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.

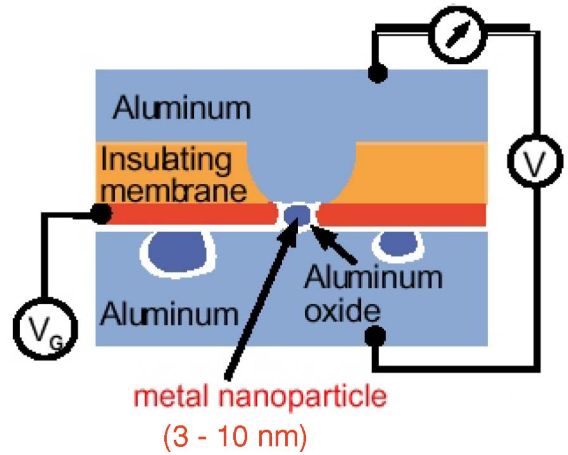
(II) Nanoparticles with spin-orbit scattering
Many-particle level response to an external magnetic field: g-factor and level curvature statistics

- 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 $T << \delta$
- Recent high-quality data in Au grains.

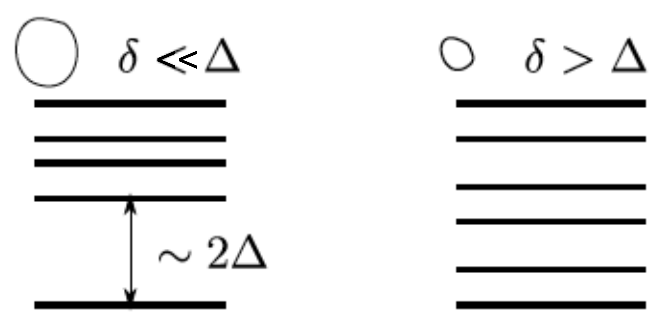


Superconducting grains

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

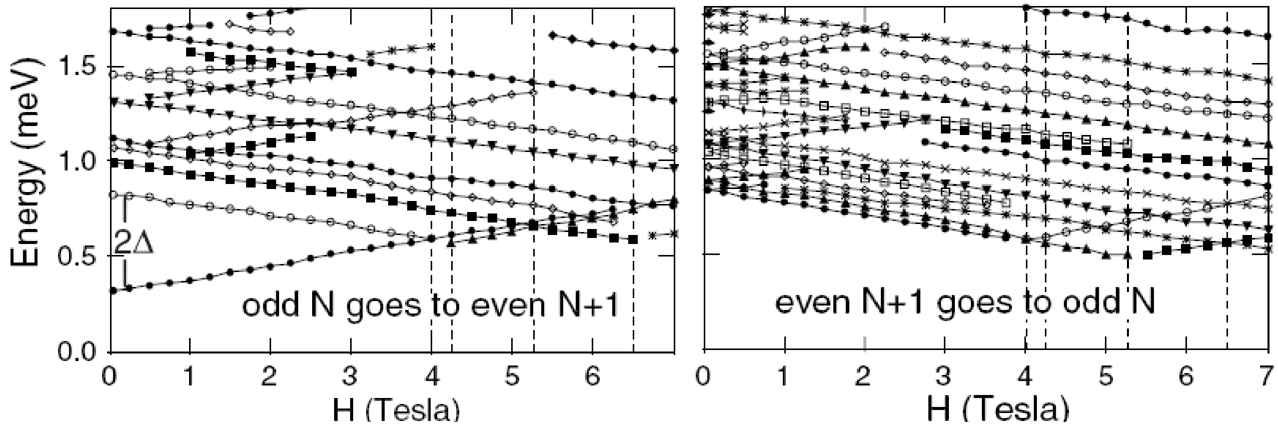
δ = single-particle level spacing.

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).

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)]

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

- Discrete single-particle levels ε_i (spin degenerate) and wave functions follow random matrix theory (RMT).
- Attractive BCS-like pairing interaction ($P^\dagger = \sum_i a^\dagger_{i\uparrow} a^\dagger_{i\downarrow}$ 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 *minimal* ground-state spin, while exchange favors *maximal* spin polarization.

Eigenstates of the universal Hamiltonian:

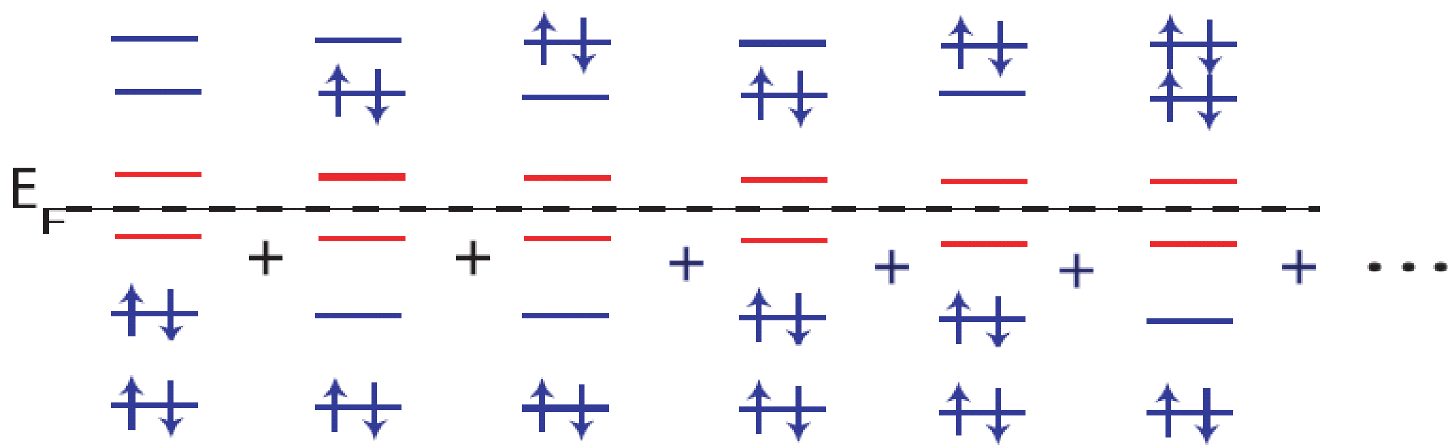
The eigenstates $|U\varsigma; B\gamma SM>$ factorizes into two parts:

U is a subset of doubly occupied and empty levels.

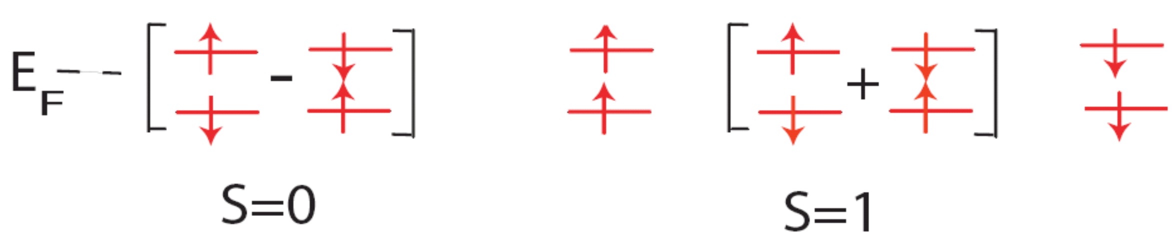
B is a subset of singly occupied levels

(i) $|U\varsigma>$ are zero-spin eigenstates of the *reduced BCS Hamiltonian*

Singly occupied levels (red) are *blocked* with respect to pairing



(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.

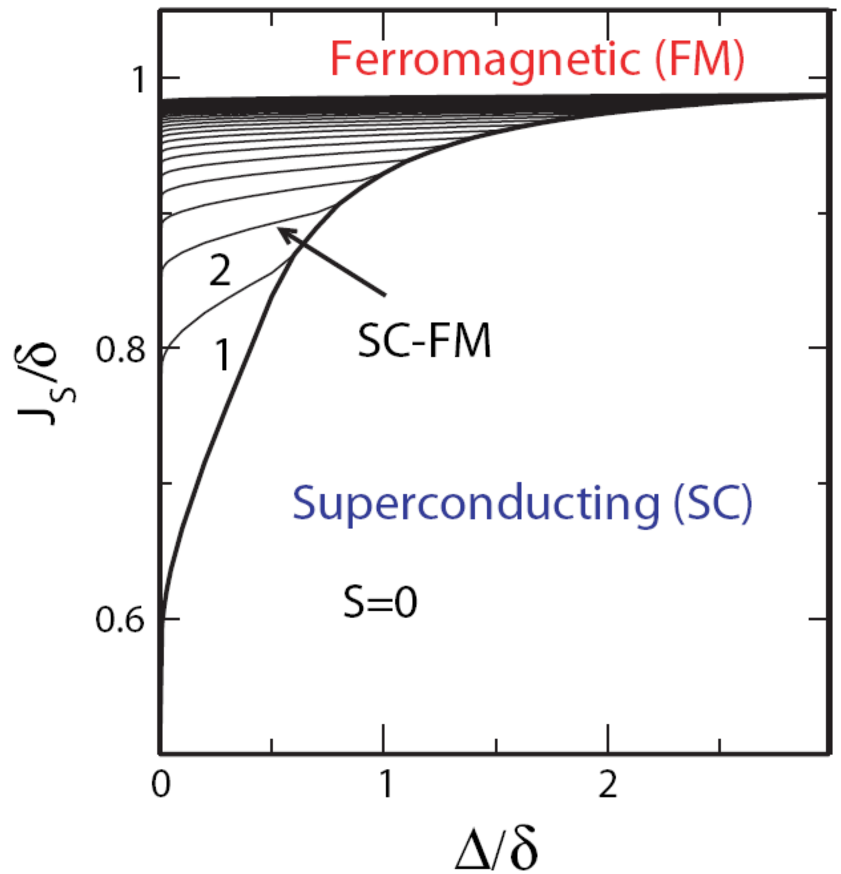


Exact solution: Richardson's solution for the reduced BCS plus spin algebra.

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

Reviewed in Y.A., K. Nesterov and S. Schmidt, Phys. Scr. T 151, 014047 (2012)

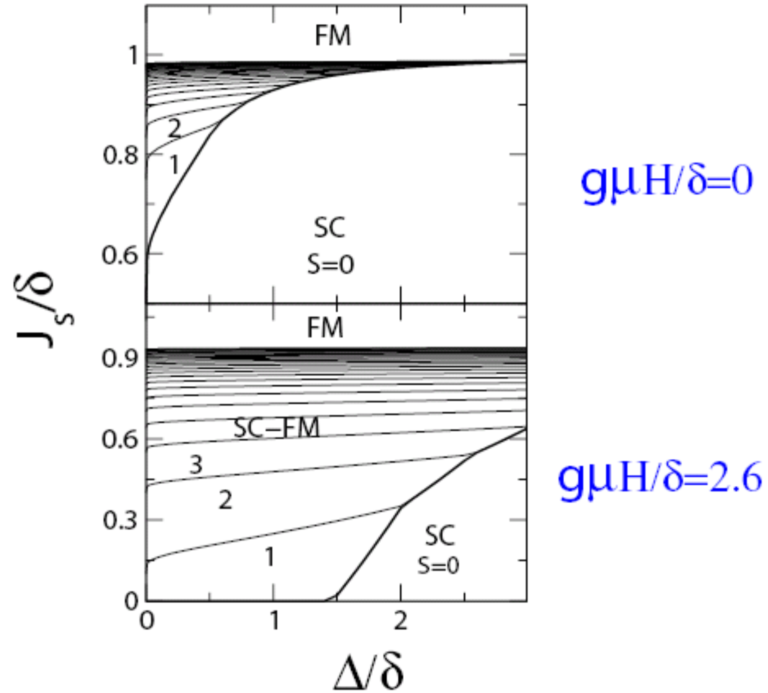
Ground-state spin in the $J_s/\delta - \Delta/\delta$ plane (for an equally spaced single-particle spectrum)



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

Zeeman field

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

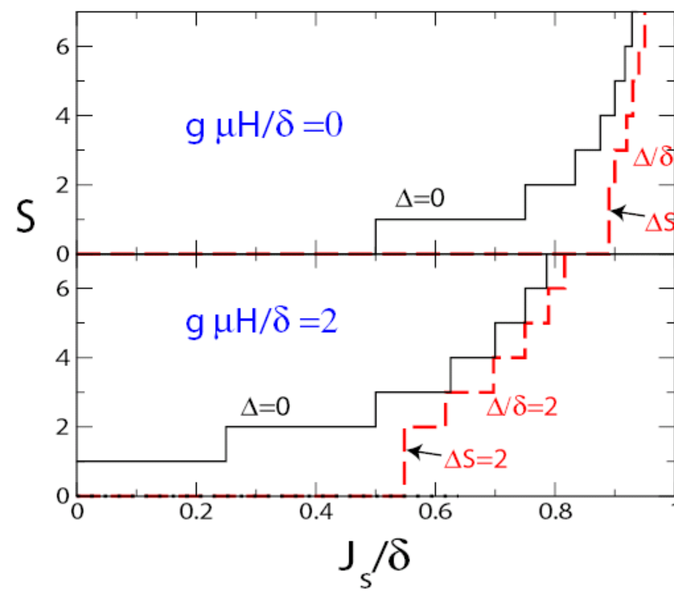


Stoner staircase

(Ground-state spin versus J_s/δ)

For a fixed Δ/δ the spin increases by discrete steps as a function of J_s/δ

- Spin jumps: the first step can have $\Delta S > 1$



The coexistence of pairing and exchange correlations: thermodynamic signatures

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

Richardson's solution becomes impractical at higher temperatures.

A finite-temperature method:

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

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

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

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

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

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

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

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

exact integration over Δ_0 (static-path approximation (SPA))

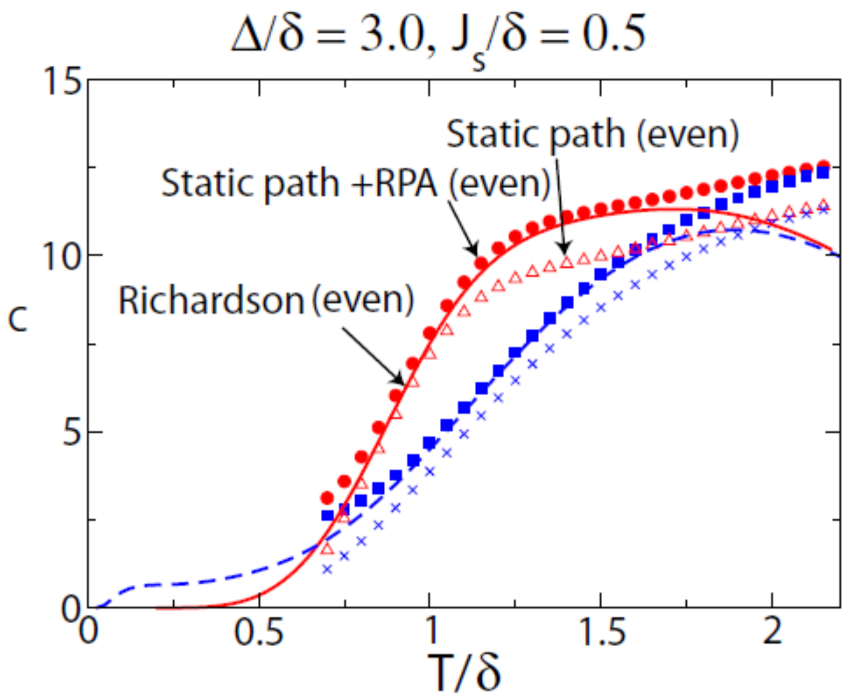
saddle-point integration over Δ_m for each static Δ_0 (random-phase approximation (RPA))

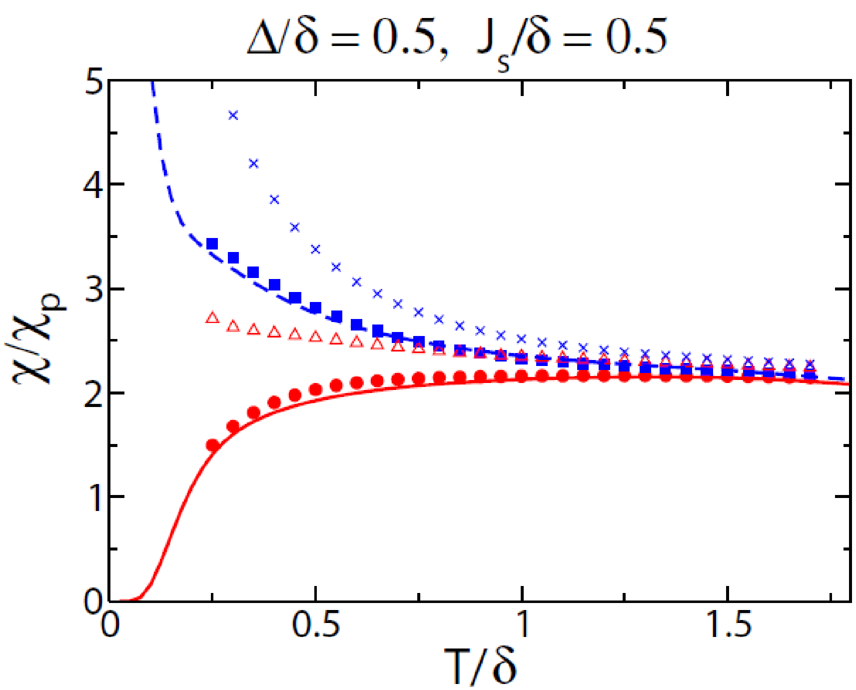
(iii) Number-parity projection to capture odd-even effects.

$$\hat{P}_\eta=\frac{1}{2}\left(1+\eta e^{i\pi\hat{N}}\right)\qquad(\eta=1\text{ for even }N,\ \eta=-1\text{ for odd }N)$$

See also Rossignoli, Canosa and Ring, PRL 80, 1853 (1998).

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

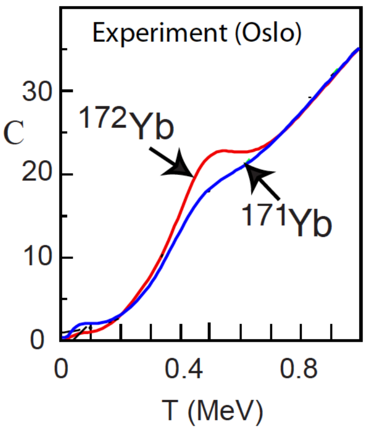


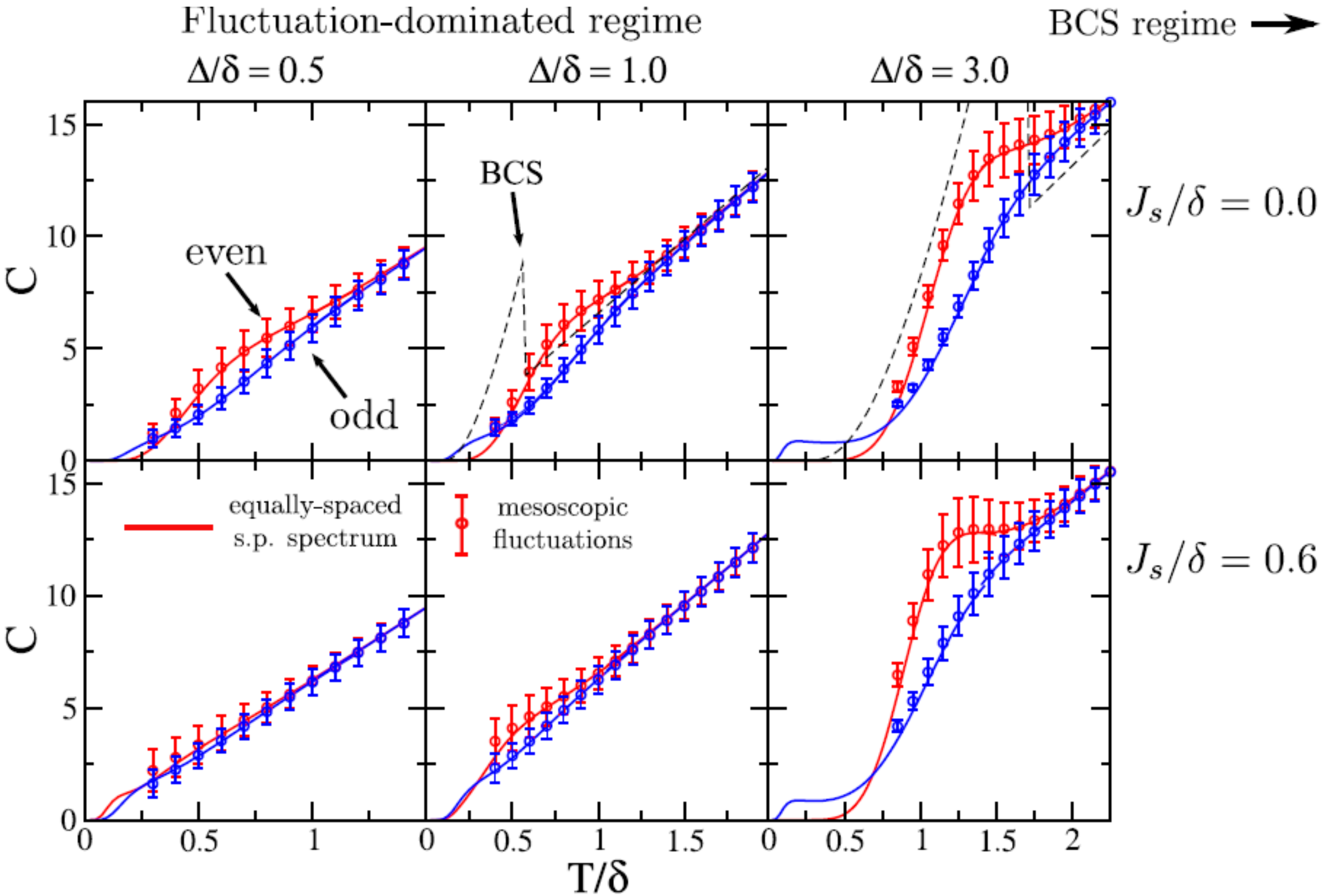


- The static path + RPA+number-parity projection is an accurate method yet very efficient.

Heat capacity

Heat capacity
in nuclei

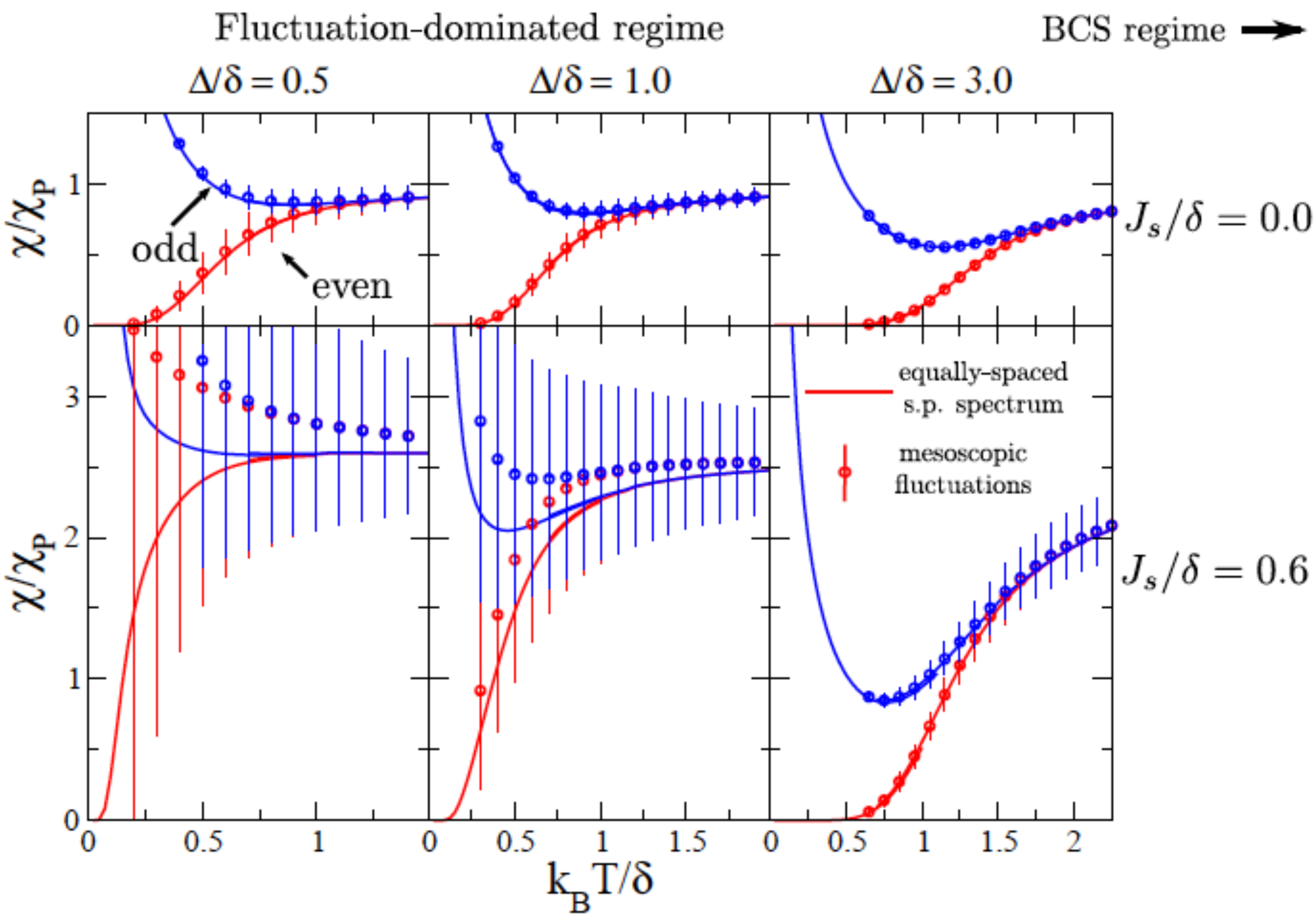




Fluctuation-dominated regime: exchange correlations suppress the odd-even signatures of pairing correlations.

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.

(II) Superconducting nanoparticles with spin-orbit scattering

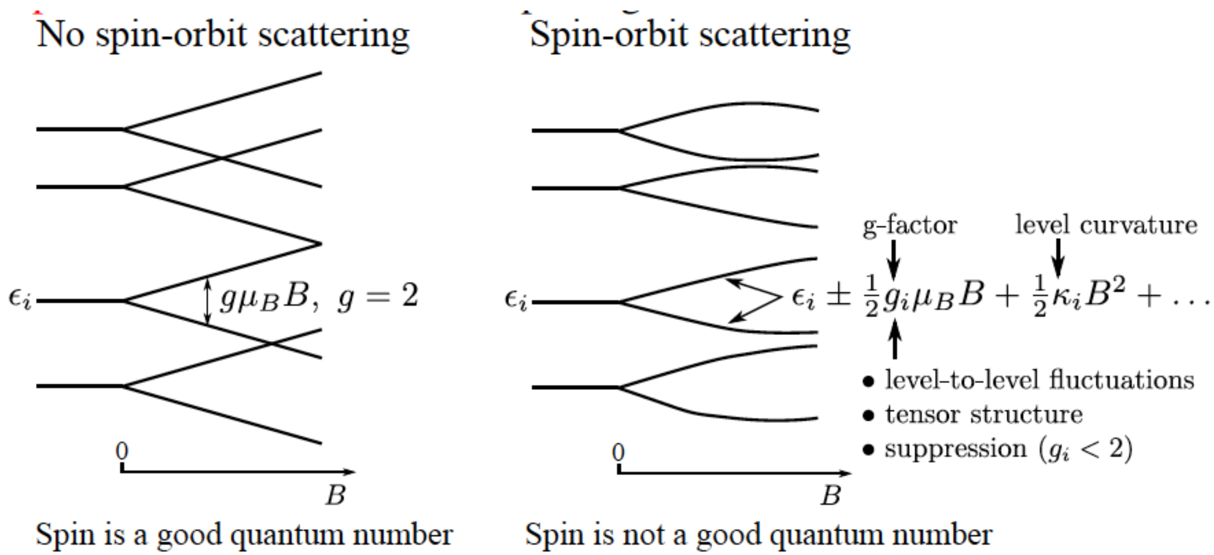
K. Nesterov and Y.A. (2014)

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.

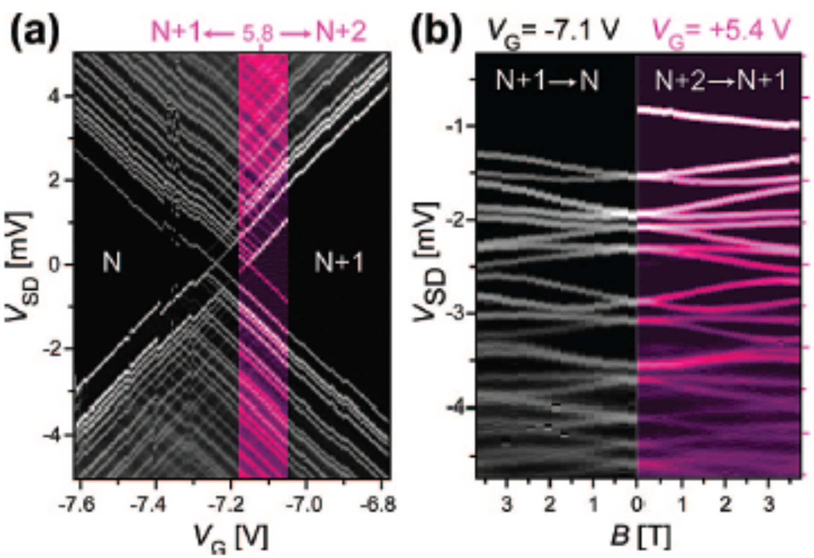
Single-particle levels vs magnetic field B

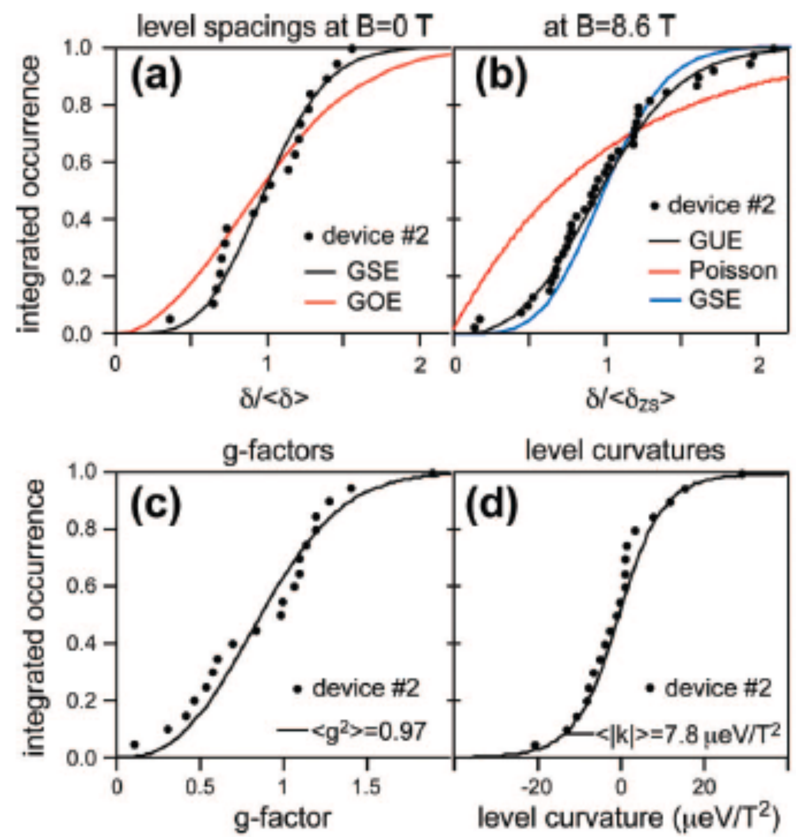


Brouwer, Waintal and Halperin (2000); Matveev, Glazman and Larkin (2000)

• 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 grain are in agreement with the symplectic ensemble of RMT (Ralph et al, 2008).

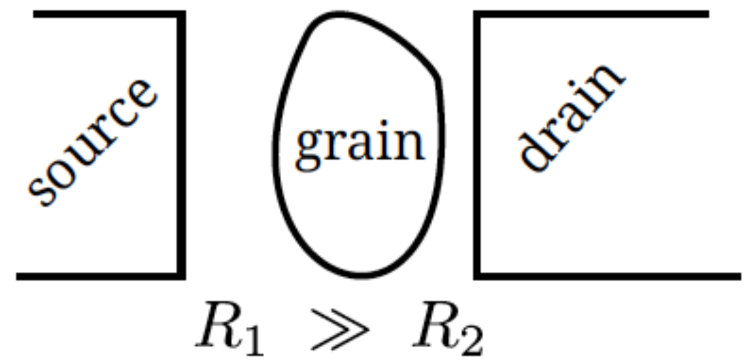




g factor and level curvature in the presence of interactions

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

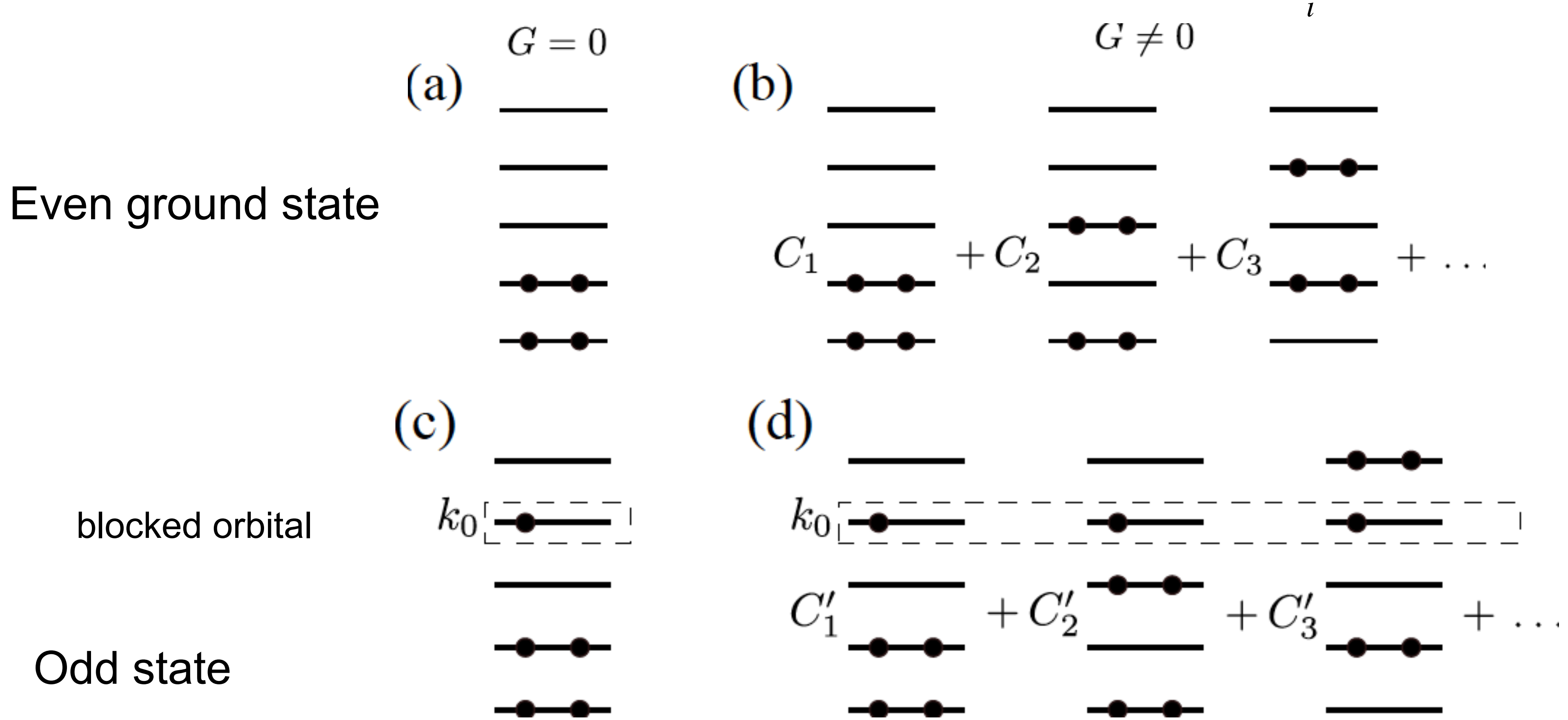
$$\Delta E = \Delta E(0) \pm \frac{1}{2} g \mu_B B + \frac{1}{2} \kappa B^2$$

g and κ reduce to the single-particle level quantities in the constant-interaction model.

Universal Hamiltonian with strong spin-orbit scattering

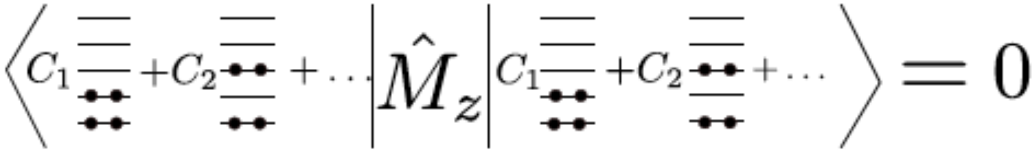
$$H = \sum_{i,\alpha} \varepsilon_i a_{i\alpha}^{\dagger} a_{i\alpha} - G P^{\dagger} P - B M_z$$

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



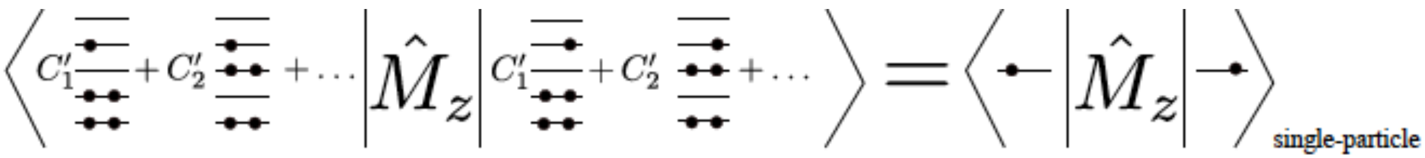
g-factor (linear correction)

For the even ground state:



by time-reversal symmetry
(M 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 ddd-particle blocked orbital.

g-factor distributions are not affected by pairing correlations.

Level curvature κ (quadratic correction)

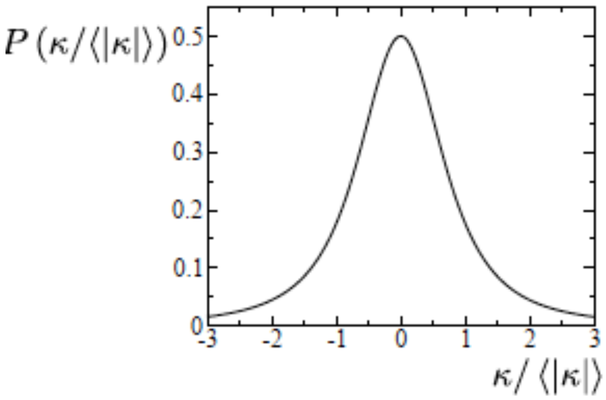
In second-order perturbation theory (even ground state to odd ground state)

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

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 k=0.



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

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

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 k come from the odd curvature

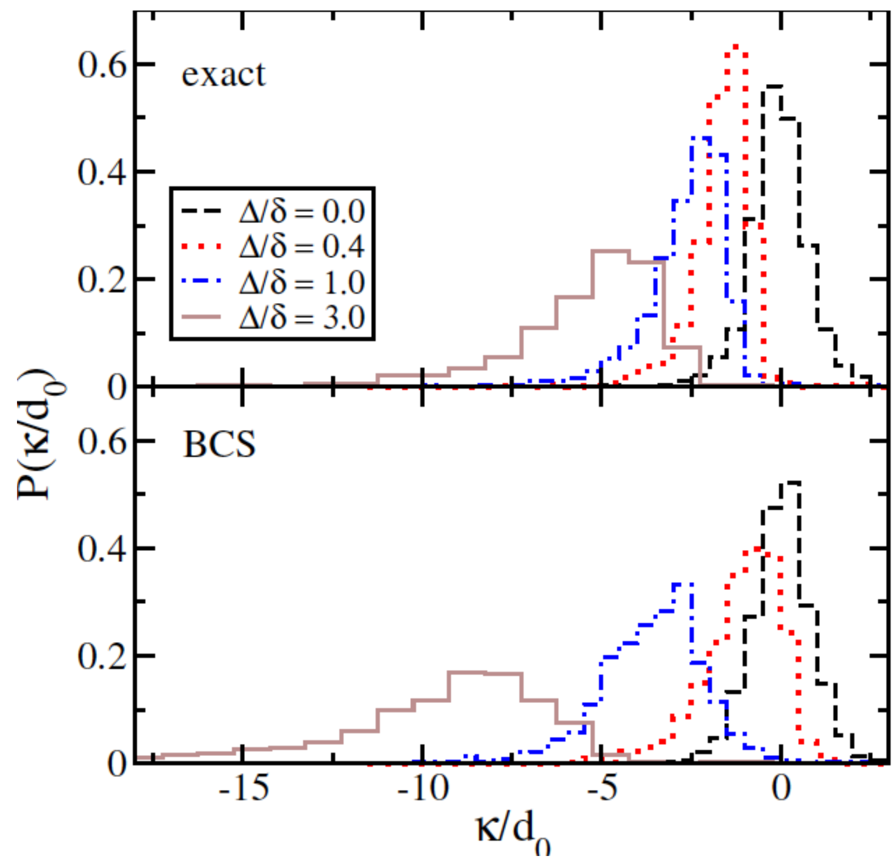
$| E_0^{N_e+1} - E_{\Omega'}^{N_e+1} |$ (no pairing gap in the odd grain) can be small and κ is enhanced

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 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 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