Charge 4e superconductor: a wavefunction approach

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The BCS theory of superconductivity is one of milestones in condensed matter physics, which successfully unveils the nature of this macroscopic quantum phenomenon at a microscopic level [1, 2]. The essential ingredients for any superconductors (SCs) are the two-electron Cooper pairs and their phase coherence [2], where electrons bind together two by two and condense to form a coherent quantum state, as illustrated in Fig.1(a). However, condensing two-electron Cooper pairs is not the only way to achieve superconductivity. Theoretically, it was proposed that the four-electron Cooper pairs can also condensate to form an SC, namely the charge 4e SC [3–6]. Experimentally, how to realize and condense to form a coherent quantum state, as illustrated in Fig.1(b) [3–6].

Although there is much progress in this field, how to describe this charge 4e SC microscopically and what are the electronic properties of this charge 4e SC remain open questions. For instance, whether this SC is gapped and the superfluid density of it are not fully understood. The first attempt to solve these issues microscopically is from a quantum Monte Carlo study [6]. Motivated by this numerical study and recent progress, we address the general microscopic properties of the charge 4e SC from a wavefunction approach in this work.

The BCS wavefunction faithfully describes the essential physical properties of SCs, especially Cooper pairs and their phase coherence. Inspired by it, we construct a ground state wavefunction |GS⟩ for charge 4e SC

|GS⟩ = ∏ k (u_k + v_k e^{iθ} c_{1↓k}^† c_{1↑k}^† c_{2↓2k}^† c_{2↑2k}^†) |0⟩, (1)

which has the similar structure as BCS wavefunction. Here, we introduce the orbit index 1, 2 to fulfill the Pauli exclusion principle. This orbital index can be any charge 4e index, like real atom orbitals, the PDW order momentum ±Q, valley degree of freedom, etc. Besides the four electron pairing term $c_{1↓k}^† c_{1↑k}^† c_{2↓2k}^† c_{2↑2k}^†$, the most important ingredient of |GS⟩ is the phase factor $e^{iθ}$. This factor is the crucial U(1) spontaneously symmetry breaking term leading to the phase coherence of charge 4e condensates as in the BCS wavefunction, which leads to the Meissner effect, Josephson effect and other SC quantum properties. To simplify our discussion, we first choose this $θ = 0$ without losing the generality.

Equipped with this wavefunction |GS⟩, the next step is to find the mean-field Hamiltonian for this wavefunction and determine the coherence factors $u_k$, $v_k$. It is easy to prove that this wavefunction is the eigenstate of following charge 4e mean-field Hamiltonian

$$\hat{H}_{4e} = \sum_{kα} ε_{αk} (c_{α↑k}^† c_{α↑k} + c_{α↓k}^† c_{α↓k}) - \sum_k (Δ_{2k} c_{1↑k}^† c_{1↓k}^† c_{2↑2k}^† c_{2↓2k}^† + h.c.)$$ (2)

where $α = 1, 2$. We also choose $ε_{1k} = ε_k$ for two degenerate orbitals and leave the general cases in the supplemental materials (SM). The ground state energy is found to be $E_G = \sum_k 2ε_k - E_k$, where $E_k = \sqrt{4ε_k^2 + Δ_k^2}$. And the $u_k$, $v_k$ take the similar factors as the Bogoliubov–Valatin transformation treatment of BCS theory

$$u_k^2 = \frac{1}{2} \left( 1 + \frac{2ε_k}{E_k} \right)$$ (3)

$$v_k^2 = \frac{1}{2} \left( 1 - \frac{2ε_k}{E_k} \right)$$ (4)

Furthermore, the excited states can be constructed from the |GS⟩ wavefunction and $\hat{H}_{4e}$ Hamiltonian. For each $k$, there are several types of excited states including single-particle excitation, pair excitation and single-hole excitation.

The Green’s functions of charge 4e SC can be calculated using the Lehmann representation. We start from the single particle retard Green’s function $G^R(k, t)_{αβ} = -iθ(t)\langle |c_{αkσ}(t), c_{βkσ}(0)⟩ |0⟩$. After the Fourier transform, it is obtained as

$$G^R(kσ, ω)_{αβ} = \frac{u_k^2}{ω + iη - (E_k - ε_k)} + \frac{v_k^2}{ω + iη + (E_k + ε_k)}$$ (5)

More detailed calculations can be found in SM. Note that the two poles of the Green’s function are not particle-hole symmetric counterpart, which is an important feature of charge 4e SC and affects the superfluid density we will show later.
However, since the 2e condensation is absence, the anomalous Green’s function \( F(k, \omega) = -i\langle \hat{T}_c^\dagger C_{\alpha,-k}\hat{T}_c C_{\beta,k}(0)\rangle_{GS} \) is always zero. The charge 4e condensation relevant anomalous Green’s function is the two-particle anomalous Green’s function \( \Gamma_F = -\langle \hat{T}_c^\dagger C_{\alpha,-k}\hat{T}_c C_{\beta,k}\hat{T}_c^\dagger C_{\gamma,-l}\hat{T}_c C_{\delta,l}(0)\rangle_{GS} \), whose diagram is shown in Fig.1(c). The Fourier transform is expressed as \( \Gamma_F(k, \omega_1, \omega_2, \omega_3) \) whose explicit form can be found in SM.

From the Green’s functions, we can determine the density of states (DOS) of this system from \( \rho(\omega) = -\frac{\pi}{\hbar} \sum_{\alpha\beta} \text{Im} G^R(k\alpha, \omega) \). For a constant pairing potential \( \Delta_k = \Delta \), an analytical expression is obtained in the SMs Eq.S6. We can find this system is a full gap system as expected. However, the gap decreases compared to charge 2e SC. At \( \omega = \pm \sqrt{3} \Delta \), different from \( \omega = \pm \Delta \) in the 2e case, the DOS shows square root divergence. To compare with d-wave pairing with \( \Delta_k = \Delta (\cos k_x - \cos k_y) \), we also carry out a numerical calculation on the square lattice. The DOS for s-wave SC \( \Delta_k = \Delta \) is plotted in Fig.1(d) with U-shape DOS. The DOS for d-wave SC is plotted in Fig.1(e) with V-shape DOS. Hence, the charge 4e is gapped or not is determined by the gap function \( \Delta_k \) in our two orbital degenerate limit. In the following discussion, we always choose a constant pairing \( \Delta \) to capture the main feature of charge 4e superconductivity.

Regarding to the phase coherence of SC, an important prediction is the flux quantization. Taking the dynamic terms with gauge field \( \mathbf{A} \) into account, the free energy for charge 4e SC must contain the gauge invariant terms as

\[
\mathcal{F} = -\frac{\rho_s}{2} \int dx (\nabla \phi(x) - \frac{4e}{\hbar} \mathbf{A}(x))^2 + F_0
\]

where \( \rho_s \) is the superfluid density and \( F_0 \) is the other irrelevant term. The current density can be found

\[
\mathbf{j}(x) = -\frac{\delta \mathcal{F}}{\delta \mathbf{A}} = \rho_s \frac{4e}{\hbar} \nabla \phi(x) - \mathbf{A}(x)
\]

In a superconducting ring with magnetic field through its hole is shown in Fig.1(f), we choose a loop C as in Fig.1(f) without any current. Then, the loop integral of Eq.7 gives \( \Phi = \oint_C A = \frac{\Phi_0}{2} \). Hence, the flux trapped in this ring is quantized as the integer multiple of flux quantum \( \Phi_0 = \frac{\hbar}{2e} \), which is half of charge 2e SC. This quantization condition provides a direct “smoking gun” for charge 4e SC.

The superfluid density in Eq.7 can be obtained from the linear response theory.

\[
J_{\mu}(\mathbf{x}) = \sum_{\nu} \left[ \left( -e^2 \right) \Pi_{\mu\nu} - \frac{e^2 \rho}{m} \delta_{\mu\nu} \right] A_{\nu}.
\]

where \( \rho \) is the electron density. The \( \Pi_{\mu\nu} \) is the paramagnetic current-current correlation function, which is obtained from the Kubo formula as

\[
\Pi_{\mu\nu} (\mathbf{q}, \omega) = -\frac{i}{\hbar} \int_0^\infty dt e^{i\omega t} \langle [J_{\mu} (\mathbf{q}, t), J_{\nu} (-\mathbf{q}, 0)] \rangle.
\]
The calculation can be done from the Feynman diagram in the top panel of Fig.1(g). The $\frac{CP}{m} \delta_{0\nu}$ is the diamagnetic contribution. Using this Kubo formula, we find the superfluid electron density $\rho_s = 3\rho/4$ at zero temperature, which is different from $\rho_s = \rho$ in charge 2e superconductors. This is because the diagram contribution from the anomalous Green’s function $F$ vanishes here.

The reduction of superfluid density can also be understood from the optical perspective. In charge-2e SC, the optical transition between the two quasiparticle band is forbidden due to the optical selection rule from particle-hole symmetry, as proved in Ref. [15]. In charge-4e case, however, the two poles of the Green’s function Eq.5 are not particle-hole symmetric counterpart. Thus the momentum conserved transition between them exists as shown in Fig.1(h), resulting in some spectral weights not being transferred to zero frequency like charge 2e SC. Then the optical sum rule requires that the superfluid density must be reduced. This may be another evidence of charge 4e SC for experimental verifications.

Besides the flux quantization, another key prediction of BCS theory is the Josephson effect, where Cooper pairs can tunnel between two SCs sandwiched by a tunneling barrier. We also calculate the Josephson current in our charge 4e model through the Feynman diagram in the bottom panel of Fig.1(g). The DC Josephson current has the relation as $I = I_c \sin(\phi)$ where $\phi$ is the phase difference between the two SCs in the Josephson junction and the detailed calculation of critical current $I_c$ can be found in SM. Notice here, there are only four-electron Cooper pairs can tunnel through the junction since 2e condensates are zero.

More importantly, the gauge invariance also requires that $\frac{dI}{dt} = \frac{4e}{\hbar} V$. The AC Josephson effect with voltage bias $V$ must be $I(t) = I_c \sin(\frac{2\pi}{\Phi_0} V t + \phi)$. From this expression, we can find that the AC Josephson effect measurement can be served as another hallmark for charge 4e SC, where the current frequency $\omega_0$ is equal to the $\frac{4e}{\hbar} V$ [6].

Finally, a natural question arises: whether we can have the coexistence of charge 2e and charge 4e SCs. Then, the wavefunction for this case can be written as

$$|GS\rangle_{2e-4e} = \prod_k (u_k + v_{1k} c_{1k}^\dagger c_{1-k} + v_{2k} c_{2k}^\dagger c_{2-k} + v_{4k} c_{1k}^\dagger c_{1-k} + v_{2k} c_{2k}^\dagger c_{2-k}) |0\rangle$$

(10)

This $|GS\rangle_{2e-4e}$ should be the ground state wavefunction for the charge 2e/4e mixed hamiltonian $\hat{H}_{2e-4e}$ as

$$\hat{H}_{2e-4e} = \sum_{k\alpha} \xi_{\alpha k} (c_{\alpha k}^\dagger c_{\alpha k} + c_{\alpha-k}^\dagger c_{\alpha-k})$$

$$- \sum_{k\alpha} (\Delta_{\alpha k} c_{\alpha k}^\dagger c_{\alpha-k} + h.c.)$$

$$- \sum_{k\alpha} (\Delta_{\alpha k} c_{\alpha-k}^\dagger c_{\alpha-k} + h.c.)$$

(11)

where $u_k$, $v_{1/2/4k}$ factors can be calculated numerically. The corresponding Green’s functions and physical properties can be obtained following above procedures.

In conclusion, we apply a wavefunction approach to study the charge 4e SCs. The wavefunction takes a similar structure to the BCS wavefunction for charge 2e SCs. The mean-field Hamiltonian and the Green’s functions of charge 4e are constructed. The physical properties including the density of states, gauge invariance, flux quantization and Josephson effects are systematically studied. All these findings provide a microscopic description of charge 4e SC. We hope our work could stimulate the investigation of charge 4e SC and call for further experimental tests.

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