Quantum Interference in Off-Resonant Transport through Single Molecules

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(Dated: March 18, 2014) We provide a simple set of rules for predicting interference effects in off-resonant transport through single-molecule junctions, valid even when including electron-electron interactions in the description of the molecule. Such junctions fall in two classes, showing respectively an odd or an even number of transmission minima, and we demonstrate here how to decide the interference class from the contacting geometry. For neutral alternate hydrocarbons, we employ the Coulson-Rushbrooke pairing theorem to devise a simple starring procedure. More generally, we investigate a range of smaller molecules by means of exact diagonalization combined with a perturbative treatment of the molecule-lead tunnel coupling. While these results generally agree well with GW calculations, they are shown to be at odds with simpler mean-field treatments. For molecules with spin-degenerate ground states, we show that interference causes no transmission nodes, but argue that it may lead to a non-standard gate-dependence of the Kondo temperature.

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Interference effects in single molecule junctions have recently attracted a lot of attention as they offer a sensitive handle with which to tune transport properties. Single molecule junctions with interference effects may come in many forms, and the transported electrons will often be strongly correlated due to Coulomb interaction and tunneling between molecule and leads. Yet we imagine that it is a feature of the molecule itself that controls the observable interference effects. In this letter, we provide a simple set of rules for predicting interference effects in off-resonant transport through alternate (bipartite) hydrocarbons. The rule is based on the Coulson-Rushbrooke pairing theorem, which we rephrase in terms of matrix elements for adding or removing an electron to or from a particle-hole symmetric molecule. For small enough molecules, we perform an exact diagonalization (ED) of the interacting molecular π-system, and demonstrate how this rephrased theorem works for strictly off-resonant transport. For a number of different molecules, we compare the result to those obtained using other popular methods like density functional theory (DFT), Hückel theory (HT), and GW, which all include higher order tunneling (hybridization) effects but treat the interactions only approximately. For most situations even a simple HT is shown to predict the correct interference class, but most often the effective single-particle calculations (HT, DFT, HF) return the incorrect dip positions and even spurious dip-degeneracies, which are usually lifted by GW and ED calculations. Our simple classification rules provide a valuable tool for gauging the validity of approximate calculations, and since the rephrased pairing theorem is topological in nature, we expect it to be of more general validity beyond the restricted class of neutral homonuclear alternate hydrocarbons.

In a molecular junction the molecule is tunnel-coupled to two electrodes at a bias voltage $V_{sd}$, and with a back gate voltage $V_g$ controlling the electrostatic environment. The molecular π-system is modeled by the semi-empirical Pariser-Parr-Pople model \[ \hat{H}_\pi = \hat{H}_T + \hat{H}_U + \hat{H}_V + \hat{H}_g, \] where

\[
\hat{H}_T = \sum_{(i,j)} \sum_{\sigma=\uparrow,\downarrow} \left( t_{ij} \hat{c}_{i\sigma}^\dagger \hat{c}_{j\sigma} + \text{h.c.} \right),
\]

\[
\hat{H}_U = \sum_i U(\hat{n}_{i\uparrow} - \frac{1}{2})(\hat{n}_{i\downarrow} - \frac{1}{2}),
\]

\[
\hat{H}_V = \frac{1}{2} \sum_{i\neq j} V_{ij}(\hat{n}_i - 1)(\hat{n}_j - 1),
\]

\[
\hat{H}_g = -eV_g \sum_i (\hat{n}_i - 1).
\]

Here $\hat{H}_T$ describes the electron kinetic energy, $\hat{H}_U$ and $\hat{H}_V$ the intra-molecular electron-electron interactions, and $\hat{H}_g$ the effect of the back gate $V_g$. The operator $\hat{c}_{i\sigma}^\dagger$ creates an electron with spin $\sigma$ on the $p_2$-orbital $|i\rangle$, $\hat{n}_{i\sigma} = \hat{c}_{i\sigma}^\dagger \hat{c}_{i\sigma}$ and $\hat{n}_i = \hat{n}_{i\uparrow} + \hat{n}_{i\downarrow}$. The Coulomb interaction is given by the Ohno parametrization $V_{ij} = U/(\sqrt{1 + |\vec{r}_{ij}|^2}207.3 \text{ eV})$, where $|\vec{r}_{ij}|$ is the real-space distance between two $p_2$-orbitals $|i\rangle$ and $|j\rangle$ measured in Ångstrom. For sp2 hybridised carbon, the nearest-neighbor overlap, $t_{ij}$, is $t \approx -2.4 \text{ eV}$, and $U \approx 11.26 \text{ eV}$. The isolated molecular π-system with $N$ electrons, described by $\hat{H}_T + \hat{H}_U + \hat{H}_V$, has eigenenergies $E_n^N$, with corresponding many-body eigenstates $|\Psi_n^N\rangle$. The $N$-electron excitation spectrum is given by $E_n^N = E_n^0$, the energy costs of adding an electron to the π-system.
is given by $\varepsilon^n_m = E^n_{m+1} - E^n_{m}$, and the costs of removing an electron by $\varepsilon^h_n = E^n_{n+1} - E^n_{n}$. For the molecules investigated below and in the Supplementary Information Table 1, these eigenenergies and many-body eigenstates are determined numerically by exact diagonalization [23].

The source, and drain ($\alpha = s, d$) electrodes are modeled by non-interacting electrons with constant densities of states $\rho_{\alpha}$. Since interference effects depend crucially on the entry, and exit points for the transport electrons, we assume that only one $p_{\alpha}$-orbital $|i_{\alpha}\rangle$ couples to each lead $\alpha = s, d$. The electrode-molecule coupling is $H_U = \sum_{\alpha k \sigma} (t_{\alpha in}^\dagger \hat{c}_{i_{\alpha}\sigma}^\dagger + h.c.)$. When the coupling strengths $\hbar \Gamma_{\alpha} = 2\pi \rho_{\alpha} |t_{\alpha}|^2$ to source and drain electrodes are much smaller than the excitation energies $\hbar \Gamma_{s,d} \ll |\varepsilon^0_{p_{s,d}}|$, the molecular junction is blocked, and transport is restricted to cotunneling processes via virtual charge-fluctuations of the molecule. The molecule holds a definite number of electrons, and the off-resonant current is determined by leading order perturbation theory in $\Gamma$, $\Gamma_d(\varepsilon_{p_{s,d}})/\hbar^2$.

For a non-degenerate molecular ground state, there are only two contributing transport processes. One process transfers an electron ($p$) from source to drain, while the second process transfers a hole ($\bar{p}$) in the reverse direction. Safely away from the charge degeneracy points, $eV_G = \varepsilon^0_{p_{s,d}}$, the zero-temperature off-resonant current can be calculated from the generalized Fermi golden rule [9]

$$I(V_g, V_{sd}) = \frac{\hbar}{2\pi} \Gamma_s \Gamma_d \sum_{m, \sigma} \int_{-\varepsilon_m/2}^{\varepsilon_m/2} \theta(eV_{sd} - \varepsilon_m) d\omega \times |h^\sigma_{m,0}(V_g, \omega - \varepsilon_m) + p^\sigma_{m,0}(V_g, \omega)|^2,$$

(5)

to second order in the cotunneling amplitudes,

$$h^\sigma_{m,d}(V_g, \omega) = \sum_n \langle \Psi^N_m | \hat{c}_{i_n\sigma}^\dagger | \Psi^{N-1}_m \rangle \langle \Psi^{N-1}_m | \hat{c}_{i_{d\sigma}}^\dagger | \Psi^N_d \rangle, eV_g - \omega - \varepsilon_m - i0^+,$$

and

$$p^\sigma_{m,d}(V_g, \omega) = \sum_n \langle \Psi^N_m | \hat{c}_{i_{d\sigma}}^\dagger | \Psi^{N+1}_m \rangle \langle \Psi^{N+1}_m | \hat{c}_{i_{n\sigma}}^\dagger | \Psi^N_d \rangle, eV_g - \omega - \varepsilon_m - i0^+.$$

This formula for the current omits any bias-dependence of excited state occupations, which would play a role for the detailed shape of inelastic cotunneling steps (cf. Ref. [23], but is immaterial for the present discussion. From Eq. (5), the zero-bias conductance, $G = \lim_{V_{sd} \rightarrow 0} dI/dV_{sd}$, is readily found to take the following simple form

$$G = \frac{e^2 \hbar}{2\pi} \Gamma_s \Gamma_d \sum_{\sigma} |h^\sigma_{0,0}(V_g, 0) + p^\sigma_{0,0}(V_g, 0)|^2.$$

(6)

Based on this current formula, and the energy-denominators in the cotunneling amplitudes, we divide interference effects in off-resonant molecular junctions into classes of even or odd, reflecting the number of conductance zeros found by varying the gate voltage all the way across a given charge state. As summarized graphically in Fig. 1, divergences of the $h^\sigma_{0,0}$ amplitude at $\varepsilon^0_0$ and similarly of $p^\sigma_{0,0}$ at $\varepsilon^0_0$ determine the interference class uniquely. The red line shows the amplitudes in the valid regime of $V_g$. The different interference mechanisms are marked with a diamond or a circle. Note the anomalous even case with exactly one node, which shows up in some DFT and HT calculations.

FIG. 1. Interference classes. The even and odd quantum interference classes. The signs of the pole of $h^\sigma_{0,0}$ at $\varepsilon^0_0$ and of $p^\sigma_{0,0}$ at $\varepsilon^0_0$ determine the interference class uniquely. The red line shows the amplitudes in the valid regime of $V_g$. The different interference mechanisms are marked with a diamond or a circle. Note the anomalous even case with exactly one node, which shows up in some DFT and HT calculations.
conductance. When hole $h$, and particle $p$ transport amplitudes cancel, the result is exactly one node. All remaining interference nodes of either class can be interpreted as happening completely within a hole $h$ (or a particle $p$) transport amplitude. Note that the $Q_i$ classification parameter is readily generalized to the case when many orbitals connect to each electrode, by replacing the $\langle \Psi_m | \hat{c}_{i\sigma} | \Psi_{n+1} \rangle$ values with an average over all connected orbitals $|i\rangle$ weighted by their coupling strengths $|t_{i\alpha}|^2$.

For neutral alternant (bipartite) hydrocarbon $\pi$-systems, the classification simplifies tremendously. In an alternant system every other $p_z$-orbital can be marked by a star, such that all starred orbitals only have non-starred neighbors and vice versa. An equal number of starred and non-starred orbitals assures a spin-singlet ground state $|1\rangle$, and the current formula (6) is valid. Attaching the molecule to electrodes through $p_z$-orbitals on disjoint sub-lattices (star and non-star) makes the interference class even, whereas contacting two $p_z$-orbitals on the same sub-lattice (both starred or both unstarred) makes it odd. This simple rule follows from the pairing between the neutral+1 and neutral−1 charge states, ensuring that $\langle \Psi_m | \hat{c}_{i\sigma} | \Psi_{n+1} \rangle = \langle \Psi_{m-1} | \hat{c}_{i\sigma} | \Psi_0 \rangle$ for unstarred sites and $\langle \Psi_m | \hat{c}_{i\sigma} | \Psi_{n+1} \rangle = -\langle \Psi_{m-1} | \hat{c}_{i\sigma} | \Psi_0 \rangle$ for starred sites. This is a consequence of the Coulson-Rushbrooke pairing theorem [7] for alternant hydrocarbon Hückel models. The pairing theorem is easily extended to PPP models [17][18], and for completeness we include the proof in the Supplementary Information S3.

As illustrated by the examples in the Supplementary Information S2, the starring procedure can readily determine the interference class of more complex molecules, still including the full effects of intra-molecular interactions. We emphasize that these straightforward starring rules for classification of interferences only apply for neutral even-alternant hydrocarbons.

As an example, we now provide a detailed analysis of the stilbene molecule shown in Fig. 2(a). Being an alternant hydrocarbon, we can employ the starring rule described above, and from Fig. 2(b) we immediately conclude that this molecule will have an even number of conductance nodes when contacted in AA’ or BB’ configuration, and an odd number of nodes in the AB’ configuration. Within a PPP-model description of the $\pi$-system, this molecule is still amenable to exact diagonalization. Inserting the exact spectrum and wave-functions into Eq. (5), we obtain the stability diagrams in Fig. 2(c), showing the logarithm of the differential conductance $dI/dV_{sd}$ as a function of a back gate voltage $V_g$ and the source drain voltage $V_{sd}$ at zero temperature. The bright colors indicate a high differential conductance with the inner diamond demarcating the (red-black) regions, inside which our off-resonant current formula for elastic cotunneling becomes valid. The dark spots in the middle and right most panels in Fig. 2 show unusual, strong suppression of the differential conductance, related to the destructive interference in the cotunneling conductance. Note also how inelastic cotunneling processes become relevant at certain values of $V_{sd}$ and instantly cut off any
interference features present in the elastic cotunneling current. We have confirmed that the salient features of Fig. 2(c), are indeed reproduced for a simple quinoid type molecule by a full generalized master equation calculation (not shown).

Fig. 2(d) shows the zero-bias conductance in three different contacting geometries, and calculated using respectively DFT or HT, or HF, GW or ED. More details on the calculations are given in the Supplementary Information S1. Whereas all methods agree on the interference class of AA’ and AB’ configuration, a clear disagreement arises in BB’ configuration, where HT shows only one node and DFT and HF both predict no nodes or at best a single local minimum. Only GW and exact diagonalization agree on two nodes, consistent with our simple starring procedure. Interpreting the DFT and HF results as predicting no nodes, and HT as predicting two degenerate nodes, they may all be said to give the correct class, but comparing with GW and ED, it is clear that the correct result depends crucially on a careful consideration of Coulomb interactions, as noted also in Refs. 2, 26. Note that calculating $\mathcal{Q}_i$ within HT correctly predicts an even interference class, and the degenerate node is an accidental degeneracy that will be lifted by interactions as found by GW and ED, whereas DFT and HF both remove the node altogether. We note that the DFT results can depend on the functional used and it is conceivable that all three possibilities (no node, degenerate nodes or split nodes) can be observed with different functionals. As illustrated by this simple example, our simple and robust classification scheme serves as a valuable tool for settling such ambiguities.

The previous analysis may be extended to molecules with degenerate ground states, e.g. π-systems with an odd number of electrons. For such systems the ground state is usually a spin doublet $|\Psi_0^N\rangle$ with spin index $\sigma = \uparrow, \downarrow$. For simplicity, we consider only the zero-bias transmission, and combine particle and hole amplitudes into the transport amplitude $A_{\sigma\sigma}^{\uparrow,\downarrow}(V_g) = h_{\sigma\sigma}^{\uparrow,\downarrow}(V_g, 0) + p_{\sigma\sigma}^{\uparrow,\downarrow}(V_g, 0)$, which allows writing the linear conductance as:

$$G = \frac{e^2\hbar}{2\pi}\Gamma_\uparrow\Gamma_\downarrow \sum_{\sigma} (|A_{\sigma\sigma,\uparrow}^\sigma|^2 + |A_{\bar{\sigma}\bar{\sigma},\downarrow}^\bar{\sigma}|^2 + |A_{\bar{\sigma}\bar{\sigma},\uparrow}^\sigma|^2)$$

$$= \frac{e^2\hbar}{2\pi}\Gamma_\uparrow\Gamma_\downarrow (|W|^2 + 3|J|^2),$$

(8)

where the subscript $\sigma$ refers to the spin of the degenerate ground state, and $\bar{\sigma}$ is the opposite spin. The second line follows immediately by introducing the potential scattering amplitude $W = \sum_{\sigma} A_{\sigma\sigma,\uparrow}^\sigma = \sum_{\sigma} A_{\bar{\sigma}\bar{\sigma},\downarrow}^\bar{\sigma}$, and the exchange amplitude $J = A_{\bar{\sigma}\bar{\sigma},\uparrow}^\sigma = A_{\bar{\sigma}\bar{\sigma},\uparrow}^\sigma$, where the identities among the different amplitudes follow from spin rotational invariance (see Supplementary Information S3). This rewriting makes it clear that an interference dip in the conductance now demands coincident dips in both $W$ and $J$, something which is generally not possible, since the requirement for interference dips in the two are mutually exclusive (see Supplementary Information S3).

As an example, we show the calculated linear conductance for a biphenyl molecule with an odd number of electrons in the neutral π-system in Fig. 3. For such odd-alternant hydrocarbons, the pairing theorem results in a similar starring rule for the spin-flip component $A_{\sigma\sigma}^{\bar{\sigma}}$ with a classification $\mathcal{Q}_{\uparrow\downarrow} = -\mathcal{Q}_{\downarrow\uparrow}$ (see Supplementary Information S3). Once again, entering and leaving on alike or disjoint (starred/unstarred) sublattice sites decides whether $W$ or $J$ has a zero near the middle of the charge state (see Fig. 3). We note that this is at odds with the interference dip suggested in Ref. 5 to appear already within a single-orbital Anderson model, and it seems that the exchange term, $J$, has been missed there.

In an Anderson model it is always the potential scattering term, $W$, which vanishes at the particle-hole symmetric point of a single-orbital $\sigma$. With a molecule, the situation can be reversed, and produce a node in $J$ while keeping $W$ finite. This is shown for the BB’-contacted biphenyl in the right panel of Fig. 3. Since this exchange amplitude gives rise to Kondo effect in spinful dots and molecules, an interference dip in $J$ may cause an unusual gate-dependence of the Kondo temperature, as has indeed been observed in certain single-molecule devices [10, 19, 33].

In conclusion, we have provided a simple set of rules for classifying interacting off-resonant single-molecule junctions into two distinct interference classes with either an
even or an odd number of transmission minima. For alternate hydrocarbons, this classification reduces to a simple starring rule, with an extension to the spin-degenerate case, which revealed mutually exclusive interference dips in the competing potential scattering and exchange amplitudes. This provides a useful tool to discriminate between different numerical results, for which more reliable calculations are not readily available.

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DFT and GW calculations

We use DFT as implemented in the GPAW code to provide a quantum chemical description of charge transport through molecular junction systems \([S2]\). Molecules were optimized in the gas phase using the PBE exchange correlation (xc) functional \([S6]\). For all calculations the molecules were attached to the FCC hollow site of Au(111) with a Au-S bond length of 2.5 Å (1.83 Å above the surface). The scattering region supercell was modeled using 3-4 atomic Au layers on both sides of the molecule with 4 × 4 surface layer atoms. Periodic boundary conditions where used in the transverse directions and the 2D Brillouin zone was sampled using 4×4 \(k\)-points. We use semi-infinite atomistic leads and a double zeta polarized (DZP) basis set for all atoms in both the lead and the scattering region. Au atoms were frozen in the bulk lattice structure using the DFT derived lattice constant of \(a = 4.18\) Å.

For calculations based on GW and HF we use the same semi-empirical Pariser-Parr-Pople (PPP) model Hamiltonian as for the exact-diagonalization (ED) results in the main text.
Figure S1: Relaxed geometry of substituted stilbene in the AA' configuration used for DFT calculations.

The GW transport method is described in more detail in Refs. [S8–S10]. Briefly, the Green’s function of the contacted molecule is calculated from

\[
G_{ij}(\omega) = (\omega - H_0 - \Sigma_L(\omega) - \Sigma_R(\omega) - \Sigma_{xc}(\omega))^{-1}_{ij},
\]

where \(H_0\) is the noninteracting part of the Hamiltonian including the Hartree potential. \(\Sigma_\alpha\) is the embedding self-energy from lead \(\alpha\) accounting for the coupling to the semi-infinite leads. The semi-infinite leads are described using a nearest neighbor tight-binding chain with a large hopping element \(t_L = -20\) eV, i.e. a featureless wide band lead. The last site of semi-infinite tight-binding chains are coupled to the source \(s\) and drain \(d\) sites on the molecule, using a hopping element of \(t_{s/d} = -\sqrt{\gamma |t_L|/2}\). This results in a broadening of \(\sim \gamma\) of the \(s\) and \(d\) sites. We use \(\gamma = 1.0\) eV.

The self-energy is evaluated either using the Hartree-Fock or the GW approximation. We evaluate the GW self-energy fully self-consistently ensuring that conservation laws, such as charge conservation, are fulfilled. The energy dependence of \(G\) and \(\Sigma_{xc}\) is sampled on a uniform grid \(\omega_n = \varepsilon_n + i\eta\), where \(\eta = 0.001\) eV is an infinitesimal and \(\varepsilon_n\) ranges from -100 to 100 eV, with a spacing of \(\eta/2 = 0.0005\) eV.

Transport properties are for the DFT and GW methods calculated using the Landauer Büttiker (LB) transmission formula expressed in terms of Green’s functions

\[
\tau(\varepsilon) = Tr [G^R(\varepsilon)\Gamma^L(\varepsilon)G^a(\varepsilon)\Gamma^R(\varepsilon)],
\]

where \(\Gamma^a = i(\Sigma_\alpha - \Sigma_\alpha^a)\) is given in terms of the lead \(\alpha\) self-energy \(\Sigma_\alpha\). We calculate the conductance in the zero bias voltage limit as \(G = G_0 \int (-n_F'(\varepsilon, T))\tau(\varepsilon)d\varepsilon\), where \(n_F'(\varepsilon, T)\) is the derivative of the Fermi function with respect to energy. \(T\) is the temperature and \(G_0 = \)
2e²/h is the quantum of conductance, where h and e is Planck’s constant and the electronic charge, respectively. For the benzene-quinoid structure, we have verified that a calculation of the low bias $dI/dV$ as a function of a gate voltage $V_g$ in the GW approximation, where the current is obtained using the Meir-Wingreen formula, gives the same destructive interference features as using the LB transmission function expression. We show in Fig. 2 the comparison between the LB transmission function result (red) and the explicit $dI/dV$ (black). The interference induced dip is clearly visible, although it appears at slightly different gate potentials.

**S.2 Classification examples**

Many more systems exhibit destructive interference. Here we catalog two different types, namely the simple cross-conjugated hydrocarbons and the Quinoid-type molecules in the same family as the naphtalene molecular junction for which [S3] and [S7], have found experimental evidence for quantum interference.
| Molecule | Class | Nodes | Conductance $[G_0]$ |
|----------|-------|-------|---------------------|
| 1        | Odd   | 1     | ![Graph](image1.png) |
| 2        | Even  | 0     | ![Graph](image2.png) |
| 3        | Odd   | 1     | ![Graph](image3.png) |
| 4        | Even  | 2     | ![Graph](image4.png) |
| 5        | Even  | 2     | ![Graph](image5.png) |
| 6        | Odd   | 3     | ![Graph](image6.png) |
| 7        | Even  | 2     | ![Graph](image7.png) |

Table 1: Examples of interference classification. The zero bias conductance is calculated using the perturbative method based on exact diagonalization discussed in the paper.
S.3 The pairing theorem for alternant molecules

In general we describe the π-electrons on the molecule by the extended Hubbard (or Pariser-Parr-Pople) model, which can be written

\[ H = \hat{H}_T + \hat{H}_e + \hat{H}_U + \hat{H}_V. \] (S3)

Here

\[ \hat{H}_T = \sum_{ij,\sigma} t_{ij} \hat{c}_i^\dagger \hat{c}_j^\sigma + h.c. \] (S4)
\[ \hat{H}_e = \sum_i \varepsilon_i \hat{n}_i \] (S5)
\[ \hat{H}_U = \sum_i U_i \hat{n}_i^\uparrow \hat{n}_i^\downarrow \] (S6)
\[ \hat{H}_V = \sum_{i \neq j} V_{ij} (\hat{n}_i - 1)(\hat{n}_j - 1), \] (S7)

with \( \hat{n}_{i\sigma} = \hat{c}_i^\dagger \hat{c}_i^\sigma \), and \( \hat{n}_i = \hat{n}_i^\uparrow + \hat{n}_i^\downarrow \). The molecule consists of \( N_A \) atoms, each with a \( p_z \) orbital, hence \( \hat{c}_i^\dagger \) creates an electron with spin \( \sigma \) in the \( p_z \) orbital of atom number \( i \).

It turns out, that this Hamiltonian has a particular symmetry, when the molecule can be divided into two subsets, \( A \) and \( B \), of atoms, such that the hopping amplitudes only connect atoms which belong to different subsets, i.e. \( t_{ij} = 0 \), if \( i,j \) both are in \( A \) or both in \( B \). Such a molecule is called alternant or bipartite. To understand this symmetry, consider the anti-unitary transformation, which transforms complex numbers, \( z \), and creation operators as follows

\[ U(z \hat{c}_i^\dagger) U^\dagger = z^* (-1)^i \hat{c}_i^\sigma, \quad \text{for } i = 1 \ldots N_a. \] (S8)

Here we use the notation

\[ (-1)^i = \begin{cases} 1 & i \text{ in } A \\ -1 & i \text{ in } B \end{cases} \] (S9)

The transformation \( U \) is then composed of particle-hole transformation and an overall sign \((-1)^i\) followed by complex conjugation.

The number operators thus transforms as

\[ U\hat{n}_i^\sigma U^\dagger = 1 - \hat{n}_i^\sigma. \] (S10)
The various terms in the Hamiltonian transform as

\[ U \hat{H} U^\dagger = \sum_{ij,\sigma} (-1)^i (-1)^j \hat{c}_{j\sigma} \hat{c}_{j\sigma}^\dagger = \hat{H}_T, \quad (S11) \]

\[ U \hat{H}_v U^\dagger = U \sum_i (1 - \hat{n}_i^\uparrow)(1 - \hat{n}_i^\downarrow) = \hat{H}_U + U (N_a - \hat{N}_e), \quad (S12) \]

\[ U \hat{H}_v U^\dagger = \sum_{i \neq j} V_{ij} (2 - \hat{n}_i - 1)(2 - \hat{n}_j - 1) = \hat{H}_V, \quad (S13) \]

\[ U \hat{H}_\varepsilon U^\dagger = \sum_i \varepsilon_i (2 - \hat{n}_i), \quad (S14) \]

where \( \hat{N}_e = \sum_i \hat{n}_i \).

The invariance of \( \hat{H}_T \) relies heavily on the fact, that the molecule is alternant. The term \( \hat{H}_\varepsilon \) is not invariant. If, however, the energies \( \varepsilon_i \) are independent of \( i \), i.e. all being equal to a fixed energy \( \varepsilon_0 \), then the transformation is

\[ U \hat{H}_\varepsilon U^\dagger = \hat{H}_\varepsilon + 2\varepsilon_0 (N_a - \hat{N}_e). \quad (S15) \]

The full Hamiltonian now transforms as

\[ U \hat{H} U^\dagger = \hat{H} + 2\varepsilon_0 (N_a - \hat{N}_e). \quad (S16) \]

If we finally choose the zero of the one-electron energies such that \( \varepsilon_0 = -U/2 \), then the Hamiltonian is invariant under the transformation (8).

We have specified how operators transform. We also need to specify how states in the Hilbert space transform. We only need to do that for the vacuum state \( |0\rangle \) and for the completely filled state \( |2N_a\rangle = \Pi_{\sigma\sigma'} \hat{c}_{i\sigma}^\dagger \hat{c}_{i\sigma'} |0\rangle \), since all other states can be obtained from these by application of creation operators and by use of the superposition principle. The states transform as follows

\[ U |0\rangle = |2N_a\rangle, \quad U |2N_a\rangle = |0\rangle. \quad (S17) \]

It is easy to show that the last equation is consistent with the first and with the transformation rules for the creation operators.

For later use we also introduce the total spin operator. The spin operator is written in second quantized form

\[ \vec{S} = \frac{\hbar}{2} \sum_{i\sigma\sigma'} \hat{c}_{i\sigma}^\dagger \vec{\sigma}_{\sigma\sigma'} \hat{c}_{i\sigma'}. \quad (S18) \]
This operator transforms as follows (here the anti-unitarity of $\mathcal{U}$ is important),

$$
\mathcal{U} \hat{S} \mathcal{U}^\dagger = \frac{\hbar}{2} \sum_{i\sigma\sigma'} \hat{c}_{i\sigma} \sigma^\dagger \sigma' \hat{c}^\dagger_{i\sigma'} = -\hat{S}.
$$

(S19)

Let us now consider a state with $N$ electrons, $|\Psi^{(N)}\rangle$. The transformed state $\mathcal{U}|\Psi^{(N)}\rangle$ will then be a state with $2N_a - N$ electrons. Let us in particular consider an eigenstate of the Hamiltonian:

$$
\hat{H}|\Psi^{(N)}_n\rangle = E_n^N |\Psi^{(N)}_n\rangle.
$$

(S20)

We denote the transformed state

$$
|\Phi^{(2N_a-N)}_n\rangle = \mathcal{U}|\Psi^{(N)}_n\rangle.
$$

(S21)

Since the Hamiltonian is invariant under $\mathcal{U}$, this state is also an eigenstate of $\hat{H}$ with the same eigenvalues

$$
\hat{H}|\Phi^{(2N_a-N)}_n\rangle = E_n^N |\Phi^{(2N_a-N)}_n\rangle.
$$

(S22)

The total spin-operator $\hat{S}^2$ commutes with $\hat{H}$, so we can classify the eigenstates by spin-quantum numbers $S$ and $M$. An energy level with spin $S$ will be $2S + 1$ times degenerate, and so will the transformed level. Furthermore, if the state $|\Psi^{(N)}_n\rangle$ is an eigenstate of $\hat{S}_z$ with eigenvalue $M$, then the transformed state will be an eigenstate of $\hat{S}_z$ with eigenvalue $-M$.

### S.3.1 Singlet groundstate

Let us consider the special case of half-filling, i.e. $N = N_a$. Let us further assume, that $N_a$ is even, and that the ground state is a non-degenerate spin singlet. In this case $|\Psi^{(N_a)}_0\rangle$ and $|\Phi^{(N_a)}_0\rangle$ is the same state and they may differ only by a phase factor.

We can now investigate $\langle \Psi^{(N+1)}_n | \hat{c}^\dagger_{i\sigma} | \Psi^{(N)}_0 \rangle$ and $\langle \Psi^{(N-1)}_n | \hat{c}_{i\sigma} | \Psi^{(N)}_0 \rangle$, sometimes called Feynman-Dyson (FD) orbitals.

In the special case of half-filling, i.e. $N = N_a$, we can rewrite in terms of the transformed states:

$$
\langle \Psi^{(N_a+1)}_n | \hat{c}^\dagger_{i\sigma} | \Psi^{(N_a)}_0 \rangle = \langle \Psi^{(N_a+1)}_n | \mathcal{U} \hat{c}^\dagger_{i\sigma} \mathcal{U}^\dagger | \Psi^{(N_a)}_0 \rangle
$$

$$
= (-1)^i \langle \Phi^{(N_a-1)}_n | \hat{c}_{i\sigma} | \Phi^{(N_a)}_0 \rangle
$$

$$
= (-1)^i \langle \Phi^{(N-1)}_n | \hat{c}_{i\sigma} | \Phi^{(N)}_0 \rangle e^{i(\gamma_0 - \gamma_n)}. \quad \text{(S23)}
$$
Here $\gamma_0$ and $\gamma_1$ are the phase factors of the two involved $\Phi$ states. We see, that apart from a phase factor the two FD orbitals are in fact closely related.

As discussed in the main text, the following combination of FD orbitals is crucial when determining interference in electron transport through molecules which have a singlet ground state.

Consider

$$Q_i = \frac{\langle \Psi_0^N | \hat{c}^\dagger_{i\sigma} | \Psi_0^{N-1} \rangle \langle \Psi_0^{N-1} | \hat{c}_{i\sigma} | \Psi_0^N \rangle}{\langle \Psi_0^N | \hat{c}^\dagger_{i\sigma} | \Psi_0^{N+1} \rangle \langle \Psi_0^{N+1} | \hat{c}_{i\sigma} | \Psi_0^N \rangle}. \quad (S24)$$

Utilizing the result from above we can rewrite $Q_i$ like

$$Q_i = (-1)^{\sigma_x} (-1)^{\sigma_d} e^{-i(\gamma_{\sigma} - \gamma_{\sigma_d})} e^{i(\gamma_{\sigma} - \gamma_{\sigma_d})} \frac{\langle \Psi_0^N | \hat{c}^\dagger_{i\sigma} | \Psi_0^{N-1} \rangle \langle \Psi_0^{N-1} | \hat{c}_{i\sigma} | \Psi_0^N \rangle}{\langle \Psi_0^N | \hat{c}^\dagger_{i\sigma} | \Psi_0^{N+1} \rangle \langle \Psi_0^{N+1} | \hat{c}_{i\sigma} | \Psi_0^N \rangle} = (-1)^{\sigma_x} (-1)^{\sigma_d}, \quad (S25)$$

where we have used that the Feynman-Dyson orbitals are in fact real.

**S.3.2 Doublet groundstate**

If $N_a$ is odd, then the total spin must be half-integer. Let us assume that the ground state is a spin doublet. In that case the ground state can be classified by a spin quantum number $\sigma$, $|\Psi_0^{(N_a)}\rangle$. The transformed states must have opposite spins, i.e. $|\Phi_0^{(N_a)}\rangle = e^{i\gamma} |\Psi_0^{(N_a)}\rangle$ and $|\Phi_0^{(N_a)}\rangle = e^{-i\gamma'} |\Psi_0^{(N_a)}\rangle$. We can determine the phase factor $e^{i\gamma}$ by considering the spin rotation operator:

$$R_x = e^{i\pi S_x}. \quad (S26)$$

This will convert an up-spin state into a down-spin state and vice versa. In the two-dimensional subspace spanned by $\{|\Psi_0^{(N_a)}\rangle, |\Psi_0^{(N_a)}\rangle\}$, the spin operator is $S_x = \frac{1}{2} \sigma_x$ and hence the rotation operator can be written

$$R_x = i \sigma_x. \quad (S27)$$

we can e.g. write

$$R_x |\Psi_0^{(N_a)}\rangle = i |\Psi_0^{(N_a)}\rangle. \quad (S28)$$

The spin rotation operator transforms as follows under the unitary transformation $U$

$$UR_x U^\dagger = U e^{i\pi S_x} U^\dagger = e^{-i\pi S_x} = R_x^\dagger, \quad (S29)$$
which follows from (19).

Transforming equation (28) we obtain
\[ -ie^{i\gamma} |\Psi_{0_1}^{(N_a)}\rangle = ie^{i\gamma'} |\Psi_{0_{1'}}^{(N_a)}\rangle, \]
(S30)
from which we conclude that
\[ \gamma' = \gamma + \pi. \]
(S31)

We can do the same exercise for a spin-triplet set of states. Let e.g. the three states $|\Psi_{0_1}^{(N)}, |\Psi_{0_0}^{(N)}\rangle, |\Psi_{0_{-1}}^{(N)}\rangle$ be a basis in a triplet level of a molecule with $N$ electrons. In this subspace we have chosen phases such that $S_x$ has the standard representation
\[ S_x = \frac{1}{\sqrt{2}} \begin{pmatrix} 0 & 1 & 0 \\ 1 & 0 & 1 \\ 0 & 1 & 0 \end{pmatrix}, \]
(S32)
and hence the rotation operator is
\[ R_x = -\begin{pmatrix} 0 & 0 & 1 \\ 0 & 1 & 0 \\ 1 & 0 & 0 \end{pmatrix}. \]
(S33)

In the $2N_a - N$ electron sector we have a similar representation. The operator $U$ will be a mapping from the $N$ triplet to the $2N_a - N$ triplet, and it can be represented in terms of a set of phases:
\[ U = \begin{pmatrix} 0 & 0 & e^{i\gamma_1} \\ 0 & e^{i\gamma_0} & 0 \\ e^{i\gamma_{-1}} & 0 & 0 \end{pmatrix}. \]
(S34)

The general equation (29) will in this case become
\[ -\begin{pmatrix} 0 & 0 & e^{i(\gamma_1 - \gamma_{-1})} \\ 0 & e^{i(\gamma_0 - \gamma_0)} & 0 \\ e^{i(\gamma_{-1} - \gamma_1)} & 0 & 0 \end{pmatrix} = -\begin{pmatrix} 0 & 0 & 1 \\ 0 & 1 & 0 \\ 1 & 0 & 0 \end{pmatrix}, \]
(S35)
which results in $\gamma_1 = \gamma_{-1}$.

For the doublet ground state the zero-bias conductance is the sum of three different
The quantum interference class of the potential scattering, \( W \), is then classified according to,

\[
Q_W = \frac{\langle \Psi_0 | \left( c_{i\uparrow}^\dagger + c_{i\downarrow}^\dagger \right) \left| \Psi_0^{(N)} \right\rangle \langle \Psi_0^{(N-1)} | \left( c_{i\uparrow}^\dagger + c_{i\downarrow}^\dagger \right) | \Psi_0^{(N-1)} \rangle}{\langle \Psi_0 | \left( c_{i\uparrow}^\dagger + c_{i\downarrow}^\dagger \right) \left| \Psi_0^{(N+1)} \right\rangle \langle \Psi_0^{(N)} | \left( c_{i\uparrow}^\dagger + c_{i\downarrow}^\dagger \right) | \Psi_0^{(N+1)} \rangle} \tag{S43}
\]
However, by following the same reasoning as in equation (S23)-(S25), it is straightforward to show that for alternant lattices $Q_W = Qi$.

In the case of exchange processes, the relevant combination of Feynman-Dyson orbitals is

$$Q_{ij} = \frac{\langle \Psi_{\sigma}^N | \hat{c}_{i,\bar{\sigma}} \rangle \langle \Psi_{\sigma}^{N-1} | \hat{c}_{i,\sigma} \rangle \langle \Psi_{\sigma}^{N-1} | \hat{c}_{i,\sigma} \rangle \langle \Psi_{\sigma}^{N} | \hat{c}_{i,\bar{\sigma}} \rangle}{\langle \Psi_{\sigma}^{N} | \hat{c}_{i,\bar{\sigma}} \rangle \langle \Psi_{\sigma}^{N} | \hat{c}_{i,\bar{\sigma}} \rangle \langle \Psi_{\sigma}^{N} | \hat{c}_{i,\sigma} \rangle \langle \Psi_{\sigma}^{N} | \hat{c}_{i,\sigma} \rangle}.$$  

(S44)

In this case the $N_a+1$ and $N_a-1$ states are either singlet or triplet states with the appropriate relationship between phases discussed above, while the $N_a$ states forms a spin-doublet, with its particular phases containing a factor $-1$ also discussed above. The resulting factor becomes

$$Q_{ij} = -(-1)^{i_j}(-1)^{i_d},$$  

(S45)

i.e. $Q_{ij} = -Q_i = -Q_{iW}$, and hence in alternant lattices the two contributions to the conductance always belong to different interference classes.

### S.4 Further results on spin doublet ground states

![Diagram](image)

Figure S3: **Pentadienyldithiol molecular junction transmission.** Bergfield et al. [SI] have previously considered this particular molecular junction, with another perturbative method and found an interference feature in the low-bias conductance. However, it seems that they have ignored the exchange contribution to the conductance, which masks the interference node present in the potential scattering term.

Bergfield et al. [SI] have previously attempted to describe quantum interference in molecular radicals. However our analysis does not reproduce their results. For completeness we have
included a calculation of the different components of the zero-bias conductance for a simple molecular junction considered by Bergfield et al. [S1].

The considered hydrocarbon \( \pi \)-system is alternant, and by use of Liebs theorem [S4] the ground state of the half-filled (neutral) \( \pi \)-system is a spin doublet. Because the two substitution sites belong to different sub-lattices the \( Q_W = 1 \) and \( Q_J = -1 \), meaning that the potential scattering \(|W|^2\) belongs to the odd quantum interference class, while the exchange \(|J|^2\) belong to the even class. This classification is also immediately evident from the zero-bias conductance presented in Figure 3.
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