Superconducting molecular quantum dots

Reinhold Egger
Heinrich-Heine-Universität Düsseldorf
A. Zazunov, A. Schulz, T. Martin,
T. Jonckheere, L. Dell'Anna, F. Siano

Obergurgl, 7th June 2010

Outline

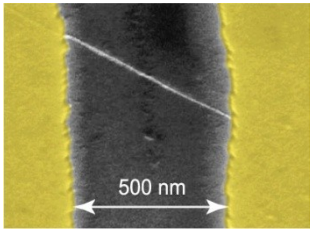
- Introduction: Josephson current through a single nanoscale quantum dot (JDOT)
- Correlated JDOT: Competition Kondo vs superconductivity
- Quantum engineering: Dissipationless manipulation of internal JDOT modes via superconducting phase difference
- Strong spin orbit coupling effects: anomalous Josephson current

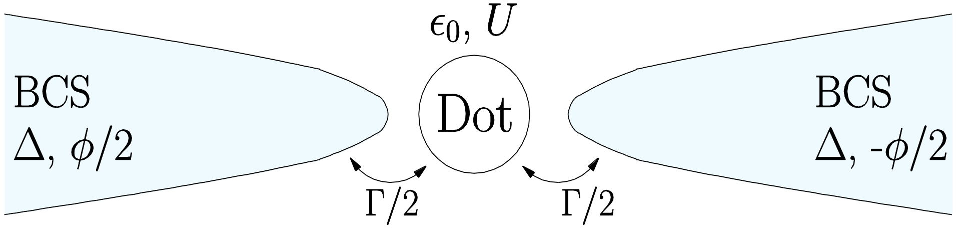
A few words on experiment…

- Josephson effect for single-level JDOT has been successfully realized, critical current ≈ nA and gate-tunable, current phase relation has been obtained in SQUID geometries
- Material classes
  - Multi-wall carbon nanotube dots

    Buitelaar, Schönenberger et al., PRL 2002
  - Single-wall nanotube dots *Kasumov et al., Science 1999; Morpurgo et al., Science 1999; Jarillo-Herrero et al., Nature 2006; Jorgensen et al., PRL 2006; Cleuziou et al., Nature Nanotechn. 2006*
  - InAs nanowires *Doh et al., Science 2005; van Dam et al., Nature 2006*
  - Metallofullerene molecule *Kasumov et al., PRB 2005*
  - Break junctions *Chauvin et al., PRL 2007*

Anderson JDOT





Anderson dot between BCS superconductors (here: symmetric case)

- Single spin-degenerate electronic level on the dot: Charging energy U, gate voltage tunes ε_0, and hybridization Γ between dot and BCS electrodes
- BCS gap Δ, phase difference φ across dot

$$H = H_{dot} + H_{BCS} + H_{tunnel}$$

$$H_{dot} = \varepsilon_0 \left(n_\uparrow + n_\downarrow\right) + U n_\uparrow n_\downarrow$$

Andreev states: U=0

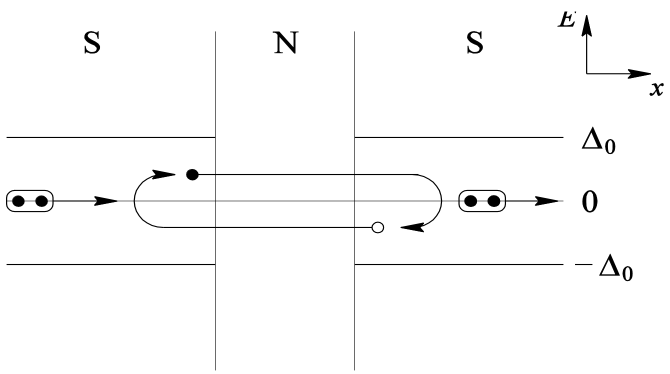
Golubov et al., Rev. Mod. Phys. 2004

– Andreev states at $\pm E_A(\varphi)$

– NN contact transmission probability: Breit Wigner formula

$$\tau = \frac{\Gamma^2}{\Gamma^2 + \varepsilon_0^2}$$

– Current-carrying fermionic bound states inside gap



$$E_A(\varphi) = \widetilde{\Delta}\sqrt{1 - \tau \sin^2 \frac{\varphi}{2}}$$

$$\widetilde{\Delta} = \begin{cases} \Delta, & \Gamma >> \Delta \\ \dfrac{\Gamma}{\sqrt{\tau}} & \Delta >> \Gamma \end{cases}$$

Josephson current: U=0

carried by Andreev state:

$$I(\varphi) = \frac{2e}{\hbar}\partial_\varphi E_g = -\frac{2e}{\hbar}\partial_\varphi E_A = \frac{e\tilde{\Delta}}{2\hbar}\frac{\tau\sin\varphi}{\sqrt{1-\tau\sin^2\frac{\varphi}{2}}}$$

– For tunnel junction (τ<<1), standard Josephson relation $I = I_c \sin\varphi$ with critical current $I_c = \frac{e\tilde{\Delta}\tau}{2\hbar}$ (Ambegaokar-Baratoff formula)

– Perfect contact (resonant tunneling, τ=1) has non-sinusoidal relation: „unitary limit“

$$I(\varphi) = I_c \sin\frac{\varphi}{2}\,\mathrm{sgn}\left(\cos\frac{\varphi}{2}\right), \quad I_c = \frac{e\Delta}{\hbar}$$

Kondo versus proximity effect

How do correlations affect Josephson current?

– Magnetic dot: consider correlated single-occupancy regime $U/\Gamma >> 1,\quad -U < \varepsilon_0 < 0$

– Perturbation theory in Γ yields π-junction with negative critical current $I = I_c \sin\varphi$

Cooper pair tunneling forbidden but fourth-order cotunneling possible: reversed spin ordering of Cooper pair *Kulik, JETP 1965*

– Interplay Kondo effect with superconductivity characterized by universal ratio Δ/T_K with normal-state Kondo temperature

$$T_K^{\left(\varepsilon_0=-\frac{U}{2}\right)} = \sqrt{\frac{\Gamma U}{2}} \exp\left[-\frac{\pi U}{8\Gamma}\right]$$

Universality and phase diagram

- Limiting cases are analytically solvable:

Glazman & Matveev, JETP Lett. 1989

  - $T_K \ll \Delta$: Coulomb blockade regime, cotunneling
    - „π phase“ ($\varphi=\pi$: minimum of free energy), Cooper pair acquires factor $e^{i\pi}$
  - $T_K \gg \Delta$: Many-body Kondo resonance pinned to Fermi level can coexist with superconductivity
    - Josephson current increases (despite of repulsive interactions)
    - Effectively: resonant tunneling (noninteracting result with $\tau=1$)
    - „0 phase“ ($\varphi=0$: minimum of free energy)
- $T_K \approx \Delta$: superconducting gap removes low-energy degrees of freedom, largely quenching the Kondo spin entanglement
- From 0- to π-phase via quantum phase transitions

Consistent picture has by now emerged & universal scaling has been confirmed:

- Mean field theory: intermediate 0'- and π' -phases (both φ=0 and π remain local minima)

  Rozhkov & Arovas, PRL 1999; Vecino et al., PRB 2003
- Noncrossing approximation & slave boson approaches

  Clerk et al., PRB 2000, Sellier et al., PRB 2005
- Numerical & functional RG approaches

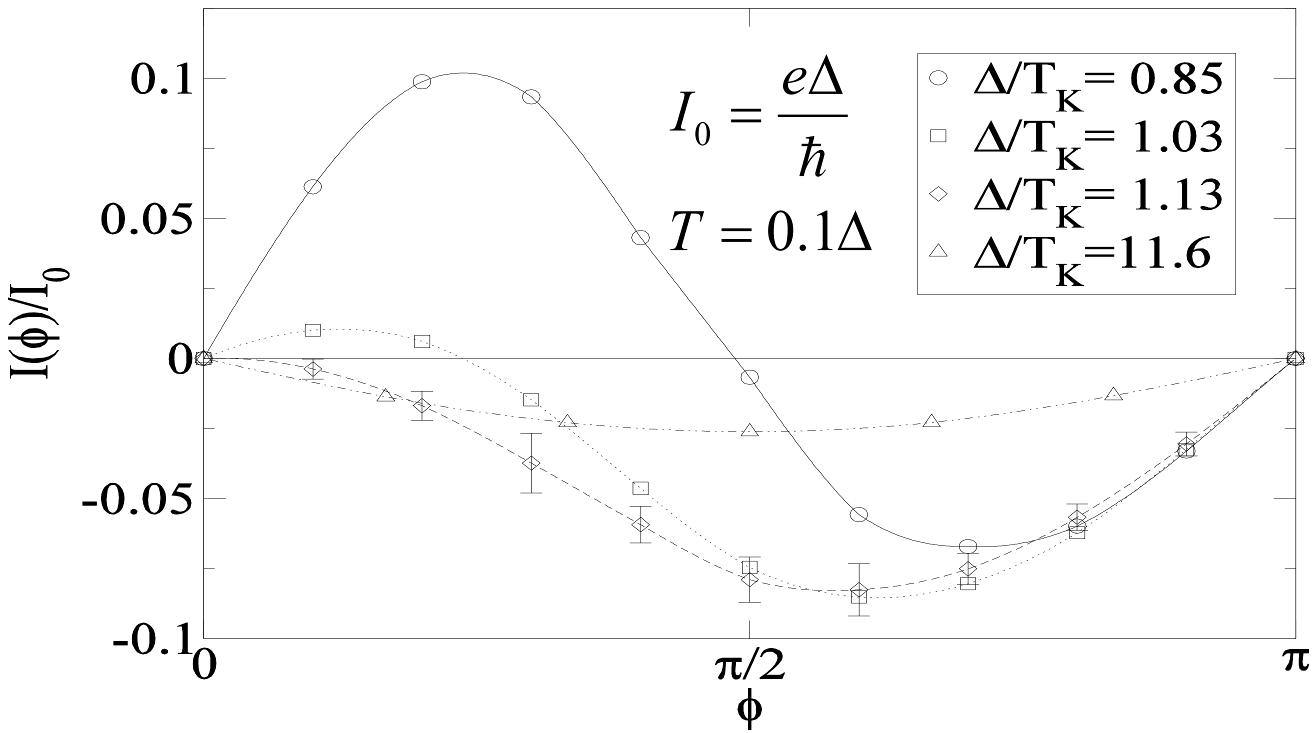
  Choi et al., PRB 2004, Karrasch et al., PRB 2008
- Hirsch-Fye quantum Monte Carlo simulations (numerically exact finite temperature technique) *Siano & Egger, PRL 2004*
- Qualitative agreement with experiments: supercurrent through JDOT, both Kondo regime and π-phase

  Buitelaar et al., PRL 2003; van Dam et al., Nature 2006; Jarillo-Herrero et al., Nature 2006; Cleuziou et al., Nat. Nanotech. 2006; Jorgensen et al., Nano Lett. 2007; Eichler et al., PRL 2009

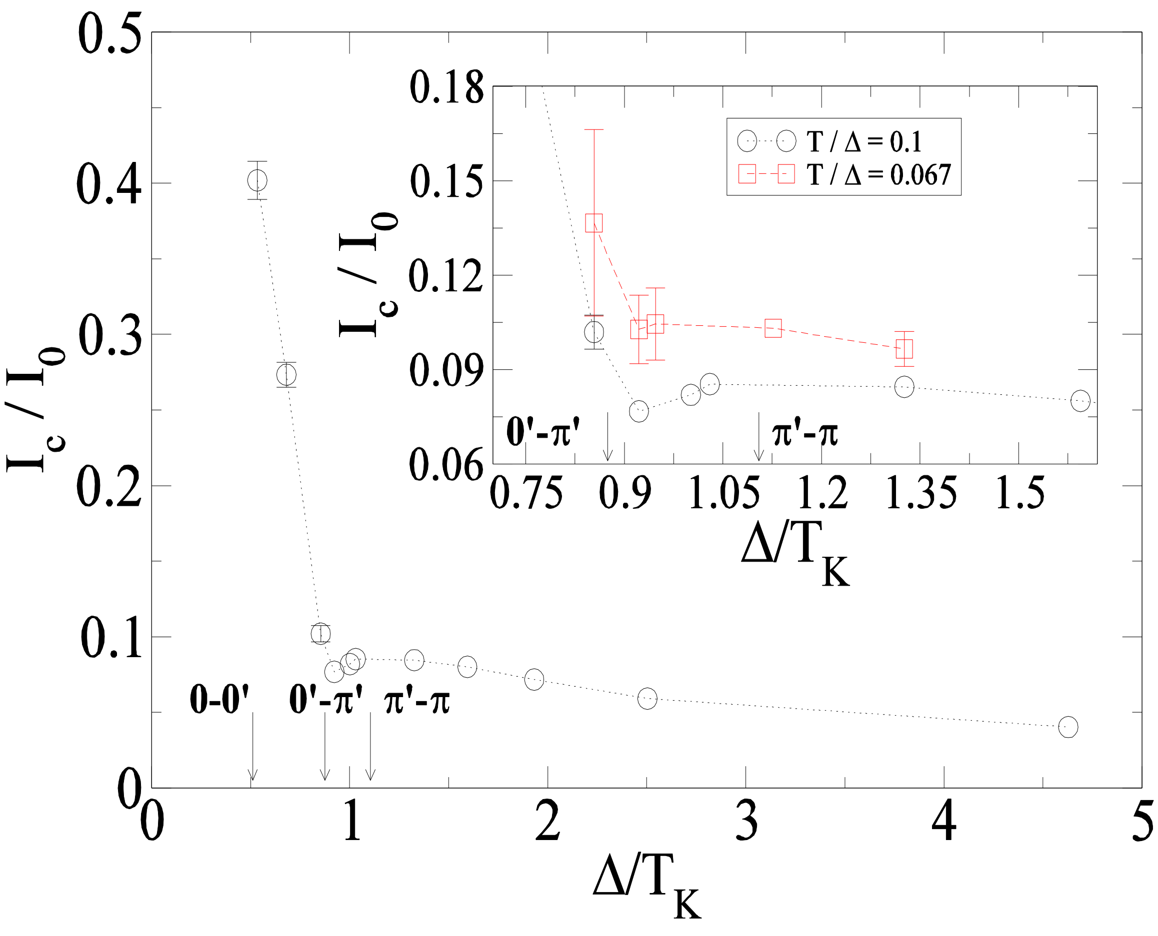
Josephson current: π and π'-phase

Siano & Egger, PRL 2004

QMC results at finite T (when T=0: jumps do occur):



Critical current: universal scaling

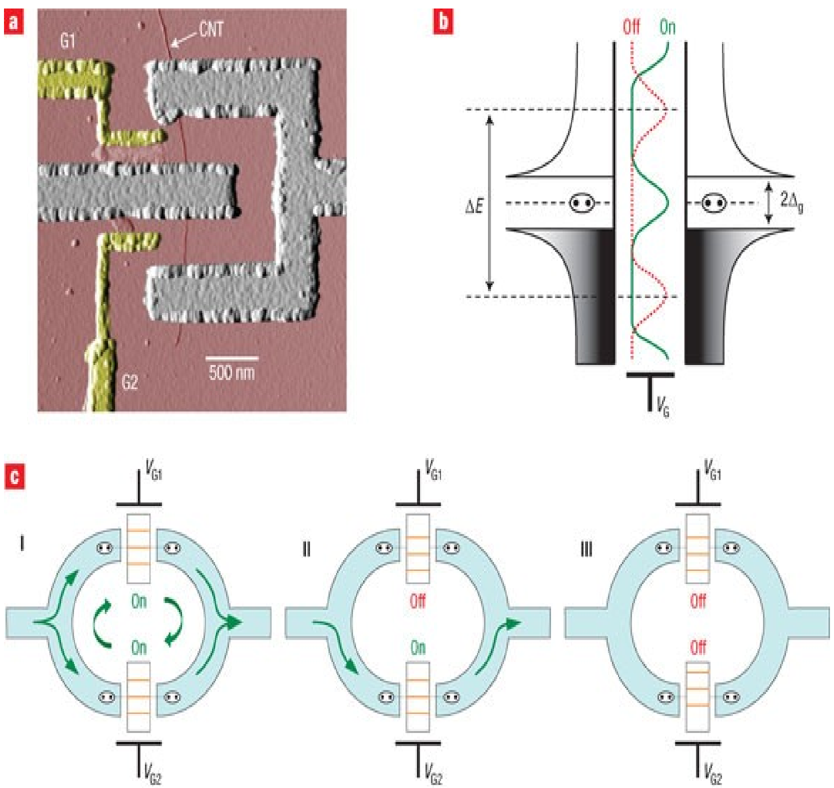


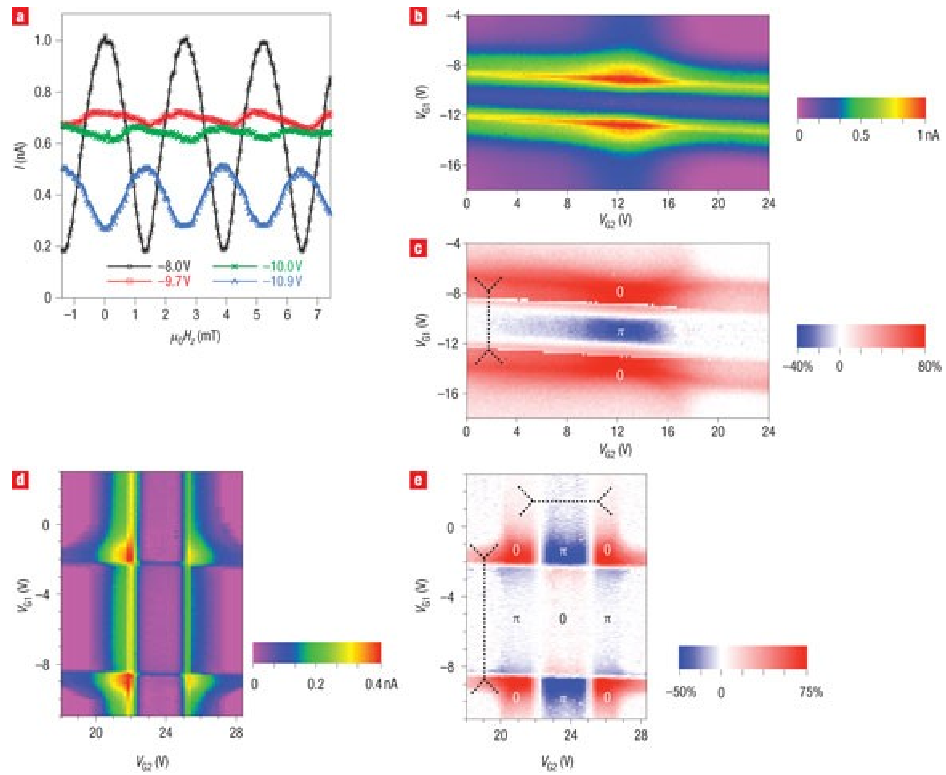
$$\left(\Delta / T_K \right)_{00'} \approx 0.51$$

$$\left(\Delta / T_K \right)_{0'\pi'} \approx 0.87$$

$$\left(\Delta / T_K \right)_{\pi'\pi} \approx 1.11$$

(One) experiment





Cleuziou, Wernsdorfer, et al.,
Nature Nanotechn. 2006

„Quantum engineering“ with JDOTs

- JDOT may have internal degrees of freedom
  - Vibration modes
  - Two-level system (TLS)
  - Electronic degrees of freedom
  - Magnetic modes
- These are affected by superconducting phase variations, both in equilibrium (dissipationless!) and out of equilibrium
- Largely unexplored territory in experiments
- Theoretical predictions: here for TLS

JDOT coupled to TLS

Zazunov, Schulz & Egger, PRL 2009

- Single electronic level coupled to TLS (Pauli matrices σ_i)
  - Model for bistable conformational mode (reaction coordinate) or two stable configurations of a break junction *Thijssen et al., PRL 2006; Lucignano et al., PRB 2008*
- Coupling to dot charge (occupation), not spin!
  - Here: symmetric coupling Γ to both leads

$$H_{dot} = -\frac{E_0}{2}\sigma_z - \frac{W_0}{2}\sigma_x + \left(\varepsilon_0 + \frac{\lambda}{2}\sigma_z\right)\left[n_\uparrow + n_\downarrow\right] + U n_\uparrow n_\downarrow$$

Supercurrent and conformation

- Partition function after integrating out the leads, using Nambu spinor $d(\tau)=\left(d_\uparrow, d_\downarrow^+\right)$ for dot:

$$Z = Tr_{dot}\left[e^{-\beta H_{dot}} T e^{-\int d\tau d\tau' d^+(\tau)\Sigma(\tau-\tau')d(\tau')} \right]$$

$$\Sigma(\omega) = \frac{\Gamma}{\sqrt{\omega^2+\Delta^2}} \begin{pmatrix} -i\omega & \Delta\cos\frac{\varphi}{2} \\ \Delta\cos\frac{\varphi}{2} & -i\omega \end{pmatrix}$$

- This yields ground state energy $E_g(\varphi, E_0)$
- Josephson current $I(\varphi) = \frac{2e}{\hbar}\frac{\partial E_g}{\partial \varphi}$
- Conformational state

$$S(\varphi) \equiv \langle \sigma_z \rangle = -2\frac{\partial E_g}{\partial E_0}$$

Exactly solvable limit

- Analytically solvable case: no TLS tunneling (W_o=0) and no interaction (U=0)
  - TLS dynamics frozen, eff. dot level $\varepsilon_{\sigma=\pm} = \varepsilon_0 \pm \lambda / 2$
  - Ground state energy $E_g = \min\left(E_{\sigma_z=+1}, E_{\sigma_z=-1}\right)$

$$E_{\sigma=\pm} = \pm\frac{1}{2}\left(\lambda - E_0\right) - E_A\left(\varphi;\varepsilon_\pm\right)$$

  follows from Andreev bound state energy $E_A\left(\varphi;\varepsilon\right)$

    - Simple expressions for Δ>>Γ or Γ>>Δ

Conformational switching

Energy bands $E_+(\varphi)$ and $E_-(\varphi)$ may cross at certain phase difference φ^*

- Then: perfect switching between S=1 and S=-1 conformational states
- Josephson current-phase relation then exhibits discontinuities (jumps)

Favorable for switching:
one effective level close to resonance

Effective Hamiltonian

- Another solvable limit (arbitrary U): $\Delta \to \infty$
  - Self energy becomes time local, integration over leads captured in effective Hamiltonian

$$H_{eff} = H_{dot} + \Gamma \cos\frac{\varphi}{2}\left(d_\downarrow d_\uparrow + h.c.\right)$$

  - Hilbert space separates into Andreev sector (spanned by 0- and 2-particle states) plus single-particle sector
  - Ground state in Andreev sector for

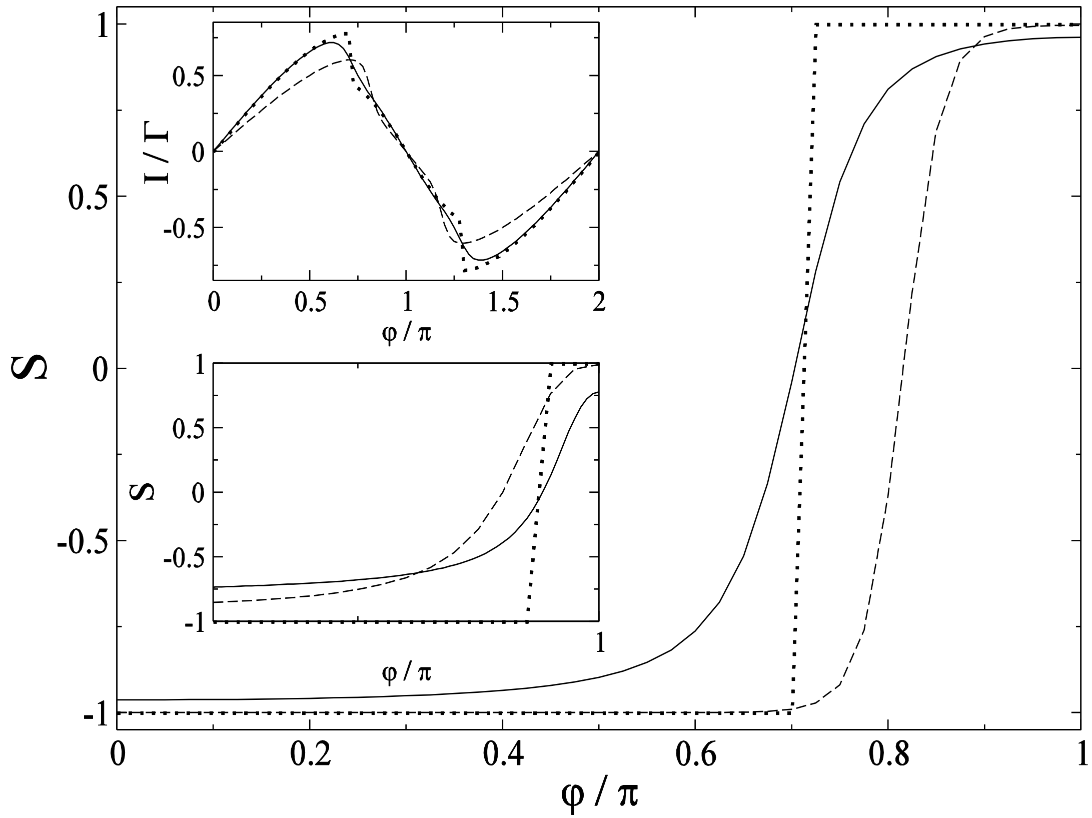
$$U < U_c = \max\left[2\sqrt{\varepsilon_0^2 + \Gamma^2\cos^2\frac{\varphi}{2}}, \lambda\right]$$

  - Diagonalize 4x4 Hamiltonian
- For stronger interactions: perturbative approach yields π-phase

Schulz, Zazunov & Egger, PRB 2009

Conformational switching

Zazunov, Schulz & Egger, PRL 2009



$$E_0 = 0.14\Gamma$$

$$\lambda = \varepsilon_0 = \Gamma/2$$

Results from effective Hamiltonian approach for $\Delta >> \Gamma$

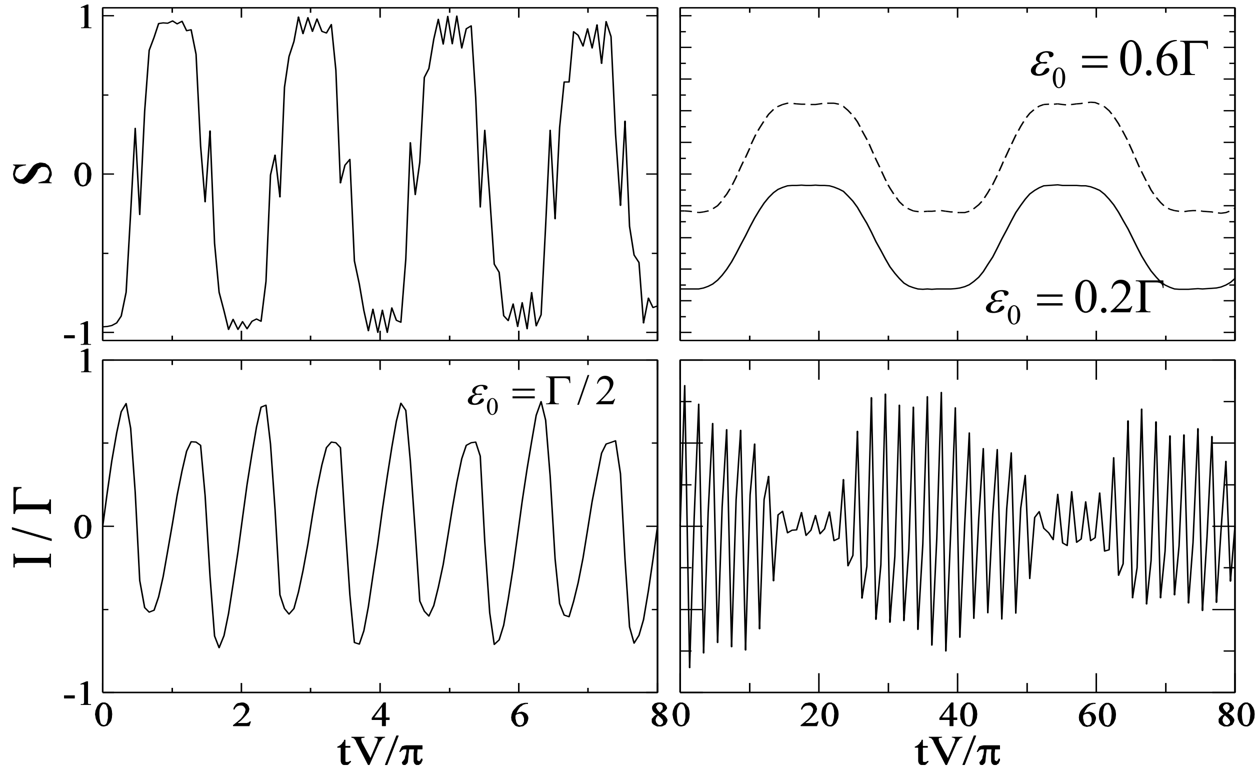
Dotted: $W_o=0$
Solid: $W_o=0.04\Gamma$
Dashed: $W_o=0$, finite T

Lower inset: different effective Hamiltonian for $\Gamma >> \Delta$

Voltage-biased junction

- Consider small voltage V<<Δ (here for Δ>>Γ)
- Phase difference time-dependent $\varphi(t) = \frac{2eV}{\hbar} t$
- Andreev and single-particle sector remain decoupled during time evolution
  - numerical solution of Schrödinger equation in Andreev subspace sufficient
  - Escape rate for Andreev state quasiparticles into continuum states stays exponentially small

Conformational dynamics



$E_0 = W_0 = 0.2\Gamma$

$eV = 0.01\Gamma$

$eV = 5\Gamma$

Adiabatic TLS dynamics:
Time-periodic level crossings & reproducible „noisy“ features

Landau-Zener transitions between Andreev levels: Slow frequency scale due to LZ transitions, also appears in time-dependent Josephson current

Spin-orbit coupled JDOT

Josephson current through spin-orbit coupled JDOT shows interesting & unexpected effects:

Anomalous Josephson current at zero phase difference: spontaneously broken time reversal symmetry, supercurrent flow without phase gradient!

Krive et al., PRB 2005; Reynoso et al., PRL 2008; Buzdin, PRL 2008; Zazunov, Egger, Jonckheere & Martin, PRL 2009

Model

- 2D JDOT with Rashba spin-orbit coupling α and in-plane Zeeman field B, neglect e-e interaction
- N relevant dot energy levels ε_n (for α=B=Γ=0), real-valued wavefunctions $\chi_n(x,y)$
- Contact to leads: NxN hybridization matrices Γ_L, Γ_R

$$H_{dot} = \sum_{n=1}^{N} d_n^+ (\varepsilon_n + B\sigma_x) d_n - i \sum_{nn'} d_n^+ \vec{a}_{nn'} \cdot \vec{\sigma}\ d_{n'}$$

$$\vec{a}_{nn'} = \frac{\alpha}{m} \int dxdy\ \chi_n(\vec{r}) \begin{bmatrix} \partial_y \\ -\partial_x \end{bmatrix} \chi_{n'}(\vec{r})$$

Exact solution for Josephson current

Dell'Anna, Zazunov, Egger & Martin, PRB 2007

Noninteracting problem, exactly solvable

- Doubled Nambu space, Pauli matrices σ_i and τ_i
- 4Nx4N matrix S(ω): $I(\varphi) = -\frac{2e}{\hbar}\partial_\varphi \int_0^\infty d\omega \, Tr \ln S(\omega)$

$$S(\omega) = -i\omega\left(1 + \frac{\Gamma_L + \Gamma_R}{\sqrt{\omega^2 + \Delta^2}}\right) + E\tau_z\sigma_z + Z + \frac{\Delta}{\sqrt{\omega^2 + \Delta^2}} Y$$

$$Y = (\Gamma_L + \Gamma_R)\cos\frac{\varphi}{2}\sigma_x\tau_z + (\Gamma_L - \Gamma_R)\sin\frac{\varphi}{2}\sigma_y, \quad E = diag\left(\varepsilon_n - \frac{\alpha^2}{2m}\right)$$

$$Z = (iA_x\sigma_x + b_y\sigma_y)\tau_x + (iA_y\sigma_x - b_x\sigma_y)\tau_y + iA_z\sigma_z + b_z\tau_z$$

Anomalous supercurrent

- Can we have anomalous supercurrent?

  equivalent to phase shift: φ_o junction $\quad I_a \equiv I(\varphi = 0) \neq 0$

  For αB=0, exact solution yields I_a=0

- Analytical approach for weak asymmetry and small αB:

  $$S = S_0 + S_1$$

  – expand in S_1 for $\varphi \approx 0$

  $$S_1 = Z + \frac{\varphi}{2} \frac{\Delta}{\sqrt{\omega^2 + \Delta^2}} (\Gamma_L - \Gamma_R)\sigma_y$$

  – Leading non-vanishing term: third order of the perturbation series !

Analytical result

- Anomalous supercurrent then follows in analytical (but lengthy) form
- Simple limit: for $\max \Gamma_{L/R,nn} >> \Delta$

$$I_a = \frac{2e\Delta}{\hbar} Tr_{dot}\left[\frac{1}{\Gamma_0^2 + E^2} [\Gamma_R, \Gamma_L] \frac{1}{\Gamma_0^2 + E^2} BA_x \right]$$

  – in this order: $I_a \propto \alpha B$

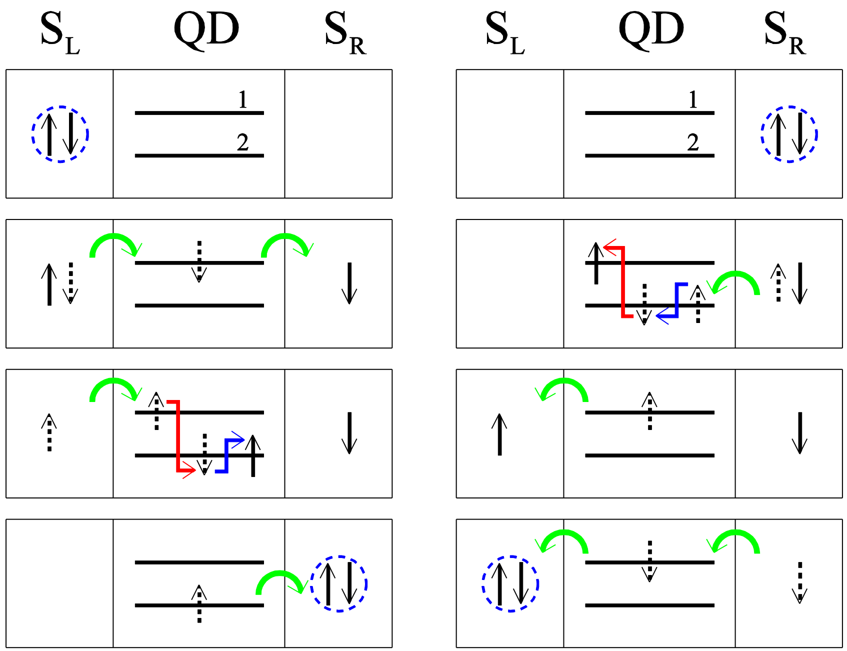
$$\Gamma_0 = diag(\Gamma_L + \Gamma_R)$$

- Apart from SO coupling and appropriately oriented Zeeman field, another necessary condition can be read off…

Conditions for existence of an anomalous supercurrent

- Finite spin-orbit coupling and Zeeman field
- „Chirality" condition: $\left[\Gamma_L, \Gamma_R\right] \neq 0$
  - Anomalous current requires at least two dot levels
  - Numerical study of full expression shows that this condition applies in general
- Existence of anomalous supercurrent implies spontaneously broken time reversal symmetry
- How can one understand this?

Basic explanation



(a) (b)

Transfer of Cooper pair through N=2 dot for φ=0: SOI and Zeeman field combine to

$$H' = \sigma_x \begin{pmatrix} B & iA \\ -iA & B \end{pmatrix}, \quad A \propto \alpha$$

Process (a) yields correction $\delta t_{L\to R} = (t_{L1} t_{R1})(t_{L1} iAB t_{R2})$

Process (b) yields correction $\delta t_{R\to L} = (t_{R2} B(-iA) t_{L1})(t_{R1} t_{L1})$

- SO coupling and Zeeman field conspire to produce effective orbital field
- Anomalous supercurrent contributions add:

$$\delta I_a^{(a)} \propto v A B \Gamma_{L,11} \Gamma_{R,12}$$

$$\delta I_a^{(b)} \propto (-v) \cdot (-A) B \Gamma_{L,11} \Gamma_{R,12}$$

- Summing up all relevant processes:

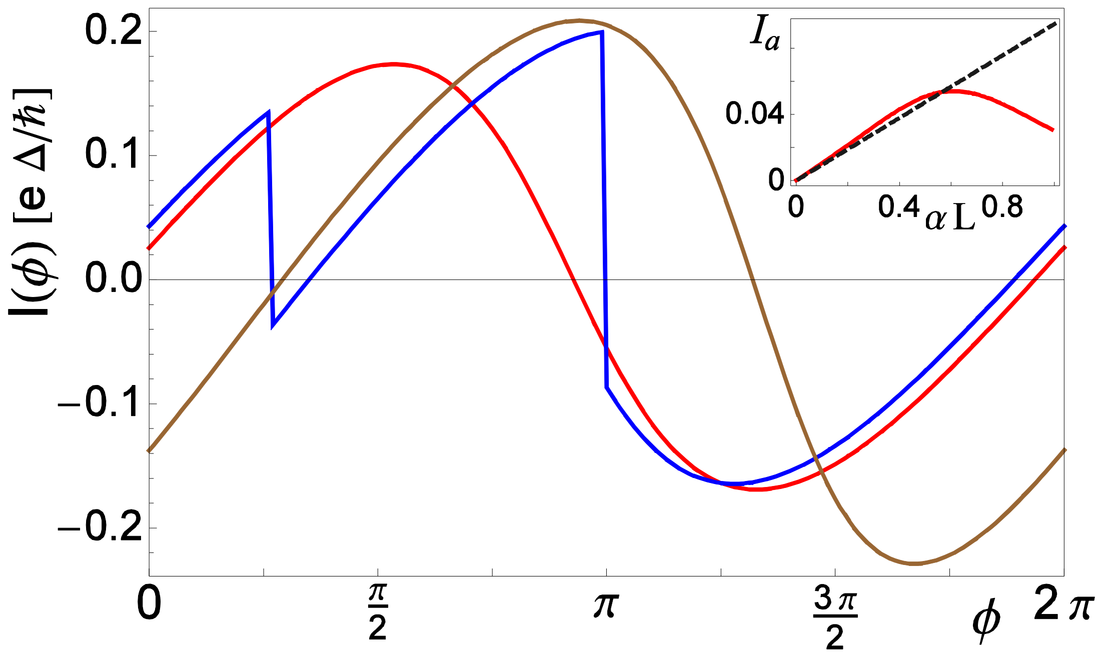
$$I_a \propto B(t_{L1}t_{R1} + t_{L2}t_{R2})(t_{L1}At_{R2} + t_{L2}(-A)t_{R1})$$
$$\propto AB((\Gamma_{L,11} - \Gamma_{L,22})\Gamma_{R,12} - (\Gamma_{R,11} - \Gamma_{R,22})\Gamma_{L,12})$$

  – Nonzero iff $\alpha B[\Gamma_L, \Gamma_R] \neq 0$
  – Symmetry argument: condition also holds when weak interactions are included

Numerical results from full expression for Josephson current-phase relation

Zazunov, Egger, Jonckheere & Martin, PRL 2009

Harmonic transverse & hard-wall longitudinal confinement, N=2, several choices for hybridization matrices



- Jumps in the current-phase relation
- Different positive/negative critical current: rectification
- Analytical prediction accurate even for large αB

Conclusions

„JDOT“ contains rich physics & potential for applications:

- Correlation effects: interplay Kondo effect vs proximity induced superconductivity
- Dissipationless „quantum engineering“ of internal modes
- Spin-orbit coupling: anomalous Josephson current