

# The Number of Transmission Channels Through a Single-Molecule Junction

Justin P. Bergfield,<sup>†,\*</sup> Joshua D. Barr,<sup>‡</sup> and Charles A. Stafford<sup>‡</sup>

<sup>†</sup>College of Optical Sciences, University of Arizona, 1630 East University Boulevard, Arizona 85721, United States, and <sup>‡</sup>Department of Physics, University of Arizona, 1118 East Fourth Street, Tucson, Arizona 85721, United States

The transmission eigenvalues  $\tau_n$  constitute a mesoscopic PIN code<sup>1</sup> 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.<sup>2,3</sup> Recently, highly conductive single-molecule junctions (SMJ) with multiple transport channels have been formed from benzene molecules between Pt electrodes.<sup>4</sup> This raises the question if there exists a similarly simple criterion determining the number of transmission eigenchannels in a SMJ.

Previous calculations<sup>5,6</sup> 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<sup>5–8</sup>

$$\mathbf{T}(E) = \Gamma_1(E) G(E) \Gamma_2(E) G^\dagger(E) \quad (1)$$

where  $G$  is the retarded Green's function<sup>9</sup> 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 2-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.<sup>6,10</sup> In Pt–benzene–Pt junctions, however, each Pt electrode forms multiple bonds to the benzene molecule.<sup>4</sup>

In this article, we investigate how transmission eigenvalue distributions of SMJs

**ABSTRACT** 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  $\pi$ -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.

**KEYWORDS:** many-body theory · transmission channels · single-molecule junction · lead-molecule coupling · wave-particle duality

depend on the number of lead-molecule bonds and on molecular symmetry using a many-body theory of transport.<sup>9</sup> Specifically, we focus on junctions with benzene ( $C_6H_6$ ) and butadiene ( $C_4H_6$ ) bonded to two Pt leads (see Figure 1). Consistent with refs 4 and 6, 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<sup>4</sup> for very strong lead-molecule hybridization.

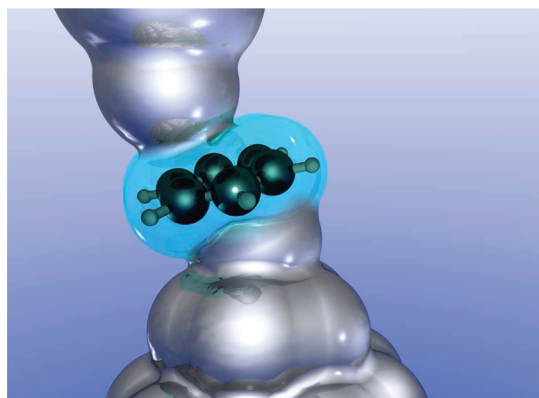
**Many-Body Theory of Transport.** When macroscopic leads are attached to a single molecule, a SMJ is formed, transforming the few-body molecular problem into a true many-body problem. Until recently, a theory of transport in SMJs that properly accounts for both the particle and wave character of the electron has been lacking, so that the Coulomb blockade and coherent transport regimes were considered “complementary.”<sup>11</sup> In this article, we utilize a

\* Address correspondence to justinb@email.arizona.edu.

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**Figure 1.** Schematic diagram of a Pt–benzene–Pt junction. The lead–molecule coupling is mediated predominantly by individual Pt atoms at the tips of each electrode.

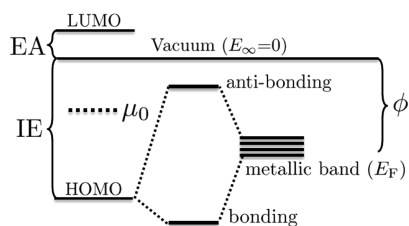
nonequilibrium many-body theory<sup>9</sup> that correctly accounts for wave-particle duality, reproducing the key features of both the Coulomb blockade and coherent transport regimes. Previous applications<sup>9,12–14</sup> to SMJs utilized a semiempirical Hamiltonian<sup>15</sup> for the  $\pi$ -electrons, which accurately describes the gas-phase spectra of conjugated organic molecules. This approach should be adequate to describe molecules weakly coupled to metal electrodes, for example, *via* thiol linkages. However, in junctions where the  $\pi$ -electrons bind directly to the metal electrodes,<sup>4</sup> 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  $\pi$ -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.<sup>15</sup> 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.<sup>4</sup>

The Green's function of a SMJ has the form<sup>9</sup>

$$G(E) = [G_{\text{mol}}^{-1}(E) - \Sigma_{\text{T}}(E) - \Delta\Sigma_{\text{C}}(E)]^{-1} \quad (2)$$

where  $G_{\text{mol}}$  is the molecular Green's function,  $\Sigma_{\text{T}}$  is the tunneling self-energy matrix, whose imaginary part is given by  $\text{Im}\Sigma_{\text{T}} = -\sum_{\alpha}\Gamma_{\alpha}/2$ , and  $\Delta\Sigma_{\text{C}}$  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,  $\Delta\Sigma_{\text{C}} \approx 0$  in the cotunneling regime<sup>9</sup> (*i.e.*, for nonresonant transport). Furthermore, the inelastic transmission probability is negligible compared to eq 1 in that limit.

The molecular Green's function  $G_{\text{mol}}$  is found by exactly diagonalizing the molecular Hamiltonian, projected onto a basis of relevant atomic orbitals:<sup>9</sup>



**Figure 2.** Energy-level diagram of a molecule with ionization energy IE and electron affinity EA bound to a metal surface/electrode with work function  $\phi$ . In forming the metal–molecule bond, the HOMO resonance of the molecule shifts and hybridizes.

$$G_{\text{mol}}(E) = \sum_{\nu, \nu'} \frac{[\mathcal{P}(\nu) + \mathcal{P}(\nu')]C(\nu, \nu')}{E - E_{\nu'} + E_{\nu} + i0^{+}} \quad (3)$$

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

$$[C(\nu, \nu')]_{n\sigma, m\sigma'} = \langle \nu | d_{n\sigma} | \nu' \rangle \langle \nu' | d_{m\sigma'}^{\dagger} | \nu \rangle \quad (4)$$

Here  $d_{n\sigma}$  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 2–4 imply that each molecular resonance  $\nu \rightarrow \nu'$  contributes at most one transmission channel in eq 1.

An effective field theory of interacting  $\pi$ -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  $\pi$ -electrons was derived, keeping all interaction terms up to the quadrupole–quadrupole interaction. The minimal set of parameters necessary to characterize the  $\pi$ -electron system consists of the  $\pi$ -orbital on-site repulsion  $U_0$ , the  $\pi$ -orbital quadrupole moment  $Q$ , the nearest-neighbor  $\pi$ – $\pi$  hybridization  $t$ , and the dielectric constant  $\epsilon$ , which accounts for the polarizability of the  $\sigma$ -electrons, which are not included explicitly in the calculation. The values  $U_0 = 8.9$  eV,  $Q = 0.67e \text{ \AA}^2$ ,  $t = 2.64$  eV, and  $\epsilon = 1.63$  were determined by fitting to the gas-phase spectrum of benzene.<sup>15</sup> In the molecular junction, screening of intramolecular Coulomb interactions by the nearby metal electrodes<sup>16,17</sup> was included *via* the image charge method, with no additional adjustable parameters.

**Junction Ensemble.** In this article, we consider junctions in which two macroscopic multichannel leads each couple to several atomic orbitals of a single molecule. 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<sup>18</sup> vary over the ensemble of junctions produced in an experiment.<sup>4</sup> The lead–molecule coupling involves both *screening*<sup>16,17</sup> and *hybridization* of the molecular and metallic states, described by

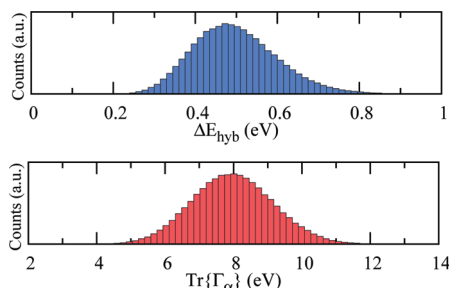
the matrix  $\Sigma_T$  (see Figure 2). We assume both effects are dominated by the interaction of the molecule with a single Pt atom at the tip of each electrode, as illustrated in Figure 1. Since  $\Sigma_T$  depends exponentially on the tip–molecule distance, we assume its variation is most important, 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.<sup>19</sup>

**Molecule-Electrode Coupling.** 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.<sup>20–22</sup> As indicated schematically in Figure 2, when a molecule binds with a metal surface, the relevant energy levels of the molecule shift and hybridize, forming bonding and antibonding states. These two effects contribute to the binding energy  $\Delta E_b = \Delta E_{vdW} + \Delta E_{hyb}$ , where  $\Delta E_{vdW} = \langle H_{mol} \rangle - \langle \tilde{H}_{mol} \rangle$  is the van der Waals energy shift and  $\Delta E_{hyb}$  is the hybridization energy. Here  $H_{mol}$  is the gas-phase molecular Hamiltonian and  $\tilde{H}_{mol}$  is the molecular Hamiltonian including screening from the Pt surface. Taking the benzene–Pt distance as 2.25 Å and assuming the screening is dominated by the nearest Pt atom, we find that the gap between the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) of benzene reduces from 10.05 eV in the gas-phase to 7.52 eV on Pt(111) and  $\Delta E_{vdW} = 0.49$  eV. This implies  $\Delta E_{hyb} \leq 0.77$  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 that

$$\Delta E_{hyb} = \sum_{\nu \in \mathcal{H}_{N-1}} \int_{\mu}^{\infty} \frac{dE}{2\pi} \frac{\text{Tr}\{\Gamma(E)C(\nu, 0_N)\}}{E - E_{0_N} + E_{\nu}} + \sum_{\nu' \in \mathcal{H}_{N+1}} \int_{-\infty}^{\mu} \frac{dE}{2\pi} \frac{\text{Tr}\{\Gamma(E)C(0_N, \nu')\}}{-E - E_{0_N} + E_{\nu'}} \quad (5)$$

where  $\mu$  is the chemical potential of the lead metal,  $\mathcal{H}_N$  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,<sup>23</sup> allowing us to perform the energy integral in eq 5 using  $\Gamma(E) \approx$



**Figure 3.** Distributions of hybridization energy (top) and tunneling-width matrix trace (bottom) for a Pt–benzene–Pt junction. The 99th-percentile values for  $\Delta E_{hyb}$  and  $\text{Tr}\{\Gamma_\alpha\}$  are 0.77 and 10.82 eV, respectively. Here  $\alpha = 1, 2$  labels the lead–molecule contacts.

$\Gamma(\varepsilon_F) Z \delta(E - \varepsilon_F) / g(\varepsilon_F)$ , where we take  $Z = +4$  for a Pt atom and  $g(\varepsilon_F) = 2.88/\text{eV}$ .<sup>24</sup> The hybridization energy is thus determined by the tunneling-width matrix evaluated at the Pt Fermi level,  $\Gamma(\varepsilon_F) \equiv \Gamma$ . Using  $\phi_{\text{Pt}(111)} = 5.93$  eV<sup>25</sup> and the chemical potential of benzene  $\mu_0 = (IE + EA)/2 = -4.06$  eV<sup>26,27</sup> (which is unaffected by screening), we find  $\text{Tr}\{\Gamma\} \leq 21.6$  eV to fit the hybridization energy for benzene adsorbed on Pt.

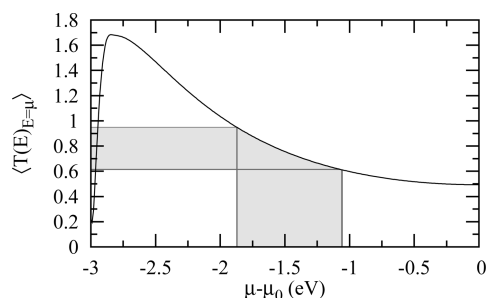
## RESULTS AND DISCUSSION

**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 6.46 eV. Since the most favorable binding of benzene on the closest-packed Pt(111) surface gives  $\Delta E_{hyb} = 0.77$  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

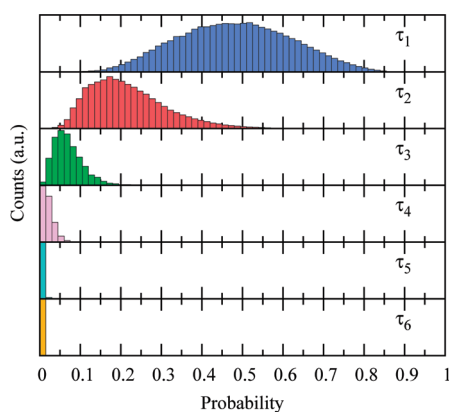
$$\Gamma = \sum_{m=1}^M \gamma_m^\dagger \gamma_m \quad (6)$$

where  $\gamma_m$  are linearly independent real row vectors of dimension  $P$ , representing linear combinations of the atomic orbitals of the molecule.<sup>28</sup> 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  $\Delta E_{hyb}$  and  $\text{Tr}\{\Gamma_\alpha\}$  shown in Figure 3 have long Gaussian tails, so the value  $A = 0.82$  eV was chosen to fix the 99th-percentile of  $\Delta E_{hyb}$  at 0.77 eV.<sup>29</sup> The 99th-percentile of  $\text{Tr}\{\Gamma_\alpha\}$  is 10.82 eV which, per orbital, is nearly  $3 \times$  the coupling found for a Au–BDT–Au junction.<sup>9</sup>

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 5.93 to 5.12 eV for the (111) and (331)



**Figure 4.** The total transmission averaged over 3000 bonding configurations through a Pt–benzene–Pt junction is shown near the HOMO resonance as a function of lead chemical potential  $\mu$ . The gray box indicates the range of possible chemical potentials for Pt electrodes. Although the lead-molecule coupling is strong, the transmission resonance is still well-defined.



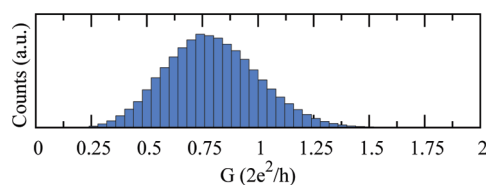
**Figure 5.** Calculated transmission eigenvalue distributions for an ensemble of  $24 \times 10^4$  Pt–benzene–Pt junctions; 3000 bonding configurations  $\times$  80 Pt surfaces were included. Each lead was assumed to form  $M = 6$  bonds with the molecule. There are two dominant transmission channels arising from the 2-fold degenerate HOMO resonance closest to the Pt Fermi level, with a small but experimentally resolvable third channel arising from further off-resonant tunneling.

surfaces, respectively,<sup>25</sup> so that

$$-1.88\text{eV} \leq \mu_{\text{Pt}} - \mu_0 \leq -1.07\text{eV} \quad (7)$$

and we assume a uniform distribution of  $\mu_{\text{Pt}}$  on this interval. The total transmission averaged over 3000 bonding configurations through a Pt–benzene–Pt junction is shown in Figure 4.

The transmission eigenvalue distributions are shown in Figure 5 for an ensemble of  $24 \times 10^4$  Pt–benzene–Pt junctions. Each lead was assumed to form  $M = 6$  bonds with the molecule. Despite the existence of six covalent bonds between the molecule and each lead, there are only two dominant transmission channels, which arise from the 2-fold degenerate HOMO resonance closest to the Pt Fermi level. There is also a small but experimentally resolvable third channel arising from further off-resonant tunneling. This channel is non-negligible because of the very large lead-molecule coupling  $\Gamma$  in the Pt–benzene junction. Explicit



**Figure 6.** Calculated conductance histogram for the same ensemble of Pt–benzene–Pt junctions discussed in Figure 5, where  $G = (2e^2/h) \sum_n \tau_n$ .

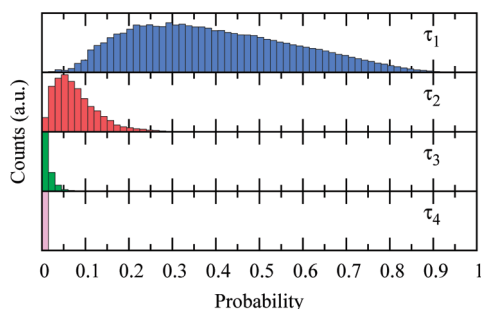
calculations with smaller values of  $\text{Tr}\{\Gamma\}$  yielded only two non-negligible transmission eigenvalues. Thus, for metals with a smaller DOS at the Fermi level, such as Cu, Ag, or Au, junctions with benzene would be expected to exhibit only two measurable transmission channels.

The calculated transmission eigenvalue distribution shown in Figure 5 is consistent with the experiment,<sup>4</sup> which determined the transmission eigenvalues for three particular junctions:  $\{\tau_n\} = \{0.68, 0.40\}$ ,  $\{0.36, 0.25, 0.10\}$ ,  $\{0.20\}$ , where a third channel was observable only once. The conductance histogram for the same ensemble of junctions is shown in Figure 6. The peak conductance value is some 20% less than that reported experimentally.<sup>4</sup> 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 Figure 5, we also investigated ensembles of junctions with  $M_\alpha = 1, \dots, 6$ , including the case  $M_1 \neq M_2$ . Consistent with the discussion in refs 4 and 6, we find that the total number of nonzero transmission eigenvalues is  $M_{\min} = \min\{M_1, M_2\}$ . However, whenever  $M_{\min} \geq 2$  there are always two dominant transmission channels, and the total transmission probability does not increase appreciably beyond  $M_{\min} = 2$ .

The above analysis demonstrates that the two dominant transmission channels evolve from the 2-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.<sup>6</sup> Alternatively, the projections of the transmission eigenvectors onto the molecular resonances can be computed.<sup>5</sup> 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.<sup>5</sup> Since charging effects in SMJs are well-described in our many-body theory,<sup>9</sup> 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 Figure 5 onto the benzene HOMO





**Figure 7.** Transmission eigenvalue distributions for an ensemble of  $24 \times 10^4$  Pt–butadiene–Pt junctions; 3000 bonding configurations  $\times$  80 Pt surfaces were included. Each lead was assumed to form  $M = 4$  bonds with the molecule. The linear butadiene ( $C_4H_6$ ) molecule lacks the orbital degeneracy of the benzene ring and consequently exhibits only 1 dominant channel. A second channel due to further off-resonant tunneling may be experimentally resolvable. The total conductance distribution peaks around  $\sim 0.4G_0$ .

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 most relevant molecular orbital, we have investigated transmission eigenvalue distributions for Pt–butadiene–Pt junctions. Butadiene is a linear conjugated polymer, lacking the discrete (6-fold) rotational symmetry of benzene. Since the molecular orbitals of butadiene are nondegenerate, we anticipate a single dominant transmission channel. Using the same per-orbital hybridization as for benzene gives  $\text{Tr}\{\Gamma_\alpha\} \leq 7.21$  eV. The image charge method gives  $\Delta E_{vdW} = 0.52$  eV and we find  $\Delta E_{hyb} \leq 0.59$  eV, so that  $\Delta E_b \leq 1.12$  eV  $\equiv$  107.7 kJ/mol, in line with existing values reported in the literature.<sup>31</sup> The range of Pt work functions for all possible Pt surfaces gives a chemical potential range of

$$-1.70 \text{ eV} \leq \mu_{Pt} - \mu_0 \leq -0.89 \text{ eV} \quad (8)$$

Despite forming four bonds with each electrode, it is evident from Figure 7 that the Pt–butadiene–Pt junction has a single dominant transmission channel. The mean-square projection of this transmission channel onto the nondegenerate butadiene HOMO resonance is 80% (see Methods).

## METHODS

### Decomposing Transmission Channels in Terms of Molecular Resonances.

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.<sup>5,6</sup> The transmission eigenvalues  $\tau_n$  and eigenvectors  $|n\rangle$  are solutions of the equation

$$T|n\rangle = \tau_n|n\rangle \quad (9)$$

## CONCLUSIONS

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–butadiene–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 Figure 5) are in quantitative agreement with experiment.<sup>4</sup>

It is interesting to relate our findings for SMJs to known results for metallic point contacts.<sup>3</sup> The transmission spectra of SMJs, especially those involving small molecules, clearly possess discrete molecular resonances, broadened by the lead-molecule coupling (see Figure 4). In contrast, metallic point contacts typically do not exhibit well-defined transmission resonances, but instead can be thought of as electron waveguides with several propagating modes.<sup>3</sup> Only in the case of a single-atom contact is there a close analogy with a SMJ, in that the valence of the central atom determines the number of transmission channels of the junction.

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.<sup>32</sup>  $C_{60}$ -based SMJs with gold electrodes have been fabricated, and shown to exhibit fascinating electromechanical<sup>33</sup> and spin-dependent<sup>34</sup> 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.<sup>35,36</sup>

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,<sup>5</sup>  $|n\rangle$  may also be expressed as a linear combination of molecular orbitals  $|\phi_j\rangle$

$$|n\rangle = \sum_j \alpha_n^j |\phi_j\rangle \quad (10)$$

Here  $|\alpha_n^j|^2$  can be identified as the contribution of the  $j$ th molecular orbital to the  $n$ th transmission channel,<sup>5</sup> which can

be conveniently expressed in terms of the projection operator  $\hat{P}_j = |\phi_j\rangle\langle\phi_j|$  as  $|\alpha_n^j|^2 = \langle n|\hat{P}_j|n\rangle$ .

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

$$\hat{P}_{\nu \rightarrow \nu'} \equiv \frac{C(\nu, \nu')}{\text{Tr}\{C(\nu, \nu')\}} \quad (11)$$

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

$$|\alpha_n^{\nu \rightarrow \nu'}|^2 = \langle n|\hat{P}_{\nu \rightarrow \nu'}|n\rangle \quad (12)$$

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).<sup>5</sup> 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,<sup>11,37–39</sup> that is, 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 5, 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,<sup>9</sup> 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 (6-fold) rotational symmetry of the molecule. To be consistent with the discussion of ref 4, the additional 2-fold spin degeneracy of each resonance is considered implicit.

We define the following projection operators:

$$\hat{P}_{\text{HOMO}} \equiv \sum_{\nu \in 0_5} \hat{P}_{\nu \rightarrow 0_6} \quad (13)$$

$$\hat{P}_{\text{LUMO}} \equiv \sum_{\nu' \in 0_7} \hat{P}_{0_6 \rightarrow \nu'} \quad (14)$$

$$\hat{P}_{\perp} \equiv \mathbf{1} - \hat{P}_{\text{HOMO}} - \hat{P}_{\text{LUMO}} \quad (15)$$

where  $0_N$  is the ground state with  $N$   $\pi$ -electrons and  $\mathbf{1}$  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. Equations 13–15 define a complete, orthogonal set of projection operators in six-dimensions with the properties

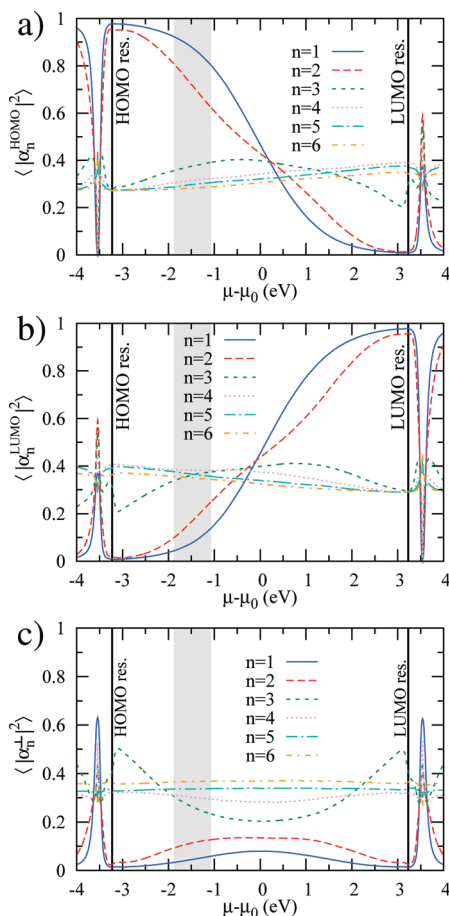
$$\sum_j \hat{P}_j = \mathbf{1} \quad (16)$$

$$\hat{P}_i \hat{P}_j = \hat{P}_i \delta_{ij} \quad (17)$$

In particular, eq 17 implies that the HOMO and LUMO subspaces of benzene are orthogonal. The absolute square of the projection of the  $n$ th transmission eigenvector onto the subspace spanned by  $\hat{P}_j$  is

$$|\alpha_n^j|^2 = \langle n|\hat{P}_j|n\rangle \quad (18)$$

These coefficients satisfy the condition



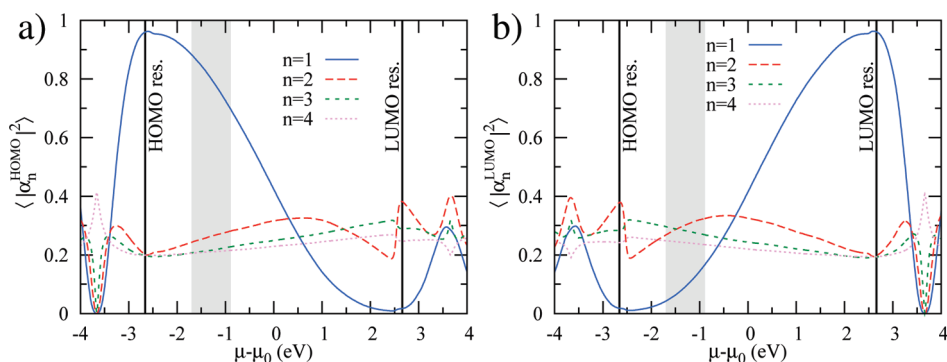
**Figure 8.** The mean-square projections  $|\alpha_n^j|^2 = \langle n|\hat{P}_j|n\rangle$  of the transmission eigenvectors onto the two-dimensional subspaces (a) spanned by the benzene HOMO resonance; (b) spanned by the benzene LUMO resonance; and (c) orthogonal to the HOMO and LUMO subspaces, for the same ensemble of Pt–benzene–Pt junctions discussed in Figure 5. 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 gray boxes in each subfigure, the first two channels have very strong overlap with the HOMO resonance: 87% and 71%, respectively.

$$\sum_j |\alpha_n^j|^2 = 1 \quad (19)$$

where the sum runs over  $j = \text{HOMO, LUMO, } \perp$ .

Figure 8 shows the mean-square projections  $\langle |\alpha_n^j|^2 \rangle$  of the transmission eigenvectors onto (a) the benzene HOMO resonance, (b) the benzene LUMO resonance, and (c) the two-dimensional subspace orthogonal to both the HOMO and LUMO resonances, as a function of electrode chemical potential for the same ensemble of Pt–benzene–Pt junctions discussed in Figure 5. We find that the mean-square projections of the first and second transmission channels onto the benzene HOMO resonance are 87% and 71%, respectively, confirming the conclusion that these eigenchannels correspond to tunneling primarily through the HOMO resonance.

Midway between the HOMO and LUMO resonances at  $\mu = \mu_0$ , the first two transmission channels have mean-square projections of  $\sim 0.5$  onto both the HOMO and LUMO resonances, consistent with the expectation that the HOMO and LUMO resonances should contribute equally to transmission. The remaining channels do not have negligible overlap with the HOMO resonance, but instead cluster around  $\langle |\alpha_n^{\text{HOMO}}|^2 \rangle \approx 0.3$ .



**Figure 9.** The mean-square projections  $|\alpha_n^j|^2 = \langle n | \hat{P}_j | n \rangle$  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 Figure 7. 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 gray box.

The transmission channels with  $\langle \tau_n \rangle \ll 1$  correspond to contributions from several far off-resonant poles, each of which has some overlap with the HOMO resonance due to the over-completeness of the projectors  $\hat{P}_{v \rightarrow v}$ .<sup>40</sup> They are essentially random unit vectors in the six-dimensional space of benzene  $\pi$ -orbitals, whose mean-square overlap with the two-dimensional HOMO subspace should be  $\langle |\alpha_n^{\text{HOMO}}|^2 \rangle = 2/6 = 1/3$ .

The first two transmission channels only have an appreciable overlap with the subspace orthogonal to the HOMO and LUMO resonances in the vicinity of a pronounced dip in the transmission spectrum at  $\mu - \mu_0 \approx \pm 3.5 \text{ eV}$ .

**Butadiene Resonances.** 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

$$\hat{P}_{\text{HOMO}} \equiv \hat{P}_{0_3 \rightarrow 0_4} \quad (20)$$

$$\hat{P}_{\text{LUMO}} \equiv \hat{P}_{0_4 \rightarrow 0_3} \quad (21)$$

respectively. Figure 9 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 Figure 7. In this case, the single dominant channel has a strong overlap with the nondegenerate HOMO resonance:  $\langle |\alpha_1^{\text{HOMO}}|^2 \rangle = 0.80$  when averaged over the range  $-1.70 \text{ eV} \leq \mu_{\text{Pt}} - \mu_0 \leq -0.89 \text{ eV}$ , while the far off-resonant channels with  $\langle \tau_n \rangle \ll 1$  have  $\langle |\alpha_n^{\text{HOMO}}|^2 \rangle \approx 1/4$ , as expected based on the arguments given above.

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