Mesoscopic superconductivity in nano-scale metallic grains

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- Nano-scale superconducting metallic grains (nanoparticles): BCS (bulk) regime and fluctuation-dominated regime.

Can we observe pairing correlations in the fluctuation-dominated regime?

I. Nanoparticles without spin-orbit scattering

Competition between pairing (superconductivity) and spin exchange correlations (ferromagnetism).

- How do spin exchange correlations affect the thermodynamic signatures of pairing correlations ?

II. Nanoparticles with spin-orbit scattering

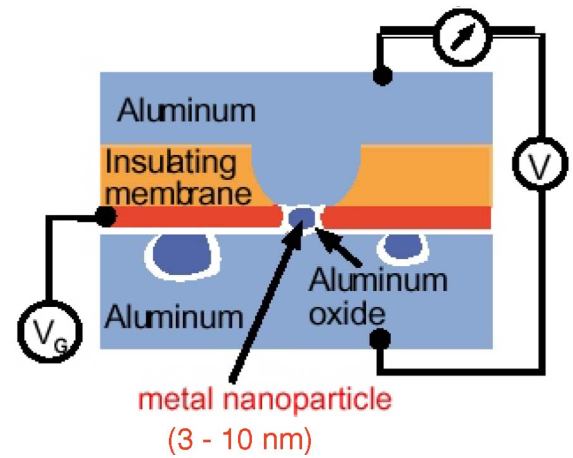
Magnetic response of many-particle levels: g-factor and level curvature.

- How do pairing correlations affect the g-factor and level curvature statistics ?

- Conclusion

Introduction: nano-scale 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 $T << \delta$
- Recent high-quality data in Au grains.

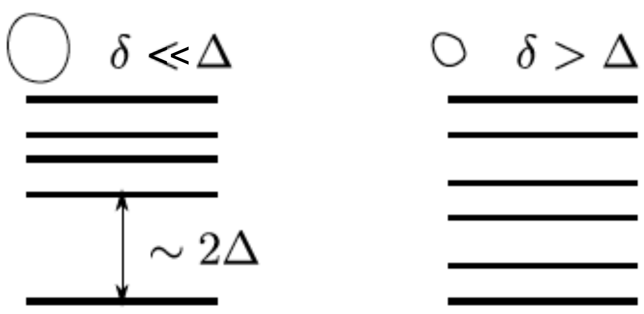


Superconducting grains

Consider materials that are superconductors in the bulk and characterized by a pairing gap Δ.

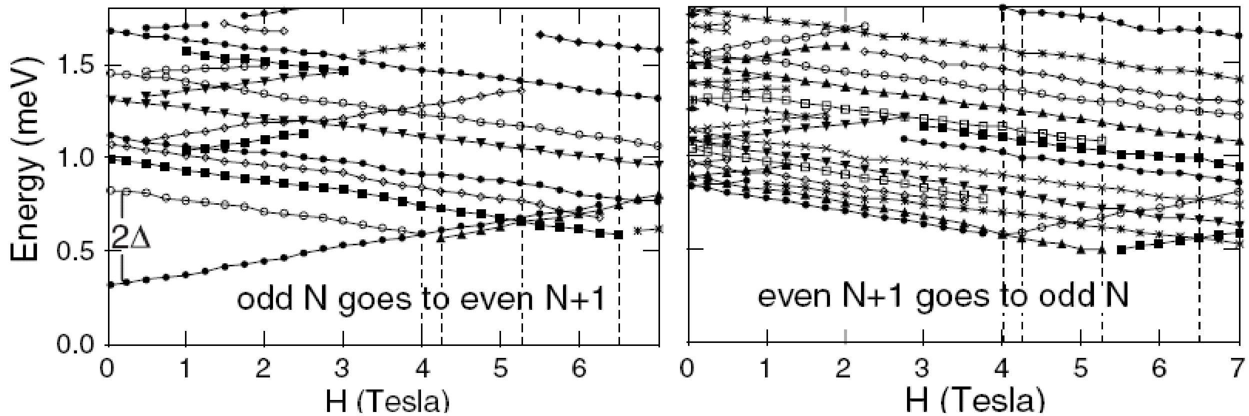
δ = single-particle level spacing.

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).

Can we observe signatures of pairing correlations in this regime despite the large fluctuations ?

For a review, see J. von Delft and D.C. Ralph, Phys. Rep **345**, 61 (2001).

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)]

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

- Discrete single-particle levels ε_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 *minimal* ground-state spin, while exchange favors *maximal* spin polarization.

Thermodynamic signatures of the competition between pairing and exchange correlations

K.N. Nesterov and Y.A., PRB 87, 014515 (2013)

Method of solution:

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

Reduced pairing Hamiltonian

(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)

See Y.A., Liu and Nakada, PRL 99, 162504 (2007).

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

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

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

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

(ω_m are Matsubara frequencies).

Integrate over Δ_0 exactly (static path approximation) and over Δ_m by saddle point [i.e., random phase approximation (RPA)] around each static Δ_0

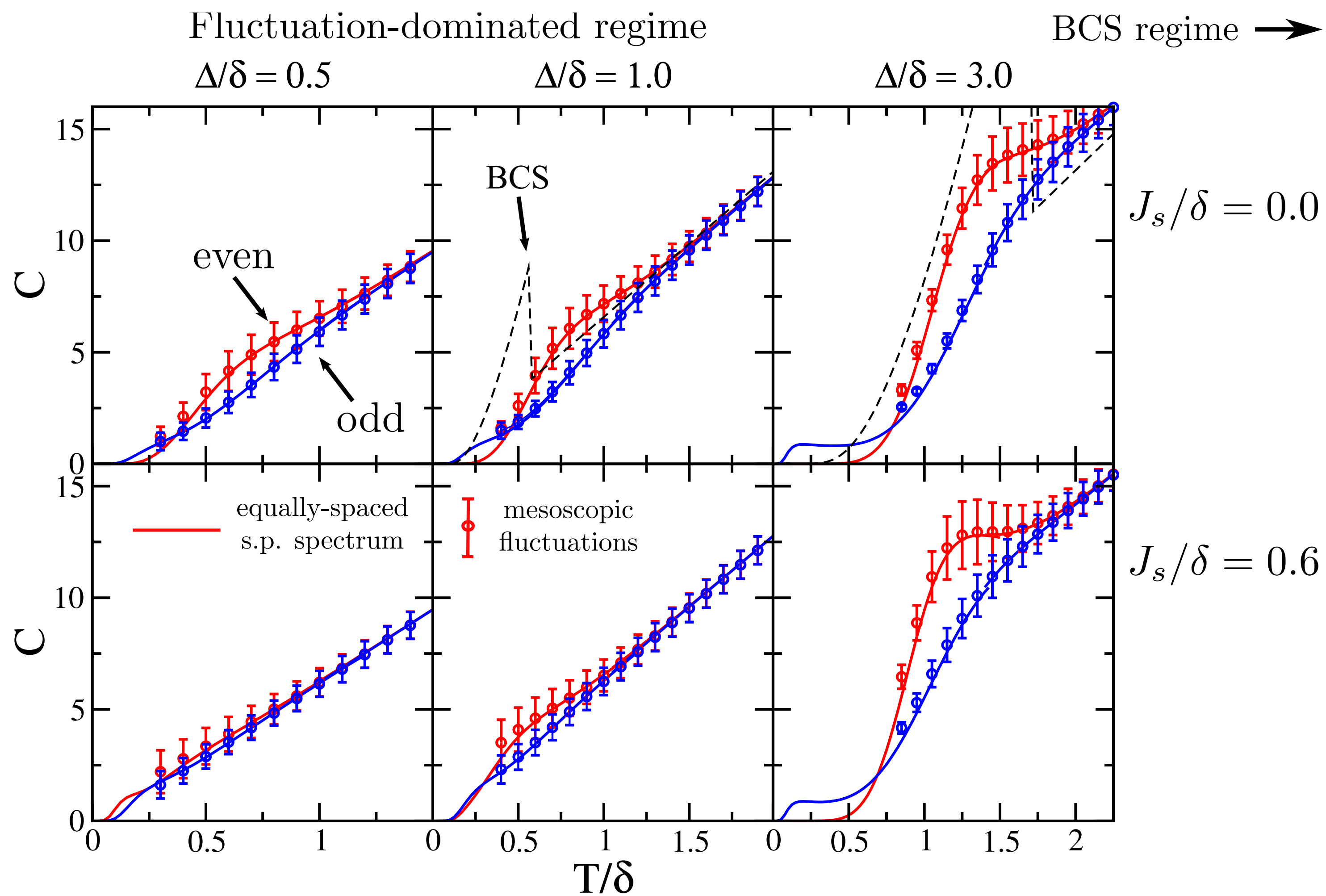
(iii) Number-parity projection to capture odd-even effects.

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

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

See also G. Falci, A. Fubini, and A. Mastellone, Phys. Rev. B 65, 140507 (2002).

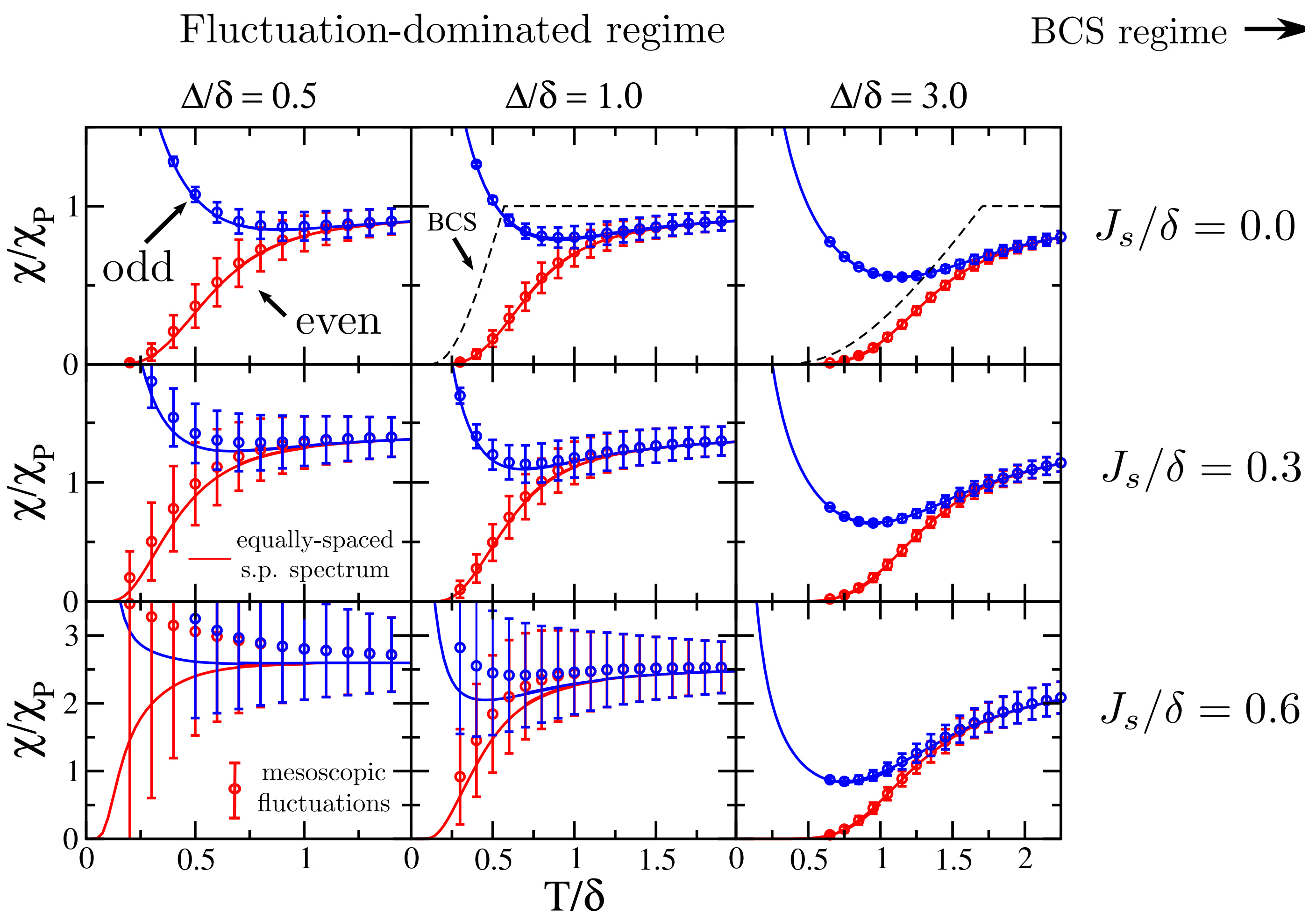
Heat capacity



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

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

Spin susceptibility



- BCS regime: exchange correlations enhance re-entrant effect.

- Fluctuation-dominated regime: exchange correlations enhance the fluctuations of the susceptibility.

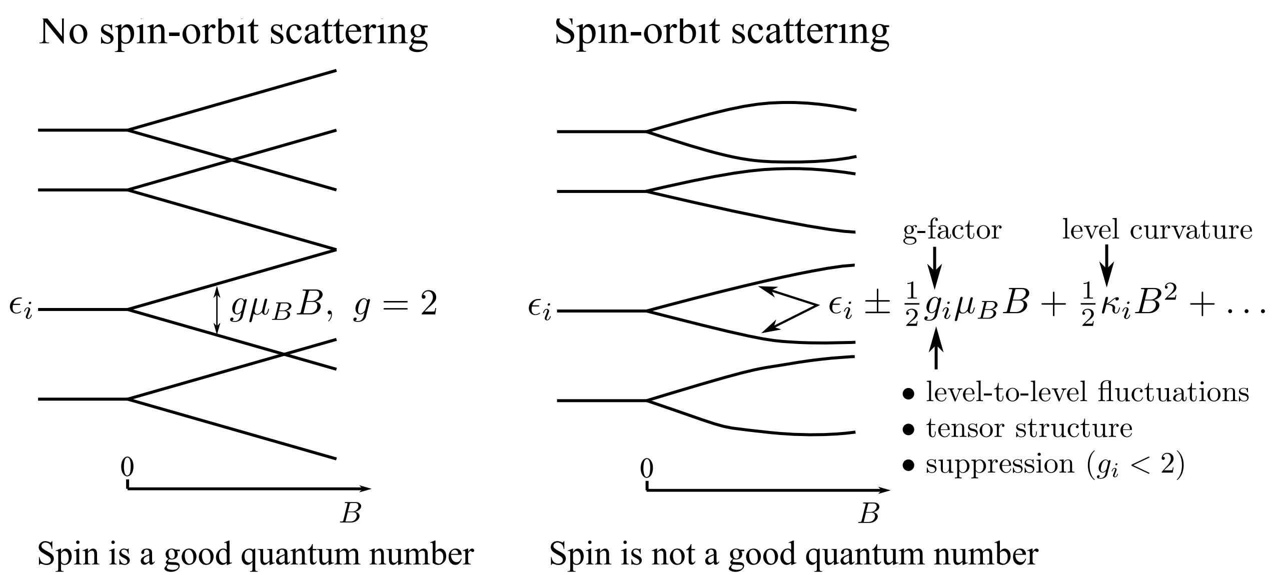
II. Superconducting nanoparticles with spin-orbit scattering

K.N. Nesterov and Y.A., arXiv:1507.01575 (2015)

Spin-orbit coupling breaks spin symmetry but preserves time-reversal symmetry.
$\Longrightarrow$ 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 κ) terms.

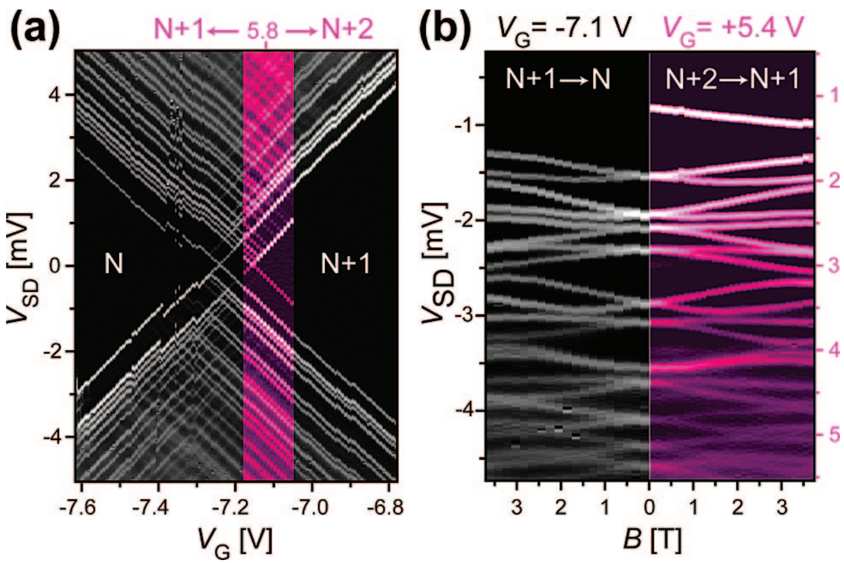
Single-particle levels vs. magnetic field B

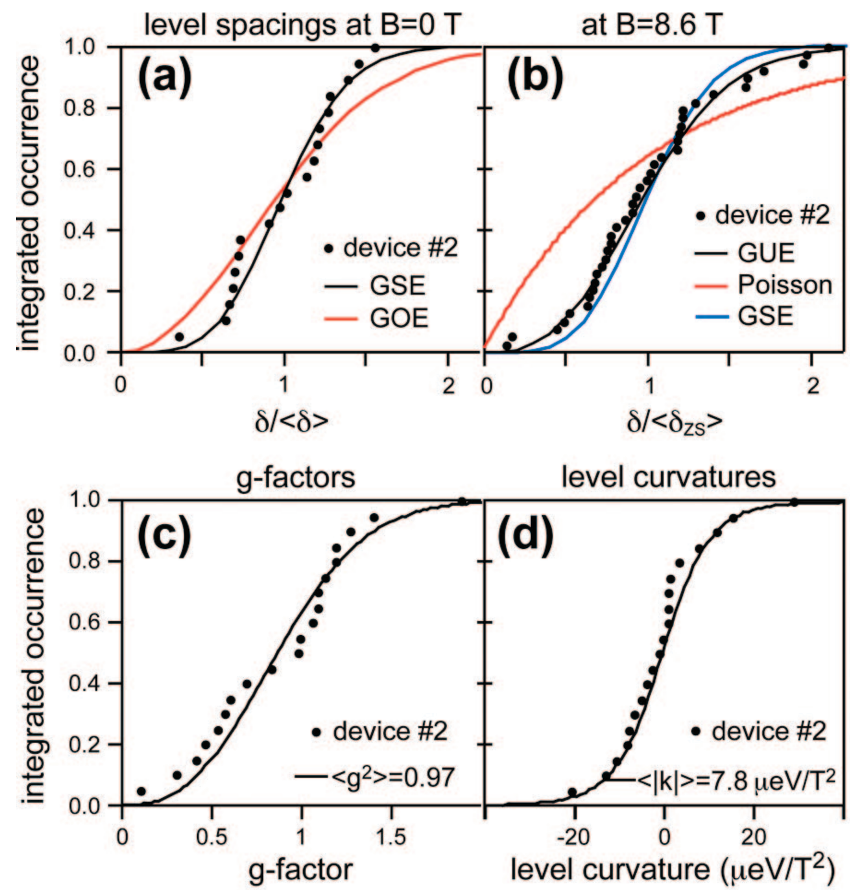


Brouwer, Waintal and Halperin (2000); Matveev, Glazman and Larkin (2000)

• 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 nanoparticle (non-superconducting) are in agreement with the symplectic ensemble of RMT (Ralph et al, 2008).

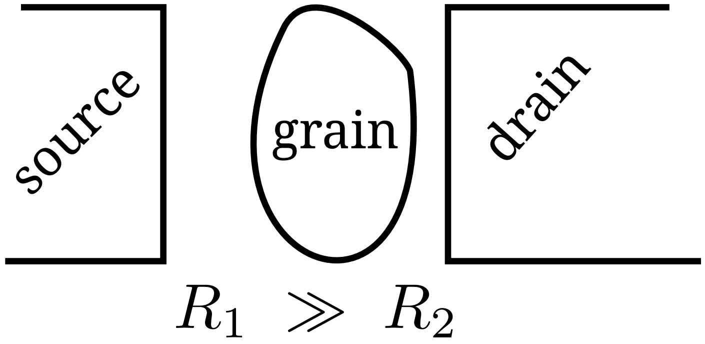




g factor and level curvature in the presence of interactions

dI/dV curves in tunneling spectroscopy experiments measure the energy differences ΔE_Ω 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 κ reduce to the single-particle level quantities in the non-interacting limit (i.e., constant-interaction model).

Universal Hamiltonian with strong spin-orbit scattering

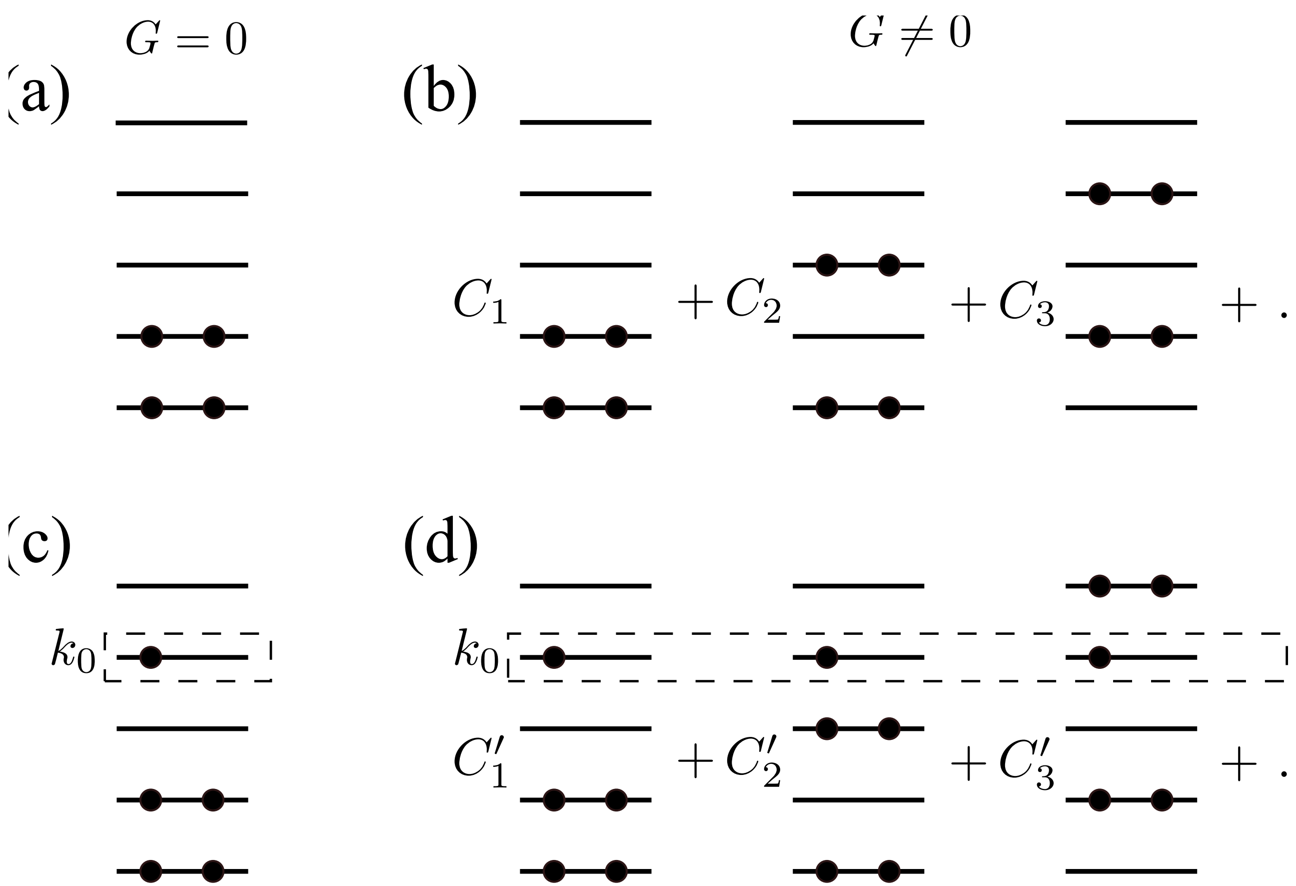
$$H = \sum_{i,\alpha} \varepsilon_i a^{\dagger}_{i\alpha} a_{i\alpha} - G P^{\dagger} P - B M_z$$

where α =1,2 is the Kramers doublet with energy ε_i and $P^{\dagger} = \sum_i a^{\dagger}_{i1} a^{\dagger}_{i2}$

Even ground state

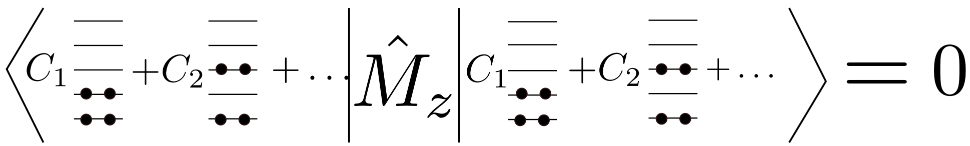
blocked orbital

Odd state



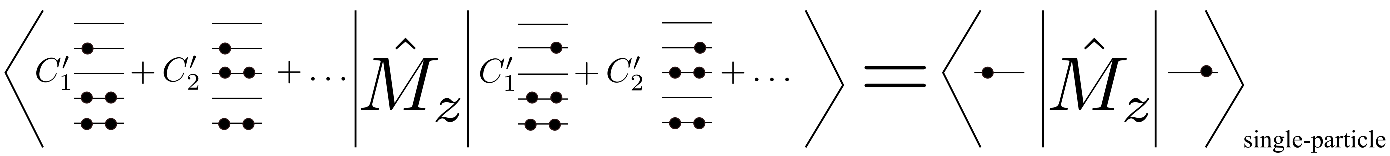
g-factor (linear correction)

For the even ground state:



by time-reversal symmetry
($\hat{M}_z$ is odd under time reversal)

For the odd state:



since $M^z_{m1,m1} + M^z_{m2,m2} = 0$ by time-reversal symmetry

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

g-factor distributions are not affected by pairing correlations.

Level curvature κ (quadratic correction)

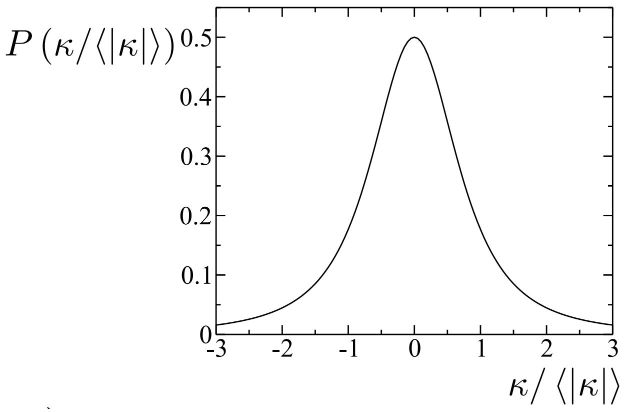
In second-order perturbation theory (even ground state to odd ground state)

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

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

$$\kappa_k = 2 \sum_{k' \neq k} \frac{|M^z_{k1,k'1}|^2 + |M^z_{k1,k'2}|^2}{\epsilon_k - \epsilon_{k'}}$$

The single-level curvature distribution
is symmetric around κ=0.



κ in the presence of pairing correlations with $\Delta > \delta$

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

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:

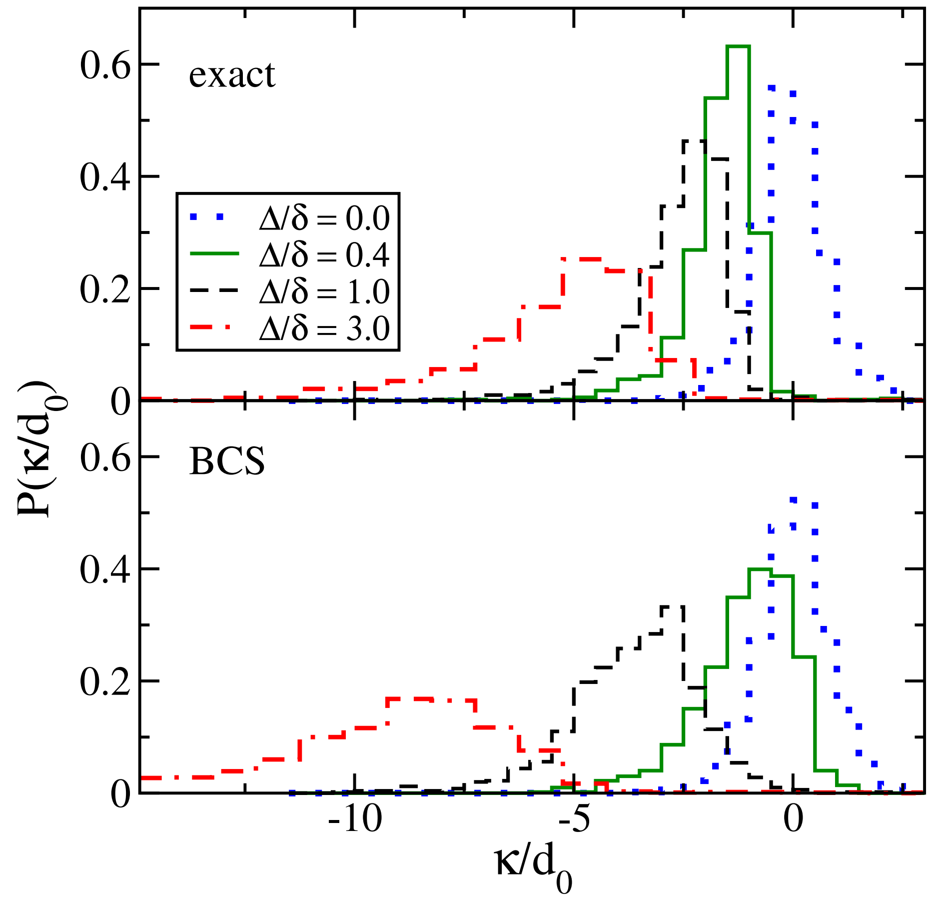
$| E_0^{N_e+1} - E_{\Omega'}^{N_e+1} |$ can be small (no pairing gap in the odd grain) and κ is enhanced

⇒ The curvature distribution is asymmetric and shifted towards 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 simulations versus a generalized BCS approach.

Similar qualitative behavior is observed in the 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)

$\Rightarrow$ A tool to probe pairing correlations in the single-electron tunneling spectroscopy experiments.

Conclusion

- A superconducting nano-scale metallic grain is characterize 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