A model for the doping dependence of the superconducting transition temperature in cobaltates

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**Abstract**

Some properties of hydrated cobalt oxides \( \text{Na}_x\text{CoO}_2\cdot\text{yH}_2\text{O} \) in the superconductor phase are studied using an extended Hubbard model on a triangular lattice. We derive the superconductive ordering temperatures for singlet and triplet symmetries by means of the Green's functions of the system, calculated within a combined mean field and Hubbard I type approximation. It is found that both symmetries are possible. The coexistence of \( d + id \) and \( p + ip \) pairing, in a certain doping region, is observed, but the \( s\)-extended pairing seems to be the more stable. The critical temperatures for superconductivity are calculated for both symmetries and compared to experimental results.

1. Introduction

The discovery of an unconventional superconductivity around 5 K on layered cobalt oxides \( \text{Na}_x\text{CoO}_2\cdot\text{yH}_2\text{O} \) [1] has received widespread interest due to the unexpected and fascinating properties showed by experiments. These compounds exhibit a layered structure with two-dimensional \( \text{CoO}_2 \) planes, where the \( \text{Co} \) atoms form a triangular lattice. These planes are separated by thick insulating layers of \( \text{Na}^+ \) ions and \( \text{H}_2\text{O} \) molecules placed between them.

The structural similarity with the high-\( T_c \) copper oxide superconductors is striking, but here it is enriched by triangular symmetry, containing all the ingredients of an ideal system for the study of strong correlation and geometrical frustration in the charge, spin and orbital degrees of freedom. Experimental results concerning the pairing symmetry of \( \text{Na}_x\text{CoO}_2\cdot\text{yH}_2\text{O} \) are often controversial. The results of specific heat experiments are compatible with an unconventional superconductivity [2,3], while the results from the Knight shift of NMR are themselves conflicting: some results are consistent with the presence of triplet symmetry [4,5], while other authors report a singlet pairing [6]. These conflicting results seem to emerge from the diagram of the critical field, \( H_{c2} \) vs. \( T_c \) [7,8], where the slope variation suggests a transition from singlet to triplet symmetry. This rich panorama has been a stimulus for many theoretical proposals concerning the superconducting pairing type [9–12].

Theoretical results obtained within the Resonant Valence Bond (RVB) model [9,11,13] show only singlet symmetry whereas Monte Carlo results [14,15] admit both possibilities but present a tendency to singlet symmetry. In the models where multi-orbital effects are considered [16,17], the presence of triplet symmetry prevails over singlet symmetry.

The superconductor phase diagram is also controversial. The dependence of the critical temperature on sodium concentration \( T_c \) vs. \( x \) exhibits a plateau in \( T_c \) for many \( x \) values in the work of Chen et al. [18], whereas a maximum of \( T_c \) for a specific sodium concentration \( x = 0.3 \) was found by Schak et al. [19].

We have investigated the unconventional superconductivity within an extended one-band Hubbard model on the basis of the Hubbard-I and mean-field approximation. The one-band model we study here is based on theoretical results on the Fermi surface of non-hydrated cobaltates [20,21], which exhibit a central region covering almost all of the first Brillouin zone, and six small pockets near the corners. The model is also reinforced both from an experimental point of view, by the results of ARPES experiments [22–24], that show that the central region is the only one observed for different Na concentrations, and from a theoretical point of view by the results obtained by Korshunov and Eremin [25] about the superconducting symmetry, which is not much affected when the \( c'_p \) pockets are present in the Fermi surface. Moreover, the inclusion of multiple neighbor hopping in
the study of Na$_x$CoO$_2$$\cdot$yH$_2$O compounds may change the Fermi surface as reported by many authors [26–29].

Within this one-band model, we calculate the superconductive Green’s functions of the system, using a mean field approach for the intersite interactions and a Hubbard-I type approach for the local correlations. We obtain results for singlet (s- and d-states) and triplet (p- and f-states) configurations. The results for the critical transition temperatures exhibit a coexistence between the two symmetries, while a maximum value for the critical temperature is obtained for a finite sodium concentration, in good qualitative agreement with the experimental results.

2. The model

The extended Hubbard Hamiltonian is defined by

$$H = -\sum_{\langle ij \rangle \sigma} \left( \frac{1}{2} \left( V - \frac{J}{2} \right) c_{i \sigma}^{\dagger} c_{j \sigma} + c_{j \sigma}^{\dagger} c_{i \sigma} + c_{i \sigma} c_{j \sigma} \right) + \frac{1}{2} \left( V + \frac{J}{2} \right) c_{i \sigma}^{\dagger} c_{j \sigma} c_{j \sigma}^\prime + \frac{1}{2} \left( U - \frac{J}{2} \right) c_{i \sigma}^{\dagger} c_{j \sigma} c_{j \sigma}^\prime c_{j \sigma}^\prime \right].$$

where the \(\langle ij \rangle\) sum runs over pairs of nearest-neighbor sites on the triangular lattice. The first term is the one-electron band term and \(t > 0\) represents the nearest neighbor hopping. The second term describes the local Coulomb interaction whose strength is \(U\). The last two terms, referred to here as \(H_{ij}\), correspond to the charge and spin interaction between nearest neighbors, \(V\) being the intersite Coulomb interaction and \(J\) the intersite exchange interaction. These intersite interactions may arise from the overlap of the wave functions on different sites, but the exchange interaction may also have a contribution from the lowest order expansion of the Hubbard model in the strong coupling limit. The latter contribution should be small in the limit of high \(U\) values. As usual, \(n_{\sigma} = \langle c_{i \sigma}^{\dagger} c_{i \sigma} \rangle\) is the electron doping with spin \(\sigma\).

We can rewrite \(H_{ij}\) in an extended form by expressing the spin operators in terms of their fermionic representation:

$$H_{ij} = \sum_{\langle ij \rangle \sigma} \left( \frac{1}{2} \left( V - \frac{J}{2} \right) c_{i \sigma}^{\dagger} c_{j \sigma}^\prime + c_{j \sigma}^{\dagger} c_{i \sigma} + c_{i \sigma} c_{j \sigma} \right) - \frac{1}{2} \left( V + \frac{J}{2} \right) c_{i \sigma}^{\dagger} c_{j \sigma} c_{j \sigma}^\prime + \frac{1}{2} \left( U - \frac{J}{2} \right) c_{i \sigma}^{\dagger} c_{j \sigma} c_{j \sigma}^\prime c_{j \sigma}^\prime \right].$$

A mean field approximation is carried through the \(J\) and \(V\) terms where we consider the possibility of singlet and triplet spin pairing. The resulting mean field effective Hamiltonian \(H_{ij}\) now reads:

$$\hat{H}_{ij} = V_t \sum_{\langle k \ell \sigma \sigma' \rangle} \left( \Lambda_{\sigma \sigma'}^{\delta \delta} c_{k \sigma}^{\dagger} c_{\ell \sigma}^{\dagger} c_{\ell \sigma'} c_{k \sigma'} - \Lambda_{\sigma \sigma'}^{\delta \delta} c_{k \sigma}^{\dagger} c_{\ell \sigma'} c_{\ell \sigma} + \Lambda_{\sigma \sigma'}^{\delta \delta} c_{\ell \sigma}^{\dagger} c_{k \sigma'} c_{k \sigma} \right),$$

where \(V_t = -\frac{1}{2} \left( V + \frac{J}{2} \right), \quad V_t = -\frac{1}{2} \left( V - \frac{J}{2} \right)\) and the relevant fields are the pairing terms, defined as:

$$\Lambda_{\sigma \sigma'}^{\delta \delta} = \Lambda_{\sigma \sigma'}^{\delta \delta} = \frac{1}{2N} \sum_{i} \left( c_{i \sigma}^{\dagger} c_{i \sigma}^{\dagger} c_{i \sigma} c_{i \sigma} + c_{i \sigma}^{\dagger} c_{i \sigma} c_{i \sigma}^{\dagger} c_{i \sigma}^{\dagger} - c_{i \sigma}^{\dagger} c_{i \sigma}^{\dagger} c_{i \sigma} c_{i \sigma} \right).$$

The labels 1(2) indicate the extended (1) singlet and the triplet (2) spin pairings. The triangular vector directions \(\vec{\delta} = \vec{a}, \vec{b}, \vec{c}\) with

Fig. 1. Pairing representation for triangular symmetry.

Fig. 2. Dispersion relation \(E(\vec{k})\) within the first Brillouin zone. The almost circular lines in the plane correspond to different values of chemical potential for different dopings.

The labels 1(2) indicate the extended (1) singlet and the triplet (2) spin pairings. The triangular vector directions \(\vec{\delta} = \vec{a}, \vec{b}, \vec{c}\) with

$$|\vec{\delta}| = 1$$

are used to specify the pairing according to the lattice symmetry (see Fig. 1).

For simplicity, we do not consider the triplet parallel spin pairing \((\Delta_{\sigma \sigma'}^{\delta \delta})\) in our calculations. Within these assumptions, and transforming the term \(H_{ij}\) to momentum space representation, the effective Hamiltonian is:

$$\hat{H} = \sum_{k \sigma} \varepsilon(\vec{k}) c_{k \sigma}^{\dagger} c_{k \sigma} + \frac{U}{2} \sum_{k} \sum_{\sigma} n_{k \sigma} n_{k \sigma}$$

$$+ \sum_{k \sigma} \Lambda_{\sigma \sigma'}^{\delta \delta}(\vec{k}) c_{k \sigma}^{\dagger} c_{k \sigma'}^{\dagger} c_{k \sigma'} c_{k \sigma} - \Lambda_{\sigma \sigma'}^{\delta \delta}(\vec{k}) c_{k \sigma}^{\dagger} c_{k \sigma} c_{k \sigma'}^{\dagger} c_{k \sigma'}$$

$$+ \sum_{k \sigma \sigma'} \Lambda_{\sigma \sigma'}^{\delta \delta}(\vec{k}) c_{k \sigma}^{\dagger} c_{k \sigma'}^{\dagger} c_{k \sigma'} c_{k \sigma}.$$
μ being the chemical potential. The remaining two body terms in Hamiltonian (7) are treated within the Hubbard-1 approximation in the limit $U \to \infty$, in order to avoid local double occupancy. This is justified because one expects that the local interaction would be much larger than the intersite one, so one expects a large value of $U$ and a small (but non-zero) value of $J$.

### 3. Order parameters

Here we assume that the superconducting pairings previously defined have the same absolute values and differ only in a phase factor, i.e., $|A_{\mathbf{k}}^{\sigma \sigma} | = |A_{\mathbf{k}}^{\sigma \bar{\sigma}} | = A_{\mathbf{k}}^{\sigma}$. Hence, we can relate the different pairings in the triangular lattice using relative phases that contain the lattice symmetry. So, if $|A_{\mathbf{k}}^{\sigma}(| \mathbf{r} \rangle = A_{\mathbf{k}}^{\sigma}(| \mathbf{r} \rangle$ for the superconductor order parameters in the limit $\delta = \tilde{c}$, we obtain a compact form for the superconductor order parameters: $A_{\mathbf{k}}^{\sigma} = \tilde{c} A_{\mathbf{k}}^{\sigma}$, $A_{\mathbf{k}}^{\bar{\sigma}} = \tilde{c} A_{\mathbf{k}}^{\bar{\sigma}}$, where $\tilde{c}$ is justified because one expects that the local interaction would be much larger than the intersite one, so one expects a large value of $U$ and a small (but non-zero) value of $J$.

### 4. Results and discussion

We present here the numerical results obtained from the self-consistent equations (16)–(19). As was stated before, we analyze separately the singlet and triplet cases. Results are obtained for a fixed concentration (occupation of the conduction band) as a function of temperature, i.e., the superconducting parameter $\Delta_{1(2)}$ and the chemical potential are evaluated self-consistently for a given concentration and as a function of temperature. The superconducting critical temperatures are obtained by requiring that $\Delta_{1(2)} = 0$.

We are interested in the variation of the critical temperature with electron doping ($n$) in the limit $U \to \infty$. The remaining parameters are related to the intersite correlations: $V_i$ and $V_i$.

\[ P = \frac{2}{\Phi} \sum \epsilon_{\mathbf{p}}^{\mathbf{p}} |\Phi_{\mathbf{p}}|^2 \quad \text{and} \quad W = -\frac{2}{\Phi} \sum \epsilon_{\mathbf{p}}^{\mathbf{p}} |\Phi_{\mathbf{p}}|^2. \]

The electron doping ($n$) and the pairing ($\Delta$) are obtained from these functions. For simplicity, in this work, the singlet and triplet symmetries are treated separately and the coexistence (or possible competition) between pairings with different symmetries is not included in the calculation.

After a straightforward calculation and fixing the values of the temperature and chemical potential, we obtain the following set of self-consistent equations:

\[ n = \frac{2 k_b T}{N} \sum \epsilon_{\mathbf{p}}^{\mathbf{p}} |\Phi_{\mathbf{p}}|^2 (n/2 - 1) - \epsilon_{\mathbf{p}}^{\mathbf{p}} - \epsilon_{\mathbf{p}}^{\mathbf{p}} = \frac{2 k_b T}{N} \sum \epsilon_{\mathbf{p}}^{\mathbf{p}} |\Phi_{\mathbf{p}}|^2 (n/2 - 1), \quad (16) \]

\[ 1 = \frac{2 k_b T}{N} \sum \epsilon_{\mathbf{p}}^{\mathbf{p}} |\Phi_{\mathbf{p}}|^2 (n/2 - 1) \cos k_x \]

for the singlet case, with

\[ E_{\mathbf{k}}^S = \sqrt{\epsilon_{\mathbf{k}}^2 (n/2 - 1)^2 + \epsilon_{\mathbf{k}}^2 |\Phi_{\mathbf{k}}|^2}, \]

and

\[ n = \frac{2 k_b T}{N} \sum \epsilon_{\mathbf{p}}^{\mathbf{p}} |\Phi_{\mathbf{p}}|^2 (n/2 - 1) - \epsilon_{\mathbf{p}}^{\mathbf{p}} - \epsilon_{\mathbf{p}}^{\mathbf{p}} = \frac{2 k_b T}{N} \sum \epsilon_{\mathbf{p}}^{\mathbf{p}} |\Phi_{\mathbf{p}}|^2 (n/2 - 1), \quad (16) \]

\[ 1 = \frac{2 k_b T}{N} \sum \epsilon_{\mathbf{p}}^{\mathbf{p}} |\Phi_{\mathbf{p}}|^2 (n/2 - 1) \cos k_x, \quad (17) \]

for the triplet case, with

\[ E_{\mathbf{k}}^T = -\Delta_{1}^2 W + \sqrt{\epsilon_{\mathbf{k}}^2 (n/2 - 1)^2 - 4 \epsilon_{\mathbf{k}}^2 |\Phi_{\mathbf{k}}|^2}, \]

\[ -\Delta_{1}^2 W - \sqrt{\epsilon_{\mathbf{k}}^2 (n/2 - 1)^2 - 4 \epsilon_{\mathbf{k}}^2 |\Phi_{\mathbf{k}}|^2}. \]

where $\epsilon_{\mathbf{p}} = \pi k_b T (2m + 1)$ are the Matsubara frequencies. In order to obtain the physical quantities of interest, like the doping and the pairings, we perform a summation over both the Matsubara frequencies and the lattice $\mathbf{k}$-vectors. To evaluate the $\mathbf{k}$-sum, we applied the technique of special points developed by Chadi and Cohen [31]. This method provides a systematic way to choose a set of points in the Brillouin zone which makes it possible to obtain accurate results, in a relatively simple way, for the mean values of periodic $k$-functions. In Fig. 2, we plot the dispersion relation $E_{\mathbf{k}}$, that exhibits the expected profile, and the Fermi surfaces, which are in agreement with the experimental results discussed above [22–24]. The results for the superconducting order parameters will be discussed in the next section.
are expressed in terms of $V$ and $J$ as defined after Eq. (3). Here, we use the values $V_i = -t/9$ and $V_f = t/9$ with $t > 0$.

Also, the numerical results obtained for the symmetry $d + id'$ are identical to those obtained for the symmetry $d - id'$, so we will refer only to the symmetry $d + id'$. This is also true for the symmetries $p + ip'$ and $p - ip'$ and we will refer only to the symmetry $p + ip'$. The reason for these equalities is the absence of distortion of the triangular lattice.

Therefore, the superconducting critical temperatures ($T_c$) as a function of electron doping ($n$) were calculated for the two singlet symmetries, $s$-extended and $d + id'$, and they are shown in Fig. 3. We observe that the critical temperatures vanish in the limits $n = 0$ and $n = 1$ and present a maximum for values of $n$ that are quite different for the two symmetries: $n \approx 0.43$ and $k_B T_c \approx 0.18t$ for $d + id'$, and $n \approx 0.7$ and $k_B T_c \approx 1.01t$ for the $s$-extended symmetry. The results for the $d + id'$ symmetry seem to be in qualitative agreement with experimental data for the cobaltates (where a maximum of $T_c$ is found for $n$ of the order of 0.3 [19]), but the low value of $T_c$ and the small size of the superconductive region, in comparison with the $s$-extended case, suggest that the $s$-extended symmetry is the dominant one in the singlet superconductor phase.

We have also calculated the critical temperature, $T_c$, for the triplet case (Fig. 4). Here the two symmetries, $p + ip'$ and $f$, exhibit a non-zero critical temperature in different regions in the concentration axis. This result suggests that two different and non-coexisting superconducting phases are present at very low temperatures for different values of concentration. Also, the values of the superconductive transition temperatures are much smaller in this case than in the singlet case. Although the calculation was performed by considering the two possibilities separately, these results suggest that singlet $s$-extended superconductivity is dominant for those compounds, in agreement with the arguments of Ref. [32] where a predominant $s$-extended phase was found.

Finally, in Fig. 5, we plot the singlet- and triplet-pairing parameter, $\Delta_{1(2)}$, as a function of $n$ for $k_B T \simeq 0.005t$. We can conclude from this figure that the $s$-symmetry is the dominant one, but there is also a possible coexistence of a triplet $p + ip'$ and a singlet $d + id'$ pairing symmetry for $0.35 \leq n \leq 0.5$. Nevertheless, we are aware that we have analyzed the singlet and triplet symmetries separately. A full calculation contains mixed terms between the $s$- and $f$-pairing as well as between the $d$- and $p$-pairing. These mixed pairings could explain the coexistence and/or a possible transition mechanism between the two pairing symmetries for adequate values of the parameters $V_i$ and $V_f$.

![Fig. 3](image-url) (Color online) Critical temperature in the singlet case for $V_i = -t/9$. The solid (red) curve corresponds to the $d + id'$ symmetry and the dashed (blue) curve corresponds to the $s$-extended symmetry.

![Fig. 4](image-url) (Color online) Critical temperature in the triplet case for $V_i = t/9$. The $p + ip'$ symmetry is represented by the solid (red) curve and $f$ symmetry by the dashed (blue) curve.

![Fig. 5](image-url) (Color online) Singlet and triplet superconducting pairing for $V_i = -t/9$ and $V_f = t/9$. The different symmetries are represented by: solid (red) curve for $d + id'$, dashed (blue) curve for $s$-extended, dotted (green) curve for $p + ip'$ and dot-dashed (black) curve for $f$.

5. Conclusions

In conclusion, we have presented some theoretical results for the superconducting critical temperatures of Na$_2$CoO$_2$·yH$_2$O within an extended Hubbard model on a triangular lattice. The non-local and local interactions in the model are treated in different degrees of approximation, mean field and Hubbard I, respectively. We obtained a set of self-consistent equations in the infinity $U$ limit relating the chemical potential, the temperature, the superconducting order parameter and the band filling (corresponding to the sodium concentration) for the singlet and triplet superconductor phases. The critical temperatures have been calculated for different symmetries. The singlet case exhibits $s$-extended symmetry in a large region of $n$ which includes the $d + id'$ symmetry, localized in a narrow region near half-band filling. The triplet case presents a different scenario, because the $p + ip'$ and $f$ symmetries are in separate regions. We show that both symmetries may be present and a maximum of $T_c$ for an optimum Na concentration is obtained for triplet and singlet symmetries, in agreement with experimental results. Our results suggest a possible coexistence and/or transition between the two superconductor phases.

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