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# Spin inelastic currents in molecular ring junctions

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Within a simple model we discuss spin inelastic currents in molecular ring junctions. We generalize considerations of the spin-flip inelastic electron tunneling spectroscopy (IETS) to the case of multi-site molecular system, and formulate a conserving approximation, which takes into account renormalization of elastic channel. We also extend recent studies of circular currents in molecular junctions beyond scattering theory formulation. We demonstrate control of the spin-flip IETS signal and discuss spin polarization of total and circular currents in a benzene ring junction.

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## I. INTRODUCTION

Advances in experimental techniques at nanoscale shift focus of research in molecular electronics<sup>1-5</sup> from ballistic transport<sup>6,7,99</sup> to inelastic effects<sup>9,10,12,93</sup> (and closely related energy transfer processes<sup>13-18</sup>), to noise characteristics<sup>19-21</sup> and optical response<sup>22-26</sup> in current carrying junctions. Recent spin-transport experiments<sup>27,28</sup> demonstrated potential possibility of using organic molecules to construct molecular spin devices, indicating the emergence of molecular spintronics<sup>30-35</sup> (see Ref. 29 for a comprehensive review).

The small size of molecules implies potential importance of coherence in molecular junctions. Interference effects in molecular systems were observed experimentally for electron transfer<sup>36</sup> and molecular junction currents<sup>37</sup> involving derivatives of benzene connected in the meta or para positions. Effects of exciton coherence in photosynthesis were demonstrated in Ref. 38. Coherent control in molecular junctions was extensively discussed in the theoretical literature.<sup>39-45</sup> In particular, quantum interference plays a decisive role in conduction through molecular ring structures. Magnetic field control of electron conduction in such systems was considered in Refs. 46,47. Possibility to utilize interference effects in nanosized rings for constructing molecular spin filters was also discussed in the literature.<sup>48-51</sup>

Another closely related issue in spintronics is the control of a local spin. In particular, spin control with electric currents achieved in experiments on single atoms<sup>52</sup> and single-molecule magnets,<sup>53</sup> was studied theoretically in Refs. 54,55. On the other side, characteristics of local spin in junction conductance manifest themselves in spin-flip inelastic electron tunneling spectroscopy (IETS). Like in the usual IETS where electron coupling to molecular vibration results in appearance of step-like features in conductance on the scale of molecular vibrations (0.01 – 0.1 eV), energy exchange between tunneling electrons and the local spin system yields similar IETS signal in the meV range. Such spin-flip spectroscopy was demonstrated using STM on single atoms,<sup>56</sup> atomic structures,<sup>57,58</sup> and molecular thin films.<sup>59</sup> Model based<sup>60-65</sup> and ab initio<sup>66</sup> theoretical treatments are available in the literature for STM setup, where electron

tunneling between tip and substrate interacts with a system of local spins via spin-spin exchange. A nonequilibrium Green function (NEGF) formulation for a model explicitly including system (single level) coupled to two electronic reservoirs (tip and substrate) with treating spin-spin exchange interaction taken into account within the first Born approximation (BA) was presented in Ref. 67.

In this paper we study spin inelastic current in a junction formed by a molecular ring (benzene) coupled to two metal leads. The spin-flip IETS signal is due to exchange interaction between conduction electrons and a local spin placed at the center of the ring. Thus the model combines consideration of quantum interference effects inherent in electron conduction in the molecular ring structures with spin-flip IETS due to interaction with local spin. We note that magnetic impurity placed at the ring center is an idealization, the only condition for the practical relevance of our model requires impurity in the vicinity of the benzene ring, which induces the spin-spin exchange interaction. Such structures have been studied both experimentally<sup>68,69</sup> and theoretically.<sup>70-74</sup>

We study inelastic effects in the (spin-resolved) total and circular currents within the NEGF approach. Circular currents are defined following the procedure outlined in Ref. 75. Since BA is a non-conserving approximation a more advanced treatment is required for any system beyond single level (see e.g. Ref. 77 for discussion). Here we consider the spin-spin exchange interaction within the self-consistent BA (SCBA). The SCBA enforces conservation laws<sup>76</sup> and accounts for the renormalization of the elastic channel disregarded in Refs. 60-65,67. We also discuss effects of the lead-molecule configuration (para, meta or ortho positions) on transport characteristics of the junction.

The paper is organized as follows. In Section II we introduce the model and formulate the NEGF scheme. Numerical results for inelastic (total and circular) currents are presented and discussed in Section III. Section IV concludes and outlines directions for future study.

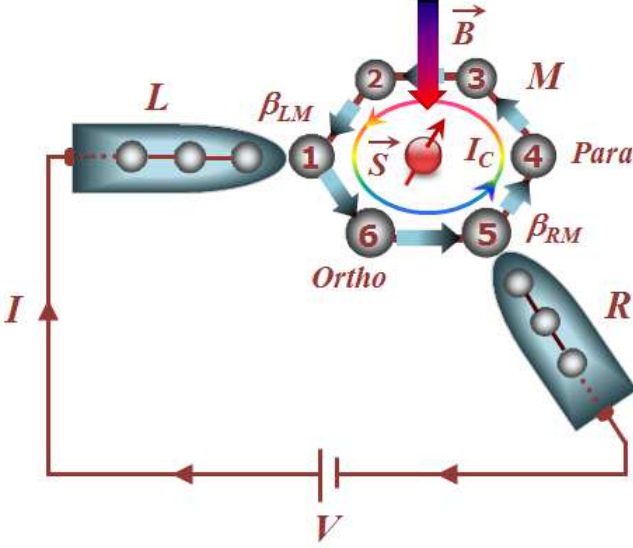


FIG. 1: (Color online) A tight-binding model for current conduction through a molecular ring  $M$  with a spin impurity  $\vec{S}$  at its center coupled to metal leads  $L$  and  $R$  in a meta position (sites of ortho and para configurations are indicated in the figure). External uniform magnetic field  $\vec{B}$  is applied perpendicular to the ring plane.

## II. MODEL AND METHOD

We consider benzene molecule,  $M$ , connected to two metal leads,  $L$  and  $R$ , at either para, meta, or ortho positions. The molecule is described by a tight-binding model with on-site energy  $\alpha_M$  and the elastic hopping matrix element  $\beta_M$ . The metal leads are modeled as semi-infinite one-dimensional tight-binding chains with the on-site energy  $\alpha_K$  and hopping  $\beta_K$  ( $K = L, R$ ). The leads are reservoirs of free electrons, each at its own thermal equilibrium. Coupling between molecule and leads is characterized by tunneling matrix elements  $\beta_{LM}$  and  $\beta_{RM}$  for  $L - M$  and  $R - M$  interfaces, respectively. An impurity atom with spin  $\vec{S}$  is placed at the center of the ring. Following Ref. 67 we disregard dynamics of the local spin, and assume fast thermalization. Figure 1 presents a sketch of the model. The Hamiltonian of the model is (here and below  $|e| = \hbar = m_e = 1$ )

$$\hat{H} = \hat{H}_M + \sum_{K=L,R} (\hat{H}_K + \hat{V}_{KM}) + \hat{V}_{SM} \quad (1)$$

$$\equiv \hat{H}_0 + \hat{V}_{SM}$$

where  $\hat{H}_M$  and  $\hat{H}_K$  introduce electronic degrees of freedom in the molecule and in the contact  $K$  ( $K = L, R$ ), respectively.  $\hat{V}_{KM}$  is coupling between molecule and contact  $K$  and  $\hat{V}_{SM}$  describes exchange interaction of conduction electrons with the local spin. Explicit expressions

are

$$\hat{H}_M = \sum_{m \in M, \sigma} \alpha_M (V_g) \hat{d}_{m\sigma}^\dagger \hat{d}_{m\sigma} \quad (2)$$

$$+ \sum_{\langle m_1 < m_2 \rangle \in M, \sigma} \left( \beta_M \hat{d}_{m_1\sigma}^\dagger \hat{d}_{m_2\sigma} + H.c. \right)$$

$$\hat{H}_K = \sum_{k \in K, \sigma} \alpha_K \hat{c}_{k\sigma}^\dagger \hat{c}_{k\sigma} \quad (3)$$

$$+ \sum_{\langle k_1, k_2 \rangle \in K, \sigma} \left( \beta_K \hat{c}_{k_1\sigma}^\dagger \hat{c}_{k_2\sigma} + H.c. \right)$$

$$\hat{V}_{KM} = \sum_{\sigma} \left( \beta_{KM} \hat{c}_{k_K\sigma}^\dagger \hat{d}_{m_K\sigma} + H.c. \right) \quad (4)$$

$$\hat{V}_{SM} = \sum_{m_1, m_2 \in M, \sigma_1, \sigma_2} J_{m_1 m_2} \left( \hat{\vec{S}} \cdot \vec{\sigma}_{\sigma_1 \sigma_2} \right) \hat{d}_{m_1\sigma_1}^\dagger \hat{d}_{m_2\sigma_2} \quad (5)$$

Here  $\hat{d}_{m\sigma}^\dagger$  ( $\hat{d}_{m\sigma}$ ) and  $\hat{c}_{k\sigma}^\dagger$  ( $\hat{c}_{k\sigma}$ ) are the creation (annihilation) operators for an electron of spin  $\sigma$  ( $\uparrow, \downarrow$ ) at site  $i$  in the molecule and site  $k$  in the lead, respectively.  $\alpha_M (V_g) \equiv \alpha_M + V_g$  is the gated molecular on-site energy ( $V_g$  is the gate voltage).  $\hat{\vec{S}}$  is vector spin operator of the impurity and  $\vec{\sigma}_{\sigma_1 \sigma_2}$  is  $\sigma_1 \sigma_2$  matrix element of the vector of Pauli spin matrices  $\vec{\sigma} \equiv (\sigma_x, \sigma_y, \sigma_z)$ .  $\langle i, j \rangle$  indicates that  $i$  and  $j$  are the nearest neighbors.  $k_K$  is the site in the atomic chain in the immediate neighborhood of the molecular site  $m_K$  ( $K = L, R$ );  $m_L = 1$  and  $m_R = 5$  for meta configuration shown in Fig. 1.  $J_{m_1 m_2}$  is the spin-spin exchange interaction coupling strength. Below we consider two types of this interaction: the s-d model<sup>78</sup>

$$J_{m_1 m_2} = \delta_{m_1, m_2} J \quad (6a)$$

and the spin-dependent tunneling matrix element model<sup>79</sup>

$$J_{m_1 m_2} = \delta_{\langle m_1, m_2 \rangle} J \quad (6b)$$

Here  $\delta_{\langle m_1, m_2 \rangle}$  indicates that  $m_1$  and  $m_2$  are nearest neighbors.

We note that the molecular Hamiltonian, Eq.(2), is a standard Pariser-Parr-Pople (PPP) model routinely used in quantum chemistry as a semi-empirical quantum mechanical method for description of conjugated and aromatic hydrocarbons.<sup>80,81</sup> Note also that spin-spin exchange coupling of the type given in Eq.(5) was employed in a number of theoretical considerations of similar systems.<sup>64,65,67,82,83</sup>

A static uniform magnetic field  $\vec{B}$  is applied perpendicular to the ring plane.<sup>101</sup> We assume that the field is confined to the molecule region only. In the presence of the field on-site energy  $\alpha_M$  becomes spin dependent (the Zeeman effect) and hopping matrix element  $\beta_M$  acquires phase factor  $\theta$ <sup>46,47</sup>

$$\alpha_{M\sigma} \equiv \alpha_M - 2\mu_B B_{tot} \sigma \quad (7)$$

$$\beta_M \rightarrow \beta_M e^{i\theta} \quad \theta \equiv 2\pi \frac{\phi_{B_{tot}}}{6\phi_0} \quad (8)$$

where  $\mu_B = e\hbar/2m_e$  is the Bohr magneton,  $B_{tot} \equiv B + B_{ind}$  is the total magnetic field (external plus current induced),  $\phi_0 = h/|e|$  is the flux quantum, and  $\phi_{B_{tot}}$  is the total magnetic flux through the benzene ring. The magnetic field also removes degeneracy of the local spin eigenstates  $|SM_S\rangle$

$$E_{SM_S} = -2\mu_B B_{tot} M_S \quad (9)$$

We assume quick relaxation of the local spin, so that probability  $P_{SM_S}$  for the eigenstates occupations follows the Boltzman distribution. Note that fast thermalization of the local spin is a reasonable approximation as long as the spin-spin exchange is relatively weak and the impurity is strongly coupled to a bath (the latter may be represented, e.g., either by chain of atoms, or metallic surface with the impurity chemisorbed on it). This assumption has also been considered in a number of previous studies.<sup>60–65,67</sup>

The central quantity of interest is single-particle electronic Green function, defined on the Keldysh contour as

$$G_{m\sigma, m'\sigma'}(\tau, \tau') = -i\langle T_c \hat{d}_{m\sigma}(\tau) \hat{d}_{m'\sigma'}^\dagger(\tau') \rangle \quad (10)$$

where  $T_c$  is the contour ordering operator. Note that in the absence of spin-spin correlations in the zero-order Hamiltonian  $\hat{H}_0$ , Eqs. (2)-(4), and within the SCBA treatment of the spin-spin interaction  $\hat{V}_{SM}$ , Eq.(5), the electron Green function, Eq.(10), is block diagonal in the spin space<sup>102</sup>

$$G_{m\sigma, m'\sigma'}(\tau, \tau') = \delta_{\sigma, \sigma'} G_{mm', \sigma}(\tau, \tau') \quad (11)$$

It satisfies the Dyson equation

$$\begin{aligned} G_{mm', \sigma}(\tau, \tau') &= G_{mm', \sigma}^{(0)}(\tau, \tau') \\ &+ \sum_{m_1, m_2 \in M} \int_c d\tau_1 \int_c d\tau_2 G_{mm_1, \sigma}^{(0)}(\tau, \tau_1) \\ &\times \Sigma_{m_1 m_2, \sigma}^{(S)}(\tau_1, \tau_2) G_{m_2 m', \sigma}(\tau_2, \tau') \end{aligned} \quad (12)$$

where  $G_{mm', \sigma}^{(0)}$  is the electron Green function in the absence of the spin-spin exchange interaction  $\hat{V}_{SM}$ , Eq.(5), and  $\Sigma_{m_1 m_2, \sigma}^{(S)}$  is the electron self-energy due to this interaction. Note that the free electron Green function  $G_{mm', \sigma}^{(0)}$  incorporates self-energies due to coupling to the contacts (see Appendix A for details)

$$\Sigma_{m_1 m_2, \sigma}^{(K)}(\tau_1, \tau_2) = \delta_{m_1, m_K} \delta_{m_2, m_K} |\beta_{KM}|^2 g_{K, \sigma}(\tau_1, \tau_2) \quad (13)$$

where  $g_{K, \sigma}(\tau_1, \tau_2) \equiv -i\langle T_c \hat{c}_{K\sigma}(\tau_1) \hat{c}_{K\sigma}^\dagger(\tau_2) \rangle$  is the surface Green function of the contact  $K$ . Note also that the Dyson equation in the form of Eq.(12) is valid only within the non-crossing approximation.<sup>85</sup> Indeed, Eq.(12) assumes that the coupling to contacts, Eq.(4), and spin-spin exchange, Eq.(5), contribute additively to the total electron self-energy.

The spin-spin exchange interaction, Eq.(5), is treated within the SCBA. Corresponding expression for the self-energy is (see Appendix B for derivation)

$$\begin{aligned} \Sigma_{m_1 m_2, \sigma}^{(S)}(\tau_1, \tau_2) &= \delta(\tau_1, \tau_2) \Sigma_{m_1 m_2, \sigma}^{(S)\delta} \\ &+ \Sigma_{m_1 m_2, \sigma}^{(S)el}(\tau_1, \tau_2) + \Sigma_{m_1 m_2, \sigma}^{(S)inel}(\tau_1, \tau_2) \end{aligned} \quad (14)$$

where

$$\Sigma_{m_1 m_2, \sigma}^{(S)\delta} = J_{m_1 m_2} \sigma \sum_{M_S} P_{SM_S} M_S \quad (15)$$

$$\begin{aligned} \Sigma_{m_1 m_2, \sigma}^{(S)el}(\tau_1, \tau_2) &= \sum_{m_3, m_4 \in M} J_{m_1 m_3} G_{m_3 m_4, \sigma}(\tau_1, \tau_2) J_{m_4 m_2} \\ &\times \sum_{M_S} P_{SM_S} [1 - P_{SM_S}] M_S^2 \end{aligned} \quad (16)$$

$$\begin{aligned} \Sigma_{m_1 m_2, \sigma}^{(S)inel}(\tau_1, \tau_2) &= \sum_{m_3, m_4 \in M} J_{m_1 m_3} G_{m_3 m_4, \bar{\sigma}}(\tau_1, \tau_2) J_{m_4 m_2} \\ &\times \sum_{\substack{M_S, M'_S \\ (|M_S - M'_S| = 1)}} B_{M_S}(\tau_1, \tau_2) B_{M'_S}(\tau_2, \tau_1) \\ &\times \frac{(S + \xi M_S)(S - \xi M_S + 1)}{2} [1 - \xi \sigma] \end{aligned} \quad (17)$$

with  $\xi \equiv \text{sgn}(M_S - M'_S)$ ,  $\bar{\sigma} \equiv -\sigma$ , and

$$B_{M_S}(\tau_1, \tau_2) \equiv i \left( P_{SM_S} - \theta_C(\tau_1, \tau_2) \right) e^{-iE_{SM_S}(\tau_1 - \tau_2)} \quad (18)$$

Here  $\theta_C(\dots)$  is the Heaviside step function defined on the contour, and  $t_{1,2}$  are the real times corresponding to the  $\tau_{1,2}$  contour variables. Eqs. (12) and (14) are then solved self-consistently. The self-consistency results from inter-dependence of the Green function, self-energy, and magnetic field induced by circular current in the ring.

The converged Green function, Eq.(11), is used to calculate currents in the molecule. In particular, within the same effective second order perturbative expansion in  $\hat{V}_{SM}$  the spin-resolved molecular bond current is (see Appendix C for derivation)

$$I_{m_1 \rightarrow m_2}^\sigma(t) \approx \frac{2e}{\hbar} \text{Re} [\beta_{m_1 m_2, \sigma} G_{m_2 m_1, \sigma}^<(t, t)] \quad (19)$$

where

$$\beta_{m_1 m_2, \sigma} \equiv \beta_M + \Sigma_{m_1 m_2, \sigma}^{(S)\delta} \quad (20)$$

with  $m_1, m_2$ , the nearest neighboring sites.

Following Ref. 75 we can write an approximate expression for the spin-resolved circular current (see Appendix C for a short discussion)

$$I_c^\sigma(t) \approx \sum_{\langle m_1, m_2 \rangle \in M} I_{m_1 \rightarrow m_2}^\sigma(t) \frac{\ell_{\langle m_1, m_2 \rangle}}{L} \quad (21)$$

Here counterclockwise direction is taken as positive (see Fig. 1), the sum is over all bonds of the molecular

ring,  $\ell_{\langle m_1, m_2 \rangle}$  is the length of the bond  $\langle m_1, m_2 \rangle$  (here length of the  $C - C$  bond in benzene,  $1.4\text{\AA}$ ), and  $L \equiv \sum_{\langle m_1, m_2 \rangle \in M} \ell_{\langle m_1, m_2 \rangle}$ .

The spin-resolved current at the molecule-contact interface  $K$  is<sup>88</sup>

$$I_K^\sigma(t) = \frac{2e}{\hbar} \sum_{m_1, m_2 \in M} \text{Re} \int_{-\infty}^t dt_1 \left[ \Sigma_{m_1 m_2, \sigma}^{(K) <}(t, t_1) G_{m_2 m_1, \sigma}^{>}(t_1, t) - \Sigma_{m_1 m_2, \sigma}^{(K) >}(t, t_1) G_{m_2 m_1, \sigma}^{<}(t_1, t) \right] \quad (22)$$

Our consideration below is restricted to steady-state, where projections of the electron Green function (11) and self-energies (13) and (14) depend only on time difference, thus it is convenient to make the Fourier transformation to energy space. Currents (21)-(22) are time-independent, and the current at the interface  $K$  is given by the Kirchhoff's law as a sum of currents in bonds connected to the site  $m_K$ . Note, however, that circular current expression, Eq.(21), is approximate, while expression for the terminal current, Eq.(22), is exact. Thus a priori there is no guarantee that the Kirchhoff's law is strictly fulfilled even when GFs in these expressions are evaluated within a conserving approximation.

In summary, Eqs. (12) and (14) set up a self-consistent procedure at the SCBA level. Converged results are utilized in Eqs. (21) and (22) to calculate circular and terminal currents, respectively.

### III. RESULTS AND DISCUSSION

We now present results of steady-state simulations of the circular and terminal currents for the model (1)-(5) with local spin chosen as  $S = 1$ . Unless stated otherwise, parameters for the calculations are  $T = 0.5$  K,  $\alpha_M = -2$  eV and  $\beta_M = 2.5$  eV,  $\alpha_K = 0$  and  $\beta_K = 6$  eV ( $K = L, R$ ),  $\beta_{LM} = \beta_{RM} = 0.3$  eV, and  $J = 5$  meV. For these parameters electron escape rate due to coupling to contacts is  $\Gamma_K = 2|\beta_{KM}|^2/|\beta_K| = 30$  meV. The Fermi energy is taken in the middle of the conduction band,  $E_F = 0$ , and the bias  $V$  is applied symmetrically  $\mu_{L,R} = E_F \pm V/2$ . Calculations are performed on energy grid spanning the range from  $-1.5$  to  $1.5$  eV in steps of  $10^{-5}$  eV.

We note that the parameters are chosen to represent a realistic molecular junction. In particular, the hopping matrix element  $\beta_M$  is chose to represent the carbon-carbon bond in benzene within the PPP model.<sup>80,96</sup> The onsite energy  $\alpha_M$  is chosen to set the lowest unoccupied molecular orbital (LUMO) at  $\sim 0.5$  eV above the Fermi in the metal following Ref. 97.<sup>103</sup> The unphysically large value of hopping matrix element  $\beta_K$  we consider for contacts is just a way to enforce wide band limit (bandwidth 24 eV). The onsite energy in contacts  $\alpha_K$  defines origin of the energy scale. Strength of molecule-contacts coupling

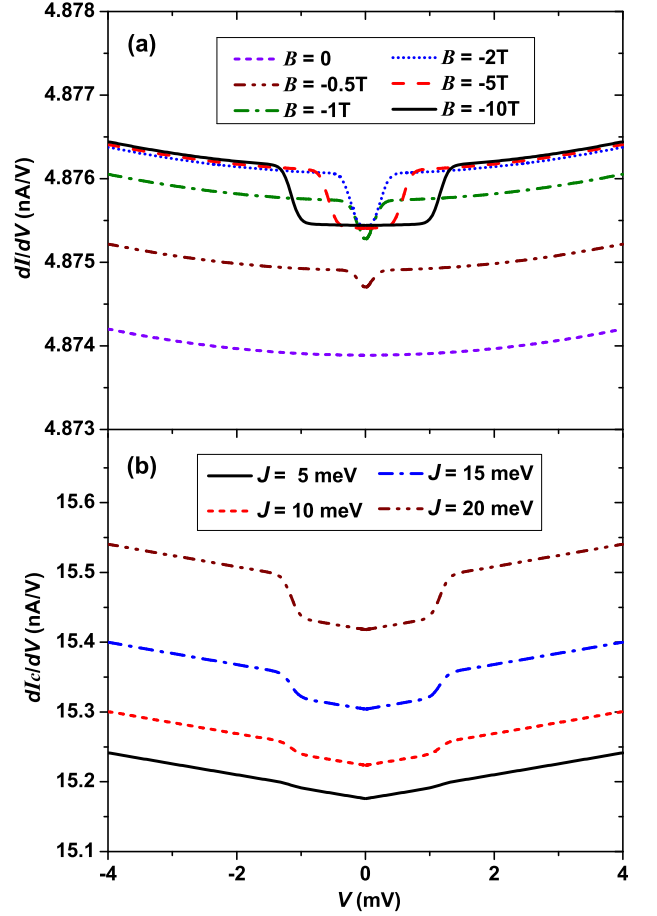


FIG. 2: (Color online) Inelastic transport in a meta-connected benzene ring molecular junction. Shown are (a) conductance  $dI/dV$  ( $I_L = I_R \equiv I$ ) vs. bias for several magnetic field strengths (negative  $B$  represents a field pointing into the plane of the ring), (b) circular conductance  $dI_C/dV$  vs. bias at  $B = -10$  T for several values of electron-spin exchange parameter  $J$ .

$\beta_{KM}$  is not well-controlled in realistic junctions, and may change by up to 3 orders of magnitude for the same device depending on experimental setup (compare, for example, experimental data on benzenedithiol molecular junction reported in Refs. 98 and 99). Thus we choose these parameters utilizing data of Ref. 67. Interestingly, results for conductance in the low bias region obtained with these parameters (see Fig. 2) are in agreement with the experimental data reported in Ref. 99. Finally, spin-spin exchange coupling parameter  $J$  is taken within the range considered in similar previous studies.<sup>82,83</sup>

The self-consistent iterations of Eqs. (12) and (14) are performed till currents, Eqs. (19)-(22), are converged with a tolerance of 0.01%. We note in passing that for the chosen parameters both models (6) yield qualitatively similar results. Below we present results of calculations for the tunneling model (6b). Note also that for these parameters currents calculated using Eq.(22) and as a sum



of bond currents at the junction (the Kirchhoff's law) are identical.

First we present inelastic features in the total current  $I_L = I_R \equiv I$ , Eq.(22), for a meta connected benzene ring molecular junction (results for the para- and ortho-connected rings are qualitatively similar). Fig. 2a depicts the conductance ( $dI/dV$ ) at low bias for several values of applied magnetic field  $B$ . The conductance step, an indication of opening of an inelastic channel, demonstrates linear shift towards higher voltages with increase of the magnetic field strength. The effect is due to increase of level separation in the local spin system, Eq.(9). Note that the field reversal,  $B \rightarrow -B$ , does not affect the conductance spectra. Results presented in Fig. 2a are similar to experimental data,<sup>56–58</sup> where spin-flip IETS was observed for atomic structures studied with STM, and corresponding theoretical simulations.<sup>60,64–67</sup>

Inelastic effects are observed also in circular current. Figure 2b shows circular conductance at low bias for several spin-exchange coupling strengths. As expected, stronger inelastic coupling strength results in a more pronounced step in the conductance. Note steeper increase of circular compared to total current (note, solid curve in Fig. 2a is calculated for the same parameters as in Fig. 2b). This can be understood by considering that for a small molecule-contact coupling electrons entering the ring spend a long time circulating in the ring, before being escaped to the other terminal,<sup>91</sup> which results in large circular currents in the ring.

Note that IETS signal presented in Fig. 2 in principle should be observable also for  $B = 0$  due to the magnetic field induced by the circular current. However, realistic estimate of the induced field yields  $B_{ind} \sim 0.2$  T, which results in splitting of spin states of the local impurity of the order of 0.01 meV. Thus observation of inelastic effects in the absence of external magnetic field is not feasible.

Renormalization of elastic scattering with opening of inelastic channel may lead to either increase or decrease of the total current (step up or down in the conductance) at the threshold.<sup>92</sup> Previous considerations,<sup>60,63–65,67</sup> which employed lowest order perturbation theory, have not accounted for the renormalization of the elastic channel. For a model of single molecular level  $\varepsilon_0$  coupled to single molecular vibration change in conductance near the threshold is proportional to (see Eq.(36) in Ref. 92)

$$\frac{[\mu - \varepsilon_0 - \text{Re} \Sigma_{inel}^r(\mu)]^2 - (\Gamma/2)^2}{[\mu - \varepsilon_0 - \text{Re} \Sigma_{inel}^r(\mu)]^2 + (\Gamma/2)^2} \quad (23)$$

where  $\mu$  is electro-chemical potential and  $\Sigma_{inel}^r$  is retarded projection of the self-energy due to coupling to molecular vibration. Thus, transition between the two features in vibrational IETS can be achieved either by applying gate voltage (i.e. changing  $\mu - \varepsilon_0$ ) or equivalently by changing strength of the molecule-contacts coupling  $\Gamma$  (e.g. in STM experiment). Figure 3a demonstrates this transition for spin-flip IETS of the model (1)-(5).

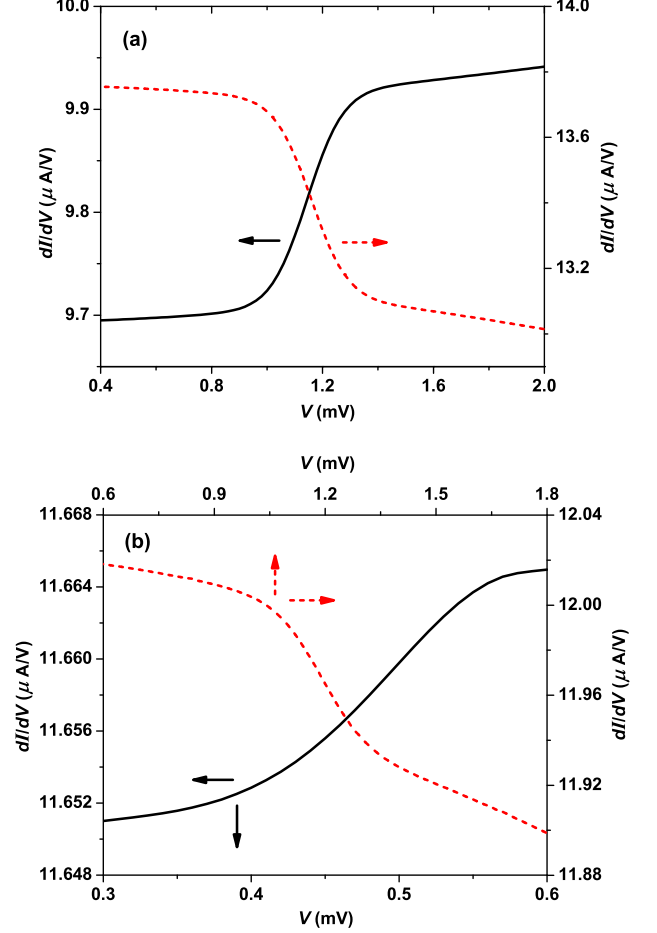


FIG. 3: (Color online) Elastic channel renormalization in a meta-connected benzene ring molecular junction. Shown is conductance  $dI/dV$  ( $I_L = I_R \equiv I$ ) vs. bias (a) at  $B = -10$  T for two different values of gate voltage:  $V_g = 0.486$  V (solid line, black) and 0.490 V (dashed line, red); (b) at  $V_g = 0.488$  V for two different values of applied magnetic field:  $B = -5$  T (solid line, black; left and bottom axes) and  $-10$  T (dashed line, red; right and top axes).

Contrary to vibrational spectroscopy, where inelastic channel threshold is set by frequency of the vibration, excitation energy of a spin inelastic process can be adjusted by magnetic field. This allows tuning of the corresponding self-energy (see e.g.  $\Sigma_{inel}^r$  in Eq.(23)). Figure 3b shows control of conductance behavior at the threshold by external magnetic field.

Peaks and dips in IETS spectrum were observed experimentally in vibrational IETS measurements (see e.g. Refs. 93,94), and should be expected also in the spin-flip IETS. Since external magnetic field is a simpler control than either gate potential or molecule-contacts coupling strength observation of transition between the two types of the IETS signal should be easier for spin-flip IETS.

We now turn to resonant tunneling regime with LUMO entering the bias window at  $V \sim 1$  V. Spin-spin exchange

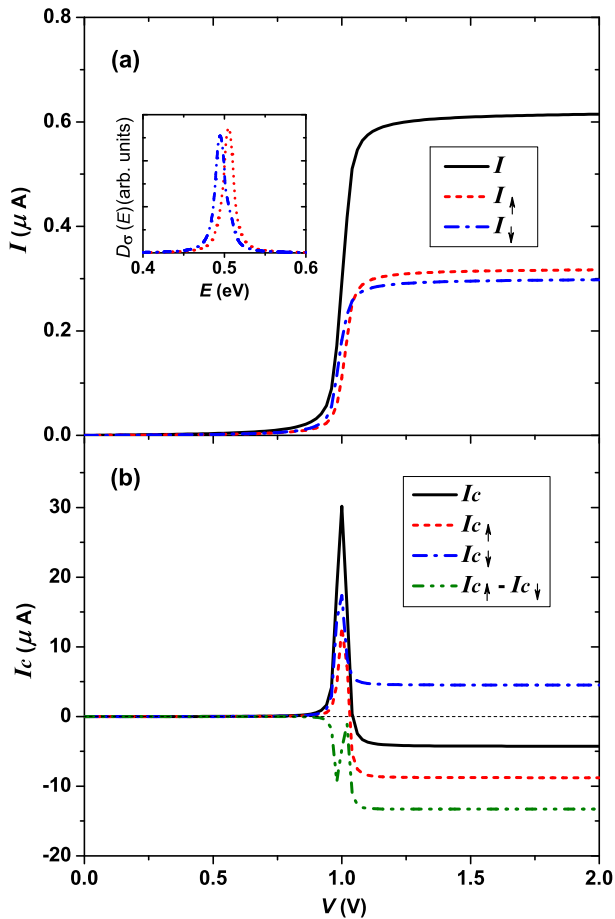


FIG. 4: (Color online) Current-voltage characteristics of a meta-connected molecular ring junction. Shown are (a) terminal current  $I_L = I_R \equiv I$ , Eq.(22), and (b) circular current  $I_c$ , Eq.(21), at  $B = -5$  T for spin-up (dashed line, red), spin-down (dash-dotted line, blue), total charge (solid line, black), and total spin (dash-double-dotted line, green) currents. The inset in panel (a) shows the spin resolved local density of states  $D_{\sigma}(E)$ , Eq.(24), at  $V = 1$  V (spin-up - dashed line, red, spin-down - dash-dotted line, blue)

coupling  $V_{SM}$ , Eq.(5), induces spin-dependent renormalization of the local density of states

$$D_{\sigma}(E) \equiv -\frac{1}{\pi} \text{Im Tr} [G_{\sigma}^r(E)] \quad (24)$$

Figure 4a shows terminal current  $I_L = I_R \equiv I$ , Eq.(22), as function of bias. Spin polarization at the resonant threshold,  $V \sim 1$  V, is due to splitting of the local density of states (see inset in the Figure).

The effect of the renormalization is even more drastic for circular current (see Fig. 4b). Here the polarization above the threshold differs qualitatively: spin-up and spin-down components move in opposite directions (compare dashed and dash-dotted lines). As a result circular charge current is suppressed, while simultaneously

large spin circular current is observed in the ring. The effect can be understood in terms of orbital momentum states (degenerate for an isolated ring) represented by Bloch waves going in opposite directions. As discussed in Ref. 75 molecule-contacts coupling removes this degeneracy. In the presence of the spin-spin exchange interaction the corresponding states appear to be spin polarized (see inset in Fig. 4a). It is interesting to note that in contrast to the symmetrically connected ring that lacks biased induced circular current and the associated magnetic field, the spin resolved currents in the asymmetrically connected rings remain split around 1 V bias even when applied field is removed due to magnetic field induced by circular current.

Possibility of experimental detection of charge circular current at resonant threshold by measuring current-induced magnetic field was discussed in Ref. 75. Presence of spin-spin exchange interaction yields almost pure spin circular current above the threshold. In principle spin circular current may be measurable by e.g. detecting its induced electric field as discussed in Ref. 95, however, we are not aware of experimental feasibility of such measurement.

To delve further into the spin resolved currents in the rings, we define spin polarization of the total current as

$$P = (I_{\uparrow} - I_{\downarrow}) / (I_{\uparrow} + I_{\downarrow}) \equiv \eta_{\uparrow} - \eta_{\downarrow} \quad (25)$$

where  $\eta_{\sigma} \equiv I_{\sigma}/I$  is spin filter efficiency. Figure 5a shows spin polarization in the ring with leads at para, meta and ortho positions for bias voltage tuned for level resonance transmission. The insets depict polarizations at bias above and below 1 V. Several points are noteworthy. First, polarization at resonant bias is far larger than that at off-resonant bias. Second, the asymmetrically connected rings offer better control of spin resolved currents over a symmetrically connected ring. Third, the renormalization in the density of states (in particular, which spin projection have a peak at lower energy) dictates change of sign of the polarization with the field reversal. Fourth, positive polarization for meta (negative for ortho) coupling above the resonance irrespective to sign of the magnetic field indicates leading role of interference effect induced by phase  $\theta$ , Eq.(8), rather than the renormalization of the local density in this regime.

Figure 5b shows spin filter efficiency as function of strength of molecule-contacts coupling. As expected stronger coupling between the ring and paramagnetic contacts reduces spin selectivity. Non-monotonic behavior for meta and ortho and fast drop in polarization for para coupled ring at weak coupling strengths,  $\beta_{KM} \sim 0.05$  eV, indicate presence of inelastic (spin-flip) effects, which are pronounced at  $\Gamma \sim J$ .

Note that terminal current polarization is easily measurable experimentally. Inelastic effects are of secondary importance here (although they are pronounced for weak molecule-contacts coupling). We note that the use of benzene substituted organic molecules as spin-filter devices has recently been discussed in the literature.<sup>51</sup> We

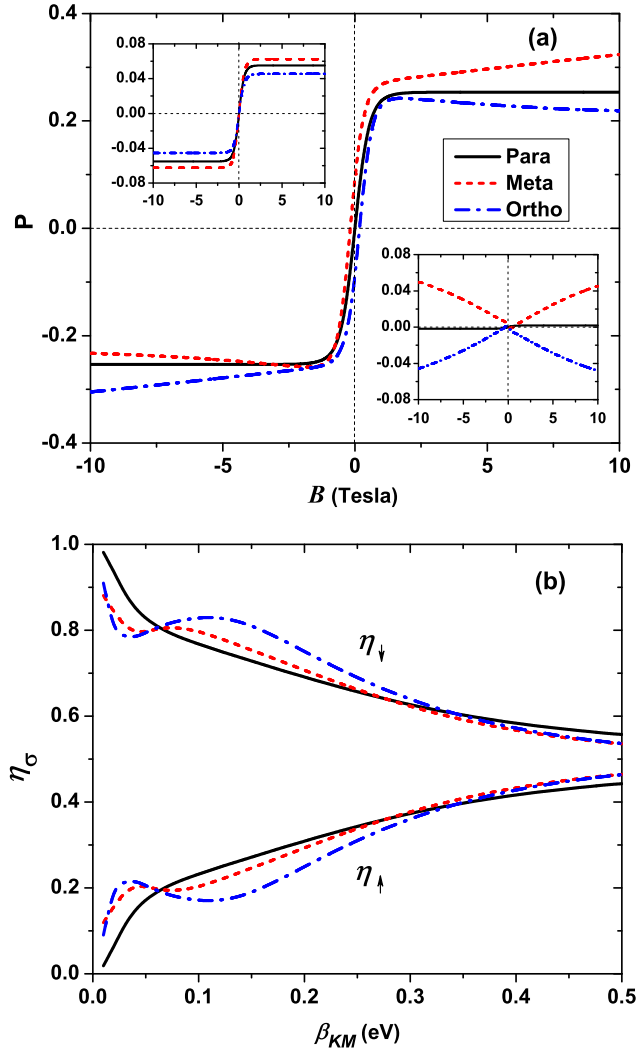


FIG. 5: (Color online) Spin polarized transport in the para (solid line, black), meta (dashed line, red) and ortho (dash-dotted line, blue) connected molecular ring junctions. Shown are: (a) Spin polarization  $P$ , Eq.(25), as a function of applied magnetic field for at resonant bias ( $V = 1$  V), and (b) Spin filter efficiency  $\eta_\sigma$ , Eq.(25), as function of the molecule-contacts coupling strength. Insets in panel (a) show spin polarization for bias below ( $V = 0.8$  V, upper inset) and above ( $V = 1.2$  V, lower inset) the resonance.

see that the effect is robust with respect to decoherence, and is sensitive to topology of the molecule-contact coupling, which indicates a possibility of coherently controlled molecular electronics.

#### IV. CONCLUSIONS

We present a study of spin inelastic currents in molecular ring junctions. Within a simple model of a benzene molecule coupled to paramagnetic contacts at meta, or-

tho and para positions, we discuss the role of external magnetic field and local spin impurity placed at the center of the ring on spin-flip IETS and spin polarization of circular and total currents.

Our study extends recent considerations of spin-flip IETS<sup>60–67</sup> formulating a conserving approximation applicable to multi-site molecular systems. It also takes into account renormalization of elastic scattering channel, which is known to cause a qualitative change in the IETS signal.

This work is also an extension of recent studies of circular currents in molecular junctions.<sup>46,47,75</sup> Our NEGF formulation allows to go beyond previous scattering theory consideration. The main results of the study are:

(a) Like vibrational also spin-flip IETS yields the possibility of control of the IETS signal. Moreover, in addition to gate bias and molecule-contacts coupling strength, also magnetic field can be used as a control of the spin-flip IETS spectrum. This feature should be measurable in any junction with spin-spin exchange interaction.

(b) The spin-spin exchange interaction in ring structures results in spin circular currents. The effect in principle is detectable by measuring current induced electric fields.<sup>95</sup>

(c) Molecular ring structures may be used as sources of spin-polarized terminal currents. Note that recently benzene substituted organic molecules have been proposed as molecular spin filters.<sup>51</sup> Here we demonstrate that the effect is robust with respect to decoherence, and is sensitive to topology of the molecule-contact coupling.

Although our consideration is restricted to simple theoretical model, the effects should be observable experimentally. Indeed, we discuss two types of effects: (a) those related to inelastic transport and (b) spin polarization due to coherence in the molecule. First, opening of inelastic channel is a robust effect observed (in the case of vibrational IETS) in many experimental studies (see e.g. Refs. 93,94). In this respect experimental observation of the spin-flip IETS is similar to those of the vibrational inelastic electron spectroscopy. Second, spin-polarization of terminal currents is caused by the presence of molecular ring. Effects of coherence related to ring molecular structures in junctions have been observed experimentally in Refs. 36,37. Also recently similar spin polarization in helical molecular junctions was reported in Ref. 100.

Extension of the study to *ab initio* simulations of transport in similar structures will be considered in the future research.

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## Appendix A: Electron self-energy due to coupling to contacts

For the model of semi-infinite atomic chain, Eq.(3), retarded, lesser and greater projections<sup>86</sup> of the self-energy (13) in energy space

$$\Sigma_{m_1 m_2, \sigma}^{(K)r}(E) = \delta_{m_1, m_K} \delta_{m_2, m_K} \quad (A1)$$

$$\times \left( \Lambda_K(E) - \frac{i}{2} \Gamma_K(E) \right)$$

$$\Sigma_{m_1 m_2, \sigma}^{(K)<}(E) = i \delta_{m_1, m_K} \delta_{m_2, m_K} \Gamma_K(E) f_K(E) \quad (A2)$$

$$\Sigma_{m_1 m_2, \sigma}^{(K)>}(E) = -i \delta_{m_1, m_K} \delta_{m_2, m_K} \quad (A3)$$

$$\times \Gamma_K(E) [1 - f_K(E)]$$

are expressed in terms of the Newns-Anderson formula<sup>87</sup>

$$\Lambda_K(E) = \frac{|\beta_{KM}|^2}{|\beta_K|} \begin{cases} \epsilon + \sqrt{\epsilon^2 - 1} & \epsilon < -1 \\ \epsilon & |\epsilon| \leq 1 \\ \epsilon + \sqrt{\epsilon^2 - 1} & \epsilon > 1 \end{cases} \quad (A4)$$

$$\Gamma_K(E) = \frac{2|\beta_{KM}|^2}{|\beta_K|} \begin{cases} \sqrt{1 - \epsilon^2} & |\epsilon| \leq 1 \\ 0 & \text{otherwise} \end{cases} \quad (A5)$$

Here  $\epsilon \equiv (E - \alpha_K)/|2\beta_K|$  and  $f_K(E)$  is the Fermi-Dirac distribution.

## Appendix B: Electron self-energy due to spin-spin exchange interaction

In the definition of the single-electron Green function, Eq.(10), operators  $\hat{d}_{m\sigma}(\tau)$  and  $\hat{d}_{m'\sigma'}^\dagger(\tau')$  are in the Heisenberg representation. Transforming this expression to the interaction representation with respect to the zero-order Hamiltonian  $\hat{H}_0$ , Eq.(1), yields

$$G_{m\sigma, m'\sigma'}(\tau, \tau') = -i \langle T_c \hat{d}_{m\sigma}(\tau) \hat{d}_{m'\sigma'}^\dagger(\tau') \rangle_0 \quad (B1)$$

$$\times e^{-i \int_c d\tau_1 \hat{V}_{SM}^I(\tau_1)}$$

where  $\hat{V}_{SM}^I(\tau_1)$  is operator of the spin-spin exchange interaction, Eq.(5), in the interaction representation, and subscript 0 indicates evolution governed by the zero-order Hamiltonian. Expanding exponent in (B1) up to second-order in  $\hat{V}_{SM}^I$ , collecting and dressing connected diagrams in the expansion,<sup>85</sup> leads to the Dyson equation with self-energy

$$\Sigma_{m_1 \sigma_1, m_2 \sigma_2}^{(S)}(\tau_1, \tau_2) = \delta(\tau_1, \tau_2) J_{m_1 m_2} \langle \hat{O}_{\sigma_1 \sigma_2}(\tau_1) \rangle_S \quad (B2)$$

$$+ \sum_{\substack{m'_1, m'_2 \in M \\ \sigma'_1, \sigma'_2}} J_{m_1 m'_1} G_{m'_1 \sigma'_1, m'_2 \sigma'_2}(\tau_1, \tau_2) J_{m'_2 m_2}$$

$$\times \langle T_c \hat{O}_{\sigma_1 \sigma'_1}(\tau_1) \hat{O}_{\sigma'_2 \sigma_2}(\tau_2) \rangle_S$$

Here

$$\hat{O}_{\sigma_1 \sigma_2}(\tau_1) \equiv \left( \hat{\vec{S}}(\tau_1) \cdot \vec{\sigma}_{\sigma_1 \sigma_2} \right), \quad (B3)$$

$\vec{\sigma}$  is vector of the Pauli matrices, and  $\langle \dots \rangle_S$  indicates average over the equilibrium distribution of the local spin system.

Following Ref. 67 we rewrite the operator  $\hat{\vec{S}}$  as

$$\hat{\vec{S}}(\tau) = \sum_{M_S, M'_S} \langle S M'_S | \hat{\vec{S}} | S M_S \rangle \hat{b}_{M'_S}^\dagger(\tau) \hat{b}_{M_S}(\tau) \quad (B4)$$

with  $\hat{b}_{M'_S}^\dagger$  and  $\hat{b}_{M_S}$  assumed to be Fermi operators, and introduce quasiparticle Green function

$$B_{M_S M'_S}(\tau, \tau') \equiv -i \langle T_c \hat{b}_{M_S}(\tau) \hat{b}_{M'_S}^\dagger(\tau') \rangle \quad (B5)$$

which for unperturbed equilibrium local spin system takes the form of Eq.(18).

Substituting (B4) into (B2), taking into account that zero-order Hamiltonian does not contain spin-flip processes, and utilizing Eq.(18) and<sup>89</sup>

$$\langle S M'_S | \hat{\vec{S}} | S M_S \rangle = \delta_{M'_S, M_S} \vec{e}_z \hbar M_S \quad (B6)$$

$$+ \delta_{M'_S, M_S \pm 1} (\vec{e}_x \mp i \vec{e}_y) \frac{\hbar}{2} \sqrt{(S \mp M_S)(S \pm M_S + 1)}$$

leads to Eqs. (14)-(17).

## Appendix C: Bond current

To derive expression for the bond current we start from equation of motion for the spin-resolved population at site  $m_1$

$$-\frac{d}{dt} \langle \hat{n}_{m_1 \sigma}(t) \rangle = -\frac{i}{\hbar} \left\langle \left[ \hat{H}; \hat{n}_{m_1}(t) \right] \right\rangle \quad (C1)$$

$$= \frac{2}{\hbar} \text{Re} \sum_{m_2 \in M, \sigma'} (\delta_{\langle m_1, m_2 \rangle} \beta_M G_{m_2 \sigma', m_1 \sigma}^<(t, t)$$

$$+ i J_{m_1 m_2} \langle \hat{O}_{\sigma \sigma'}(t) \hat{d}_{m_1 \sigma}^\dagger(t) \hat{d}_{m_2 \sigma'}(t) \rangle)$$

where  $\hat{n}_m \equiv \hat{d}_m^\dagger \hat{d}_m$ ,  $\hat{O}_{\sigma \sigma'}$  is defined in Eq.(B3), and we used Eqs. (1)-(5).

Each term in the sum in the right of Eq.(C1) is a flux from site  $m_2$  to site  $m_1$ . Utilizing Eq.(11), expanding the last term in the right of (C1) up to second order in the spin-spin exchange interaction, Eq.(5), and neglecting contribution from  $m_2$  beyond nearest neighbor sites<sup>104</sup> leads to Eq.(19) for the bond current.

Ref. 75 introduces circular current as the sole source of flux through a ring, employing the Biot-Savart expression for time-independent current in the derivations. Time-dependent generalization of the Biot-Savart law is known as Jefimenko's equation<sup>90</sup>

$$\vec{B}(\vec{r}, t) = \frac{\mu_0}{4\pi} \int d\vec{r}_1 \left( \left[ \left( \vec{J}(\vec{r}_1, t_1) \right)_{ret} \times \frac{\vec{R}}{R^3} \right] \quad (C2)$$

$$+ \left[ \left( \frac{\partial \vec{J}(\vec{r}_1, t_1)}{\partial t_1} \right)_{ret} \times \frac{\vec{R}}{cR^2} \right] \right)$$

where  $\vec{R} \equiv \vec{r} - \vec{r}_1$  and  $(f(\vec{r}_1, t_1))_{ret} \equiv f(\vec{r}_1, t - R/c)$ . Since characteristic distance for benzene ring is  $R \sim 1.4 \text{ \AA}$ , the retardation effect is confined to times of the order of  $R/c \sim 10^{-18} \text{ s}$ , which may be safely disregarded for currents in molecular junctions. Similarly, second term

in Eq.(C2) can be dropped. This results in expression which has the form of the usual Boi-Svarat law, but with time-dependent current in it. Under these assumptions results of Ref. 75 can be utilized to introduce expression for time-dependent circular current as given by Eq.(21).

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- <sup>101</sup> In realistic situation of a molecular junction one can not guarantee that the external field will be exactly normal to the molecular plane. In this case projection of the external field on the direction perpendicular to the plane is relevant for the model considered. An in-plane magnetic field causes only diamagnetic shift of electronic states. Such fields (together with electric gate potentials) are used in experiments for tuning (see e.g. Ref. 84), and are of secondary importance in our study.
- <sup>102</sup> The Green function is block diagonal in spin space due to effective second order in spin-spin coupling considered in the present work. Spin non-diagonal matrix elements appear in higher order considerations which for relatively weak spin-spin exchange coupling may be neglected. We note, that the result is similar to that obtained previously.<sup>67</sup>
- <sup>103</sup> Note that the explicit position of the LUMO in our model calculation is of secondary importance. Indeed, the IETS signal is demonstrated for gated junction (see Figs. 2 and 3), while for behavior at resonance LUMO only defines threshold bias.
- <sup>104</sup> Note that for the models considered, Eqs. (6), at most nearest neighbor contribution to the sum exists.