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Controllable π junction in a Josephson quantum-dot device with molecular spin.

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We consider a model for a single molecule with a large frozen spin sandwiched in between two BCS superconductors at equilibrium, and show that this system has a π junction behavior at low temperature. The π shift can be reversed by varying the other parameters of the system, e.g., temperature or the position of the quantum dot level, implying a controllable π junction with novel application as a Josephson current switch. In contrast to previous works the importance of the contribution from the continuum of states above the superconducting gap is brought out. The free energy for certain configuration of parameters shows a bistable nature, which is a necessary pre-condition for achievement of a qubit.

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I. INTRODUCTION

Molecular spintronics is a promising new domain, at the convergence of two challenging disciplines. On the one hand molecular electronics, where single molecules are used to create electronics devices at the nanometric scale with unique properties. And on the other hand spintronics, where the spin of the electron is used as the relevant quantity in place of the electronic charge, allowing to take advantage of unusual properties of the spin, like a long coherence time. It is in this context that we consider in this work the equilibrium properties of a molecule with a large magnetic moment placed between two superconductors, when a Josephson current flows between the two superconductors through the molecule. The focus will be on the effect, on the Josephson current, of the coupling between the spin of the electrons producing the current and the molecular spin. We will show in particular that when this spin coupling is large enough, the superconducting junction behaves as a π junction, with a reversal of the Josephson current compared to the case without spin coupling.

Of great importance for molecular spintronics are the molecules possessing a large spin, or “single molecule magnet”. Such molecules can now be synthesized, for example the molecule Mn12ac, which has a ground state with a large spin $S = 10$, and a very slow relaxation of magnetization at low temperature¹. This slow relaxation is due to a high anisotropy barrier for the magnetization, around 5.6 meV for Mn12ac. For the system we are considering, this is a very large energy, as the typical energies in our system (temperature, coupling to the electrodes, etc.) are at most of the order of the superconducting gap (which is 0.1 meV in Aluminum for example). This motivates our choice to take the molecular spin as a fixed quantity, which will act as a local magnetic field for the electrons going through the molecule. Concerning the electronic transport across the molecule, we model the molecule as a single resonant level, i.e. a quantum dot. As we will be interested in the regime of good transparency between the molecules and the superconducting electrodes, we will neglect in this work the electronic interactions on the resonant level¹³.

The main result of our paper is to show that, when the coupling to the molecular spin is large enough, the system shows a π shift. A reversal of the super-current in a Josephson device and the free energy having a global minima at phase difference π is referred to as π shift and a Josephson junction displaying this is termed a π junction². The π junction has potential applications in superconducting electronics, in quantum logic circuits as switches and are an integral part of superconducting phase qubits. We will also show that this π shift can be controlled by the other parameters of the system (position of the dot level, temperature, coupling to the electrodes, etc.), allowing to reverse the π shift and recover a standard Josephson junction. In order to contrast our results with π shifts found in other systems, we provide in the next section a brief history of the π -shift as seen in Josephson junctions.

Generally in works related to π junction behavior the bound state current, which is due to current carrying Andreev bound states formed between the two superconductors, is investigated while the contribution from the continuum of states above the superconducting gap is ignored^{7,8}. There are good reasons for doing so, since the continuum contribution is generally much less compared to bound state current, especially in the limit of a long junction or a very short one. However recent works have shown that the continuum current cannot be ignored⁹⁻¹¹, especially in a Josephson junction which is neither very short nor very long. In this work, we calculate explicitly the contribution from the continuum, and we show that in the presence of a large coupling to the molecular spin, the continuum current is essential to understand the π junction behavior. In some regime, the bound state current can even vanish, and the continuum current is then the only contribution. We will show also that, with some fine-tuning of the

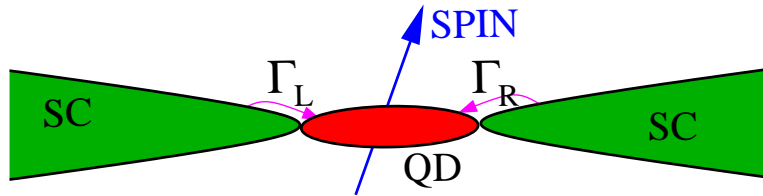


FIG. 1: Our model system

parameters of the system, the system can be in a bi-stable state, where the $\phi = 0$ and $\phi = \pi$ state are equally stable; this bi-stability is a necessary condition for a possible qubit implementation.

The rest of the work is organized as follows. The next section deals with a short history of the π -shift as seen in Josephson junctions and with the possible applications which such behavior may have. Section III is devoted to the derivation of the Josephson current when coupling to the molecular spin is present. In section IV we use the formulae obtained in section III to show the behavior of the Josephson current as a function of the coupling to the molecular spin, and of the other parameters. We give a detailed explanation of the mechanism leading to the π shift. In section V we discuss some potential applications of our system, first as a Josephson current switch, then as a superconducting qubit. Section VI is devoted to concluding remarks.

II. BRIEF HISTORY OF π -SHIFT

In order to show how our work and results differ from existing works on π junctions, we find useful to give a very short history of the π -shift. π junctions were first proposed theoretically by Bulaevskii and coworkers in Ref.[14]. They considered a tunnel junction with magnetic impurities in the barrier. In this system spin-flip tunneling leads to a formation of π junction. They also predicted that a superconducting ring containing a π junction could generate a spontaneous current and a magnetic flux opening the way for experimental detection. Spin flip tunneling in superconductor-quantum dot-superconductor(S-QD-S) system has also been shown to give rise to a π junction behavior as in Refs.[4,15,16]. It was Kulik who in 1966 was the first to discuss the spin-flip tunneling through an insulator with magnetic impurities¹⁷. The spin-flip tunneling is predicted to dominate the Josephson current when spin on the quantum dot is non-zero. In S-QD-S junction, changes in the sign of the critical current could be observed as a function of the quantum dot gate voltage which controls the occupancy of a quantum dot. Due to this gating capability one has more control over the magnetic state of a barrier in S-QD-S junction compared to a magnetically doped Superconductor-Insulator-Superconductor junction¹². Superconductor-Ferromagnet-Superconductor(SFS) have also been shown to give rise to a π junction behavior both in theory¹⁸⁻²⁰ as well as in experiments^{21,22}. The study of the superconducting π state sheds more light on the coexistence of superconductivity and ferromagnetism in general and is also important for superconducting electronics²³. Generally with increase in the strength of the exchange field the π shift is observed with a reversal and suppression of the super-current. In SFSFS systems with the ferromagnets in anti-parallel alignment, however, with increase in the strength of the exchange field an increase in super-current is observed²⁴. In SIFIS and SFcFS, where c denotes a constriction, structures also such π junctions have been observed². Recently triplet superconductor-ferromagnet-triplet superconductor junctions have been predicted to have potential applications as current switches²⁵. In contrast to SFS systems, π junction behavior in SNS systems occurs due to the creation of a non-equilibrium distribution of electrons in the barrier via a control channel⁵. Thus in these systems the π -junction can be controlled via a voltage applied to the control channel this makes such devices ideal for them to be used in superconducting digital circuits, especially as a phase inverter, i. e., π -SQUID²⁶ for complementary Josephson digital devices. Further application of π junctions as candidates for engineering quantum bits have been predicted²⁷.

III. DERIVATION OF THE JOSEPHSON CURRENT

A. Model Hamiltonian and effective action

The Josephson Current(I_J) can be calculated from the derivative of the free energy(F) with respect to the phase difference(ϕ) across the superconducting leads $I_J = 2\frac{dF}{d\phi}$, in equilibrium. The free energy in turn is defined as $F = -kT \ln Z$, where Z is the partition function of our system. Thus calculating Z is the first step in calculating the

Josephson current in our system. The full Hamiltonian of our system is written as below:

$$H = H_{D-S} + \sum_{j=L,R} H_j + H_T, \quad (1)$$

where H_{D-S} defines the Hamiltonian of the quantum-dot molecule with spin, H_j represents the superconducting leads, while H_T denotes the tunneling part. The dot-spin Hamiltonian is:

$$H_{D-S} = \epsilon \sum_{\sigma} d_{\sigma}^{\dagger} d_{\sigma} + JS(d_{\uparrow}^{\dagger} d_{\uparrow} - d_{\downarrow}^{\dagger} d_{\downarrow}) \quad (2)$$

where $d_{\sigma}, d_{\sigma}^{\dagger}$ are the electronic operators in the dot, ϵ is the energy level of the dot, J the coupling between the molecular spin \mathbf{S} and the electronic spin on the dot level. The coupling term comes from the exchange interaction $J\mathbf{S} \cdot \mathbf{s}$, where \mathbf{s} is the electronic spin on the dot, but as explained in the introduction, the molecular spin is fixed in our system, and we chose the z axis along the spin orientation. In the superconducting Hamiltonian it is convenient to perform a gauge transformation which removes the phase from the order parameter²⁸. Thus,

$$H_j = \sum_k \Psi_{jk}^{\dagger} (\xi_k \sigma_z + \Delta \sigma_x) \Psi_{jk}, \Psi_{jk} = \begin{pmatrix} \psi_{jk, \uparrow} \\ \psi_{j(-k), \downarrow}^{\dagger} \end{pmatrix} \quad (3)$$

and finally the tunneling part can be written in the standard form with a hopping parameter t_j determining the transfer properties of the junction. The effect of the gauge transformation on the tunnel Hamiltonian is the appearance of a phase dependence in the hopping parameter

$$H_T = \sum_{jk} \Psi_{jk}^{\dagger} T_j d + h.c., d = \begin{pmatrix} d_{\uparrow} \\ d_{\downarrow}^{\dagger} \end{pmatrix} \quad (4)$$

with $T_L = t_L \sigma_z e^{i\sigma_z \phi/4}$, $T_R = t_R \sigma_z e^{-i\sigma_z \phi/4}$, where ϕ is the phase difference between the superconducting leads, and t_j is the tunneling amplitude between the j th lead and dot.

To calculate the partition function we use the path integral approach. In this method the partition function is given by:

$$Z = \int \prod_{jk} (\mathcal{D}\bar{\Psi}_{jk} \mathcal{D}\Psi_{jk} \mathcal{D}\bar{d} \mathcal{D}d) e^{-S} \quad (5)$$

Z is written as a functional integral over grassmann fields for the electronic degrees of freedom ($\Psi, \bar{\Psi}$). The Euclidean action reads:

$$S = S_D + \int_0^{\beta} d\tau [\sum_{jk} \bar{\Psi}_{jk}(\tau) (\partial_{\tau} + \xi_k \sigma_z + \Delta \sigma_x) \Psi_{jk}(\tau) + H_T(\tau)]$$

β is the inverse temperature, and $H_T(\tau) = \sum_{jk} \bar{\Psi}_{jk}(\tau) T_j d(\tau) + h.c.$ while $S_D = \int_0^{\beta} d\tau [\bar{d}(\partial_{\tau} + \epsilon \sigma_z + JS)d]$. After integrating out the leads we get

$$Z = \int \mathcal{D}\bar{d} \mathcal{D}d e^{-S_{eff}} \quad \text{with} \quad S_{eff} = S_D - \int_0^{\beta} d\tau d\tau' \bar{d}(\tau) \check{\Sigma}(\tau - \tau') d(\tau') \quad (6)$$

where $\check{\Sigma}(\tau) = \sum_{j=L,R} T_j^{\dagger} G(\tau) T_j$ and $G(\tau) = \sum_k (\partial_{\tau} + \xi_k \sigma_z + \Delta \sigma_x)^{-1} \delta(\tau)$.

We perform a Fourier transform on the Matsubara frequencies (with $w_n = (2n+1)\pi/\beta$): $\delta(\tau) = \frac{1}{\beta} \sum_{w_n} e^{-iw_n \tau}$ and $G(\tau) = \frac{1}{\beta} \sum_{w_n} e^{-iw_n \tau} G_{w_n}$, which gives for the Green function G :

$$G_{w_n} = \int d\xi \nu(\xi) (-iw_n + \xi_k \sigma_z + \Delta \sigma_x)^{-1} \simeq \frac{\pi \nu(0)}{\sqrt{w_n^2 + \Delta^2}} (iw_n + \Delta \sigma_x) \quad (7)$$

In the above equation, $\nu(\xi) = \sum_k \delta(\xi - \xi_k)$ is approximated as a constant $\nu(0)$, the density of states at the Fermi level in the normal leads. This gives for the self-energy:

$$\check{\Sigma}_{w_n} = \frac{\Gamma/2}{\sqrt{\Delta^2 - (iw)^2}} [iw_n - \Delta \cos(\phi/2) \sigma_x - \gamma \Delta \sin(\phi/2) \sigma_y] \quad (8)$$

with $\gamma = \frac{\Gamma_L - \Gamma_R}{\Gamma_L + \Gamma_R}$, $\Gamma = \Gamma_L + \Gamma_R$, $\Gamma_{L/R} = 2\pi\nu(0)t_{L/R}^2$. We get finally for the effective action (introducing $d(\tau) = \frac{1}{\beta} \sum_{w_n} e^{-iw_n\tau} d_{w_n}$)

$$S_{eff} = \sum_{w_n} \bar{d}_{w_n} \mathcal{M}_{w_n} d_{w_n} \quad \text{with} \quad \mathcal{M}_{w_n} = -iw_n + \epsilon\sigma_z + JS - \tilde{\Sigma}_{w_n} \quad (9)$$

B. Andreev Levels

The dispersion equation for the Andreev levels is given by the eigenvalues of the effective action in Eq. (9) (with $iw = z$)

$$\det \left[z - \epsilon\sigma_z - JS + \frac{\Gamma/2}{\sqrt{\Delta^2 - z^2}} (z - \Delta \cos(\phi/2)\sigma_x - \gamma\Delta \sin(\phi/2)\sigma_y) \right] = 0 \quad (10)$$

which gives:

$$(z + \frac{\Gamma z}{2\sqrt{\Delta^2 - z^2}} - \epsilon - s)(z + \frac{\Gamma z}{2\sqrt{\Delta^2 - z^2}} + \epsilon - s) - \frac{\Gamma^2 \Delta^2 (\cos^2(\phi/2) + \gamma^2 \sin^2(\phi/2))}{4(\Delta^2 - z^2)} = 0 \quad (11)$$

While this cannot be solved analytically in general, there are two limiting regimes where the left hand side simplifies to a second order polynomial in z , giving an analytical expression for the two Andreev levels:

case 1: $\Gamma \gg \Delta, z, s$:

$$z = E_{1,2} = \pm \Delta \sqrt{1 - D_s \sin^2(\phi/2)} \quad , \quad D_s = \frac{1 - \gamma^2}{1 + \frac{4}{\Gamma^2}(\epsilon^2 - s^2)} \quad (12)$$

with $s = JS$. Note the above result needs $|z| \gg s/\Gamma$ to be valid.

case 2: $\Gamma, \epsilon, s \ll \Delta$:

$$z = E_{1,2} = s \pm \sqrt{\epsilon^2 + (\frac{\Gamma}{2})^2 [\cos^2(\phi/2) + \gamma^2 \sin^2(\phi/2)]} \quad (13)$$

In the general case, for arbitrary $\Gamma, \epsilon, s(=JS)$ and Δ , we calculate numerically the roots, by transforming the l.h.s. of Eq. (11) into a 8th order polynomial in z to get rid of the square roots, and then calculating the roots of this polynomial. We find that only two of these roots correspond to roots of Eq. (11) (see also ref. [10]), and that these two roots are real and belongs to $[-\Delta, \Delta]$. There are thus always two Andreev bound states, as in the zero spin case: the effect of the spin term is merely to move these two states, but it does not introduce new bound states.

In Fig. 2, we plot the two Andreev bound state positions as a function of the phase difference for four values of spin, $s = 0, 1, 2$, and 4, for large transparency of the contacts ($\Gamma = 4.0$) and very low temperature ($\beta = 1000$). $\Delta = 1$ is taken as the unit of energy in our system, as in the rest of this work. The right panel in Fig. 2 corresponds to positive coupling $J > 0$ while left panel is for negative coupling $J < 0$. We see that when the absolute value of the coupling is increased, the two Andreev levels are pushed towards $+\Delta$ or $-\Delta$ (depending on the sign of J).

C. Josephson Current

The Josephson current as defined earlier is related to the free energy which in turn is given in terms of the partition function. The partition function after integrating out the $\{d, \bar{d}\}$ variables is given by-

$$Z = \int \mathcal{D}\bar{d} \mathcal{D}d e^{-S_{eff}} = \prod_{w_n} \det \mathcal{M}_{w_n} \quad (14)$$

where \mathcal{M}_{w_n} is given in Eq. (9). The Josephson current then reduces to:

$$\begin{aligned} I_J &= -\frac{2}{\beta} \frac{\partial}{\partial \phi} \ln Z = -\frac{2}{\beta} \frac{\partial}{\partial \phi} \sum_{w_n} \ln(\det \mathcal{M}_{w_n}) \\ &= -\frac{1}{\beta} \sum_{w_n} \frac{\Gamma^2 \Delta^2 (1 - \gamma^2) \sin(\phi)}{4[\det \mathcal{M}_{w_n}](\Delta^2 - (iw_n)^2)} = -\frac{1}{\beta} \sum_{w_n=-\infty}^{\infty} f(iw_n) \end{aligned} \quad (15)$$

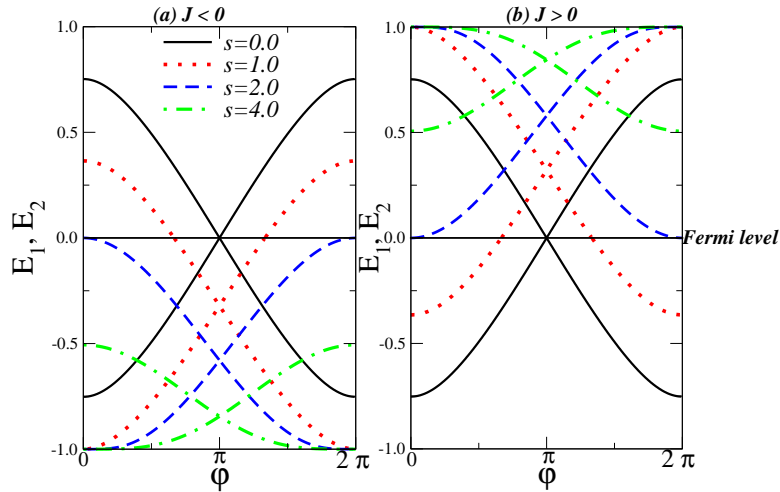


FIG. 2: The two Andreev bound states as function of phase difference. For positive coupling ($J > 0$) in the right panel and for negative coupling ($J < 0$) in the left panel. The labelling of the curves is as follows: spin $s=0$ (black,solid line), 1.0 (red,dotted line), 2.0 (blue,dashed line) and 4.0 (green, dot-dashed line). The other parameters are $\Gamma = 4.0$, $\gamma = 0.0$, $\beta = 1000$, $\epsilon = 0.0$, and $\Delta = 1.0$.

Further, the Free energy is given by:

$$F = -\frac{1}{\beta} \sum_{w_n} \ln(\det \mathcal{M}_{w_n}). \quad (16)$$

In the above equations, $\det \mathcal{M}_{w_n}$ is the same as the determinant of Eq. (11), with iw_n replacing z .

From the above equation, one can calculate the total Josephson current by summing over the Matsubara frequencies. However, we can transform the above equation in order to separate explicitly the contributions of the Andreev bound states and of the continuum, which are physically meaningful. In order to calculate these contributions, we take advantage of the fact that the Matsubara frequencies are the poles of the Fermi function $n_f(z)$ [29]. We then consider the integral $I = \int_C \frac{dz}{2\pi i} f(z)n_f(z)$, where the function $f(z)$ is defined in Eq. (15). The function $f(z)$ as seen earlier has two poles on the real axis between $-\Delta$ and Δ (these are simply the two Andreev bound states, for which $\det \mathcal{M} = 0$). Further, because of the square roots terms in the $\det \mathcal{M}$, it has branch points at $z = \pm\Delta$; we have chosen to place branch cuts on the real axis, for $z \in [\Delta, \infty]$ and $z \in [-\infty, -\Delta]$. We thus chose the contour C as two large semi-circles plus parts going around the branch cuts. We illustrate the contour, poles and branch cuts in Fig. 3. Thus integral I can be broken into the sum of the contributions from the large circle D of radius R , the two small circles at $\pm\Delta$, denoted by $d_{1,2}$ of radius ϵ , and the contribution from the branch cuts. Therefore,

$$\begin{aligned} I = \frac{1}{2\pi i} \int_C f(z)n_f(z)dz &= \frac{1}{2\pi i} \int_D dz f(z)n_f(z) + \frac{1}{2\pi i} \int_{d_1} dz f(z)n_f(z) + \frac{1}{2\pi i} \int_{d_2} dz f(z)n_f(z) \\ &+ \frac{1}{2\pi i} \lim_{\epsilon \rightarrow 0} \left[\int_{\Delta}^{\infty} dz f(z+i\epsilon)n_f(z+i\epsilon) - \int_{\Delta}^{\infty} dz f(z-i\epsilon)n_f(z-i\epsilon) \right] \\ &+ \frac{1}{2\pi i} \lim_{\epsilon \rightarrow 0} \left[\int_{-\infty}^{-\Delta} dz f(z+i\epsilon)n_f(z+i\epsilon) - \int_{-\infty}^{-\Delta} dz f(z-i\epsilon)n_f(z-i\epsilon) \right] \end{aligned} \quad (17)$$

The integrals over D and $d_{1,2}$ tend to zero as $R \rightarrow \infty$ and $\epsilon \rightarrow 0$. The last two terms in the above equation define the contribution from the continuum to the current, which we denote as I_c . From Cauchy's residue theorem the integral I can also be evaluated as follows:

(a) Function $n_f(z) = \frac{1}{e^{\beta z} + 1}$ has poles at $z = iw_n$, with residue $-1/\beta$. The contributions from these poles is thus: $-\frac{1}{\beta} \sum_{w_n} f(iw_n)$, which is precisely I_J (Eq. (15)).

(b) $f(z)$ has 2 poles of its own, written E_1 and E_2 . These gives the Andreev bound states contribution, which we denote by I_b .

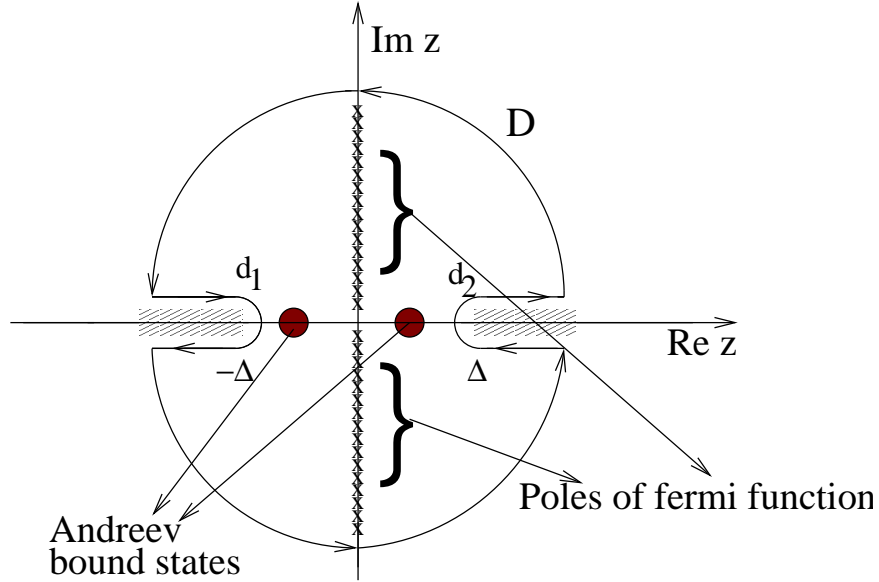


FIG. 3: The contour includes poles from the Fermi function, two Andreev bound states and the contribution from the branch cuts.

We have thus

$$\begin{cases} I_J = I_b + I_c \\ I_b = -n_F(E_1)\text{res}(f(E_1)) - n_F(E_2)\text{res}(f(E_2)) \\ I_c = \lim_{\epsilon \rightarrow 0} \frac{1}{\pi} \left[\int_{\Delta}^{\infty} dz + \int_{-\infty}^{-\Delta} dz \right] \Im(f(z+i\epsilon)n_f(z+i\epsilon)) \end{cases} \quad (18)$$

where res denotes the residue of the quantity in square brackets, and \Im stands for the imaginary part. We see from the equation giving I_b that the contribution from each Andreev bound state is simply proportional to the occupation number $n_F(E_i)$ ($i = 1, 2$) of this level. Equation (18) is the central result of this work, which we have used to calculate numerically the I_b and I_c curves shown in the following.

In the limiting cases corresponding to Eqs. (12) and (13), we can get analytical expressions for the Josephson current. As in these limits the $\det \mathcal{M}$ term reduces to a second order polynomial, the function $f(z)$ has no branch point and the continuum contribution current vanishes. Using Eq. (15), we have

$$\begin{aligned} I_J &= -\frac{2}{\beta} \frac{\partial}{\partial \phi} \sum_{w_n} \ln[\det \mathcal{M}_{w_n}] = -\frac{2}{\beta} \frac{\partial}{\partial \phi} \sum_{w_n} \ln[(iw_n - E_1)(iw_n - E_2)] \\ &= \frac{2}{\beta} \sum_{w_n} \left[\frac{1}{iw_n - E_1} \frac{\partial E_1}{\partial \phi} + \frac{1}{iw_n - E_2} \frac{\partial E_2}{\partial \phi} \right] \end{aligned} \quad (19)$$

Using $-\frac{1}{\beta} \sum_{w_n} \frac{1}{iw_n - E_i} = n_f(E_i)$ ($i = 1, 2$), this reduces to

$$I_J = I_b = I_{b1} + I_{b2} = -2[n_f(E_1) \frac{\partial E_1}{\partial \phi} + n_f(E_2) \frac{\partial E_2}{\partial \phi}] \quad (20)$$

We see that, in these limiting cases, the contribution of a given Andreev bound state E_i is simply the product of the occupation number $n_F(E_i)$ times the dispersion of this level as a function of the phase difference. The explicit analytic expression for the two limiting cases are:

case 1: $\Gamma \gg \Delta, iw, s$ (see Eq. (12) for E_1 and D_s)

$$I_J = -\frac{1}{2} \tanh\left(\frac{\beta E_1}{2}\right) \frac{\Delta D_s}{\sqrt{1 - D_s \sin^2(\phi/2)}} \sin(\phi) \quad (21)$$

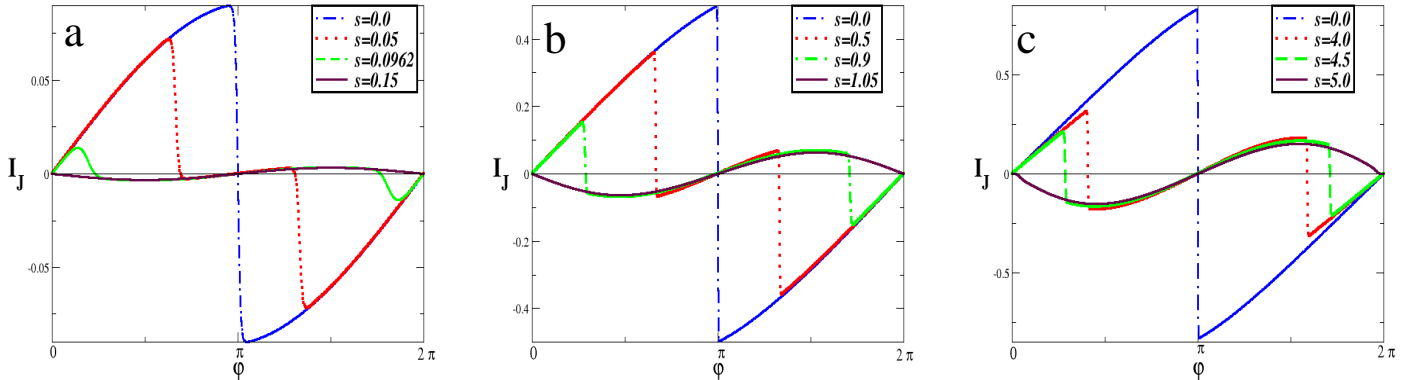


FIG. 4: The total Josephson current (I_J) as function of the phase difference for increasing spin. The π junction behavior is clearly seen. (a) $\Gamma = 0.2$. (b) $\Gamma = 2$. (c) $\Gamma = 10$. The other parameters are: $\Delta = 1.0$, $\beta = 1000$, $\gamma = 0$, and $\epsilon = 0$.

case 2: $\Gamma, \epsilon, s \ll \Delta$ (see Eq. (13) for $E_{1,2}$), we have

$$I_J = \frac{[n_f(E_1) - n_f(E_2)]\Gamma^2(1 - \gamma^2)\sin(\phi)}{8\sqrt{\epsilon^2 + \frac{\Gamma^2}{4}[\cos^2(\phi/2) + \gamma^2\sin^2(\phi/2)]}} \quad (22)$$

IV. RESULTS

In this section, we show the results obtained numerically for the Josephson current using equation (18). We will see that, when the coupling to the spin is strong enough, the junction behaves as a π junction, and that the other parameters of the system allow a control of this π junction. We will also show that the mechanism leading to this π junction behavior can be understood simply in terms of the bound states and continuum contributions to the Josephson current.

A. Total Josephson current and free energy: The π shift

In Fig. 4, we plot the Josephson current (I_J) as a function of the phase ϕ , for different values of the spin coupling $s = JS$. We clearly see a π -junction type behavior as the magnitude of the spin coupling is increased. One clear inference from Fig. 4 is that the strength of the spin coupling required to engineer a π junction behavior increases with the interface transparency Γ . We get another point of view of this π shift in Fig. 5, where we plot the free energy F as a function of the phase ϕ . We see that with increase in spin coupling strength the transition from the 0 to the π phase is clearly marked: the absolute minimum of F shifts from $\phi = 0$ to $\phi = \pi$.

This figure also brings out other features, namely the $0'$ and π' phases. As is evident from Fig. 5, the labelling of the respective junctions as 0, $0'$, π' and π configurations, follows from the respective stability of $\phi = 0$ and $\phi = \pi$ configurations. For a 0(π) junction, only $\phi = 0$ ($\phi = \pi$) is a minimum of $F(\phi)$. For the other two cases, both $\phi = 0, \pi$ are local minima and depending on whether $\phi = 0$ ($\phi = \pi$) is the global minimum, one has a $0'$ (π') junction. Of particular interest is the bistable junction, in which both $\phi = 0$ and $\phi = \pi$ are global minima; note that this bi-stability is a necessary precondition for the realization of a Josephson junction qubit²⁷.

The total Josephson current and the free energy are invariant with respect to the change of sign of the spin ($s \rightarrow -s$). This is to be expected from the rotational symmetry invariance of the system, and can be seen on Eqs. (15)-(16), using $\omega_{-(n+1)} = -\omega_n$.

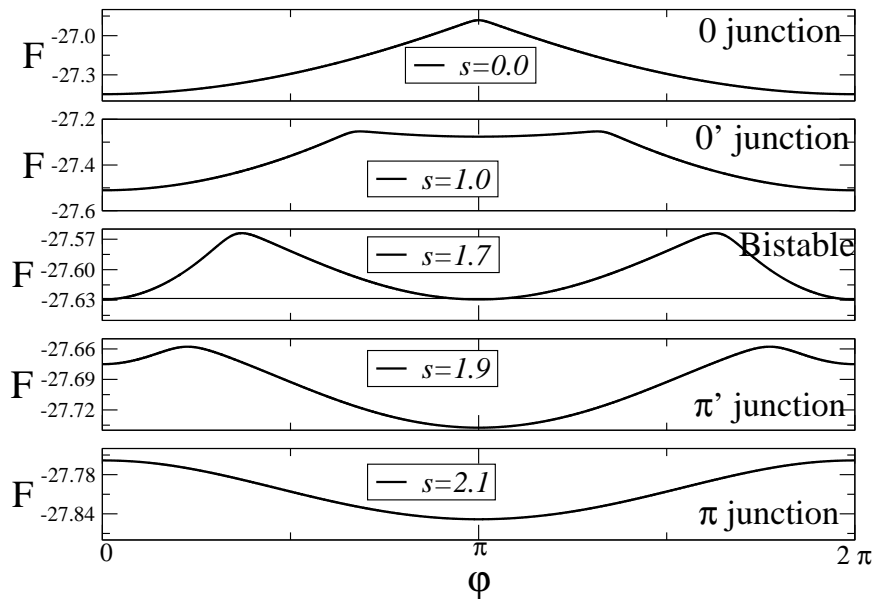


FIG. 5: The Free energy (F) as function of the phase difference (Φ) for increasing spin from top to bottom. The π junction behavior is clearly seen. The other parameters are: $\Delta = 1.0, \Gamma = 4.0, \gamma = 0, \beta = 1000$ and $\epsilon = 0$.

B. Reasons for the π -shift

The ability to distinguish, in the Josephson current, between the contributions from each Andreev bound state and from the continuum (see Eq. (18)) provides us with a simple picture for the mechanism leading to the π shift for large spin coupling. In a few words, the effect of the spin coupling is to reduce or suppress the Andreev bound states contribution, and to give more importance to the continuum contribution, and this leads to the π shift. With more details, the effect of the spin coupling on the bound states current can be understood from Eq. (18) and Fig. 2. For $s = 0$, we see in Fig. 2 that there is always one bound state below the Fermi level, and the other one above. As the contribution of a bound state to the Josephson current is proportional to the occupation number $n_F(E_i)$ of this bound state (Eq. (18)), this means that we have only one bound state contributing to the current, and this contribution appears to be much larger than the continuum contribution. With a large positive spin coupling s , we see on Fig. 2 that both Andreev bound states are above the Fermi level, which means their contribution to the Josephson current vanishes; while for a large negative spin coupling s , we see that both bound states are below the Fermi energy, which means they both contribute to the Josephson current, and this reduces the total bound state contribution as the respective contributions of the two bound states have opposite signs. Note that the total Josephson current is independent of the spin coupling sign, but that for large $s > 0$ there is only the contribution from the continuum, while for large $s < 0$ there is a combinations of the bound states and the continuum contributions. This explanation is illustrated on Fig. 6, where the contributions of the bound states and of the continuum are plotted for different values of s .

We see from this mechanism that the continuum contribution to the Josephson current, which is often ignored when studying Josephson junctions, is in fact essential to understand behavior of our junction. The reason for the π shift in our case has to be contrasted to that seen in Superconductor-Ferromagnet-Superconductor systems. In the latter case the Andreev reflection is modified at Ferromagnet-Superconductor interfaces due to spin imbalance in the ferromagnet. As a result, the current carrying Andreev bound states are split and shifted in an oscillatory way under the influence of the ferromagnet²⁰. Thus in these systems the π shift is exclusively defined by the bound state current. In contrast to this, in our case the the continuum contribution plays a central role.

The origin of the continuum current -which is non-zero even at zero temperature- is due to the phase difference between the two superconductors, which breaks the symmetry between the left and right-moving quasiparticles^{31,32}. One can draw an analogy with persistent currents flowing in normal metal rings at zero temperature. In normal metal rings the flux breaks the symmetry between clockwise and anti-clockwise moving electrons inducing the persistent

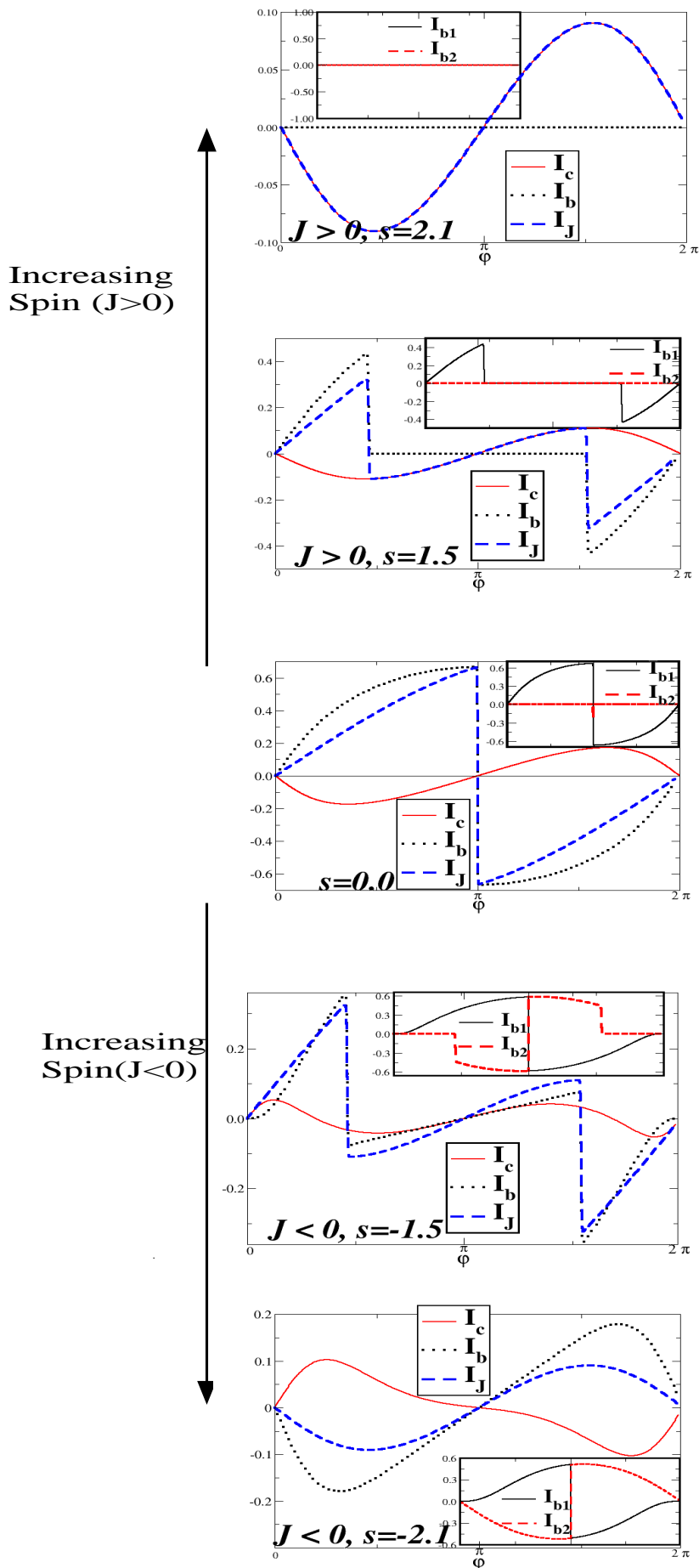


FIG. 6: The Andreev bound state current (I_b), continuum current (I_c) and total Josephson current (I_J) as function of phase difference ϕ . The individual Andreev bound state contributions (I_{b1}, I_{b2}) are plotted in the insets. Central figure is for spin $s = 0.0$. The two figures to the bottom of the central figure depict the case of anti-ferromagnetic coupling $J < 0$, the first is for spin $s = -1.5$ and last one on the bottom is for $s = -2.1$. On the top of the central figure the two figures depict the case of ferromagnetic coupling $J > 0$. The individual figures plotted are for spin $s = 1.5$ and lastly for $s = 2.1$. The other parameters are: $\Delta = 1.0, \Gamma = 4.0, \gamma = 0.0, \beta = 1000$ and $\epsilon = 0$.

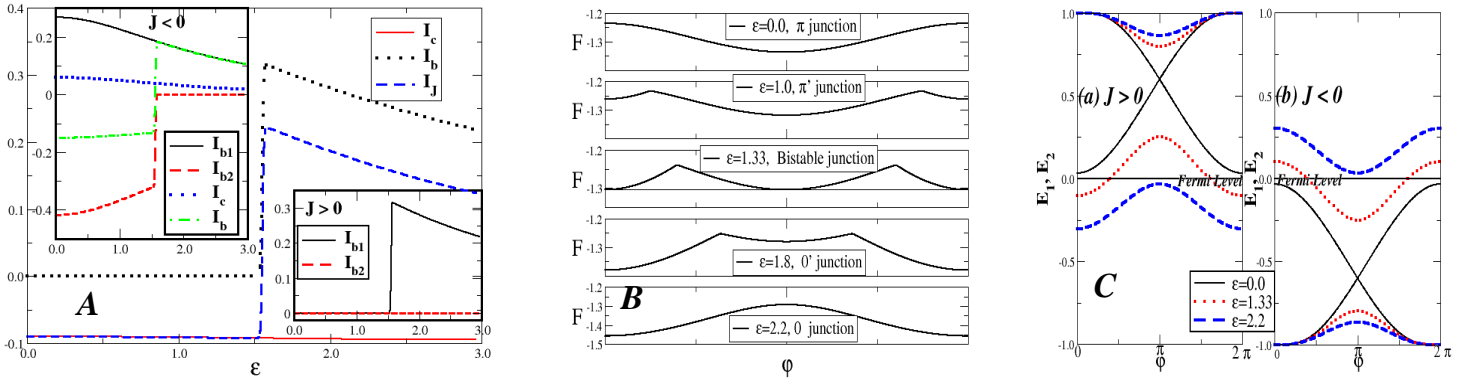


FIG. 7: (A) The Andreev bound state current (I_b , dotted line), the continuum contribution (I_c , solid line) and the total Josephson current (I_J , dashed line) as function of dot level ϵ , for positive coupling. The π junction behavior is clearly seen as dot level is varied, in the insets the individual bound state contributions (I_{b1}, I_{b2}) are plotted for negative ($J < 0$) and positive ($J > 0$) coupling, for negative coupling the continuum and total bound state currents are also plotted. The total Josephson current (I_J) is identical for both $J < 0$ as well as $J > 0$. The other parameters are: $\Delta = 1.0, s = 2.1, \phi = \pi/2, \Gamma = 4.0, \beta = 1000$ and $\gamma = 0$. (B) The Free energy as function of the phase difference (ϕ) for increasing dot energies, and (C) Andreev levels for both negative as well as positive coupling. The other parameters for B and C are: $\Delta = 1.0, s = 2.1, \Gamma = 4.0, \beta = 1000$ and $\gamma = 0$.

current. At zero temperature all states below the Fermi energy are filled, still then the persistent current is non-zero³³.

We also observe that the continuum current generally flows opposite to the bound state current. This observation is in agreement with those of other works^{9,10}.

C. Reversing the Π shift

A remarkable feature of our system is that the π shift behavior can be controlled and reversed using the different parameters of the system. This is important for potential experimental implementations, as some of these parameters can be accessed relatively easily (one can for example move the dot level by using a gate voltage³⁵), while the spin coupling is a fixed quantity which depends in the molecule used. Our results show that, when the spin coupling is large enough to have a π junction, a change in any of the parameter of the system (dot level ϵ , coupling to the leads Γ , asymmetry of this coupling γ , and even the temperature) makes it possible to have the system behave as a standard 0 junction (going through any intermediate situation between π and 0 junction). Schematically, the mechanism for this can be understood along the same lines as the explanation given above for the π shift: starting from a π junction situation, where both Andreev levels are (for example) above the Fermi energy and thus do not contribute to the Josephson current, changing a parameter of the system can move the Andreev level positions, and as soon as one of the Andreev level goes below the Fermi energy, it gives an important bound state contribution which brings the system back to a 0 junction behavior. This is illustrated on Fig. 7, where the dependence of the currents (panel A), of the free energy (panel B) and of the Andreev levels (panel C) as a function of the dot level position ϵ . Similar plots are obtained when looking at the Γ or γ dependence (not shown).

The picture is a bit different when the temperature is changed, as there the Andreev levels do not move, but the Fermi functions become broader as temperature is increased, leading to a partial revival of the bound state current. This is shown on Fig. 8, where the dependence of the currents (panel A) and of the free energy (panel B) is shown as a function of $\beta = 1/(k_B T)$. Starting from low temperature (high β), with a π junction behavior (the total current I_J is < 0 , and the free energy has its minimum at $\phi = \pi$), we see that when the temperature increases (β decreases), the total current becomes positive, and the minimum of the free energy shifts from $\phi = \pi$ to $\phi = 0$.

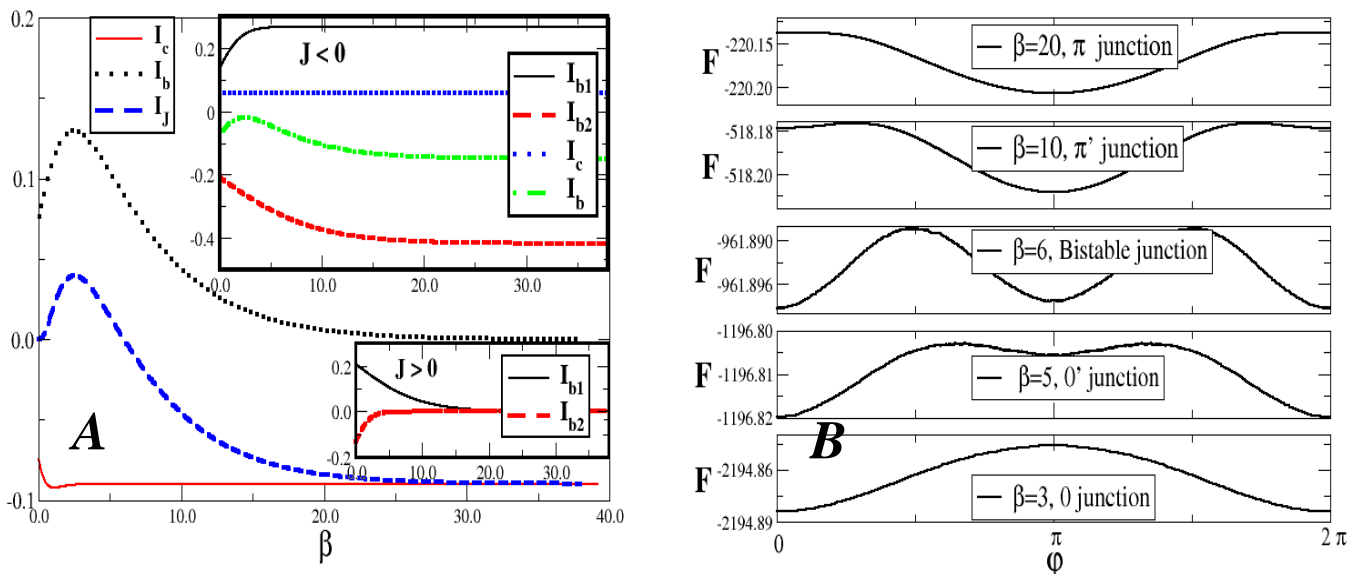


FIG. 8: (A) Andreev bound state current (I_b), the continuum contribution (I_c) and the total Josephson current (I_J) as function of inverse temperature β for positive coupling. The π junction behavior is clearly seen as inverse temperature β is varied. In the insets the individual bound state currents for the case of $J > 0$ and $J < 0$ are plotted. For $J < 0$, the continuum along with the total bound state current is also plotted. The total Josephson current I_J is identical for both $J > 0$ and $J < 0$. The other parameters are: $\Delta = 1.0$, $s = 2.1$, $\epsilon = 0.0$, $\gamma = 0.0$, $\phi = \pi/2$ and $\Gamma = 4.0$. (B) The Free energy as function of the phase difference at different temperatures. The junction is bistable at the crossover between $0 - \pi$ junction behaviors. The other parameters are: $\Delta = 1.0$, $s = 2.1$, $\epsilon = 0.0$, $\gamma = 0.0$, and $\Gamma = 4.0$.

V. DISCUSSION

We have studied in the previous sections the behavior of the Josephson current as a function of the spin coupling strength, and found that a π junction behavior appears when this coupling is large enough. In view of an experimental realization, one must ask if the actual value of the spin coupling obtained with a given molecular magnet is large enough to observe this π junction behavior. While a precise estimate, for a real molecule, of the magnetic coupling energy between the electronic spin and the molecular spin is beyond the scope of this paper, we can get a gross estimate by calculating the interaction energy of two magnetic dipoles at a distance typical of the molecular distance involved in our problem. Taking a spin $S = 10$ for the molecule (as in Mn12ac), and a distance $\sim 5 \text{ \AA}$, we find a interaction energy $\sim 0.1 meV$, which is of the same order as the superconducting gap. This estimate shows that the π junction regime due to spin coupling may be reached experimentally.

Let us now discuss some potential applications of our results. First, as we have explained before, when the system behaves as a π junction due to large spin coupling, the role of the continuum contribution to the current is essential, and it can even be the only contribution to the current (case of positive spin coupling s). This means that, in this case, our system allows to measure directly the contribution of the continuum to the Josephson current³⁶. Secondly, the system could be used as a Josephson current switch. Looking at the panel A of Fig. 7, we see that there is an abrupt change of the current sign as ϵ goes through a specific value depending on the other parameters (it is $\epsilon \simeq 1.5$ on the figure), while the current does not change much elsewhere. As ϵ should be experimentally accessible using a gate voltage, a Josephson current switch could be implemented. Moreover, this implementation should be easier than in systems where the Josephson current changes sign several times as a parameter is varied.

Finally, a more ambitious application would be to engineer a qubit with the system we describe in this work. Indeed, we have shown that, when varying some parameters, it is possible that the system behaves as a bistable junction (see for example panel B of Fig. 7), where the system has a degenerate ground state. This feature can be effectively exploited to fashion a qubit system³⁷, where the junction itself can be in a superposition²⁷ of the two ground states

at either a phase difference of 0 or π . In contrast to the superconducting persistent current qubit³⁸, it is here the two phase states of the Josephson junction which provide the two states of the qubit. These qubits are therefore called superconducting phase qubits as in Ref.[27]. Similar to that in Ref.[39], the coherent Rabi oscillations in our system could in principle be observed by a measurement of the phase sensitive sub-gap Andreev conductance across a high resistance tunnel contact between the qubit and a dirty metal wire.

VI. CONCLUSION

To conclude, we have studied in this work the properties of the Josephson current between two superconductors through a single molecular magnet, which we modeled as a quantum dot plus a large frozen spin. We have shown that the coupling between the electronic spin on the dot and the molecular spin lead the system to behave as a π junction. We have given an explanation of the mechanism leading to this π junction behavior, showing that the spin coupling tends to reduce strongly the Andreev bound states contribution to the current, and that the continuum current plays an essential role in this π shift. To our knowledge, this mechanism leading to the π shift is new.

We have shown moreover that the other parameters of the system give a precise control of this π junction, allowing for example to reverse the π shift and to bring the system to the normal 0 junction state, or to an intermediate bistable state. This control of the π shift can lead to useful applications, like a Josephson current switch, or could even be used to engineer a phase qubit.

Possible topics of future study in such systems may include incorporating the dynamical nature of molecular spin⁴⁰ and quantum tunneling of the magnetization¹, when the anisotropy barrier is not much larger than all the other energies of the problem, and inclusion of electron-electron and electron-phonon interactions.

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