

1 New Pairing Mechanism via Chiral Electron-Hole Condensation for 2 Non-BCS Superconductivity

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A novel chiral electron-hole (CEH) pairing mechanism is proposed to account for non-BCS superconductivity. In contrast to BCS Cooper pairs, CEH pairs exhibit a pronounced affinity to antiferromagnetism for superconductivity. The gap equations derived from this new microscopic mechanism are analyzed for both s- and d-wave superconductivity, revealing marked departures from the BCS theory. Unsurprisingly, CEH naturally describes superconductivity in strongly-correlated systems, necessitating an exceedingly large coupling parameter ($\lambda > 1$ for s-wave and $\lambda > \pi/2$ for d-wave) to be efficacious. The new mechanism provides a better understanding of various non-BCS features, especially in cuprate and iron-based superconductors. In particular, CEH, through quantitative comparison with experimental data, shows promise in solving long-standing puzzles such as the unexpectedly large gap-to-critical-temperature ratio Δ_0/T_c , the lack of gap closure at T_c , superconducting phase diagrams, and a non-zero heat-capacity-to-temperature ratio C/T at $T = 0$ (i.e., the “anomalous linear term”), along with its quadratic behavior near $T = 0$ for d-wave cuprates.

7 I. INTRODUCTION

8 Magnetism has traditionally been viewed as antagonistic to conventional Bardeen-
9 Cooper-Schrieffer (BCS) superconductivity [1]. However, many non-BCS superconductors
10 discovered in the past few decades have demonstrated the opposite, showing that strong
11 magnetism is actually very conducive to non-BCS superconductivity. In particular, many of
12 them are derived from parent compounds with antiferromagnetic properties, and some even
13 exhibit cases of the coexistence of superconductivity and antiferromagnetic order [2]. The
14 two primary classes of high T_c superconductors, cuprate [3] and iron-based (FeSC) [4] super-
15 conductors, both have their roots in antiferromagnetic compounds, with cuprates originating
16 from antiferromagnetic Mott insulators and FeSCs from antiferromagnetic metals.

17 The coexistence of superconductivity and long-range antiferromagnetic order was actually
18 discovered a long time ago in the late 1970s [5, 6]. The intimate relationship between
19 antiferromagnetism and superconductivity has been observed in many different types of
20 non-BCS superconducting materials, including heavy fermion compounds [7, 8], organic
21 superconductors such as quasi-1D TMTTF/TMTSF type and quasi-2D BEDT-TTF type
22 [9], and doped fullerenes [10].

23 The significance of antiferromagnetic order may provide crucial clues for solving the
24 puzzles of non-BCS superconductivity. In particular, this leads to our proposal of a new

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25 pairing mechanism via chiral electron-hole (CEH) condensation in this work. The presence
 26 of strong antiferromagnetic correlations is critical, as it guarantees that chirally opposite
 27 electron and hole states are next to each other, making the chiral condensation more feasible.
 28 This may explain why both high T_c superconducting classes (cuprates and FeSCs) are based
 29 on antiferromagnetic compounds.

30 In order to fully comprehend these superconductors, it is imperative to not only find
 31 their correct pairing mechanism, but also to identify their pairing symmetry. Angle-resolved
 32 photoemission spectroscopy measurements have indisputably proven that cuprates display
 33 a $d_{x^2-y^2}$ gap symmetry [11]. Although studies on the pairing symmetry of FeSCs that were
 34 discovered much later are not as conclusive, the majority consensus suggests that they most
 35 probably exhibit some type of s-wave pairing symmetry [12].

36 In this paper, we apply the mean-field approach to derive superconducting gap equations
 37 using the new pairing mechanism. Detailed analysis of the equations for both s-wave and
 38 d-wave superconductivity will reveal various features that differ from BCS. Furthermore, we
 39 will address puzzles concerning superconducting gap and heat capacity and present several
 40 examples that directly compare CEH predictions with cuprate and FeSC data. Natural units
 41 ($\hbar = c = k_B = 1$) are utilized throughout the work for convenience.

42 II. CHIRAL ELECTRON-HOLE (CEH) PAIRING

43 We will closely follow the Bogoliubov-BCS formalism as described in Ref. [13] for the
 44 mean-field theory of BCS superconductivity, albeit with a new microscopic superconducting
 45 mechanism. First of all, we will begin with a four-fermion interacting Hamiltonian for the
 46 simple straightforward case of s-wave CEH pairing,

$$H = \sum_{\mathbf{k}\sigma} \xi_{\mathbf{k}} c_{\mathbf{k}\sigma}^\dagger c_{\mathbf{k}\sigma} - V \sum_{\mathbf{k}\mathbf{k}'} c_{\mathbf{k}L}^\dagger c_{-\mathbf{k}R} c_{-\mathbf{k}'R}^\dagger c_{\mathbf{k}'L} \quad (1)$$

47 where we use left and right chiralities instead of the conventional up and down spin notation
 48 to emphasize the significance of chirality in this study.

49 Note that similar four-fermion interactions were also used in the Nambu-Jona-Lasinio
 50 (NJL) mechanism [14] in particle physics for quark condensation and spontaneous symmetry
 51 breaking, borrowing the idea from the earlier BCS superconductivity work [1]. Such ideas
 52 are also crucial in the recently developed mirror matter theory, which aims to address many
 53 puzzles in fundamental physics and cosmology [15–19]. In particular, the concept of staged
 54 chiral quark condensation [16, 19, 20] has directly motivated this work.

55 The most significant difference in Eq. 1 from the BCS Hamiltonian is that, by borrowing
 56 back the idea of the NJL model, the four creation and annihilation operators are arranged
 57 to incorporate the proposed condensation mechanism of chiral electron-hole pairs instead
 58 of the conventional Cooper pairs. Specifically, the superconducting pairs are formed from
 59 electrons and holes with exactly opposite chiralities, a configuration readily achievable in
 60 adjacent sites of antiferromagnetic materials, which also explains the non-local behavior of
 61 the CEH mechanism. We can then define a similar order parameter Δ based on the CEH
 62 condensation mechanism,

$$\Delta = V \sum_{\mathbf{k}} \langle c_{\mathbf{k}L}^\dagger c_{-\mathbf{k}R} \rangle, \quad \Delta^* = V \sum_{\mathbf{k}} \langle c_{-\mathbf{k}R}^\dagger c_{\mathbf{k}L} \rangle. \quad (2)$$

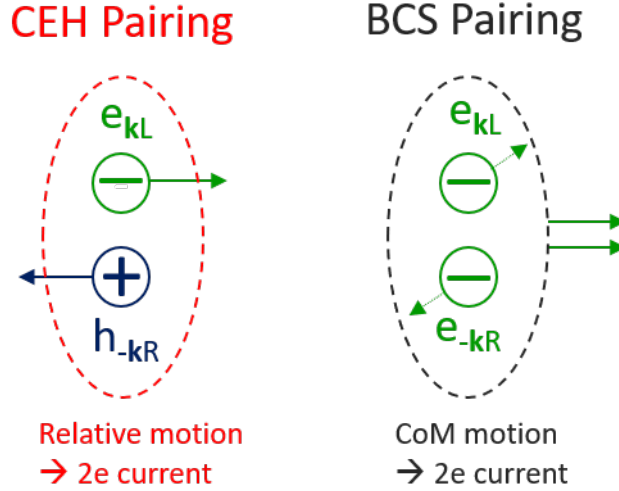


FIG. 1. Different pairing and conducting mechanisms between CEH and BCS are shown.

63 Upon initial instinctive consideration, one might assume that CEH pairs cannot conduct
 64 electric currents due to their zero net charge. However, the conduction mechanism of CEH
 65 pairs is fundamentally different from that of Cooper pairs, as illustrated in Fig. 1. While the
 66 Cooper pair conducts currents through center-of-mass motion, the CEH pair achieves this
 67 through relative motion. On a macroscopic scale, both mechanisms yield equivalent $2e$ -like
 68 currents, resulting in comparable outcomes in most macroscopic phenomena, including the
 69 Josephson effect.

70 Another important aspect concerns the pairing symmetry. In CEH condensation, the
 71 pairs must be spin singlets owing to its chiral nature (like the Higgs in particle physics),
 72 leading to symmetric orbital wave functions. Consequently, the resulting pairing symmetry
 73 can only be s-, d-, or g-wave.

74 Considering the CEH condensation, the Hamiltonian of Eq. 1 then takes the bilinear
 75 form,

$$H = \sum_{\mathbf{k}} (c_{\mathbf{k}L}^\dagger, c_{-\mathbf{k}R}^\dagger) \begin{pmatrix} \xi_{\mathbf{k}} & -\Delta^* \\ -\Delta & \xi_{\mathbf{k}} \end{pmatrix} \begin{pmatrix} c_{\mathbf{k}L} \\ c_{-\mathbf{k}R} \end{pmatrix}. \quad (3)$$

76 We can then diagonalize the Hamiltonian through the Bogoliubov transformation [21] as
 77 follows,

$$U^\dagger \begin{pmatrix} \xi_{\mathbf{k}} & -\Delta^* \\ -\Delta & \xi_{\mathbf{k}} \end{pmatrix} U = \begin{pmatrix} E_{\mathbf{k}}^+ & 0 \\ 0 & E_{\mathbf{k}}^- \end{pmatrix}, \quad U = \begin{pmatrix} u_{\mathbf{k}} & v_{\mathbf{k}}^* \\ -v_{\mathbf{k}} & u_{\mathbf{k}}^* \end{pmatrix} \quad (4)$$

78 where the eigenvalues are,

$$E_{\mathbf{k}}^\pm = \xi_{\mathbf{k}} \pm |\Delta|, \quad (5)$$

79 in contrast to $E_{\mathbf{k}}^\pm = \pm \sqrt{\xi_{\mathbf{k}}^2 + |\Delta|^2}$ in BCS. The corresponding emergent Bogoliubov quasi-
 80 particles (energy eigenstates) are therefore defined as follows,

$$\begin{pmatrix} b_{\mathbf{k}1} \\ b_{-\mathbf{k}2} \end{pmatrix} = U^\dagger \begin{pmatrix} c_{\mathbf{k}L} \\ c_{-\mathbf{k}R} \end{pmatrix} \quad (6)$$

81 where the quasi-particle operators b and b^\dagger satisfy the same anticommutation relations as

82 fermions. Applying the unitarity condition of $|u|^2 + |v|^2 = 1$, we arrive at the solution,

$$|u| = |v| = \frac{1}{\sqrt{2}} \quad (7)$$

83 which is remarkably different from the BCS findings. To facilitate later discussion, we can
84 introduce a phase factor by setting $u/v = e^{i\delta}$, which gives $u^*v = 1/2e^{-i\delta}$.

85 Using the above solution, we obtain the following condensation relation

$$\langle c_{\mathbf{k}L}^\dagger c_{-\mathbf{k}R} \rangle = u^*v(\langle b_{-\mathbf{k}2}^\dagger b_{-\mathbf{k}2} \rangle - \langle b_{\mathbf{k}1}^\dagger b_{\mathbf{k}1} \rangle) \quad (8)$$

86 where, at finite temperature, the quasi-particles follow Fermi-Dirac statistics, that is,

$$\langle b_{\mathbf{k}1}^\dagger b_{\mathbf{k}1} \rangle = \frac{1}{e^{E^+/T} + 1}, \quad \langle b_{-\mathbf{k}2}^\dagger b_{-\mathbf{k}2} \rangle = \frac{1}{e^{E^-/T} + 1}. \quad (9)$$

87 Note that both the BCS and CEH mechanisms for superconductivity are similar to those
88 for neutrino or neutron-mirror neutron oscillations [15, 18] in the sense of reaping the fruits
89 of the misalignment between interaction and energy eigenstates.

90 Then, we can obtain the s-wave CEH gap equation from Eqs. 2, 5, 8, and 9,

$$\begin{aligned} \Delta &= \frac{V}{2} e^{-i\delta} \sum_{\mathbf{k}} \frac{\sinh(|\Delta|/T)}{\cosh(|\Delta|/T) + \cosh(\xi_{\mathbf{k}}/T)} \\ &= V \rho_F e^{-i\delta} \int_0^{\omega^*} d\xi \frac{\sinh(|\Delta|/T)}{\cosh(|\Delta|/T) + \cosh(\xi/T)} \end{aligned} \quad (10)$$

91 where ρ_F denotes the density of states at the Fermi energy and the summation is replaced
92 by an integration over the energy shell ($\pm\omega^*$) near the Fermi surface where the formation
93 of superconducting pairs occurs. It is worth noting that ω^* bears resemblance to the Debye
94 energy ω_D in the BCS theory. However, we will elaborate later on the more significant
95 impact of ω^* within the CEH mechanism.

96 By working out the integration and introducing a dimensionless coupling parameter $\lambda =$
97 $V \rho_F$ and a positive energy gap Δ defined by $\Delta = \Delta e^{-i\delta}$, the s-wave gap equation can be
98 simplified as,

$$\begin{aligned} \Delta(T) &= 2\lambda T \tanh^{-1} \left(\tanh\left(\frac{\Delta(T)}{2T}\right) \tanh\left(\frac{\omega^*}{2T}\right) \right) \\ &= \lambda T \log \left(\frac{e^{(\Delta(T)+\omega^*)/T} + 1}{e^{\Delta(T)/T} + e^{\omega^*/T}} \right). \end{aligned} \quad (11)$$

99 CEH Gap equations with more intricate orbital pairing symmetries can be calculated by
100 considering an angular-dependent superconducting energy gap $\Delta_{\mathbf{k}} = \Delta \gamma_{\mathbf{k}}$. For a d-wave gap
101 symmetry of $d_{x^2-y^2}$ in cuprate superconductors, we have the symmetry factor $\gamma_{\mathbf{k}} = \cos(2\varphi)$.
102 A d-wave CEH gap equation can then be derived with ease,

$$\Delta(T) = \frac{8\lambda T}{\pi} \int_0^{\pi/4} d\varphi \tanh^{-1} \left(\tanh\left(\frac{\Delta(T) \cos(2\varphi)}{2T}\right) \tanh\left(\frac{\omega^*}{2T}\right) \right). \quad (12)$$

103 If we further consider Δ as an emergent scalar field (akin to the Higgs field in parti-
104 cle physics), its self-interactions will lead to the same phenomenological Ginzburg-Landau
105 theory as derived in BCS superconductivity.

III. ANALYSIS OF CEH GAP EQUATIONS

106

107 First, we should emphasize that both s-wave and d-wave gap equations in CEH (Eqs. 11
108 and 12) are dramatically different from those derived in the BCS theory. In particular, the
109 two parameters of ω^* and λ play a crucial role in distinguishing the CEH mechanism from
110 BCS.

111 To ensure that quasi-particles have positive energies (or negative energies for correspond-
112 ing “anti-particles”) as in Eq. 5, we establish the following superconducting requirement
113 under the CEH model,

$$\omega^* \leq \Delta(T) \quad (13)$$

114 which is entirely different from that of BCS. In BCS, positive energies are guaranteed as
115 $E_{\mathbf{k}}^+ = \sqrt{\xi_{\mathbf{k}}^2 + |\Delta|^2}$, and thus no constraint on the Debye energy ω_D is necessary. In addition,
116 it should be noted that the coupling parameter λ in CEH must be very large (i.e., $\lambda > 1$ for
117 s-wave and $\lambda > \pi/2$ for d-wave as presented below), as opposed to the small parameter of
118 $\lambda \ll 1$ used in BCS. This implies that CEH is naturally suited for modeling superconductivity
119 in strongly-correlated electron systems while BCS is more appropriate for the weak-coupling
120 limit.

121 The condition of Eq. 13 suggests that typically $\Delta(T_c) = \omega^* \neq 0$, meaning that the
122 superconducting gap does not necessarily close at the critical temperature T_c , which is
123 distinct from BCS. More details are presented below for both s- and d-wave cases.

124

A. s-wave results

125 The CEH s-wave gap equation (Eq. 11) can also be written as,

$$x^{1/\lambda}(x + w) = wx + 1 \quad (14)$$

126 where $x = \exp(\Delta(T)/T) > 1$ and $w = \exp(\omega^*/T) > 1$. The superconducting condition of
127 Eq. 13 requires that $x > w$. We can then easily solve it for λ ,

$$\lambda = \frac{\log(x)}{\log\left(\frac{wx+1}{w+x}\right)} = \frac{\log(x)}{\log(x) + \log\left(\frac{w+1/x}{w+x}\right)} > 1 \quad (15)$$

128 which means that CEH addresses a strongly-correlated system.

129 In the limit of $T \rightarrow 0$, we obtain the gap at zero temperature,

$$\Delta_0 \equiv \Delta(T = 0) = \lambda\omega^* \quad (16)$$

130 and the gap equation can then be simplified at the critical temperature T_c as,

$$2 \exp\left(\frac{\lambda + 1}{\lambda^2} \frac{\Delta_0}{T_c}\right) = \exp\left(\frac{2}{\lambda} \frac{\Delta_0}{T_c}\right) + 1. \quad (17)$$

131 This allows us to plot the solution of Δ_0/T_c as a function of λ as shown in Fig. 2 with
132 its two asymptotic limits: two as $\lambda \rightarrow \infty$ and $\log(2)\lambda^2/(\lambda - 1)$ as $\lambda \rightarrow 1$. Note that this
133 ratio is always larger than two and can become much larger at smaller λ (or lower doping
134 levels), in contrast to the value of about 1.764 in BCS for s-wave superconductors. To be
135 clear, the ratios shown as arrows in the plot represent only the weak-coupling limit in BCS

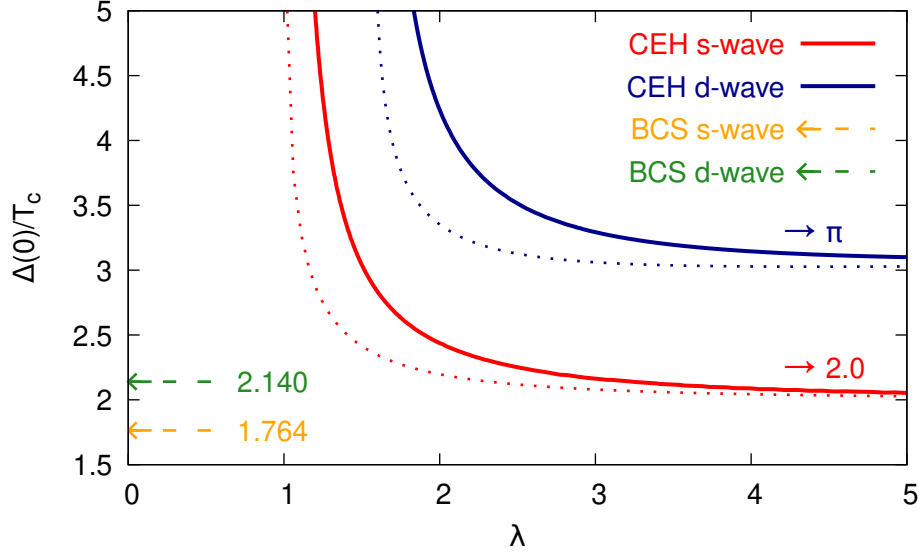


FIG. 2. Δ_0/T_c as a function of λ is shown for both s-wave and d-wave CEH superconductivity. BCS values in the weak-coupling limit are also displayed for comparison. The two dotted lines depict Δ_0/T_0 corresponding to their respective CEH results.

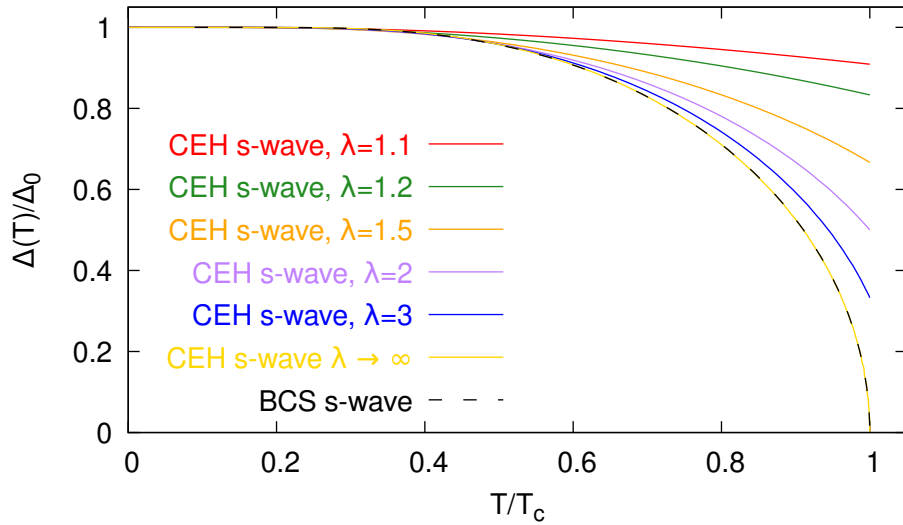


FIG. 3. The $\Delta(T)/\Delta_0$ ratios as a function of T/T_c are shown for s-wave CEH superconductivity. The gap only vanishes at T_c when $\lambda \rightarrow \infty$, in which case the curve nearly overlaps with that of BCS.

136 and higher Δ_0/T_c ratios are possible in extended models using stronger electron-phonon
 137 couplings. For simplicity, further comparisons to BCS in this paper will also be restricted
 138 to its weak-coupling limit unless stated otherwise.

139 Fig. 3 shows the $\Delta(T)/\Delta_0$ ratios as a function of T/T_c for various λ values, which are
 140 numerically calculated from the gap equation. In Fig. 3, it is evident that the supercon-
 141 ducting gap in CEH, in general, does not close at the critical temperature T_c , resulting in

142 $\Delta(T_c) = \Delta_0/\lambda$ according to Eq. 16. It only closes in the extreme case of $\lambda \rightarrow \infty$, where the
 143 relation between $\Delta(T)/\Delta_0$ and T/T_c can be simplified as,

$$\frac{T}{T_c} = \frac{\Delta(T)/\Delta_0}{\tanh^{-1}(\Delta(T)/\Delta_0)} \quad (18)$$

144 which nearly overlaps with the results from BCS as shown in Fig. 3. It is worth pointing out
 145 that, in this case, BCS extensions using strong electron-phonon couplings give very similar
 146 results to those obtained at its weak-coupling limit [22].

147 On the other hand, the superconducting gap does close at a higher temperature $T_0 > T_c$.
 148 It can be calculated from the gap equation using the condition of $\Delta(T_0) = 0$,

$$T_0 = \frac{\omega^*}{2 \tanh^{-1}(1/\lambda)} = \frac{\omega^*}{\log(\frac{\lambda+1}{\lambda-1})} \quad (19)$$

149 which, though higher, follows a similar trend as T_c as demonstrated in the following section.
 150 Another ratio can be calculated simply as follows,

$$\Delta_0/T_0 = 2\lambda \tanh^{-1}(1/\lambda) < \Delta_0/T_c \quad (20)$$

151 which is shown as the red dotted line in Fig. 2.

152 At $T \rightarrow 0$, we find, directly from the gap equation, that the energy gap exponentially
 153 approaches its maximum value of Δ_0 ,

$$\Delta(T) \simeq \Delta_0 - \lambda T \exp\left(-\frac{\Delta_0}{T}\left(1 - \frac{1}{\lambda}\right)\right) \quad (21)$$

154 which is similar to that of BCS.

155

B. d-wave results

156 Taking the limit of $T \rightarrow 0$, we obtain the coupling parameter from the gap equation (Eq.
 157 12) (see Appendix A),

$$\lambda = \frac{\pi}{2(1 - \sin 2\theta) + 4\theta \cos 2\theta} > \frac{\pi}{2} \quad (22)$$

158 where θ is defined by $\cos 2\theta = \omega^*/\Delta_0$ within the range of $0 < \theta < \pi/4$. This indicates that
 159 CEH d-wave superconductors require even stronger correlations.

160 We can also obtain the d-wave ratio of Δ_0/T_c numerically from the gap equation using
 161 $\omega^* = \Delta(T_c) = \Delta_0 \cos 2\theta$ and compare it with the s-wave and BCS results, as shown in Fig.
 162 2 and also in Fig. 4 as a function of θ . The general trend of the d-wave ratio is similar to
 163 the s-wave one, though notably higher. However, the inset plot in Fig. 4 reveals that the
 164 d-wave ratio is not monotonic and has a minimum of about 3.0774 at $\theta \approx 0.7184$.

165 Similar to the s-wave results, the normalized d-wave superconducting gap as a function
 166 of T/T_c is shown in Fig. 5. Again, it does not close at T_c which is contrary to the BCS
 167 prediction. Note that the temperature dependence of the BCS d-wave gap, unlike the s-wave
 168 case, differs greatly from the CEH predictions, even in the limit of $\lambda \rightarrow \infty$ or $\theta = \pi/4$. As
 169 a matter of fact, the distinction is so significant between BCS and CEH that measurements
 170 with decent experimental precision should be pursued.

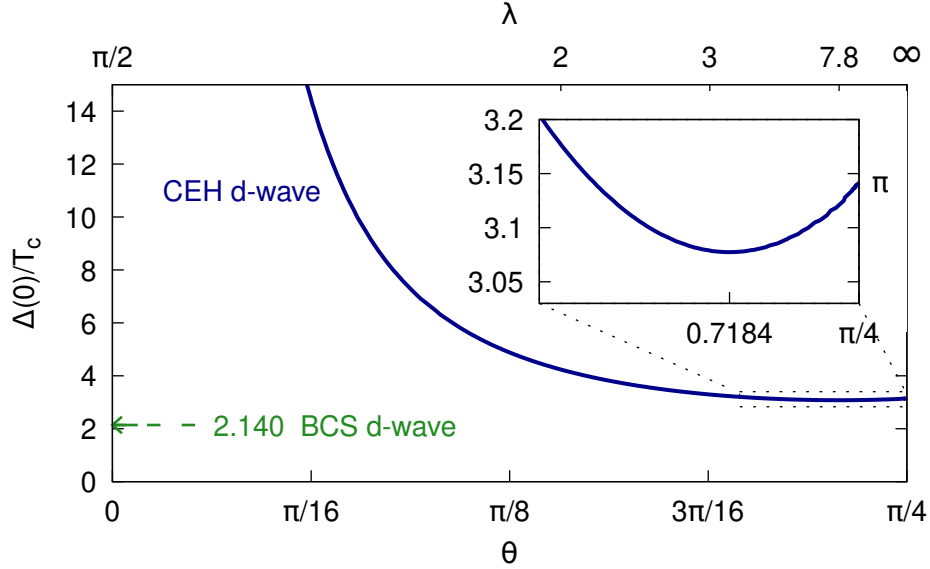


FIG. 4. The Δ_0/T_c ratios as a function of θ or λ are shown for d-wave CEH superconductivity. The inset presents a minimum of ≈ 3.0774 at $\theta \approx 0.7184$. The BCS d-wave value in the weak-coupling limit is also displayed for comparison.

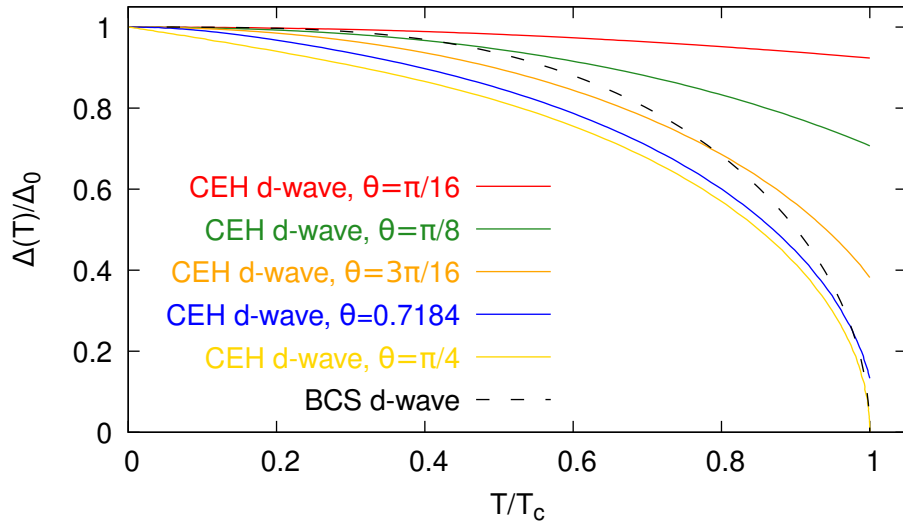


FIG. 5. The ratios of $\Delta(T)/\Delta_0$ as a function of T/T_c are shown for d-wave CEH superconductivity. The gap only closes at T_c when $\theta \rightarrow \pi/4$ or $\lambda \rightarrow \infty$. However, the gap-vanishing BCS curve behaves differently.

171 It is straightforward to calculate the temperature $T_0 > T_c$ where the d-wave supercon-
172 ducting gap vanishes,

$$T_0 = \frac{\omega^*}{2 \tanh^{-1}(\pi/(2\lambda))} \quad (23)$$

173 which is similar to the s-wave result except for a larger lower bound on the coupling param-

174 eter ($\lambda > \pi/2$). A similar ratio can also be obtained,

$$\Delta_0/T_0 = 2 \tanh^{-1}(1 + 2\theta \cos 2\theta - \sin 2\theta) / \cos 2\theta < \Delta_0/T_c \quad (24)$$

175 which is plotted as the blue dotted line in Fig. 2. Like Δ_0/T_c , this ratio has a minimum of
176 about 3.027 at $\theta \approx 0.662$.

177 The asymptotic behavior of the superconducting gap at $T \rightarrow 0$ can be obtained as follows,

$$\Delta \simeq \Delta_0 - \frac{T^2}{\theta \sin(2\theta) \cos(2\theta) \Delta_0} \quad (25)$$

178 which is derived by utilizing the following integration,

$$\int_0^{\pi/4} d\varphi \exp\left(-\frac{\Delta}{T} |\cos(2\varphi) - \cos(2\theta)|\right) \Bigg|_{T \rightarrow 0} = \frac{T}{\Delta \sin(2\theta)}. \quad (26)$$

179

IV. ENTROPY AND SPECIFIC HEAT

180 In the CEH superconducting phase, the entropy of the finite-temperature system can be
181 expressed through the statistics of Bogoliubov quasi-particles,

$$\begin{aligned} S &= -2 \sum_{\mathbf{k}} (f_+ \log f_+ + f_- \log f_-) \\ &= -2 \sum_{\mathbf{k}} (f_+ \log f_+ + (1 - f_+) \log(1 - f_+)) \end{aligned} \quad (27)$$

182 where f_{\pm} represent the Fermi-Dirac distributions of the quasi-particles as in Eq. 9. By
183 replacing the summation with an energy integration, we obtain for the simple s-wave case,

$$S = 2 \int_{\Delta-\omega^*}^{\Delta+\omega^*} d\epsilon \rho(\epsilon) \left(\frac{\epsilon/T}{1 + e^{\epsilon/T}} + \log(1 + e^{-\epsilon/T}) \right) \quad (28)$$

184 where $\rho(\epsilon)$ is the quasi-particle density of states. This entropy formula seems to be the
185 same as the BCS one but only formally. The critical differences lie in $\rho(\epsilon)$ and the bounds
186 of integration $\pm\omega^*$. In CEH, $\rho(\epsilon) = \rho_F$, whereas in BCS, the density exhibits a singular
187 behavior at the gap energy, reflecting their differences in the pairing mechanism. More
188 significantly, the integration bounds in CEH demand more careful handling, unlike BCS, due
189 to a drastically different dispersion relation in Eq. 5. Such differences are most effectively
190 showcased in the following calculations of heat capacity.

191

A. s-wave specific heat

192 The specific heat for the CEH s-wave superconductors can be obtained from the entropy
193 in Eq. 28 as follows,

$$C_{sc} = T \frac{\partial S}{\partial T} = 2T \rho_F \int_{\Delta-\omega^*}^{\Delta+\omega^*} d\epsilon \frac{e^{\epsilon/T}}{(e^{\epsilon/T} + 1)^2} \left(\left(\frac{\epsilon}{T} \right)^2 - \frac{\epsilon}{T} \frac{\partial \Delta(T)}{\partial T} \right) \quad (29)$$

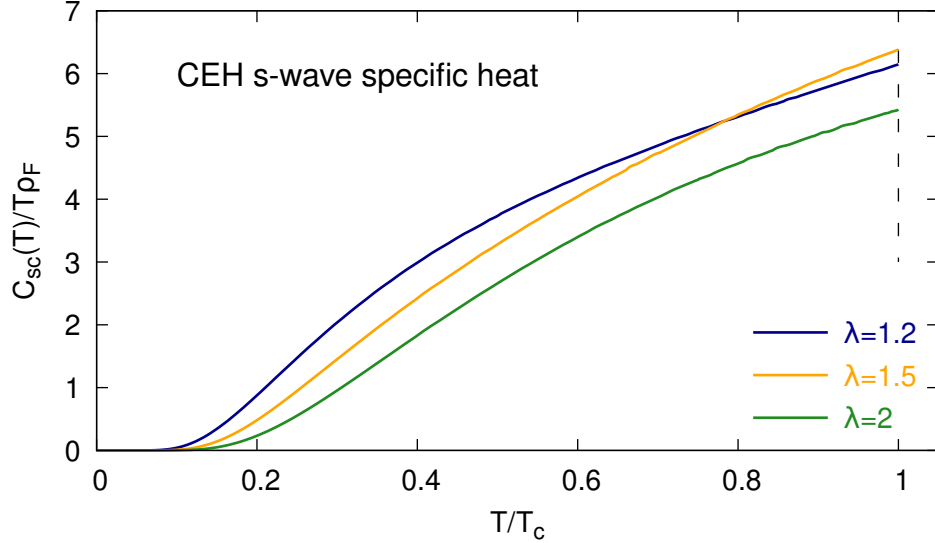


FIG. 6. The temperature dependence of heat capacity $C_{sc}(T)/(T\rho_F)$ is shown for s-wave CEH superconductivity. Cases with three different coupling parameters $\lambda = 1.2, 1.5, 2$ are presented.

194 which can be simplified as,

$$C_{sc}(T) = 2T\rho_F(s_2(T) - \frac{\partial\Delta(T)}{\partial T}s_1(T)) \quad (30)$$

195 where the two auxiliary functions are defined as

$$s_{1,2}(T) = \int_{(\Delta-\omega^*)/T}^{(\Delta+\omega^*)/T} dx \frac{e^x}{(e^x+1)^2} x^{1,2}. \quad (31)$$

196 The CEH s-wave specific heat for various λ values is shown in Fig. 6, where it exponen-
197 tially approaches zero in the limit of $T \rightarrow 0$,

$$C_{sc}(T) \rightarrow 2T\rho_F \left(\frac{\Delta_0 - \omega^*}{T} \right)^2 e^{-(\Delta_0 - \omega^*)/T} \quad (32)$$

198 and behaves similarly to the s-wave BCS superconductivity.

199 To better understand the heat capacity jump at the critical temperature, we plot its peak
200 value at T_c as a function of the coupling parameter λ in Fig. 7. It is evident that the second
201 term contribution $C_{\hat{\Delta}}$ in Eq. 30 dominates the heat capacity at larger λ . The normal state
202 electronic heat capacity, within the same energy shell $\pm\omega^*$, can be written as,

$$C_N(T) = 2T\rho_F \int_{-\omega^*/T}^{\omega^*/T} dx \frac{e^x}{(e^x+1)^2} x^2 \quad (33)$$

203 where, in the bounds of integration, $\omega^*/T = \Delta_0/(\lambda T)$ decreases rapidly as λ increases. The
204 behavior of $C_N(T_c)$, as shown in Fig. 7, resembles that of normal metals only at very low λ
205 values (still > 1), where ω^*/T_c remains large. It then drops rapidly to zero because ω^*/T_c
206 approaches $2/\lambda$ asymptotically as $\lambda \rightarrow \infty$. Note that, unlike in the case of BCS, the first
207 term in Eq. 30 does not reduce to C_N at T_c since the gap does not close at T_c or $\Delta(T_c) \neq 0$.

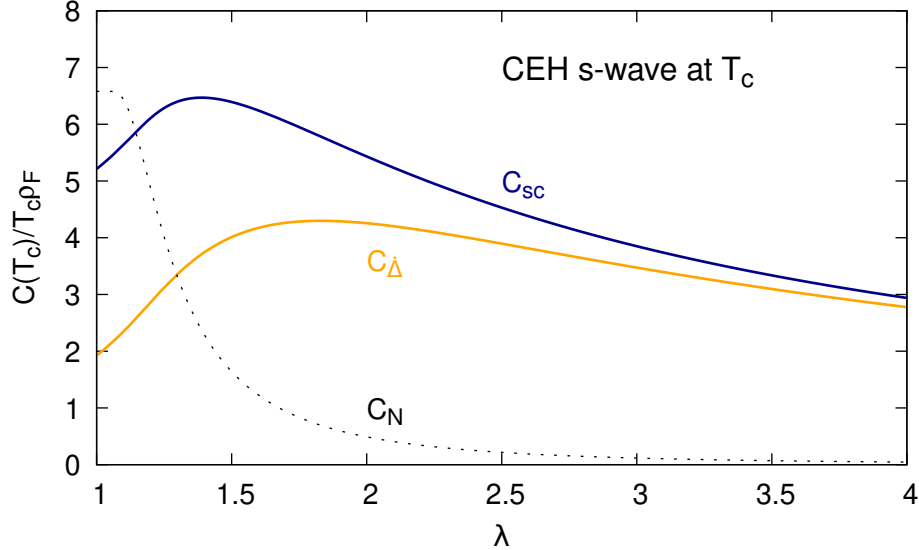


FIG. 7. The heat capacity $C_{sc}(T_c)/(T_c\rho_F)$ at $T = T_c$ as a function of λ is shown for s-wave CEH superconductivity. For comparison, the partial contribution C_{Δ} from the second term in Eq. 30 and the normal-state heat capacity C_N are also presented.

208 Fig. 7 demonstrates that optimal superconductivity for s-wave pairing favors relatively
 209 weaker correlations ($\lambda \lesssim 1.5$). The specific capacity jump at T_c from the superconducting
 210 state to the normal state is more complicated in CEH. The normal state electronic heat
 211 capacity in BCS maintains a constant C_N/T , giving rise to a fixed jump ratio of about 1.43
 212 for s-wave pairing. However, in CEH, this ratio varies depending on λ or the doping level
 213 and may reach about 3 at $\lambda \sim 1.5$ as C_N decreases. More complicatedly, the ω^* energy shell
 214 may shrink so significantly at larger λ or higher doping levels that other energy bands could
 215 become accessible for electrons, causing an increase in C_N and resulting in a smaller heat
 216 capacity jump at T_c .

217 B. d-wave specific heat

218 The d-wave specific heat can be similarly obtained as follows,

$$C_{sc}(T) = \frac{8T\rho_F}{\pi} \left(\int_0^{\pi/4} d\varphi d_2(\varphi, T) - \frac{\partial\Delta}{\partial T} \int_0^{\pi/4} d\varphi d_1(\varphi, T) \cos(2\varphi) \right) \quad (34)$$

219 where the two integrand functions, similar to the s-wave case, are defined by

$$d_{1,2}(\varphi, T) = \int_{(\Delta \cos(2\varphi) - \omega^*)/T}^{(\Delta \cos(2\varphi) + \omega^*)/T} dx \frac{e^x}{(e^x + 1)^2} x^{1,2} \quad (35)$$

220 and the derivative of the gap can be obtained by differentiating the gap equation,

$$\frac{\partial\Delta}{\partial T} = \frac{\Delta}{T} + \frac{\omega^*}{T} \frac{4\lambda g_2(T)}{\pi \exp(-\omega^*/T) - 8\lambda \sinh(\omega^*/T) g_1(T)} \quad (36)$$

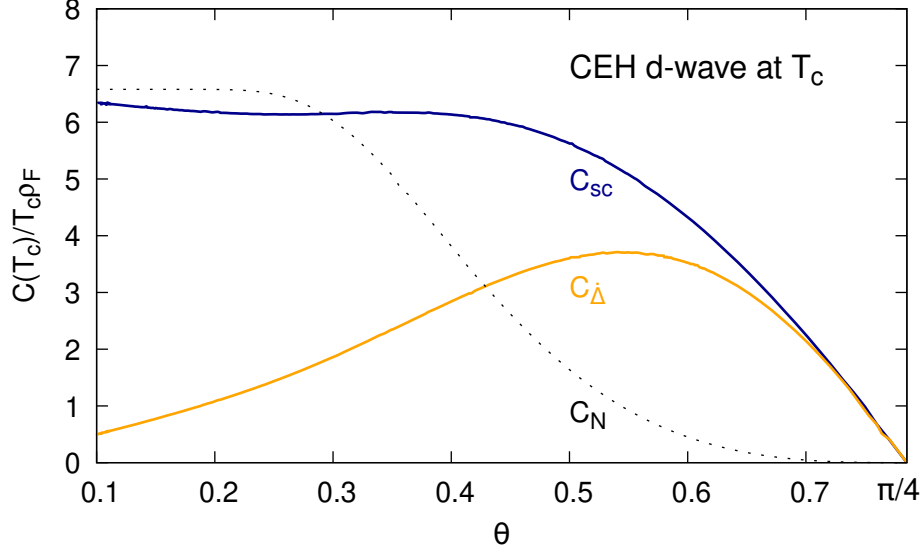


FIG. 8. The heat capacity $C_{sc}(T_c)/(T_c\rho_F)$ at $T = T_c$ as a function of θ is shown for d-wave CEH superconductivity. For comparison, the partial contribution C_{Δ} from the second term in Eq. 34 and the normal-state electronic heat capacity C_N are also presented.

221 where the two auxiliary functions are given by

$$\begin{aligned}
 g_1(T) &= \int_0^{\pi/4} d\varphi \frac{e^{\Delta \cos(2\varphi)/T} \cos(2\varphi)}{(e^{(\Delta \cos(2\varphi)+\omega^*)/T} + 1)(e^{\Delta \cos(2\varphi)/T} + e^{\omega^*/T})} \\
 g_2(T) &= \int_0^{\pi/4} d\varphi \frac{1 - e^{2\Delta \cos(2\varphi)/T}}{(e^{(\Delta \cos(2\varphi)+\omega^*)/T} + 1)(e^{\Delta \cos(2\varphi)/T} + e^{\omega^*/T})}.
 \end{aligned} \tag{37}$$

222 As presented in Fig. 8, the peak specific heat at $T = T_c$ for d-wave superconductivity
 223 follows the trend of s-wave, though large heat capacity jumps are extended to larger θ / λ
 224 or higher doping levels. Again, compared to a constant jump ratio of about 0.95 for BCS
 225 d-wave, the normalized jump ratio in CEH varies (reaching ~ 1.2 at $\lambda = 2$). The d-wave
 226 ratio is generally lower than the s-wave one due to a slower decrease in C_N as θ and λ
 227 increase.

228 One notable finding in CEH is its unique prediction of a non-zero linear term in the
 229 d-wave heat capacity at the zero-temperature limit, as shown in Fig. 9. This non-zero offset
 230 originates from the $d_2(\varphi, T)$ term of Eq. 34 (see Appendix B),

$$\gamma(0) \equiv \left. \frac{C_{sc}(T)}{T} \right|_{T \rightarrow 0} = \frac{8\pi}{3} \left(\frac{\pi}{4} - \theta \right) \rho_F \neq 0 \tag{38}$$

231 which explains the “anomalous linear term” observed in the heat capacity of cuprates [23, 24].
 232 It may not approach zero even at the extreme overdoping limit where $\theta = \pi/4$ or $\lambda \rightarrow$
 233 ∞ . Assuming a constant four-fermion interaction strength, i.e., $\lambda \propto \rho_F$, and taking into
 234 account Eq. 22, we see that $\gamma(0)$ decreases as the doping level or λ increases, and we obtain
 235 its underdoping-to-overdoping ratio $\gamma(0)_{UL}/\gamma(0)_{OL} = \pi^2/4 \approx 2.47$ calculated at the two
 236 extreme doping limits, which agrees very well with the cuprate measurements [24, 25].

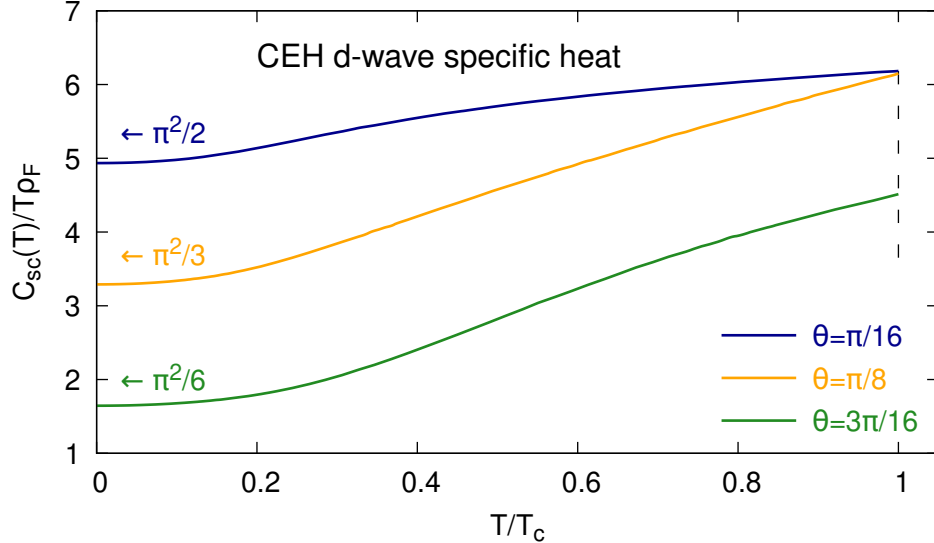


FIG. 9. The temperature dependence of heat capacity $C_{sc}(T)/(T\rho_F)$ is shown for d-wave CEH superconductivity. Cases with three different coupling strengths $\theta = \pi/16, \pi/8, 3\pi/16$ are presented.

237 The next leading order at $T \rightarrow 0$ in Fig. 9 is contributed from both terms (see Appendix
238 B),

$$\frac{C_{sc}(T)}{T\rho_F} - \frac{\gamma(0)}{\rho_F} \simeq \left(\frac{8\pi}{3\theta} + \frac{14\pi^3}{15 \tan 2\theta} \right) \frac{1}{\sin^2 2\theta} \left(\frac{T}{\Delta_0} \right)^2 \quad (39)$$

239 where the first part within the parentheses is calculated from the $d_1(\varphi, T)$ term and the
240 second from the $d_2(\varphi, T)$ term. This exactly explains the quadratic behavior observed in
241 the heat capacity curve of C/T at $T \ll T_c$ in d-wave superconducting cuprates [26–28].

242 V. DISCUSSIONS AND COMPARISONS WITH EXPERIMENTAL DATA

243 The proposed CEH mechanism provides many unique predictions that are distinct from
244 the well known BCS results. These differences have been discussed above in detail and are
245 also summarized in Table I. In particular, CEH naturally explains the necessity of antiferro-
246 magnetism and strong coupling in non-BCS superconductivity. Most strikingly, many of its
247 predictions agree very well with existing experimental data on non-BCS superconductors,
248 particularly cuprates and FeSCs. Several such examples will be illustrated below.

249 CEH conducts current via relative motion and this may explain why flat bands are favored
250 in high- T_c superconductivity. The key feature in CEH is the ω^* energy shell, which could
251 function as both the superconducting band for CEH pairs and an energy gap (closely related
252 to the widely-recognized pseudogap) for normal state electrons. This ω^* band may be one of
253 the flat bands where center-of-mass motion is forbidden, making it ideal for the formation
254 of antiferromagnetism and CEH pairs. For easier comparison with data below, we assume a
255 simple linear relationship between ω^* and the pseudogap temperature T^* : $\omega^* \propto T^*$.

256 In the undoped parent compound, ω^* typically exceeds the superconducting gap Δ , which
257 can disrupt the stability of CEH pairs with additional energy. Doping, however, plays a cru-
258 cial role in reducing ω^* , making it below the level of Δ , and thereby facilitating the onset

TABLE I. Summary of comparisons of some major results between BCS and CEH. The results from BCS are calculated in the weak-coupling limit and other extensions using stronger electron-phonon couplings may differ.

Model	BCS		CEH	
material	averse to magnetism		desirous of antiferromagnetism	
mechanism	Cooper pairs		chiral electron-hole pairs	
SC criteria	no constraint on Debye ω_D		$\omega^* < \Delta(T)$	
symmetry	s-wave	d-wave	s-wave	d-wave
coupling	weak coupling $\lambda \ll 1$		strong coupling $\lambda > 1$ $\lambda > \frac{\pi}{2}, 0 < \theta < \frac{\pi}{4}$	
$E_{\mathbf{k}}^{\pm} =$	$\pm \sqrt{\xi_{\mathbf{k}}^2 + \Delta ^2}$	$\pm \sqrt{\xi_{\mathbf{k}}^2 + \Delta \cos 2\varphi ^2}$	$\xi_{\mathbf{k}} \pm \Delta $	$\xi_{\mathbf{k}} \pm \Delta \cos 2\varphi $
gap equation	$\frac{1}{\lambda} = \int_0^{\omega_D} d\xi \frac{\tanh(E^+/2T)}{E^+}$	$\frac{1}{\lambda} = \int_0^{2\pi} d\varphi \frac{\cos^2 2\varphi}{2\pi} \times \int_0^{\omega_D} d\xi \frac{\tanh(E^+/2T)}{E^+}$	Eq. 11	Eq. 12
$\Delta_0 =$	$2\omega_D e^{-1/\lambda}$	$2.426\omega_D e^{-2/\lambda}$	$\lambda\omega^*$	$\omega^*/\cos 2\theta$
T_c or $T_0 =$	$T_c = T_0$ $T_c = 1.134\omega_D e^{-1/\lambda}$	$T_c = T_0$ $T_c = 1.134\omega_D e^{-2/\lambda}$	$T_c < T_0$ $T_0 = \frac{\omega^*}{2 \tanh^{-1}(1/\lambda)}$	$T_c < T_0$ $T_0 = \frac{\omega^*}{2 \tanh^{-1}(\pi/2\lambda)}$
$\Delta_0/T_c =$	1.764	2.140	> 2 (Fig. 2)	$\gtrsim 3.077$ (Fig. 4)
$\Delta(T_c)$	$\Delta(T_c) = 0$, gap closes at T_c		$\Delta(T_c) = \omega^* \neq 0$, does not close at T_c	
$\frac{\Delta(T)}{\Delta_0}$ vs. $\frac{T}{T_c}$	dashed line in Fig. 3		Fig. 3	Fig. 5
specific heat	exponentially approaches 0		Figs. 7-6	Figs. 8-9
$C/T(T \rightarrow 0)$	exponentially approaches 0		exponentially approaches 0	quadratically to $\frac{8\pi}{3}(\frac{\pi}{4} - \theta)\rho_F \neq 0$
jump at T_c	1.43	0.95	varies with λ	varies with θ

of superconductivity. Meanwhile, doping tends to increase the coupling parameter λ as the density of states in the ω^* band rises due to unitarity or conservation of the number of quantum states in a compressed ω^* band. High-pressure-induced superconductivity, investigated in various materials, may introduce similar effects by compressing the ω^* band with external pressure.

It have been observed in various cuprate superconductors that the ratio Δ_0/T_c exceeds three. This ratio has been shown to undergo a dramatic increase with decreasing doping and approach a limit of three near maximum doping (see Fig. 3 of Ref. [29] and the references therein). This behavior aligns well with our d-wave prediction based on the new pairing mechanism as shown in Fig. 2. To further demonstrate this, a direct comparison between CEH predictions and experimental data for $\text{HgBa}_2\text{CuO}_{4+\delta}$ (Hg-1201) [30] is presented in Fig. 10. A good fit to the experimental data is achieved using a simple $\lambda - p$ parametrization discussed below. Furthermore, large Δ_0/T_c ratios, consistent with CEH s-wave predictions, have also been observed in iron-based superconductors [12].

It has been observed in various studies (e.g., [30–32]) that the non-BCS superconducting gap does not close at the critical temperature, exhibiting a behavior similar to that shown in Fig. 5. In particular, in Fig. 3 of Ref. [30], the trend of the temperature dependence closely resembles our results and also displays a similar deviation from the BCS prediction.

Another piece of clear and convincing evidence comes from the detailed analysis of d-wave specific heat presented above, which is worth reiterating. CEH predicts a non-zero linear

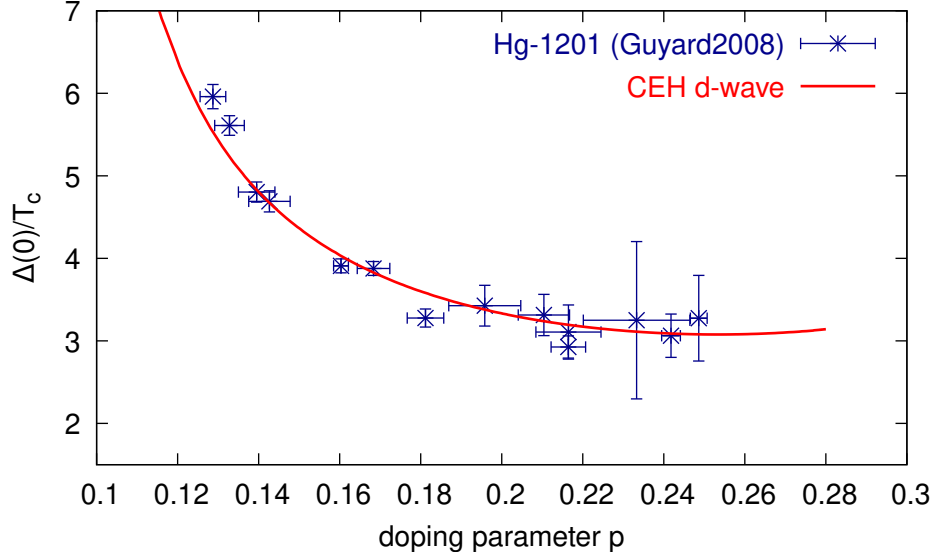


FIG. 10. Δ_0/T_c as a function of the doping level predicted by d-wave CEH is shown in good agreement with the $\text{HgBa}_2\text{CuO}_{4+\delta}$ (Hg-1201) data [30], which are much higher than the BCS weak-coupling limit value of 2.140.

term in heat capacity at $T = 0$ for d-wave superconductors, a phenomenon well observed in many cuprates [23–25]. Furthermore, the predicted quadratic temperature dependence in C/T near zero temperature is also in agreement with observations [26–28], in stark contrast to the BCS linear dependence.

To make direct comparisons between CEH predictions and the wealth of data accumulated over decades of high- T_c superconductivity studies, it is necessary to establish a concrete relationship between the coupling parameter λ and the doping level parameter p . We will start with some rough yet simple estimates to facilitate direct comparisons to the data. For strongly correlated parent compounds like cuprates or FeSCs, it is reasonable to assume that the initial coupling parameter $\lambda \sim 1$. Doping then increases the density of charge carrier states, effectively making λ larger. It has been observed that the carrier density increases very rapidly at very low doping levels and then more gradually at higher doping levels [33]. At low doping levels or in the case of CEH s-wave superconductors, we can approximate this with the following $\lambda - p$ relation

$$\lambda = 1 - \frac{1}{\log(p/p_m)} \quad (40)$$

where p_m is the maximum doping level corresponding to $\lambda \rightarrow \infty$. For the example of an s-wave FeSC discussed below, we choose to adopt $p_m = 1/3$.

However, CEH d-wave superconductors require larger correlations, specifically, $\lambda > \pi/2$, which means that superconductivity will not occur until the doping reaches a minimum level p_0 . To describe d-wave superconductors, we can apply the following parametrization,

$$p = p_0 + a \sin^2 \theta. \quad (41)$$

For the comparison shown in Fig. 10, parameters of $p_0 = 0.08$ and $a = 0.4$ are adopted.

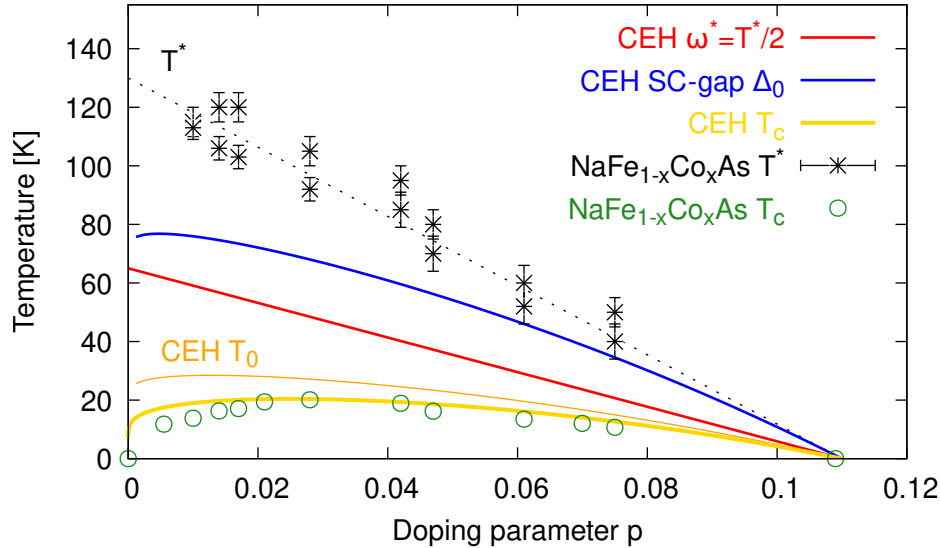


FIG. 11. Phase diagram, predicted by CEH assuming that $p_m = 1/3$ and $\omega^* = 0.5T^*$, is compared to experimental data on NaFe_{1-x}Co_xAs [34, 35].

Using the $\lambda - p$ and $\theta - p$ relations given in Eqs. 40-41, we can compare the phase diagrams constructed from CEH to experimental data in two examples. The first example involves NaFe_{1-x}Co_xAs with experimental data taken from Refs. [34, 35]. Fig. 11 shows the results from CEH assuming that $p_m = 1/3$ and $\omega^* = 0.5T^*$. The superconducting phase and T_c values derived from s-wave CEH agree well with the data. One possible issue is that T_c appears moderately overestimated at extremely low doping levels ($p \lesssim 0.01$), which could stem from the oversimplified parametrization in Eq. 40. The $\lambda - p$ relation may require more nuanced treatment at extremely low doping levels where the density of states undergoes the most significant changes. Other parameters such as the superconducting gap Δ_0 and the gap closing temperature T_0 predicted by s-wave CEH are also depicted in Fig. 11.

Another example is the phase diagram of La_{2-x}Sr_xCuO₄ (LSCO). In Fig. 12, a comparison between the measured LSCO data [36, 37] and the d-wave predictions from CEH ($p = 0.05 + 0.94 \sin^2 \theta$ and $\omega^* = 1.5T^*$) is presented. The superconducting phase, characterized by the well-known dome shape for cuprates, is well reproduced and CEH shows good agreement with both the data [36] and the universal T_c parametrization of $T_c/T_c^{\max} = 1 - 82.6(p - 0.16)^2$ [38] using $T_c^{\max} = 38K$ for LSCO.

The same $\theta - p$ relation applied in LSCO, along with $\omega^* = 2.3T^*$, also performs equally well in predicting the phase diagram of YBCO, despite significantly higher T^* and T_c values in YBCO. More systematic comparisons, especially to experimental data on Δ_0 and T_0 , will provide more compelling evidence for CEH. Further comparisons with other non-BCS superconducting materials would offer more valuable insights into understanding these parametrization relations.

Note that the T^* lines shown in both Figs. 11 and 12 do not agree with an alternative view where the T^* line could cross into the superconducting phase and end at a smaller critical doping point. This is because the pseudogap phase between the T^* and T_c lines is related to superconductivity, that is, the pseudogap is not an independent order competing with superconductivity in the CEH mechanism. It could possibly be understood as a short-range

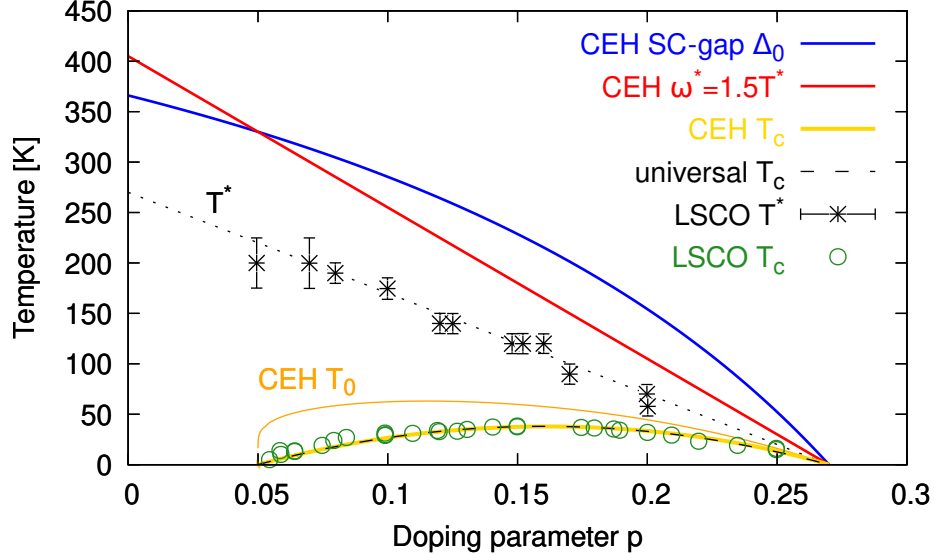


FIG. 12. Phase diagram, predicted by CEH assuming that $p = 0.05 + 0.94 \sin^2 \theta$ and $\omega^* = 1.5T^*$, is compared to experimental data on $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$ (LSCO) [36, 37].

326 antiferromagnetic order in the phase between T^* and T_0 , e.g., a liquid of antiferromagnetic
 327 singlet dimer states as proposed in the resonating valence bond theory [39]. When it enters
 328 the phase between T_0 and T_c , these antiferromagnetic dimers could transition into CEH
 329 dimers due to the appearance of superconducting gap. However, these preformed CEH pairs
 330 could not superconduct owing to the condition of $\omega^* > \Delta(T)$ in this phase, which could
 331 easily convert these pairs back to normal antiferromagnetic dimers. The long-range CEH
 332 order could only be established for unconventional superconductivity under the condition of
 333 $\omega^* < \Delta(T)$ at $T < T_c$.

334 VI. CONCLUSIONS AND OUTLOOK

335 Using the new chiral electron-hole pairing mechanism, we provide a more comprehensive
 336 understanding of non-BCS superconductivity in a strongly correlated electron system. Our
 337 new predictions are remarkably consistent with numerous puzzling properties observed in
 338 cuprate and FeSC superconductors such as the unexpectedly large Δ_0/T_c ratios, the absence
 339 of gap closure at T_c , the presence of a non-zero $\gamma(0)$ term and a quadratic trend in the heat
 340 capacity ratio of C/T as $T \rightarrow 0$ in cuprates, among others. Further measurements (e.g.,
 341 on T_0) and systematic comparisons with experimental data across diverse material types
 342 will provide more stringent tests on the CEH mechanism. A better understanding of the
 343 ω^* band and the λ -doping level relationship may help identify even more promising high- T_c
 344 superconducting materials in the near future.

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 347 of Notre Dame. The author would like to thank Edwin Huang for his insightful comments.

348

Appendix A: d-wave $\lambda - \theta$ relation

349 The d-wave gap equation (Eq. 12) can be rewritten as,

$$\Delta(T) = \frac{4\lambda T}{\pi} \int_0^{\pi/4} d\varphi \log \left(\frac{e^{(\Delta \cos 2\varphi + \omega^*)/T} + 1}{e^{\Delta \cos 2\varphi/T} + e^{\omega^*/T}} \right). \quad (\text{A1})$$

350 As $T \rightarrow 0$, the integrand becomes $\Delta \cos 2\varphi/T$ if $\Delta \cos 2\varphi < \omega^*$ and ω^*/T otherwise. By
351 introducing a new parameter θ with

$$\cos(2\theta) = \omega^*/\Delta_0 \quad (\text{A2})$$

352 where the range of θ is limited to $0 < \theta < \pi/4$, we obtain in the zero-temperature limit

$$\begin{aligned} \Delta_0 &= \frac{4\lambda T}{\pi} \left(\int_0^\theta d\varphi \frac{\omega^*}{T} + \int_\theta^{\pi/4} d\varphi \frac{\Delta_0 \cos 2\varphi}{T} \right) \\ &= \frac{4\theta}{\pi} \lambda \omega^* + \frac{2(1 - \sin 2\theta)}{\pi} \lambda \Delta_0 \end{aligned} \quad (\text{A3})$$

353 which, by using Eq. A2, immediately leads to the d-wave $\lambda - \theta$ relation as given in Eq. 22.

354

Appendix B: d-wave specific heat at $T \rightarrow 0$

355 The d-wave specific heat in Eq. 34 can be expressed as a sum of two terms: $C_{sc} = C_2 + C_1$
356 where $C_{2,1}$ involve the integration of the two functions $d_{2,1}(\varphi, T)$, respectively. For both
357 terms, the integration with respect to φ can be divided into two parts: from 0 to θ' and from
358 θ' to $\pi/4$, where $\cos 2\theta' = \omega^*/\Delta$. For convenience, we introduce the following definitions,

$$y_\pm \equiv (\cos 2\varphi \pm \cos 2\theta')\Delta/T \quad (\text{B1})$$

$$h_n(x) \equiv \frac{e^x}{(e^x + 1)^2} x^n. \quad (\text{B2})$$

359

1. C_1 contribution at $T \rightarrow 0$

360 First, we work with the C_1 term where we can simplify the second part of the integral as
361 follows,

$$\begin{aligned} \int_{\theta'}^{\pi/4} d\varphi \cos 2\varphi \int_{y_-}^{y_+} dx h_1(x) &= \int_{\theta'}^{\pi/4} d\varphi \cos 2\varphi \left(\int_{-y_+}^{y_+} - \int_{-y_+}^{-|y_-|} \right) dx h_1(x) \\ &= \int_{\theta'}^{\pi/4} d\varphi \cos 2\varphi \int_{|y_-|}^{y_+} dx h_1(x) \end{aligned} \quad (\text{B3})$$

362 because $h_1(x)$ is an odd function. By taking the limit of $y_+ \rightarrow \infty$ as $T \rightarrow 0$ and the following
363 integration,

$$\int_y^\infty dx h_1(x) = \log(1 + e^y) - ye^y/(e^y + 1) \equiv j(y), \quad (\text{B4})$$

364 where $j(y)$ is odd as well, we can obtain the full integration as,

$$\begin{aligned} \int_0^{\pi/4} d\varphi \cos 2\varphi \int_{y_-}^{y_+} dx h_1(x) &= \left(\int_0^{\theta'} \int_{y_-}^{y_+} + \int_{\theta'}^{\pi/4} \int_{|y_-|}^{y_+} \right) d\varphi dx \cos 2\varphi h_1(x) \\ &= \left(\int_0^{\theta'} + \int_{\theta'}^{\pi/4} \right) d\varphi \cos 2\varphi j(|y_-|). \end{aligned} \quad (\text{B5})$$

365 By a change of variable from φ to y_- , we obtain for the first part,

$$\begin{aligned} \int_0^{\theta'} d\varphi \cos 2\varphi j(y_-) &= \int_0^{(1-\cos 2\theta')\Delta/T} dy_- j(y_-) \frac{T}{2 \tan 2\varphi \Delta} \\ &= \frac{\pi^2 T}{12 \tan 2\theta' \Delta} \end{aligned} \quad (\text{B6})$$

366 where the main contribution arises from the vicinity of $\varphi \sim \theta'$, allowing us to approximate
367 $\tan 2\varphi$ with $\tan 2\theta'$, and the upper limit of integration becomes ∞ as $T \rightarrow 0$, allowing us to
368 use the identity $\int_0^\infty dy j(y) = \pi^2/6$. Likewise, the second part of the integral yields the same
369 result.

370 From Eq. 25, we can obtain the derivative of the gap,

$$\frac{\partial \Delta(T)}{\partial T} = -\frac{2T}{\theta' \sin(2\theta') \cos(2\theta') \Delta}. \quad (\text{B7})$$

371 Putting them all together, we can obtain the C_1 contribution to the specific heat,

$$\frac{C_1}{T \rho_f} = \frac{8\pi}{3\theta' \sin^2 2\theta'} \left(\frac{T}{\Delta} \right)^2 \quad (\text{B8})$$

372 which gives the first term in Eq. 39 by replacing θ' and Δ with $\theta' = \theta$ and $\Delta = \Delta_0$ at $T = 0$.

373

2. C_2 contribution at $T \rightarrow 0$

374 Similarly, contributions to the C_2 term can be separated into three parts,

$$\begin{aligned} \int_0^{\pi/4} d\varphi \int_{y_-}^{y_+} dx h_2(x) &= \left(\int_0^{\theta'} \int_{y_-}^{y_+} - \int_{\theta'}^{\pi/4} \int_{|y_-|}^{y_+} + \int_{\theta'}^{\pi/4} \int_{-y_+}^{y_+} \right) d\varphi dx h_2(x) \\ &\equiv C'_{2a} + C'_{2b} + C'_{2c} \end{aligned} \quad (\text{B9})$$

375 because $h_2(x)$ is an even function.

376 We can easily integrate out the last part by taking $y_+ \rightarrow \infty$ as $T \rightarrow 0$ and $\int_{-\infty}^{\infty} dx h_2(x) =$
377 $\pi^2/3$,

$$C'_{2c} = \int_{\theta'}^{\pi/4} d\varphi \int_{-\infty}^{\infty} dx h_2(x) = \frac{\pi^2}{3} \left(\frac{\pi}{4} - \theta' \right) \quad (\text{B10})$$

378 which gives the non-zero offset in Eq. 38.

379 The first part of Eq. B9 can be worked out by changing the order of integration as follows,

$$C'_{2a} = \left(\int_0^{x_1} \int_{\cos 2\theta'}^{Tx/\Delta + \cos 2\theta'} + \int_{x_1}^{x_2} \int_{\cos 2\theta'}^1 + \int_{x_2}^{x_3} \int_{Tx/\Delta - \cos 2\theta'}^1 \right) dx h_2(x) \frac{d \cos 2\varphi}{2 \sin 2\varphi} \quad (\text{B11})$$

380 where $x_1 = (1 - \cos 2\theta')\Delta/T$, $x_2 = 2 \cos 2\theta'\Delta/T$, or vice versa, and $x_3 = (1 + \cos 2\theta')\Delta/T$.
 381 As $T \rightarrow 0$, we have $x_{1,2,3} \rightarrow \infty$, rendering the last two terms in the above integral negligible.
 382 The integration with respect to φ in the first term results in $\theta' - \cos^{-1}(Tx/\Delta + \cos 2\theta')/2$.
 383 Using the following expansion,

$$\cos^{-1}(t + \cos 2\theta) = 2\theta - \frac{t}{\sin 2\theta} - \frac{\cos 2\theta t^2}{2 \sin^3 2\theta} + O(t^3), \quad (\text{B12})$$

384 we can simplify the integral as

$$C'_{2a} = \frac{T}{2 \sin 2\theta' \Delta} \int_0^\infty dx h_3(x) + \frac{\cos 2\theta'}{4 \sin^3 2\theta} \left(\frac{T}{\Delta}\right)^2 \int_0^\infty dx h_4(x) + O(T^3). \quad (\text{B13})$$

385 The second part of Eq. B9 can be treated similarly as,

$$C'_{2b} = - \left(\int_0^{x_4} dx h_2(x) \int_{\cos 2\theta' - Tx/\Delta}^{\cos 2\theta'} + \int_{x_4}^{x_2} dx h_2(x) \int_{Tx/\Delta - \cos 2\theta'}^{\cos 2\theta'} \right) \frac{d \cos 2\varphi}{2 \sin 2\varphi} \quad (\text{B14})$$

386 where $x_4 = \cos 2\theta'\Delta/T$ and again, only the first term contributes. Then it can be worked
 387 out as,

$$C'_{2b} = - \frac{T}{2 \sin 2\theta' \Delta} \int_0^\infty dx h_3(x) + \frac{\cos 2\theta'}{4 \sin^3 2\theta} \left(\frac{T}{\Delta}\right)^2 \int_0^\infty dx h_4(x) + O(T^3). \quad (\text{B15})$$

388 The linear terms in Eqs. B13 and B15 exactly cancel each other out. By summing up the
 389 two parts and using $\int_0^\infty dx h_4(x) = 7\pi^4/30$, we obtain the C_2 contribution to the quadratic
 390 temperature dependence, which gives the second term in Eq. 39.

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