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 micro- or nanometer-size has triggered formidable progress in the research of mesoscopic systems for more than a decade now. Such endeavor has given rise to a variety of nontrivial quantum effects in solid state physics at these length scales providing an active field of interplay between fundamental and applied research.

An arena closely related to mesoscopics is molecular electronics which combines molecular and solid state physics. Driven by possible technological applications and owing to recent experimental breakthrough, this area has evolved to a rapidly developing field on its own posing new challenges to theory. 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, end-group modifications, scanning probe and break-junction techniques, 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 to DNA strands. 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.

Albeit 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, the precise nature of the contact and its implications has also become a topic of investigation.

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 (∼nm), chirality (orientation of graphene roll up), and whether they consist of a single cylindrical surface (single-wall) or more (multi-wall). On the one hand, first experimental attempts to build nanotube-molecule-nanotube hybrids are on their way. On the other hand, carbon nanotubes are utilized as scanning probe tips to study molecular structures. 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 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 interface as well as on the symmetry of the channel wavefunctions 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 parameterized tight-binding Hamiltonian with a π-electron per atom which represents a good approximation to the carbon nanotubes electronic band structure [13], 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

\[
H = H_{\text{tubes}} + H_{\text{wire}} + H_{\text{coupling}}
\]

\[
= \sum_{\alpha=L,R,\text{wire}} \sum_{n_\alpha} \left( \frac{\epsilon_{\alpha}}{2} \delta_{n_\alpha,n_\alpha'} + \gamma_{\alpha}(n_\alpha,n_\alpha') \right) |n_\alpha\rangle \langle n_\alpha'|
\]

\[
+ \sum_{m_L} \Gamma |m_L\rangle \langle n_{\text{wire}} = 1| + \sum_{m_R} \Gamma |m_R\rangle \langle n_{\text{wire}} = N| + \text{H.c.}
\]

Here, \( \gamma^{L,R} = (2.66 \text{ eV}) \), \( \gamma^{\text{wire}} \), and \( \Gamma \) are the hopping matrix elements between atoms of the carbon tube leads, molecular bridge, and the bridge/lead interface, respectively. They are non-zero only for nearest neighbors. In Eq. (1), \( \epsilon_{\text{wire}} \) is the on-site or orbital energy of each of the \( n_{\text{wire}} = 1, \ldots, N \) chain-atoms relative to that of the leads, \( \epsilon^{L,R} \), 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 \( \sum m_L = \sum m_R = M \) hybridization contacts. We also compare with a square lattice model of mesoscopic electrodes with nearest-neighbor interactions (\( \gamma^{L,R} = 1 \text{ eV} \)) and periodic boundary conditions, which delivers additional insight.

In what follows, we use the Landauer theory [17] which relates the conductance of a system to an independent-electron scattering problem [15] and describes unique quantum effects in mesoscopic systems [13]. The electron wavefunction is assumed to extend coherently across the device and the two-terminal, linear-response conductance at zero temperature reads

\[
G(E_F) = 2(e^2/h)T(E_F).
\]

The factor two 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 which 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 which has been recently formulated for studies of the giant magnetoresistance [24]. Application of the method to phonon transport across disordered interfaces [11] and to electric conductance in multi-wall carbon nanotubes [20] reveals an efficient algorithm for calculating the Green function for arbitrary tight-binding Hamiltonians and, hence, the \( S \)-matrix [11]. 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 the suggestion discussed in [20] for the implementation and computation of the exact Green function of the tubules.

\[
G(E_F) = 2(e^2/h)T(E_F).
\]

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 non-zero for any \( \nu, \nu' \). For the case of the molecular wire bridging two square-lattice tubes, depicted in the upper left panel of Fig. 3, the conductance
bears some of the properties of current flowing through a one-dimensional constriction [9]. 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 tubules leads (upper right panel of Fig. 3) 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 tubules band structure [22].

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. 3. The complicated conductance spectrum for a SC carbon tube-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 wavefunctions of the tubes without modulation along the cross-section circumference allow for transport, thereby, yielding zero conductance when such channels are not available. The filtering is a consequence of a sum rule that determines the transmission of each open channel which may be viewed as the overlap \(\langle n_{\text{wire}} | H | n_{L,R} \rangle \) (see Eq. (4), due to the nature of coupling only the transverse profile is important). The overlap is also related to the spectral density [12]. For the square lattice model we note that transport usually takes place at \(E \sim 1\text{eV}\) around the Fermi 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’ [23]. 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 \(M_c = 3\cdot n\) as depicted and non-zero otherwise [24].

![Superimposed conductance curves](image1)

**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 \(\Gamma\).

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 \(\Gamma^2 \cdot D\), exhibit the same conductance profile (Fig. 4). This is a mere contact effect related to the symmetry of the contributing channel wavefunction and should hold for any effective coupling with the form considered here. For single-channel transport it follows that the conductance is proportional to \(\langle n_{\text{wire}} | H | n_{L,R} \rangle^2\). Then one readily arrives at the exact form of the scaling law taking into account that the transverse profile of the contributing channel wavefunction has no nodes and is normalized.

![Conductance spectrum for (9,0) carbon nanotube](image2)

**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 \(\gamma_{\text{L-R}} = \gamma_{\text{wire}} = \Gamma\).

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 which once more illustrates the importance of the interfacial coupling for molecular systems bridging nano-electrodes 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 \(E \sim 1\text{eV}\) around the Fermi 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’ [23]. 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 \(M_c = 3\cdot n\) as depicted and non-zero otherwise [24].

![Chemical binding effects](image3)

**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 \((M_c = 20, \text{right})\). 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.

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. 3 for both
single (left) and multiple contact (right). However, the upper panels of Fig. 3 reveal a counterintuitive behavior. By decreasing Γ from top to bottom in Fig. 3 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. 3) fall into the tube energy band. The position of resonances is suggestive for a possible explanation of this effect. It points to considering the wire end-atoms as part of the leads due to strong binding 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 discussed in Ref. 25 and are quite sensitive to multiple contacts as demonstrated.

In additional simulations 22, we have considered a dimerized chain as a model for a molecular wire as suggested in 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 to the conductance profile richer structure. The latter needs further investigation to relate it to the tubules 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 multi-wall 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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