The number of transmission channels through a single-molecule junction

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We calculate transmission eigenvalue distributions for Pt–benzene–Pt and Pt–butadiene–Pt junctions using realistic state-of-the-art many-body techniques. An effective field theory of interacting π-electrons is used to include screening and van der Waals interactions with the metal electrodes. We find that the number of dominant transmission channels in a molecular junction is equal to the degeneracy of the molecular orbital closest to the metal Fermi level.

The transmission eigenvalues \( \tau_n \) constitute a mesoscopic PIN code [1] characterizing quantum transport through any nanoscale device. For a single-atom contact between two metallic electrodes, the number of transmission channels is simply given by the chemical valence of the atom [2]. Recently, highly-conductive single-molecule junctions (SMJ) with multiple transport channels have been formed from benzene molecules between Pt electrodes [3]. This raises the question if there exists a similarly simple criterion determining the number of transmission eigenchannels in a SMJ.

Previous calculations [4, 5] using effective single-particle models based on density functional theory appear to answer the above question in the negative. However, we find that transmission channel distributions calculated using many-body theory do yield a simple, intuitive answer to this important question.

For a two-terminal SMJ, \( \tau_n \) are eigenvalues of the elastic transmission matrix [4–7]

\[
T(E) = \Gamma_1(E)G(E)\Gamma_2(E)G^\dagger(E),
\]

where \( G \) is the retarded Green’s function [8] of the SMJ and \( \Gamma_\alpha \) is the tunneling-width matrix describing the coupling of the molecule to lead \( \alpha \). The number of transmission channels is equal to the rank of the matrix (1), which is in turn limited by the ranks of the matrices \( \Gamma_\alpha \) and \( G \). The additional two-fold spin degeneracy of each resonance is considered implicit. The rank of \( \Gamma_\alpha \) is equal to the number of covalent bonds formed between the molecule and lead \( \alpha \). Thus, for example, in a SMJ where a Au electrode bonds to an organic molecule via a thiol group, only a single bond is formed, and there is only one non-negligible transmission channel [5, 9]. In Pt–benzene–Pt junctions, however, each Pt electrode forms multiple bonds to the benzene molecule [3].

In this article, we investigate how transmission eigenvalue distributions of SMJs depend on the number of lead-molecule bonds and on molecular symmetry using a many-body theory of transport [8]. Specifically, we focus on junctions with benzene (C\textsubscript{6}H\textsubscript{6}) and butadiene (C\textsubscript{4}H\textsubscript{6}) bonded to two Pt leads (see Fig. 1). Consistent with refs. [5] and [8], we find that the total number of nonzero transmission eigenvalues in a SMJ is limited only by the number of bonds to each electrode. However, increasing the number of bonds past a certain point leads to additional channels with very small transmission \( \langle \tau_n \rangle \ll 1 \). The central finding of this article is that in SMJs with sufficient numbers of lead-molecule bonds the number of dominant transmission channels is equal to the degeneracy of the molecular orbital closest to the metal Fermi level. Additional transmission channels stemming from further off-resonant molecular states are strongly suppressed, but may still be experimentally resolvable [3] for very strong lead-molecule hybridization.

MANY-BODY THEORY OF TRANSPORT

When macroscopic leads are attached to a single molecule, a SMJ is formed, transforming the few-body molecular problem into a true many-body problem. Until recently, a theory of transport in SMJs that properly accounts for both the particle and wave character of the electron has been lacking, so that the Coulomb blockade and coherent transport regimes were considered...
In this article, we utilize a nonequilibrium many-body theory [8] that correctly accounts for wave-particle duality, reproducing the key features of both the Coulomb blockade and coherent transport regimes. Previous applications [8,11–13] to SMJs utilized a semi-empirical Hamiltonian [14] for the π-electrons, which accurately describes the gas-phase spectra of conjugated organic molecules. This approach should be adequate to describe molecules weakly coupled to metal electrodes, e.g. via thiol linkages. However, in junctions where the π-electrons bind directly to the metal electrodes [8], the lead-molecule coupling may be so strong that the molecule itself is significantly altered, necessitating a more fundamental molecular model. To address this issue, we have developed an effective field theory of interacting π-electrons, in which the form of the molecular Hamiltonian is derived from symmetry principles and electromagnetic theory (multipole expansion), rather than using an ad-hoc parametrization [14]. The resulting formalism constitutes a state-of-the-art many-body theory that provides a realistic description of lead-molecule hybridization and van der Waals coupling, as well as the screening of intramolecular interactions by the metal electrodes, all of which are essential for a quantitative description of strongly-coupled SMJs [3].

The Green’s function of a SMJ has the form [8]

\[ G(E) = \left[ G_{mol}^{-1}(E) - \Sigma_T(E) - \Delta \Sigma_C(E) \right]^{-1}, \]

where \( G_{mol} \) is the molecular Green’s function, \( \Sigma_T \) is the tunneling self-energy matrix, whose imaginary part is given by \( \text{Im} \Sigma_T = -\sum \Gamma_{\alpha}/2 \), and \( \Delta \Sigma_C \) is the correction to the Coulomb self-energy due to the broadening of the molecular resonances in the junction. At room temperature and for small bias voltages, \( \Delta \Sigma_C \approx 0 \) in the cotunneling regime [8] (i.e., for nonresonant transport). Furthermore, the inelastic transmission probability is negligible compared to Eq. [1] in that limit.

The molecular Green’s function \( G_{mol} \) is found by exactly diagonalizing the molecular Hamiltonian, projected onto a basis of relevant atomic orbitals [8]:

\[ G_{mol}(E) = \sum_{\nu,\nu'} \frac{[\mathcal{P}(\nu) + \mathcal{P}(\nu')]C(\nu, \nu')}{E - E_{\nu'} + i0^+}, \]

where \( E_{\nu} \) is the eigenvalue associated with eigenstate \( \nu \) of the molecular Hamiltonian, \( \mathcal{P}(\nu) \) is the probability that the state \( \nu \) is occupied, and \( C(\nu, \nu') \) is a rank-1 matrix with elements

\[ C(\nu, \nu')_{\sigma} = \langle \nu | d_{\sigma} | \nu' \rangle \langle \nu' | d^{\dagger}_{\sigma} | \nu \rangle. \]

Here \( d_{\sigma} \) annihilates an electron of spin \( \sigma \) on the \( n \)th atomic orbital of the molecule. For linear response, \( \mathcal{P}(\nu) \) is given by the grand canonical ensemble. Equations [2] imply that each molecular resonance \( \nu \rightarrow \nu' \) contributes at most one transmission channel in Eq. [1].

An effective field theory of interacting π-electrons was used to model the electronic degrees of freedom most relevant for transport. Using symmetry principles and an electrostatic multipole expansion, an effective Hamiltonian for the π-electrons was derived, keeping all interaction terms up to the quadrupole-quadrupole interaction. The minimal set of parameters necessary to characterize the π-electron system consists of the π-orbital on-site repulsion \( U_0 \), the π-orbital quadrupole moment \( Q \), the nearest-neighbor π–π hybridization \( t \), and the dielectric constant \( \epsilon \), which accounts for the polarizability of the σ-electrons, which are not included explicitly in the calculation. The values \( U_0=8.9eV, Q = 0.67e\text{Å}^2, t = 2.64eV \), and \( \epsilon = 1.63 \) were determined by fitting to the gas-phase spectrum of benzene [14]. In the molecular junction, screening of intramolecular Coulomb interactions by the nearby metal electrodes [15, 16] was included via the image charge method, with no additional adjustable parameters.

### JUNCTION ENSEMBLE

In this article, we consider junctions in which two macroscopic multi-channel leads each couple to several atomic orbitals of a single molecule. In order to calculate the distribution of transmission eigenvalues, it is first necessary to construct a physical ensemble of junctions. Both the lead-molecule coupling and the electrode geometry [17] vary over the ensemble of junctions produced in an experiment [3]. The lead-molecule coupling involves both screening [15, 16] and hybridization of the molecular and metallic states, described by the matrix \( \Sigma_T \) (see Fig. 2). We assume both effects are dominated by the interaction of the molecule with a single Pt atom at the tip of each electrode, as illustrated in Fig. 1. Since \( \Sigma_T \) depends exponentially on the tip-molecule distance, we assume its variation is most important, and keep screening fixed over the ensemble of junctions. Moreover, we neglect the real part of \( \Sigma_T \) and focus on the variation of the tunneling-width matrices \( \Gamma_{\alpha} \). The variation of electrode geometry leads to a variation of the work function \( \phi \) and density of states (DOS) of the leads (the latter also contributes to the variation of \( \Gamma_{\alpha} \)).
We thus assume the ensemble of junctions can be modeled adequately through variations of $\Gamma_\alpha$ and $\phi$ only \[18\].

**Molecule-electrode Coupling**

In order to determine the tunneling-width matrices $\Gamma_\alpha$ for a SMJ, we first consider the details of a single benzene molecule adsorbed on a Pt(111) surface. This is the most stable Pt surface, and has been the subject of numerous investigations, where the observed binding energy for benzene ranges between 21 kcal/mol (0.91 eV/molecule) to 29 kcal/mol (1.26 eV/molecule) corresponding to the atop(0) and bridge(30) bonding configurations, respectively \[19–21\]. As indicated schematically in Fig. 2 when a molecule binds with a metal surface, the relevant energy levels of the molecule shift and hybridize, forming bonding and anti-bonding states. These two effects contribute to the bonding energy $\Delta E_{\text{vb}} = \Delta E_{\text{vdW}} + \Delta E_{\text{hyb}}$, where $\Delta E_{\text{vdW}} = \langle H_{\text{mol}} \rangle - \langle \tilde{H}_{\text{mol}} \rangle$ is the van der Waals energy shift and $\Delta E_{\text{hyb}}$ is the hybridization energy. Here $H_{\text{mol}}$ is the gas-phase molecular Hamiltonian and $\tilde{H}_{\text{mol}}$ is the molecular Hamiltonian including screening from the Pt surface. Taking the benzene-Pt distance as 2.25Å and assuming the screening is dominated by the nearest Pt atom, we find that the HOMO-LUMO gap of benzene reduces from 10.05eV in the gas-phase to 7.52eV on Pt(111) and $\Delta E_{\text{vdW}} = 0.49$eV. This implies $\Delta E_{\text{hyb}} \leq 0.77$eV.

Since the metallic work function $\phi$ lies between the HOMO and LUMO resonances, hybridization occurs via the virtual exchange of an electron or hole between the metal and the neutral molecule. Using second-order perturbation theory, we find:

$$
\Delta E_{\text{hyb}} = \sum_{\nu \in H_{N-1}} \int_{-\infty}^{\infty} \frac{dE}{2\pi} \text{Tr} \left\{ \Gamma(E) C_{\nu}(0,0_N) \right\} + \sum_{\nu' \in H_{N+1}} \int_{-\infty}^{\infty} \frac{dE}{2\pi} \text{Tr} \left\{ \Gamma(E) C_{0,N}(0,N) \right\},
$$

where $\mu$ is the chemical potential of the lead metal, $H_{N}$ is the $N$-particle molecular Hilbert space, and $0_N$ is the ground state of the $N$-particle manifold of the neutral molecule. At room temperature, the Pt DOS $g(E)$ is sharply peaked around the Fermi energy \[22\], allowing us to perform the energy integral in Eq. 5 using $\Gamma(E) \approx \Gamma(\epsilon_F) Z \delta(E - \epsilon_F) / g(\epsilon_F)$, where we take $Z=4$ for a Pt atom and $g(\epsilon_F)$=2.88/eV \[23\]. The hybridization energy is thus determined by the tunneling-width matrix evaluated at the Pt Fermi level, $\Gamma(\epsilon_F) = \Gamma$. Using $\phi_{\text{Pt}(111)}=5.93$eV \[24\] and the chemical potential of benzene $\mu_0=(IE + E_A)/2=4.06$eV \[25\] (which is unaffected by screening), we find $\text{Tr} \{ \Gamma \} \leq 21.6$eV to fit the hybridization energy for benzene adsorbed on Pt.

**RESULTS AND DISCUSSION**

**Pt-benzene-Pt Junctions**

Let us now consider lead-molecule hybridization in a Pt-benzene-Pt junction. Screening from two metal electrodes further reduces the HOMO-LUMO gap to 6.46eV. Since the most favorable binding of benzene on the closest-packed Pt(111) surface gives $\Delta E_{\text{hyb}}=0.77$eV, we assume this is essentially an upper bound on hybridization in a SMJ, where the bonding is more random. We wish to study the dependence of the transmission eigenvalue distribution on the number of bonds formed with each electrode. For $M$ covalent bonds between a macroscopic lead and a molecule with $P$ atomic orbitals, $\Gamma$ is a rank-$M$ matrix, which can be represented as

$$
\Gamma = \sum_{m=1}^{M} \gamma_m^\dagger \gamma_m,
$$

where $\gamma_m$ are linearly-independent real row vectors of dimension $P$, representing linear combinations of the atomic orbitals of the molecule \[27\]. Our approach is to populate the elements of $\gamma_m$ from a uniform random distribution on the interval [-A,A]. The bonding ensemble corresponds to a random walk of $M$ steps in a $P$-dimensional space. The distributions of $\Delta E_{\text{hyb}}$ and $\text{Tr} \{ \Gamma_\alpha \}$ shown in Fig. 3 have long Gaussian tails, so the value $A=0.82$eV was chosen to fix the 99th-percentile of $\Delta E_{\text{hyb}}$ at 0.77eV \[28\]. The 99th-percentile of $\text{Tr} \{ \Gamma_\alpha \}$ is 10.82eV which, per orbital, is nearly 3× the coupling found for a Au-BDT-Au junction \[8\].

In addition to sampling a variety of bonding configurations, we assume the ensemble of junctions samples all possible Pt surfaces. The work function of Pt ranges from 5.93eV to 5.12eV for the (111) and (331) surfaces, respec-
The conductance histogram for the same ensemble of Pt–benzene–Pt junctions discussed in Fig. 4, where \( G = (2e^2/h) \sum_n \tau_n \), is shown in Fig. 5. The peak conductance value is some 20% less than that reported experimentally \([3]\). This discrepancy might be attributable, in part, to the inclusion of a small fraction of Pt–Pt junctions in the experimental histogram.

In addition to the ensemble of junctions shown in Fig. 4, we also investigated ensembles of junctions with \( M_n = 1, \ldots, 6 \), including the case \( M_1 \neq M_2 \). Consistent with the discussion in Refs. \([3, 5]\), we find that the total number of nonzero transmission eigenvalues is \( M_{\text{min}} = \min\{M_1, M_2\} \). However, whenever \( M_{\text{min}} \geq 2 \) there are always two dominant transmission channels, and the total transmission probability does not increase appreciably beyond \( M_{\text{min}} = 2 \).

The above analysis demonstrates that the two dominant transmission channels evolve from the two-fold degenerate HOMO resonance in Eq. \( [3] \) as the lead-molecule coupling \( \Sigma_T \) is turned on. For finite \( \Sigma_T \), the poles of \( G_{\text{mol}} \) are mixed by Dyson’s equation (Eq. \( [2] \)), making it problematic to decompose the transmission eigenvalues into separate contributions from each molecular resonance \([5]\). Alternatively, the projections of the transmission eigenvectors onto the molecular resonances can be computed \([4]\). Because an “extended molecule” is often used in density-functional calculations to account for charge transfer between the molecule and electrodes, it is difficult if not impossible to interpret these contributions in terms of the resonances of the molecule itself \([4]\). Since charging effects in SMJs are well-described in our many-body theory \([8]\), there is no need to utilize an “extended molecule,” so the projections of the transmission eigenvectors onto the molecular resonances can be determined unambiguously (see Methods). We find that the mean-square projections of the first and second transmission channels in Fig. 4 onto the benzene HOMO resonance are 87% and 71%, respectively, confirming the conclusion that these eigenchannels correspond to tunneling primarily through the HOMO resonance.

**Pt-butadiene-Pt Junctions**

To test our hypothesis that the number of dominant transmission channels is limited by the degeneracy of the
CONCLUSIONS

In conclusion, we find that the number of dominant transmission channels in a SMJ is equal to the degeneracy of the molecular orbital closest to the metal Fermi level. Transmission eigenvalue distributions were calculated for Pt-benzene-Pt and Pt-butenadiene-Pt junctions using realistic state-of-the-art many-body techniques. In both cases, transmission occurs primarily through the HOMO resonance, which lies closest to the Pt Fermi level, resulting in two dominant transmission channels for benzene (2-fold degenerate HOMO) and a single dominant transmission channel for butadiene (non-degenerate HOMO). Our results for the transmission channel distributions of Pt-benzene-Pt junctions (see Fig. 6) are in quantitative agreement with experiment [3].

Despite the larger number of states available for tunneling transport in SMJs, we predict that the number of transmission channels is typically more limited than in single-atom contacts because molecules are less symmetrical than atoms. Nonetheless, certain highly-symmetric molecules exist that should permit several dominant transmission channels. For example, the C_{60} molecule possesses icosahedral symmetry, and has a 5-fold degenerate HOMO resonance and 3-fold degenerate LUMO resonance [34, 35]. C_{60}-based SMJs with gold electrodes have been fabricated, and shown to exhibit fascinating electromechanical [32] and spin-dependent [33] transport properties. For Pt-C_{60}-Pt junctions, we predict five dominant transmission channels stemming from the C_{60} HOMO resonance, which lies closest to the Pt Fermi level [34, 35].

METHODS

Decomposing transmission channels in terms of molecular resonances

In order to understand how transport in a SMJ is determined by the chemical properties of the molecule, it would be desirable to express the transmission eigenchannels in terms of molecular resonances [4]. The transmission eigenvalues $\tau_n$ and eigenvectors $|n\rangle$ are solutions of the equation

$$T|n\rangle = \tau_n|n\rangle,$$

where $T$ is the transmission matrix given by Eq. 1. By definition, $|n\rangle$ is a linear combination of the atomic orbitals of the molecule. In an effective single-particle model [4], $|n\rangle$ may also be expressed as a linear combination of molecular orbitals $|\phi_j\rangle$

$$|n\rangle = \sum_j a_{n,j} |\phi_j\rangle.$$

Here $|a_{n,j}|^2$ can be identified as the contribution of the $j$th molecular orbital to the $n$th transmission channel [4], which can be conveniently expressed in terms of the projection operator $\hat P_j = |\phi_j\rangle\langle\phi_j|$ as $|a_{n,j}|^2 = \langle n|\hat P_j|n\rangle$.

In the many-body problem, there is no orthonormal set of “molecular orbitals”; rather each molecular resonance of energy $E_{\nu} - E_\nu$ corresponds to a transition $\nu \rightarrow \nu'$ between an $N$-body and an $(N+1)$-body molecular eigenstate [see Eqs. 3 and 4]. The projection operator onto a molecular resonance is

$$\hat P_{\nu \rightarrow \nu'} = \frac{C(\nu, \nu')}{\text{Tr} \{ C(\nu, \nu') \}}.$$
where $C(\nu, \nu')$ is given by Eq. 4. The absolute square projection of the $n$th transmission eigenvector onto the resonance $\nu \rightarrow \nu'$ is given by

$$|\alpha_{n}^{\nu \rightarrow \nu'}|^{2} = \langle n | \hat{P}_{\nu \rightarrow \nu'} | n \rangle.$$

A necessary condition to identify an eigenchannel $|n\rangle$ with transmission through a particular molecular resonance is $|\alpha_{n}^{\nu \rightarrow \nu'}|^{2} \approx 1$.

The above procedure is in principle straightforward to implement in an effective single-particle model based on density functional theory (DFT). However, in practice, an “extended molecule” must be used in DFT calculations to account for charge transfer between the molecule and electrodes. This is because current implementations of DFT fail to account for the particle aspect of the electron [10, 36–38], i.e., the strong tendency for the electric charge on the molecule within the junction to be quantized in integer multiples of the electron charge $e$. Analyzing transport in terms of extended molecular orbitals has unfortunately proven problematic. For example, the resonances of the extended molecule in Ref. 4 apparently accounted for less than 9% of the current through the junction.

Since charging effects in SMJs are well-described in our many-body theory [8], there is no need to utilize an “extended molecule,” so the projections of the transmission eigenvectors onto the molecular resonances can be determined directly from Eq. 12.

### Benzene resonances

The neutral ground state of benzene is nondegenerate, while the HOMO and LUMO resonances are both doubly degenerate due to the (six-fold) rotational symmetry of the molecule. To be consistent with the discussion of Ref. 3, the additional two-fold spin degeneracy of each resonance is considered implicit.

We define the following projection operators:

$$\hat{P}_{\text{HOMO}} \equiv \sum_{\nu \in 0_5} \hat{P}_{\nu \rightarrow 0_{\nu}},$$

$$\hat{P}_{\text{LUMO}} \equiv \sum_{\nu' \in 0_7} \hat{P}_{0_{\nu'} \rightarrow \nu'},$$

$$\hat{P}_{\perp} \equiv 1 - \hat{P}_{\text{HOMO}} - \hat{P}_{\text{LUMO}},$$

where $0_{N}$ is the ground state with $N$ $\pi$-electrons and 1 is the six-dimensional unit matrix in the space of $\pi$-orbitals. $\hat{P}_{\text{HOMO}}$ and $\hat{P}_{\text{LUMO}}$ are projection operators onto the two-dimensional subspaces spanned by the HOMO and LUMO resonances, respectively. Eqs. 13–15 define a complete, orthogonal set of projection operators in six-dimensions with the properties

$$\sum_{j} \hat{P}_{j} = 1,$$

$$\hat{P}_{i} \hat{P}_{j} = \hat{P}_{i} \delta_{ij}.$$
The neutral ground state of butadiene is nondegenerate, and the HOMO and LUMO resonances have no orbital degeneracy. The projection operators onto the HOMO and LUMO resonances of butadiene are

\[
\hat{P}_{\text{HOMO}} = \hat{P}_{0_4 \rightarrow 0_4}, \\
\hat{P}_{\text{LUMO}} = \hat{P}_{0_4 \rightarrow 0_5},
\]

respectively. Fig. 8 shows the mean-square projections of the transmission eigenvectors onto the nondegenerate butadiene HOMO and LUMO resonances as a function of electrode chemical potential for the same ensemble of Pt–butadiene–Pt junctions discussed in Fig. 6. In this case, the single dominant channel has a strong overlap with the nondegenerate HOMO resonance: \( \langle |\alpha_n| \rangle \sim 1/4 \), as expected based on the arguments given above.

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**Butadiene resonances**

For the range of possible chemical potentials of Pt electrodes, \(-1.88\text{eV} \leq \mu_{\text{Pt}} - \mu_0 \leq -1.07\text{eV}\) indicated by the grey boxes in each subfigure, the first two channels have very strong overlap with the HOMO resonance: 87% and 71%, respectively.

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a) The mean-square projections $|\langle \alpha_n^j | \gamma \rangle|^2 = \langle n | P_j | n \rangle$ of the transmission eigenvectors onto (a) the butadiene HOMO resonance; and (b) the butadiene LUMO resonance, for the same ensemble of Pt–butadiene–Pt junctions discussed in Fig. 6. The dominant channel has a strong overlap (80% mean-square) with the HOMO resonance for the range of possible chemical potentials of Pt electrodes, $-1.70 \text{eV} \leq \mu_{\text{Pt}} - \mu_0 \leq -0.89 \text{eV}$, indicated on each subfigure by a solid grey box.

FIG. 8. The mean-square projections $|\langle \alpha_n^j | \gamma \rangle|^2 = \langle n | P_j | n \rangle$ of the transmission eigenvectors onto (a) the butadiene HOMO resonance; and (b) the butadiene LUMO resonance, for the same ensemble of Pt–butadiene–Pt junctions discussed in Fig. 6. The dominant channel has a strong overlap (80% mean-square) with the HOMO resonance for the range of possible chemical potentials of Pt electrodes, $-1.70 \text{eV} \leq \mu_{\text{Pt}} - \mu_0 \leq -0.89 \text{eV}$, indicated on each subfigure by a solid grey box.
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