Numerical sub-gap spectroscopy of double quantum dots coupled to superconductors

Rok Žitko\textsuperscript{1,2}

\textsuperscript{1}Jožef Stefan Institute, Jamova 39, SI-1000 Ljubljana, Slovenia
\textsuperscript{2}Faculty of Mathematics and Physics, University of Ljubljana, Jadranska 19, SI-1000 Ljubljana, Slovenia

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This is a comprehensive numerical study of the sub-gap spectra of the double quantum dot nanostructure embedded either between two superconducting leads or in a superconducting ring pierced by the magnetic flux. The two-impurity Anderson model is solved using the non-perturbative numerical renormalization group (NRG) technique and the results are analyzed in terms of the level structure in the superconducting atomic (infinite gap) limit. For reference, the results for the normal-state leads are also given. At half-filling, clear signs of the Kondo regime, antiferromagnetic, and molecular-orbital regimes can be detected. Away from half-filling we study the new features induced by transitions to the valence-fluctuation and empty-orbital regimes; this is the parameter regime with the most complex structure of sub-gap Shiba states. We study the splitting of the Shiba doublet states a) at non-zero superconducting phase difference and b) away from half-filling. When one of the dots is in the valence fluctuation regime, the ground state is a spin doublet and there are very different spectral weights for the transitions to singlet or triplet excited states: the triplet state is best visible on the valence-fluctuating dot, while the singlets are more pronounced on the half-filled dot.

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I. INTRODUCTION

The advances in fabrication and characterization of small electronic devices have enabled new ways to perform spectroscopy of strongly correlated electron systems. A prominent example is the tunneling spectroscopy\textsuperscript{1}\textsuperscript{14} of interacting quantum dots coupled to superconducting baths as well as magnetic adatoms on superconducting surfaces\textsuperscript{15}, where the competition between the Kondo screening\textsuperscript{16,17} and superconducting correlations can be studied in exquisite detail because it engenders spectroscopically sharp energy states known as the Andreev bound states (or Yu-Shiba-Rusinov states or simply Shiba states in other contexts)\textsuperscript{18,19}. At low enough temperatures even fine details can be resolved and in some cases quantitative agreement is found between the experiment and accurate theoretical modelling using non-perturbative numerical techniques.

The most thoroughly studied problem is that of a quantum dot in the deep Kondo limit where charge fluctuations are frozen out and the device behaves essentially as a local moment characterized by a single bare parameter, the Kondo exchange coupling $J_K$, and at low temperatures by a single scaling parameter, the Kondo temperature $T_K$. When such a quantum dot (QD) is coupled to a superconducting host with energy gap $\Delta$, the ground state of the system depends on the ratio $T_K/\Delta$. For $T_K \ll \Delta$, the Kondo screening is incomplete due to a lack of quasiparticle states at low energy scales, thus the system behaves as a free local moment decoupled from the BCS bath, which is an overall spin doublet state. For $T_K \gg \Delta$, the Kondo screening is fully completed on energy scales much above the onset of pairing; the superconducting state is thus formed out of the local Fermi liquid state resulting from the Kondo effect, and is an overall spin singlet. For $T_K \sim \Delta$ there is a quantum phase transition between these two different ground states. In this parameter range, the many-particle spectrum usually includes at least three states (one singlet and two doublet states) below the onset of the continuum of quasiparticle states at $\Delta$. The singlet-doublet excitations are spectroscopically visible as resonances pairs at $\omega = \pm E$. Additional complexity in the problem is brought about by coupling the quantum dot to a superconducting ring pierced by a magnetic flux. This can be theoretically modelled as a quantum dot coupled to two superconductors with a non-zero difference of the superconducting phase $\phi$ and leads to Josephson currents. The direction of the Josephson current depends on the sub-gap states and the singlet-doublet transitions can be directly related to the physics of 0 or $\pi$ junction behavior\textsuperscript{20,21}.

Recently, this research direction has intensified with a focus on more complex systems. Double quantum dot (DQD) systems that are studied in this article have long played the role of the minimal non-trivial toy models that capture the essence of extended strongly-correlated systems described by lattice models\textsuperscript{22,23}. Coupled to superconducting leads, they can serve to study the competing effects of exchange coupling, charge fluctuations, Kondo screening, and superconductivity\textsuperscript{24,25}. In the context of superconducting rings, an important question is also the variation of the sub-gap state energies as a function of the flux. We investigate a wide parameter range with the goal of identifying the regimes of strong flux dependence which would be a suitable target for experimental investigation. Strong flux dependence implies sizeable particle exchange between the superconducting contacts on either side of the DQD structure, thus the regimes of enhanced valence fluctuations away from the integer filling limit are carefully considered.

This work is structured as follows. In Sec. II we introduce the model and the numerical method. The extensive presentation of the results in Sec. III is divided in a number of subsections: A) the single-impurity limit, B) the left-right symmetric case at half-filling, and C) away from half-filling, and D) the fully generic case. Sec. IV discusses the results in terms of a simple approximation (superconducting atomic limit) which is shown to be remarkably successful in reproducing the gen-
eral trends even though it fails on the quantitative level. Appendix A discusses the deviations from the large-$\Delta$ limit in the single impurity problem using the numerical renormalization group. Appendix B is a short discussion of the two-impurity Kondo quantum criticality in the presence of superconductivity.

II. MODEL AND METHOD

The system under study is schematically represented in Fig. 1. We consider two quantum dots ($i = 1, 2$) described by the Anderson impurity model:

\[ H_i = \epsilon_i n_i + \sum_{\sigma} U n_{i\sigma} n_{i\bar{\sigma}} + \sum_{\sigma} \delta_i (n_i - 1) + \frac{U}{2} (n_i - 1)^2 + \text{const.} \]

(1)

Here $n_i = n_{i\uparrow} + n_{i\downarrow}$ with $n_{i\sigma} = d_{i\sigma}^\dagger d_{i\sigma}$ is the QD occupancy, $U$ is the Hubbard charge repulsion, and $\delta_i$ is the impurity energy level measured with respect to the particle-hole symmetric point (half filling), i.e., $\delta_i = \epsilon_i + U/2$. Each dot is coupled to a separate superconducting bath

\[ H_{SC,i} = \sum_{k\sigma} \epsilon_{k,i} c_{k\sigma,i}^\dagger c_{k\sigma,i} - \sum_{k\sigma} \Delta_i e^{i\phi_i} c_{k\uparrow,i}^\dagger c_{-k\downarrow,i} + \text{H.c.,} \]

(2)

where $\epsilon_{k,i}$ is the band dispersion, $\Delta_i$ the gap parameter and $\phi_i$ the superconducting phase. The coupling terms are

\[ H_{c,i} = \sum_{k\sigma} V_{k,i} d_{k\sigma,i}^\dagger c_{k\sigma,i} + \text{H.c.,} \]

(3)

where $V_{k,i}$ is the hopping parameter. We assume that both bands are flat: in the absence of superconductivity they have constant density of states $\rho = 1/2D$ on the interval $[-D : D]$, thus $D$ is one half of the bandwidth ($D$ will henceforth be used as the energy unit, $D = 1$). The hybridization strengths are characterized by functions

\[ \Gamma_i(\omega) = \sum_k |V_{k,i}|^2 \delta(\omega - \epsilon_{k,i}) = \pi \rho V_i^2, \]

(4)

which will be taken as constants. Finally, the two dots are interconnected by a tunneling term

\[ H_{12} = -t \sum_\sigma d_{1\sigma}^\dagger d_{2\sigma} + \text{H.c.} \]

(5)

Almost all results presented in this work (with the exception of Sec. III.B.5 and Appendix B) are calculated for

\[ U/D = 0.27 \quad \text{and} \quad \Gamma/D = 0.02, \]

(6)

while $\delta_i$ and $t$ will be variable. For easier interpretation, both normal ($\Delta = 0$) and the superconducting state ($\Delta = 0.01$) are considered. Since $U/\pi \Gamma \approx 4.3$, the dots are in the Kondo regime near half-filling. This choice of parameters has the advantage that several different physical regimes can be distinguished, while for smaller $U/\Gamma$ ratios are not well separated. The Kondo temperature (according to Wilson’s definition) of each separate QD is given by

\[ T_K = 0.182U \sqrt{\rho J_K} \exp \left[ -\frac{1}{\rho J_K} \right], \]

(7)

where

\[ \rho J_K = \frac{2\Gamma}{\pi} \left( \frac{1}{U/2 - \delta} + \frac{1}{U/2 + \delta} \right). \]

(8)

At $\delta = 0$ this gives $T_K \approx 10^{-4} \ll \Delta$.

The method of choice for this class of problems is the numerical renormalization group (NRG)\cite{9,10,41–45} which is able to quantitatively reproduce the experimental results\cite{14,31–40} but also provides additional detailed information about the system properties which are difficult or impossible to measure. The calculations were performed in the low-temperature limit with the discretization parameter $\Lambda = 4$, keeping 5000 states at each diagonalization step, with $N_z = 2$ discretization meshes\cite{46–49}. The only symmetry in the problem is the SU(2) spin symmetry. The spectra are computed using the density-matrix NRG algorithm\cite{50} using a $N/N + 1$ patching approach and with a mixed broadening scheme: for $|\omega| > \Delta$ log-Gaussian broadening kernel with $\alpha = 0.6$ is used, while for $|\omega| < \Delta$ Gaussian broadening with $\sigma = 10^{-3}$ is used (this latter choice mimicks non-zero experimental temperature and gives a finite width to the sub-gap resonances).

I will present results for the spectral functions on either dot, defined as

\[ A_i(\omega) = -\frac{1}{\pi} \text{Im} G_i(\omega + i\delta), \]

(9)

where $G_i(z) = \langle \langle d_{i\sigma}^\dagger d_{i\sigma} \rangle \rangle_z$ is the local Green’s function of dot $i$. Such spectra are measurable by tunneling spectroscopy using weakly coupled additional probes. Another quantity of interest is the interdot spectral function

\[ A_{12}(\omega) = -\frac{1}{\pi} \text{Im} G_{12}(\omega + i\delta), \]

(10)

where $G_{12}(z) = \langle \langle d_{1\sigma}^\dagger d_{2\sigma} \rangle \rangle_z$, which quantifies interdot correlations of the excitations. If the tunneling probe is coupled
to both dots, the resulting spectrum is proportional to

$$
\text{Im} \left[ |v_1|^2 G_1(z) + |v_2|^2 G_2(z) + v_1^* v_2 G_{12}(z) + v_1 v_2^* G_{21}(z) \right]_{z = \omega + i\delta}.
$$

Here $v_1$ and $v_2$ are the tunnel couplings of the probe to either QD. Such situation occurs in the experiment described in Refs. [51] and [44], where the segment of the carbon nanotube actually hosts two QDs and the probe is attached to the center of the tube.

### III. RESULTS

#### A. Single impurity limit

As an aid in the interpretation of the results for the full DQD problem, we first consider the case of decoupled impurities by setting $t = 0$, i.e., a single quantum dot coupled to one lead. The results for the normal state are well known [3]. The single-particle excitation spectrum is characterized by broad atomic peaks at $\omega = \epsilon$ and $\omega = \epsilon + U$, and if the dot occupancy is near unity (as happens around the particle-hole symmetric point at $\delta = 0$) there is a further peak near the Fermi level due to local moment screening, known as the Abrikosov-Suhl or Kondo resonance.

The same problem but with superconducting leads has been thoroughly studied in recent times, both theoretically and experimentally, thus we only describe the salient points. For our parameter set, near half-filling $T_K$ is lower than $\Delta$, the local moment remains unscreened, thus the ground state is a spin doublet, see Fig. 2(a). With increasing $|\delta|$, $T_K$ increases according to Eq. (7), until at $|\delta| \approx 0.1$ the condition

$$
T_K(\delta) \approx 0.3\Delta
$$

is satisfied and the new ground state is the spin singlet state. This level crossing (first-order quantum phase transition) is accompanied by true discontinuities in all physical properties, for instance the expectation value of the local pairing operator $\langle d_+^\dagger d_- \rangle$ (inset to panel a) and the spectral function (panels b and c). The spectral function is defined as

$$
A(\omega) = \frac{1}{Z} \sum_{i,j} \left[ \exp(-\beta E_i) + \exp(-\beta E_j) \right]
$$

$$
\times \left(\langle i | d_+^\dagger | j \rangle \right)^2 \delta(\omega - (E_j - E_i)),
$$

with $Z = \sum_{i} \exp(-\beta E_i)$, $i$ and $j$ run over all many-particle states and $\beta = 1/k_B T$. The only sub-gap excitation that contributes to $A(\omega)$ at zero temperature is the transition from singlet to doublet state (or vice versa), which produces a pair of peaks at $\omega = \pm(E_D - E_S)$. The total weight of these peaks depends on $\delta$ and also varies discontinuously across the transition. It is worth to point out that in addition to the sub-gap range, the spectrum above and around the gap edges is also non-trivial and features atomic peaks at $\omega \approx \epsilon$ and $\omega \approx \epsilon + U$ which fuse with the superconducting coherence peaks at $|\omega| = \Delta$. The spectrum outside the gap is, yet again, discontinuous across the transition.

The single impurity problem is further studied in Appendix A with the goal of better understanding the nature of the large-$\Delta$ limit, also known as the superconducting atomic limit.

![Figure 2](Color online) Single quantum dot coupled to a superconducting lead. (a) Sub-gap ($\omega < \Delta$) part of the many-particle excitation spectrum which includes one spin-singlet and one spin-doublet. The energies are plotted by subtracting the ground-state energy, thus the lowest lying state is always at $E = 0$. The continuum of quasiparticle states extends from $\Delta$ upwards. The inset shows the ground-state expectation value of the pairing operator, $\langle d_+^\dagger d_- \rangle$, whose sign reveals the type of the ground state. (b) The corresponding impurity spectral function, measurable through tunneling spectroscopy. (c) Spectral function in an extended frequency range plotted using a nonlinear grayscale to emphasize the low-intensity details outside the gap. Note that the atomic features cross the Fermi level close to (but not exactly at) the singlet-doublet quantum phase transition points.
B. Left-right symmetric case, half-filling

1. Normal state

Figure 3: (Color online) Spectral function on one of the dots, $A_1(\omega)$, in the left-right symmetric DQD system in the normal state with linear (upper panel) and logarithmic (bottom panel) frequency scales.

We now consider the full double quantum dot problem. We begin with the case where all parameters are left-right reflection symmetric, i.e., $\delta_1 = \delta_2 = \delta$, and start with half-filling of the dots, $\delta = 0$, where the physics are driven by the competition between the Kondo screening and the inter-dot superexchange coupling

$$J = \frac{4t^2}{U}. \quad (14)$$

We first plot the spectrum for the case of leads in the normal state, see Fig. 3. For small $t$, the spectrum is the same as in the single-impurity case, with broad peaks at $\omega = \pm U/2$ and a Kondo resonance at $\omega = 0$. The low-frequency part of the spectrum starts to be affected by the superexchange interaction for $t$ such that $J \sim T_K$. This occurs at $t \sim 10^{-2}$. The behavior in this range is governed by the proximity of the two-impurity Kondo model (TIKM) non-Fermi-liquid fixed point which, however, is never reached because the particle exchange between the leads is a relevant perturbation in the renormalization group sense. After this point the Kondo peak amplitude is reduced and a splitting of order $J \propto t^2$ becomes observable. As $t$ increases further, the hybridization between the local orbitals becomes the dominant effect, resulting in the splitting between the anti-bonding and bonding molecular orbitals that is linear in $t$. This occurs at $t \sim 10^{-1}$. The Kondo (K), the antiferromagnetic (AFM), and the molecular-orbital (MO) regimes can be even more clearly distinguished in the inter-impurity spectral function $A_{12}(\omega)$ shown in Fig. 4. The plot on the logarithmic scale allows easy identification of the cross-over scales defined by $J \sim T_K$ and $J \sim t$, respectively. The change of slope of the main ridge in $A_{12}(\omega)$ from quadratic to linear directly reveals the cross-over of the main coupling mechanism from the superexchange interaction to the hybridization (chemical bonding) effects. The corresponding ranges, defined as $t \lesssim 10^{-2}$, $10^{-2} \lesssim t \lesssim 10^{-1}$, $10^{-1} \lesssim t$, will be referred to in the following as small, intermediate and large $t$ regime, respectively.

Figure 4: (Color online) Interdot spectral function $A_{12}(\omega)$ in the left-right symmetric DQD system in the normal state with logarithmic frequency scale. This spectral function is odd in frequency, thus we only show $\omega > 0$. The enhancement of $A_{12}(\omega)$ at $\omega \sim T_K$, which occurs for $t \approx 9 \times 10^{-3}$, indicates the two-impurity Kondo model critical point, and the enhancement at $\omega \sim 0.1 \approx t$ indicates the transition to the molecular-orbital regime.

2. Superconducting state

As the leads become superconducting, see Fig. 5, the spectrum changes mainly in the frequency range of order of the gap $\Delta$, while it is perturbed only little at higher frequency scales (there are again atomic peaks at $\omega = \pm U/2$ for low $t$, and molecular orbitals with splitting $\propto t$ for high $t$). As expected, the differences are the most dramatic inside the gap, $|\omega| < \Delta$, where the sub-gap states become manifest. At low $t$ we see the sub-gap peaks at the same energy of $\Omega = E_S - E_D \approx 0.6\Delta$ as the excitations in the single-dot case shown in Fig. 2 at $\delta = 0$. While for a single dot the ground-state was a doubllet and the excited state was a singlet, for two QDs the ground state must have integer spin. The two doublets can couple into a singlet or a triplet state which are split by $J \approx 4t^2/U$ due to the superexchange coupling. At low $t$ the triplet Shiba state is nearly degenerate with the ground state. The singlet-triplet transition is not spectroscopically visible, since it violates the $\Delta S_z = \pm 1/2$ sum rule. Its presence is, however, revealed by a direct calculation of the many-particle spectrum using the numerical renormalization group, see the bottom-most panel in Fig. 6.

What is clearly visible in the spectral function $A_1(\omega)$, however, are the doublet states. (There are, in fact, two exactly degenerate doublets. In the following subsection it will be
shown that the degeneracy is broken in the presence of the flux and away from the particle-hole symmetric point.) In the $t \to 0$ limit, these spectral peaks are exactly the same excitations as the doublet-singlet Shiba resonances in the single-dot case. At finite $t$ they persist, although their energy is affected by the inter-dot coupling. The shift of the resonance is not linear in $t$, as would be expected for a hybridization coupling, but rather quadratic. The underlying physics is thus associated with magnetism, not hybridization. This is not surprising, since this quadratic shift occurs in the range of $t$ around $10^{-2}$, which is the region associated with the competition between the Kondo screening and the superexchange in the normal-state case discussed above (see also Figs. 3 and 4). Furthermore, the doublet-singlet energy difference is actually mostly driven by the downward shift of the singlet state. Indeed, we observe significant changes of the singlet ground state with changing with $t$, revealed by the evolution of the ground-state expectation values, in particular the spin $\langle S_1 \cdot S_2 \rangle$ and pairing correlations $\langle d_{1\uparrow}d_{1\downarrow}\rangle$.

3. Thermodynamic properties

An important difference between the normal-state and superconducting case manifests through the very different behavior of the spin correlation $\langle S_1 \cdot S_2 \rangle$ in the small $t$ limit. In the normal case, the Kondo screening wins over the superexchange and each dot is screened individually, leading to $\langle S_1 \cdot S_2 \rangle \to 0$. In the superconducting case, the Kondo screening cannot be completed due to the lack of quasiparticles, thus the two unscreened moments are free to form a tightly bound local singlet state and $\langle S_1 \cdot S_2 \rangle$ attains values close to the saturation $(-0.6)$. It is also revealing to observe that the difference in $\langle S_1 \cdot S_2 \rangle$ between the two cases starts to grow near the point where the pairing correlations $\langle d_{1\uparrow}d_{1\downarrow}\rangle$ change sign, as indicated by the arrow in Fig. 6. This is yet another sign that the Kondo screening becomes ineffective for $t$ lower than this limiting value. Due to non-zero electron hopping in this model, this passing through zero is a simple cross-over, not a quantum phase transition.

In the opposite limit of very large $t$, the behavior can be described in terms of molecular orbitals. In fact, from Fig. 6 it is immediately obvious that in this limit there is little difference between the normal-state and the superconducting case, since the superconducting gap is positioned in the region of low spectral density between the bonding and anti-bonding orbitals, thus it is ineffective. This is also signalled by the pairing correlations $\langle d_{1\uparrow}d_{1\downarrow}\rangle$ going to zero for large $t$.

While spin degrees of freedom are significantly affected...
by the superconductivity, the charge fluctuations are approximately the same in both regimes, as evidenced by nearly overlapping results for the inter-dot charge fluctuations $\langle (n_1 - 1)(\nu_2 - 1) \rangle$ and slightly reduced intra-dot charge fluctuations $\langle (n_1 - 1)^2 \rangle$ in the superconducting state in the K and AFM regimes. The reduction is due to the opening of the gap in the density of states and the corresponding reduction of electron hopping.

4. **Flux dependence**

We now study the effect of non-zero difference in the superconducting phase (i.e., flux through the ring), $\phi$. We show the results for an intermediate strong $t = 10^{-2}$ in Fig. 7. The flux leads to a splitting of the doublet Shiba states which are otherwise degenerate at the p-h symmetric point. The splitting is only faintly visible in the spectral function because of the unequal spectral weights. Splitting is proportional to $t$, it starts linearly for small $\phi$ and is the largest for $\phi = \pi$. It is worth stressing that the singlet-triplet splitting is hardly affected by non-zero $\phi$, there is only a slight downward trend.

In this regime, the flux cannot lead to a quantum phase transition. For larger $t$ the enhanced splitting of the double states is never large enough for the lower doublet state to become lower in energy than the singlet state.

5. **$\Gamma$ dependence**

In this section I briefly discuss the role of the hybridization strength $\Gamma$. Most of the results discussed in this work have been computed for $\Gamma = 0.02$, such that each quantum dot is in the deep Kondo limit and, for a decoupled dot at $\Delta = 0.01$, $T_K \ll \Delta$ thus its ground state is a spin doublet. The doublet-singlet transition in a single QD occurs for $\Gamma = \Gamma_t \approx 0.04$.

For the double quantum dot system, we find that with increasing $\Gamma$, the doublet excited state decreases in energy and at $\Gamma \approx 0.025$ an excited singlet also enters the sub-gap region. This trend continues until $\Gamma = \Gamma_t$, where in the limit $t \to 0$ we find degeneracy of five multiplets: two singlets, two (degenerate) doublets, and the triplet. For $\Gamma > \Gamma_t$, the nature of the singlet ground state changes, since it is associated with two separate Kondo clouds, rather than with the inter-dot singlet induced by the superexchange coupling. Consequently, in this range the triplet state lies close to the excited singlet state, rather than the ground state, see Fig. 8(a) where the sub-gap states are plotted for $\Gamma = 0.0045 > \Gamma_t$. Curiously, for non-zero $t$ the triplet is lower in energy than the excited singlet state, although the superexchange coupling would lead to the opposite order. The reason for this behavior is not entirely clear, but it could be a manifestation of the two-channel $S = 1$ Kondo screening of the local moment associated with the triplet. Another difference between $\Gamma < \Gamma_t$ and $\Gamma > \Gamma_t$ regimes is manifest in the $t$-dependence of $\langle S_1 \cdot S_2 \rangle$ on the approach to the decoupled-dot $t \to 0$ limit, see Fig. 8(b). These different singlet states have recently also been discussed in Ref. 30.

Irrespective of the value of $\Gamma$ and the nature of the ground-state singlet, we find that the excited singlet state always monotonously increases in energy with $t$ and the spectral functions are qualitatively always very similar. There are no quantum phase transitions, nor even avoided crossings at finite $t$ as could be expected in the two-impurity Kondo model.
This issue is discussed further in Appendix B where the model without particle hopping but only exchange interaction is studied: that model has a true quantum phase transition.

C. Left-right symmetric case, away from half-filling

1. Splitting of the doublet Shiba states

![Diagram](image)

Figure 9: (Color online) Spectral function $A_1(\omega)$ in the left-right symmetric DQD system away from half-filling at fixed small coupling $t = 10^{-3}$. Top panel: normal state (wide frequency range). Middle panel: superconducting state (close-up on the region inside the gap). Bottom panel: the sub-gap Shiba state spectrum revealing the small splitting induced by the inter-dot coupling.

We now maintain the left-right symmetry, but move away from the $\delta = 0$ particle-hole symmetric point. For low inter-dot coupling $t$, the behavior mirrors that of single dots, see Fig. 2. With increasing $\delta$ the atomic peaks shift to higher energies and the width of the Kondo resonance increases as $T_K$ grows. This continues until $\delta \approx U/2 - \Gamma \approx 0.1$ when the system enters the valence fluctuation regime and the Kondo resonance merges with the lower atomic peak. For even larger $\delta$, the system is in the empty orbital regime with no electrons occupying the quantum dot. This evolution is well visible in the normal-state results presented in Fig. 9a. Similarities with the single dot limit are also observed in the superconducting case: compare Fig. 9b with Fig. 2b), where very similar energies and spectral weights can be seen. A closer look at the sub-gap states, however, reveals some interesting details, see Fig. 9c. (i) The transition at $\delta \sim 0.1$ is between two singlet ground states (we show below that this is actually a cross-over; true quantum phase transition only occurs in the $t = 0$ limit). For $\delta < 0.1$, the ground state of a single dot is a spin doublet Shiba state, thus the DQD systems has a nearly degenerate singlet and triplet states for low $t$. The lowest spectroscopically observable excitations are the two doublet states which decrease in energy $\Omega$ as $\delta$ increases; these doublets correspond to one of the QDs having a quasiparticle attached to it. As $\Omega$ drops below $0.5\Delta$, an additional singlet state enters the sub-gap range. This state can be interpreted as the state where both QDs have one quasiparticle attached each. The ground state for $\delta > 0.1$ is of this type. (ii) While at $\delta = 0$ the doublet excitations are degenerate, there is a splitting induced by the inter-dot coupling of order proportional to $\delta t$. This can be understood as the formation of molecular orbitals by the quasiparticle attached to the dots.

![Diagram](image)

Figure 10: (Color online) Spectral function $A_1(\omega)$ in the left-right symmetric DQD in the superconducting state for increasing inter-dot coupling $t$.

For intermediate inter-dot coupling, see the $t = 10^{-2}$ case in Fig. 10, these effects become more pronounced and the splitting of the doublet Shiba states is clearly visible. We notice that the asymmetry of the particle-like ($\omega > 0$) and hole-like ($\omega < 0$) transitions exists for both branches. At larger $t$, the higher-energy doublet state is already essentially merged with the continuum and is hardly spectroscopically observable. For even larger $t \sim 0.1$ the system is in the molecular orbital regime and the two dots behave as a single large quantum dot which undergoes Kondo screening when $\delta$ is appropriately tuned; this manifests as the singlet-doublet transition similar to that discussed in Sec. III A.

Before continuing, we also remark on the general feature
of decreasing spectral weight of the sub-gap states as they approach the gap edges at \( \omega = \pm \Delta \), already observed and discussed for the case of a single quantum dot in Ref. [14]. This is well visible in Figs. [9] and [10] as well as in all other spectra in the following.

2. Cross-over between the singlet states

Another important inference from Fig. [10] is that there is no phase transition between the two possible singlet states, but rather a continuous cross-over. This is immediately clear, since the second singlet state occurs approximately at the sum of energies of the doublet Shiba states, thus it is pushed together with these two states to higher energies as \( t \) increases. This is confirmed by inspecting the spectrum of sub-gap excitations (bottom panel in Fig. [11]). Despite the continuous evolution of the ground state as a function of \( \delta \), its nature is not the same at \( \delta = 0 \) as compared to the large \( \delta \) limit, see other panels in Fig. [11]. Most notably, the pairing expectation value \( \langle d_{\uparrow}d_{\downarrow} \rangle \) has opposite signs. The \( \delta = 0 \) ground state can be interpreted as a localized singlet formed by unscreened local moments, for \( \delta \gtrsim 0.1 \) these are two separate Kondo compensated states with quasiparticles attached, and for large \( \delta \) the dots are unoccupied and play no role, thus the system is a simple BCS superconductor.

It may be noted that the singlet ground-state for \( \delta \geq 0.1 \) is actually similar in nature (and most likely “adiabatically connected” with) the singlet ground state at \( \delta = 0 \) at \( \Gamma > \Gamma_t \) discussed in previous subsection.

3. Flux dependence

We now consider the flux dependence. The main effect for small \( \delta \) and \( t \) is some initial (\( \phi = 0 \)) splitting of the doublet Shiba state, otherwise the results are rather similar to those shown in Fig. [7]. For \( \delta \approx 0.1 \), in the valence fluctuation region, the behavior is more interesting: the flux can induce a quantum phase transition by strongly increasing the splitting between the doublet states, see Fig. [12]. This type of the phase transition will be studied more carefully in the following section, since it also occurs for unequal \( \delta_1 \) and \( \delta_2 \), where one dot is tuned to the VF regime, and the other remains at 0. Here we comment on some other features: a) the singlet-triplet splitting is now more significantly affected by non-zero \( \phi \), b) the second singlet state is also significantly \( \phi \) dependent (in fact, the two single states merge at \( \phi = \pi \) in the \( t \to 0 \) limit). There is a significant spectral weight redistribution across the phase transition, thus it should be easily experimentally observable.

Figure 11: (Color online) Expectation values in the left-right symmetric DQD system away from the particle-hole symmetric point. The value of \( t \) is the same as in the top panel of Fig. [10].

Figure 12: (Color online) Spectral function \( A(\omega) \) and the diagram of the sub-gap Shiba states for \( \delta_1 = \delta_2 = 0.1 \) as a function of the superconducting phase difference \( \phi \).
D. Generic case

1. Normal state

We now consider the fully generic case of two quantum dots with different on-site energies $\delta_i$. The results will be presented by fixing $\delta_2$ and plotting the sweeps of $\delta_1$ for different values of the inter-dot coupling $t$. In the limit of small $t$, the two dots are essentially decoupled, thus the spectral function of dot 1 will be the same as in the single dot case, while the dot 2 will not vary.

We first fix $\delta_2 = 0$, thus the dot 2 is half filled and in the Kondo regime. At intermediate $t$ the exchange coupling $J$ starts to influence the spectra. In the local-moment regime $J$ further increases somewhat with increasing $\delta_1$, since

$$J = t^2 \left( \frac{1}{\delta_1 + U/2} + \frac{1}{U/2 - \delta_1} \right) = \frac{4t^2}{U} \left( \frac{1}{U/2 - \delta_1} \right) \approx \frac{4t^2}{U} \left( \frac{1}{U/2} \right) \quad (15)$$

At $\delta_1 \approx U/2 - \Gamma$, as the system enters the valence-fluctuation regime, the exchange coupling becomes less effective. The results for $t = 10^{-2}$ are shown in the top row in Fig. 13.

For small $\delta_1$ we observe on both dots the expected exchange splitting of the Kondo resonance, $T_K$ on dot 1 increases with increasing $\delta_1$. Near $\delta_1 = 0.07$, the condition $J \sim T_K$ is fulfilled, as revealed by the disappearance of splitting on $A_2(\omega)$ for $\delta_1 > 0.07$. Interestingly, the splitting in $A_1(\omega)$ persist to higher values of $\delta_2$, even in the valence fluctuation regime of dot 1. A closer inspection of the results reveals that the splitting in this regime corresponds to the width of the Kondo resonance on dot 2. This splitting is thus not due to the exchange coupling, but is a simple coherence (proximity) effect due to particle hopping between the dots. This observation is important: spectral dips of similar magnitude can be generated by quite different mechanisms, thus for proper interpretation it is necessary to consider the spectral functions of all parts of the coupled QD nanostructure.

At larger $t = 4.62 \times 10^{-2}$, the effects of the inter-dot tunneling become even more pronounced, see bottom row in Fig. 13. The two dots behave increasingly as a single entity, thus there is a pronounced “mirroring” of spectral features in $A_1(\omega)$ and $A_2(\omega)$. The most pronounced effects occur in the range $\delta_1 \approx 0.1$ to $\delta_1 \approx 0.15$ when the dot 1 is in the valence fluctuation regime. The shade for $\omega < 0$ in this range is the nascent molecular orbital state that becomes better defined for even larger $t$. The spectral weight in $A_1(\omega)$ for $\omega > 0$ is the disappearing atomic on-site orbital of dot 1 that eventually disappears for increased $t$. This is thus the transient regime where both localized atomic and delocalized molecular spectral features coexist.

2. Superconducting case

In Fig. 14 we plot the results for the superconducting case focusing on the sub-gap states. At small $t = 10^{-3}$, top row, the dots are nearly decoupled, thus the dot 1 shows the same evolution of the sub-gap states as discussed in relation to Fig. 2 while the spectrum on dot 2 shows peaks at constant energy of $\Omega = 0.6\Delta$, as expected for $\delta_2 = 0$. The first signs of the inter-dot effects become visible around $t = 2 \times 10^{-3}$ in the form of weak features of $A_1(\omega)$ mirrored in $A_2(\omega)$, which then amplify and mix with the Shiba states of dot 2. By $t = 10^{-2}$, center row in Fig. 14, the structure of the sub-gap states is already quite complex and the superexchange $J$ needs to be invoked to explain all features. There is a non-trivial evolution of the spectral weights, including the discontinuities that stem from the ground state change from singlet to doublet. As an aid in the interpretation, we show in Fig. 15 the sub-gap many-particle spectrum. The quantum phase transition occurs at $\delta_1 \approx 0.1$. For $\delta_1 < 0.1$, the spectrum is similar to that in the $t \to 0$ limit: the ground state is singlet, and with increasing $\delta_1$ one of the doublet ground states comes down in energy and becomes the new ground state. The effect of non-zero $t$ is visible in the slightly increasing (vs. $\delta_1$) energy of the other doublet state (also its initial $\delta_1 = 0$ values is enhanced from $0.6\Delta$ at $t = 10^{-3}$ to $0.7\Delta$ at $t = 10^{-2}$, as already shown in Fig. 6), and in the singlet-triplet splitting. The most interesting features occur for $\delta_1 \gtrsim 0.1$. In particular, we point out the differences between $A_1(\omega)$ and $A_2(\omega)$. In $A_2(\omega)$, the most pronounced features correspond to the transitions from the doublet GS to the two excited singlet states, while the transition to the triplet state is not visible at all. In $A_1(\omega)$, on the other hand, the dominant feature is the transition from the doublet GS to the triplet excited state, while the weights for the transitions to the singlet excited states are much weaker. (By continuity, the same must be true at smaller $t = 10^{-3}$, although there the singlet and triplet states are degenerate and the nature of the excitation cannot be inferred.) Since in the atomic limit the triplet state does not depend at all on $\delta_1$, nor on $t$, and the lowest lying singlet state depends on these parameters only very weakly, the differences between the two spectra are predominantly due to the different site amplitudes of the doublet wavefunction. The very strong transition on the particle side ($\omega > 0$) of $A_1(\omega)$ is due to the charge depletion by high electrostatic potential which leads to strong enhancement of the matrix element for the particle addition. For $\delta_1 \gg 0.1$, the only resonance remaining inside the gap is that corresponding to the Shiba state on dot 2: it is positioned at $0.6\Delta$ in the large $\delta_1$ limit where the dot 1 has little effect on dot 2 in the sub-gap energy range. Other sub-gap states are pushed into the continuum, since the dot 1 no longer has a magnetic moment. Finally, for large $t$, bottom row in Fig. 14 we enter the regime of a single effective QD, thus the variation of the sub-gap state manifests in a similar way in both spectral functions, except for some differences in spectral weights due to different on-site energies.

Observing that interesting effects occur around $\delta_1 \approx 0.1$, we now fix one of the dots to this value, i.e., $\delta_2 = 0.1$, and sweep the other in the full interval. At small $t$, the dots are decoupled: $A_1(\omega)$ shows the same evolution as a single QD, while $A_2(\omega)$ is always in the valence fluctuation regime with a resonance near $\omega = 0$ which resulted from the merging of the Kondo resonance with the lower atomic peak. At interme-
Figure 13: (Color online) Spectral function on dot 1 (left panels) and dot 2 (right panels) in the normal state for two values of the inter-dot couplings $t$. The quantum dot 2 is kept at $\delta_2 = 0$, which is the Kondo regime.

Figure 14: (Color online) Spectral function on dot 1 (left panels) and dot 2 (right panels) in the superconducting state for a range of inter-dot couplings $t$. The quantum dot 2 is kept at $\delta_2 = 0$, which is the Kondo regime.
diate value of $t = 10^{-2}$ we start to observe the effects of the exchange coupling: $A_2(\omega)$ shows a splitting of order $J$, see Fig. 16. In the central range $-0.1 < \delta_1 < 0.1$, there is consequently a non-negligible antiferromagnetic spin correlation $\langle S_1 \cdot S_2 \rangle \approx -0.1$. They are somewhat stronger for negative $\delta_1$, since in that case the overall occupancy is closer to 2, which is favorable for local singlet formation. As $t$ grows, both spectral functions become visibly perturbed ($u = 2.15 \times 10^{-2}$, bottom row). The spin correlations in the centre is now much stronger, reaching values around $-0.3$. The exchange splitting is asymmetric, which can be explained by the following expression for $J$:

$$J = t^2 \left( \frac{1}{U/2 + \delta_1 - \delta_2} + \frac{1}{U/2 + \delta_2 - \delta_1} \right) = \frac{4t^2}{U} \left( 1 - 4(\delta_1 - \delta_2)^2 / U \right),$$

which indicates that the largest exchange coupling is found for $\delta_1$ of opposite signs, i.e., for $\delta_1 \sim -0.1$. The interdot coupling also affects the occupancy and charge fluctuations on dot 2: compared to the $t = 0$ values, the occupancy is increased (toward half-filling) in the $\delta_1 \sim 0$ region (charge fluctuations are little affected) and decreased near $\delta_1 \sim -0.1$ and $\delta_1 \sim 0.1$ points, where an increase of charge fluctuations is also observed. These results show that the behavior in this regime cannot be explained by the exchange coupling alone, but the charge fluctuations also play an important role.

For large (absolute) values of $\delta_1$, the dot 1 becomes non-interacting, while the dot 2 returns to the single-impurity valence fluctuation regime with a resonance close to $\omega = 0$.

Finally, we briefly discuss the results for the case where one of the dots (dot 2, for definitiveness) is driven to the empty orbital regime by tuning $\delta_2$ to a large value sufficiently above $U/2 + \Gamma \approx 0.15$. The system then essentially behaves as a single quantum dot; this includes also the level diagram of the Shiba states. Even though the dot 2 is unoccupied, we still find at finite inter-dot coupling some faint features from $A_1(\omega)$ being mirrored into the spectral function $A_2(\omega)$ (results not shown). As $t$ grows one can smoothly reach the regime of molecular orbitals. To conclude, for large $\delta_2$ the DQD always effectively behaves as a single quantum dot: for small $t$, the physical QD 1, and for large $t$ the “large” QD made of molecular orbitals spanning both dots.

### 3. Flux dependence

Without showing any results, I briefly comment on the flux dependence. General features are already known: finite $\phi$ leads to the splitting of doublet Shiba states, reduces the singlet-triplet splitting, and reduces the energy of the first excited singlet Shiba state. In some parameter ranges this leads to spectroscopically observable features. For example, for $\delta_1 = 0.05$, $\delta_2 = 0$, $t = 10^{-2}$, the doublet splitting becomes well visible since it is large and both resonances are well inside the gap. For $\delta_1 = \delta_2 = 0$, $t = 10^{-1}$, at finite $\phi$ a doublet state emerges from the continuum and becomes well defined. The most interesting case of flux-induced singlet-doublet transition were already discussed in the previous section and commonly appear close to valence fluctuation regimes.

## IV. SUPERCONDUCTING ATOMIC LIMIT

This section demonstrates that on the qualitative level most features in the sub-gap many-particle spectra can be properly described in the superconducting atomic limit which consists in taking the $\Delta \to \infty$ limit in the leads. \cite{14,15,17,18,19,20}. This eliminates the continuum of the quasiparticle levels above the gap (see Appendix A), thus the sole remaining effect of each lead is the proximity pairing term of the form $\Gamma d_i^\dagger d_i^\dagger + H.c$. We obtain a two-site discrete model with the following Hamiltonian:

$$H = \sum_i \delta_i (n_i - 1) + \frac{U}{2} \sum_i (n_i - 1)^2 + \sum_i \left( \Gamma d_i^\dagger d_i^\dagger + H.c. \right) - t \sum_\sigma \left( d_i^\dagger d_{i\sigma}^\dagger + H.c. \right),$$

which can be easily diagonalized. The Kondo correlations are excluded in this description, thus the results are quantitatively quite different compared to the accurate NRG calculations. Nevertheless, the lowest levels match the observed sub-gap Shiba states, and their splittings and evolution with model parameters tend to be remarkably close to the true behavior of the full model.

We first analyse the eigenvalues in the different invariant subspaces. The singlet space is spanned by the following five states (one from the zero-occupancy sector, three from the half-filling sector, and one from the full-occupancy sector)

$$|0\rangle, \quad d_{21}^\dagger d_{21}^\dagger |0\rangle, \quad \frac{1}{\sqrt{2}} \left( d_{11}^\dagger d_{12}^\dagger - d_{12}^\dagger d_{11}^\dagger \right) |0\rangle,$n

$$d_{14}^\dagger d_{11}^\dagger |0\rangle, \quad d_{14}^\dagger d_{11}^\dagger d_{12}^\dagger d_{21}^\dagger |0\rangle.$$

The Hamiltonian in this subspace is
Figure 16: (Color online) Spectral function on dot 1 (left panels) and dot 2 (right panels) in the normal state for two values of the inter-dot couplings $t$. The quantum dot 2 is kept at $\delta_2 = 0.1$, which is in the valence fluctuation regime.

\[
H_S = \begin{pmatrix}
    U - \delta_1 - \delta_2 & \Gamma & 0 & 0 \\
    \Gamma & U - \delta_1 + \delta_2 & -\sqrt{2}t & 0 \\
    0 & -\sqrt{2}t & 0 & -\sqrt{2}t \\
    \Gamma & 0 & -\sqrt{2}t & U + \delta_1 - \delta_2 \\
    0 & \Gamma & U + \delta_1 + \delta_2 & \Gamma
\end{pmatrix}.
\] (19)

In general, the eigenvalues cannot be expressed in (reasonably simple) closed form and need to be computed numerically. For $\delta_i = 0$ and $t = 0$, they are

\[
0, U, U - 2\Gamma, U + 2\Gamma.
\] (20)

The first state is the inter-dot singlet with one electron on each dot. For $\delta = 0$, to lowest order in $t$ only the first state shifts in energy (by the superexchange coupling $4t^2/U$). For $t = 0$, to lowest order in $\delta$ the third and the fifth state shift to $U - 2\Gamma - \delta^2/\Gamma$ and $U + 2\Gamma + \delta^2/\Gamma$, respectively. When both $\delta$ and $t$ are non-zero, the first state shifts down by the corresponding superexchange coupling $\propto t^2$, the third and the fifth shift by $\propto \delta^2$, while the two remaining states remain fixed at $U$. Since $U \gg \Delta$ in our NRG calculations, the states that are relevant for the sub-gap part of the spectrum are only two: the inter-dot singlet (first state) at $\approx -4t^2/U$, and the (third) state at $\approx U - 2\Gamma - \delta^2/\Gamma$ which becomes important at $\delta$ of order $\sqrt{U\Gamma}$, which is the charge fluctuation scale in the single-impurity Anderson model (going beyond the perturbation theory, the correct scale is $\delta \approx U/2$, but the interpretation in terms of charge fluctuations remains correct). As expected, the main component of this latter state for large $\delta$ is $|0\rangle$, i.e., this is the empty orbital.

The doublet space is spanned by the following four states (two each from single-occupancy and triple-occupancy sectors):

\[
d_{2\uparrow}|0\rangle, \quad d_{1\uparrow}|0\rangle, \quad d_{1\uparrow}d_{2\downarrow}|0\rangle, \quad d_{1\downarrow}d_{1\uparrow}d_{2\uparrow}|0\rangle.
\] (21)

The corresponding Hamiltonian is

\[
H_D = \begin{pmatrix}
    U - \delta_1 & -t & 0 & 0 \\
    -t & U - \delta_2 & 0 & \Gamma \\
    0 & 0 & \Gamma & t \\
    \Gamma & 0 & t & U/2 + \delta_1
\end{pmatrix}.
\] (22)

The four eigenvalues are

\[
\frac{1}{2} \left( U \pm \sqrt{\left(2(2t^2 + 2\Gamma^2 + \delta_1^2 + \delta_2^2) + \sqrt{\left(4t^2 + (\delta_1 - \delta_2)^2\right)(\delta_1^2 + \delta_2^2)}\right)^{1/2}} \right).
\] (23)

(The two $\pm$ signs in this expression are independent.) For $t = 0, \delta_1 = \delta_2 = 0$, these energies are

\[
\frac{U}{2} \pm \Gamma,
\] (24)
Figure 17: (Color online) Spectral function on dot 1 (left panels) and dot 2 (right panels) in the superconducting state for a range of inter-dot couplings $t$. The quantum dot 2 is kept at $\delta_2 = 0.1$, which is the valence fluctuation regime. The last row shows the corresponding many-particle Shiba state diagrams.

Each being doubly degenerate. These states are of the form

$$\frac{1}{\sqrt{2}} d_{1\sigma}^\dagger \left( 1 \pm d_{2\uparrow}^\dagger d_{2\downarrow}^\dagger \right) |0\rangle,$$

and the analogous states with $1 \leftrightarrow 2$. The degeneracy is lifted when both $t$ and $\delta_1 = \delta_2 = \delta$ are non-zero, the splitting being

$$\frac{2\delta t}{\Gamma}$$

to lowest order in $t$ and $\delta$. This can be interpreted as the bond formation.

Finally, there is a single triplet which we represent through $d_{1\uparrow}^\dagger d_{2\uparrow}^\dagger |0\rangle$. Its energy is always 0.

We now proceed in the same order as when presenting the results of the NRG calculation in Sec. II. In Fig. 18(a) we consider the left-right symmetric case at half-filling for increasing inter-dot coupling $t$. This should be compared with the bottom panel in Fig. 6. The lowest three states are in direct correspondence: the ground state is always the inter-dot singlet state, there is a triplet state growing in energy as $\propto 4t^2/U$, and a doublet excited state. The singlet-triplet splitting behaves similarly in both approaches. There are more differences related to the doublet state: at $t = 0$, in the NRG we find it at $\Omega = 0.6\Delta = 0.006$ while here it is found at a much higher energy of $\approx U/2 - \Gamma$. Nevertheless, we find the same increasing trend at large $t$, thus qualitative behavior is the same. The remaining states are irrelevant for our purposes since they are merged with the continuum; this will also be the case in all following examples.

In Fig. 18(b) we study the $\delta = \delta_1 = \delta_2$ dependence at constant $t$. These results should be compared with the diagrams in Fig. 9 and 11. There is an important qualitative difference
In this work I have presented a selection of the most interesting results curated out of an extensive survey of the behavior of the double quantum dots with superconducting leads, focusing on the regimes of strong dependence on model parameters that could be targeted by future experiments. The results were interpreted by first considering these systems in the normal state and then discussing the spectroscopically sharp sub-gap states which emerge when the leads become superconducting. Qualitative trends were reproduced using very simple calculations on a two site cluster in the superconducting atomic limit which projects out the continua of the quasi-particle states above \( \Delta \) by taking the \( \Delta \rightarrow \infty \) limit, while for quantitative correctness it is crucial to use a non-perturbative technique such as the NRG, especially in the regimes where the Kondo effect plays an important role. A general observation that one can make after considering the totality of the results is that the valence fluctuation regime, where one or both quantum dots are close to the occupancy change, shows the most complex behavior that should be more closely examined both theoretically and experimentally, the advantage for the superconducting ring geometry being that this also happens to be the range where the flux dependence of the sub-gap levels is the strongest. This regime is just as intriguing, if not more, as the deep Kondo regime.

V. CONCLUSION

The NRG shows that the ground state is always a singlet and that there is an avoided level crossing between the two singlet Shiba states, yet in the atomic limit we find a finite parameter range where one of the doublet states becomes the ground state and, furthermore, there is a crossing of the singlet states in the same parameter range. This indicates that the avoided crossing in the true solution is due to virtual transitions through the quasiparticle continuum.

In Fig. 18(c) we consider the asymmetric case with \( \delta_2 \) fixed to 0 and variable \( \delta_1 \), to be compared with the Shiba level diagram in Fig. 15. It correctly reproduces the splitting of the doublet states at low \( \delta_1 \), the singlet-doublet quantum phase transition induced by driving one of the dots away from the Kondo regime toward the empty orbital regime, as well as the behavior of the triplet state.

Finally, in Fig. 18(d) we plot the generic case with the QD2 in the valence fluctuation regime, to be compared with the Shiba level diagrams in Fig. 17. The quantum phase transition at \( \delta_1 \approx 0.1 \) is correctly reproduced, although the one at \( \delta_1 \approx -0.15 \) is an artifact of the atomic limit method and does not exist in the true solution.

In spite of minor shortcomings, the superconducting atomic limit works surprisingly well, thus it appears to be a good general method for surveying large parameter spaces in complex multi-dot systems. Its validity is, however, expected to become limited as the role of the Kondo effect via quasiparticle states is increased, either by increasing \( \Gamma \) or by decreasing \( \Delta \). This is further studied in the Appendix A. A systematic method for improving perturbatively upon the superconducting atomic limit has been described in Ref. 17.

Figure 18: (Color online) Eigenvalues of the effective Hamiltonian in the superconducting atomic limit (\( \Delta \rightarrow \infty \)). The color scheme is the same as for the NRG results: black lines are \( S = 0 \), red lines \( S = 1/2 \), blue line is \( S = 1 \). a) Left-right symmetric case, half-filling, evolution as a function of \( t \). b) Left-right symmetric case away from half-filling, \( t = 0.02 \). The singlet states (black lines) actually cross, the appearance of avoided crossing is a plotting artifact. c) Generic case with \( \delta_2 = 0 \), \( t = 0.02 \). d) Generic case with \( \delta_2 = 0.1 \), \( t = 0.02 \). In all calculations \( U = 0.27 \), \( \Gamma = 0.02 \), \( \Delta = 0.01 \).
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Appendix A: NRG study of the $\Delta \to \infty$ limit in the single impurity model

We consider the single impurity Anderson model and study the evolution of the results for fixed Kondo exchange coupling $J_K \propto \Gamma/U$ and variable $\Delta/U$ ratio. In the $\Delta \to \infty$ limit the continuum of the quasiparticle states plays no role, thus there is strictly speaking no Kondo physics and the only effect of the superconducting lead is the proximity effect, i.e., a local pairing field proportional to the hybridization strength $\Gamma$. In the opposite limit of $\Delta \to 0$, there is no superconductivity, only Kondo screening. The cross-over between the two regimes occurs for $\Delta \sim T_K$. Our goal here is the assessment of the renormalization effects due to the Kondo effect in order to better understand the limitations of the superconducting atomic limit. (See also Ref. 14 for a similar discussion.)

The $\Delta/U$ ratio can be controlled in two ways: i) by fixing $\Delta$ and varying $U$, which shifts the scale of the Kondo temperature linearly in $U$ since $J_K \propto \Gamma/U$ is constant and only the prefactor in the expression for $T_K$, Eq. (7), is affected (this is only true for $U \ll D$; for $U \gg D$ the Kondo temperature saturates), and ii) by fixing $U$ and varying $\Delta$, which keeps the Kondo temperature scale constant but suppresses the Kondo screening by bringing the density of states in the gap to zero. As long as all the relevant model parameters ($\Delta$ and $U$) are sufficiently below the half-bandwidth $D$, these two points of view are fully equivalent.

We first fix $\Delta/D = 0.01$ and tune $U$. The results are shown in Fig. 19. The Kondo temperature for the chosen parameters ($U/\Gamma = 0.27/0.02$) is always sufficiently smaller than $\Delta$, so that the system has always a doublet ground state at the particle-hole symmetric point. The singlet-doublet transitions in the $\Delta \to \infty$ limit is then simply due to the occupancy variation. In the superconducting atomic limit, there are two singlet states with energies
\[
\frac{U}{2} \pm \sqrt{\Gamma^2 + \delta^2},
\] (A1)
and a doublet at zero energy. For large $\Delta$, these values are indeed reproduced in the NRG, see Fig. 19, where the dashed line corresponds to the exact analytical result, while the full lines are the NRG results for a range of $\Delta/U$ ratios.

The main effect of increasing $U$ (this here means an increasing role of the quasiparticle excitations and thus more pronounced Kondo physics) is the energy reduction of the singlet sub-gap states. This is precisely what is expected since a Kondo singlet state is being formed and this process is associated with the “binding energy” of order $T_K$. The deviation from the atomic limit starts to be visible (5% difference) already for $U/D \approx 0.003$, when $T_K \approx 10^{-6}$, thus $\Delta \approx 10^4 T_K$. In terms of the different phases, Kondo screening leads to the shrinking doublet region around $\delta = 0$ from the $\delta_{1,2} = \pm \sqrt{U^2/4 - \Gamma^2}$ points. At $\delta = 0$ there is always at least one singlet state inside the gap, while the second one merges with the continuum for $U \gtrsim 0.03$. The Kondo screening thus brings about both significant quantitative (renormalization effects) and qualitative differences (merging of sub-gap states with the quasiparticle continuum).

We now focus on the particle-hole symmetric point and use the approach ii) by fixing $U$. Since $T_K$ is now constant, $\Delta$ can be tuned across the singlet-doublet quantum phase transition, see Fig. 20. The asymptotic superatomic limit regime with both singlet excitations present inside the sub-gap region occurs only for very large $\Delta/T_K \gtrsim 10^5$. This scale is determined by $\Delta \sim U$, i.e., the superatomic limit is reached when the energy scale of the atomic processes is comparable or lower than the superconducting gap. This cross-over is unrelated to Kondo physics, as evident from the large separation of the relevant energy scales. The most interesting information is contained in the charge fluctuations of the singlet states, shown in the bottom panel. The cross-over to the atomic limit corresponds to a change in the nature of the singlet states from delocalized Kondo singlets formed by the local moment on the quantum dot and the conduction-band electrons (hence charge fluctuations are low and determined by the ratio of the hybridization strength over e-e repulsion, $\Gamma/U$), to BCS like singlet states $1/\sqrt{2}\langle|0\rangle \pm |\uparrow\downarrow\rangle\rangle$ with saturating charge fluctuations that are cause by the proximity effect, not by quasiparticle hopping. (In the NRG, the information about the expectation values of all sub-gap states is available in a reliable way through the diagonal matrix elements of the corresponding singlet operators.)

The general trend of $\Delta$ decreasing from the $\Delta \to \infty$ (atomic) limit can be generalized: it will lead to decreasing energy of states associated with the Kondo screening. In the DQD case, these are chiefly the two doublet states, as well as the first excited singlet state. This behavior is indeed observed.
use the same Hamiltonian as in the main text of this work but with the inter-dot coupling term replaced by
\[ H_{12} = J \mathbf{S}_1 \cdot \mathbf{S}_2, \]
where \( \mathbf{S}_i \) are the spin operators of the impurities.

The results are shown in Fig. 21 for a value of \( \Gamma/U \) in the suitable range for a competition between the singlet ground state a) consisting of two separate Kondo clouds or b) intersite singlet generated by the superexchange coupling \( 4t^2/U \). We indeed observe a quantum phase transition between the two singlets at \( J = J_c \approx 1.1 \times 10^{-3} \). The state a is characterized by near-zero spin correlations, \( \langle \mathbf{S}_1 \cdot \mathbf{S}_2 \rangle \approx 0 \), while the state b is an inter-site singlet state with large spin-spin values. All other system properties also change discontinuously across the transition (see the example of the charge fluctuations \( \langle n_1 - 1 \rangle \)), also shown in Fig. 21.

The two-impurity Kondo effect quantum phase transition is thus in principle spectroscopically observable, if only a system with sufficiently suppressed particle exchange could be physically realized.

I conclude this appendix with an amusing observation: in the normal-state case, the two-impurity Kondo quantum phase transition is a second-order transition with true quantum criticality, while in the superconducting case it is technically a first order quantum phase transition (level crossing between two sub-gap singlet states that are separated from the quasiparticle continuum). An interesting question for future work

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**Appendix B: Two-impurity Kondo criticality**

In the double quantum dot nanostructure with normal-state leads the low-temperature physics is governed by the two-impurity Kondo effect. The non-Fermi-liquid (NFL) fixed point of this model is never actually reached because the particle exchange between the leads is a relevant perturbation (in the RG sense \[53\]), but its presence still has important effects. In Sec. III B we observed that at the particle-hole symmetric point the ground state is the same singlet many-particle state for any value of \( t \); this is the case for any \( \Gamma/U \) ratio, even if the single-impurity Kondo temperature is larger than \( \Delta \) and each QD in the decoupled dot \( t \rightarrow 0 \) limit would have a spin-singlet ground state. This continuity is the superconducting counterpart of the cross-over behavior found in the normal state. The presence of the two-impurity Kondo model fixed point is thus only felt through the non-trivial evolution of the expectation values, in particular that of the spin-spin correlation function \( \langle \mathbf{S}_1 \cdot \mathbf{S}_2 \rangle(t) \).

The NFL fixed point can be approached arbitrarily closely, however, if the particle exchange between the two channel is suppressed while the exchange coupling is maintained \[53\]. We consider here how this scenario manifests in the superconducting case through the properties of the sub-gap states. We

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Figure 20: (Color online) Single quantum dot case at the particle-hole symmetric point, \( \delta = 0 \), for fixed \( U \) and \( \Gamma \) and variable \( \Delta \). (a) Sub-gap states showing the singlet-doublet transition at \( \Delta \approx 3T_K \). The second singlet state enters the sub-gap region only at very large \( \Delta \sim 10^3T_K \). (b) Ground state expectation value of the pairing operator, rescaled by \( \Delta \). (c) Charge fluctuations in the sub-gap Shiba states, evaluated as the expectation values of the corresponding many-particle states. The parameters are: \( U/D = 0.00027 \), \( \Gamma/D = 0.00002 \), and consequently \( T_K/D \approx 10^{-7} \).

Figure 21: (Color online) Two-impurity Kondo effect manifesting through the quantum phase transition between two different many-particle sub-gap singlet states in the model with exchange coupling \( J \) between the dots and no particle transfer \( (t = 0) \).
is to explore the structure of the excitations in the continuum above $\Delta$: are the Bogoliubov states formed out of Fermi li-
uid or non-Fermi liquid quasiparticles?

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