Superconducting molecular quantum dots

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Outline

• Introduction: Superconducting transport through a single nanoscale quantum dot (JDOT)
• Josephson effect through correlated JDOT
  – Competition Kondo vs proximity effect, phase diagram
  – SU(4) Kondo effect and Josephson current in carbon nanotube dots
  – Nonequilibrium effects: multiple Andreev reflections (MAR) with interactions
• 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 $\approx nA$ 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  
  - 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 dot between BCS superconductors (here: symmetric case)

- Single spin-degenerate electronic level on the dot: Charging energy $U$, gate voltage tunes $\varepsilon_0$, and hybridization $\Gamma$ between dot and BCS electrodes
- BCS gap $\Delta$, phase difference $\varphi$ across dot

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

$$H_{dot} = \varepsilon_0 (n_{\uparrow} + n_{\downarrow}) + Un_{\uparrow}n_{\downarrow}$$
Andreev states: U=0

- Josephson current for noninteracting JDOT
  - Competition Andreev state $\pm E_A(\varphi)$ & Breit-Wigner resonance
  - NN contact transmission probability

- Andreev states: Current-carrying fermionic bound states inside gap

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

$$\tilde{\Delta} = \begin{cases} \frac{\Delta}{\sqrt{\tau}} & \Delta \gg \Gamma \\ \frac{\Gamma}{\sqrt{\tau}} & \Gamma \gg \Delta \end{cases}$$

Golubov et al., Rev. Mod. Phys. 2004
Josephson current: U=0

carried by Andreev state:

\[ I(\phi) = \frac{2e}{\hbar} \partial_\phi E_g = -\frac{2e}{\hbar} \partial_\phi E_A = \frac{e\tilde{\Delta}}{2\hbar} \sqrt{1 - \tau \sin^2 \varphi} \left( \frac{\tau \sin \varphi}{2} \right) \]

– For tunnel junction (\( \tau \ll 1 \)), standard Josephson relation \( I = I_c \sin \phi \) with critical current \( I_c = \frac{e\tilde{\Delta}}{2\hbar} \tau \)

(\text{Ambegaokar-Baratoff formula})

– Perfect contact (resonant tunneling, \( \tau = 1 \)) has non-sinusoidal relation: unitary limit

\[ I(\phi) = I_c \sin \frac{\phi}{2} \text{sgn} \left( \cos \frac{\phi}{2} \right), \quad I_c = \frac{e\Delta}{\hbar} \]
Nonequilibrium effects: U=0

- Subgap transport involves multiple Andreev reflections
- Specific features at onset voltages $eV=2\Delta/n$ for transfer due to $n$ Andreev reflections

*Cuevas et al., PRB 1996*
Kondo versus proximity effect

How do correlations affect Josephson current?

– Magnetic dot: consider correlated single-occupancy regime

\[ \frac{U}{\Gamma} >> 1, \quad -U < \varepsilon_0 < 0 \]

– Perturbation theory in $$\Gamma$$ yields \( \pi \)-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 \( \frac{\Delta}{T_K} \) with normal-state Kondo temperature

\[ T_K(\varepsilon_0 = -\frac{U}{2}) = \sqrt{\frac{\Gamma U}{2}} \exp \left[ -\frac{\pi U}{8\Gamma} \right] \]
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 $\pi$-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 \( \phi=0 \) and \( \pi \) 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
  
Josephson current: $\pi$ and $\pi'$-phase

Siano & Egger, PRL 2004

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

$I_0 = \frac{e\Delta}{\hbar}$

$T = 0.1\Delta$
Critical current: universal scaling

\[
\left( \frac{\Delta}{T_K} \right)_{00'} \approx 0.51
\]

\[
\left( \frac{\Delta}{T_K} \right)_{0',\pi'} \approx 0.87
\]

\[
\left( \frac{\Delta}{T_K} \right)_{\pi',\pi} \approx 1.11
\]
(One) experiment

SU(4) symmetry in nanotubes

- Ultraclean carbon nanotube dots: extra orbital (KK′) degree of freedom can be conserved during tunneling
- Enlarged symmetry group SU(4) from spin and orbital angular momentum possible
- Experimental signatures: Coulomb blockade spectroscopy and noise measurements

SU(4) Kondo effect (normal state)

SU(4) Kondo regime: enhanced Kondo temperature, exotic local Fermi liquid behavior with asymmetric Kondo resonance. Fermi liquid theory (at T=0): transmission probabilities for even/odd KK' linear combinations are

\[
\tau_{v=\pm} = \frac{1 \pm \sin^2 \theta}{(\tilde{\varepsilon} / T_K)^2 + 1 \pm \sin^2 \theta}
\]

\[
\frac{\tilde{\varepsilon}}{T_K} = \frac{(1 - \sin \theta)(1 + \sin \theta)^4}{(1 + \sin \theta)^{(1-\sin \theta)/4}}
\]

\(\Theta\): orbital mixing angle, full SU(4) for \(\Theta=0\)
Josephson current for SU(4) JDOT

Zazunov, Levy Yeyati & Egger, PRB 2010

- Deep Kondo regime $T_K \gg \Delta$: Josephson current follows from Fermi liquid theory or equivalent mean-field slave boson approach

- Current phase relation covering crossover from SU(2) to SU(4)

$$ I(\varphi) = \frac{e\Delta}{2\hbar} \sum_{\nu=\pm} \frac{\tau_\nu \sin \varphi}{\sqrt{1 - \tau_\nu \sin^2 \varphi}} \sqrt{\frac{\nu^2}{2}} $$

- SU(4): $\tau_+ = \tau_- = 1/2$

- SU(2): $\tau_+ = 1, \tau_- = 0$
Deep Kondo regime

Critical current in SU(4) case suppressed by factor $2 - 2^{1/2} = 0.59\ldots$

Qualitatively different current phase relation when going from SU(2) to SU(4)
Perturbative regime

- Perturbation theory in $\Gamma$ for SU(4): critical current suppressed by factor 2 against SU(2), but $\pi$-regime persists for $U >> \Delta$

- Full phase diagram can be obtained from simpler effective Hamiltonian derived for $\Delta >> U, \Gamma$

Zazunov, Levy Yeyati & Egger, PRB 2010
Phase diagram of SU(4) JDOT

Phases for large $\Delta$ can be classified by spin and orbital pseudospin $(S,T)$:

**White:** $(0,0)$

**Green:** $(1/2,1/2)$

**Blue:** $(0,0)$ at $\varphi=0$, but $(1,0)$ or $(0,1)$ at $\varphi=\pi$

**Black:** $(0,0)$ at $\varphi=0$ but $(1/2,1/2)$ at $\varphi=\pi$

**Red:** like black but $\pi'$-phase (global minimum of free energy at $\varphi=\pi$)

**Green region:** smooth crossover instead of phase transition from 0- to $\pi$-phase!
Nonequilibrium effects

• Superconducting transport through JDOT with finite voltage bias V: multiple Andreev reflections

• How do interactions affect MAR (for Anderson JDOT)?
  – Previous mean field theories: no interaction correction for weak interactions, but suppression of current for strong interactions
    
    Avishai, Golub & Zaikin, PRB 2001
  – Difficult problem to go beyond: need to simultaneously account for correlations and MAR
    • Progress possible in deep Kondo regime (Fermi liquid theory)
      Levy Yeyati, Martin-Rodero & Vecino, PRL 2003
  – Here: diagrammatic Keldysh perturbation theory in interaction strength U up to second order (with first order kept self-consistent), nonperturbative in hybridization scale Γ
    Dell’Anna, Zazunov & Egger, PRB 2008
Interaction corrections to MAR

Corrections most sizeable near MAR features: $eV = 2\Delta/n$

Left: self-consistent first order perturbation theory in $U$

Right: include also second order diagram (solid) on top of first order (dots) for $\varepsilon_0 = -U/2$
Interaction effects on MAR

- Significant enhancement of the MAR-mediated subgap current by repulsive interactions for $\Gamma < \Delta$ and most bias voltages
  - For $\Gamma > \Delta$ current is (usually) suppressed by $U$
  - MAR features qualitatively survive (no shifts)

- Systematic mean field approach must keep on-dot pairing order parameter. Then: interaction effects for all $U$

- Corrections most pronounced near MAR onset voltages

Dell’Anna, Zazunov & Egger, PRB 2008
„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 $\sigma_i$)

— 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 $\Gamma$ to both leads

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

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

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

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

• 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 ($W_0=0$) and no interaction ($U=0$)
  - TLS dynamics frozen, eff. dot level \( \varepsilon_{\sigma=\pm} = \varepsilon_0 \pm \lambda/2 \)
  - Ground state energy \( E_g = \min(E_{\sigma_z=+1}, E_{\sigma_z=-1}) \)
    \[
    E_{\sigma=\pm} = \pm \frac{1}{2} (\lambda - E_0) - E_A(\varphi; \varepsilon_{\pm})
    \]
    follows from Andreev bound state energy \( E_A(\varphi; \varepsilon) \)
- Simple expressions for \( \Delta >> \Gamma \) or \( \Gamma >> \Delta \)
Conformational switching

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

– 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

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

– 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 $\pi$-phase

Schulz, Zazunov & Egger, PRB 2009
Conformational switching

Zazunov, Schulz & Egger, PRL 2009

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

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

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

$$E_0 = 0.14\Gamma$$
$$\lambda = \varepsilon_0 = \frac{\Gamma}{2}$$
Voltage-biased junction

- Consider small voltage $V \ll \Delta$ (here for $\Delta \gg \Gamma$)
- Phase difference time-dependent, $\varphi(t) = 2eVt$
- 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

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

\[ \Omega \]

\[ \varepsilon_0 = 0.6 \Gamma \]

\[ \varepsilon_0 = 0.2 \Gamma \]

\[ \varepsilon_0 = \Gamma / 2 \]

\[ eV = 0.01 \Gamma \]

\[ eV = 5 \Gamma \]

\[ E_0 = W_0 = 0.2 \Gamma \]
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
    Krive et al., PRB 2005; Reynoso et al., PRL 2008; Buzdin, PRL 2008; Zazunov, Egger, Jonckheere & Martin, PRL 2009
  – Dependence of critical current on SO couplings
    Dell’Anna, Zazunov, Egger & Martin, PRB 2007

• Naive expectation: SO coupling is time reversal invariant, does not affect Josephson effect - we find different picture...
Model

- 2D JDOT with Rashba-Dresselhaus spin-orbit coupling $\alpha$ and in-plane Zeeman field $B$, neglect e-e interactions
- N relevant dot energy levels $\varepsilon_n$ (for $\alpha=B=\Gamma=0$): real-valued wavefunctions $\chi_n(x,y)$
- Tunnel contacts to leads: generic asymmetric situation with $N\times N$ hybridization matrices $\Gamma_L$ and $\Gamma_R$

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

$$\vec{a}_{nn'} = \frac{\alpha}{m} \int d\vec{r} \; \chi_n(\vec{r}) \left[ \begin{array}{c} \sin(\vartheta) \partial_x + \cos(\vartheta) \partial_y \\ -\cos(\vartheta) \partial_x - \sin(\vartheta) \partial_y \end{array} \right] \chi_{n'}(\vec{r})$$

Pure Rashba: $\vartheta=0$
Pure Dresselhaus: $\vartheta=\pi/2$
Exact solution for Josephson current

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

Noninteracting problem, exactly solvable

– Doubled Nambu space, Pauli matrices $\sigma_i$ and $\tau_i$
– 4Nx4N matrix $S(\omega)$:

$$I(\varphi) = -\frac{2e}{\hbar} \partial_\varphi \int_0^\infty d\omega \ Tr \ln S(\omega)$$

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

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

$$Z = (iA_x \sigma_x + B_y \sigma_y) \tau_x + (iA_y \sigma_x - B_x \sigma_y) \tau_y + iA_z \sigma_z + B_z \tau_z$$
Spin-orbit and magnetic field effects enter via

- SO vector of real antisymmetric N\times N matrices

\[ \vec{A}_{nn'} = \frac{\alpha}{m} \int d\vec{r} \chi_n \partial_y \chi_{n'} \begin{bmatrix} -\cos \vartheta (1 - \cos(2\vartheta)\sin^2(\alpha x)) \\ \sin \vartheta (1 + 2\cos(2\vartheta)\sin^2(\alpha x)) \\ \cos(2\vartheta)\sin(2\alpha x) \end{bmatrix} \]

- Magnetic field in „optimal direction“:

\[ \vec{b} = B \begin{pmatrix} \cos \vartheta \\ -\sin \vartheta \\ 0 \end{pmatrix} \]

\[ \vec{B}_{nn'} = B \int d\vec{r} \chi_n \chi_{n'} \begin{bmatrix} \cos \vartheta \cos^2(\alpha x) - \cos(3\vartheta)\sin^2(\alpha x) \\ -\sin \vartheta \cos^2(\alpha x) - \sin(3\vartheta)\sin^2(\alpha x) \\ \cos(2\vartheta)\sin(2\alpha x) \end{bmatrix} \]
Anomalous supercurrent

• Can we have anomalous supercurrent?
  equivalent to phase shift: $\phi_o$ junction $I_a \equiv I(\phi = 0) \neq 0$
  For $\alpha B=0$, exact solution yields $I_a=0$

• Analytical approach for weak asymmetry and small $\alpha B$:
  $$S = S_0 + S_1$$
  $$S_1 = Z + \frac{\phi}{2} \frac{\Delta}{\sqrt{\omega^2 + \Delta^2}} (\Gamma_L - \Gamma_R) \sigma_y$$
  
  – Leading non-vanishing term: third order of the perturbation series !
Analytical result

• Anomalous supercurrent then follows in analytical (but lengthy) form

• Simple limit: for \( \max \Gamma_{L/R,nn} \gg \Delta \)

\[
I_a = \frac{2e\Delta}{\hbar} \text{Tr}_{dot} \left[ \frac{1}{\Gamma_0^2 + E^2} [\Gamma_R, \Gamma_L] \frac{1}{\Gamma_0^2 + E^2} \vec{b} \cdot \vec{A} \right]
\]

—in this order: \( I_a \propto \alpha B \) \hspace{1cm} \Gamma_0 = \text{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: \[ [\Gamma_L, \Gamma_R] \neq 0 \]
  – 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

Transfer of Cooper pair through N=2 dot for $\varphi=\vartheta=0$:
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

$$\delta t_{L\rightarrow R} = (t_{L1} t_{R1}) (t_{L1} iAB t_{R2})$$

Process (b) yields correction

$$\delta t_{R\rightarrow L} = (t_{R2} B (-iA) t_{L1}) (t_{R1} t_{L1})$$
• SO coupling and Zeeman field conspire to produce effective orbital field

• Anomalous supercurrent contributions add:

\[ \delta I^{(a)}_a \propto \nu AB \Gamma_{L,11} \Gamma_{R,12} \]
\[ \delta I^{(b)}_a \propto (-\nu) \cdot (-A) B \Gamma_{L,11} \Gamma_{R,12} \]

• Summing up all relevant processes:

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

– 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

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 $\alpha B$

Zazunov, Egger, Jonckheere & Martin, PRL 2009
Conclusions

„JDOT“ contains rich physics & potential for applications:

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