Mesoscopic superconductivity in ultra-small metallic grains

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• Introduction

• Superconducting metallic grains (nanoparticles): BCS (bulk) regime and fluctuation-dominated regime.

(I) Nanoparticles without spin-orbit scattering: competition between pairing (superconductivity) and spin exchange correlations (ferromagnetism).

• Thermodynamic signatures of the coexistence of pairing and spin exchange correlations.

(II) Nanoparticles with spin-orbit scattering

Many-particle level response to an external magnetic field: g-factor and level curvature statistics

• Effects of pairing correlations on the g-factor and level curvature distributions.

• Conclusion
Introduction: ultra-small metallic grains (nanoparticles)

- Discrete energy levels extracted from non-linear conductance measurements (Ralph et al).
- Experiments on Al, Co, Au, Cu, Ag.
- Ultra-small (nano-scale) grains: probe the quantum regime $T \ll \delta$
- Recent high-quality data in Au grains.

Superconducting grains

Consider materials that are superconductors in the bulk and characterized by a pairing gap $\Delta$.

$\delta = \text{single-particle level spacing}$.

Many-particle spectrum for an even number of electrons:
(i) Large grains (~ 10 nm) \( \Delta \gg \delta \)

The pairing gap is directly observed in the spectra of such grains with even number of electrons.

- The Bardeen-Cooper-Schrieffer (BCS) theory is valid (BCS regime)

(ii) Small grains (~ 1 nm) \( \Delta \leq \delta \)

- BCS theory breaks down.
  Anderson: “superconductivity would no longer be possible.”

A mesoscopic regime dominated by large fluctuations of the pairing gap (fluctuation-dominated regime).

Do signatures of pairing correlations survive the large fluctuations?
(I) Superconducting nanoparticles without spin-orbit scattering

An isolated chaotic grain with a large number of electrons is described by the universal Hamiltonian [Kurland, Aleiner, Altshuler, PRB 62, 14886 (2000)]

\[
H = \sum_i \mathcal{E}_i (a_i^{\dagger} a_i^{\uparrow} + a_i^{\dagger} a_i^{\downarrow}) + \frac{e^2}{2C} N^2 - G P^\dagger P - J_s \vec{S}^2
\]

- Discrete single-particle levels \( \mathcal{E}_i \) (spin degenerate) and wave functions follow random matrix theory (RMT).
- Attractive BCS-like pairing interaction (\( P^\dagger = \sum_i a_i^{\dagger} a_i^{\dagger} \) is the pair operator) with coupling \( G > 0 \).
- Ferromagnetic exchange interaction (\( \vec{S} \) is the total spin of the grain) with exchange constant \( J_s > 0 \).

Competition between pairing and exchange correlations: pairing favors \textit{minimal} ground-state spin, while exchange favors \textit{maximal} spin polarization.
Eigenstates of the universal Hamiltonian:

The eigenstates $|U_\zeta; B \gamma SM >$ factorizes into two parts:

$U$ is a subset of doubly occupied and empty levels.

$B$ is a subset of singly occupied levels

(i) $|U_\zeta >$ are zero-spin eigenstates of the reduced BCS Hamiltonian

(ii) $|B \gamma SM >$ are eigenstates of $\tilde{S}^2$, obtained by coupling spin-1/2 singly-occupied levels in $B$ to total spin $S$ and spin projection $M$.

Exact solution: Richardson's solution for the reduced BCS plus spin algebra.
Ground-state spin in the $J_s / \delta - \Delta / \delta$ plane (for an equally spaced single-particle spectrum)

Mean field approximation (S-dependent BCS) fails to reproduce coexistence.

A Zeeman field broadens the coexistence regime and makes it accessible to typical values of $J_s$.

Stoner staircase
(Ground-state spin versus $J_s / \delta$)

For a fixed $\Delta / \delta$ the spin increases by discrete steps as a function of $J_s / \delta$.

Spin jumps: the first step can have $\Delta S > 1$
The coexistence of pairing and exchange correlations: thermodynamic signatures


Richardson’s solution becomes impractical at higher temperatures.

A finite-temperature method:

\[ H = \sum_i \epsilon_i (a_{i \uparrow}^\dagger a_{i \uparrow} + a_{i \downarrow}^\dagger a_{i \downarrow}) - G P^\dagger P - J_s \vec{S}^2 = H_{BCS} - J_s \vec{S}^2 \]

(i) Exact spin projection method

\[ \text{Tr} e^{-\beta H} = \sum_S e^{\beta J_s S(S+1)} \text{Tr}_S e^{-\beta H_{BCS}} \]

Trace over states with fixed spin \( S \)

\[ \text{Tr}_S X = (2S + 1)(\text{Tr}_{S_z=S} X - \text{Tr}_{S_z=S+1} X) \]

Trace with fixed spin component \( S_z \)

(ii) Functional integral representation (Hubbard-Stratonovich) for the reduced pairing Hamiltonian:

\[
\exp \left[ -\beta \left( \hat{H}_{\text{BCS}} - \mu \hat{N} \right) \right] = \int D[\Delta(\tau), \Delta^*(\tau)] \exp \left[ -\int_0^\beta d\tau \left( \frac{|\Delta(\tau)|^2}{G} + \hat{H}_{\Delta(\tau)} \right) \right]
\]

**one-body Hamiltonian in pairing field \( \Delta(\tau) \)**

\[
\hat{H}_\Delta = \sum_i \left[ \left( \epsilon_i - \mu - \frac{G}{2} \right) (a_{i\uparrow} a_{i\downarrow} + a_{i\downarrow} a_{i\uparrow}) - \Delta a_{i\uparrow} \Delta^* a_{i\downarrow} + \frac{G}{2} \right]
\]

\[
\Delta(\tau) = \Delta_0 + \sum_{m \neq 0} \Delta_m e^{i\omega_m \tau}
\]

**exact integration over \( \Delta_0 \) (static-path approximation (SPA))**

**saddle-point integration over \( \Delta_m \) for each static \( \Delta_0 \) (random-phase approximation (RPA))**

(iii) Number-parity projection to capture odd-even effects.

\[
\hat{P}_\eta = \frac{1}{2} \left( 1 + \eta e^{i\pi \hat{N}} \right)
\]

\( (\eta = 1 \text{ for even } N, \ \eta = -1 \text{ for odd } N) \)

See also Rossignoli, Canosa and Ring, PRL 80, 1853 (1998).
Comparison with exact results for particular realizations of the single-particle spectrum

$\Delta/\delta = 3.0, \; J_s/\delta = 0.5$

- The static path + RPA+number-parity projection is an accurate method yet very efficient.
Heat capacity

Fluctuation-dominated regime: exchange correlations suppress the odd-even signatures of pairing correlations.

BCS regime: exchange correlations enhance the S-shoulder in the even case.
Spin susceptibility

- **Fluctuation-dominated regime**: exchange correlations enhance the fluctuations of the susceptibility.
- **BCS regime**: exchange correlations enhance re-entrant effect.

![Graph showing the spin susceptibility in different regimes.](image)
Spin-orbit scattering breaks spin symmetry but preserves time-reversal.

The exchange interaction is suppressed but the pairing interaction remains unaffected.

We studied the response of energy levels in the nanoparticle to external magnetic field: linear (g factor) and quadratic (level curvature) terms.

\[ \epsilon_i \pm \frac{1}{2} g_i \mu_B B + \frac{1}{2} \kappa_i B^2 + \ldots \]

- g-factor
- level curvature
- level-to-level fluctuations
- tensor structure
- suppression \((g_i < 2)\)

Spin is a good quantum number

Spin is not a good quantum number

Brouwer, Waintal and Halperin (2000); Matveev, Glazman and Larkin (2000)
• Recent advances (use of organic substrates) are providing much better control over the size and shape the metallic grain.

• Level and g-factor statistics in a gold grain are in agreement with the symplectic ensemble of RMT (Ralph et al, 2008).
g factor and level curvature in the presence of interactions

dl/dV curves in tunneling spectroscopy experiments measure the energy differences $\Delta E_\Omega$ between many-particle states with N+1 and N electrons.

Assume one-bottleneck geometry: decay into the ground state before another electron is added.

For tunneling into the even ground state

$$\Delta E_\Omega = E_\Omega^{N+1} - E_0^N$$

Many-body levels of the odd nanoparticle are doubly degenerate (Kramers’ degeneracy), and they split in a magnetic field

$$\Delta E = \Delta E(0) \pm \frac{1}{2} g \mu_B B + \frac{1}{2} \kappa B^2$$

g and $\kappa$ reduce to the single-particle level quantities in the constant-interaction model.
Universal Hamiltonian with strong spin-orbit scattering

$$H = \sum_{i, \alpha} \varepsilon_i a_{i\alpha}^\dagger a_{i\alpha} - GP^\dagger P - BM_z$$

where $\alpha = 1, 2$ is the Kramers doublet with energy $\varepsilon_i$ and $P^\dagger = \sum_i a_{i1}^\dagger a_{i2}^\dagger$

Even ground state

$C_1 + C_2 + C_3 + \ldots$

Odd state

$C'_1 + C'_2 + C'_3 + \ldots$
For the even ground state:

\[
\left\langle \sum_{i=1}^{\text{even}} \frac{C_i}{m_1} + C_2 + \ldots \left| \hat{M}_z \right| \sum_{i=1}^{\text{even}} \frac{C_i}{m_1} + C_2 + \ldots \right\rangle = 0
\]

by time-reversal symmetry

(M is odd under time reversal)

For the odd state:

\[
\left\langle \sum_{i=1}^{\text{odd}} \frac{C'_i}{m_1} + C'_2 + \ldots \left| \hat{M}_z \right| \sum_{i=1}^{\text{odd}} \frac{C'_i}{m_1} + C'_2 + \ldots \right\rangle = \left\langle \cdot \left| \hat{M}_z \right| \cdot \right\rangle_{\text{single-particle}}
\]

since

\[
M^z_{m_1,m_1} + M^z_{m_2,m_2} = 0
\]

by time-reversal symmetry

The many-particle g factor reduces to the single-particle g factor of the dddparticle blocked orbital.

\[
g\text{-factor distributions are not affected by pairing correlations.}
\]
**Level curvature $\kappa$ (quadratic correction)**

In second-order perturbation theory (even ground state to odd ground state)

$$
\kappa = \sum_{\Omega'} \left| \frac{\langle \Omega' | \hat{M}_z | 0 \rangle_{N_{e+1}}}{E_0^{N_{e+1}} - E_{\Omega'}^{N_{e+1}}} \right|^2 - \sum_{\Theta'} \left| \frac{\langle \Theta' | \hat{M}_z | 0 \rangle_{N_{e}}}{E_0^{N_{e}} - E_{\Theta'}^{N_{e}}} \right|^2
$$

In the CI model (i.e., non-interacting), $\kappa$ reduces to the single-level curvature

$$
\kappa_k = 2 \sum_{k' \neq k} \frac{|M_{k_1, k'_1}|^2 + |M_{k_1, k'_2}|^2}{\epsilon_k - \epsilon_{k'}}
$$

The single-level curvature distribution is symmetric around $k=0$. 
κ in the presence of pairing correlations with \( \Delta > \delta \)

\[
\kappa = \sum_{\Omega'} \left| \frac{\langle \Omega' | \hat{M}_z | 0 \rangle_{N_e+1}}{E_0^{N_e+1} - E_{\Omega'}^{N_e+1}} \right|^2 - \sum_{\Theta'} \left| \frac{\langle \Theta' | \hat{M}_z | 0 \rangle_{N_e}}{E_0^{N_e} - E_{\Theta'}^{N_e}} \right|^2 = \kappa_0^{\text{odd}} - \kappa_0^{\text{even}}
\]

Positive contributions to κ come from the even curvature

\[| E_0^{N_e} - E_{\Theta'}^{N_e} | \geq 2\Delta \] (there is a pairing gap in the even grain) and κ is suppressed.

Negative contributions to κ come from the odd curvature

\[| E_0^{N_e+1} - E_{\Theta'}^{N_e+1} | \] (no pairing gap in the odd grain) can be small and κ is enhanced

The curvature distribution is asymmetric and shifted towards the left (negative values)
Results for the level curvature distributions

- Single-particle levels follow the Gaussian symplectic ensemble (GSE).
- Only spin contribution to magnetization is included.
- Exact calculations versus a generalized BCS approach.

Similar qualitative behavior is observed in the exact results and in the BCS approximation.

Many-particle level curvature distribution is highly sensitive to pairing correlations (even in the fluctuation-dominated regime).

Can be used as a tool to probe pairing correlations in the single-electron tunneling spectroscopy experiments.
Conclusion

- A superconducting nano-scale metallic grain is characterized by two regimes: BCS regime $\Delta / \delta > > 1$ and fluctuation-dominated regime $\Delta / \delta \leq 1$.

(I) In the absence of spin-orbit scattering:
- Competition between pairing and spin exchange correlations
- Coexistence of superconductivity and ferromagnetism in the fluctuation-dominated regime
- Effects of exchange correlations on the odd-even signatures of pairing correlations are qualitatively different in the BCS and fluctuation-dominated regimes.

(II) In the presence of spin-orbit scattering:
- Spin exchange correlations are suppressed.
- g-factor statistics are unaffected by pairing correlations.
- Level curvature statistics is highly sensitive to pairing correlations.