Critical Josephson current through a bistable single-molecule junction

Andreas Schulz, Alex Zazunov, and Reinhold Egger
Institut für Theoretische Physik, Heinrich-Heine-Universität, D-40225 Düsseldorf, Germany
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We compute the critical Josephson current through a single-molecule junction. As a model for a molecule with a bistable conformational degree of freedom, we study an interacting single-level quantum dot coupled to a two-level system and weakly connected to two superconducting electrodes. We perform a lowest-order perturbative calculation of the critical current and show that it can significantly change due to the two-level system. In particular, the π-junction behavior, generally present for strong interactions, can be completely suppressed.

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I. INTRODUCTION

The swift progress in molecular electronics achieved during the past decade has mostly been centered around a detailed understanding of charge transport through single-molecule junctions,[1,2] where quantum effects generally turn out to be important. When two *superconducting* (instead of normal) electrodes with the same chemical potential but a phase difference φ are attached to the molecule, the Josephson effect[3] implies that an equilibrium current $I(\varphi)$ flows through the molecular junction. Over the past decade, experiments have observed gate-tunable Josephson currents through nanoscale junctions,[4–22] including out-of-equilibrium cases, and many different interesting phenomena have been uncovered. In particular, the current-phase relation has been measured by employing a superconducting quantum interference device.[14,15,19] For weakly coupled electrodes, the current-phase relation is[3]

$$I(\varphi) = I_c \sin(\varphi), \tag{1}$$

with the *critical current* I_c.

The above questions have also been addressed by many theoretical works. It has been shown that the repulsive electron-electron (e-e) interaction $U>0$, acting on electrons occupying the relevant molecular level, can have a major influence on the Josephson current.[23–36] For intermediate-to-strong coupling to the electrodes, an interesting interplay between the Kondo effect and superconductivity takes place.[24,28,30–32,35] In the present paper, we address the opposite limit where, for sufficiently large U, a so-called π-phase can be realized, with $I_c<0$ in Eq. (1). In the π-regime, $\varphi=\pi$ corresponds to the ground state of the system (or to a minimum of the free energy for finite temperature), in contrast to the usual 0-state with $I_c>0$, where $\varphi=0$ in the ground state.[37] The sign change in I_c arises due to the blocking of a direct Cooper pair exchange when U is large. Double occupancy on the molecular level is then forbidden, and the remaining allowed processes generate the sign change in I_c.[23–25,27,29,34] The most natural way to explain the π-junction behavior is by perturbation theory in the tunnel couplings connecting the molecule to the electrodes. Experimental observations of the π-phase were recently reported for InAs nanowire dots[14] and for nanotubes,[15,38] but a π-junction is also encountered in superconductor-ferromagnet-superconductor structures.[39,40] Accordingly, theoretical works have also analyzed spin effects in molecular magnets coupled to superconductors.[41–43]

The impressive experimental control over supercurrents through molecular junctions reviewed above implies that modifications of the supercurrent due to vibrational modes of the molecule play a significant and observable role.[34,44–46] We have recently discussed how a *two-level system* (TLS) coupled to the dot's charge is affected by the Josephson current carried by Andreev states.[47] For instance, two conformational configurations of a molecule may realize such a TLS degree of freedom. Experimental results for molecular break junctions with normal leads were interpreted using such models,[48–53] but the TLS can also be created artificially using a Coulomb-blockaded double dot.[47] A detailed motivation for our model, where the Pauli matrix σ_z in TLS space couples to the dot's charge, and its experimental relevance has been given in Refs. 47 and 53. While our previous work[47] studied the Josephson-current-induced switching of the TLS, we here address a completely different parameter regime characterized by weak coupling to the electrodes, and focus on the Josephson current itself. We calculate the critical current I_c in Eq. (1) using perturbation theory in these couplings, allowing for arbitrary e-e interaction strength and TLS parameters. A similar calculation has been reported recently,[34] but for a harmonic oscillator (phonon mode) instead of the TLS. Our predictions can be tested experimentally in molecular break junctions using a superconducting version of existing[48–50] setups.

The remainder of this paper has the following structure. In Sec. II, we discuss the model and present the general perturbative result for the critical current. For tunnel matrix element $W_0=0$ between the two TLS states, the result allows for an elementary interpretation, which we provide in Sec. III. The case $W_0\neq 0$ is then discussed in Sec. IV, followed by some conclusions in Sec. V. Technical details related to Sec. III can be found in the Appendix. We mostly use units where $e=\hbar=k_B=1$.

II. MODEL AND PERTURBATION THEORY

We study a spin-degenerate molecular dot level with single-particle energy ϵ_d and on-site Coulomb repulsion $U>0$, coupled to the TLS and to two standard s-wave BCS superconducting banks (leads). The TLS is characterized by the (bare) energy difference E_0 of the two states, and by the tunnel matrix element W_0. The model Hamiltonian studied in this paper is motivated by Refs. 48 and 53 where it was employed to successfully describe break junction experiments (with normal-state leads). It reads

$$H = H_0 + H_{\text{tun}} + H_{\text{leads}}, \tag{2}$$

where the coupled dot-plus-TLS part is

$$H_0 = -\frac{E_0}{2}\sigma_z - \frac{W_0}{2}\sigma_x + \left(\epsilon_d + \frac{\lambda}{2}\sigma_z\right)(n_\uparrow + n_\downarrow) + U n_\uparrow n_\downarrow \tag{3}$$

with the occupation number $n_s = d_s^\dagger d_s$ for dot fermion d_s with spin $s = \uparrow, \downarrow$. Note that the TLS couples with strength λ to the dot's charge. Indeed, assuming some reaction coordinate X describing molecular conformations, the dipole coupling to the dot is $\propto X(n_\uparrow + n_\downarrow)$, just as for electron-phonon couplings.[44,45,48,49] If the potential energy $V(X)$ is bistable, the low-energy dynamics of X can be restricted to the lowest quantum state in each well and leads to Eq. (3). The TLS parameters and the dipole coupling energy λ can be defined in complete analogy to Refs. 48 and 53, and typical values for λ in the meV range are expected, comparable to typical charging energies U. Moreover, the electron operators $c_{\boldsymbol{k}\alpha s}$, corresponding to spin-$s$ and momentum-$\boldsymbol{k}$ states in lead $\alpha = L/R$, are governed by a standard BCS Hamiltonian with complex order parameter $\Delta_{L/R} e^{\pm i\varphi/2}$ (with $\Delta_{L/R} > 0$), respectively,

$$H_{\text{leads}} = \sum_{\boldsymbol{k}\alpha s} \epsilon_{\boldsymbol{k}\alpha} c_{\boldsymbol{k}\alpha s}^\dagger c_{\boldsymbol{k}\alpha s} - \sum_{\boldsymbol{k}\alpha} (e^{i\alpha\varphi/2} \Delta_\alpha c_{\boldsymbol{k}\alpha\uparrow}^\dagger c_{-\boldsymbol{k},\alpha\downarrow}^\dagger + \text{H.c.}), \tag{4}$$

where $\epsilon_{\boldsymbol{k}\alpha}$ is the (normal-state) dispersion relation. Finally, the tunneling Hamiltonian is

$$H_{\text{tun}} = \sum_{\alpha s} (H_{T\alpha s}^{(-)} + H_{T\alpha s}^{(+)}), \quad H_{T\alpha s}^{(-)} = \sum_{\boldsymbol{k}} t_{\boldsymbol{k}\alpha} c_{\boldsymbol{k}\alpha s}^\dagger d_s, \tag{5}$$

where $H_{T\alpha s}^{(-)}$ describes tunneling of an electron with spin s from the dot to lead α with tunnel amplitude $t_{\boldsymbol{k}\alpha}$, and the reverse process is generated by $H_{T\alpha s}^{(+)} = H_{T\alpha s}^{(-)\dagger}$.

The Josephson current $I(\varphi)$ at temperature $T = \beta^{-1}$ follows from the equilibrium (imaginary-time) average,

$$I = 2\,\text{Im}\left\langle \mathcal{T} e^{-\int_0^\beta d\tau H_{\text{tun}}(\tau)} H_{T\alpha s}^{(-)} \right\rangle, \tag{6}$$

where $\alpha = L/R$ and $s = \uparrow, \downarrow$ can be chosen arbitrarily by virtue of current conservation and spin-$SU(2)$ invariance, and $\mathcal{T}$ is the time-ordering operator. Equation (6) is then evaluated by lowest-order perturbation theory in H_{tun}. The leading contribution is of fourth order in the tunnel matrix elements and can be evaluated in a similar manner as in Ref. 34. We assume the usual wide-band approximation for the leads with $\boldsymbol{k}$-independent tunnel matrix elements, and consider temperatures well below both BCS gaps, $T \ll \Delta_{L,R}$. Putting $\alpha = L$ and $s = \uparrow$, after some algebra, the Josephson current takes form (1) with the critical current,

$$I_c = \frac{2}{\pi^2} \int_{|\Delta_L|}^\infty \frac{\Gamma_L \Delta_L dE}{\sqrt{E^2 - \Delta_L^2}} \int_{|\Delta_R|}^\infty \frac{\Gamma_R \Delta_R dE'}{\sqrt{E'^2 - \Delta_R^2}} C(E, E'). \tag{7}$$

We define the hybridizations $\Gamma_\alpha = \pi \rho_F |t_\alpha|^2$, with (normal-state) density of states ρ_F in the leads. The function C in Eq. (7) can be decomposed according to

$$C(E, E') = \sum_{N=0}^{2} C_N(E, E'), \tag{8}$$

with contributions C_N for fixed dot occupation number $N = n_\uparrow + n_\downarrow = \{0, 1, 2\}$. For given N, the two eigenenergies (labeled by $\sigma = \pm$) of the dot-plus-TLS Hamiltonian H_0 in Eq. (3) are

$$E_N^{\sigma=\pm} = N\epsilon_d + U\delta_{N,2} + \frac{\sigma}{2}\Phi_N, \tag{9}$$

with the scale

$$\Phi_N = \sqrt{(E_0 - N\lambda)^2 + W_0^2}. \tag{10}$$

The occupation probability for the state (N, σ) is

$$p_N^\sigma = \frac{1}{Z} e^{-\beta E_N^\sigma} (1 + \delta_{N,1}), \tag{11}$$

where Z ensures normalization, $\sum_{N\sigma} p_N^\sigma = 1$. With the propagator

$$G_\xi(E) = \frac{1}{E - \xi}, \tag{12}$$

we then find the contributions C_N in Eq. (8),

$$C_0(E, E') = \sum_{\sigma_1 \cdots \sigma_4} [p_0^{\sigma_2} T_{1010}^{\sigma_1\sigma_2\sigma_3\sigma_4} G_{E_0^{\sigma_2} - E_1^{\sigma_3}}(E) G_{E_0^{\sigma_2} - E_1^{\sigma_1}}(E') G_{E_0^{\sigma_2} - E_0^{\sigma_4}}(E + E') + 2p_0^{\sigma_4} T_{1210}^{\sigma_1\sigma_2\sigma_3\sigma_4} G_{E_0^{\sigma_4} - E_1^{\sigma_1}}(E) G_{E_0^{\sigma_4} - E_1^{\sigma_3}}(E') G_{E_0^{\sigma_4} - E_2^{\sigma_2}}(0)], \tag{13}$$

$$C_1(E, E') = -\sum_{\sigma_1 \cdots \sigma_4} \Bigg[T_{1210}^{\sigma_1\sigma_2\sigma_3\sigma_4} (p_1^{\sigma_1} G_{E_1^{\sigma_1} - E_0^{\sigma_4}}(E) G_{E_1^{\sigma_1} - E_2^{\sigma_2}}(E) G_{E_1^{\sigma_1} - E_1^{\sigma_3}}(E + E') + p_1^{\sigma_3} G_{E_1^{\sigma_3} - E_0^{\sigma_4}}(E') G_{E_1^{\sigma_3} - E_2^{\sigma_2}}(E') G_{E_1^{\sigma_3} - E_1^{\sigma_1}}(E + E'))$$
$$+ \frac{p_1^{\sigma_1}}{2} T_{1010}^{\sigma_1\sigma_2\sigma_3\sigma_4} G_{E_1^{\sigma_1} - E_0^{\sigma_4}}(E) G_{E_1^{\sigma_1} - E_0^{\sigma_2}}(E') G_{E_1^{\sigma_1} - E_1^{\sigma_3}}(E + E') + \frac{p_1^{\sigma_2}}{2} T_{2121}^{\sigma_1\sigma_2\sigma_3\sigma_4} G_{E_1^{\sigma_2} - E_2^{\sigma_3}}(E) G_{E_1^{\sigma_2} - E_2^{\sigma_1}}(E') G_{E_1^{\sigma_2} - E_1^{\sigma_4}}(E + E') \Bigg], \tag{14}$$

$$C_2(E,E') = \sum_{\sigma_1\cdots\sigma_4} [p_2^{\sigma_1} T_{2121}^{\sigma_1\sigma_2\sigma_3\sigma_4} G_{E_2^{\sigma_1}-E_1^{\sigma_4}}(E) G_{E_2^{\sigma_1}-E_1^{\sigma_2}}(E') G_{E_2^{\sigma_1}-E_2^{\sigma_3}}(E+E') + 2p_2^{\sigma_2} T_{1210}^{\sigma_1\sigma_2\sigma_3\sigma_4} G_{E_2^{\sigma_2}-E_1^{\sigma_1}}(E) G_{E_2^{\sigma_2}-E_1^{\sigma_3}}(E') G_{E_2^{\sigma_2}-E_0^{\sigma_4}}(0)]. \quad (15)$$

Here, we have used the matrix elements

$$T_{N_1N_2N_3N_4}^{\sigma_1\sigma_2\sigma_3\sigma_4} = \mathrm{Tr}(A_{N_1}^{\sigma_1} A_{N_2}^{\sigma_2} A_{N_3}^{\sigma_3} A_{N_4}^{\sigma_4}), \quad (16)$$

with the 2×2 matrices (in TLS space)

$$A_N^{\pm} = \frac{1}{2}\left(1 \mp \frac{(E_0 - N\lambda)\sigma_z + W_0\sigma_x}{\Phi_N}\right).$$

For $T=0$, it can be shown that C_0 and C_2 are always positive, while C_1 yields a negative contribution to the critical current. When C_1 outweighs the two other terms, we arrive at the π-phase with $I_c<0$.

Below, we consider identical superconductors, $\Delta_L=\Delta_R=\Delta$, and assume $\lambda>0$. It is useful to define the reference current scale,

$$I_0 = \frac{\Gamma_L\Gamma_R}{\Delta^2}\frac{2e\Delta}{\pi^2\hbar}. \quad (17)$$

Within lowest-order perturbation theory, the hybridizations Γ_L and Γ_R only enter via Eq. (17) and can thus be different. Equation (7) provides a general but rather complicated expression for the critical current, even when considering the symmetric case $\Delta_L=\Delta_R$. In the next section, we will therefore first analyze the limiting case $W_0=0$.

III. NO TLS TUNNELING

When there is no tunneling between the two TLS states, $W_0=0$, the Hilbert space of the system can be decomposed into two orthogonal subspaces $\mathcal{H}_+\oplus\mathcal{H}_-$, with the fixed conformational state $\sigma=\pm$ in each subspace. Equation (9) then simplifies to

$$E_N^{\sigma} = \left(\epsilon_d + \frac{\sigma\lambda}{2}\right)N + U\delta_{N,2} - \frac{\sigma E_0}{2}. \quad (18)$$

One thus arrives at two decoupled copies of the usual interacting dot problem (without TLS), but with a shifted dot level $\epsilon_\sigma=\epsilon_d+\sigma\lambda/2$ and the "zero-point" energy shift $-\sigma E_0/2$. As a result, the critical current I_c in Eq. (7) can be written as a weighted sum of the partial critical currents $I_c(\epsilon_\sigma)$ through an interacting dot level (without TLS) at energy ϵ_σ,

$$I_c = \sum_{\sigma=\pm} p^{\sigma} I_c(\epsilon_\sigma), \quad (19)$$

where $p^{\sigma}=\Sigma_N p_N^{\sigma}$ with Eqs. (11) and (18) denotes the probability for realizing the conformational state σ. The current $I_c(\epsilon)$ has already been calculated in Ref. 34 (in the absence of phonons), and has been reproduced here. In order to keep the paper self-contained, we explicitly specify it in the Appendix.

In order to establish the relevant energy scales determining the phase diagram, we now take the $T=0$ limit. Then the probabilities [Eq. (11)] simplify to $p_N^{\sigma}=\delta_{N\bar{N}}\delta_{\sigma\bar{\sigma}}$, where $E_{\bar{N}}^{\bar{\sigma}}=\min_{(N,\sigma)}(E_N^{\sigma})$ is the ground-state energy of H_0 for $W_0=0$. Depending on the system parameters, the ground state then realizes the dot occupation number $\bar{N}$ and the TLS state $\bar{\sigma}$. The different regions $(\bar{N},\bar{\sigma})$ in the $E_0-\epsilon_d$ plane are shown in the phase diagram in Fig. 1. The corresponding critical current in each of these regions is then simply given by $I_c=I_c(\epsilon_{\bar{\sigma}})$.

By analyzing the dependence of the ground-state energy on the system parameters, one can always (even for $W_0\neq 0$) write the function $C(E,E')$ in Eq. (7) as

$$C(E,E') = \Theta(\xi_- - \epsilon_d)C_2 + \Theta(\epsilon_d - \xi_-)\Theta(\xi_+ - \epsilon_d)C_1 + \Theta(\epsilon_d - \xi_+)C_0, \quad (20)$$

where Θ is the Heaviside function and the energies $\xi_\pm=\xi_\pm(U,\lambda,E_0)$ are the boundaries enclosing the π-phase region with $\bar{N}=1$, i.e., $\xi_+(\xi_-)$ denotes the boundary between the $\bar{N}=0$ and $\bar{N}=1$ (the $\bar{N}=1$ and $\bar{N}=2$) regions, see Fig. 1. Explicit results for $\xi_\pm$ follow from Eq. (18) for $W_0=0$. For E_0

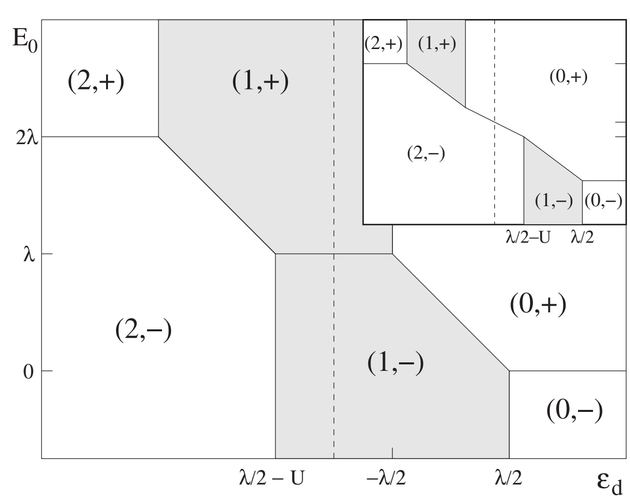

FIG. 1. Ground-state phase diagram in the $E_0-\epsilon_d$ plane for $W_0=0$. Different regions $(\bar{N},\bar{\sigma})$ are labeled according to the ground-state dot occupation number $\bar{N}=0,1,2$ and the conformational state $\bar{\sigma}=\pm$. Dark areas correspond to π-junction behavior. The charge-degeneracy line $\epsilon_d=-U/2$ is indicated as dashed line. Main panel: $\lambda<U$. Inset: $\lambda>U$, where no π-junction behavior is possible for $U<E_0<2\lambda-U$.

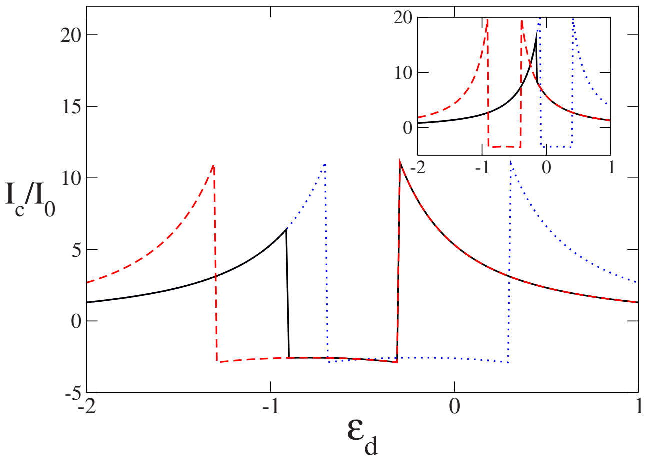

FIG. 2. (Color online) Ground-state critical current I_c as a function of ϵ_d for $W_0=0$. I_c is given in units of I_0, see Eq. (17). In all figures, the energy scale is set by $\Delta=1$. Dashed (red), dotted (blue) and solid (black) curves represent the partial critical currents $I_c(\epsilon_+)$, $I_c(\epsilon_-)$, and the realized critical current I_c, respectively. Main panel: $E_0=0.8, \lambda=0.6, U=1$, such that $\xi_+>\xi_-$. This corresponds to the π-phase region with $\lambda<E_0<2\lambda$ in the main panel of Fig. 1. Inset: $E_0=0.6, \lambda=0.8, U=0.5$, where $\xi_+<\xi_-$ and no π-junction behavior is possible. This corresponds to $U<E_0<2\lambda-U$, see inset of Fig. 1.

$<0 (E_0>2\lambda)$ and arbitrary $\bar{N}$, the ground state is realized when $\bar{\sigma}=-(\bar{\sigma}=+)$, leading to $\xi_+=\lambda/2 (\xi_+=-\lambda/2)$. In both cases, the other boundary energy follows as $\xi_-=\xi_+-U$. In the intermediate cases, with $\xi_0=\frac{1}{2}(\lambda-U-E_0)$, we find for $0<E_0<\lambda$,

$$\xi_+ = \max(\lambda/2 - E_0, \xi_0), \quad \xi_- = \min(\lambda/2 - U, \xi_0), \quad (21)$$

while for $\lambda<E_0<2\lambda$, we obtain

$$\xi_+ = \max(-\lambda/2, \xi_0), \quad \xi_- = \min(\xi_0, \lambda/2 + 2\xi_0). \quad (22)$$

These results for $\xi_\pm$ are summarized in Fig. 1. Remarkably, in the $E_0-\epsilon_d$ plane, the phase diagram is inversion-symmetric with respect to the point $(E_0=\lambda, \epsilon_d=-U/2)$. Furthermore, we observe that for many choices of E_0, one can switch the TLS between the $\bar{\sigma}=\pm$ states by varying ϵ_d, see Fig. 1.

We now notice that Eq. (20) implies the same decomposition for the critical current [Eq. (7)]. We can therefore immediately conclude that the π-junction regime (where $\bar{N}=1$) can exist only when $\xi_+>\xi_-$. This condition is always met away from the window $0<E_0<2\lambda$. However, inside that window, Eqs. (21) and (22) imply that for sufficiently strong dot-TLS coupling, $\lambda>U$, the π-phase may disappear completely. Indeed, for $U<E_0<2\lambda-U$, no π-phase is possible for any value of ϵ_d once λ exceeds U. The resulting ground-state critical current is shown as a function of the dot level ϵ_d for two typical parameter sets in Fig. 2. The inset shows a case where the π-phase has been removed by a strong coupling of the interacting dot to the TLS. The above discussion shows that the π-junction regime is very sensitive to the presence of a strongly coupled TLS.

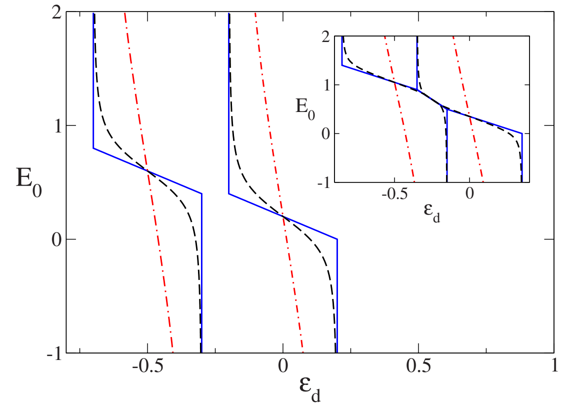

FIG. 3. (Color online) Phase diagram and boundary energies $\xi_\pm$ enclosing the π-phase for finite W_0. Main figure: $\lambda=0.4$ and $U=0.5$, where a π-phase is present; $W_0=0, 0.2$ and 5, for solid (blue), dashed (black), and dash-dotted (red) curves, respectively. Inset: $\lambda=0.7$ and $U=0.5$, where the π-phase vanishes; $W_0=0, 0.3$ and 3, for solid (blue), dashed (black), and dash-dotted (red) curves, respectively.

IV. FINITE TLS TUNNELING

Next we address the case of finite TLS tunneling, $W_0\neq 0$. Due to the σ_x term in H_0, the critical current cannot be written anymore as a weighted sum [see Eq. (19)] and no abrupt switching of the TLS happens when changing the system parameters. Nevertheless, we now show that the size and even the existence of the π-phase region still sensitively depend on the TLS coupling strength (and on the other system parameters). In particular, the π-phase can again be completely suppressed for strong λ.

For finite W_0, the ground-state critical current is obtained from Eq. (20), where the C_N are given by Eqs. (13)–(15) and the π-phase border energies $\xi_\pm$ are replaced by

$$\xi_+ = \frac{1}{2}(\Phi_1 - \Phi_0), \quad \xi_- = \frac{1}{2}(\Phi_2 - \Phi_1 - 2U). \quad (23)$$

The Φ_N are defined in Eq. (10). Compared to the $W_0=0$ case in Fig. 1, the phase diagram boundaries now have a smooth (smeared) shape due to the TLS tunneling. Nevertheless, the critical current changes sign abruptly when the system parameters are tuned across such a boundary. The energies [Eq. (23)] are shown in Fig. 3 for various values of W_0 in the $E_0-\epsilon_d$ plane. In between the ξ_+ and ξ_- curves, the π-phase is realized. From the inset of Fig. 3, we indeed confirm that the π-phase can again be absent within a suitable parameter window. Just as for $W_0=0$, the π-phase vanishes for $\xi_+<\xi_-$, and the transition between left and right 0-phase occurs at $\bar{\xi}=(\xi_++\xi_-)/2$. For $|E_0|\gg\max(\lambda, W_0)$, we effectively recover the phase diagram for $W_0=0$, since the TLS predominantly occupies a fixed conformational state.

The corresponding critical current I_c is shown in Fig. 4 for both a small and a very large TLS tunnel matrix element W_0. In the limit of large $W_0\gg\max(\lambda,|E_0|)$, see lower panel in Fig. 4, the dot and the TLS are effectively decoupled since $\langle\sigma_z\rangle\simeq 0$ and $\langle\sigma_x\rangle\simeq \mathrm{sgn}(W_0)$. While this limit is unrealistic

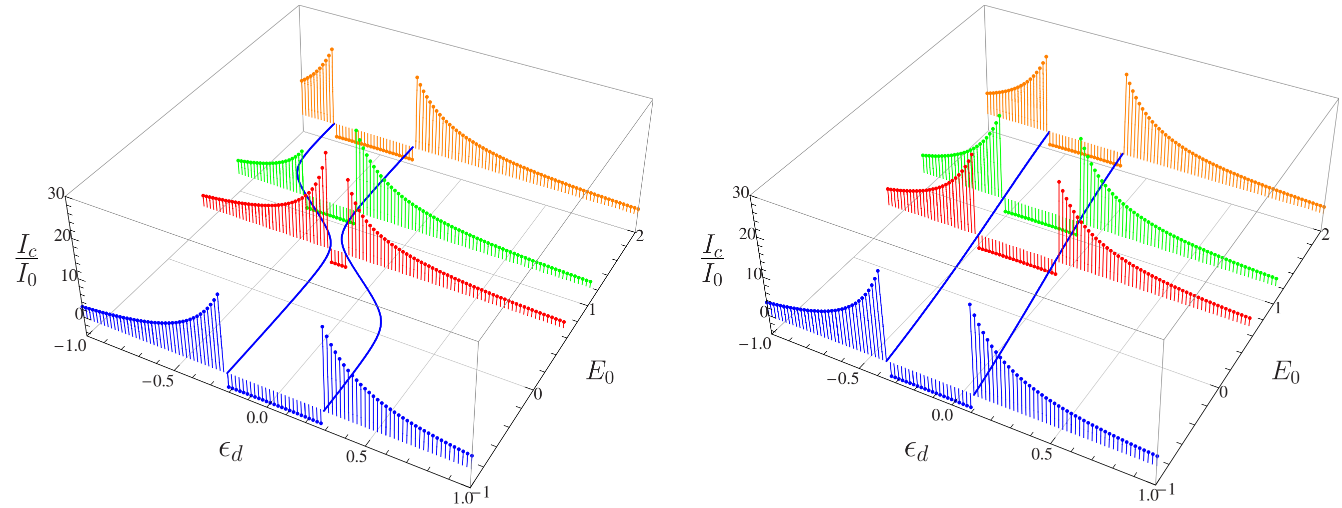

FIG. 4. (Color online) List line plots of the $W_0 \neq 0$ ground-state critical current I_c (in units of I_0) in the $E_0 - \epsilon_d$ plane, with $\lambda = 0.6$ and $U = 0.5$. The boundaries $\xi_\pm$ enclosing the π-phase, see also Fig. 3, are indicated as solid (blue) curves. Top panel: small tunnel amplitude, $W_0 = 0.2$. Bottom panel: large tunnel amplitude, $W_0 = 3$.

for molecular junctions, it may be realized in a side-coupled double-dot system.[47] Finally we note that, unlike for $W_0 = 0$, the perturbative result for the critical current *diverges* at the point where the π-phase vanishes, i.e., for $\epsilon_d = \bar{\xi}$. This divergence is an artifact of perturbation theory and is caused by the appearance of the factor $G_{E_0^- - E_2^-}(0) = (\epsilon_d - \bar{\xi})^{-1}$ in Eqs. (13) and (15).

V. CONCLUSIONS

In this paper, we have presented a perturbative calculation of the critical Josephson current, I_c, through an interacting single-level molecular junction side coupled to a two-level system. Such a TLS is a simple model for a bistable conformational degree of freedom, and has previously been introduced in the literature.[47,48,53] Our perturbative calculation assumes very weak coupling to attached superconducting reservoirs. The ground-state critical current can then be computed exactly for otherwise arbitrary parameters. Our main finding is that the π-phase with $I_c < 0$ is quite sensitive to the presence of the TLS. In particular, for strong coupling λ of the molecular level to the TLS as compared to the Coulomb energy U on the level, the π-phase can disappear altogether.

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APPENDIX: PARTIAL CRITICAL CURRENTS

In this appendix, we provide the partial critical current $I_c(\epsilon_\sigma)$ which appears in the calculation for $W_0 = 0$, see Sec. III. In the absence of TLS tunneling, the matrix elements [Eq. (16)] simplify to

$$T^{\sigma_1\sigma_2\sigma_3\sigma_4}_{N_1N_2N_3N_4} = \prod_{i=1}^{4} \delta_{\tilde{\sigma}_i,1} + \prod_{i=1}^{4} \delta_{\tilde{\sigma}_i,-1},$$

where $\tilde{\sigma}_i = \sigma_i \,\mathrm{sgn}(N_i\lambda - E_0)$. We now rename $\tilde{\sigma} \to \sigma$ to denote the conformational state (eigenstate of σ_z).

The partial current $I_c(\epsilon_\sigma)$ corresponding to fixed conformational state $\sigma = \pm$ is then given by

$$\frac{I_c(\epsilon_\sigma)}{I_0} = \Delta^3 \sum_N \int_\Delta^\infty \frac{dE dE' \, C_N^\sigma(E,E')}{\sqrt{(E^2 - \Delta^2)(E'^2 - \Delta^2)}},$$

where

$$C_N^\sigma(E,E') = \tilde{p}_N^\sigma c_N^\sigma(E,E'),$$

$$\tilde{p}_N^\sigma = \frac{1}{Z_\sigma} e^{-\beta E_N^\sigma}(1 + \delta_{N,1}),$$

with Z_σ such that $\Sigma_N \tilde{p}_N^\sigma = 1$. Moreover, the c_N^σ are given by

$$c_0^\sigma(E,E') = \frac{1}{(E+\epsilon_\sigma)(E'+\epsilon_\sigma)} \left[\frac{1}{E+E'} + \frac{2}{2\epsilon_\sigma + U} \right],$$

$$c_1^\sigma(E,E') = -\frac{1}{E+E'} \left[\frac{1}{(E-\epsilon_\sigma)(E+\epsilon_\sigma+U)} + \frac{1}{(E'-\epsilon_\sigma)(E'+\epsilon_\sigma+U)} + \frac{1/2}{(E-\epsilon_\sigma)(E'-\epsilon_\sigma)} + \frac{1/2}{(E+\epsilon_\sigma+U)(E'+\epsilon_\sigma+U)} \right],$$

$$c_2^\sigma(E,E') = \frac{1}{(E-\epsilon_\sigma-U)(E'-\epsilon_\sigma-U)} \times \left[\frac{1}{E+E'} - \frac{2}{2\epsilon_\sigma + U} \right].$$

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