

**Electron transport in nanotube–molecular-wire hybrids**

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We study contact effects on electron transport across a molecular wire sandwiched between two semi-infinite (carbon) nanotube leads as a model for nanoelectrodes. Employing the Landauer scattering matrix approach, we find that the conductance is very sensitive to parameters such as the coupling strength and geometry of the contact. The conductance exhibits markedly different behavior in the two limiting scenarios of single contact and multiple contacts between the molecular wire and the nanotube interfacial atoms. In contrast to a single contact, the multiple-contact configuration acts as a filter selecting single transport channels. It exhibits a scaling law for the conductance as a function of coupling strength and tube diameter. We also observe an unusual narrow-to-broad-to-narrow behavior of conductance resonances upon decreasing the coupling.

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The “top-down” miniaturization of electronic devices to nanometer size has triggered formidable progress in the research of mesoscopic systems for more than a decade now. An arena closely related to mesoscopics is molecular electronics.<sup>1</sup> Driven by possible technological applications and owing to recent experimental breakthroughs, this area has evolved to a rapidly developing field on its own. Molecular electronics is based on the “bottom-up” manufacture philosophy whose underlying principle is to use molecules or supramolecular structures as (reproducible) circuit elements. Hence, employing the diverse electronic properties of molecular complexes and the capacity of synthetic (bio)chemistry, it may be able to circumvent inherent limitations and imperfections of conventional semiconductor device fabrication techniques at nanometer scales.

Although the original idea is quite old, significant progress has only been demonstrated experimentally in recent years. Owing to the advances in self-assembly techniques,<sup>2</sup> end-group modifications,<sup>3</sup> and scanning probe and break-junction techniques,<sup>4,5</sup> atomic-scale control and positioning of single molecules and their assemblies become possible. First electron transport measurements through molecular complexes between metallic electrodes have been reported. Proposals and studies of molecular wires range from “simple” molecules<sup>5</sup> to DNA strands.<sup>6</sup> In a parallel development, the use of carbon nanotube networks has been the focus of intense experimental and theoretical activity as another promising direction for building blocks of molecular circuits.<sup>7</sup>

Although a molecular device is typically divided into three parts—the donor and acceptor electrodes and the molecular compound serving as a bridge—it is clear that to understand conductance measurements, an account of the system as a whole is required. This is intuitively plausible when looking at the problem as an electron transfer process. The coupling of the molecular complex to the environment as well as its intrinsic ability to convey charge are equally important factors. Hence, whereas the molecular character has been the main focus,<sup>8–10</sup> the precise nature of the contact and its implications has also become a topic of investigation.<sup>11,12</sup>

Yet the electrodes are usually formed from bulk material. In contrast, we take here the viewpoint that the electrodes in the vicinity of the molecular interface can be mesoscopic themselves. To be more specific, we focus on carbon tubules as suitable candidates for such nanoelectrodes. Carbon nanotubes are known to exhibit a wealth of properties depending on their diameter ( $\sim$  nm), chirality (orientation of graphene roll up), and whether they consist of a single cylindrical surface (single-wall) or more (multiwall).<sup>13,14</sup> On the one hand, the first experimental attempts to build nanotube-molecule-nanotube hybrids are in progress.<sup>15</sup> On the other hand, carbon nanotubes are utilized as scanning probe tips to study molecular structures.<sup>16</sup> This represents a related setup where contact effects of a molecule-nanoelectrode junction play a key role.

In the present study, we address the influence of the molecular-wire–electrode contact on the conductance for the class of systems where the structure of the electrodes plays an important role. For mesoscopic leads with reduced dimensionality lateral to the current direction, it makes sense to discriminate between electron transport channels, e.g., carbon nanotubes support up to two channels for electrons with energy around the equilibrium Fermi energy. Evidently, for such low-dimensional transport, the geometry of the contact should crucially determine the measured conductance. We find that electron transport shares distinct properties depending on the number and strength of contacts between the molecular bridge and the electrodes as well as on the symmetry of the channel wave functions transverse to transport. We demonstrate that single contacts give rise to complex conductance spectra exhibiting quantum features of both the molecule and the electrodes; multiple contacts provide a mechanism for transport channel selection, leading to a scaling law for the conductance and allowing for its control. Channel selection also highlights the role of molecular resonant states by suppressing details assigned to the electrodes. Such information may be used as a guideline for systematic chemical synthesis or complementary experimental analysis.

We shall now specify more the system we have in mind. The electrodes are open-ended single-wall carbon nanotubes described by a parametrized tight-binding Hamiltonian with

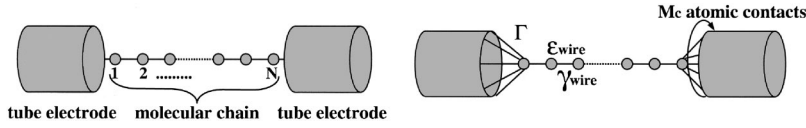


FIG. 1. Scheme of the molecular-wire-tube hybrid with single (left) and multiple (right) contacts.

a  $\pi$  electron per atom, which represents a good approximation to the carbon nanotubes electronic band structure,<sup>13</sup> whereas the molecular system sandwiched in between is modeled by a homogeneous tight-binding chain. The latter choice reflects our aim to provide a qualitative understanding of the phenomenology of the physical problem as opposed to more quantitative quantum-chemical methods that take into account the precise structure and properties of the molecular bridge.

The electronic Hamiltonian of the full system, including the left (L) and right (R) tube (see Fig. 1), reads

$$\begin{aligned}
 H &= H_{\text{tubes}} + H_{\text{wire}} + H_{\text{coupling}} \\
 &= \sum_{\alpha=L,R,\text{wire}} \sum_{n_{\alpha}, n'_{\alpha}} \left( \frac{\varepsilon_{n_{\alpha}}^{\alpha}}{2} \delta_{n_{\alpha}, n'_{\alpha}} - \gamma_{\langle n_{\alpha}, n'_{\alpha} \rangle}^{\alpha} \right) |n_{\alpha}\rangle \\
 &\quad \times \langle n'_{\alpha}| - \sum_{m_L} \Gamma |m_L\rangle \langle n_{\text{wire}}=1| \\
 &\quad - \sum_{m_R} \Gamma |m_R\rangle \langle n_{\text{wire}}=N| + \text{H.c.}
 \end{aligned} \quad (1)$$

Here,  $\gamma^{\text{L,R}} (= 2.66 \text{ eV})$ ,  $\gamma^{\text{wire}}$ , and  $\Gamma$  are the hopping matrix elements between atoms of the carbon tubule leads, molecular bridge, and the bridge/lead interface, respectively. They are nonzero only for nearest neighbors. In Eq. (1),  $\varepsilon_{n_{\text{wire}}}^{\text{wire}}$  is the on-site or orbital energy of each of the  $n_{\text{wire}} = 1, \dots, N$  chain atoms relative to that of the leads,  $\varepsilon^{\text{L,R}}$ , which is fixed to zero. Summations over  $m_L$  and  $m_R$  run over interfacial end atoms of the leads. In general, there are  $M$  such atomic positions, depending on the perimeter of the tubes, and  $1 \leq M_c \leq M$  hybridization contacts. We also compare with a square lattice model of mesoscopic electrodes with nearest-neighbor interactions ( $\gamma^{\text{L,R}} = 1 \text{ eV}$ ) and periodic boundary conditions, which delivers additional insight.

In what follows, we use the Landauer theory,<sup>17</sup> which relates the conductance of a system to an independent-electron scattering problem<sup>18</sup> and describes unique quantum effects in mesoscopic systems.<sup>19</sup> The electron wave function is assumed to extend coherently across the device, and the two-terminal, linear-response conductance at zero temperature reads

$$G(E_F) = 2(e^2/h)T(E_F). \quad (2)$$

The factor 2 accounts for spin degeneracy, and  $T(E_F)$  is the total transmittance for injected electrons with Fermi energy  $E_F$ . The transmission function is given by  $T(E) = \sum_{\nu, \nu'} |S_{\nu\nu'}(E)|^2$ , where  $\nu, \nu'$  are quantum numbers labeling open channels for transport that belong to mutually exclusive leads, in our case the two semi-infinite perfect nanotubes. The molecular system attached acts as a scatterer, and  $S$  is the corresponding quantum-mechanical scattering matrix.

For the numerical calculation of the central quantity,  $T(E)$ , we use a general scattering technique that has been recently formulated for studies of the giant magneto-resistance.<sup>20</sup> Application of the method to phonon transport across disordered interfaces<sup>21</sup> and to electric conductance in multiwall carbon nanotubes<sup>22</sup> reveals an efficient algorithm for calculating the Green function for arbitrary tight-binding Hamiltonians and, hence, the  $S$  matrix.<sup>19</sup> The computational scheme comprises two essential steps: first, the calculation of an effective (renormalized) interaction between the electrodes by projecting out the degrees of freedom of the scatterer, and second, the computation of the unperturbed electrodes Green function. Then, one uses the Dyson equation to express the Green function of the composite system (leads plus scatterer). We followed a previous suggestion<sup>22</sup> for the implementation and computation of the exact Green function of the tubules.

Gross properties of the conductance spectrum of the system can be understood by looking at the two extreme cases of a single interfacial contact,  $M_c = 1$  [single contact (SC)], and multiple contacts,  $M_c = M$  (MC). In the SC scenario, all open channels contribute to the transmission, i.e.,  $S_{\nu\nu'}(E)$  is nonzero for any  $\nu, \nu'$ . For the case of the molecular wire bridging two square-lattice tubes, depicted in the upper left panel of Fig. 2, the conductance bears some of the properties of current flowing through a one-dimensional constriction.<sup>19</sup> In particular, the conductance shows resonances of quantum unit ( $2e^2/h$ ) height at eigenenergies of the isolated molecular chain (indicated as triangles). They arise because of back-reflections at the molecular interface. However, for carbon tubule leads (upper right panel of Fig. 2), we observe additional structure in the conductance spectra. Preliminary results suggest that distinctive features such as antiresonances are signatures of van Hove singularities in the carbon tubule band structure.<sup>23</sup>

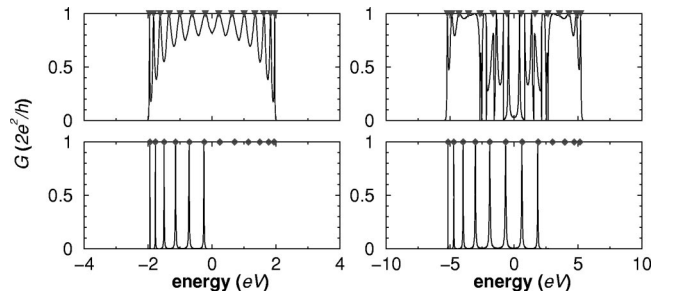


FIG. 2. Typical conductance spectra for an  $N=14$  molecular bridge between square-lattice tube (left) and (10,10) carbon nanotube electrodes (right). An effective multiple contact ( $M_c=20$ , bottom) acts as a filter selecting a single transport channel in contrast to a single contact (top). Diamonds and triangles indicate eigenenergies of an  $N=12$  and  $N=14$  isolated chain.  $\varepsilon_{\text{wire}}^{\text{wire}}=0$  and  $\gamma^{\text{L,R}} = \gamma^{\text{wire}} = \Gamma$ . The carbon nanotube, square-lattice tube, and molecular wire bands (centered at zero) have widths 16 eV, 8 eV, and  $4\gamma^{\text{wire}}$ , respectively.

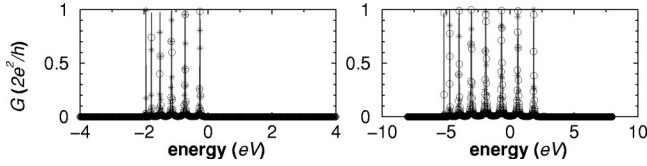


FIG. 3. Superimposed conductance curves with  $\varepsilon^{\text{wire}}=0$ ,  $\gamma^{\text{L,R}}=\gamma^{\text{wire}}$ , and  $\Gamma^2 M=\text{const}$  showing the validity of the sum rule (see text) for the multiple contact configuration for square lattice tube (left) and carbon nanotube (right) electrodes. Symbols and line indicate different  $\Gamma$ .

In contrast, the MC configuration acts as a channel filter resulting in a profoundly different behavior: The conductance vanishes for part of the spectrum as shown in the lower panels of Fig. 2. The complicated conductance spectrum for a SC carbon-tubule-molecule configuration turns into a regular sequence of peaks at eigenenergies of the isolated molecular wire (marked as diamonds). Further analysis of the  $S$ -matrix elements revealed that only wave functions of the tubes without modulation along the cross-section circumference allow for transport, thereby yielding zero conductance when such channels are not available. Evidently, this leads to asymmetric conductance spectra in general. The filtering is a consequence of a sum rule that determines the transmission of each open channel, which may be viewed as the wave-function overlap  $\langle \psi_{\text{wire}} | H | \psi_{\text{L,R}} \rangle$  [see Eq. (1); due to the nature of coupling only the transverse profile is important]. The overlap is directly related to the spectral density.<sup>12</sup> For the square-lattice model tubes, e.g., only the channel with zero “transverse” momentum gives a nonzero sum. From symmetry considerations it is clear that the channel selection is a generic feature of cylindrical electrodes. Moreover, we found that channel filtering approximately prevails also for noncylindrical, mesoscopic electrodes with lateral confinement. More generally, multiple contacts allow for control of low-dimensional transport via channel selection.

An additional particular feature of the MC configuration is that the conductance conforms to a scaling law. Two MC hybrid structures differing in tube diameters  $D$  and contact strengths  $\Gamma$ , but conserving the product  $\Gamma^2 D$ , exhibit the same conductance profile (Fig. 3). This is a mere contact effect related to the symmetry of the contributing channel wave function that should hold for any effective coupling with the form considered here and for any kind of tubule electrode. Since the conductance depends only on  $\langle \psi_{\text{wire}} | H | \psi_{\text{L,R}} \rangle$ ,<sup>8,12,23</sup> the exact form of the scaling law for such single-channel transport readily follows by taking into account that the transverse profile of the contributing channel wave function has no nodes and is normalized.

The “intermediate contact” case, i.e.,  $1 < M_c < M$ , exhibits much richer behavior but can be understood with the above arguments. For completeness, we discuss a specific example that once more illustrates the importance of the interfacial coupling for molecular systems bridging nanoelectrodes and further supports channel selection. In Fig. 4, typical conductance spectra for zigzag carbon nanotube electrodes are shown. To interpret these results, we note that transport usually takes place at  $E \sim 1$  eV around the Fermi

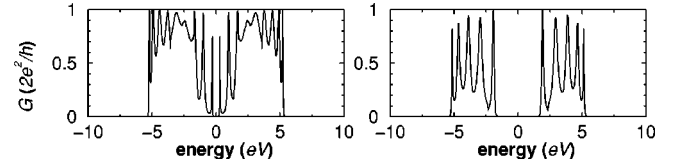


FIG. 4. Conductance spectrum for (9,0) carbon nanotube electrodes with  $M_c=1$  (left) and  $M_c=3$  (right).  $\varepsilon^{\text{wire}}=0$  and  $\gamma^{\text{L,R}}=\gamma^{\text{wire}}=\Gamma$ .

energy  $E_F=0$ . For this part of the spectrum we notice a complete suppression of conductance for  $M_c=3$ , owing to contact “dimensionality.”<sup>24</sup> The origin of this effect derives from metallic zigzag nanotubes supporting two degenerate transport channels in this energy region with wavefunction symmetries such that the wire/tube overlap gives a zero contribution for  $M_c=3n$  as depicted and nonzero otherwise.<sup>25</sup>

Finally, we examine the dependence of the conductance on the coupling strength  $\Gamma$ . It is expected that as the coupling is reduced, resonances are resolved with decreasing width-to-height ratio. This is indeed visible when comparing the middle and lower panels of Fig. 5 for both single (left) and multiple contact (right). However, the upper panels of Fig. 5 reveal a counterintuitive behavior. By decreasing  $\Gamma$  from top to bottom in Fig. 5, we observe an intermediate broadening of the resonance widths, accompanied by a clear-cut change in the position and number of resonances picked up. There is a crossover from  $N-2 \rightarrow N$  resonances, if all the wire resonant states (marked as diamonds and triangles in Fig. 5) fall into the tube energy band. The position of the resonances is suggestive for a possible explanation of this effect. It points to considering the wire/lead interfacial atoms as strongly coupled with the transition driven by the interaction strength. Similar binding effects, which determine the effective length (or the nature) of the molecular bridge, have been previously discussed<sup>11</sup> and are quite sensitive to multiple contacts as demonstrated.

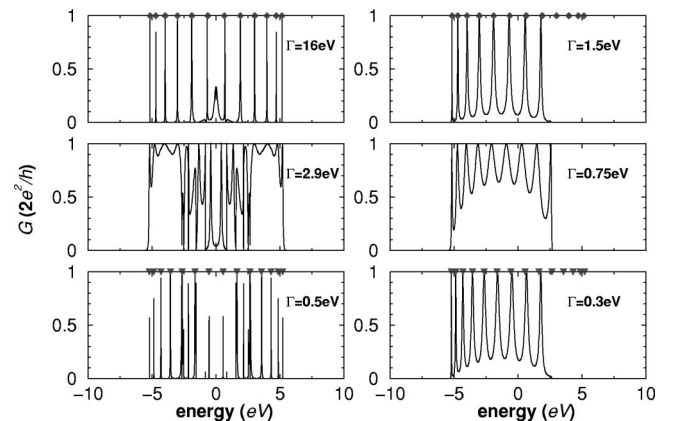


FIG. 5. Chemical binding effects: the effective length of the molecular bridge ( $N=14$ ) depends on the contact strength. Conductance resonances are followed by a narrow-to-broad-to-narrow behavior as  $\Gamma$  decreases from top to bottom for both single (left) and multiple contact ( $M_c=20$ , right). Diamonds and triangles indicate eigenenergies of an  $N=12$  and  $N=14$  isolated chain, respectively.  $\varepsilon^{\text{wire}}=0$ ,  $\gamma^{\text{L,R}}=\gamma^{\text{wire}}$ , and  $\Gamma$  is given as an inset.

In additional simulations,<sup>26</sup> we have considered a dimerized chain as a model for a molecular wire as suggested in Ref. 10 and more complex artificial molecular compounds, which nevertheless do not show distinct behavior from what we have discussed.

We have not discussed electron transport for finite temperatures and bias voltages, since our objective has been to point out generic geometry-induced features linked to the contact resistance of molecular wires. In that case, the calculation of  $I$ - $V$  characteristics requires generalized methods with the Landauer conductance delivering the initial insight. We further point out that in the scattering approach used it is implicitly assumed that no inelastic scattering or other phase-breaking mechanisms occur. For instance, coupling to molecular vibrational modes is neglected and, therefore, studies relying on the independent-electron picture may be only indicative of the underlying conduction mechanisms. We have also assumed that the molecular system is strongly coupled to the electrodes so that charging effects are not important.

In summary, we have studied contact effects on the conductance of a hybrid built by a molecular wire coupled to

low-dimensional leads. We have pointed out immediate consequences of the contact geometry and dimensionality on electron transport across such systems. These include channel selection, conductance spectra tuning, and the existence of a scaling law  $G = G(\Gamma^2 M)$ . We also demonstrated that a square lattice tube exhibits most of the above features and can be used as a tractable analytic model. Replacing such a model for electrodes by natural and realistic candidates of molecular electronic circuits, carbon nanotubes, adds richer structure to the conductance profile. The latter needs further investigation to relate it to the tubule band structure and details depending on the tubule chirality. We hope that our observations may drive systematic chemical synthesis based on geometrical factors and stimulate corresponding experimental analysis. Especially for multiwall nanotube leads, an axial magnetic field of reasonable magnitude can be applied which modulates the symmetry of the tube states and, hence, can act as an external tuning parameter.

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<sup>24</sup>The position of the contacts does not influence conductance for zigzag carbon tubule leads, while for armchair carbon tubules there is no distinction only if  $M_c$  is odd.

<sup>25</sup>For armchair tubules, conductance is always finite but for  $M_c$  even, only one channel instead of two is contributing.

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