Manipulating the magnetic state of a carbon nanotube Josephson junction using the superconducting phase

R. Delagrange,1 D. J. Luitz,2 R. Weil,1 A. Kasumov,1 V. Meden,3 H. Bouchiat,1 and R. Debloch1

1Laboratoire de Physique des Solides, Univ. Paris-Sud, CNRS, UMR 8502, F-91405 Orsay Cedex, France.
2Laboratoire de Physique Théorique, IRSAMC, Université de Toulouse and CNRS, 31062 Toulouse, France.
3Institut für Theorie der Statistischen Physik, RWTH Aachen University and JARA—Fundamentals of Future Information Technology, 52056 Aachen, Germany.

We study the supercurrent of a carbon nanotube quantum dot Josephson junction in a parameter regime in which the Kondo energy and the superconducting gap are of comparable size. For gate voltages in the vicinity of a Kondo ridge the superconducting phase difference can then be used to tune the magnetic state from a singlet to a doublet. Accordingly our measured current phase relation crosses over from 0 to π-junction behavior, exhibiting strong anharmonicities. The experimental results are in excellent agreement with our numerically exact finite temperature quantum Monte Carlo simulations and provide insights on the phase-controlled level-crossing transition at zero temperature.

When a localized magnetic moment interacts with a Fermi sea of conduction electrons, the Kondo effect can develop. Spin-flip processes lead to a many-body singlet state in which the delocalized electrons screen the moment. Quantum dots (QD) in the Coulomb blockade regime and particularly carbon nanotube (CNT) dots constitute ideal systems for the investigation of Kondo physics at the single spin level [1–3]. The Kondo screening is active provided that it is not prohibited by an energy scale larger than the Kondo energy \( k_B T_K \). Temperature is the most obvious obstacle to the development of the Kondo effect since \( T_K \) can be smaller than 1K. However, if temperature is sufficiently low, the Kondo effect can compete with other quantum many-body phenomena such as superconductivity, for which the formation of Cooper pairs of energy \( \Delta \) may prevent the screening of the dot’s spin. In fact, this competition leads to two distinct ground states, depending on the respective strength of the two effects. This situation can be investigated using superconducting hybrid junctions, where a supercurrent is induced by the proximity effect, for example in CNT-based QDs [4] or semiconductor-based ones [5].

Inserting the hybrid junction in a superconducting quantum interference device (SQUID) introduces another physical parameter: the superconducting phase difference across the junction \( \varphi \). A high-resistance tunnel barrier between two superconductors, also called Josephson junction (JJ) carries a supercurrent \( I = I_C \sin \varphi \), \( I_C \) being the critical current. This is the Josephson relation, the most famous and common example of a current-phase relation (CPR). In some peculiar systems such as ferromagnetic superconducting junctions, the transmission of Cooper pairs gives rise to a π phase shift of the CPR [6]. When the Kondo effect is negligible, such a π shift is also observed in QD JJs containing an odd number of electrons since the tunneling of a Cooper pair implies reversing the order of particles within this pair. This leads to a gate-controlled sign reversal of the CPR when the parity of the number of electrons is changed, as was observed experimentally [7–10]. However, if the Kondo effect prevails, the spin of the dot is screened by unpaired electrons leading to a singlet ground state: the 0-junction is then recovered even though the parity of the dot is still odd. This indicates that the measurement of the CPR of the hybrid junction constitutes a very powerful tool to investigate the competition between superconducting proximity and the Kondo effect. Furthermore, the \( \varphi \) dependence of the supercurrent through the junction provides insights on the evolution of the Andreev bound states, which strongly contribute to this current.

The switching from 0- to \( \pi \)-junction behavior as a function of a variety of energy scales of the QD JJ was extensively studied theoretically [11–20]. The scales are the broadening \( \Gamma \) of the energy levels in the dot due to the coupling to the reservoirs, the superconducting gap \( \Delta \) of the contacts, the dot’s charging energy \( U \) and its level energy \( \epsilon \). When these parameters fall into the 0-\( \pi \) transition regime, it was predicted that the ground state of the system—singlet or doublet—depends on the phase difference \( \varphi \) across the junction, undergoing a level-crossing transition. This leads to a characteristic anharmonicity of the CPR for temperature \( T > 0 \) and a jump at a critical phase \( \varphi_C \) for \( T = 0 \). Consequently, in this particular regime of parameters, the magnetic state of the dot is governed by the superconducting phase difference across the junction.

The 0-\( \pi \) transition as a function of the different parameters was earlier observed experimentally [9, 21, 22] and the spectroscopy of Andreev bound states enabled a better understanding of the involved physics [23–26]. Measurements of the CPR of a QD JJ embedded in a SQUID were also performed [22] and indeed showed anharmonicities. However, in the region of 0-\( \pi \) transition, the obtained CPRs are not odd functions of flux as it should be, indicating that the physics is affected by other effects [27].
Here we report on our successful measurement of the CPR of a CNT-based hybrid junction over the entire 0-π transition in the most interesting regime of strongest competition between superconductivity and the Kondo effect characterized by Δ ≈ k_B T_K. To achieve this, we have used a modified SQUID. The experimental CPRs are compared to theoretical calculations using a quantum Monte Carlo (QMC) method.

We fabricated a CNT-based QD, connected to superconducting leads and embedded in an asymmetric modified SQUID (Fig. 1 c) [31]. This device, a SQUID containing the QD JJ (here the CNT) and a reference JJ with critical current high compared to the one of the QD JJ, allows us to determine the CPR of interest [28, 29]. The switching current $I_s$ of the SQUID versus magnetic flux is measured. The CPR of the QD JJ is then obtained by extracting the modulation of $I_s$ around its mean value < $I_s$ >. Our device possesses a second reference JJ and a third connection as described in Ref. [29]. This allows us to characterize each junction independently at room temperature, and to measure both the CPR of the CNT and its differential conductance in the superconducting state.

The CNTs are grown by chemical vapor deposition on an oxidized doped silicon wafer [30]. A three-junctions SQUID is constructed around a selected nanotube with the following materials: Pd(7 nm)/Nb(20 nm)/Al(40 nm), AlOx and Al[120 nm][31]. The sample is thermally anchored to the mixing chamber of a dilution refrigerator of base temperature 50 mK and measured through low-pass filtered lines. A magnetic field $B$ is applied perpendicular to the loop to modulate the phase difference across the CNT-junction by $2\pi BS/\Phi_0$, with the superconducting flux quantum $\Phi_0 = h/2e$ and $S$ the loop area.

We first characterize the sample in the normal state, measuring the differential conductance $dI/dV_{sd}$ versus bias voltage $V_{sd}$ for various backgate voltages $V_g$, using a lock-in-amplifier technique. The contacts are made of Pd/Nb/Al with a gap of $\Delta = 0.17$ meV ± 10%, a value very close to the gap of Al but considerably smaller than the Nb gap because of the Pd layer. A magnetic field of 1T is needed to suppress superconductivity in these contacts. Even though such a magnetic field significantly affects the Kondo effect, the results of Fig. 1 a and b show clear Coulomb diamonds and an increase of the conductance at zero-bias for odd occupation of the dot, a signature of the Kondo effect. Moreover, the CNT exhibits on a wide range of gate voltage the four-fold degeneracy

Vg=6.242V
Vg=6.234V
Vg=6.238V
Vg=6.234V
Vg=6.232V
Vg=6.242V
Vg=6.249V
Vg=6.238V
Vg=6.234V
Vg=6.232V
Vg=6.222V
Vg=6.222V

Figure 1: Differential conductance $\frac{dI}{dV_{sd}}$ in the normal state of the CNT junction versus gate voltage $V_g$ and bias voltage $V_{sd}$ for two Kondo zones A (a) and B (b). In light blue, $\frac{dI}{dV_{sd}}$ at zero bias is plotted versus $V_g$ (axis on the right). In the normal state, the reference JJ contribution is a constant which was subtracted to obtain the plots. The white symbols in a correspond to the theoretical fit of the conductance (see text). c Scanning electron microscopy image of the measured asymmetric SQUID, containing two reference JJs in parallel with a CNT based hybrid junction (see text and [29]). To control the phase biasing of the CNT, a magnetic field is applied perpendicular to the SQUID.

Figure 2: a Modulation of the switching current of the SQUID, proportional to the CPR of the CNT junction, versus the magnetic field for various gate voltages in zone A. b Modulation of the switching currents near the transition for several gate voltages. c CPR extracted from the previous data and rescaled by 1.33 (see the text) near the transition (green continuous line). The theoretical predictions resulting from QMC calculations are shown as black lines. The dashed lines are guides to the eyes and represent the contributions of the singlet (0-junction, in blue) and the doublet state (π-junction, in red).
observed in clean carbon nanotubes [33].

We focused on two interesting ranges of gate voltages where non-zero conductance is observed at zero bias, zone A (around \( V_g = 6.2 \) V) and zone B (around \( V_g = 1.4 \) V) (see Figs. 1 a and b). The height in \( V_{sd} \) of the Coulomb diamonds gives the charging energy \( U = 3.2 \) meV \( \pm 10\% \) in zone A and 2.5 meV \( \pm 10\% \) in zone B. Due to the complex interplay of the Kondo scale \( k_B T_K \) and the Zeeman energy, that are of comparable size, \( \Gamma \) and the contact asymmetry cannot be determined directly from the experimental results; theoretical modeling is required.

The junction is modeled by an Anderson impurity model with right (\( R \)) and left (\( L \)) BCS superconducting leads and superconducting order parameter \( \psi \pm i \phi / 2 \Delta \). The interaction of electrons on the QD is given by a standard Hubbard term with charging energy \( U \) and the coupling of the leads to the QD is described by the energy independent hybridization strength \( \Gamma_{L/R} \). The model was introduced in detail in Refs. [12–20]. We solve it using the numerically exact CT-INT Monte Carlo method [19] in the normal state (\( \Delta = 0 \)) in a magnetic field and calculate the finite temperature linear conductance for different \( \Gamma_{L/R} \) as a function of the dot energy \( \epsilon \), defined relative to particle-hole symmetry. The amplitudes of the magnetic field and the charging energy are fixed to the experimentally determined values \( B = 1 \) T and \( U = 3.2 \) meV of zone A [34]. A comparison with the measured conductance at zero source drain voltage (i.e. in equilibrium) yields a set of parameters that fit the experiment best. We find \( \Gamma_R + \Gamma_L = 0.44 \) meV, \( \Gamma_R/\Gamma_L = 4 \). We also slightly varied \( T \) to estimate the electronic temperature in the sample and obtain \( T = 150 \) mK. Additionally, this procedure gives a reliable way of extracting the conversion factor \( \alpha = 39 \) meV between the applied gate voltage and the dot on-site energy \( \epsilon \). Our best fit is displayed in Fig. 1 a (white symbols).

Next, superconductivity is restored by suppressing the IT magnetic field and the CPR is measured in both Kondo zones, extracting the modulation of the switching current \( \delta I_s \) versus magnetic field (Fig. 2) from the critical current of the SQUID. To measure the switching current, the SQUID is biased with a linearly increasing current with a rate \( \frac{dI}{dt} = 37 \) \( \mu \)A/s and the time at which the SQUID switches to a dissipative state is measured. This process is reproduced and averaged around 1000 times, the whole procedure being repeated at different values of magnetic field below a few Gauss, small enough to preserve superconductivity. To obtain the modulation of the switching current \( \delta I_s \) versus magnetic field, the contribution of the reference junctions (around 90 nA) is subtracted. As demonstrated in Ref.[29], \( \delta I_L \) is proportional to the CPR of the CNT junction. It should be noted that this kind of system, in particular near the 0-\( \pi \) transition, is very sensitive to the electromagnetic environment, which therefore needs to be optimized [27].

The main results of this work are presented in Figs. 2 and 3, where we show the extracted CPRs for gate values over the entire transition regime (curves c.1 to c.6 of Fig. 2 for zone A and curves b.1 to b.3 of Fig. 3 for zone B). We now analyze qualitatively the shape of these curves.

On the edges of Kondo zone A, far from the transition (Fig. 1 c.1), the junction behaves as a regular JJ with a CPR proportional to \( \sin(\varphi) \) (0-junction). In contrast, at the center of the Kondo zone (Fig. 1 c.6) the CPR is \( \pi \)-shifted (\( \delta I \propto \sin(\varphi + \pi) \)) and has a smaller amplitude characteristic for a \( \pi \)-junction. In between, the CPR is composite with one part corresponding to 0- and another part to \( \pi \)-junction behavior. The latter first occurs around \( \varphi = \pi \), giving rise to a very anharmonic CPR. In the middle of the transition region, we find period halving (Fig. 1 c.4) [35]. This evolution of the CPR between a 0- and \( \pi \)-junction is consistent with the finite temperature transition of the dot’s magnetic state (between singlet and doublet) which is controlled by the superconducting phase difference [12, 17, 19].

A more precise analysis of the transition allows to attribute this 0-\( \pi \) transition to a competition between the Kondo effect and the superconductivity. Indeed, around the center of Kondo zone A (Fig. 2 a), the \( \pi \)-junction extends over a range of 60 mV of gate voltage. According to the \( dI/dV_{sd} \) in the normal state (Fig. 1) and the conversion factor \( \alpha \), the odd diamond has a width in gate voltage of about 82 mV, larger than the \( \pi \)-junction regime. Consequently, this 0 to \( \pi \) transition is not simply due to a change in the parity of the dot filling but to an increase in the ratio \( \Delta/T_K \) (\( T_K \) being minimal at odd filling). This is even more obvious for Kondo zone B.
describe the experiment perfectly; see Fig. 4 a 2 phase dependence of the measured Josephson current. Thus exactly captures the nontrivial finite temperature and black: harmonics 1, 2 and 3) continuous lines correspond to the QMC calculation (red, blue transition for different level energies

The comparison of the measurements and calculations can even be refined employing Fourier decompositions $I(\phi) = a_1 \sin(\phi) + a_2 \sin(2\phi) + a_3 \sin(3\phi) + \ldots$ of the 2π-periodic CPRs. The first three amplitudes suffice to describe the experiment perfectly; see Fig. 4 a where they are shown as functions of $\epsilon$. The theoretical model thus exactly captures the nontrivial finite temperature phase dependence of the measured Josephson current.

An important information that can also be extracted from the experiment is the gate voltage dependence of the critical phase $\varphi_C$ at which the system switches from 0 to $\pi$-junction behavior, i.e. the CPR has 0-behavior for $\varphi \in [0,\varphi_C]$ and $\pi$-behavior for $\varphi \in [\varphi_C,2\pi-\varphi_C]$ (Fig. 4 b). At $T = 0$ this switching at $\varphi_C$ is associated to a first order level crossing transition and appears as a jump of the current from positive to negative. For $T > 0$ the transition is washed out and the CPR is smoothed. However, at small enough $T$, $\varphi_C$ depends only weakly on $T$ (cf. Refs. [17, 19] and supplementary materials). In Fig. 4 b, we compare $\varphi_C(\epsilon)$ from experiment and theory. Both display the same characteristic shape, that can be understood based on the atomic limit of the Anderson impurity model with $\Delta \gg \Gamma$. A straightforward extension of the $T = 0$ atomic limit calculation (such as presented in [17]) to the case of asymmetric level-lead couplings gives $\varphi_C(\epsilon) = 2 \arccos \sqrt{g - (\epsilon/h)^2}$. For the experimental $\Delta \lesssim \Gamma$ the dependence of $g$ and $h$ on the model parameters cannot be trusted; we rather fit both ($g = 2.2$, $h = 0.72$ meV) and obtain very good agreement. This shows that the $\epsilon$-dependence of $\varphi_C$ is a strong characteristic of the 0-π transition.

In conclusion we have measured with unprecedented accuracy the evolution of the Josephson current of a CNT junction at the 0-π transition. We have shown that the CPR has a composite behavior, with a "0" and a "$\pi$" component. The phase at which this transition occurs is gate dependent. The measurements are successfully compared to QMC calculations, confirming the validity of both the experiment as well as the theoretical modeling. Our study shows that the magnetic state, doublet or Kondo-singlet, is controlled not only by the gate voltage but also by the superconducting phase difference across the junction.

The possibility to measure precisely the CPR of correlated systems may motivate the study of systems with different symmetry such as Kondo SU(4) or with strong spin-orbit coupling.

Acknowledgments: Ra.D., H.B. and Ri.D. thank M. Aprili, S. Autier-Laurent, J. Basset, M. Ferrier, S. Guéron, C. Li, A. Murani, and P. Simon for fruitful discussions. V.M. is grateful to D. Kennes for discussions.

This work was supported by the French program ANR MASH (ANR-12-BS04-0016) and DYMESYS (ANR 2011-ISO4-001-01). D.J.L. also acknowledges funding by the ANR program ANR-11-ISO4-005-01 and the allocation of CPU time by GENCI (grant x2014050225).

References:

[1] M. Pustilnik and L. Glazman. *Journal of Physics: Condensed Matter* **16**(16), R513 (2004).
[2] D. Goldhaber-Gordon, J. Göres, M. A. Kastner, H. Shtrikman, D. Mahalu and U. Meirav *Phys. Rev. Lett.* **81**, 5225-5228 (1998).
[3] S. M. Cronenwett, T. H. Oosterkamp, and L. P. Kouwenhoven. *Science* **281**, 540–544 (1998).
[4] A.Yu. Kasumov, R. Debloek, M. Kociak, B. Reulet,
H. Bouchiat, I.I. Khodos, Yu.B. Gorbatov, V.T. Volkov, C. Journet, and M. Burghard. Science, 284, 1508–1511 (1999).

[5] Y.-J. Doh, J. A. van Dam, A. L. Roest, E. P. A. M. Bakkers, Leo P. Kouwenhoven, and Silvano De Franceschi. Science 309, 272–275 (2005).

[6] V. V. Ryazanov, V. A. Oboznov, A. Yu. Rusanov, A. V. Veretennikov, A. A. Golubov, and J. Aarts. Phys. Rev. Lett. 86, 2427–2430 (2001).

[7] J. A. van Dam, Y. V. Nazarov, Erik P. A. M. Bakkers, S. De Franceschi, and L. P. Kouwenhoven. Nature 442, (2006).

[8] J.-P. Cleuziou, W. Wernsdorfer, V. Bouchiat, T. Ondarçuhu, and M. Monthioux. Nature Nanotechnology 1(1):53 (2006).

[9] H. Ingerslev Jorgensen, T. Novotny, K. Grove-Rasmussen, K. Flensberg, and P. E. Lindelof. Nano Letters 7(8) 2441–2445 (2007).

[10] S. De Franceschi, L. Kouwenhoven, C. Schonenberger, and W. Wernsdorfer. Nature Nanotechnology, 5(10):703–711 (2010).

[11] Clerk, A. & Ambegaokar, V. Phys. Rev. B 61, 9109-9112 (2000).

[12] Glazman,L.I. and K.A. Matveev. JETP Lett. 49, 659 (1989).

[13] E. Vecino, A. Martin-Rodero, and A. Levy Yeyati. Phys. Rev. B 68, 035105 (2003).

[14] Computing the normal state linear conductance as well as the CPRs with CT-INT is numerically costly. We thus focus on zone A showing the complete transition.