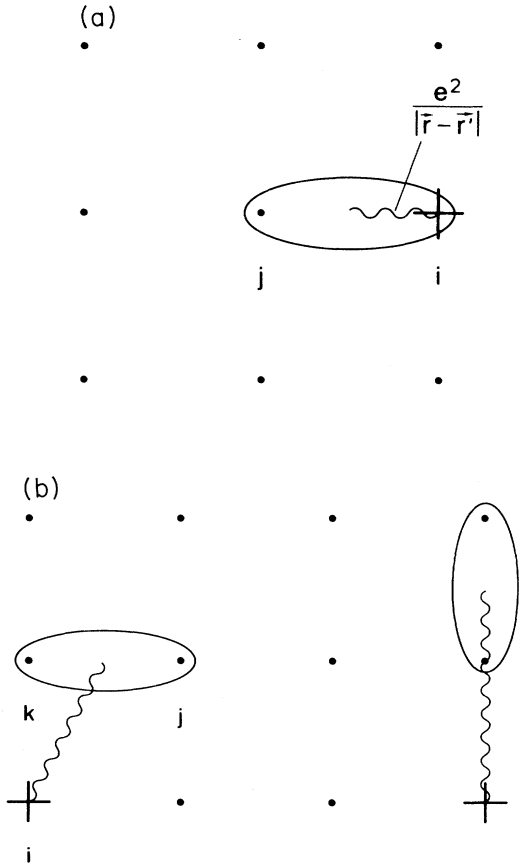

FIG. 6. Site configuration for the bond-charge matrix elements (a) for nearest neighbors Δt and (b) for next-nearest neighbors Δt_3 (left) and $\Delta t_3'$ (right).

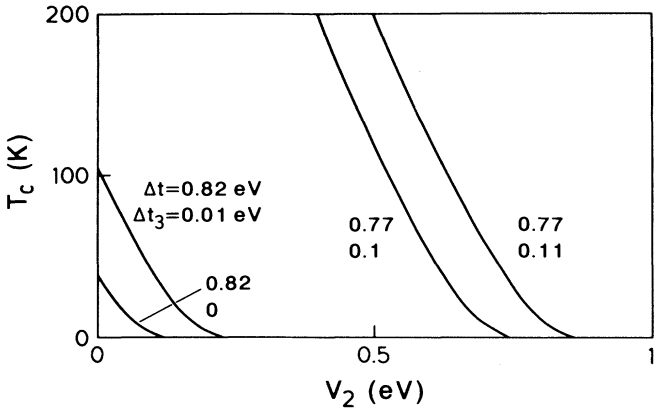

FIG. 7. T_c vs the next-nearest-neighbor Coulomb repulsion V_2 for different values of the nearest- and next-nearest-neighbor bond-charge repulsions Δt and Δt_3, respectively; the same U, V, μ as Fig. 2, $t_{\text{eff}}=0.125$ eV.

charge matrix elements and density-density Coulomb interactions beyond Δt_3 and V_2. A bond-charge matrix element depends on the overlap between two bond-charge wave functions, $S_{kj} \approx \exp(-|\mathbf{R}_k - \mathbf{R}_j|)$, and on $1/R$, where R is the distance between the center of the bond charge, $e\phi^*(\mathbf{r}-\mathbf{R}_k)\phi(\mathbf{r}-\mathbf{R}_j)$, and the site charge, $e|\phi(\mathbf{r}-\mathbf{R}_i)|^2$; hence $R=|\frac{1}{2}(\mathbf{R}_k+\mathbf{R}_j)-\mathbf{R}_i|$. Therefore it appears justified to neglect (i) all other two-, three-, and four-center integrals between two bond charges, because of their S^2 dependences. The validity of this neglect is confirmed by the analytical evaluation of S in Sec. VI. Furthermore, we neglect (ii) all of the matrix elements with an overlap between next-nearest and higher-order neighbors. This neglect is justified because the overlap between next-nearest neighbors is by approximately a factor of 10 smaller than that between nearest neighbors (cf. Sec. VI). Finally, we neglect (iii) matrix elements [of the form Eq. (18)] with a nearest-neighbor bond-charge overlap between $\mathbf{R}_j$ and $\mathbf{R}_k$ and a site charge at $\mathbf{R}_i$, with a distance larger than that between nearest neighbors [cf. Fig. 6(b)]. In this case, screening should diminish the value of these matrix elements as compared with Δt_3 and V_2.

The lowest-order bond-charge matrix element ignored in Eq. (15) is $\Delta t_3'$ shown in Fig. 6(b). Its effect on T_c is expected to be approximately $\frac{1}{2}$ of Δt_3 because, for a given site, there are four matrix elements Δt or $\Delta t_3'$, and eight matrix elements Δt_3. As for the density-density matrix elements, we ignore all elements of higher order than V_2 because of screening effects.

In summary, *of the higher-order matrix elements, only the three-center bond-charge matrix element is relevant with nearest-neighbor overlap.*

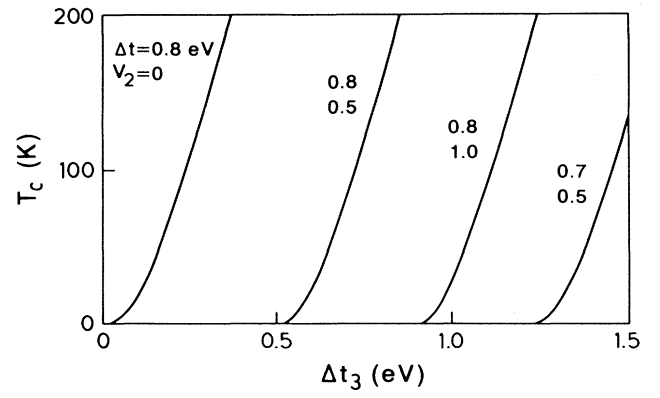

FIG. 8. T_c vs the bond-charge parameter Δt_3 for different values of the nearest-neighbor bond-charge repulsion Δt and of the Coulomb parameter V_2; the same U, V, μ as Fig. 2, $t_{\text{eff}}=0.125$ eV.

VI. ANALYSIS OF BOND-CHARGE PARAMETERS

So far, we have confirmed Hirsch's conclusion on the importance of the two-center bond-charge repulsion Δt for high-T_c superconductivity. Moreover, we find that the three-center bond-charge matrix element Δt_3 reinforces the Δt effect. We proceed to discuss the physical basis of this model. The crucial question is whether the parameter values of Δt and Δt_3—required for the pairing interaction to be *attractive*—can independently be confirmed as physically reasonable. In order to answer this question, we proceed in two different ways. First, the matrix elements $\Delta t^{(0)}$ and $\Delta t_3^{(0)}$ are evaluated analytically. In addition, values for t_{LDA} are derived from a cluster calculation. The LDA matrix element corresponds approximately to the Hartree-Fock matrix element t_{HF}.

The analytical evaluation of $\Delta t^{(0)}$ between two oxygen atoms with the nearest-neighbor distance $R=5.19$ a.u.,

$$\Delta t^{(0)}=\int d^3r\, d^3r'\, \phi^*(\mathbf{r})\phi^*(\mathbf{r}')|\mathbf{r}-\mathbf{r}'|^{-1}\phi(\mathbf{r})\phi(\mathbf{r}'-\mathbf{R}) , \tag{19}$$

requires the knowledge of the orbitals $\phi(\mathbf{r})$. Assuming atomiclike O($2p$) orbitals

$$\phi(\mathbf{r})=are^{-\zeta r}Y_{1m}(\hat{\mathbf{r}})=R(r)\cdot Y_{1m}(\hat{\mathbf{r}}) , \tag{20}$$

with an approximately chosen exponent ζ, the analytical form of $\Delta t^{(0)}$ is in good approximation (cf. the Appendix),

$$\Delta t^{(0)}=\frac{\zeta}{2}x^2(1+x)e^{-x}, \quad x=\zeta R . \tag{21}$$

Taking $\zeta=1.86$ a.u.—which is the value that follows from our cluster calculation— we obtain

$$\Delta t^{(0)}=5.93\times 10^2 \text{ Ry}=0.806 \text{ eV} .$$

The analogous evaluation of $\Delta t_3^{(0)}$ gives

$$\Delta t_3^{(0)}=0.13 \text{ eV} .$$

Since two bond-charge matrix elements Δt_3 and one $\Delta t_3'$ contribute to each Δt (cf. Fig. 6), the three-center integrals increase $\Delta t^{(0)}$ by approximately 0.35 eV. Hence, in view of the sensitivity of T_c against Δt, the three-center integrals are not *a priori* negligible.

Hopping matrix elements can also be derived from a calculation on the $Cu_4O_{12}H_{12}Ba_6$ cluster (cf. Fig. 9). The

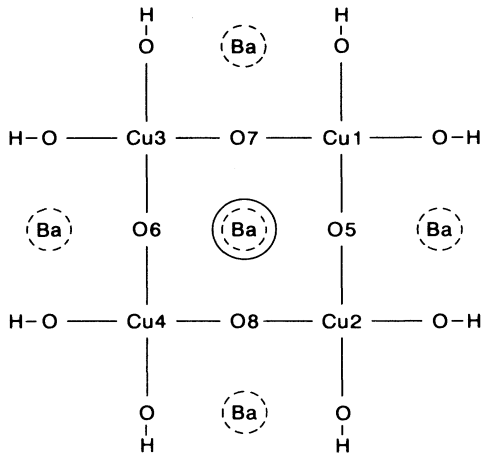

FIG. 9. Cluster model; each Cu atom has a H neighbor in the z direction.

calculation is performed by the self-consistent charge X_α method[13] that uses the X_α exchange potential and a minimal basis set of Slater-type orbitals. The variable exponents of these orbitals are automatically adjusted to the respective electronic configuration of the atom in the cluster. The potential energy gives two contributions to the hopping that contain Δt and Δt_3, respectively. The comparison of two- and three-center contributions to the Cu-O and O-O matrix elements (cf. Table I) emphasize the importance of the three-center matrix element for the O-O hopping. Taking into account that delocalization effects are somewhat overestimated by the LDA, the value of 0.9 eV for the O-O hopping may be too large by about 10–15 %.

The LDA calculations of $\Delta t^{(0)}$ and $\Delta t_3^{(0)}$ presume an unscreened Coulomb interaction. The dielectric response of the electrons in the conduction band with respect to the bond-charge repulsions is not known, and therefore the magnitude of the screening reductions of $\Delta t^{(0)}$ and $\Delta t_3^{(0)}$ remains an open question. At this point, we consider the values of $\Delta t^{(0)}$ and $\Delta t_3^{(0)}$ to be reasonable upper bounds for these matrix elements.

VII. DISCUSSION OF T_c RESULTS

The importance of the two-center bond-charge matrix element Δt for the Coulomb interaction between the $p\pi$ electrons of the O^{2-} anion lattice is confirmed in agreement with Marsiglio and Hirsch.[10] By applying the method of Ref. 12 to evaluate the transition temperature T_c for tightly bound electrons in the atomic representation, we find a strong increase of T_c with increasing value of Δt, as shown in Fig. 2 for different values of the bandwidth, $8t_{\text{eff}}$. Figure 3 gives the variation of T_c with the on-site Coulomb repulsion U for different values of V and Δt.

TABLE I. Two- and three-center contributions to the hopping matrix elements.

t_{LDA} (eV)	CuO		O-O
	$pd\sigma$	$pd\pi$	pp
Two-center	2.32	1.26	0.31
Three-center	0.31	0.12	0.60
Sum	2.64	1.38	0.91

The dependence of T_c on the band occupation is shown in Fig. 4. Using the electron picture, we find the maximum in T_c vs the electron occupation $\langle n \rangle$ obtained in Ref. 7. Moving from the maximum toward larger electron fillings $\langle n \rangle$, i.e., smaller hole occupations δ, we observe the decrease of T_c due to the diminishing number of Bloch states available for the pairing processes. This number is determined by the electron distribution function $f(\varepsilon-\mu)$, where the Fermi energy μ moves toward the band edge at $\varepsilon=4t_{\text{eff}}$. We note that $T_c \to 0$ for $\mu \to \infty$ because of the Pauli blocking for the electrons in the conduction band. Moving from the maximum toward smaller $\langle n \rangle$, T_c decreases because the Δt attraction, which reaches its maximum value for a filled electron band decreases as the band is emptied. Our calculation does not include the band-narrowing effect given by Eq. (5), and therefore the maximum is less pronounced than in Ref. 7.

The minimum value $\Delta t_{\min}$ where superconductivity can occur by virtue of the bond-charge repulsion, i.e., $T_c > 0$, is given in Fig. 5 as a function of the Fermi energy μ. The result is compared with that of Hirsch[7] and good agreement is found, except for the almost-empty electron band. This difference can be due to the neglect of δb (cf. Ref. 19).

By using the atomic representation to find T_c for the tightly bound $p\pi$ electrons, we proceed beyond the three-parameter study of the Coulomb interactions U, V, and Δt defined by the basic model Hamiltonian [Eq. (4)]. It is found that the next-nearest-neighbor bond-charge repulsion Δt_3 reinforces the effect of Δt (Figs. 7 and 8).

This paper is based on the one-band model Hamiltonian [Eq. (4)] for the $p\pi$ electrons. The Cu spin degrees of freedom are thereby ignored. For holes in the $pd\sigma$ band, it is shown elsewhere that the spin fluctuations can lead to an attractive pair interaction either by virtue of *two*-magnon exchange—if one presumes an antiferromagnet metal—or by the exchange of two antiferromagnetic paramagnons if the superconductivity is approached from the paramagnetic metal phase.[20,21]

Finally, we wish to comment on the superconductivity in a d-band metal, niobium. Whereas the superconductivity in ordinary metals is usually well accounted for the BCS and Eliashberg theories in terms of the electron-phonon parameter λ and the Coulomb parameter μ^*, there may be problems with Nb. For this metal two different experimental groups have used the tunneling technique to find the microscopic parameters λ, μ^* and the energy gap Δ_0. Whereas Bostock *et al.*[22] get a negative value of $\mu^* = -0.084$ together with $\lambda = 0.43$ and the experimental gap $\Delta_0 = 1.56$ meV, Harmon, Geballe, and Rowell[23] obtain $\mu^* = 0.05$, $\lambda = 0.81$, and $\Delta_0 = 1.46$ meV. In either case, the value of μ^* is much smaller than the standard values, $\mu^* \approx 0.10$–0.15. Niobium metal is a hole conductor with a positive Hall coefficient and with a Fermi surface consisting of octahedral and ellipsoidal

hole pockets and a multiply connected hole sheet. Hence the bond-charge repulsion between the tightly bound $4d$ electrons can be responsible for the small value of μ^*. For Nb_3Sn, Marsiglio[24] discusses in some detail the effect of Δt on the Coulomb pseudopotential within Eliashberg theory of the electron-phonon interaction in superconductors.

VIII. CONCLUSION AND SUMMARY

In this paper we confirm the basic conclusion of Marsiglio and Hirsch, according to which the Coulomb repulsion between holes in almost filled and narrow energy bands can lead to an attractive pairing interaction for BCS-type superconductivity. The crucial role of the nearest-neighbor bond-charge repulsion Δt for the pairing kernel is shown with a parameter study of the transition temperature T_c. This temperature is obtained as the eigenvalue of the e-e vertex equation in the atomic representation for the energy band spanned by the oxygen $p\pi$ orbitals in the CuO_2 plane. Thereby, we also take into account the next-nearest-neighbor bond-charge repulsions Δt_3. *Our T_c results depend in a sensitive manner on the magnitudes of both the two- and three-center matrix elements Δt and Δt_3*, assuming reasonable values for the on-site and nearest-neighbor Coulomb interactions U and V. It would be of some interest to see these results also confirmed by Monte Carlo calculations. The matrix elements Δt and Δt_3 are calculated analytically for the $p\pi$ orbitals, and the hopping matrix element t is determined by a LDA cluster calculation. The quantitative results for Δt and Δt_3 can be considered as upper bounds for the two bond-charge matrix elements. The value for Δt is larger than the minimum values required for superconductivity, $T_c > 0$. The diminution of Δt by screening effects is at least partially compensated for when the three-center matrix element Δt_3 is taken into account. Because of the sensitive dependence of T_c on the magnitudes of both Δt and Δt_3 and because of the unknown screening effects, we leave open the question whether the bond-charge interactions are sufficiently strong to lead by themselves to an *attractive* pairing interaction between holes. This observation does not rule out the possible importance of the bond-charge interaction for the superconductivity in the CuO_2 layers as discussed by Hirsch.[25] If the bond charge repulsion does *not* lead to an *attractive* pairing between holes, it can still have the very important effect of mitigating the Coulomb interactions U and V.

The foregoing discussion applies to holes in the $p\pi$ band. Band-structure calculations—which can be notoriously bad for transition-metal oxides[26]—suggest that the holes are in the $pd\sigma$ band. Also, for this orbital symmetry, the bond-charge repulsion will mitigate the net Coulomb interaction between two holes. This effect can be responsible for tilting the delicate balance between the Coulomb repulsion and the attraction due to the bosonic exchange of two magnons or two spinfluctuations, in favor of high-T_c superconductivity.

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APPENDIX: ANALYTICAL EVALUATION OF Δt AND Δt_3

The matrix element Δt [Eq. (19)] is evaluated by expanding $|\mathbf{r}-\mathbf{r}'|^{-1}$ into spherical harmonics and using Eq. (20) for the orbital wave functions $\phi(\mathbf{r})$:

$$\Delta t^{(0)} = \int d^3r \int d^3r'\, R^2(r) |Y_{1m}(\hat{\mathbf{r}})|^2 \times \left[4\pi \sum_{\lambda\mu} \frac{r_<^\lambda}{(2\lambda+1) r_>^{\lambda+1}} Y^*_{\lambda\mu}(\hat{\mathbf{r}}) Y_{\lambda\mu}(\hat{\mathbf{r}}') \right] \times \phi^*(\mathbf{r}')\phi(\mathbf{r}'-\mathbf{R}) \, .$$

The selection rules for the Clebsch-Gordan coefficients restrict λ to 0 and 2. The term with $\lambda=2$ contributes usually less than 10% to Δt and, therefore, is ignored here. Then we have

$$\Delta t^{(0)} \cong \int d^3r'\, \phi^*(\mathbf{r}')\phi(\mathbf{r}'-\mathbf{R}) \int_0^\infty r_>^{-1} R^2(r) r^2 dr = \int d^3r'\, \phi^*(\mathbf{r}')\phi(\mathbf{r}'-\mathbf{R}) \times \left[\frac{1}{r'} - \frac{e^{-x'}}{r'} \sum_{\nu=0}^{3} \frac{(x')^\nu}{\nu!} \frac{4-\nu}{\nu} \right] ,$$

where $x' = 2\zeta r'$. Because of the large nearest-neighbor distance $R = 5.19$ a.u., the exponential gives a negligible contribution ($\approx 2\%$) and we get

$$\Delta t^{(0)} \cong \int d^3r\, \phi^*(\mathbf{r})\phi(\mathbf{r}-\mathbf{R}) r^{-1} \, .$$

For the same orbital exponents, one readily evaluates such integrals by using the Fourier-transform technique.[27] The result is given by Eq. (21) for $\hat{\mathbf{R}} = (1\,1\,0)/\sqrt{2}$.

The three-center matrix element [Eq. (18)] for an unscreened Coulomb interaction V_{ee} has the form,

$$\Delta t_3^{(0)} = \int d^3r\, d^3r'\, \phi^*(\mathbf{r}-\mathbf{R}_1)\phi(\mathbf{r}-\mathbf{R}_2) \frac{1}{|\mathbf{r}-\mathbf{r}'|} |\phi(\mathbf{r}')|^2 \, .$$

This integral can be evaluated with the procedure analogous to that of Δt. The result is given by

$$\Delta t_3^{(0)} \cong R^{-1} S(2p, 2p, \pi) = R^{-1} \left[\left(1 + x + \frac{x^2}{3} \right) e^{-x} + \frac{x^2}{15} (1+x) e^{-x} \right] ,$$

where S is the overlap matrix element between two O($2p$) orbitals, $x = \zeta R$.

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$$b = N(0,\mu)\left[16\Delta t\left[\frac{\mu}{4t_{\text{eff}}}\right]-4V\left[\frac{\mu}{4t_{\text{eff}}}\right]^2-U\right]$$
$$+N(0,\mu)^2\left\{\frac{1}{2}\left[1+\left[\frac{\mu}{4t_{\text{eff}}}\right]^2\right](64\Delta t^2-4UV)\right\}.$$

We ignore a term δb determined by the ε integral over $N(0,\varepsilon)/N(0,\mu)-1$. Here we use our definitions for the density of states and the Coulomb parameters; the energy scale is fixed so that $\varepsilon=0$ at the center of the band, $-4t_{\text{eff}} \le \mu \le 4t_{\text{eff}}$. Whereas the Δt^2 term enhances T_c for all band fillings and can become large for narrow bands, $N(0,\mu)^2 \approx 1/t_{\text{eff}}^2$, the term linear in Δt favors superconductivity only for a more than one-half-filled band.
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