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

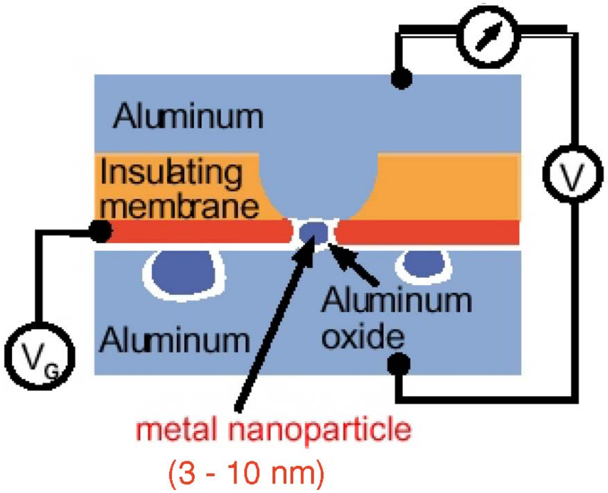
Response to an external magnetic field: g-factor and level curvature

- 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.



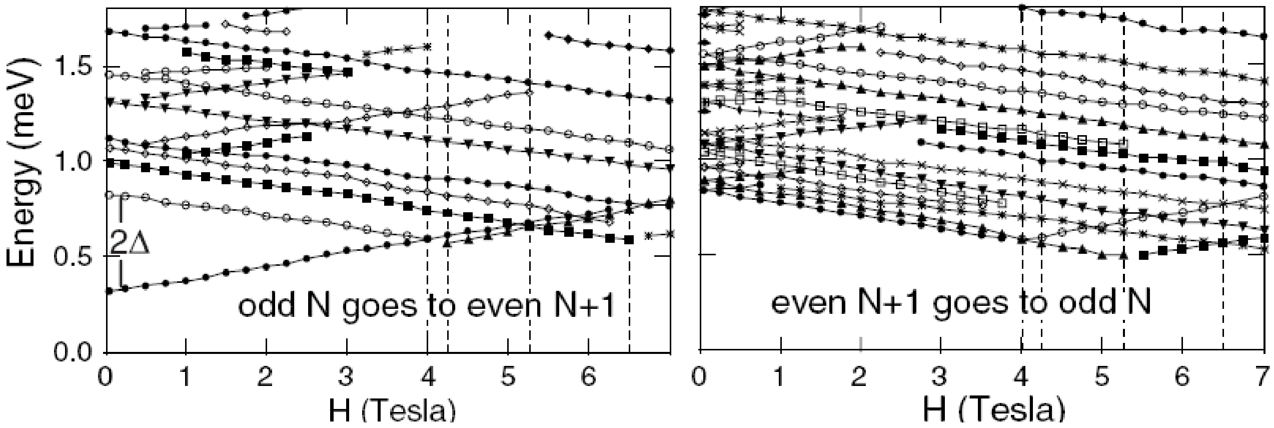
- Ultra-small (nano-scale) grains: probe the quantum regime $T << \delta$ (δ = single-particle level spacing)

Superconducting grains

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

(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.



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

(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 ?

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)]

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

- 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 $J_s > 0$.
- 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.

A derivation from symmetry principles
[Y. A., H.A. Weidemuller, A. Wobst, PRB 72, 045318 (2005)]

$$H = \sum_{\alpha\sigma} \varepsilon_\alpha a^\dagger_{\alpha\sigma} a_{\alpha\sigma} + \frac{1}{2} \sum_{\alpha\beta\gamma\delta\sigma\sigma'} \mathrm{v}_{\alpha\beta;\gamma\delta} a^\dagger_{\alpha\sigma} a^\dagger_{\beta\sigma'} a_{\gamma\sigma'} a_{\delta\sigma}$$

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:

$$\overline{\mathrm{v}}_{\alpha\beta;\gamma\delta} = \mathrm{v}_0 \delta_{\alpha\gamma}\delta_{\beta\delta} + J_s \delta_{\alpha\delta}\delta_{\beta\gamma} - G\,\delta_{\alpha\beta}\delta_{\gamma\delta}$$

$$\Leftrightarrow \quad \bar{V} = \frac{1}{2}\left(\mathrm{v}_0 - J_S/2\right)\hat{N}^2 - \left(\mathrm{v}_0/2 - J_S\right)\hat{N} - J_S\hat{S}^2 - G\,\hat{P}^\dagger\hat{P}$$

Eigenstates of the universal Hamiltonian:

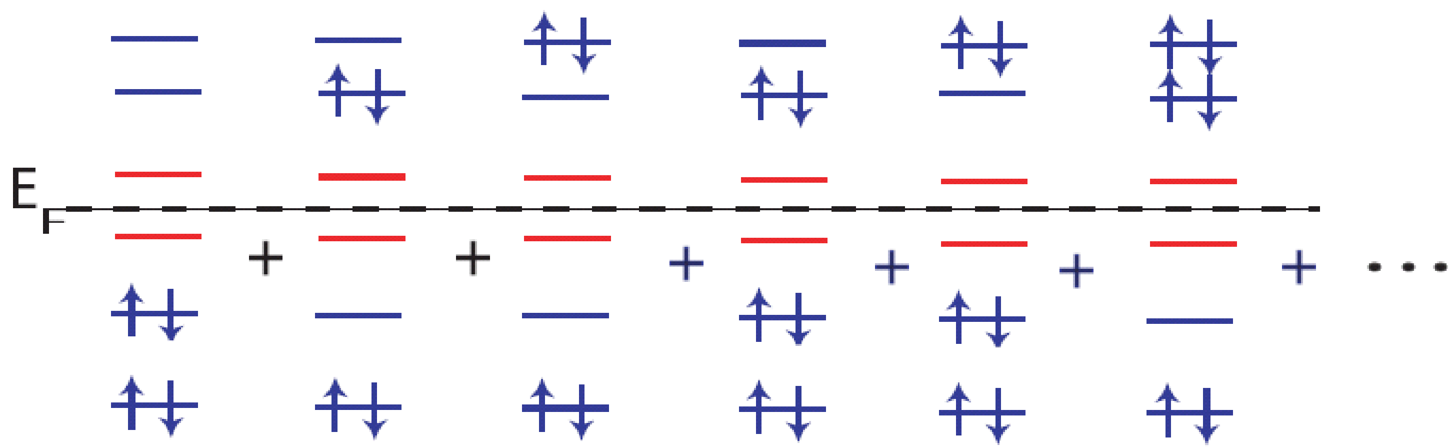
The eigenstates $|U\varsigma; B\gamma SM>$ factorizes into two parts:

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.

For a review, see J. Dukelsky, S. Pittel, and G. Sierra, Rev. Mod. Phys. 76, 643 (2004)

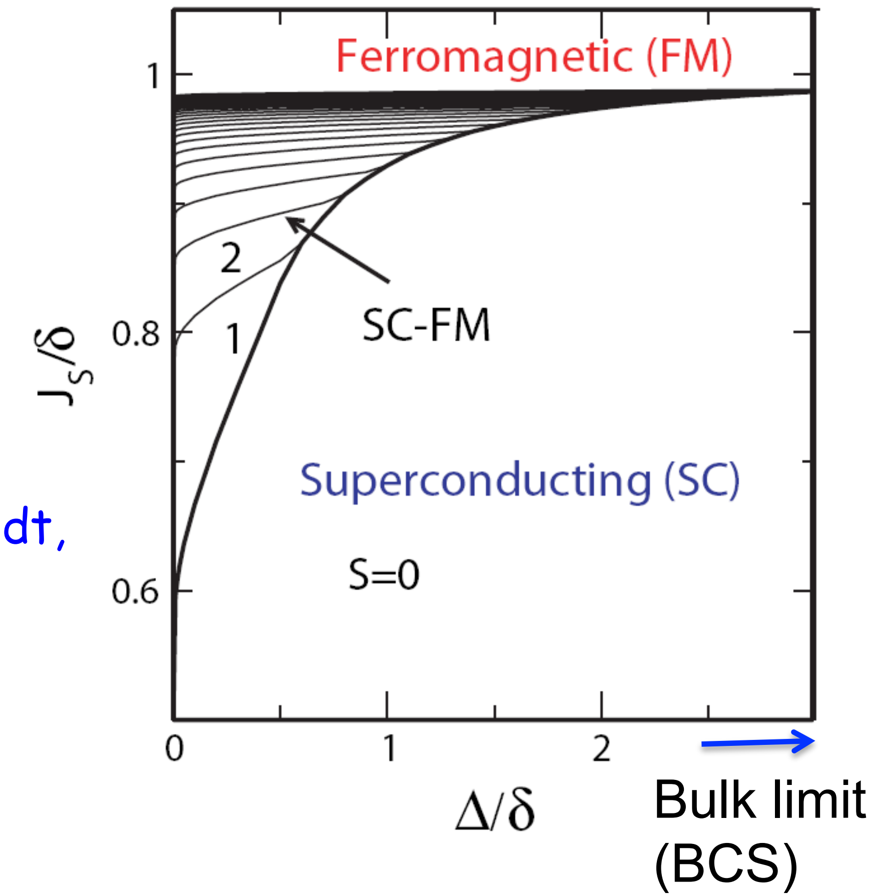
Quantum phase diagram

Z. Ying et al, Phys. Rev. B 74, 012503 (2006)
S. Schmidt, Y.A., K. van Houcke, Europhys. Lett.,80, 47004 (2007)

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

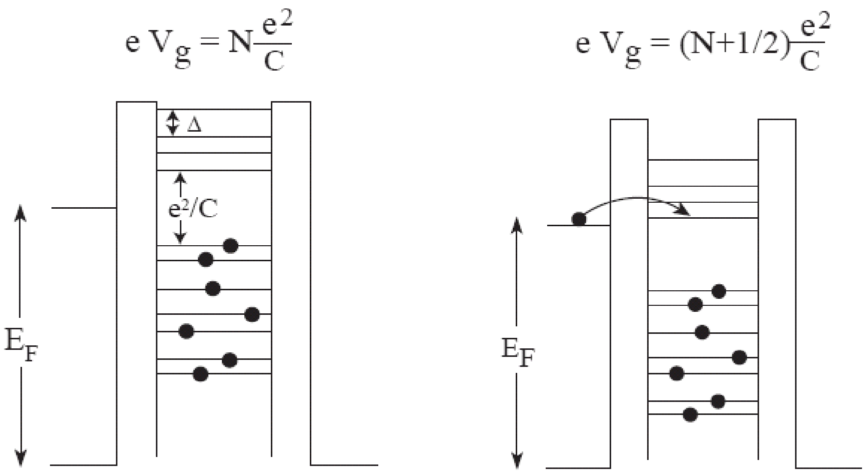
Ground-state spin in the $J_s/\delta - \Delta/\delta$ plane (for an equally spaced single-particle spectrum)

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



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

Transport: Coulomb blockade conductance



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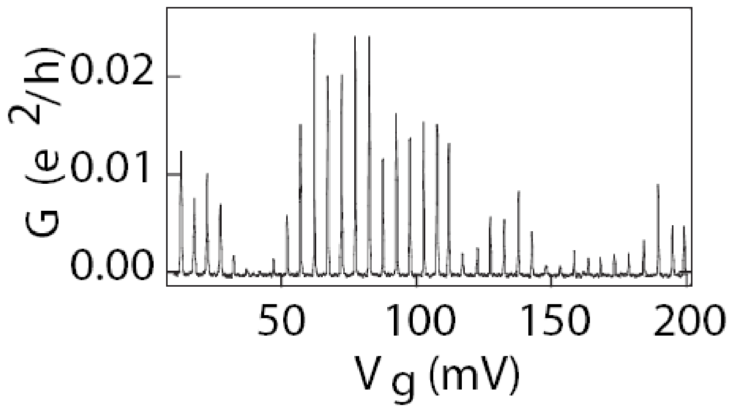
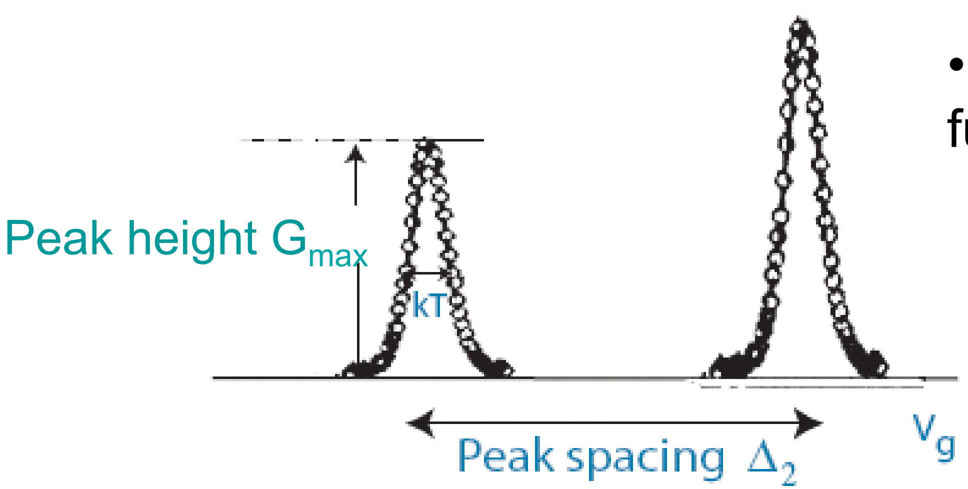


• A conductance peak is observed for each electron that tunnels into the dot



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

⇓

Mesoscopic fluctuations of G_{max} and Δ_2

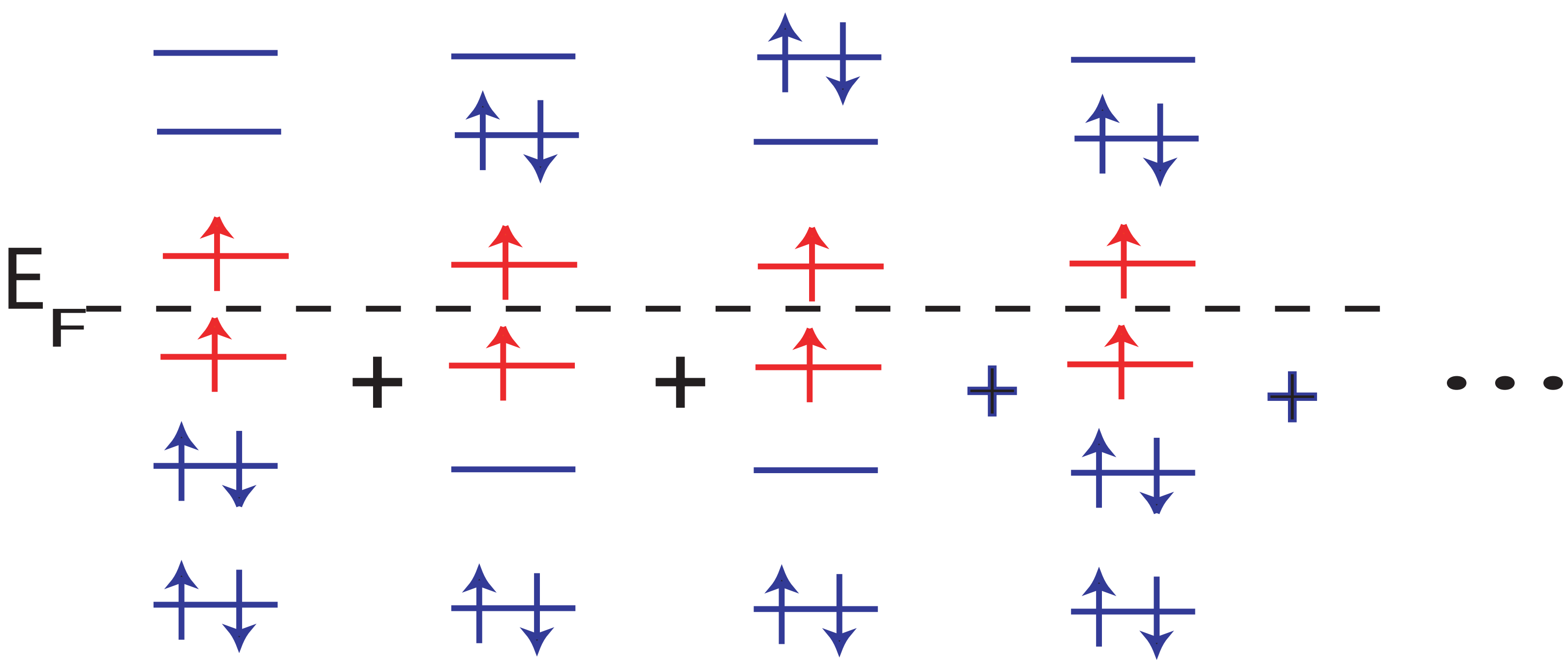
Conductance in a metallic grain

[S. Schmidt and Y.A, PRL 101, 207003 (2008)]

In sequential tunneling, there are two classes of transport processes:

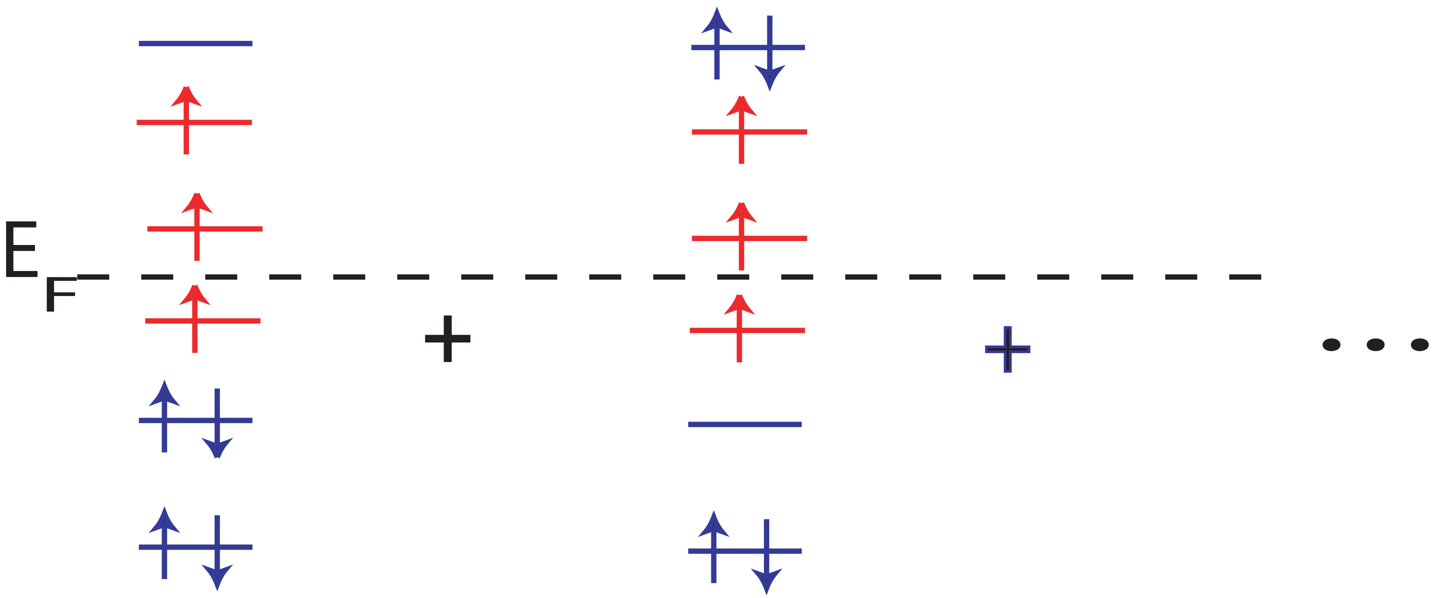
(i) The electron tunnels into an empty level λ and blocks it

Before tunneling:



S=1

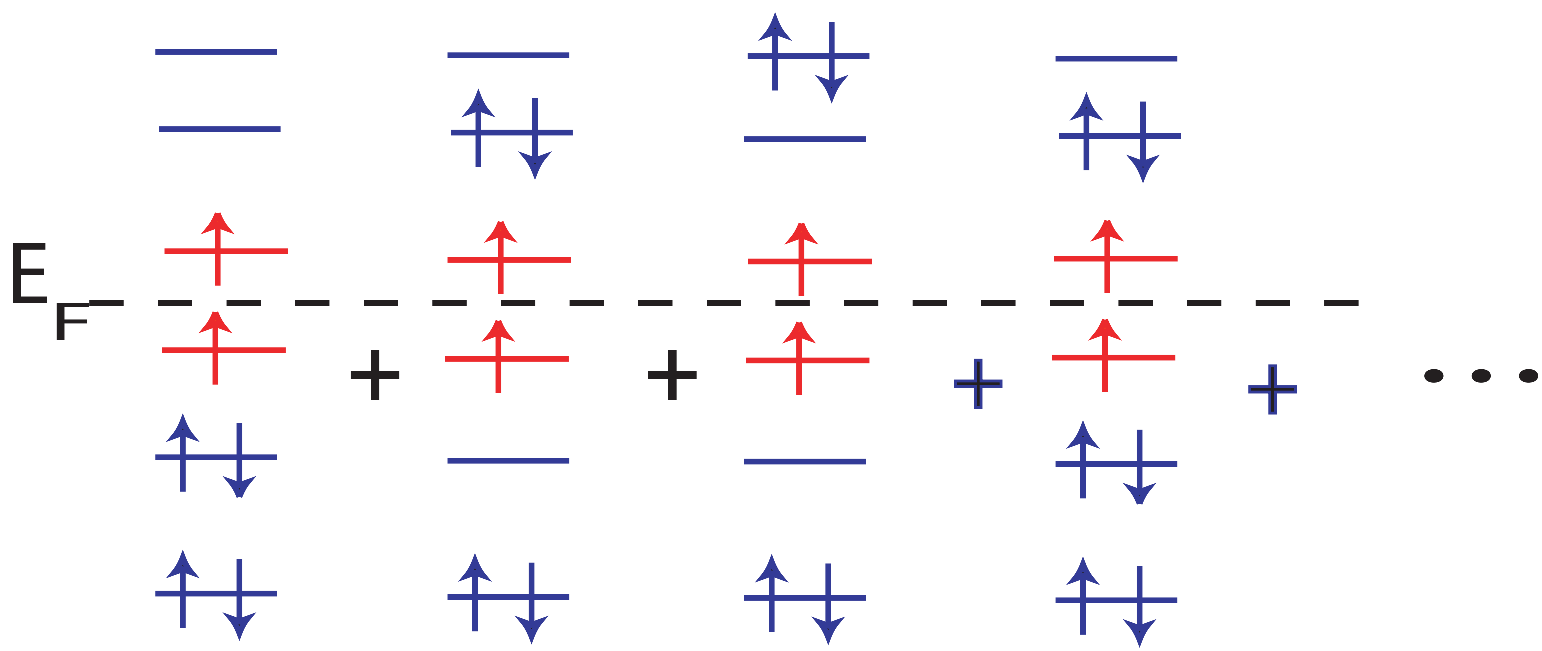
After tunneling:



S=3/2

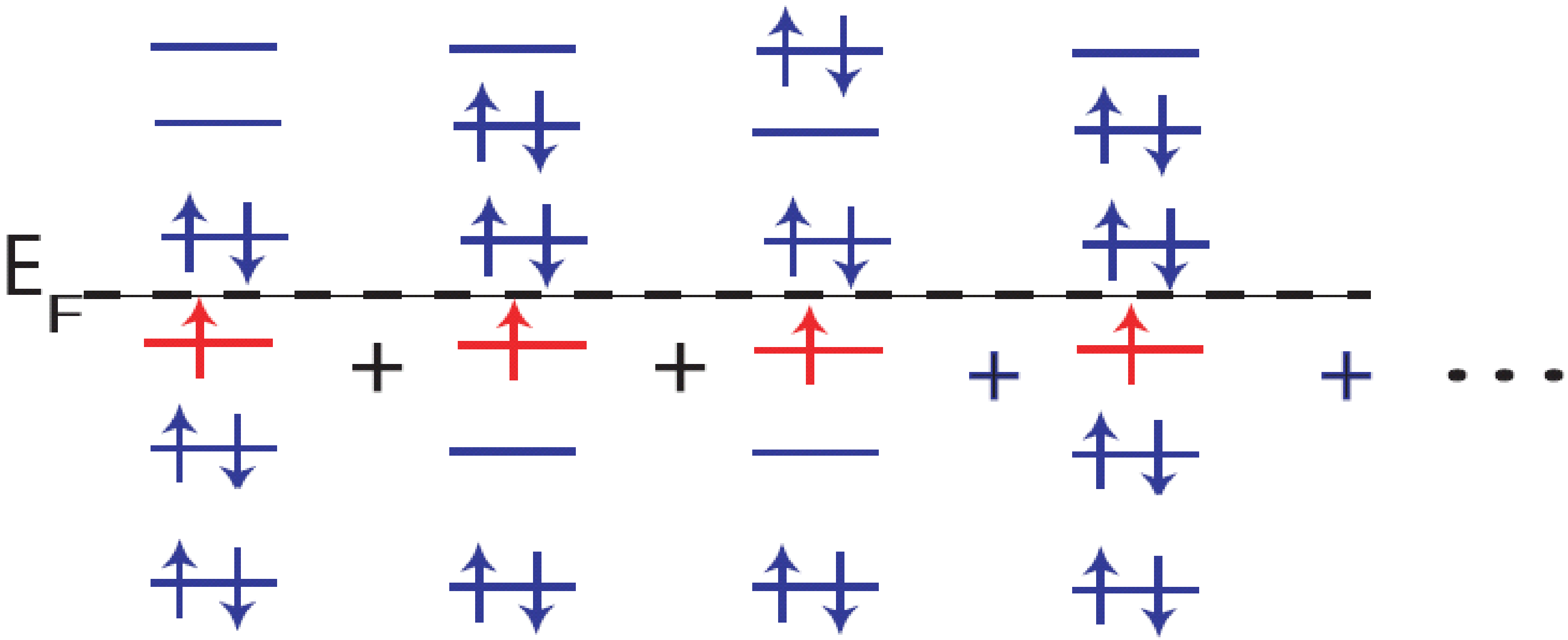
(ii) The electron tunnels into a singly occupied level λ and unblocks it

Before tunneling:



S=1

After tunneling:



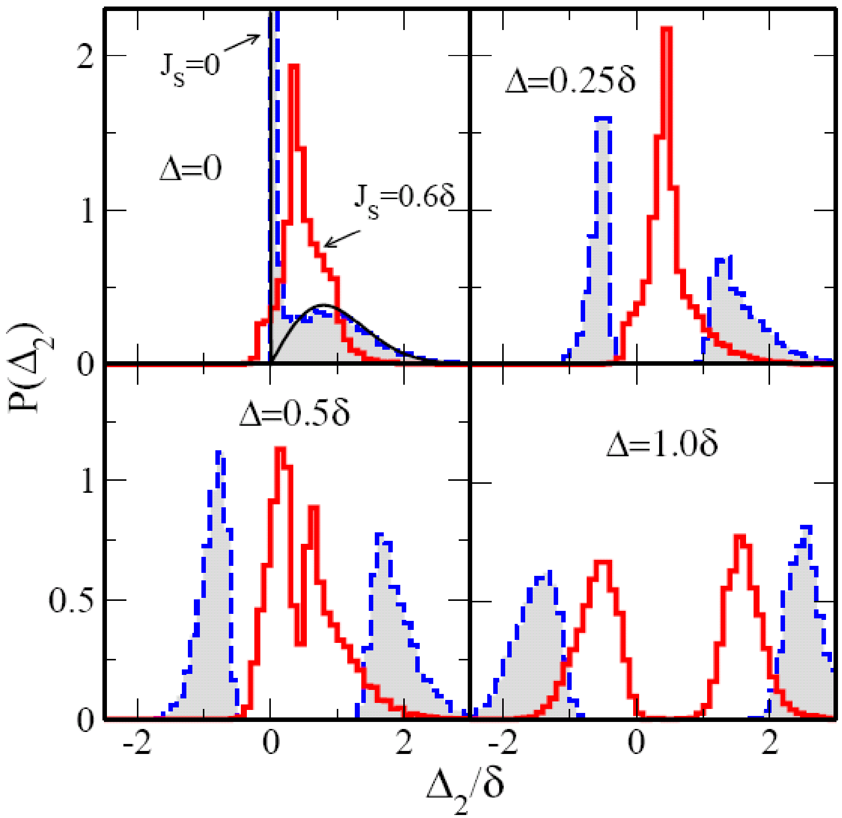
S=1/2

Mesoscopic fluctuations of the conductance peaks

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

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

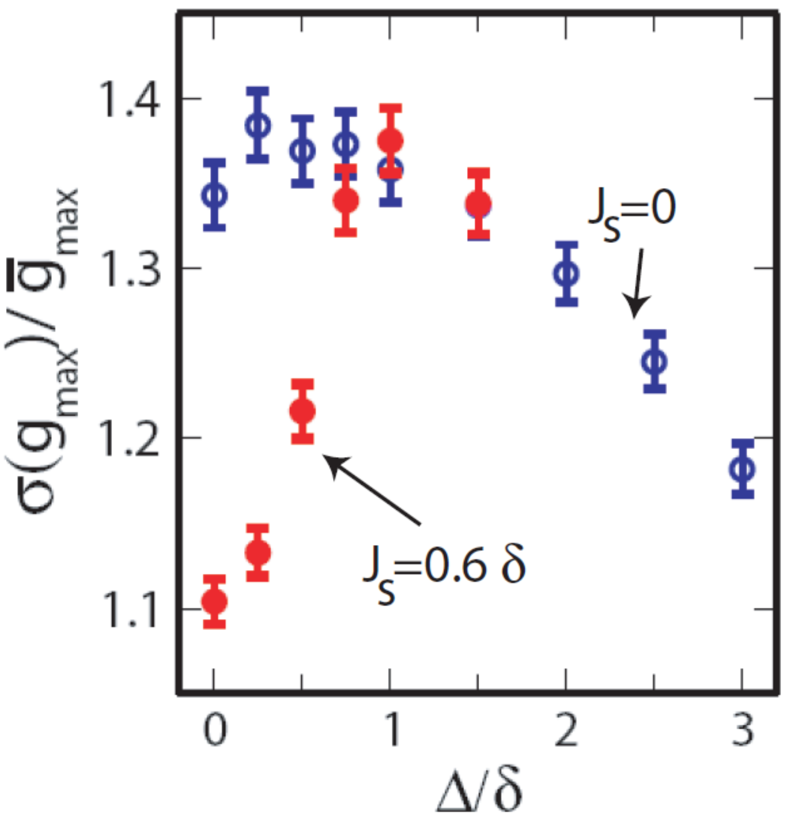
Peak-spacing distributions



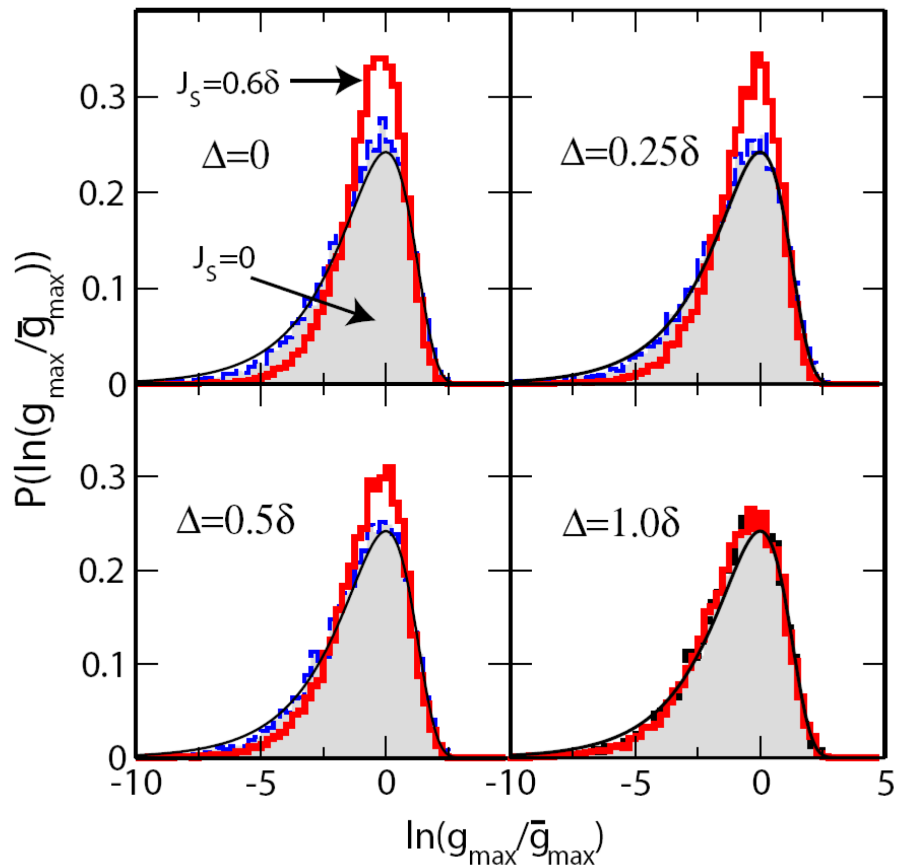
• Exchange suppresses bimodality while pairing enhances it.

Peak-height statistics ($T = 0.1\delta$)

Peak height fluctuation width



Peak-height distributions



- 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).

Thermodynamics

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 (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.

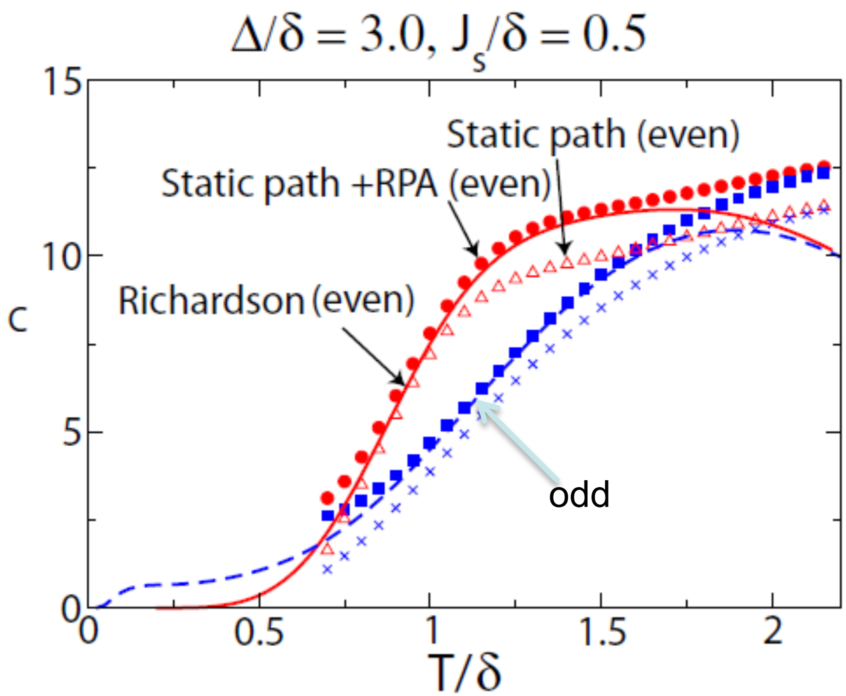
$$P_\eta = (1 + \eta e^{i\pi N})/2$$

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

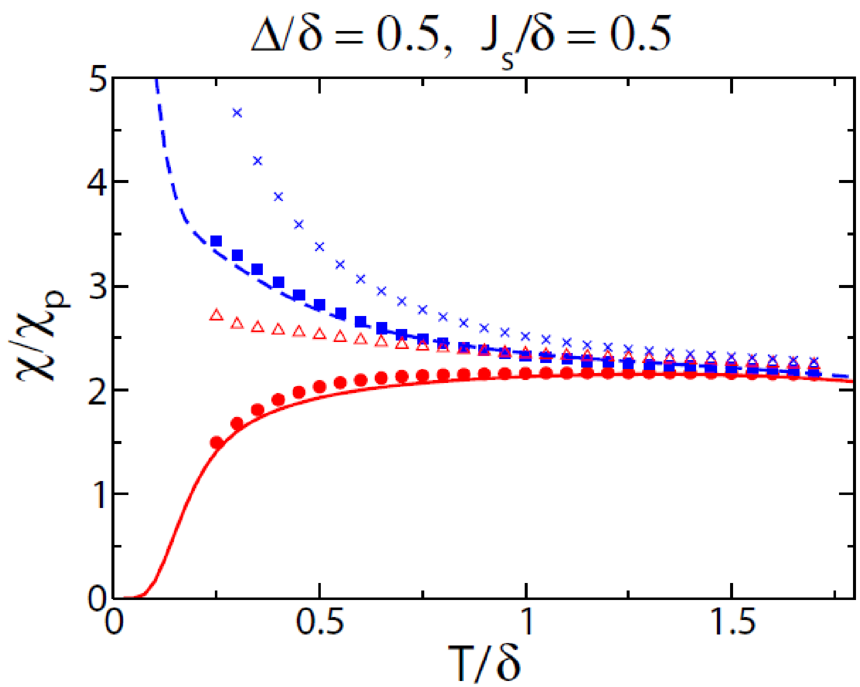
See also R. Rossignoli, N. Canosa and P. Ring, Phys. Rev. Lett. 80, 1853 (1998); G. Falci, A. Fubini, and A. Mastellone, Phys. Rev. B 65, 140507 (2002).

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

Heat capacity



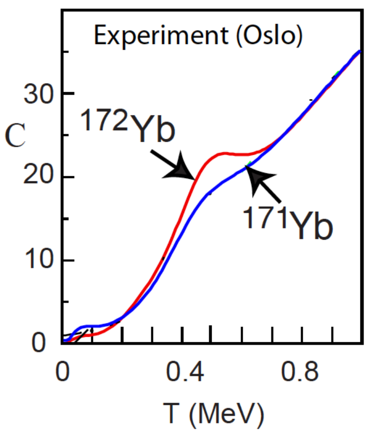
Spin susceptibilty

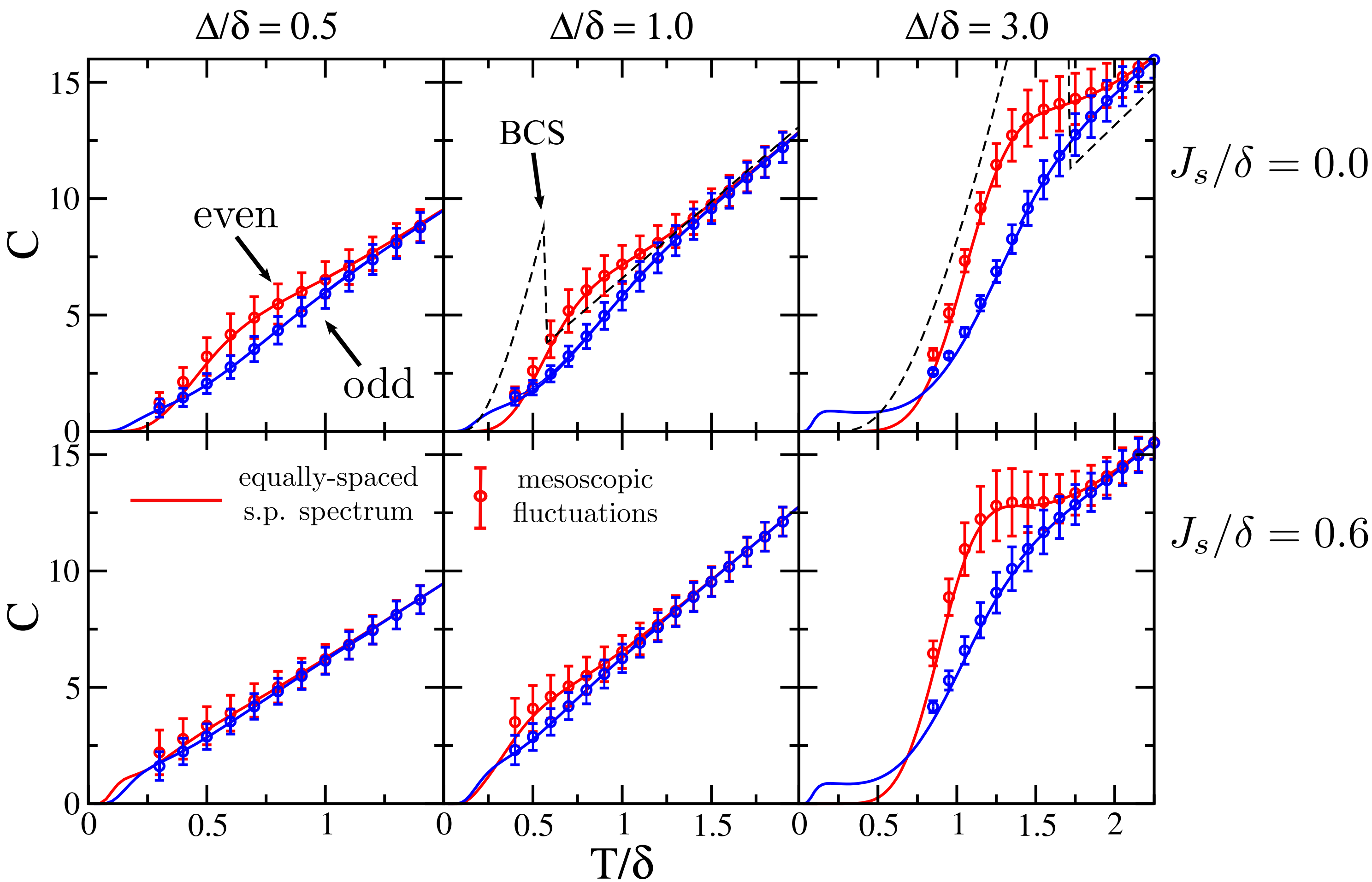


- The static path + RPA+number-parity projection is an accurate method yet very efficient.

Heat capacity

Heat capacity
in nuclei

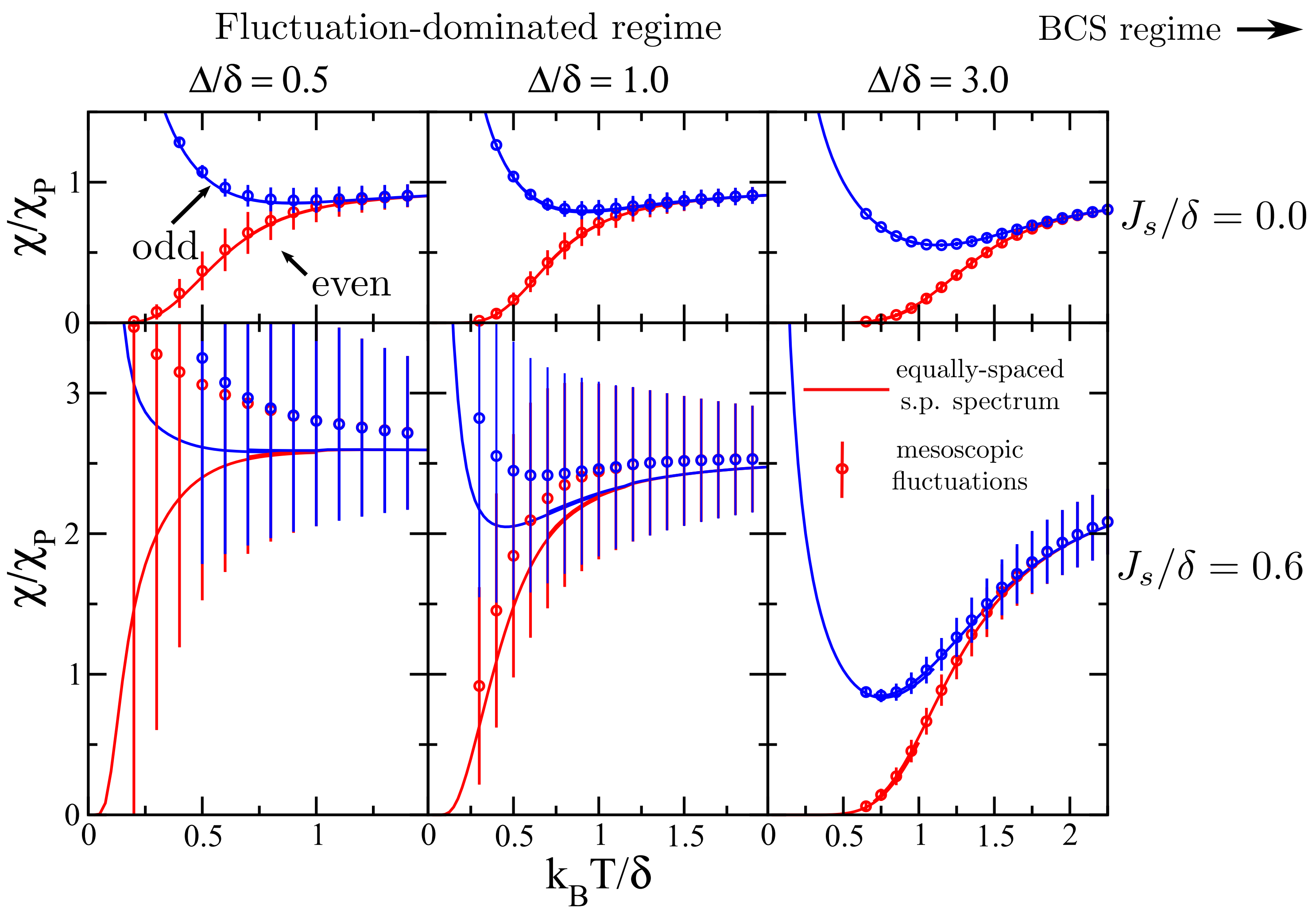




Fluctuation-dominated regime: exchange correlations suppress the odd-even signatures of pairing correlations.

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

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

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

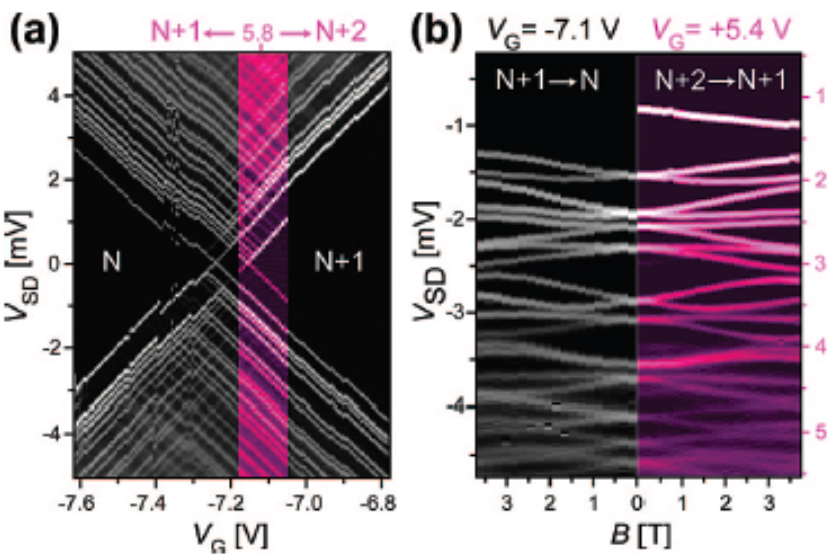
- Without spin orbit scattering, spin is a good quantum number and g=2.

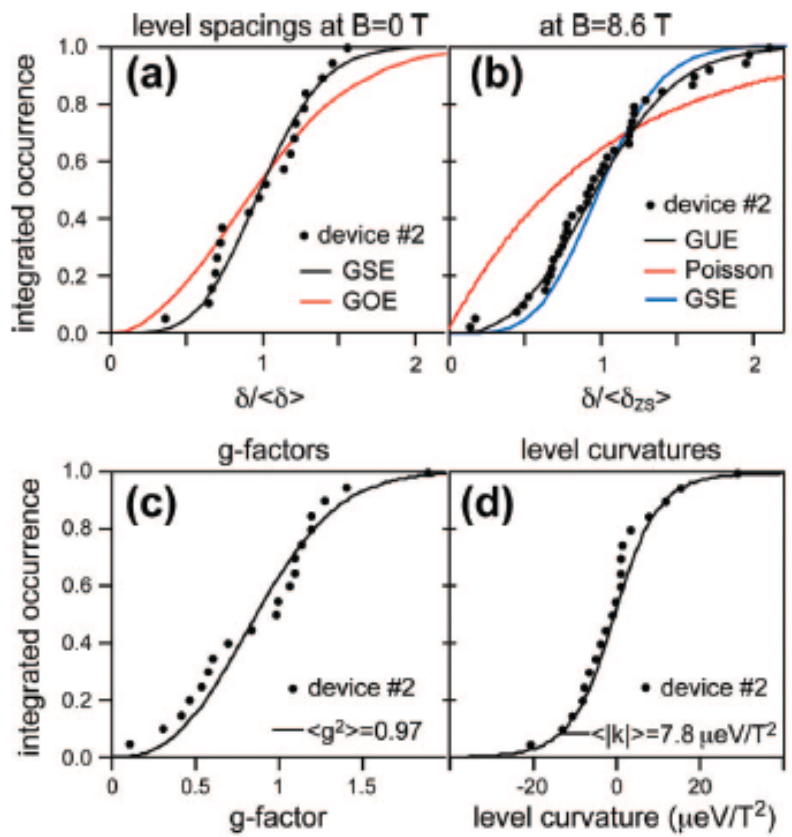
- With spin-orbit scattering, spin is no longer conserved. The g factor is suppressed (g<2) and exhibits level-to-level fluctuations.
  In general, g has a tensor structure.
  The statistical distribution of the g factor was studied using random matrix theory.

[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).





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

We assume a 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

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

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

Universal Hamiltonian with strong spin-orbit scattering

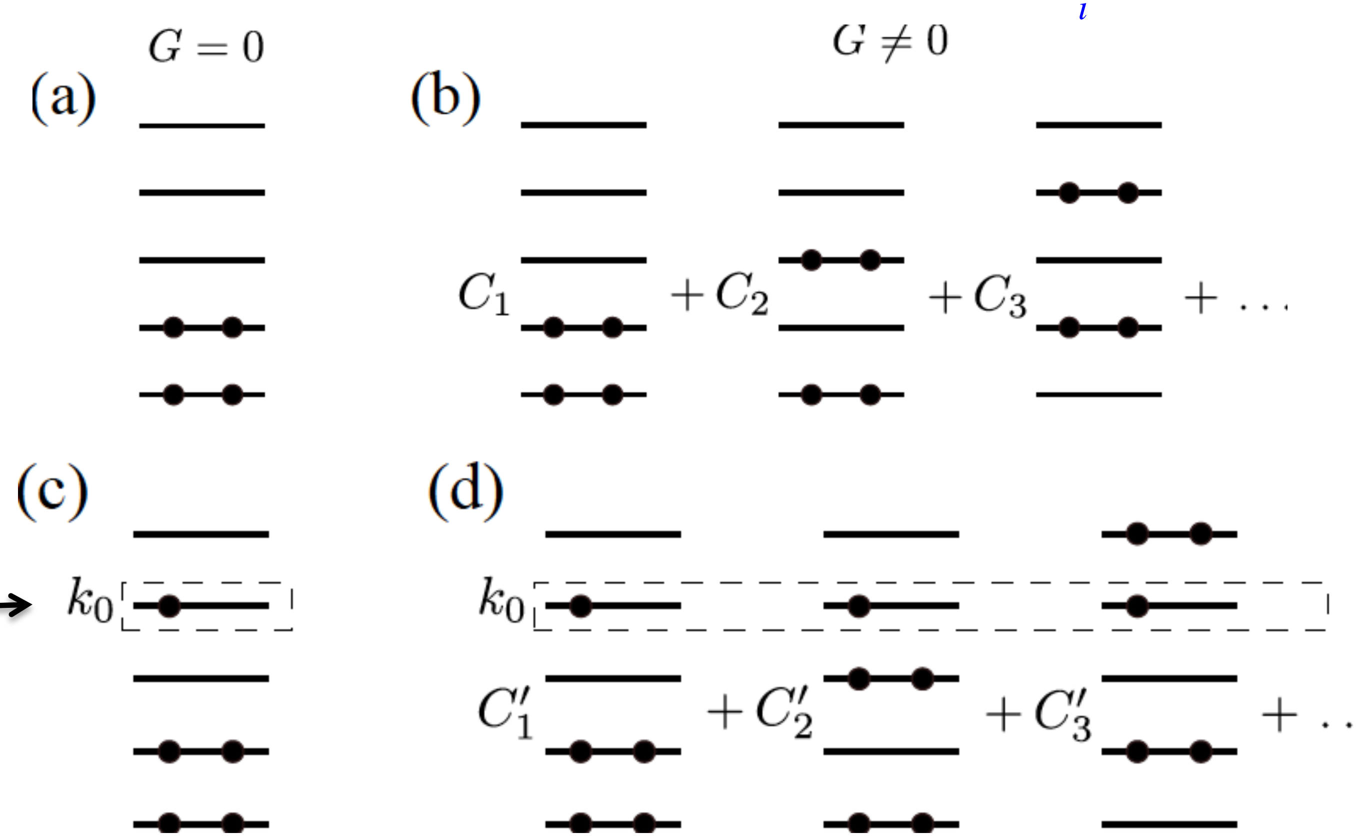
$$H = \sum_{i,\alpha} \varepsilon_i a_{i\alpha}^{\dagger} a_{i\alpha} - G P^{\dagger} P - B M_z$$

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

Even ground state

blocked orbital →

Odd state



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

The many-particle g factor reduces to the single-particle g factor of the odd-particle blocked orbital k_0.

g-factor distributions are not affected by pairing correlations.

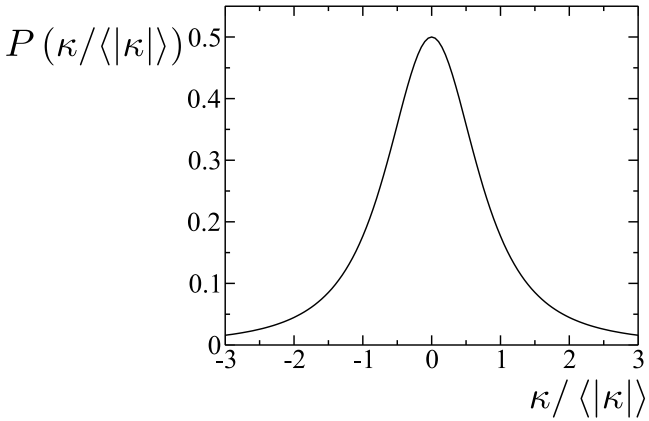
Level curvature κ (quadratic correction)

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

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

In the non-interacting case, κ reduces to the single-level curvature

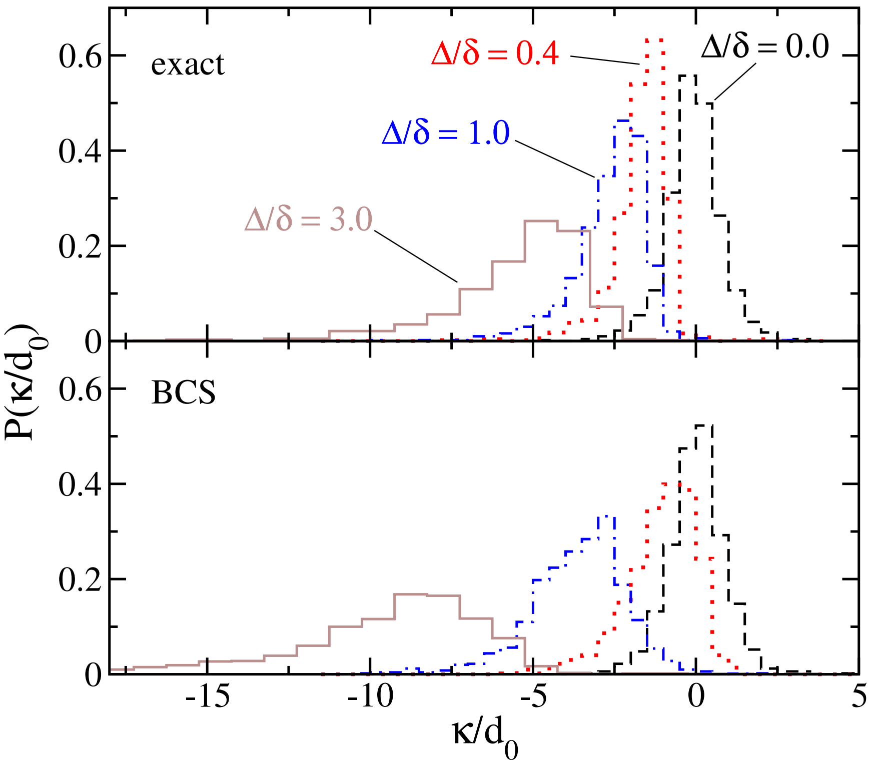
The single-level curvature distribution is symmetric around $\kappa = 0$.



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 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.

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 statistic is highly sensitive to pairing correlations