

## Exchange interaction and Fano resonances in diatomic molecular systems

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We propose a mechanism to use scanning tunneling microscopy for direct measurements of the two-electron singlet-triplet exchange splitting  $J$  in diatomic molecular systems, using the coupling between the molecule and the substrate electrons. The different pathways for electrons lead to interference effects and generate kinks in the differential conductance at the energies for the singlet and triplet states. These features are related to the Fano resonance due to the branched electron wave functions. The ratio between the tunneling amplitudes through the two atoms can be modulated by spatial movements of the tip along the surface.

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There are various techniques that allow one to detect and manipulate spin states in the solid state, which have attracted a lot of interest. A partial list includes the optical detection of electron spin resonance (ESR) in a single molecule,<sup>1</sup> tunneling through a quantum dot,<sup>2</sup> and, more recently, ESR scanning tunneling microscopy (ESR-STM) technique.<sup>3,4</sup> The interest in ESR-STM is due to the possibility of manipulating single spins,<sup>5-7</sup> something which is crucial in spintronics and quantum information. Experimentally, modulation in the tunneling current has been observed by STM using spin-unpolarized electron beam.<sup>2,3</sup> Lately, there has also been a growing interest in using spin-polarized electron beams for direct detection of spin structures,<sup>8</sup> as well as utilizing inelastic electron scanning tunneling spectroscopy (IETS) for detection of local spatial variations in electron-boson coupling in molecular systems.<sup>9,10</sup>

Typically in STM measurements with an object located on a substrate surface, the tunneling current can either go directly between the STM tip and the substrate or go via the object. The tunneling electrons are thus branched between different pathways, which gives rise to interference effects when the partial waves merge into one in the tip or the substrate.<sup>9</sup> This interference leads to a suppressed transmission probability for the tunneling electrons at certain energies. The suppressed transmission is a fingerprint of Fano resonances<sup>11</sup> and generally appear in systems where tunneling electrons are branched between different pathways. Recently, Fano resonances have been studied in double- and triple-quantum-dot systems,<sup>12</sup> where the different pathways are constituted of the different quantum dots.

In this paper we propose a method to measure the two-electron singlet-triplet ( $S$ - $T$ ) exchange splitting  $J$  in a diatomic molecule by means of STM. The presence of two pathways for the tunneling current between the tip and the substrate, through the diatomic molecule, gives rise to interference effects (Fano resonance) between the electron waves traveling through the singlet and triplet states. In the direct tunneling between the tip and substrate via the molecule, the probability for the tunneling is proportional to  $\Gamma_0$ . In addition, because of the phase-space branching of tunneling possibilities, the tunneling probability is multiplied by the interference probability  $\gamma^2$ ; hence, the characteristic energy width of the antiresonance is  $\gamma^2\Gamma_0$ . Clearly, the antiresonances will be measurable in the second derivative of the

current whenever  $\gamma \ll 1$ . Such measurements will be extremely useful in situations where the level broadening is larger than the singlet-triplet splitting, since a large broadening smears all features and therefore prevents identification of those states in the differential conductance.

Fano resonances can be realized in a variety of systems, ranging from systems with interactions between continuum states and a localized state to systems where the branching of the wave function through diatomic molecules. In the case we consider here, we also have to include the fact that the one-electron states in a two-level system, with the levels being resonant, consist of an antibonding and a bonding state (both being spin degenerate). This modifies the expected transport properties such that transitions between the triplet and the antibonding one-electron states generate a dip in the transmission at the energy for this transition; see Fig. 1(b) (dashed line). On the other hand, transitions between the singlet and the bonding one-electron states give rise to a dip in the transmission at the energy for this transition; see Fig. 1(b) (solid line). In turn, the features that appear at voltages corresponding to both the singlet and triplet states provide a

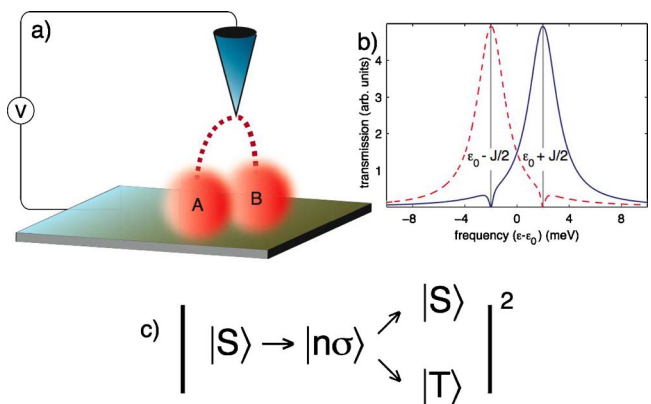


FIG. 1. (Color online) (a) Diagram of the diatomic  $A+B$  molecule coupled to the tip and substrate. The particles interact via exchange interaction  $J$ . (b) Transmission for transitions between the singlet and triplet and the antibonding (dashed line) and bonding (solid line) one-electron states. (c) Phase-space branching of the tunneling wave functions between the singlet  $|S\rangle$  and triplet  $|T\rangle$  states. The respective amplitudes of the tunneling through these states have to be added, resulting in the Fano-like features.

unique fingerprint which allows a readout of the  $S$ - $T$  exchange splitting  $J$ .

In a regular Fano resonance, interference occurs between the different tunneling paths in real space, one path going through the molecule to the substrate whereas the other going directly into the substrate. Here, on the other hand, the interference occurs between different pathways in phase space where the tunneling can occur through a singlet  $|S\rangle$  or triplet  $|T\rangle$ . The respective amplitudes of the tunneling through these states have to be added, resulting in the Fano-like features; see Fig. 1(c).

In general, the Fano resonance appearing at voltages that correspond to both the singlet and the triplet states is expected to be found in any model which includes one-electron states and two-electron singlet and triplet configurations and which accounts for the  $S$ - $T$  exchange splitting  $J$ . For simplicity, we assume large intralevel charging energies  $U_A$  and  $U_B$  so that double occupancy on each atom can be excluded, and we assume that the interlevel hopping is negligible. The last assumption is not crucial for the effect; it is merely a matter of convenience. We thus describe the system by the Hamiltonian

$$\mathcal{H}_{AB} = \sum_{\sigma} \varepsilon_0 (d_{A\sigma}^{\dagger} d_{A\sigma} + d_{B\sigma}^{\dagger} d_{B\sigma}) - J/2 (n_{A\uparrow} + n_{A\downarrow})(n_{B\uparrow} + n_{B\downarrow}) - 2J \mathbf{S}_A \cdot \mathbf{S}_B. \quad (1)$$

Here,  $d_{A\sigma/B\sigma}^{\dagger}$  ( $d_{A\sigma/B\sigma}$ ) creates (annihilates) an electron in atom  $A/B$  at the energy  $\varepsilon_0$ ,  $n_{A\sigma}$  and  $n_{B\sigma}$  are the number operators, and  $J$  denotes the spin-spin interaction (exchange splitting) parameter for the interactions between the spins  $\mathbf{S}_A$  and  $\mathbf{S}_B$ . In this model, the one-electron states are the (spin-degenerate) antibonding and bonding states  $|1\sigma\rangle = (d_{A\sigma}^{\dagger} - d_{B\sigma}^{\dagger})|0\rangle/\sqrt{2}$  and  $|2\sigma\rangle = (d_{A\sigma}^{\dagger} + d_{B\sigma}^{\dagger})|0\rangle/\sqrt{2}$ , respectively, whereas the two-electron states consist of the singlet state  $|S\rangle = [d_{B\downarrow}^{\dagger} d_{A\uparrow}^{\dagger} - d_{B\uparrow}^{\dagger} d_{A\downarrow}^{\dagger}]|0\rangle/\sqrt{2}$  and triplet states  $|T_1\rangle = d_{B\uparrow}^{\dagger} d_{A\uparrow}^{\dagger}|0\rangle$ ,  $|T_2\rangle = d_{B\uparrow}^{\dagger} d_{A\downarrow}^{\dagger}|0\rangle$ , and  $|T_3\rangle = (d_{B\downarrow}^{\dagger} d_{A\uparrow}^{\dagger} + d_{B\uparrow}^{\dagger} d_{A\downarrow}^{\dagger})|0\rangle/\sqrt{2}$ .

For simplicity, however, we will perform our calculations for the interference between the singlet  $|S\rangle$  and triplet  $|T\rangle = |T_3\rangle$  ( $=|S=1, S_z=0\rangle$ ). The interference arising from the other triplet state  $|T_{1,2}\rangle = |S=1, S_z=\pm 1\rangle$  leads to results which only renormalize the coefficients in the final expressions for the transmission and can thus be omitted in our description of the effect.

In order to keep the number of parameters to a minimum, we ignore the splitting between the bonding and antibonding one-electron states. This assumption is not crucial for our subsequent analysis, since the Fano resonance we discuss arises due to interference between the singlet and triplet states, and not between the one-electron states. In order to make contact with experiments, we assume that  $J$  corresponds to the exchange splitting which is renormalized by the coupling to the substrate—that is, the  $J$  that will be detected by any measurement in a given setup.

To illustrate the electron interference along different paths consider an electron tunneling from the tip to the substrate via the molecule. Because of the different paths, the electron acquires a different phase depending on whether it travels

through  $A$  or  $B$  and, in addition, whether it makes a transition between the triplet or singlet state and the bonding or antibonding one-electron states. To be specific, suppose a spin  $\uparrow$  electron leaves the molecule from the singlet state to a medium that hybridizes equally strong to  $A$  and  $B$ —e.g.,

$$(d_{A\uparrow} + d_{B\uparrow})|S\rangle = (-d_{B\downarrow}^{\dagger} - d_{A\downarrow}^{\dagger})|0\rangle/\sqrt{2} = -|2\downarrow\rangle. \quad (2)$$

The final state is orthogonal to the antibonding state  $|1\downarrow\rangle$ . Hence, the singlet state couples to the bonding one-electron state. Likewise, supposing that a spin- $\uparrow$  electron tunnels out from the triplet state—e.g.,

$$(d_{A\uparrow} + d_{B\uparrow})|T\rangle = (-d_{B\downarrow}^{\dagger} + d_{A\downarrow}^{\dagger})|0\rangle/\sqrt{2} = |1\downarrow\rangle \quad (3)$$

shows that the triplet only couples to the antibonding one-electron state.

The tunneling between the tip and substrate and the molecule is modeled by  $\mathcal{H}_T = \sum_{k\sigma} [v_{Ak\sigma} c_{k\sigma}^{\dagger} d_{A\sigma} + v_{Bk\sigma} c_{k\sigma}^{\dagger} d_{B\sigma} + \text{H.c.}]$ , where  $c_{k\sigma}^{\dagger}$  creates an electron in the tip and substrate, whereas  $v_{Ak\sigma}$  and  $v_{Bk\sigma}$  are the tunneling rates between the tip and substrate and  $A$  and  $B$ , respectively. Reformulating the molecule in terms of its eigenstates—e.g.,  $\mathcal{H}_{AB} = \sum_{\sigma, n=1,2} E_n |n\sigma\rangle\langle n\sigma| + E_S |S\rangle\langle S| + E_T |T\rangle\langle T|$  with the eigenenergies  $E_n = \varepsilon_0$ ,  $n=1,2$ , corresponding to the states  $|n\sigma\rangle$ , and  $E_{S/T} = 2\varepsilon_0 \mp J/2$ —and neglecting the transitions between the empty and one-electron states, the tunneling Hamiltonian becomes  $\mathcal{H}_T = \sum_{k\sigma n X} [v_{k\sigma n X} c_{k\sigma}^{\dagger} |n\sigma\rangle\langle X| + \text{H.c.}]$ , where  $X=S, T$ , whereas

$$v_{k\sigma n X} = v_{Ak\sigma} \langle n\sigma | d_{A\sigma} | X \rangle + v_{Bk\sigma} \langle n\sigma | d_{B\sigma} | X \rangle. \quad (4)$$

This form of the tunneling rate reflects the real-space branching of the electrons tunneling between the tip and the substrate via the molecule. From this description of the tunneling rate we define the couplings  $\Gamma_{nXX'n'}^{L/R} = 2\pi \sum_{k \in L/R} v_{k\sigma n X}^* v_{k\sigma n' X'} \delta(\omega - \varepsilon_{k\sigma})$ , where  $L/R$  denote states in the tip/substrate. In the present study, the spin currents through the system are identical; thus, we do not explicitly indicate the spin in the couplings.

Suppose that the molecule is in the two-electron singlet state. The tunneling current between the tip and the substrate is then mediated by sequences like  $|S\rangle \rightarrow |n\sigma\rangle \rightarrow |X\rangle$ , where  $X$  either of the singlet ( $S$ ) or the triplet ( $T$ ) states. Hence, there occur indirect  $S$ - $T$  transitions, in the sense that the tunneling may cause a singlet configuration to be turned into a triplet and vice versa; see Fig. 2. These indirect  $S$ - $T$  transitions give rise to the interference effects between the different transport channels, which implies that multiple-scattering events have to be taken into account in the description of the tunneling through the molecule. These tunneling events leading to the interference resemble cotunneling often discussed in this context.<sup>13</sup> Here, the multiple-scattering events are accounted for through the Green functions (GFs)  $G_{nXX'n}(t, 0)$ ,<sup>14</sup> where subscripts  $nX$  denote the transitions  $|n\bar{\sigma}\rangle\langle X|$ , whereas subscripts  $Xn$  denote the conjugate transitions  $|X\rangle\langle n\bar{\sigma}|$ .

We assume, for simplicity, that both atoms couple equally to the substrate and model this by letting  $v_{Aq\sigma} = v_{Bq\sigma} = v_{q\sigma}$  for  $q\sigma \in R$ . From Eqs. (3) and (4) this leads to a vanishing probability for transitions between the triplet and bonding one-electron states, since  $|v_{q\sigma 2T}| = |v_{q\sigma}| |(\langle 2\bar{\sigma} | d_{A\sigma} | T \rangle + \langle 2\bar{\sigma} | d_{B\sigma} | T \rangle)|$

$=|v_{q\sigma}|[-1/2+1/2]=0$ . Likewise, from Eqs. (2) and (4), we note that the probability for transitions between the singlet and antibonding one-electron state vanishes. Hence, the only nonvanishing coupling matrix elements between the molecule and the substrate are given by  $\Gamma_{1T}^R=\Gamma_{2S}^R=\Gamma_0/2$ , where  $\Gamma_0=2\pi\sum_{k\in L,R}|v_{k\sigma}|^2\delta(\omega-\varepsilon_{k\sigma})$ . As we mentioned, the Fano resonance feature should be present for any bonding and antibonding splitting, since the interference we discuss occurs between the different tunneling processes  $|S\rangle\rightarrow|n\sigma\rangle\rightarrow|S\rangle$  and  $|S\rangle\rightarrow|n\sigma\rangle\rightarrow|T\rangle$ , and not between the one-electron states; see Fig. 2.

The tunneling between the tip and the molecule, however, is assumed to depend on the spatial position of the tip relative to  $A$  and  $B$ . Introducing the functions  $\gamma_{A/B}(|\mathbf{r}-\mathbf{r}_{A/B}|)$ , we model the spatial dependence by putting  $v_{Ap\sigma}=\gamma_A(|\mathbf{r}-\mathbf{r}_A|)v_{p\sigma}$  and  $v_{Bp\sigma}=\gamma_B(|\mathbf{r}-\mathbf{r}_B|)v_{p\sigma}$  for  $p\sigma\in L$ . The coupling matrix between the antibonding one-electron state and the two-electron states for the tunneling between the tip and the molecule then becomes

$$\mathbf{\Gamma}_1^L = \begin{pmatrix} \Gamma_{1T}^L & \Gamma_{1TS1}^L \\ \Gamma_{1ST1}^L & \Gamma_{1S}^L \end{pmatrix} = \frac{\Gamma_0}{8} \begin{pmatrix} (\gamma_A + \gamma_B)^2 & \gamma_A^2 - \gamma_B^2 \\ \gamma_A^2 - \gamma_B^2 & (\gamma_A - \gamma_B)^2 \end{pmatrix}. \quad (5)$$

The coupling matrix between the bonding state and the two-electron states is obtained by letting  $\pm\rightarrow\mp$  in the diagonal elements in Eq. (5). The assumption that the atoms couple equally to the substrate is not crucial. For unequal couplings between the atoms the substrate would result in the coupling matrices  $\mathbf{\Gamma}_{1/2}^R$  being full (structurally equal to  $\mathbf{\Gamma}_{1/2}^L$ ). However, since the tip is movable, inequalities in the coupling between the atoms and the substrate can be canceled by relocating the tip to a position where it couples equally to both atoms.

Using the equation-of-motion technique we find that the Fourier-transformed retarded GF, to a good approximation, can be solved by<sup>15</sup>

$$G_{nTTn}^r(\omega) = \frac{\omega - (E_S - E_n) - \Sigma_{nS}^r(\omega)}{C_n(\omega)}, \quad (6a)$$

$$G_{nTSn}^r(\omega) = \frac{\Sigma_{nTSn}^r(\omega)}{C_n(\omega)}, \quad (6b)$$

$$\Sigma_{nS}^r(\omega) = \sum_{k\sigma} \frac{|v_{k\sigma nS}|^2}{\omega - \varepsilon_{k\sigma} + i0^+}, \quad (6c)$$

$$\Sigma_{nTSn}^r(\omega) = \sum_{k\sigma} \frac{v_{k\sigma nT}^* v_{k\sigma nS}}{\omega - \varepsilon_{k\sigma} + i0^+}, \quad (6d)$$

where  $E_S - E_n = \varepsilon_0 - J/2$ . The GFs  $G_{nSSn}^r$  and  $G_{nSTn}^r$  are obtained from Eq. (6) by letting  $T(S)\rightarrow S(T)$ , where  $E_T - E_n = \varepsilon_0 + J/2$ . In Eq. (6) we have used the function  $C_n(\omega) = \det \mathbf{G}_n^{r,-1} = (\omega - \omega_{n+})(\omega - \omega_{n-})$ —that is, the poles of the GF, which are given by

$$\omega_{1\pm} = \varepsilon_0 - i \frac{\Gamma_0}{8} \left( 1 + \frac{\gamma_A^2 + \gamma_B^2}{2} \right) \pm \frac{1}{2} \sqrt{\left[ J - i \frac{\Gamma_0}{4} (1 + \gamma_A \gamma_B) \right]^2 - \left( \frac{\Gamma_0}{2} \frac{\gamma_A^2 - \gamma_B^2}{4} \right)^2}, \quad (7a)$$

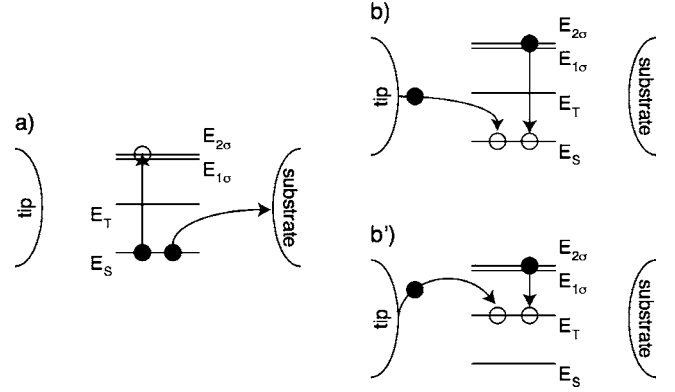


FIG. 2. Example of tunneling events leading to the interference. First (a) an electron leaves the molecule through a transition to the antibonding one-electron state  $|2\sigma\rangle$ . Second, an electron enters the molecule through a transition to either the singlet state (b) or to the triplet state (b').

$$\omega_{2\pm} = \varepsilon_0 - i \frac{\Gamma_0}{8} \left( 1 + \frac{\gamma_A^2 + \gamma_B^2}{2} \right) \pm \frac{1}{2} \sqrt{\left[ J + i \frac{\Gamma_0}{4} (1 + \gamma_A \gamma_B) \right]^2 - \left( \frac{\Gamma_0}{2} \frac{\gamma_A^2 - \gamma_B^2}{4} \right)^2}. \quad (7b)$$

These expressions are obtained by neglecting the real parts of the self-energies  $\Sigma_{nS}^r$  and  $\Sigma_{nTSn}^r$ ; we have  $\Sigma_{1(2)}^r(\omega) = -i(\mathbf{\Gamma}_{1(2)}^L + \mathbf{\Gamma}_{1(2)}^R)/2$ . Here, subscript 1 (2) refers to the antibonding (bonding) one-electron state, whereas  $+(-)$  refers to the triplet (singlet) two-electron state. Hence, the energy  $\omega_{1+}$  corresponds to transitions between the triplet and antibonding states.

From Eqs. (7) we extract the widths of the transitions between the one- and two-electron states. Assuming  $\gamma_B = \kappa\gamma_A$ , where  $\gamma_A \ll 1$  and  $0 \leq \kappa \leq 1$ , we find that the widths of the transitions between the triplet (singlet) and bonding (antibonding) states are significantly smaller than the transitions between the triplet (singlet) and the antibonding (bonding) states. Indeed, while the widths of the main peaks at  $\omega_{1+}$  and  $\omega_{2-}$  are approximately  $\Gamma_0/4$ , the widths of the narrow peaks at  $\omega_{1-}$  and  $\omega_{2+}$  are approximately  $(\Gamma_0/4)(1 + \kappa^2)\gamma_A^2/4$ . Hence, for small  $\gamma_A$  we expect sharp features in the differential conductance for the system. However, due to the small width of the dips, these features will be easier to observe in the derivative of the differential conductance—i.e., the second derivative of the current  $I \sim \text{tr} \int \mathcal{T}(\omega)[f_L(\omega) - f_R(\omega)]d\omega$  which here is given by

$$\frac{\partial^2 I}{\partial V^2} \sim \int \mathcal{T}(\omega) \left( \frac{\tanh[\beta(\omega - \mu_L)/2]}{\cosh^2[\beta(\omega - \mu_L)/2]} - \frac{\tanh[\beta(\omega - \mu_R)/2]}{\cosh^2[\beta(\omega - \mu_R)/2]} \right) d\omega, \quad (8)$$

where  $\mathcal{T}_n(\omega) = \text{tr} \mathbf{\Gamma}_n^L \mathbf{G}_n^r(\omega) \mathbf{\Gamma}_n^R \mathbf{G}_n^a(\omega)$  is the transmission coefficient,<sup>16</sup> whereas  $\mu_{L/R}$  is the chemical potential of the tip and substrate. We also note that measuring  $\partial^2 I / \partial V^2$  is particularly useful in situations where the level broadening is larger than the singlet-triplet splitting, since a large level

broadening precludes identification of those states in the differential conductance  $\partial I/\partial V$ .

Under the given conditions we find that the total transmission  $\mathcal{T}=\sum_n \mathcal{T}_n$  through the molecule is given by

$$\mathcal{T}(\omega) = \left(\frac{\Gamma_0}{4}\right)^2 (\gamma_A + \gamma_B)^2 \times \left( \left| \frac{\omega - \varepsilon_0 + J/2}{C_1(\omega)} \right|^2 + \left| \frac{\omega - \varepsilon_0 - J/2}{C_2(\omega)} \right|^2 \right), \quad (9)$$

which shows dips at the energies corresponding to the transitions between the one-electron and two-electron singlet and triplet states—e.g., at  $\omega = \varepsilon_0 \mp J/2$ , respectively— independent of  $\gamma_{A/B}$ . From the above analysis of the widths, these dips are expected to be sharp since their positions in the transmission exactly correspond to the roots  $\omega_{1-}$  and  $\omega_{2+}$ , respectively, for small  $\gamma_A$ .

We note here that the approach by Tersoff and Hamann<sup>17</sup> would have been sufficient in the case of proportional couplings between the molecule and the tip and substrate—e.g.,  $\Gamma^L = \lambda \Gamma^R$ , where  $\lambda$  is a real scalar. In the present situation, however, the couplings are not proportional to one another and the transmission coefficient must be described as above.

Asymmetric coupling between both the tip and substrate and the atoms generates a shift in the positions of the transmission dips.<sup>18</sup> This result shows that the distance between

the transmission dips deviates from  $J$  by at most 6% for asymmetries  $v_{Ap(q)\sigma}/v_{Bp(q)\sigma} = \gamma_{L(R)} \leq 0.7$ .<sup>18</sup> Thus, even for asymmetric coupling, this will still be a good measure of  $J$ .

In conclusion we propose to use the interference between different paths of the tunneling electron wave function as a tool to detect the  $S$ - $T$  splitting in a single molecule. This splitting could be observed as features in the tunneling conductance. Because the features we find are rather narrow, they can be, more prominently, revealed in the  $\partial^2 I/\partial V^2$  peaks that would correspond to the  $S$ - $T$  splitting. Our proposed measurements are particularly useful in cases where the level broadening is larger than the singlet-triplet splitting. The splitting produces interference between the possible pathways for electrons to tunnel through virtual states with different energies, identical to classical Fano resonance arguments.<sup>11</sup> This effect is similar to IETS features seen in inelastic scattering off nonmagnetic and magnetic excitations in molecules.<sup>10</sup> With current experimental capabilities in STM one can easily address single diatomic molecules with either spin-polarized STM<sup>8</sup> or with position-dependent IETS measurements.<sup>10</sup>

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<sup>15</sup>These GFs should be calculated self-consistently with respect to the population numbers of the various many-body (Ref. 14). However, this procedure is omitted here for simplicity since the self-consistent treatment of the GFs only changes quantitative details concerning the transport properties, not the main qualitative features.

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<sup>17</sup>J. Tersoff and D. R. Hamann, *Phys. Rev. B* **31**, 805 (1985); C. Bracher, M. Riza, and M. Kleber, *ibid.* **56**, 7704 (1997).

<sup>18</sup>The asymmetries  $v_{Ap(q)\sigma} = \gamma_{L(R)} v_{Bp(q)\sigma}$  result in

$$\mathcal{T}(\omega) = 2(1 + \gamma_L \gamma_R) (\Gamma_0/8)^2 \left[ \left| (\omega - \varepsilon_0 + qJ/2)/C_1(\omega) \right|^2 + \left| (\omega - \varepsilon_0 - qJ/2)/C_2(\omega) \right|^2 \right],$$

with  $q = (\gamma_L + \gamma_R)/(1 + \gamma_L \gamma_R)$ . Assuming  $\gamma_{L(R)} \sim 0.7$ , we obtain a 6% shift of the transmission dips as quoted in the text.