Interference single electron transistors based on quantum dot molecules

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Abstract We consider nanojunctions in the single electron tunneling regime which, due to a high degree of spatial symmetry, have a degenerate many-body spectrum. They comprise single molecule quantum dots as well as artificial quantum dot molecules. As a consequence, interference phenomena which cause a current blocking can occur at specific values of the bias and gate voltage. We present here a general formalism providing necessary and sufficient conditions for interference blockade also in the presence of spin-polarized leads. As examples we analyze a triple quantum dot as well as a benzene molecule single electron transistor.

1 Introduction

Single particle interference is one of the most genuine quantum mechanical effects. Since the original double-slit experiment [1], it has been observed with electrons in vacuum [2, 3] and even with the more massive \( C_{60} \) molecules [4]. Mesoscopic rings threaded by a magnetic flux provided the solid-state analogous [5, 6]. Intramolecular interference has been recently discussed in molecular junctions for the case of strong [7, 8, 9, 10, 11, 12, 13, 14, 15, 16, 17, 18] and weak [19, 20, 21] molecule-lead coupling. What unifies these realizations of quantum interference is that the travelling particle has two (or more) spatially equivalent paths at disposal to go from one point to another of the interferometer.

Interference, though is hindered by decoherence. Generally, for junctions in the strong coupling regime decoherence can be neglected due to the short time
of flight of the particle within the interferometer. In the weak coupling case, instead, the dwelling time is long. It is the regime of the single electron tunnelling devices (SETs) in which, usually, the decoherence introduced by the leads dominates the picture and the dynamics essentially consists of sequential tunnelling events connecting the many-body eigenstates of the isolated system. Yet, interference is achieved whenever two energetically equivalent paths involving degenerate states contribute to the dynamics (see Fig. 1) [22]. The associated fingerprints in the transport characteristics are a strong negative differential conductance (NDC) and eventually a current blocking in the case of fully destructive interference.

In the simplest case, NDC and current blocking triggered by interference take place any time a SET presents an $N$-particle non-degenerate state and two degenerate $N + 1$-particle states such that the ratio between the transition amplitudes $\gamma_\chi$ ($i = 1, 2$, $\chi = S, D$) between those $N$- and $N + 1$-particle states is different for tunneling at the source ($S$) and at the drain ($D$) lead:

$$\frac{\gamma_S}{\gamma_D} \neq \frac{\gamma_D}{\gamma_S}.$$  \hspace{1cm} (1)

Notice that no asymmetry in the tunnelling rates, which are proportional to $|\gamma_\chi|^2$, is implied by Eq. (1). This fact excludes the interpretation of the physics of the interference SET in terms of standard NDC with asymmetric couplings. Instead, due to condition (1) there exist linear combinations of the degenerate $N + 1$-particle states which are connected to the $N$-particle state via a tunnelling event to one of the leads but not to the other. The state which is decoupled from the drain lead (i.e. the lead with the lower chemical potential) represents a blocking state which prevents the current to flow since electrons can populate this state by tunnelling from the source but cannot tunnel out towards the drain.

It should be noticed that several blocking states can be associated to the same system. Let us consider again the example associated to (1) and analyze an inversion of the bias polarity which interchanges the source and the drain lead. If the state decoupled from the right lead blocks the current $L \rightarrow R$, viceversa the state decoupled from the left lead is a blocking state for the current $R \rightarrow L$. Typically these two different blocking states are not orthogonal and cannot form together a valid basis set of the $N + 1$ particle space. The basis set that diagonalizes the stationary density matrix (what we call in the manuscript the physical basis) contains at large positive biases the $L \rightarrow R$ blocking state and is thus different from the physical basis at large negative biases which necessarily contains the $R \rightarrow L$ blocking state. More generally, the physical basis depends continuously on the bias. Thus only a treatment that includes also coherences and not only populations of the density matrix can capture the full picture at all biases.

It could be argued about the fragility of an effect which relies on the presence of degeneracies in the many-body spectrum. Interference effects are instead rather robust. The exact degeneracy condition can be in fact relaxed and interference survives as far as the splitting between the many body levels is smaller that the tunnelling rate to the leads. In this limit, the system still does not distinguish between the two ener-
I-SET based on quantum dot molecules

getically equivalent paths sketched in Fig. 1. Summarizing, despite the decoherence introduced by the leads, in such devices, that we called interference single electron transistors [20] (I-SET), interference effects show up even in the Coulomb blockade regime.

Fig. 1 Interference in a single electron transistor (SET). The dynamics is governed by equivalent paths in the many-body spectrum that involve two (or more) degenerate states. From [22].

In the present chapter we develop a general theory of interference blockade. We give in fact an a priori algorithm for the detection of the interference blocking states of a generic I-SET. As concrete examples, we analyze the triple dot and the benzene I-SET. The first is chosen as the simplest structure exhibiting interference blockade and in the second we emphasize the crucial role of the coupling geometry in the interference phenomena. In both cases we further analyze the blockade that involves orbitally and spin degenerate states and we show how to realize all electrical preparation of specific spin states. Thus we obtain an interference mediated control of the electron spin in quantum dots, a highly desirable property for spintronics [25, 26, 27] and spin-qubit applications [28, 29, 30, 31, 32]. Similar blocking effects have been found also in multiple quantum dot systems in dc [23] and ac [24] magnetic fields. The method of choice for the study of the dynamics in those systems is the generalized master equation approach for the reduced density matrix (RDM), where coherences between degenerate states are retained [19, 20, 21, 33, 34, 35, 36, 37, 38, 39, 40, 41, 42, 43]. Such coherences give rise to precession effects and ultimately cause interference blockade.

The chapter is organized as follows: in Section 2 we introduce a generic model of I-SET. In Section 3 we set the necessary and sufficient conditions which define the interference blocking states and a generic algorithm to detect them. In Sections 4 and 5 we apply the theory to the benzene and to the triple dot molecule I-SET.
Section 6 is dedicated to the implications on spin transport of the interference effects in presence of ferromagnetic leads. In Section 7 we analyze the robustness of the interference phenomena upon relaxation of the exact orbital degeneracy condition. Section 8 closes the chapter with a summary of the results and conclusive remarks.

2 Generic model of I-SET

Let us consider the interference single electron transistor (I-SET) described by the Hamiltonian:

\[
H = H_{\text{sys}} + H_{\text{leads}} + H_{\text{tun}},
\]

where \(H_{\text{sys}}\) represents the central system and also contains the energy shift operated by a capacitively coupled gate electrode at the potential \(V_g\). The Hamiltonian \(H_{\text{sys}}\) is invariant with respect to a set of point symmetry operations that defines the symmetry group of the device. This fact ensures the existence of degenerate states. To fix the ideas, the system Hamiltonian describing the triple dot and the benzene molecule considered later in this chapter (see Figs. 3 and 9) are of the Pariser-Parr-Pople form [44, 45, 46]:

\[
H_{\text{sys}} = \xi \sum_{i \sigma} d^\dagger_{i \sigma} d_{i \sigma} + b \sum_{i \sigma} \left( d^\dagger_{i \sigma} d_{i+1 \sigma} + d^\dagger_{i+1 \sigma} d_{i \sigma} \right) \\
+ U \sum_i \left( n_{i\uparrow} - \frac{1}{2} \right) \left( n_{i\downarrow} - \frac{1}{2} \right) \\
+ V \sum_i \left( n_{i\sigma} + n_{i+1\sigma} - 1 \right) \left( n_{i+1\sigma} + n_{i+1\sigma} - 1 \right),
\]

where \(d^\dagger_{i \sigma}\) creates an electron of spin \(\sigma\) in the \(p_z\) orbital of site \(i\) or in the ground state of the quantum dot \(i\) and \(i = 1, \ldots, 6\) runs over the six carbon atoms (three quantum dots) of the system. Moreover, \(n_{i\sigma} = d_{i \sigma}^\dagger d_{i \sigma}\) counts the number of electrons of spin \(\sigma\) on site \(i\). The effect of the gate is included as a renormalization of the on-site energy \(\xi = \xi_0 - eV_g\) with \(V_g\) being the gate voltage. The parameters \(U\) and \(V\) describe the Coulomb interaction between electrons, respectively, on the same and on neighboring sites.

We leave a detailed analysis of the manybody spectrum of (3) to the Sections 4 and 5. Here we just mention that, for these planar structures belonging to the \(D_6\) group, the (non-accidental) orbital degeneracy is at maximum twofold and can be resolved using the eigenvalues \(\ell\) of the projection of the angular momentum along the principal axis of rotation. A generic eigenstate is then represented by the ket \(|N(\sigma E)\rangle\) where \(N\) is the number of electrons on the system, \(\sigma\) is the spin and \(E\) the energy of the state. The size of the Fock space can make the exact diagonalization of \(H_{\text{sys}}\) a numerical challenge in its own. We will not treat here this problem and
I-SET based on quantum dot molecules concentrate instead on the transport characteristics. $H_{\text{leads}}$ describes two reservoirs of non-interacting electrons with a difference $eV_b$ between their electrochemical potentials. Finally, $H_{\text{tun}}$ accounts for the weak tunnelling coupling between the system and the leads, characteristic of SETs:

$$H_{\text{tun}} = \sum_{\chi,k} t_{\chi k}^\sigma c_{\chi k\sigma}^\dagger d_{i\sigma} + h.c.,$$

where $c_{\chi k\sigma}^\dagger$ creates an electron with spin $\sigma$ and momentum $k$ in lead $\chi = L, R$ and $t_{\chi k}^\sigma$ is the bare tunnelling amplitude of a $k$ electron in the lead $\chi$ to the site $i$. We assume it for simplicity independent of the spin $\sigma$. Naturally, $|t_{\chi k}^\sigma|$ is highest for the atom (quantum dot) closest to the lead $\chi$, due to the exponential decay on the atomic scale of the tunnelling probability with the distance between the system and the lead. Moreover, in the case of atomically localized coupling where the tunnelling from the lead is most probable only to a small part of the system it is also reasonable to assume a very weak $k$-dependance of the tunnelling amplitude. We will simply neglect it in Sec. 3 when discussing the general criteria for the identification of blocking states.

In the weak coupling regime, the dynamics essentially consists of sequential tunnelling events at the source and drain lead inducing a flow of probability between the many-body eigenstates of the system. The coupling between the system and the leads, though, also contributes to an internal dynamics of the system that leaves unchanged its particle number. In fact the equation of motion for the reduced density matrix $\rho$ of the system can be cast, to lowest non vanishing order in the coupling to the leads, in the form [35, 33, 21]:

$$\dot{\rho} = -\frac{i}{\hbar} [H_{\text{sys}}, \rho] - \frac{i}{\hbar} [H_{\text{eff}}, \rho] + L_{\text{tun}} \rho. \quad \text{(5)}$$

The commutator with $H_{\text{sys}}$ in Eq. (5) represents the coherent evolution of the system in absence of the leads. The operator $L_{\text{tun}}$ describes the sequential tunnelling processes and is defined in terms of the transition amplitudes between the different many-body states. The commutator with $H_{\text{eff}}$ is responsible instead for the effective internal dynamics associated to the presence of the leads. It is convenient to analyze the different terms in greater detail. In particular:

$$\langle L_{\text{tun}} \rho \rangle^{\text{NE}} = -\frac{1}{2} \sum_{\chi} \sum_{ij} \left\{ \mathcal{P}^{\text{NE}} \left[ d_{i\sigma}^\dagger t_{ij}^{\chi\sigma} (E - H_{\text{sys}}) f_{\chi}^E (E - H_{\text{sys}}) d_{j\sigma} \right] + \frac{d_{i\sigma}^\dagger t_{ij}^{\chi\sigma} (H_{\text{sys}} - E) f_{\chi}^E (H_{\text{sys}} - E) d_{j\sigma}}{E - E'} \right\} \rho^{\text{NE}} + h.c. + \sum_{\chi} \sum_{ij} \mathcal{P}^{\text{NE}} \left[ d_{i\sigma}^\dagger t_{ij}^{\chi\sigma} (E' - E) \rho^{N+1} f_{\chi}^{E'} (E' - E) d_{j\sigma} + d_{j\sigma}^\dagger t_{ij}^{\chi\sigma} (E' - E) \rho^{N+1} f_{\chi}^{E'} (E' - E) d_{i\sigma} \right] \mathcal{P}^{\text{NE}}.$$  

where $\rho^{NE} := \mathcal{P}_{NE} \rho_{NE}$, being $\rho_{NE} := \sum_{i\sigma} |N(i\sigma E)\rangle \langle N(i\sigma E)|$ the projection operator on the subspace of $N$ particles and energy $E$. Moreover, $f_{\chi}^+(x) := f(x - \mu_{\chi})$, and $f_{\chi}^-(x) := 1 - f_{\chi}^+(x)$. The terms proportional to $f_{\chi}^+(x)$ describe in (6) tunnelling events into the system, while the tunnelling out of the system is associated to $f_{\chi}^-(x)$. Additionally, $\mu_{\chi}$ stands for the electro-chemical potential of the lead $\chi$, defined via the applied bias voltage as $\mu_L = \mu_0 + (1 - c)eV_b$, $\mu_R = \mu_0 - ceV_b$ and consequently $eV_b = \mu_L - \mu_R$, with the electron charge $e$, the equilibrium potential $\mu_0$ and the coefficient $c$ governing the relative bias drop at the left and right lead. A symmetrical potential drop is obtained for $c = 1/2$, while for $c = 1$ the bias drops completely at the right-lead interface.

Finally, $\mu_0 = -\Phi_0$ relates the equilibrium chemical potential to the work function and, in equilibrium, the work functions of the two leads are assumed equal. Besides the Fermi function, the tunnelling rates are characterized by the geometrical component:

$$\Gamma_{ij}^{\chi\sigma}(\Delta E) = \frac{2\pi}{\hbar} \sum_k (\tau_{ij}^\chi)^* \tau_{ji}^\chi \delta(\varepsilon_{i\sigma}^\chi - \Delta E).$$

(7)

The argument $\Delta E$ of the rate $\Gamma_{ij}^{\chi\sigma}$ is the energy difference $E_{N+1} - E_N$ of the many body states involved in the tunnelling process, sometimes written in Eq. (6) in terms of the operator $H_{sys}$.

Until now we only concentrated on the sequential tunnelling processes in the system. We still have to discuss the term in Eq. (5) which contains the effective Hamiltonian $H_{eff}$. The latter is defined as:

$$H_{eff} = \frac{1}{2\pi} \sum_{NE} \sum_{k\sigma} \sum_{ij} \mathcal{P}_{NE} \left[ d_{i\sigma}^\dagger \Gamma_{ij}^{\chi\sigma} (E - H_{sys}) p_{\chi} (E - H_{sys}) d_{j\sigma} \right] \mathcal{P}_{NE},$$

(8)

where the principal part function $p_{\chi}(x) = -\text{Re} \Psi \left[ \frac{1}{\pi} + \frac{1}{2\pi i \sigma T} (x - \mu_{\chi}) \right]$, has been introduced, with $T$ being the temperature and $\Psi$ the digamma function. Eq. (8) shows that the effective Hamiltonian is block diagonal in particle number and energy, exactly as the density matrix in the secular approximation. Consequently, it only influences the dynamics of the system in presence of degenerate states. The effective Hamiltonian depends on the details of the system, yet in all cases it is bias and gate voltage dependent and this property has important consequences on the interference blocking phenomena that we are considering.

A natural expression for the current operators is obtained in terms of the time derivative of the reduced density matrix:

$$\langle I_S + I_D \rangle = \sum_{NE} \text{Tr} \left\{ N\rho^{NE} \right\},$$

(9)
where $I_{S/D}$ are the current operators calculated for the source and the drain interfaces. Conventionally we assume the current to be positive when it increases the charge on the molecule. Thus, in the stationary limit, $\langle I_S + I_D \rangle$ is zero. The stationary current is obtained as the average:

$$\langle I_S \rangle = \text{Tr} \{ \rho_{\text{stat}} I_S \} = -\langle I_D \rangle,$$

(10)

where $\rho_{\text{stat}} = \lim_{t \to \infty} \rho(t)$ is the stationary density operator that can be found from

$$\dot{\rho}_{\text{stat}} = L \rho_{\text{stat}} = 0,$$

(11)

where $L$ is the full Liouville operator defined in (5). Finally, by following for example the procedure described in detail in [20], one finds the explicit expressions for the current operators:

$$I_x = \sum_{\sigma \sigma' ij} \rho_{NE} \left[ d_{i\sigma} r^{\sigma \sigma'}_{ij} (H_{\text{sys}} - E) f^+ (H_{\text{sys}} - E) d_{j\sigma}^\dagger + d_{j\sigma}^\dagger r^{\sigma \sigma'}_{ij} (E - H_{\text{sys}}) f^- (E - H_{\text{sys}}) d_{i\sigma} \right] \rho_{NE},$$

(12)

where the energy renormalization terms, present in the generalized master equation (5), do not appear.

### 3 Blocking states

The dynamics of SETs is essentially described by sequential tunnelling events at the source and drain lead which connect the many-body eigenstates of the system. It is natural to define, in this picture, a blocking state as a state which the system can enter but from which it can not escape. When the system occupies a blocking state the particle number can not change in time and the current vanishes. If degenerate states participate in transport, they can lead to interference since, like the two arms of an electronic interferometer, they are populated simultaneously (see Fig. 1). In particular, depending on the external parameters they can form linear superpositions which behave as blocking states. If a blocking state is the linear combination of degenerate states we call it interference blocking state.

We present in this section the general criteria for the identification of a blocking state and more specifically of an interference blocking state. First of all we will proceed to a classification of the tunnelling processes needed for a many-body description of the electron transport through a nanojunction.
3.1 Classification of the tunnelling processes

For the description of the tunnelling dynamics contained in the superoperator $\mathcal{L}_{\text{tun}}$ (see Eqs. (5) and (6)), it is convenient to classify all possible tunnelling events according to four categories: i) Creation (Annihilation) tunnelling events that increase (decrease) by one the number of electrons in the system, ii) Source (Drain) tunnelling that involves the lead with the higher (lower) chemical potential, iii) $\uparrow$ ($\downarrow$) tunnelling that involves an electron with spin up (down) with respect of the corresponding lead quantization axis, iv) Gain (Loss) tunnelling that increases (decreases) the energy in the system.

Using categories i)-iii) we can efficiently organize the matrix elements of the system component of $H_{\text{tun}}$ in the matrices:

$$
T_{N,EE'}^+ = \begin{pmatrix}
\gamma_{S\uparrow}^+ & \gamma_{S\downarrow}^+ & \gamma_{D\uparrow}^+ & \gamma_{D\downarrow}^+
\end{pmatrix}
$$

$$
T_{N,EE'}^- = \begin{pmatrix}
\gamma_{S\uparrow}^- & \gamma_{S\downarrow}^- & \gamma_{D\uparrow}^- & \gamma_{D\downarrow}^-
\end{pmatrix}
$$

(13)

where $S, D$ means source and drain, respectively, and

$$
\gamma_{S\sigma}^\pm = \sum_i \langle \ell', \tau', E'|d_{i\sigma}^\dagger|N+1, \{\ell', \tau', E', \ell, \tau\rangle \rangle
$$

is a matrix in itself, defined for every creation transition from a state with particle number $N$ and energy $E$ to one with $N+1$ particles and energy $E'$. We indicate correspondingly in the following transitions involving $\gamma_{S\sigma}^\pm$ and $\gamma_{D\sigma}^\pm$ as source-creation and drain-creation transitions. The compact notation $\{\ell, \tau\}$ indicates all possible combinations of the quantum numbers $\ell$ and $\tau$. It follows that the size of $\gamma_{S\sigma}^\pm$ is $\text{mul}(N+1,E') \times \text{mul}(N,E)$ where the function $\text{mul}(N,E)$ gives the degeneracy of the many-body energy level with $N$ particles and energy $E$. Analogously

$$
\gamma_{D\sigma}^\pm = \sum_i \langle \ell', \tau', E'|d_{i\sigma}|N-1, \{\ell', \tau', E', \ell, \tau\rangle \rangle
$$

(15)

accounts for the annihilation transitions.

The fourth category concerns energy and it is intimately related to the first and the second. Not all transitions are in fact allowed: due to the energy conservation and the Pauli exclusion principle holding in the fermionic leads, the energy gain (loss) of the system associated to a gain (loss) transition is governed by the bias voltage. These energy conditions, for the case of equal potential drop at the source and drain lead ($c = 1/2$) are summarized in the table 1 and illustrated in Fig. 2.

The quantity $\Delta E := E_f - E_i$, is the difference between the energy of the final and initial state of the system and the condition $\leq$ is in reality smoothed due to the thermal broadening of the Fermi distributions. For simplicity we set the zero of the energy at the chemical potential of the unbiased device. In the table 1 one reads for example that in a source-creation tunnelling event the system can gain at maximum
Table 1 Energy conditions for tunnelling transitions between the many-body eigenstates of the system. The quantity $\Delta E = E_f - E_i$ is the difference between the energies of the final and initial many-body states of the system involved in the transition. The bias energy $eV_b$ is assumed to be positive. From [22].

<table>
<thead>
<tr>
<th>Tunnelling process</th>
<th>Energy condition</th>
</tr>
</thead>
<tbody>
<tr>
<td>Source-Creation</td>
<td>$\Delta E \leq +eV_b/2$</td>
</tr>
<tr>
<td>Source-Annihilation</td>
<td>$\Delta E \leq -eV_b/2$</td>
</tr>
<tr>
<td>Drain-Creation</td>
<td>$\Delta E \leq -eV_b/2$</td>
</tr>
<tr>
<td>Drain-Annihilation</td>
<td>$\Delta E \leq +eV_b/2$</td>
</tr>
</tbody>
</table>

$\frac{eV_b}{2}$ or that in a source-annihilation and drain-creation transition the system looses at least an energy of $\frac{eV_b}{2}$.

From table 1 one also deduces that, from whatever initial state, it is always possible to reach the lowest energy state (the global minimum) via a series of energetically allowed transitions. Vice versa, not all states can be reached starting from the global minimum. Thus, the only relevant states for the transport in the stationary regime are the states that can be reached from the global minimum via a finite number of energetically allowed transitions.

Fig. 2 Energetically available transitions from an $N$ particle level. The patterned rectangles indicate the energy range of energetically available source (S) and drain (D) transitions both to states with $N + 1$ and $N - 1$ particles. The arrows show examples of both allowed and forbidden transitions. From [22].
3.2 Subspace of decoupled states

In the process of detecting the blocking states we observe first that some states do not participate in the transport and can be excluded a priori from any consideration. These are states with zero transition elements to all other relevant states. Within the subspace with $N$ particles and energy $E$ the decoupled states span the vector space:

$$D_{N,E} = \bigcap_{E'} \left[ \ker T_{N,EE'}^+ \cap \ker T_{N,EE'}^- \right]$$

where $E'$ is the energy of a relevant state with $N+1$ or $N-1$ particles, respectively. The function $\ker M$ returns the null space of the linear application associated to the matrix $M$.

The decoupled space $D_{N,E}$ as presented in equation (16) is constructed as follows. Let us consider a generic many-body state $|\psi_{NE}\rangle$ with $N$ particles and energy $E$ and let $v$ be the vector of its components in the basis $|N\ell\tau_E\rangle$. The vector $T_{N,EE'}^+ v$ has thus $4 \times \text{mul}(N+1,E')$ components and consists of all possible transition amplitudes from $|\psi_{NE}\rangle$ to all possible states with $N+1$ particles and energy $E'$. Consequently $\ker T_{N,EE'}^+$ contains the vectors $v$ associated to states with $N$ particles and energy $E$ which are decoupled from all possible states with $N+1$ particles and energy $E'$. Analogously holds for the significance of $\ker T_{N,EE'}^-$. The intersections in (16) and the condition on $E'$ ensure that $D_{N,E}$ contains only states decoupled at the same time from all other states relevant for transport in the stationary regime. We emphasize that, due to the condition on the energy $E'$, the decoupled space $D_{N,E}$ is a dynamical concept that depends on the applied gate and bias across the I-SET. The coupled space $C_{N,E}$ is the orthogonal complement of $D_{N,E}$ in the Hilbert space with $N$ particles and energy $E$. The blocking states belong to it.

As a first simple application of the ideas presented so far, let us consider the SET at zero bias. According to the table 1 the system can only undergo loss tunnelling events and the global energy minimum is the only blocking state, in accordance with the observation that the system is in equilibrium with the leads and that we measure the energy starting from the equilibrium chemical potential$^1$. The potential $V_g$ of the gate electrode defines the particle number of the global minimum and, by sweeping $V_g$ at zero bias, one can change the number of electrons on the system one by one. This situation, the Coulomb blockade, remains unchanged until the bias is high enough to open a gain transition that unblocks the global minimum. Then, the current can flow. Depending on the gate this first unblocking transition can be of the kind source-creation or drain-annihilation. Correspondingly, the current is associated to $N \leftrightarrow N+1$ or $N \leftrightarrow N-1$ oscillations, where $N$ is the particle number of the global minimum.

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$^1$ If the equilibrium chemical potential is not set to zero the many-body energy spectrum should be substituted with the spectrum of the many-body free energy $(H_{\text{sys}} - \mu_0 N)$ where $\mu_0$ is the chemical potential of the leads at zero bias. The rest of the argumentation remains unchanged.
3.3 Blocking conditions

At finite bias the condition which defines a blocking state becomes more elaborate:

1. The blocking state must be achievable from the global minimum with a finite number of allowed transitions.
2. All matrix elements corresponding to energetically allowed transitions outgoing from the blocking state should vanish: in particular all matrix elements corresponding to \( E_f - E_{\text{block}} < -\frac{eV_b}{2} \) and for \( |E_f - E_{\text{block}}| < \frac{eV_b}{2} \) only the ones corresponding to the drain-annihilation and source-creation transitions.

The first condition ensures the blocking state to be populated in the stationary regime. The second is a modification of the generic definition of blocking state restricted to energetically allowed transitions and it can be written in terms of the tunnelling matrices \( T_{N,EE'}^+ \) and \( T_{N,EE'}^- \). For each many-body energy level \( |NE\rangle \), the space spanned by the blocking states reads then:

\[
\mathcal{B}_{N,E} = \mathcal{B}_{N,E}^{(1)} \cap \mathcal{B}_{N,E}^{(2)} \cap \mathcal{C}_{N,E} \tag{17}
\]

with

\[
\mathcal{B}_{N,E}^{(1)} = \bigcap_{E'} \left\{ \mathcal{P}_{NE} \left[ \text{ker} \left( T_{N,EE'}^+, T_D \right) \right] \cap \mathcal{P}_{NE} \left[ \text{ker} \left( T_{N,EE'}^-, T_S \right) \right] \right\},
\]

\[
\mathcal{B}_{N,E}^{(2)} = \bigcap_{E''} \left[ \text{ker} \left( T_{N,EE''}^+, T_D \right) \cap \text{ker} \left( T_{N,EE''}^-, T_S \right) \right]. \tag{18}
\]

In Eq. (18) we introduced the matrices \( T_D = (0, 1)^T \) and \( T_S = (1, 0)^T \) with \( I \) being the identity matrix and \( 0 \) the zero matrix, both of dimension \( 2 \times \text{mul}(N + 1, E') \) for \( T_D \) and \( 2 \times \text{mul}(N - 1, E') \) for \( T_S \). The energies \( E' \) and \( E'' \) satisfy the inequalities \( |E' - E| < \frac{eV_b}{2} \) and \( E'' - E < -\frac{eV_b}{2} \), respectively, and \( \mathcal{P}_{NE} \) is the projection on the \( N \) particle space with energy \( E \).

The first kernel in \( \mathcal{B}_{N,E}^{(1)} \) together with the projector \( \mathcal{P}_{NE} \) gives all linear combinations of \( N \) particle degenerate states which have a finite creation transition involving the drain but not the source lead. This condition can in fact be expressed as a non-homogeneous linear equation for the vector \( v \) of the components in the many body basis of the generic \( N \) particle state with energy \( E \):

\[
T_{N,EE'}^+ v = b, \tag{19}
\]

where \( b \) is a generic vector of length \( 4 \times \text{mul}(N + 1, E') \) whose first \( 2 \times \text{mul}(N + 1, E') \) components (the source transition amplitudes) are set to zero. Due to the form of \( b \), it is convenient to transform Eq. (19) into an homogeneous equation for a larger space of dimension \( \text{mul}(N, E) + 2 \times \text{mul}(N + 1, E') \) which also contains the non-zero elements of \( b \) and finally project the solutions of this equation on the orig-
inal space. With this procedure we can identify the space of the solutions of (19) with:

\[ V = \mathcal{P}_{NE} \left( \ker \left( T_{N,EE'}, T_D \right) \right) . \]  

(20)

The second kernel in \( \mathcal{P}^{(1)}_{N,E} \) takes care of the annihilation transitions in a similar way. Notice that \( V \) also contains vectors that are decoupled at both leads. This redundancy is cured in (17) by the intersection with the coupled space \( \mathcal{C}_{NE} \).

The conditions (18) are the generalization of the conditions over the tunnelling amplitudes that we gave in the introduction (Eq. (1)). That very simple condition captures the essence of the effect, but it is only valid under certain conditions: the spin channels should be independent, the relevant energy levels only two and the transition has to be between a non degenerate and a doubly degenerate level. Equation (18), on the contrary, is completely general. At the end of the this section we will show explicitly the equivalence of the two approaches in the simple case.

For most particle numbers \( N \) and energies \( E \), and sufficiently high bias, \( \mathcal{P}_{N,E} \) is empty. Yet, blocking states exist and the dimension of \( \mathcal{P}_{N,E} \) can even be larger than one as we will show explicitly in Section 5 for the triple dot I-SET. Moreover, it is most probable to find interference blocking states among ground states due to the small number of intersections appearing in (18) in this situation. Nevertheless also excited states can block the current as we will show in the next section.

The case of spin polarized leads is already included in the formalism both in the parallel and non parallel configuration. In the parallel case one quantization axis is naturally defined on the whole structure and \( \sigma \) in Eqs. (14) and (15) is defined along this axis. In the case of non parallel polarized leads instead it is enough to consider \( d^\dagger_{i\sigma} \) and \( d_{i\sigma} \) in equations (14) and (15), respectively, with \( \sigma \) along the quantization axis of the lead \( \chi \). It is interesting to note that in that case, no blocking states can be found unless the polarization of one of the leads is \( P = 1 \). The spin channel can in fact be closed only one at the time via linear combination of different spin states.

A last comment on the definition of the blocking conditions is necessary. A blocking state is a stationary solution of the equation (5) since by definition it does not evolve in time. The density matrix associated to one of the blocking states discussed so far i) commutes with the system Hamiltonian since it is a state with given particle number and energy; ii) it is the solution of the equation \( Z_{\text{tun}} \rho = 0 \) since the probability of tunnelling out from a blocking state vanishes, independent of the final state. Nevertheless, a third condition is needed to satisfy the condition of stationarity:

3. The density matrix \( \rho_{\text{block}} \) associated to the blocking state should commute with the effective Hamiltonian \( H_{\text{eff}} \) which renormalizes the coherent dynamics of the system to the lowest non vanishing order in the coupling to the leads:

\[ [\rho_{\text{block}}, H_{\text{eff}}] = 0. \]  

(21)

The specific form of \( H_{\text{eff}} \) varies with the details of the system. Yet its generic bias and gate voltage dependence implies that, if present, the current blocking oc-
occurs only at specific values of the bias for each gate voltage. Further, if an energy level has multiple blocking states and the effective Hamiltonian distinguishes between them, selective current blocking, and correspondingly all electrical preparation of the system in one specific degenerate state, can be achieved. In particular, for spin polarized leads, the system can be prepared in a particular spin state without the application of any external magnetic field as we will show explicitly in Section 6.

Before continuing with the discussion, in the following sections, we derive here the equation (1) as a specific example of the general theory presented so far. That equation represents the interference blocking condition for the simplest possible configuration involving only a non degenerate and a doubly degenerate state. Let us consider for simplicity a spinless system and a gate and bias condition that restricts the set of relevant many-body states to three: one with \( N \) particles and two (degenerate) with \( N + 1 \) or \( N - 1 \) particles. The interference blocking state, if it exists, belongs to the \( N \pm 1 \) level. There is only one interesting tunnelling matrix to be analyzed, namely \( T_{N \pm 1} \). Let us take for it the generic form:

\[
T_{N \pm 1} = \begin{pmatrix}
\gamma_1 & \gamma_2 \\
\gamma_0 & \gamma_2
\end{pmatrix}
\]  

(22)

where \( S \) and \( D \) indicate source and drain, respectively and 1 and 2 label the two degenerate states with \( N \pm 1 \) particles. \( \gamma_{S(D)} \) are the elements of the \( \gamma^T_{S(D)} \) matrices introduced in Eqs. (14) and (15). The decoupled space reads:

\[
D_{N \pm 1} = \ker T_{N \pm 1}.
\]

(23)

Since the \( N \pm 1 \) particles relevant Hilbert space has dimension 2 the only possibility to find a blocking state is that \( D_{N \pm 1} = 0 \). In other terms:

\[
\det T_{N \pm 1} = \gamma_1 \gamma_2 - \gamma_0 \gamma_2 \neq 0
\]

(24)

This condition is identical to Eq. (1). The blocking state can finally be calculated as:

\[
\mathcal{B}_{N+1} = \mathcal{P}_{N+1} \ker \begin{pmatrix}
\gamma_1 & \gamma_2 \\
\gamma_0 & \gamma_2
\end{pmatrix} \cap \mathcal{C}_{N+1}
\]

(25)

or

\[
\mathcal{B}_{N-1} = \mathcal{P}_{N-1} \ker \begin{pmatrix}
\gamma_1 & \gamma_2 \\
\gamma_0 & \gamma_2
\end{pmatrix} \cap \mathcal{C}_{N-1},
\]

(26)

where the \( \mathcal{C}_{N \pm 1} \) is, in the relevant case, the entire space and the projector \( \mathcal{P}_{N \pm 1} \) simply removes the last component of the vector that defines the one dimensional kernel.

\footnote{The assumption of a spinless system is not restrictive for parallel polarized leads and transitions between a spin singlet and a doublet since the different spin sectors decouple from each other.}
4 The benzene I-SET

The general ideas on interference blocking presented in the previous section apply to a large class of devices. As a first example of interference SET based on quantum dot molecules we consider a benzene single molecule transistor. We treat the transport through the benzene I-SET in two different setups, the para and the meta configuration, depending on the position of the leads with respect to the benzene molecule (see Fig. 3). Similar to [47], we start from an interacting Hamiltonian of isolated benzene where only the localized $p_z$ orbitals are considered and the ions are assumed to have the same spatial symmetry as the relevant electrons. We calculate the $4^6 = 4096$ energy eigenstates of the benzene Hamiltonian numerically. Subsequently, with the help of group theory, we classify the eigenstates according to their different symmetries and thus give a group-theoretical explanation to the large degeneracies occurring between the electronic states. For example, while the six-particles ground state ($A_{1g}$ symmetry) is non-degenerate, there exist four seven-particle ground states due to spin and orbital ($E_{2u}$ symmetry) degeneracy. Fingerprints of these orbital symmetries are clearly visible in the strong differences in the stability diagrams obtained by coupling the benzene I-SET to the leads in the meta and para configurations (see Fig. 4). Striking are the selective reduction of conductance and the appearance of regions of interference driven current blocking with associated negative differential conductance (NDC) when changing from the para to the meta configuration.

![Fig. 3](image_url)  
Schematic representation of the two different setups for the benzene I-SET considered in this paper. The molecule, lying on a dielectric substrate, is weakly contacted to source and drain leads as well as capacitively gated. From [20].
4.1 Model Hamiltonian

For the description of the benzene molecule weakly coupled to source and drain leads, we adopt the total Hamiltonian (2) introduced in Section 2 where the first term is now the interacting Hamiltonian for isolated benzene \([44, 45, 46]\) that we recall here for clarity:

\[
H^0_{\text{ben}} = \xi_0 \sum_{i, \sigma} d_{i \sigma}^{\dagger} d_{i \sigma} + b \sum_{i, \sigma} \left( d_{i \sigma}^{\dagger} d_{i+1 \sigma} + d_{i+1 \sigma}^{\dagger} d_{i \sigma} \right) \\
+ U \sum_i \left( n_{i \uparrow} - \frac{1}{2} \right) \left( n_{i \downarrow} - \frac{1}{2} \right) \\
+ V \sum_i \left( n_{i \uparrow} + n_{i \downarrow} - 1 \right) \left( n_{i+1 \uparrow} + n_{i+1 \downarrow} - 1 \right),
\]

(27)

where \(d_{i \sigma}^{\dagger}\) creates an electron of spin \(\sigma\) in the \(p_z\) orbital of carbon \(i, i = 1, \ldots, 6\) runs over the six carbon atoms of benzene and \(n_{i \sigma} = d_{i \sigma}^{\dagger} d_{i \sigma}\). Only the \(p_z\) orbitals (one per carbon atom) are explicitly taken into account, while the core electrons and the nuclei are combined into frozen ions, with the same spatial symmetry as the relevant electrons. They contribute only to the constant terms of the Hamiltonian and enforce particle-hole symmetry. Mechanical oscillations are neglected and all atoms are considered at their equilibrium position.

This Hamiltonian for isolated benzene is respecting the \(D_{6h}\) symmetry of the molecule. Since for every site there are 4 different possible configurations (|0\rangle, |↑\rangle, |↓\rangle, |↑↓\rangle), the Fock space has the dimension \(4^6 = 4096\), which requires a numerical treatment. Though the diagonalization of the Hamiltonian is not a numerical challenge, it turns out to be of benefit for the physical understanding of the transport processes to divide \(H_{\text{ben}}\) into blocks, according to the number \(N\) of \(p_z\) electrons (from 0 to 12), the \(z\) projection \(S_z\) of the total spin and the orbital symmetries of benzene (see Table 2).

The parameters \(b, U,\) and \(V\) for isolated benzene are given in the literature \([48]\) and are chosen to fit optical excitation spectra. The presence, in the molecular I-SET, of metallic electrodes and the dielectric is expected to cause a substantial renormalization of \(U\) and \(V\) \([49, 50, 51]\). Nevertheless, we do not expect the main results of this work to be affected by this change. We consider the benzene molecule weakly coupled to the leads. Thus, to first approximation, we assume the symmetry of the isolated molecule not to be changed by the screening. Perturbations due to the lead-molecule contacts reduce the symmetry in the molecular junction. They are included in \(H'_{\text{ben}}\) (see Eq. (64) and (65)) and will be treated in Section 7.

The effect of the gate is included as a renormalization of the on-site energy \(\xi = \xi_0 - eV_g\) \((V_g\) is the gate voltage) and we conventionally set \(V_g = 0\) at the charge neutrality point. Source and drain leads are two reservoirs of non-interacting electrons:

\[
H_{\text{leads}} = \sum_{\chi, k, \sigma} (\epsilon_k - \mu_{\chi}) c_{\chi, k \sigma}^{\dagger} c_{\chi, k \sigma},
\]

where \(\chi = L, R\) stands for the left or right lead and the chemical potentials \(\mu_{\chi}\) of the leads depend on the applied bias voltage \(\mu_{L, R} = \mu_0 \pm \frac{V_b}{2}\). In the following we will measure the energy starting from the equi-
librium chemical potential $\mu_0 = 0$. We specialize the tunnelling Hamiltonian (4) to the following form

$$H_{\text{tun}} = t \sum_{\chi \lambda \sigma} \left( d_{\chi \lambda \sigma}^\dagger c_{\chi \lambda \sigma} + c_{\chi \lambda \sigma}^\dagger d_{\chi \lambda \sigma} \right),$$  \hspace{1cm} (28)

where we define $d_{\chi \lambda \sigma}$ as the creator of an electron in the benzene carbon atom which is closest to the lead $\chi$. In particular $d_{R \sigma}^\dagger := d_{4 \sigma}^\dagger, d_{5 \sigma}$ respectively in the para and meta configuration, while $d_{L \sigma}^\dagger := d_{1 \sigma}$ in both setups (see Fig. 6 for the numbering of the benzene carbon atoms).

### 4.2 Symmetry of the benzene eigenstates

In this section, we will review the symmetry characteristics of the eigenstates of the interacting Hamiltonian of benzene, focusing on the symmetry operations $\sigma_v$ and $C_n$ which have a major impact on the electronic transport through the molecular I-SET. Benzene belongs to the $D_{6h}$ point group. Depending on their behavior under symmetry operations, one can classify the molecular orbitals by their belonging to a certain irreducible representation of the point group. Table 2 shows an overview of the states of the neutral molecule (the 6 particle states) sorted by $S_z$ and symmetries. The eigenstates of the interacting benzene molecule have either $A$-, $B$- or $E$-type symmetries. While orbitals having $A$ or $B$ symmetries can only be spin degenerate, states with an $E$ symmetry show an additional twofold orbital degeneracy, essential for the explanation of the transport features occurring in the meta configuration.

Transport at low bias is described in terms of transitions between ground states with different particle number. Table 3 shows the symmetries of the ground states (and of some first excited states) of interacting benzene for all possible particle numbers. Ground state transitions occur both between orbitally non-degenerate states (with $A$ and $B$ symmetry), as well as between orbitally degenerate and non-degenerate states ($E$- to $A$-type states).

The interacting benzene Hamiltonian commutes with all the symmetry operations of the $D_{6h}$ point group, thus it has a set of common eigenvectors with each operation. The element of $D_{6h}$ of special interest for the para configuration is $\sigma_v$, i.e., the reflection about the plane through the contact atoms and perpendicular to the molecular plane. The molecular orbitals with $A$ and $B$ symmetry are eigenstates of $\sigma_v$ with eigenvalue $\pm 1$, i.e., they are either symmetric or antisymmetric with respect to the $\sigma_v$ operation. The behavior of the $E$-type orbitals under $\sigma_v$ is basis dependent, yet one can always choose a basis in which one orbital is symmetric and the other one antisymmetric.

Let us now consider the generic transition amplitude $\langle N | d_{\alpha \tau} | N + 1 \rangle$, where $d_{\alpha \tau}$ destroys an electron of spin $\tau$ on the contact atom closest to the $\alpha$ lead. It is useful to rewrite this amplitude in the form
Table 2. Overview of the 6 particle states of benzene, sorted by $S_z$ and symmetry. Orbitals with $A$- and $B$-type of symmetry show no degeneracy, while $E$-type orbitals are doubly degenerate. From [20].

<table>
<thead>
<tr>
<th>$N$</th>
<th>$S_z [h]$</th>
<th>number of states</th>
<th>states with given symmetry</th>
</tr>
</thead>
<tbody>
<tr>
<td>6</td>
<td>3</td>
<td>1</td>
<td>$1 B_{1u}$</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>$4 A_{1g}$</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>$2 A_{2g}$</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>$2 \times 6 E_{2g}$</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>$4 B_{1u}$</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>$2 B_{2u}$</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>$2 \times 6 E_{1u}$</td>
</tr>
<tr>
<td>2</td>
<td>36</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>225</td>
<td></td>
<td>$16 A_{1g}$</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>$20 A_{2g}$</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>$2 \times 36 E_{2g}$</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>$22 B_{1u}$</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>$17 B_{2u}$</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>$2 \times 39 E_{1u}$</td>
</tr>
<tr>
<td>0</td>
<td>400</td>
<td></td>
<td>$38 A_{1g}$</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>$30 A_{2g}$</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>$2 \times 66 E_{2g}$</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>$38 B_{1u}$</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>$30 B_{2u}$</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>$2 \times 66 E_{1u}$</td>
</tr>
<tr>
<td>-1</td>
<td>225</td>
<td></td>
<td>$\vdots$</td>
</tr>
<tr>
<td>-2</td>
<td>36</td>
<td></td>
<td>$\vdots$</td>
</tr>
<tr>
<td>-3</td>
<td>1</td>
<td></td>
<td>$\vdots$</td>
</tr>
</tbody>
</table>

\[
\langle N | d_{\alpha \tau} | N + 1 \rangle = \langle N | \sigma^\dagger \sigma_{\alpha} d_{\alpha \tau} \sigma^\dagger \sigma_{\tau} | N + 1 \rangle,
\]

(29)

where we have used the property $\sigma^\dagger \sigma = 1$. Since in the para configuration both contact atoms lie in the mirror plane $\sigma_v$, it follows $\sigma_{v} d_{\alpha} \sigma^\dagger_{v} = d_{\alpha}$. If the participating states are both symmetric under $\sigma_v$, Eq. (29) becomes

\[
\langle N, \text{sym} | \sigma_v^\dagger d_{\alpha \tau} \sigma_v | N + 1, \text{sym} \rangle = \langle N, \text{sym} | d_{\alpha \tau} | N + 1, \text{sym} \rangle
\]

(30)

and analogously in the case that both states are antisymmetric. For states with different symmetry it is

\[
\langle N, \text{sym} | d_{\alpha \tau} | N + 1, \text{antisym} \rangle = -\langle N, \text{sym} | d_{\alpha \tau} | N + 1, \text{antisym} \rangle = 0.
\]

(31)

In other terms, there is a selection rule that forbids transitions between symmetric and antisymmetric states. Further, since the ground state of the neutral molecule is symmetric, for the transport calculations in the para configuration we select the effective Hilbert space containing only states symmetric with respect to $\sigma_v$. Correspondingly, when referring to the $N$ particle ground state we mean the energetically
lowest symmetric state. For example in the case of 4 and 8 particle states it is the first excited state to be the effective ground state. In the para configuration also the orbital degeneracy of the $E^{-}$-type states is effectively cancelled due to the selection of the symmetric orbital (see Table 3).

Small violations of this selection rule, due e.g. to molecular vibrations or coupling to an electromagnetic bath, result in the weak connection of different metastable electronic subspaces. We suggest this mechanism as a possible explanation for the switching and hysteretic behaviour reported in various molecular junctions. This effect is not addressed in this work.

For a simpler analysis of the different transport characteristics it is useful to introduce a unified geometrical description of the two configurations. In both cases, one lead is rotated by an angle $\phi$ with respect to the position of the other lead. Hence we can write the creator of an electron in the right contact atom $d_{R\tau}^\dagger$ in terms of the creation operator of the left contact atom and the rotation operator:

$$d_{R\tau}^\dagger = R_{\phi}^\dagger d_{L\tau}^\dagger R_{\phi}, \quad (32)$$

where $R_{\phi}$ is the rotation operator for the anticlockwise rotation of an angle $\phi$ around the axis perpendicular to the molecular plane and piercing the center of the benzene ring; $\phi = \pi$ for the para and $\phi = (2\pi/3)$ for the meta configuration.

Table 3 Degeneracy, energy and symmetry of the ground states of the isolated benzene molecule for different particle numbers. We choose the on-site and inter-site Coulomb interactions to be $U = 10eV, V = 6eV$, and the hopping to be $b = -2.5eV$. Notice, however, that screening effects from the leads and the dielectric are expected to renormalize the energy of the benzene many-body states. From [20].

<table>
<thead>
<tr>
<th>$N$</th>
<th>Degeneracy</th>
<th>Energy[eV] (at $\xi = 0$)</th>
<th>Symmetry</th>
<th>Symmetry behavior under $\sigma_v$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>1</td>
<td>0</td>
<td>$A_{1g}$</td>
<td>sym</td>
</tr>
<tr>
<td>1</td>
<td>2</td>
<td>-22</td>
<td>$A_{2u}$</td>
<td>sym</td>
</tr>
<tr>
<td>2</td>
<td>1</td>
<td>-42.25</td>
<td>$A_{1g}$</td>
<td>sym</td>
</tr>
<tr>
<td>3</td>
<td>4</td>
<td>-57.42</td>
<td>$E_{1g}$</td>
<td>2 sym, [2 antisym]</td>
</tr>
<tr>
<td>4</td>
<td>4</td>
<td>-57.42</td>
<td>$E_{1g}$</td>
<td>2 sym, [2 antisym]</td>
</tr>
<tr>
<td>5</td>
<td>1</td>
<td>-81.725</td>
<td>$A_{1g}$</td>
<td>sym</td>
</tr>
<tr>
<td>7</td>
<td>4</td>
<td>-76.675</td>
<td>$E_{2u}$</td>
<td>2 sym, [2 antisym]</td>
</tr>
<tr>
<td>8</td>
<td>[3]</td>
<td>[-68.87]</td>
<td>$A_{2u}$</td>
<td>[antisym]</td>
</tr>
<tr>
<td>9</td>
<td>4</td>
<td>-57.42</td>
<td>$E_{2u}$</td>
<td>2 sym, [2 antisym]</td>
</tr>
<tr>
<td>10</td>
<td>1</td>
<td>-42.25</td>
<td>$A_{1g}$</td>
<td>sym</td>
</tr>
<tr>
<td>11</td>
<td>2</td>
<td>-22</td>
<td>$B_{2g}$</td>
<td>sym</td>
</tr>
<tr>
<td>12</td>
<td>1</td>
<td>0</td>
<td>$A_{1g}$</td>
<td>sym</td>
</tr>
</tbody>
</table>

The energy eigenstates of the interacting Hamiltonian of benzene can be classified also in terms their quasi-angular momentum. In particular, the eigenstates of
the \( z \)-projection of the quasi angular momentum are the ones that diagonalize all operators \( \hat{R}_\phi \) with angles multiples of \( \pi/3 \). The corresponding eigenvalues are phase factors \( e^{-i\ell\phi} \) where \( h\ell \), the quasi-angular momentum of the state, is an integer multiple of \( \hbar \). The discrete rotation operator of an angle \( \phi = \pi \) (\( C_2 \) symmetry operation), is the one relevant for the para configuration. All orbitals are eigenstates of the \( C_2 \) rotation with the eigenvalue \( \pm 1 \).

The relevant rotation operator for the meta configuration corresponds to an angle \( \phi = 2\pi/3 \) (\( C_3 \) symmetry operation). Orbitals with an \( A \) or \( B \) symmetry are eigenstates of this operator with the eigenvalue \( +1 \) (angular momentum \( \ell = 0 \) or \( \ell = 3 \)). Hence we can already predict that there will be no difference based on rotational symmetry between the para and the meta configuration for transitions between states involving \( A \)- and \( B \)-type symmetries. Orbitals with \( E \) symmetry however behave quite differently under the \( C_3 \) operation. They are the pairs of states of angular momenta \( \ell = \pm 1 \) or \( \ell = \pm 2 \). The diagonal form of the rotation operator on the two-fold degenerate subspace of \( E \)-symmetry reads:

\[
    C_3 = \begin{pmatrix}
    e^{-|\ell| \frac{2\pi}{3} i} & 0 \\
    0 & e^{i|\ell| \frac{2\pi}{3} i}
    \end{pmatrix}
\]

For the two-fold orbitally degenerate 7-particle ground states \( |\ell| = 2 \). This analysis in terms of the quasi-angular momentum makes easier the calculation of the fundamental interference condition (1) given in the introduction. In fact the following relation holds between the transition amplitudes of the 6 and 7 particle ground states:

\[
    \gamma_R \equiv \langle 7, \ell |\tau |d^\dagger_R |6_R \rangle = \langle 7, \ell |\tau |d^\dagger_L \phi \rangle = e^{-i\phi} \gamma_L \]

(34)

and (1) follows directly.

### 4.3 Transport calculations

With the knowledge of the eigenstates and eigenvalues of the Hamiltonian for the isolated molecule, we implement Eq. (5) and look for a stationary solution. The symmetries of the eigenstates are reflected in the transition amplitudes contained in the generalized master equation. We find numerically its stationary solution and calculate the current and the differential conductance of the device. In Fig. 4 we present the stability diagram for the benzene I-SET contacted in the para (upper panel) and meta position (lower panel). Bright ground state transition lines delimit diamonds of zero differential conductance typical for the Coulomb blockade regime, while a rich pattern of satellite lines represents the transitions between excited states. Though several differences can be noticed, most striking are the suppression of the linear conductance, the appearance of negative differential conductance (NDC) and the strong suppression of the current at the right(left) border of the 7 (5) particle diamond when passing from the para to the meta configuration. All these features
are different manifestations of the interference between orbitally degenerate states and ultimately reveal the specific symmetry of benzene.

![Fig. 4](image-url)

Fig. 4 Stability diagram for the benzene I-SET contacted in the para (above) and meta (below) configuration. Dot-dashed lines highlight the conductance cuts presented in Fig. 5, the dashed lines the regions corresponding to the current traces presented in Fig. 6 and Fig. 8, the dotted line the region corresponding to the current trace presented in Fig. 7. The parameters used are $U = 4|\ell|$, $V = 2.4|\ell|$, $k_B T = 0.04|\ell|$, $\hbar \Gamma_L = \hbar \Gamma_R = 10^{-3}|\ell|$. From [20].

### 4.3.1 Linear conductance

We study the linear transport regime both numerically and analytically. For the analytical calculation of the conductance we consider the low temperature limit where only ground states with $N$ and $N+1$ particles have considerable occupation probabilities, with $N$ fixed by the gate voltage. Therefore only transitions between these states are relevant and we can treat just the terms of (5) with $N$ and $N+1$ particles and the ground state energies $E_{gN}$ and $E_{gN+1}$, respectively. A closer look at (5) reveals that the spin coherences are decoupled from the other elements of the density matrix. Thus we can set them to zero, and write (5) in a block diagonal form in the basis of the ground states of $N$ and $N+1$ particles. Additionally, since the total Hamiltonian $H$ is symmetric in spin, the blocks of the GME with the same particle
but different spin quantum number \( \tau \) must be identical. Finally, since around the resonance the only populated states are the \( N \) and \( N+1 \) particle states, the conservation of probability implies that:

\[
1 = \sum_n \rho^N_n + \sum_m \rho^{N+1}_m,
\]

where \( \rho^N_n \) is the population of the \( N \)-particle ground state and \( n \) contains the orbital and spin quantum numbers. With all these observations we can reduce (5) to a much smaller set of coupled differential equations, that can be treated analytically. The stationary solution of this set of equations can be derived more easily by restricting in (5) to the dynamics generated by the sequential tunnelling Liouvillian \( \mathcal{L}_{\text{tun}} \).

We derive an analytical formula for the conductance close to the resonance between \( N \) and \( N+1 \) particle states as the first order coefficient of the Taylor series of the current in the bias:

\[
G_{N,N+1}(\Delta E) = 2e^2 \left( \frac{I_L I_R}{I_L + I_R} \right) A_{N,N+1} \left[ -\frac{S_{N}S_{N+1}f'(\Delta E)}{(S_{N+1} - S_{N})f(\Delta E) + S_{N}} \right]
\]

where \( \Delta E = E_{g,N} - E_{g,N+1} + eV_g \) is the energy difference between the benzene ground states with \( N \) and \( N+1 \) electrons diminished by a term linear in the gate voltage. Interference effects are contained in the overlap factor \( A_{N,N+1} \):

\[
A_{N,N+1} = \sum_{nm} |\langle N,n|d_L^\tau|N+1,m\rangle|^2 S_N S_{N+1} \sum_{nm} \langle N,n^\dagger d_{\tau}^\dagger|N+1,m\rangle^2
\]

where \( n \) and \( m \) label the \( S_N \)-fold and \( S_{N+1} \)-fold degenerate ground states with \( N \) and \( N+1 \) particles, respectively. In order to make the interference effects more visible we remind that \( d_{\tau}^\dagger = \mathcal{R}_\phi^N d_L^\tau \mathcal{R}_\phi^N \), with \( \phi = \pi \) for the para while \( \phi = 2\pi/3 \) for the meta configuration. Due to the behaviour of all eigenstates of \( H_{\text{ben}}^0 \) under discrete rotation operators with angles multiples of \( \pi/3 \), we can rewrite the overlap factor:

\[
A_{N,N+1} = \sum_{nm} |\langle N,n|d_L^\tau|N+1,m\rangle|^2 e^{i\phi_{nm}} S_N S_{N+1} \sum_{nm} \langle N,n|d_L^\tau|N+1,m\rangle^2
\]

where \( \phi_{nm} \) encloses the phase factors coming from the rotation of the states \( |N,n\rangle \) and \( |N+1,m\rangle \).

The effective Hamiltonian \( H_{\text{eff}} \) neglected in (36) only influences the dynamics of the coherences between orbitally degenerate states. Thus, Eq. (36) provides an exact description of transport for the para configuration, where orbital degeneracy is cancelled. Even if Eq. (36) captures the essential mechanism responsible for the conductance suppression, we have derived an exact analytical formula also for the meta configuration which can be found in Appendix B of [20].
In Fig. 5 we present an overview of the results of both the para and the meta configuration. A direct comparison of the conductance (including the $H_{\text{eff}}$ term of (5)) in the two configurations is displayed in the upper panel. The lower panel illustrates the effect of the energy non-conserving terms on the conductance in the meta configuration. The number of $p_z$ electrons on the molecule and the symmetry of the lowest energy states corresponding to the conductance valleys are reported. The symmetries displayed in the upper panel belong to the (effective) ground states in the para configuration, the corresponding symmetries for the meta configuration are shown in the lower panel.

Fig. 5 shows that the results for the para and the meta configuration coincide for the $10 \leftrightarrow 11$ and $11 \leftrightarrow 12$ transitions. The ground states with $N = 10, 11, 12$ particles have $A$- or $B$-type symmetries, they are therefore orbitally non-degenerate, no interference can occur and thus the transitions are invariant under configuration change. For every other transition we see a noticeable difference between the results of the two configurations (Fig. 5). In all these transitions one of the participating states is orbitally degenerate. First we notice that the linear conductance peaks for the $7 \leftrightarrow 8$ and $8 \leftrightarrow 9$ transitions in the para configuration are shifted with respect to the corresponding peaks in the meta configuration. The selection of an effective symmetric Hilbert space associated to the para configuration reduces the total degeneracy by cancelling the orbital degeneracy. In addition, the ground state energy of the 4 and 8 particle states is different in the two configurations, since in the para configuration the effective ground state is in reality the first excited state. The degeneracies $S_N, S_{N+1}$ of the participating states as well as the ground state energy are both entering the degeneracy term of Eq. (36)

$$\Delta = -\frac{f'(\Delta E)}{(S_{N+1} - S_N) f(\Delta E) + S_N}, \quad (39)$$

and determine the shift of the conductance peaks.

Yet, the most striking effect regarding transitions with orbitally degenerate states participating is the systematic suppression of the linear conductance when changing from the para to the meta configuration. The suppression is appreciable despite the conductance enhancement due to the principal part contributions to the GME (see Fig. 5, lower panel). Thus, we will for simplicity discard them in the following discussion.

The conductance suppression is determined by the combination of two effects: the reduction to the symmetric Hilbert space in the para configuration and the interference effects between degenerate orbitals in the meta configuration. The reduction to the symmetric Hilbert space implies also a lower number of conducting channels (see Table 4). One would expect a suppression of transport in the para configuration. As we can see from Table 4 on the example of the $6 \leftrightarrow 7$ transition peak, $\Delta_{\text{max}}$ is higher in the para configuration but not enough to fully explain the difference between the two configurations. The second effect determining transport is the interference between the $E$-type states, which is accounted for in the overlap factor $\Lambda$. The overlap factor is basis independent, thus we can write the transition probabili-
Fig. 5 Conductance of the benzene I-SET as a function of the gate voltage. Clearly visible are the peaks corresponding to the transitions between ground states with \( N \) and \( N + 1 \) particles. In the low conductance valleys the state of the system has a definite number of particles and symmetry as indicated in the upper panel for the para, in the lower for the meta configuration. Selective conductance suppression when changing from the meta to the para configuration is observed. From [20].

Table 4 Number of channels participating in transport, overlap factor and resonance value of the degeneracy term in the para and the meta configuration for the \( 6 \leftrightarrow 7 \) transition peak. It is \( C = |\langle 6 | d_{\tau} | 7 \rangle |^2 \), where \( \tau \) and \( \ell \) are the spin and the quasi angular momentum quantum numbers, respectively. The transition probabilities have the same value, since all four 7 particle states are in this basis equivalent (see Appendix C of [20] for a detailed proof). Under the \( C_2 \) rotation the symmetric 7 particle ground state does not acquire any phase factor. Under the \( C_3 \) rotation however, the two orbitally degenerate states acquire different phase factors, namely \( e^{\frac{2\pi}{3}i} \) and \( e^{-\frac{2\pi}{3}i} \), respectively. Thus the overlap factors \( A \) for the \( 6 \leftrightarrow 7 \) transition are:

<table>
<thead>
<tr>
<th>Configuration</th>
<th>Number of channels ((S_N, S_{N+1}))</th>
<th>Overlap factor ( A )</th>
<th>Degeneracy term ( \Delta_{\text{max}} [1/k_B T] )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Para</td>
<td>2</td>
<td>( C )</td>
<td>0.17</td>
</tr>
<tr>
<td>Meta</td>
<td>4</td>
<td>( \frac{1}{2}C )</td>
<td>0.11</td>
</tr>
</tbody>
</table>
\[ \Lambda_{\text{para}} = \frac{1}{2 \cdot 8C} \cdot |4C|^2 = C, \]
\[ \Lambda_{\text{meta}} = \frac{1}{4 \cdot 8C} \cdot \left| 2Ce^{+\frac{4\pi i}{3}} + 2Ce^{-\frac{4\pi i}{3}} \right|^2 = \frac{1}{8} C. \]

The linear conductance is determined by the product between the number of conducting channels, the overlap factor and the degeneracy term. Yet, it is the destructive interference between degenerate \( E \)-type orbitals, accounted for in the overlap factor \( \Lambda \), that gives the major contribution to the strong suppression of the conductance in the meta configuration.

### 4.3.2 Negative differential conductance (NDC) and current blocking

Interference effects between orbitally degenerate states are also affecting non-linear transport and producing in the meta configuration current blocking and thus NDC at the border of the 6 particle state diamond (Fig. 4). The upper panel of Fig. 6 shows the current through the benzene I-SET contacted in the meta configuration as a function of the bias voltage. The current is given for parameters corresponding to the white dashed line of Fig. 4. In this region only the 6 and 7 particle ground states are populated. At low bias the 6 particle state is mainly occupied. As the bias is raised, transitions \( 6 \leftrightarrow 7 \) occur and current flows. Above a certain bias threshold a blocking state is populated and the current drops. For the understanding of this non-linear current characteristics, we have to take into account energy conservation, the Pauli exclusion principle and the interference between participating states. For the visualization of the interference effects, we introduce the transition probability (averaged over the \( z \) coordinate and the spin \( \sigma \)):

\[ P(x, y; n, \tau) = \lim_{L \to \infty} \frac{1}{2L} \sum_{\sigma} \int_{-L/2}^{L/2} dz \langle 7g_n \tau | \psi_{\sigma}(r) | 6g \rangle^2 \]

(40)

for the physical 7 particle basis, \( i.e. \), the 7 particle basis that diagonalizes the stationary density matrix at a fixed bias. Here \( \tau \) is the spin quantum number, \( n = 1, 2 \) labels the two states of the physical basis which are linear combinations of the orbitally degenerate states \( |7g_\tau \rangle \) and can be interpreted as conduction channels. Each of the central panels of Fig. 6 are surface plots of (40) at the different bias voltages \( a-c \). The 7 particle ground states can interfere and thus generate nodes in the transition probability at the contact atom close to one or the other lead, but, in the meta configuration, never at both contact atoms at the same time.

Energetic considerations are illustrated in the lower panels of Fig. 6 for two key points of the current curve at positive biases. The left panel corresponds to the resonance peak of the current. Due to energy conservation, electrons can enter the molecule only from the left lead. On the contrary the exit is allowed at both leads. The current is suppressed when transitions occur to a state which cannot be depopulated (a blocking state). Since, energetically, transmissions to the 6 particle state
Fig. 6  Upper panel - Current through the benzene I-SET in the meta configuration calculated at bias and gate voltage conditions indicated by the dashed line of Fig. 4. A pronounced NDC with current blocking is visible. Middle panels - Transition probabilities between the 6 particle and each of the two 7 particle ground states for bias voltage values labelled $a - c$ in the upper panel. The transition to a blocking state is visible in the upper (lower) part of the $c$ $(a)$ panels. Lower panels - Sketch of the energetics for the $6 \rightarrow 7$ transition in the meta configuration at bias voltages corresponding to the resonance current peak and current blocking as indicated in the upper panel of this figure. From [20].
are allowed at both leads, each 7 particle state can always be depopulated and no blocking occurs.
The current blocking scenario is depicted in the lower right panel of Fig. 6. For large positive bias the transition from a 7 particle ground state to the 6 particle ground state is energetically forbidden at the left lead. Thus, for example, the c panel in Fig. 6 visualizes the current blocking situation yielding NDC: while for both channels there is a non-vanishing transition probability from the source lead to the molecule, for the upper channel a node prevents an electron from exiting to the drain lead. In the long time limit the blocking state gets fully populated while the non-blocking state is empty. At large negative bias the blocking scenario is depicted in the panel a that shows the left-right symmetry obtained by a reflection through a plane perpendicular to the molecule and passing through the carbon atoms atoms 6 and 3. The temperature sets the scale of the large bias condition and, correspondingly, the width of the current peak presented in Fig. 6 grows with it. The peak is not symmetric, though, its shape depends also on the energy renormalization introduced by the coupling to the leads[21] and described by the effective Hamiltonian (8). In fact the interference blocking is not a threshold effect in the bias. The complete blocking corresponds to a very precise bias which is determined by the form of $H_{\text{eff}}$. We will return to this point in Section 6, while discussing the spin dependent transport. Moreover, we remark that only a description that retains coherences between the degenerate 7 particle ground states correctly captures NDC at both positive and negative bias.

In contrast to the 6 → 7 transition, one does not observe NDC at the border of the 7 particle Coulomb diamond, but rather a strong suppression of the current. The upper panel of Fig. 7 shows the current through the benzene I-SET contacted in the meta configuration as a function of the bias voltage corresponding to the white dotted line of Fig. 4. The middle panels show the transition probabilities between each of the 7 particle and the 6 particle ground state. The lower panel of Fig. 7 shows a sketch of the energetics at positive bias corresponding to the “expected” resonance peak. Here electrons can enter the molecular dot at both leads, while the exit is energetically forbidden at the left lead. Thus, if the system is in the 7 particle state which is blocking the right lead, this state cannot be depopulated, becoming the blocking state. On the other hand, transitions from the 6 particle ground state to both 7 particle ground states are equally probable. Thus the blocking state will surely be populated at some time. The upper plot of the b panel in Fig. 7 shows the transition probability to the blocking state that accepts electrons from the source lead but cannot release electrons to the drain. As just proved, in this case the current blocking situation occurs already at the resonance bias voltage. For a higher positive bias, the transition probability from the blocking state at the drain lead increases and current can flow. This effect, though, can be captured only by taking into account also the $H_{\text{eff}}$ contribution to (5).

In the para configuration, the current as a function of the bias voltage is shown in Fig. 8. The current is given for parameters corresponding to the white dashed line of Fig. 4. In this case, no interference effects are visible. We see instead the typical step-like behavior of the current in the regime of single electron tunnelling. The panels on the right are the surface plots of
The upper plot shows the transition probability to the symmetric 7 particle state, the lower to the antisymmetric. Remember that in the para configuration only the symmetric states contribute to transport. Evidently the symmetric state is in the para configuration non-blocking. Additionally, since the coherences between orbitally degenerate states and therefore the energy non-conserving terms do not play any role in the transport, the physical basis states are not bias dependent. Thus in the para configuration there are always non-blocking states populated and no NDC can occur.

Fig. 8 Left panel - Current through the benzene I-SET in the para configuration calculated at bias and gate voltage conditions indicated by the dashed line of Fig. 4. No interference effects are visible. Right panels - Transition probabilities between the 6 particle and the symmetric and antisymmetric 7 particle ground states. From [20].

5 The triple dot I-SET

As a second example of I-SET we consider an artificial quantum dot molecule: i.e. the triple dot I-SET. The triple dot SET has been recently in the focus of intense theoretical [23, 24, 52, 53, 54, 55, 56] and experimental [57, 58, 59, 60] investigation
due to its capability of combining incoherent transport characteristics and signatures of molecular coherence. The triple dot I-SET that we consider here (Fig. 9) is the simplest structure with symmetry protected orbital degeneracy exhibiting interference blockade. Despite its relative simplicity this system displays different kinds of current blocking and it represents for this reason a suitable playground for the ideas presented in Section 3. In particular we will concentrate on the blockade that involves an excited triplet state: a regime which is not achievable in the benzene I-SET.

5.1 The model

The total Hamiltonian of the I-SET is in the generic form (2). We describe the system with an Hamiltonian in the extended Hubbard form:

\[ H = \sum_{i} \epsilon_i n_i + U \sum_{i<j} n_{i}\delta_{ij} + \sum_{i<j} V_{ij} \delta_{ij} \]

This denomination of the Pariser-Parr-Pople Hamiltonian is more common in the solid state community.
\begin{align}
H_{3d} &= \xi_0 \sum_{\sigma} d_{i\sigma}^{\dagger} d_{i\sigma} + b \sum_{\sigma} \left( d_{i\sigma}^{\dagger} d_{i+1\sigma} + d_{i+1\sigma}^{\dagger} d_{i\sigma} \right) \\
&+ U \sum_i \left( n_{i\uparrow} - \frac{1}{2} \right) \left( n_{i\downarrow} - \frac{1}{2} \right) \\
&+ V \sum_i \left( n_{i\uparrow} + n_{i\downarrow} - 1 \right) \left( n_{i+1\uparrow} + n_{i+1\downarrow} - 1 \right),
\end{align}

where $d_{i\sigma}^{\dagger}$ creates an electron of spin $\sigma$ in the ground state of the quantum dot $i$. Here $i = 1, \ldots, 3$ runs over the three quantum dots of the system and we impose the periodic condition $d_{3\sigma} = d_{1\sigma}$. Moreover $n_{i\sigma} = d_{i\sigma}^{\dagger} d_{i\sigma}$. The effect of the gate is included as a renormalization of the on-site energy $\xi = \xi_0 - eV_g$ where $V_g$ is the gate voltage. We measure the energies in units of the modulus of the (negative) hopping integral $b$. The parameters that we use are $\xi_0 = 0$, $U = 5 |b|$, $V = 2 |b|$. $H_{\text{leads}}$ in (2) describes two reservoirs of non-interacting electrons with a difference $eV_b$ between their electrochemical potentials. Finally, $H_{\text{tun}}$ accounts for the weak tunnelling coupling between the system and the leads, characteristic of SETs, and we consider the tunnelling events restricted to the atoms or to the dots closest to the corresponding lead.

The number of electrons considered for the triple dot structure goes from 0 to 6. Thus the entire Fock space of the system contains $4^3 = 64$ states. By exact diagonalization we obtain the many body-eigenstates and the corresponding eigenvalues that we present in Fig. 10 for a gate voltage of $V_g = 4.8 b/e$. In the table 5 we also give the degeneracies of all levels relevant for the blocking states analysis which will follow. We distinguish between spin and orbital degeneracy since the latter is the most important for the identification of the blocking states. The total degeneracy of a level is simply the product of the two.

5.2 Excited state blocking

In Fig. 11 we show the stationary current through the triple dot I-SET as a function of bias and gate voltage. At low bias the current vanishes almost everywhere due to Coulomb blockade. The particle number is fixed within each Coulomb diamond by the gate voltage and the zero particle diamond is the first to the right. The zero current lines running parallel to the borders of the 6, 4 and 2 particle diamonds are instead signatures of ground state interference that involves an orbitally non-degenerate ground state (with 2, 4, and 6 particles) and an orbitally double-degenerate one (with 3 and 5 particles).

The striking feature in Fig. 11 is the black area of current blocking sticking out of the right side of the two particles Coulomb diamond. It is the fingerprint of the occupation of an excited interference blocking state. Fig. 12 is a zoom of the current plot in the vicinity of this excited state blocking. The dashed lines indicate at which bias and gate voltage a specific transition is energetically allowed, with the notation $N_i$ labelling the $i$th excited many-body level with $N$ particles. These lines are
I-SET based on quantum dot molecules

Fig. 10  Spectrum of the triple dot system for the specific gate voltage $eV_g = 4.8b$ chosen to favor a configuration with two electrons. The other parameters in the system are $U = 5|b|$ and $V = 2|b|$, where $b$ is the hopping integral between the different dots. From [22].

Table 5  Degeneracy of the triple dot system energy levels as it follows from the underlying $D_3$ symmetry. A level $N_i$ is the $i$th excited level with $N$ particles. The total degeneracy of the level is the product of its orbital and spin degeneracies. From [22].

<table>
<thead>
<tr>
<th>Many-body energy level</th>
<th>Orbital degeneracy</th>
<th>Spin degeneracy</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>1_0</td>
<td>1</td>
<td>2</td>
</tr>
<tr>
<td>2_0</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>2_1</td>
<td>2</td>
<td>3</td>
</tr>
<tr>
<td>3_0</td>
<td>2</td>
<td>2</td>
</tr>
<tr>
<td>4_0</td>
<td>1</td>
<td>3</td>
</tr>
<tr>
<td>5_0</td>
<td>2</td>
<td>2</td>
</tr>
<tr>
<td>6</td>
<td>1</td>
<td>1</td>
</tr>
</tbody>
</table>

physically recognizable as abrupt changes in the current and run all parallel to two fundamental directions determined by the ground state transitions. For positive bias, positive (negative) slope lines indicates the bias threshold for the opening of source-creation (drain-annihilation) transitions. The higher the bias the more transitions are open, the higher, in general, the current.

The anomalous blockade region is delimited on three sides by transitions lines associated to the first excited two particle level $2_1$. Our group theoretical analy-
sis shows that the two particle first excited state is a twofold orbitally degenerate spin triplet (see Table 5). In other terms we can classify its six states with the notation $|2_1, \ell, S\rangle$ with $\ell = \pm \hbar$ being the projection of the angular momentum along the main rotation axis, perpendicular to the plane of the triple dot, and $S_z = -\hbar, 0, \hbar$ the component of the spin along a generic quantization axis. The 1\_0 energy level is instead twice spin degenerate and invariant under the symmetry operations of the point group $D_3$.

In order to identify the 2 particle blocking states we perform the analysis presented in the previous section for the 2\_1 energy level with the gate and bias in the blocking region. Firstly, we find that the 2\_1 energy level can be reached from 2\_0 via the drain-annihilation transition $2_0 \rightarrow 1_0$ followed by the source-creation transition $1_0 \rightarrow 2_1$. Secondly, the space of the decoupled states $\mathcal{R}_{2_1}$ is empty and the only energetically allowed outgoing transition is the drain-annihilation $2_1 \rightarrow 1_0$ transition. Thus the blocking space is given by the expression:

$$B_{2_1} = \mathcal{R}_{2_1} \left[ \ker \left( T_{2_1, 1_0, T_3} \right) \right]$$

and has dimension three. It is instructive to calculate explicitly the $T_{2_1, 1_0}$ matrix necessary for the calculation of the triplet blocking states and the associated blocking states. The states in the 1\_0 doublet and in the two times orbitally degenerate triplet 2\_1 are labeled and ordered as follows:

$$1_0 \left\{ \begin{array}{c} |1_0, \ell = 0, \uparrow\rangle \\ |1_0, \ell = 0, \downarrow\rangle \end{array} \right\} , \quad 2_1 \left\{ \begin{array}{c} |2_1, \ell = +\hbar, S_z = +\hbar\rangle \\ |2_1, \ell = +\hbar, S_z = 0\rangle \\ |2_1, \ell = +\hbar, S_z = -\hbar\rangle \\ |2_1, \ell = -\hbar, S_z = +\hbar\rangle \\ |2_1, \ell = -\hbar, S_z = 0\rangle \\ |2_1, \ell = -\hbar, S_z = -\hbar\rangle \end{array} \right\}$$
The elements of the $\gamma_{\alpha\sigma}$ matrices that compose $T_{2\rightarrow 1,1_0}^-$ have thus the general form:

$$\gamma_{\alpha\sigma}(S_z, S'_z, \ell) = \langle 1_0, \ell' = 0, S'_z | d_{\alpha\sigma} | 2_1, \ell, S_z \rangle.$$  \hfill (46)

By orbital and spin symmetry arguments it is possible to show that

$$\gamma_{\alpha\sigma}(S_z, S'_z, \ell) = t e^{i\phi_\alpha} \delta_{S'_z - \sigma} (\sqrt{2} \delta_{S_z, \uparrow} + \delta_{S_z, \downarrow}).$$ \hfill (47)

where $t = \langle 1_0, \ell' = 0, \downarrow | d_{\alpha\sigma} | 2_1, \ell = 1, S_z = 0 \rangle$. The subscript $M$ labels a reference dot and $\phi_\alpha$ is the angle of the rotation that brings the dot $\alpha$ on the dot $M$. The explicit form of $T_{2\rightarrow 1,1_0}^-$ reads:

$$T_{2\rightarrow 1,1_0}^- = t \begin{pmatrix}
\sqrt{2} e^{-i2\pi/3} & 0 & 0 & 0 & 0 \\
0 & e^{-i2\pi/3} & 0 & 0 & 0 \\
0 & e^{-i2\pi/3} & 0 & 0 & e^{i2\pi/3} \\
0 & 0 & \sqrt{2} e^{-i2\pi/3} & 0 & 0 \\
0 & 0 & 0 & \sqrt{2} e^{i2\pi/3} & 0 \\
\sqrt{2} e^{i2\pi/3} & 0 & 0 & 0 & 0 \\
e^{-i2\pi/3} & 0 & 0 & e^{i2\pi/3} & 0 \\
e^{-i2\pi/3} & 0 & 0 & 0 & e^{-i2\pi/3} \\
e^{i2\pi/3} & 0 & 0 & e^{-i2\pi/3} & 0 \\
e^{i2\pi/3} & 0 & 0 & 0 & e^{i2\pi/3} \\
0 & 0 & \sqrt{2} e^{i2\pi/3} & 0 & 0 \\
0 & 0 & 0 & \sqrt{2} e^{i2\pi/3} & 0
\end{pmatrix}. \hfill (48)$$

**Fig. 12** Blow up of the stationary current through the triple dot I-SET around the 2 to 1 particle degeneracy point. The black area sticking out of the 2 particles Coulomb diamond denotes the excited states blocking. From [22].
The rank of this matrix is six since all columns are independent. Thus \( C_{2,2} \) coincides with the full Hilbert space of the first excited two electron energy level. The blocking space \( \mathcal{B}_{2,2,1,0} \) reads:

\[
\mathcal{B}_{2,2,1,0} = \mathcal{P}_{2,1} \ker(T_{2,2,1,0}, T_S)
\]

where \( T_S \) reads

\[
T_S = \begin{pmatrix}
1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
0 & 1 & 0 & 0 & 0 & 0 & 0 & 0 \\
0 & 0 & 1 & 0 & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & 1 & 0 & 0 & 0 & 0
\end{pmatrix}
\]

in accordance to its general definition given in Eq. (17), and the projector \( \mathcal{P}_{2,1} \) removes the last four components from the vectors that span \( \ker(T_{2,2,1,0}, T_S) \). It is then straightforward to calculate the vectors that span the blocking space \( \mathcal{B}_{2,2,1,0} \):

\[
v_1 = \begin{pmatrix}
\frac{\sqrt{2}}{2}e^{-i\pi/6} \\
0 \\
0 \\
\frac{\sqrt{2}}{2}e^{+i\pi/6} \\
0
\end{pmatrix}, \quad v_2 = \begin{pmatrix}
\frac{\sqrt{2}}{2} \\
0 \\
0 \\
0 \\
\frac{\sqrt{2}}{2}
\end{pmatrix}, \quad v_3 = \begin{pmatrix}
0 \\
0 \\
\frac{\sqrt{2}}{2}e^{-i\pi/6} \\
0 \\
\frac{\sqrt{2}}{2}e^{+i\pi/6}
\end{pmatrix}
\]

The vectors \( v_1, v_2 \) and \( v_3 \) are the components of the blocking states written in the \( 2_1 \) basis set presented in (45). Thus, the three blocking states correspond to the three different projectors of the total spin \( S_z = \bar{h}, 0, \) and \( -\bar{h}, \) respectively. Essentially, there is a blocking state for each of the three projection of the spin \( S_z, \) This result is natural since, for unpolarized or parallel polarized leads, coherences between states of different spin projection along the common lead quantization axis do not survive in the stationary limit.

### 6 Spin dependent transport

In the previous sections we have shown different types of interference blocking, involving both ground and excited many-body states. All of them were essentially described in terms of the sequential tunnelling dynamics generated by \( \mathcal{L}_{\text{tun}} \) (see Eq. (6)). We neglected \( H_{\text{eff}} \) in the analysis of the numerical results and correspondingly the role of the third condition \( \langle H_{\text{eff}}, \rho_{\text{block}} \rangle = 0 \) in the definition of a blocking state. Indeed, the consequences of the dynamics generated by \( H_{\text{eff}} \) on the transport characteristics of the benzene and triple dot I-SETs are marginal for unpolarized leads.

The scenario changes completely for the case of spin polarized leads (Fig. 13). Thanks to (21) the destructive interference between orbitally degenerate electronic states typical of I-SETs produces current blocking at specific bias voltages (see
Fig. 13 Two examples of interference single electron transistors (I-SETs): a benzene molecular junction contacted in the meta configuration (A) and a triple quantum dot artificial molecule (B). The source and drain are parallel polarized ferromagnetic leads. From [21].

In the presence of parallel polarized ferromagnetic leads the interplay between interference and the exchange coupling on the system generates an effective energy renormalization yielding different blocking biases for majority and minority spins. Hence, by tuning the bias voltage full control over the spin of the trapped electron is achieved. Notice that we assume the leads to be parallel polarized so that no spin torque is active in the device and we can exclude the spin accumulation associated to that [35, 33]. In conclusion, the spin dependent renormalization of the system dynamics introduced by $H_{\text{eff}}$ allows to exploit interference to achieve all-electrical control of a single electron spin in quantum dots, a highly desirable property for spintronics [25, 26, 27] and spin-qubit applications [28, 29, 30, 31, 32].

6.1 Spin polarized leads

The lead polarization $P_\chi$ with $\chi = L, R$ is defined by means of the density of states $D_\chi\sigma$ at the Fermi energy for the different spin states:

$$P_\chi = \frac{D_\chi\uparrow - D_\chi\downarrow}{D_\chi\uparrow + D_\chi\downarrow}$$

and is taken equal for the two leads $P = P_L = P_R$. The spin polarization influences the dynamics of the system via the tunnelling rate matrices $\Gamma_{ij}^{\chi\sigma}$ which are proportional to the density of states $D_\chi\sigma$ and enter both the definition of the tunnelling component of the Liouvillian $Z_{\text{tun}}$ (see Eq. (6)) and the effective Hamiltonian $H_{\text{eff}}$ (see Eq. 8).

The particular form of the effective Hamiltonian for the benzene and the triple dot I-SET is the key to the understanding of the spin selective interference blockade. For the sake of simplicity we give in the following the explicit form of $H_{\text{eff}}$ only for the benzene I-SET and for the ground state transition $6_g \rightarrow 7_g$ that is characterized by interference blocking. The argumentation is nevertheless very general and can be repeated for all the systems exhibiting interference due to rotational symmetry. Let
us start from (8) and project it on the subspace of the fourfold degenerate 7 particle ground state. One obtains a $4 \times 4$ matrix that can be cast into the tensor product of a spin and an orbital component:

$$H_{\text{eff}}|7\rangle = \sum_{\chi} \begin{pmatrix} \omega_{\chi} & 0 \\ 0 & \omega_{\chi} \end{pmatrix} \otimes L_{\chi}. \tag{53}$$

The spin component has the units of a frequency

$$\omega_{\chi\sigma} = \frac{1}{\pi} \sum_{\sigma(E)} \Gamma_{\chi\sigma}^0 \left[ \langle 7_\ell \ell | d_{M\sigma'} | 8 \{E\} \rangle \langle 8 \{E\} | d_{M\sigma'}^\dagger | 7_\ell \ell \rangle \sigma \right] p_{\chi}(E - E_7) + \langle 7_\ell \ell | d_{M\sigma'} | 6 \{E\} \rangle \langle 6 \{E\} | d_{M\sigma'}^\dagger | 7_\ell \ell \rangle \sigma \right] p_{\chi}(E_7 - E), \tag{54}$$

and it weights the energy renormalization given to the states of spin $\sigma$ by their coupling to the lead $\chi$. In (54) we have introduced $d_{M\sigma}$ which destroys an electron of spin $\sigma$ in a reference carbon atom $M$ placed in the middle between the two contact atoms, $|7_\ell \ell \sigma\rangle$ are the orbitally degenerate 7 particle ground states, $\ell = \pm 2$ is the $z$ projection of the angular momentum in units of $\hbar$ and $\ell \equiv -\ell$. The compact notation $|N\{E\}\rangle$ indicates all possible states with particle number $N$ and energy $E$.

$$p_{\chi}(x) = -\text{Re} \psi \left[ \frac{1}{2} + \frac{\beta}{\pi} (x - \mu_{\chi}) \right] \text{ where } \beta = 1/k_B T, \text{ is the temperature and } \psi \text{ is the digamma function. Moreover } \Gamma_{\chi\sigma'}^0 = \frac{2\pi}{\hbar} |t|^2 D_{\chi\sigma'} \text{ is the bare tunneling rate to the lead } \chi \text{ of an electron of spin } \sigma' \text{, where } t \text{ is the tunnelling amplitude and } D_{\chi\sigma'} \text{ is the density of states for electrons of spin } \sigma' \text{ in the lead } \chi \text{ at the corresponding chemical potential } \mu_{\chi}. \text{ Due to the particular choice of the arbitrary phase of the 7 particle ground states, } \omega_{\chi\sigma} \text{ does not depend on the orbital quantum numbers } \ell. \text{ It depends instead on the bias and gate voltage through the energy of the 6, 7-ground and 8 particle states. The orbital component of (53) has the units of an angular momentum and it reads:}$$

$$L_{\chi} = \frac{\hbar}{2} \begin{pmatrix} 1 \\ e^{-i2\phi_{\chi}} \end{pmatrix} \begin{pmatrix} e^{i2\phi_{\chi}} \\ 1 \end{pmatrix}. \tag{55}$$

where $\phi_{\alpha}$ is the angle of which we have to rotate the molecule to bring the reference atom $M$ into the position of the contact atom $\chi$. The present choice of the reference atom implies that $\phi_{L} = -\phi_{R} = \frac{\pi}{3}$.

It is important to notice for the following discussions that $L_{\chi}$ not only has the units of an angular momentum but it is a quasi-angular momentum since it generates the rotations of the 7 particle ground states of the benzene molecule along the horizontal $C_2$ symmetry axis passing through the contact atom $\chi$. Let us prove the last statement. It is convenient, for the purpose, to choose the arbitrary phases of the states $|7_\ell \ell \sigma\rangle$ in such a way that the rotation of $\pi$ around the axis passing through a reference atom $M$ and the center of the molecule transforms $|7_\ell \ell \sigma\rangle$ into $-|7_\ell \ell \sigma\rangle$. In other terms
\[ \exp(i\pi \frac{L_M}{\hbar}) = -\sigma_x, \]  
(56)

where \( \sigma_x \) is the first Pauli matrix. The relation is in fact an equation for \( L_M \) and the solution reads:

\[ L_M = \frac{\hbar}{2} \begin{pmatrix} 1 & 1 \\ 1 & 1 \end{pmatrix}. \]  
(57)

Eventually we obtain \( L_\alpha \) by rotation of \( L_M \) in the molecular plane, namely:

\[ L_\alpha = e^{-\frac{i}{\hbar} \theta_e L_z} L_M e^{i \theta_e L_z} = \frac{\hbar}{2} \begin{pmatrix} 1 & e^{i2|\ell|\phi_x} \\ e^{-i2|\ell|\phi_x} & 1 \end{pmatrix}, \]  
(58)

where \( L_z = 2\hbar \sigma_z \) is the generator of the rotations along the principal rotational axis for the 7 particle ground states of the benzene molecule.

### 6.2 All-electrical spin control

We come now to the phenomenology of the spin dependent transport through a benzene and a triple dot I-SET. The different panels of Figs. 14 and 15 show the current through the benzene and triple dot I-SET, respectively, as a function of bias and gate voltage. As in all SETs at low bias so called Coulomb diamonds, where transport is energetically forbidden, occur. Within the diamonds the particle number is fixed as indicated in the figures.

The characteristic fingerprint of I-SETs is represented by the interference blockade where the current decreases for increasing bias generating negative differential conductance (NDC) and eventually vanishes (see green lines in the panels B and C of Fig. 14 and 15). Panels B in the same figures indicate moreover that, for a given gate voltage and in absence of polarization in the leads, the current is blocked only at one specific bias voltage. For parallel polarized leads, however, at a given gate voltage, the current is blocked at two specific bias voltages, one for each spin configuration (panels C). As demonstrated below, the blocking of the minority electrons occurs for the smaller bias voltages. As such full control of the spin configuration in the I-SET can be electrically achieved. The interference blockade and its spin selectivity is also demonstrated in panels A and B of Fig. 16. Along the dotted (dashed) line a majority (minority) spin electron is trapped into the molecule. The molecular spin state can thus be manipulated simply by adjusting the bias across the I-SET. In the following we discuss the physics of the spin-selective interference blocking and present the necessary ingredients for its occurrence.

From the analysis of the negative differential conductance and current blocking associated to interference presented in Sections 4 and 5 one would conclude that the interference blocking is a threshold effect appearing when the bias opens transitions to a specific set of degenerate states and surviving until transitions to other states lift the blocking. However, as shown in Fig. 14 and 15, the current is completely blocked
Fig. 14 Benzene I-SET: polarized vs. unpolarized configuration. Panel A - Current vs. bias and gate voltage for unpolarized leads. Panel D - Current vs. bias and gate voltage for polarized leads (polarization $P = 0.85$). Panels B and C - Blow up of the $6 \rightarrow 7$ particle transition for both configurations. The unpolarized case shows a single current blocking line and the trapped electron has either up or down polarization. The polarized case shows two current blocking lines, corresponding to the different spin of the trapped electron. The current is given in units of $e/\Gamma$ where $\Gamma$ is the bare average rate, and the temperature $k_B T = 0.01b$ where $b$ is the hopping parameter. From [21].

only at specific values of the bias voltage. The explanation of this phenomenon relies on two observations:

i) The blocking state (Fig. 16) must be antisymmetric with respect to the plane perpendicular to the system and passing through its center and the atom (quantum dot) closest to the drain; this state is thus also an eigenstate of the projection of the angular momentum in the direction of the drain lead $^4$. At positive (negative) bias voltages we call this state the $R(L)$-antisymmetric state $|\psi_{R(L),a}\rangle$.

---

$^4$ The corresponding eigenvalue depends on the symmetry of the atomic (quantum dot) wave function with respect to the molecular (artificial molecule) plane: $\hbar$ or 0 for symmetric or antisymmetric wave functions respectively.
ii) The complete interference blocking is only achieved when $[\rho_{\text{block}}, H_{\text{eff}}] = 0$.

In Fig. 17 the black curve depicts $\omega_{L,\sigma}$ as a function of the bias in absence of polarization: the frequencies corresponding to the two spin species coincide and thus vanish at the same bias. The same condition,

$$\omega_{L,\sigma} = 0,$$

also determines the bias at which the current is completely blocked. In fact, at that bias the effective Hamiltonian contains only the projection of the angular momentum in the direction of the right lead (the drain) and the density matrix corresponding to the full occupation of the 7 particle $R$-antisymmetric state ($\rho = |\psi_{R,a}\rangle \langle \psi_{R,a}|$) is the stationary solution of Eq. (5). As we leave the blocking bias the effective Hamiltonian contains also the projection of the angular momentum in the direction of the
left lead and the $R$-antisymmetric state is no longer an eigenstate of $H_{\text{eff}}$. The corresponding density matrix is not a stationary solution of (5) and current flows through the system. The $L \leftrightarrow R$ symmetry of the system implies, for negative biases, the blocking condition $\omega_{R\sigma} = 0$.

![Fig. 16 Spin control. Panel A - Current through the benzene I-SET vs bias and polarization at the $6 \rightarrow 7$ electrons transition. Panel B - Population of the majority spin 7 particle state. The two zero current lines at high bias correspond to the maximum or minimum population of the 7 particle majority spin state and thus identify the spin state of the trapped electron on the molecule. Panels C and D - Schematic representation of the spin selective blocking corresponding to the dashed (C) and dotted (D) lines of the panels A and B. From [21].]

All-electric-spin control is achieved, in an I-SET, only in presence of ferromagnetic leads and with exchange interaction on the system as we prove by analyzing the splitting of the renormalization frequencies $\omega_{X\sigma}$. (see Eq. (54).) By introducing the average bare rate $\Gamma = \frac{r_{0\uparrow}^2 + r_{0\downarrow}^2}{2}$, for simplicity equal in both leads, and using the fact that benzene is paramagnetic we get:

$$\omega_{\uparrow \uparrow} - \omega_{\downarrow \downarrow} = 2\Gamma_0^p P_0 \sum_{\{E\}} \left[ \langle 7_g \ell \uparrow | d_{M\uparrow}^\dagger | 8\{E\} \rangle \langle 8\{E\} | d_{M\uparrow} | 7_g m \uparrow \rangle p_\alpha (E - E_{7_g}) \right.$$  

$$+ \langle 7_g \ell \uparrow | d_{M\downarrow}^\dagger | 6\{E\} \rangle \langle 6\{E\} | d_{M\downarrow} | 7_g m \uparrow \rangle p_\alpha (E_{7_g} - E) \right.$$
\[ \langle 7g^\ell \uparrow | \hat{d}^\dagger_{M\downarrow} | 8\{E\} \rangle \langle 8\{E\} | \hat{d}^\dagger_{M\downarrow} | 7g^m \uparrow \rangle p_\alpha (E - E_{7g}) \]
\[ -\langle 7g^\ell \uparrow | \hat{d}^\dagger_{M\downarrow} | 6\{E\} \rangle \langle 6\{E\} | \hat{d}^\dagger_{M\downarrow} | 7g^m \uparrow \rangle p_\alpha (E_{7g} - E) \], \quad (60) \]

where one appreciates the linear dependence of the spin splitting on the lead polarization \( P_\alpha \). The first and the third term of the sum would cancel each other if the energy of the singlet and triplet 8 particle states would coincide. An analogous condition, but this time on the 6 particle states, concerns the second and the fourth terms. For this reason the exchange interaction on the system is a necessary condition to obtain spin splitting of the renormalization frequencies and thus the full all-electric spin control.

In Fig. 17 we show the frequencies \( \omega_{L\sigma} = 0 \) vs. bias voltage also for a finite values of the polarization \( P \) calculated for the benzene I-SET, where exchange splitting is ensured by the strong Coulomb interaction on the system. The interference blocking conditions \( \omega_{L\sigma} = 0 \) for the \( L \rightarrow R \) current are satisfied at different biases for the different spin species. The dotted and dashed lines in Fig. 16 are the representation of the relations \( \omega_{L\uparrow} = 0, \omega_{L\downarrow} = 0 \) as a function of the bias and polarization, respectively.

**Fig. 17** Blocking condition. Renormalization frequencies \( \omega_{L\sigma} \) of a benzene I-SET as function of the bias and for different lead polarizations. The current blocking condition \( \omega_{L\sigma} = 0 \) is fulfilled at different biases for the different spin states. From [21].
7 Robustness

One could argue about the fragility of an effect which relies on the degeneracy of the many-body spectrum. Interference effects are instead rather robust. The exact degeneracy condition can in fact be relaxed and interference survives also for a quasi-degeneracy condition: i.e as far as the splitting between the many body levels is smaller that the tunnelling rate to the leads. In this limit, the system still does not distinguish between the two energetically equivalent paths sketched in Fig. 1.

To quantify the robustness of the effect we will address, in this section, two issues: the first is the modification of the master equation, Eq. (5), necessary to capture the interference between quasidegenerate states, the second is the detailed study of an example of I-SET (the benzene single molecule junction) under several perturbations that lower the symmetry of the system.

7.1 GME and current in the non-secular approximation

The bias and the contact perturbations in our model for a benzene I-SET lower the symmetry of the active part of the junction and consequently lift the degeneracy that appeared so crucial for the interference effects. The robustness of the latter relies on the fact that the necessary condition is rather quasi-degeneracy, expressed by the relation \( \delta E \ll \hbar \Gamma \).

Nevertheless, if the perfect degeneracy is violated, the secular approximation applied to obtain Eq. (5)-(8) does not capture this softer condition. We report here the general expression for the generalized master equation and the associated current operator in the Born-Markov approximation and under the only further condition that coherences between states with different particle number are decoupled from the populations and vanish exactly in the stationary limit:

\[
\dot{\rho}_{EE'}^{N} = -\frac{i}{\hbar}(E - E')\rho_{EE'}^{N} + \\
-\sum_{\chi} \sum_{ij} \sum_{F} \frac{1}{2} \mathcal{P}_{NF} \left\{ d_{i\sigma}^{\dagger} \Gamma_{ij}^{\chi\sigma} (F - H_{\text{sys}}) \left[ -\frac{i}{\pi} p_{\chi} (F - H_{\text{sys}}) + f_{\chi}^{+} (F - H_{\text{sys}}) \right] d_{j\sigma} + \\
\right. \\
\left. d_{j\sigma} \Gamma_{ij}^{\chi\sigma} (H_{\text{sys}} - F) \left[ -\frac{i}{\pi} p_{\chi} (H_{\text{sys}} - F) + f_{\chi}^{+} (H_{\text{sys}} - F) \right] d_{i\sigma} \right\} \rho_{EE'}^{N} + \\
-\sum_{\chi} \sum_{ij} \sum_{F} \frac{1}{2} \mathcal{P}_{NE'}^{N} \left\{ d_{\sigma}^{\dagger} \Gamma_{ij}^{\chi\sigma} (F - H_{\text{sys}}) \left[ +\frac{i}{\pi} p_{\chi} (F - H_{\text{sys}}) + f_{\chi}^{+} (F - H_{\text{sys}}) \right] d_{\sigma} + \\
\right. \\
\left. d_{\sigma} \Gamma_{ij}^{\chi\sigma} (H_{\text{sys}} - F) \left[ +\frac{i}{\pi} p_{\chi} (H_{\text{sys}} - F) + f_{\chi}^{+} (H_{\text{sys}} - F) \right] d_{\sigma} \right\} \rho_{EE'}^{N} + 
\]

Eq. (5) represents a special case of Eq. (61) in which all energy spacings between states with the same particle number are either zero or much larger than the level broadening $\hbar \Gamma$. The problem of a master equation in presence of quasi-degenerate states in order to study transport through molecules has been addressed in the work of Schultz et al.[43]. The authors claim in their work that the singular coupling limit should be used in order to derive an equation for the density matrix in presence of quasi-degenerate states. Equation (61) is derived in the weak coupling limit and bridges all the regimes as illustrated by Fig. 18-20.

The current operators associated to the master equation just presented read:

$$I_{\chi} = \frac{1}{2} \sum \sum \sum \sum \mathcal{P}_{\text{NE}}$$

$$ \left\{ d_{i \sigma} \Gamma_{ij}^{\chi \sigma} (E - H_{\text{sys}}) \left[ + \frac{i}{\pi} p_{\chi} (E - H_{\text{sys}}) + f_{\chi} (E - H_{\text{sys}}) \right] d_{j \sigma} + ight.$$ \left.$$ + d_{i \sigma} \Gamma_{ij}^{\chi \sigma} (F - H_{\text{sys}}) \left[ - \frac{i}{\pi} p_{\chi} (F - H_{\text{sys}}) + f_{\chi} (F - H_{\text{sys}}) \right] d_{j \sigma} + ight.$$ \left.$$ - d_{i \sigma} \Gamma_{ij}^{\chi \sigma} (H_{\text{sys}} - E) \left[ + \frac{i}{\pi} p_{\chi} (H_{\text{sys}} - E) + f_{\chi} (H_{\text{sys}} - E) \right] d_{j \sigma} + ight.$$ \left.$$ - d_{i \sigma} \Gamma_{ij}^{\chi \sigma} (H_{\text{sys}} - F) \left[ - \frac{i}{\pi} p_{\chi} (H_{\text{sys}} - F) + f_{\chi} (H_{\text{sys}} - F) \right] d_{j \sigma} \right\} \mathcal{P}_{\text{NE}} \quad (62)$$

where $\chi = L, R$ indicates the left or right contact. Nevertheless, within the limits of derivation of the master equation, this formula can be simplified. Actually, if $E - F \leq \hbar \Gamma$, then $F$ can be safely substituted with $E$ in the argument of the principal values and of the Fermi functions, with an error of order $\frac{E - F}{\hbar \Gamma} \ll \frac{\hbar \Gamma}{k_B T}$ which is negligible (the generalized master equation that we are considering is valid for $h\Gamma \ll k_B T$). The approximation $E \sim F$ breaks down only if $E - F \sim k_B T$, but this implies $E - F \gg \hbar \Gamma$ which is the regime of validity of the secular approximation. Consequently, in this regime, terms with $E \neq F$ do not contribute to the average current because they vanish in the stationary density matrix. Ultimately we can thus reduce the current operators to the simpler form:
\[ I_\chi = \sum_{NE} \sum_{ij} \sum_{\sigma} \mathcal{P}_{NE} \left[ d_{j\sigma} \gamma_{ij}^{\chi\sigma} (H_{\text{sys}} - E) f_\chi^+ (H_{\text{sys}} - E) d_{i\sigma}^{\dagger} + \right. \]
\[ - d_{i\sigma} \gamma_{ij}^{\chi\sigma} (E - H_{\text{sys}}) f_\chi^- (E - H_{\text{sys}}) d_{j\sigma} + \left. \right], \tag{63} \]

which is almost equal to the current operator corresponding to the secular approximation. The only difference is here the absence of the second projector operator that allows contributions to the current coming from coherences between different energy eigenstates.

### 7.2 Interference in a reduced symmetry I-SET

In this section we study the effect of reduced symmetry on the transport characteristics of a benzene I-SET. For this purpose, we generalize the model Hamiltonian by taking into account the perturbations on the molecule due to the contacts and the bias voltage. The contact between molecule and leads is provided by different anchor groups. These linkers are coupled to the contact carbon atoms over a \( \sigma \) bond thus replacing the corresponding benzene hydrogen atoms. Due to the orthogonality of \( \pi \) and \( \sigma \) orbitals, the anchor groups affect in first approximation only the \( \sigma \) orbitals of benzene. In particular the different electron affinity of the atoms in the linkers imply a redistribution of the density of \( \sigma \) electrons. Assuming that transport is carried by \( \pi \) electrons only, we model the effect of this redistribution as a change in the on-site energy for the \( p_z \) orbitals of the contact carbon atoms:

\[ H'_{\text{ben}} := H_{\text{contact}} = \xi_{\chi} \sum_{\sigma} d_{\chi\sigma}^{\dagger} d_{\chi\sigma}, \quad \chi = L, R \tag{64} \]

where \( d_{R\sigma} = d_{4\sigma}, d_{5\sigma} \), respectively, in the para and meta configuration, while \( d_{L\sigma} = d_{1\sigma} \) in both setups.

We also study the effect of an external bias on the benzene I-SET. In particular we release the strict condition of potential drop all concentrated at the lead-molecule interface. Nevertheless, due to the weak coupling of the molecule to the leads, we assume that only a fraction of the bias potential drops across the molecule. For this residual potential we take the linear approximation \( V_b(r) = -\frac{V_b}{a} (\mathbf{r} \cdot \hat{r}_{sd}/a_0) \), where we choose the center of the molecule as the origin and \( \hat{r}_{sd} \) is the unity vector directed along the source to drain direction. \( a_0 = 1.43 \text{ Å} \) is the bond length between two carbon atoms in benzene, \( a \) is the coefficient determining the intensity of the potential drop over the molecule. Since the \( p_z \) orbitals are strongly localized, we can assume that this potential will not affect the inter-site hopping, but only the on-site term of the Hamiltonian:

\[ H'_{\text{ben}} := H_{\text{bias}} = \epsilon \sum_{\sigma} \xi_{\sigma} d_{\alpha\sigma}^{\dagger} d_{\alpha\sigma} \tag{65} \]
with $\xi_b = \int dr \ p_z(r - R_i)V_b(r)p_z(r - R_i)$.

Under the influence of the contacts or the bias potential, the symmetry of the molecule changes. Table 6 shows the point groups to which the molecule belongs in the perturbed setup. This point groups have only $A$- and $B$-type reducible representations. Thus the corresponding molecular orbitals do not exhibit orbital degeneracy.

No interference effects influence the transport in the para configuration. Thus we do not expect its transport characteristics to be qualitatively modified by the new set up with the corresponding loss of degeneracies. In the meta configuration on the other hand, interferences between orbitally degenerate states play a crucial role in the explanation of the occurring transport features. Naively one would therefore expect that neither conductance suppression nor NDC and current blocking occur in a benzene I-SET with reduced symmetry.

**Table 6** Point groups to which the molecule belongs under the influence of the contacts and the external bias potential. From [20].

<table>
<thead>
<tr>
<th>Type of perturbation</th>
<th>Symmetry (Para config.)</th>
<th>Symmetry (Meta config.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Contact perturbation</td>
<td>$D_{2h}$</td>
<td>$C_{2v}$</td>
</tr>
<tr>
<td>Bias perturbation</td>
<td>$C_{2v}$</td>
<td>$C_{2v}$</td>
</tr>
</tbody>
</table>

Yet we find that, under certain conditions, the mentioned transport features are robust under the lowered symmetry.

The perturbations due to the contacts and the bias lead to an expected level splitting of the former orbitally degenerate states. Very different current-voltage characteristics are obtained depending of the relation between the energy splitting $\delta E$ and other two important energy scales of the system: the tunnelling rate $\Gamma$ and the temperature $T$. In particular, when $\delta E < \Gamma \ll T$, interference phenomena persist. In contrast when $\Gamma < \delta E \ll T$ interference phenomena disappear, despite the fact that, due to temperature broadening, the two states still can not be resolved. In this regime, due to the asymmetry in the tunnelling rates introduced by the perturbation, standard NDC phenomena, see Fig. 19, occur.

Fig. 18 shows from left to right closeup views of the stability diagram for the setup under the influence of increasing contact perturbation around the 6 ↔ 7 resonance. The orbital degeneracy of the 7 particle states is lifted and the transport behavior for the 6 ↔ 7 transition depends on the energy difference between the formerly degenerate 7 particle ground states. In panel a the energy difference is so small that the states are quasi-degenerate: $\delta E \ll h\Gamma \ll k_B T$. As expected, we recover NDC at the border of the 6 particle diamond and current suppression at the border of the 7 particle diamond, like in the unperturbed setup. Higher on-site energy-shifts correspond to a larger level spacing. Panel b displays the situation in which the latter is of the order of the level broadening, but still smaller than the thermal energy ($\delta E \simeq h\Gamma \ll k_B T$): no interference causing NDC and current blocking can occur. Yet, due to thermal broadening, we cannot resolve the two 7 particle states. Even-
Fig. 18 Closeup views of the stability diagram around the 6 ↔ 7 resonance for the system under contact perturbation. The perturbation strength grows from left to right. The parameter that describes the contact effect assumes the values $\xi_c = 0.15 \Gamma$, $2 \Gamma$, $15 \Gamma$ from left to right respectively and $k_B T = 10 \hbar \Gamma$. From [20].

Fig. 19 shows closeup views of the stability diagram for the setup under the influence of the bias perturbation at the border of the 6 and 7 particle diamonds. The same region is plotted for different strengths of the external potential over the molecule. In contrast to the contact perturbation, the amount of level splitting of the former degenerate states is here bias dependent. This fact imposes a bias window of interference visibility. The bias must be small enough, for the 7 particle states to be quasi-degenerate and at the same time bigger than the thermal energy, so that the occurring NDC is not obscured by the thermally broadened conductance peak. A strong electrostatic potential perturbation closes the bias window and no interference effect can be detected. Panel a of Fig. 19 represents the weak perturbation regime with no qualitative differences with the unperturbed case. The typical fingerprints of interference (NDC at the border of the 6 particle diamond and current blocking for the 7 → 6 transition) are still visible for intermediate perturbation strength (panel b) but this time only in a limited bias window. Due to the perturbation strength, at some point in the bias, the level splitting is so big that the quasi-degeneracy is lifted and the interference effects destroyed. In panel c the...
Fig. 19 Closeup views of the stability diagram around the $6 \leftrightarrow 7$ resonance for the system under the effect of the bias potential, displayed for different strengths of the electrostatic potential drop over the molecule. The parameter that describe the strength of the electrostatic drop over the molecule assumes the values $a = 25, 12, 0.6$ from left to right respectively. From [20].

quasi-degeneracy is lifted in the entire bias range. There is NDC at the border of the 6 particle diamond, but is not accompanied by current blocking as proved by the excitation line at the border of the 7 particle diamond (see arrow): no interference occurs. The NDC is here associated to the sudden opening of a slow current channel, the one involving the 6 particle ground state and the 7 particle (non-degenerate) excited state (standard NDC).

Fig. 20 refers to the setup under both the bias and contact perturbations. The left panel shows the energy of the lowest 7 particle states as a function of the bias. In the right panel we present the stability diagram around the $6 \leftrightarrow 7$ resonance. NDC and current blocking are clearly visible only in the bias region where, due to the combination of bias and contact perturbation, the two seven particle states return quasi-degenerate. Also the fine structure in the NDC region is understandable in terms of interference if in the condition of quasi-degeneracy we take into account the renormalization of the level splitting due to the energy non-conserving terms.

Interference effects predicted for the unperturbed benzene I-SET are robust against various sources of symmetry breaking. Quasi-degeneracy, $\delta E \ll h\Gamma \ll k_B T$, is the necessary condition required for the detection of the interference in the stability diagram of the benzene I-SET.
8 Conclusions

In this chapter we addressed the interference effects that characterize the electronic transport through a symmetric single electron transistor based on quantum dot molecules. Interestingly, in this class of devices interference effects survive even in the weak tunnelling coupling regime when usually the decoherence introduced by the leads dominate the picture and transport consists of a set of incoherent tunnelling events.

After introducing the concept of interference single electron transistor (I-SET) we formulate a simple interference condition (24) for I-SETs in terms of the tunnelling transitions amplitudes of degenerate states with respect to the source and drain lead. A generic model of I-SET is then introduced, together with our method of choice to study the dynamics of the molecular I-SET: i.e. the density matrix approach which starts from the Liouville equation for the total density operator which enables the treatment of quasi-degenerate states, so crucial for the description of the interference effects which are the focus of our investigation. As a further step, we derive the most generic conditions for interference blockade and an algorithm for the identification of the interference blocking states as linear combination of degenerate many-body eigenstates of the system. The theory is sufficiently general to be applied to any device consisting of a system with degenerate many-body spectrum.
weakly coupled to metallic leads e.g. molecular junctions, graphene or carbon nanotube quantum dots, artificial molecules. In particular, the algebraic formulation of the blocking condition in terms of kernels of the tunnelling matrices $T^{\pm}$, Eq. (18), allows a straightforward numerical implementation and makes the algorithm directly applicable to complex junctions with highly degenerate spectrum. For example, we have recently applied the same theory to study the transport through STM junctions of single molecules on thin insulating films [61, 62].

As an application of the theory we study the benzene and the triple dot I-SET.

For the first system, two different setups are considered, the para and the meta configuration, depending on the position of the leads with respect to the molecule. Within an effective $p_z$ orbital model, we diagonalize exactly the Hamiltonian for the molecule. We further apply a group theoretical method to classify the many-body molecular eigenstates according to their symmetry and quasi-angular momentum. With the help of this knowledge we detect the orbital degeneracy and, in the para configuration, we select the states relevant for transport. The application of the simple interference condition (24) enables us to predict the existence of interference effects in the meta configuration. The stability diagrams for the two configurations show striking differences. In the linear regime a selective conductance suppression is visible when changing from the para to the meta configuration. Only transitions between ground states with well defined particle number are affected by the change in the lead configuration. With the help of the group theoretical classification of the states we recognize in this effect a fingerprint of the destructive interference between orbitally degenerate states. We derive an analytical formula for the conductance that reproduces exactly the numerical result and supports their interpretation in terms of interference. Other interference effects are also visible in the non-linear regime where they give rise to NDC and current blocking at the border of the 6 particle Coulomb diamond as well as to current suppression for transitions between 7 and 6 particle states.

Despite its relative simplicity, the triple dot I-SET exhibits different types of interference blocking and it represents an interesting playground of the general theory. Specifically, we concentrated on the interference blockade that involves an excited triplet state, a condition not accessible in the benzene I-SET.

In both cases we further analyze the blockade that involves orbitally and spin degenerate states and we show how to realize all electrical preparation of specific spin states. Thus we obtain an interference mediated control of the electron spin in quantum dots, a highly desirable property for spintronics [25, 26, 27] and spin-qubit applications [28, 29, 30, 31, 32]. Similar blocking effects have been found also in multiple quantum dot systems in dc [23] and ac [24] magnetic fields.

Finally, we provide a detailed discussion of the impact of the reduced symmetry due to linking groups between the molecule and the leads or to an electrostatic potential drop over the molecule. We classify different transport regimes and set up the limits within which the discussed transport features are robust against perturbations. We identify in the quasi-degeneracy of the many-body states the necessary condition for interference effects.
9 Acknowledgment

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References

1. T. Young, Phil. Trans. Royal Society of London 94, 12 (1804).