High-temperature excess current and quantum suppression of electronic backscattering

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Abstract – We consider the electronic current through a one-dimensional conductor in the ballistic transport regime and show that the quantum oscillations of a weakly pinned single-scattering target results in a temperature- and bias-voltage independent excess current at large bias voltages. This is a genuine quantum effect on transport that derives from an exponential reduction of electron backscattering in the elastic channel due to quantum delocalisation of the scatterer and from a suppression of low-energy electron backscattering in the inelastic channels caused by the Pauli exclusion principle. We show that both the mass of the target and the frequency of its quantum vibrations can be measured by studying the differential conductance and the excess current. We apply our analysis to the particular case of a weakly pinned C\textsubscript{60} molecule encapsulated by a single-wall carbon nanotube and find that the discussed phenomena are experimentally observable.

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Geometrical confinement is known to alter the interactions in a wide range of interesting systems. Restricting molecules to the hollow interior of a single-wall carbon nanotube (SWNT), e.g. has proven to be an enabling technology for novel chemistry where reactions not allowed in free space can be studied [1]. Electron transport through such encapsulated molecular systems has also been studied to some extent, both experimentally [2,3] and theoretically [4–6], mainly for the case of the “carbon peapod”, a chain of fullerenes inside a SWNT. Even so, little is known about the effect of encapsulated neutral molecules on electron transport along the tube, which is the question addressed in this letter.

We focus on the fact that weakly pinned encapsulated molecules can move rather easily along the nanotube and examine the effect on electron transport along a SWNT due to scattering from such a target. To model this we assume the motion of the molecule to be confined by a shallow harmonic potential well, with the amplitude of its quantum fluctuations, $X_0$, comparable to the Fermi wavelength, $\lambda_F = 2\pi/k_F$, of the electrons ($k_F \sim 8.5\,\text{nm}^{-1}$ is the Fermi wave vector for electrons in a metallic SWNT [7]). Below we will show that the transport properties of the system will be significantly modified by an exponential reduction of electron backscattering in the elastic channel due to quantum delocalisation of the scatterer in conjunction with a suppression of low-energy electron backscattering in the inelastic channels caused by the Pauli exclusion principle. In particular we predict a measurable temperature- and bias-voltage independent excess current at large bias voltages, where the vibration energy quantum of the molecule sets the energy scale for the bias voltage.

In order to develop a theory of electronic transport through a SWNT with an enclosed movable scatterer (sketched in fig. 1) we describe our system by the Hamiltonian

$$\hat{H} = \hat{H}_{el} + \hat{H}_{osc} + \hat{H}_{int}.\quad (1)$$

Here the first term,

$$\hat{H}_{el} = -\frac{\hbar^2}{2m} \int \Psi^\dagger(x) \frac{\partial^2}{\partial x^2} \Psi(x) \, dx,\quad (2)$$

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expressed as
\[ \hat{H} = \hat{H}_0 + \hat{H}_I + \hat{H}_{II} + \hat{H}_{osc}, \]
\[ \hat{H}_0 = iv_F\hbar \int \left( \psi_R^\dagger(x) \frac{\partial}{\partial x} \psi_R(x) - \psi_L^\dagger(x) \frac{\partial}{\partial x} \psi_L(x) \right) dx, \]
\[ \hat{H}_I = U_0 a \left( e^{2i k_F x} \psi_R^\dagger(0) \psi_L(0) + \text{h.c.} \right), \]
\[ \hat{H}_{II} = U_0 a \left( \psi_R^\dagger(0) \psi_R(0) + \psi_L^\dagger(0) \psi_L(0) \right), \]
where \( v_F = \hbar k_F/m \) is the Fermi velocity of the electrons. Below we investigate how the motion of the scattering molecule affects the 1-dimensional transport of electrons through our system. To do this we calculate the current, \( I(x_0) \), through the nanotube at some point \( x_0 \) outside the scattering region, where
\[ I(x_0) = \text{Tr}(\hat{J}(x_0) \hat{\rho}), \]
\[ \hat{J}(x_0) = e v_F \left( \psi_R^\dagger(x_0) \psi_R(x_0) - \psi_L^\dagger(x_0) \psi_L(x_0) \right). \]
Here, \( \hat{J}(x_0) \) is the current operator at point \( x_0 \) and \( \hat{\rho} \) is the stationary density matrix satisfying \( [\hat{\rho}, \hat{H}] = 0 \). Considering that the flow of right (left) moving electrons to the left (right) of the scattering region is determined by the emission of electrons from the left (right) reservoirs, kept at the constant chemical potentials \( \mu_{l(r)} \), one finds that the current can be expressed as
\[ I = I_0 + \text{Im} \frac{4 e u_0 a}{\hbar} \text{Tr} \left( e^{2i k_F x} \psi_R^\dagger(0) \psi_L(0) \hat{\rho} \right). \]
The first term in (7), \( I_0 = G_0 V \), is the current without the scattering center (\( G_0 = 4 e^2/\hbar \) is the quantum conductance for a metallic SWNT) while the second term describes the back-flow current generated by electronic reflection from the molecule. We calculate the back-flow current to lowest order in the electron-molecule interaction, which is assumed to be weak on the energy scale of the electrons, \( U_0 \ll \hbar v_F/a \). The current is evaluated by expanding the density matrix in (7) to first order in \( U_0 \),
\[ \hat{\rho} = \hat{\rho}_0 - \frac{i}{\hbar} \int_{-\infty}^{0} [\hat{H}_I(t), \hat{\rho}_0] dt, \]
\[ \hat{H}_I(t) = e^{i(\hat{H}_0 + \hat{H}_{osc})t/\hbar} \hat{H}_I e^{-i(\hat{H}_0 + \hat{H}_{osc})t/\hbar}, \]
where \( \hat{H}_I(t) \) is the time-dependent scattering Hamiltonian in the interaction representation and \( \hat{\rho}_0 \) is a density matrix for the non-interacting system. The latter takes the proper boundary conditions into account, i.e. right/left-moving electrons are in thermal equilibrium with the left/right lead with the chemical potential \( \mu_{l(r)} = \epsilon_F \pm e V/2 \) and the harmonic oscillator is in thermal equilibrium with the environment. Note that in this approximation contributions from \( \hat{H}_{II} \) do not affect the current.

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1Our analysis shows that the details of the SWNT electronic spectrum do not affect the phenomena discussed here.
Using (7) together with (8) allows us to calculate the current by evaluating the trace and integrating out the time variable,

$$I = G_0 V = \frac{G_0 R}{\epsilon} \sum_{n=0}^{\infty} P(n) \times \sum_{\Delta=-n}^{\infty} |\langle n | e^{i \sqrt{\pi} (b + b^\dagger)} | n + \Delta \rangle|^2 F(\Delta \omega, eV, \beta),$$

$$F(\Delta \omega, eV, \beta) = \int d\epsilon [f_R(\epsilon) (1 - f_L(\epsilon - \hbar \omega)) - f_L(\epsilon) (1 - f_R(\epsilon - \hbar \omega))] = \frac{\hbar \omega \Delta - eV}{e^\beta(\hbar \omega \Delta - eV) - 1} - \frac{\hbar \omega \Delta + eV}{e^\beta(\hbar \omega \Delta + eV) - 1}. \quad (9)$$

In (9), $R = (U_0 a / h v_F)^2$ is the (small) reflection coefficient for electrons, $P(n) = (1 - e^{-\beta h \omega(n)}) e^{-n \beta h \omega}$ (where $\beta = 1/k_B T$) is the probability that the oscillator is in state $n$ with energy $n \hbar \omega$, and $f_R, f_L(\epsilon) = (1 + e^{\beta(\epsilon - \mu_r, \mu_l)})^{-1}$ are Fermi distribution functions for right and left moving electrons, respectively. The electron-oscillator coupling is described by the matrix element $\langle n | e^{i \sqrt{\pi} (b + b^\dagger)} | n + \Delta \rangle$ between the oscillator states $| n \rangle$ and $| n + \Delta \rangle$ where the (dimensionless) parameter $\alpha = \sqrt{2k_F x_0}^2$ measures the strength of the coupling and $b^\dagger (b)$ is a boson creation (annihilation) operator.

Clearly, the function $F(\Delta \omega, eV, \beta)$ in (9) contains the effects of reflections of right/left-moving electrons with the arguments in the respective Fermi distributions dictating the allowed transitions of the oscillator and the combination of the Fermi distributions ensuring that the Pauli exclusion principle is not violated. By evaluating (9) one finds the current through the system as a function of voltage and temperature.

First and foremost we find that at high voltages, $eV > eV_0$ ($eV_0 \propto \max\{k_B T, \hbar \omega, \alpha \hbar \omega\}$) there is an excess current, $\delta I$, compared to the “static” current $I_{st} = G_0 (1 - R) V$ that would flow if the scatterer was immobile. This is because with a mobile scatterer some of the inelastic reflection channels are blocked due to Pauli principle restrictions and this reduces the back-flow current. It is particularly interesting to note that in the limit of very high voltages, $V \gg V_0$, the excess current is temperature and voltage independent,

$$\lim_{V \gg V_0} \delta I = \lim_{V \gg V_0} I - I_{st} = \frac{4G_0 R}{\epsilon} \left( \frac{\hbar^2 k_F^2}{2 M} \right). \quad (10)$$

This is a remarkable result, not only in that it predicts the high-voltage excess current—a truly quantum-mechanical phenomenon—to be independent of temperature, but also in that it should be feasible to probe experimentally.

Also interesting to note is that the amount of excess current scales as $\hbar^2 k_F^2/(2 M)$; hence it is inversely proportional to the mass of the target and does not depend on the curvature of the harmonic potential. Even more, one can prove that the result in (10) is quite general and valid for any confining potential.

One can only speculate about the possible value of $\hbar \omega$ for the longitudinal oscillatory fullerene motion along the nanotube. Here, we estimate its value to be one to two orders of magnitude lower than the $5 \text{ meV}$ reported by Park et al. for a $C_{60}$ molecule bound to a gold electrode by van der Waals forces [8]. The excess current is shown in fig. 2 for two different temperatures and two different confining potentials.

From (9) one can also calculate the low-temperature differential conductance. By using the restrictions imposed by the allowed transitions between oscillator states and by noting that as $T \to 0$, $P(n) = \delta_{n,0}$, one finds that

$$\lim_{T \to 0} \frac{\partial I}{\partial V} = G_0 \left( 1 - R \sum_{\Delta=0}^{\infty} e^{-\alpha \Delta} \left( \frac{\Delta!}{\Delta^\Delta} \right) \right). \quad (11)$$

Here, $[eV/\hbar \omega]$ is the integer part of the ratio between the applied bias voltage and the characteristic energy scale of the oscillator, which dictates the number of open scattering channels. Thus, as the applied voltage across the system is increased the low-temperature differential conductance is seen to approach the expected result for an immobile scatterer, $G_0 (1 - R)$, as shown in fig. 3. This is understandable since a larger bias voltage will increase...
the number of possible final oscillator states, making the motion of the fullerene less important on the energy scale of the electrons and the result from a static barrier due to Landauer [9] is recovered.

The linear conductance of the system refers to the limit of zero bias voltage and generally has to be evaluated numerically. However, its low- and high-temperature asymptotic limits can be found using the completeness of the set of vibronic states, \( \sum_{\Delta=0}^{\infty} |\langle n| e^{i\sqrt{\alpha} (b+b^\dagger)} |\Delta\rangle|^2 = 1 \). These limiting results, which are similar to those found by Shekhter et al. [10] for the case of a suspended nanotube in a transverse magnetic field, can be expressed as

\[
\frac{\partial I}{\partial V} = G_0 \begin{cases} (1 - R e^{-\alpha}), & \alpha \ll 1 \\ (1 - R \left[1 - \frac{\alpha}{3k_B T}\right]), & \alpha \gg 1. \end{cases}
\]

In the low-temperature limit, \( \alpha \ll 1 \), only the ground-state elastic channel is allowed and the conductance goes as the zero-bias limit of (11). In the high-temperature limit, \( \alpha \gg 1 \), many inelastic channels for back-scattering are available, which reduces the excess conductance of the system as compared to a static barrier case. These asymptotes are clearly visible in the numerical solutions for the linear conductance, fig. 4. Also of interest is the low-temperature conductance as a function of \( \alpha \), also shown in fig. 4. We propose that this region could be studied experimentally by tuning the Fermi wavelength, hence \( \alpha \), using a gate voltage.

It is interesting to note that in all the above cases the energy scale is set by the frequency of the fullerene oscillator, i.e. \( \hbar \omega \) separates out low- and high-temperature effects in the conductance of our carbon nanotube system. For \( \hbar \omega \sim 0.1 \text{ meV} \) the crossover energy would correspond to a temperature of order \( \sim 1 \text{K} \).

It is also of interest to compare our result with that found by Krive et al. [11] for resonant electron tunneling through carbon peapods. In agreement with preliminary experimental results [12] they found an anomalous \( T^{-1/2} \) temperature dependence of the conductance, which they attribute to a polaron-assisted tunneling. Their model is, however, specific to resonant tunneling and is complementary to ours, which applies to the ballistic transport regime.

To conclude, our analysis has shown that in the weak-scattering limit, confinement of a molecule inside a carbon nanotube leads to quantum corrections to both the current and the conductance through the system. In particular we have shown that due to the quantum fluctuations of the scattering target, a temperature- and voltage-independent excess current is predicted at high bias. We find that the magnitude of the excess current in the high-voltage limit is itself not a function of the confining potential but scales inversely with the mass of the target, thus making this an observable quantity for any confined scattering target for which the onset of the excess current is dictated by the confining potential. An extension of our perturbative approach to the case of many encapsulated molecules should be possible for low enough molecule concentrations, in which case they can be treated independently, allowing us to sum up their individual contributions.

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