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).

- Quantum phase diagram
- Transport
- Thermodynamics.

(II) Nanoparticles with spin-orbit scattering
   Response to an external magnetic field: $g$-factor and level curvature

- Effects of pairing correlations on the $g$-factor and level curvature statistics.

- 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, and Ag grains.
- Ultra-small (nano-scale) grains: probe the quantum regime $T \ll \delta$ ($\delta$ = single-particle level spacing)

Superconducting grains

Consider materials that are superconductors in the bulk and characterized by a pairing gap $\Delta$. 
(i) Large Al grains (~ 10 nm) \( \Delta \gg \delta \)

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

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

• BCS theory breaks down.
  “Superconductivity would no longer be possible” (Anderson)

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)]

\[ H = \sum_i \varepsilon_i (a_{i\uparrow}^{\dagger} a_{i\uparrow} + a_{i\downarrow}^{\dagger} a_{i\downarrow}) + \frac{e^2}{2C} N^2 - GP^{\dagger}P - J_s \vec{S}^2 \]

• Discrete single-particle levels \( \varepsilon_i \) (spin degenerate) and wave functions follow random matrix theory (RMT).
• Attractive BCS-like pairing interaction ( \( P^{\dagger} = \sum_i a_{i\uparrow}^{\dagger} a_{i\downarrow}^{\dagger} \) is the pair operator) with coupling \( G > 0 \).
• Ferromagnetic exchange interaction ( \( \vec{S} \) is the total spin of the grain) with exchange constant \( J_s > 0 \).
• Corrections \( \sim O(1/g) \) are small for large Thouless conductance \( g \).

Competition between pairing and exchange correlations: pairing favors \emph{minimal} ground-state spin, while exchange favors \emph{maximal} spin polarization.
A derivation from symmetry principles
[Y. A., H.A. Weidemuller, A. Wobst, PRB 72, 045318 (2005)]

\[ H = \sum_{\alpha\sigma} \varepsilon_\alpha a^\dagger_\alpha\sigma a_{\alpha\sigma} + \frac{1}{2} \sum_{\alpha\beta;\gamma\delta\sigma\sigma'} v_{\alpha\beta;\gamma\delta} a^\dagger_\alpha\sigma a^\dagger_\beta\sigma' a_{\gamma\sigma'} a_{\delta\sigma} \]

where \( v \) is the (screened) Coulomb interaction

- The randomness of the single-particle wave functions induces randomness in the two-body interaction matrix elements.

- Cumulants of the interaction matrix elements are determined by requiring invariance under a change of the single-particle basis (single-particle dynamics are chaotic).

**Averages:** There are three (two) invariants in the orthogonal (unitary) symmetry:

\[ \bar{V}_{\alpha\beta;\gamma\delta} = v_0 \delta_{\alpha\gamma} \delta_{\beta\delta} + J_s \delta_{\alpha\delta} \delta_{\beta\gamma} - G \delta_{\alpha\beta} \delta_{\gamma\delta} \]

\[ \iff \bar{V} = \frac{1}{2} \left( v_0 - J_s / 2 \right) \hat{N}^2 - \left( v_0 / 2 - J_s \right) \hat{N} - J_s \hat{S}^2 - G \hat{P}^\dagger \hat{P} \]
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 $\vec{S}^2$, 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.

For a review, see J. Dukelsky, S. Pittel, and G. Sierra, Rev. Mod. Phys. 76, 643 (2004)
Ground-state spin in the $J_s/\delta - \Delta/\delta$ plane (for an equally spaced single-particle spectrum)

Exact solution: coexistence of superconductivity and ferromagnetism in the fluctuation-dominated regime.


Quantum phase diagram


• Mean-field approximation (S-dependent BCS) fails to reproduce coexistence.
Transport: Coulomb blockade conductance

- A conductance peak is observed for each electron that tunnels into the dot

- Single-particle energies and wave functions are described by RMT

Mesoscopic fluctuations of $G_{\text{max}}$ and $\Delta_2$
In sequential tunneling, there are two classes of transport processes:

(i) The electron tunnels into an empty level $\lambda$ and blocks it
After tunneling:

\[ \text{S} = \frac{3}{2} \]
(ii) The electron tunnels into a singly occupied level $\lambda$ and unblocks it.
After tunneling:

\[ S = 1/2 \]
Mesoscopic fluctuations of the conductance peaks

Single-particle energies and wave functions described by random matrix statistics (GOE).

**Peak-spacing statistics (** $T = 0.1\delta$**)**

Peak-spacing distributions

- Exchange suppresses bimodality while pairing enhances it.
Peak-height statistics \( (T = 0.1 \delta) \)

- Exchange interaction suppresses the peak-height fluctuations.

Mesoscopic signatures of coexistence of pairing and exchange correlations for \( \Delta / \delta = 0.5 \) and \( J_s / \delta = 0.6 \): bimodality of peak spacing distribution (pairing) and suppression of peak height fluctuations (exchange).
Richardson’s solution becomes impractical at higher temperatures.

**A finite-temperature method:**

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

(i) Exact spin projection method

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

Trace over states with fixed spin S

\[
Tr_S X = (2S + 1)(Tr_{S_z=S} X - Tr_{S_z=S+1} X)
\]

Trace with fixed spin component \(S_z\) (calculated by Fourier transform)

(ii) Functional integral representation (Hubbard-Stratonovich) for the reduced pairing Hamiltonian $H_{BCS}$:

$$e^{-\beta H_{BCS}} = \int D[\Delta(\tau), \Delta^*(\tau)] T e^{\beta \int_0^\beta d\tau (|\Delta(\tau)|^2/G + h[\Delta(\tau), \Delta^*(\tau)])}$$

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

Expand $\Delta(\tau) = \Delta_0 + \sum_m \Delta_m e^{i\omega_m \tau}$

($\omega_m$ are Matsubara frequencies).

Integrate over $\Delta_0$ exactly (static path approximation) and over $\Delta_m$ by saddle point [i.e., random phase approximation (RPA)] around each static $\Delta_0$

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

$$P_\eta = (1 + \eta e^{i\pi N}) / 2$$

$\eta = 1 (\eta = -1)$ describes a projection on even (odd) number of particles

Comparison with exact results for particular realizations of the single-particle spectrum

- The static path + RPA+number-parity projection is an accurate method yet very efficient.
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.
• **Fluctuation-dominated regime**: exchange correlations enhance the fluctuations of the susceptibility.
• **BCS regime**: exchange correlations enhance re-entrant effect.
Superconducting nanoparticles with spin-orbit scattering


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 $B$: linear (g factor) and quadratic (level curvature) terms.

In the absence of pairing correlations, the single-particle levels are given by

$$
\varepsilon_i \pm \frac{1}{2} g \mu_B B + \frac{1}{2} \kappa B^2 + ... 
$$

- Without spin orbit scattering, spin is a good quantum number and $g=2$.

- With spin-orbit scattering, spin is no longer conserved. The g factor is suppressed ($g<2$) and exhibits level-to-level fluctuations.

In general, $g$ has a tensor structure.

The statistical distribution of the $g$ factor was studied using random matrix theory.

[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).
We assume a one-bottleneck geometry: decay into the ground state before another electron is added.

\[ \Delta E_{\Omega} = E_{\Omega}^{N+1} - E_{0}^{N} \]

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

\[ \Delta E = \Delta E(0) \pm \frac{1}{2} g \mu_{B} B + \frac{1}{2} \kappa B^{2} + \ldots \]

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

\[ H = \sum_{i,\alpha} \varepsilon_i a_{i\alpha}^\dagger a_{i\alpha} - G P^\dagger P - B M_z \]

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

(a) \( G = 0 \)

(b) \( G \neq 0 \)

Even ground state

Odd state

blocked orbital

\( k_0 \)

\( k_0' \)
g-factor (linear correction)

For the even ground state:

\[ \langle 0 | M_z | 0 \rangle = 0 \]

by time-reversal symmetry

\( (M_z) \) is odd under time reversal

For the odd state:

\[ \langle \Omega | M_z | \Omega' \rangle = M^z_{k_0 \alpha, k_0 \alpha'} \]

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 odd-particle blocked orbital \( k_0 \).

g-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)

$$
\kappa = \sum_{\Omega' \neq 0} \left| \frac{\langle \Omega' | M_z | 0 \rangle_{N+1}}{E_0^{N+1} - E_{\Omega'}^{N+1}} \right|^2 - \sum_{\Theta' \neq 0} \left| \frac{\langle \Theta' | M_z | 0 \rangle_{N}}{E_0^{N} - E_{\Theta'}^{N}} \right|^2
$$

In the non-interacting case, $\kappa$ reduces to the single-level curvature

The single-level curvature distribution is symmetric around $\kappa = 0$.
Results for the many-particle level curvature distributions

- Single-particle levels follow the Gaussian symplectic ensemble (GSE).
- Exact CI calculation versus a generalized BCS approach.

Similar qualitative behavior is observed in the exact results and in the BCS approximation: the curvature distribution is asymmetric and shifted towards negative values.

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.
Conclusions

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 statistic is highly sensitive to pairing correlations