Carbon nanotube sensor for vibrating molecules

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\textbf{Abstract.} The transport properties of a carbon nanotube (CNT) capacitively coupled to a molecule vibrating along one of its librational modes are studied and its transport properties analyzed in the presence of a scanning tunnel microscope tip. We evaluate the linear charge and thermal conductances of the system and its thermopower. They are dominated by \textit{position-dependent} Franck–Condon factors, governed by a position-dependent effective coupling constant peaked at the molecule position. Both conductance and thermopower allow us to extract some information on the position of the molecule along the CNT. Crucially, however, thermopower also sheds light on the vibrational level spacing, allowing a more complete characterization of the molecule to be obtained, even in the linear regime.

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1. Introduction

Carbon nanotubes (CNTs) are outstanding examples of one-dimensional conductors [1, 2]. When embedded into a circuit and connected to external leads via tunneling barriers, CNTs behave as quantum dots [3–5]. Owing to their one-dimensional nature, their behavior can be well described by means of a Luttinger liquid (LL) model [6–10], which can also include electron–electron interactions. The latter can lead to several interesting effects, including the formation of Wigner molecules [11–13], peculiar correlated electron states characterized by unusual transport properties [14], which in a CNT can be either probed by means of an atomic force microscope [15–17] or the tip of a scanning tunnel microscope (STM) [18, 19].

Among the most prominent applications of CNTs is their use as mass [20, 21] or gas nanoscale sensors [22, 23]. Seminal work on gas sensing using CNT detectors included the study of the change in resistance of single wall nanotubes [24] or mats of multiwall CNTs exposed to an environment containing H$_2$ or NH$_3$ molecules [25, 26]. The ultimate goal of CNT-based nano-sensing is to achieve the resolution of few molecules and to be able to identify the chemical species of the molecule itself. One of the possible ‘fingerprints’ of a molecule is its vibrational spectrum.

Molecules exhibit several different vibrational modes, with a broad spectrum of vibrational frequencies. The intrinsic vibrational modes strongly depend on the molecule mass, as well as its spatial orientation and on the nature of the chemical bonds composing it. The typical frequency of these modes can be as high as 100 THz (65 meV) [27]. Molecules coupled to a surface, such as the one of the CNT, show additional libration vibrational modes involving the center of mass of the molecule itself, which oscillates as a whole with respect to the surface [28]. Such modes are much softer, with a vibrational frequency of the order of 1 THz and excitation energies smaller than 1 meV.

Molecular vibrations are typically detected with optical methods such as Raman scattering [27]. However, it is also, in principle, possible to employ the transport properties of a CNT to detect at least some of these vibrational modes. Low-energy modes have excitation energies smaller than the typical level spacing $\delta E$ of a CNT which, for a length $L \approx 200$ nm can be estimated as $\delta E = \hbar \pi v_F / L \approx 10$ meV ($v_F = 8 \times 10^5$ m s$^{-1}$ the CNT Fermi velocity). This allows their signatures in the transport properties to be singled out, in contrast with the internal vibration modes with excitation energies well exceeding $\delta E$, whose signatures are intertwined with those due to the electronic degrees of freedom of the CNT. In turn, this would lead to ‘smart’ molecular sensors, able to detect the presence and the type of molecule attached to it.
This coupling of molecular vibrations and electronic states in a CNT is strongly reminiscent of the situation that occurs in a nano-electromechanical system (NEMS) [29--34], in which mechanical and electronic degrees of freedom are strongly coupled. Suspended CNTs themselves can behave as NEMS when current flowing through them excites their vibrational modes [10, 35].

Another powerful tool to detect the excitation spectrum of a mesoscopic system is the thermopower [36]. In the context of quantum dots, thermopower has been studied theoretically [37--43] as well as experimentally [44--47]. It constitutes a powerful tool to investigate the spectrum of excited states of quantum dots in the linear regime [37], in contrast with the more conventional nonlinear transport spectroscopy. In the context of NEMS, the thermopower has been shown experimentally to provide a way to investigate mechanical vibrations in sequential and the cotunneling regimes [48]. The information brought by thermopower has been employed in the study of molecular junctions [49, 50], in the presence of an STM tip [51] and even in gas sensors based on CNT mats [52].

In this paper we study the behavior of a single-wall CNT capacitively coupled to a vibrating molecule. The CNT–molecule system is coupled via tunnel barriers to a lateral contact and to a STM tip free to scan the CNT length. Focusing on the linear regime, we evaluate the linear charge, the thermal conductance and the thermopower. Our task is to investigate to what extent the linear transport properties bring about information about the molecule attached to the CNT surface. Our main results are the following.

1. The capacitive coupling of the electrons and the molecule leads to the appearance of space-dependent [10, 35, 53] Franck–Condon (FC) factors [54, 55], whose behavior is dominated by an effective, space-dependent CNT–molecule coupling constant $\lambda(x)$ ($x$ the coordinate of the tip), which affects the tunneling rate through the tip and the lateral contact. Such a coupling constant is peaked around the position where the molecule sits.

2. The linear conductance exhibits a maximum following a simple analytical function of $\lambda(x)$, allowing to identify where the molecule is by scanning the STM tip.

3. The thermopower shows resonant features at energies corresponding to the vibrational spectrum of the molecule, allowing a precise characterization of the latter.

Our findings show that thermopower measurements would be able to detect the position of a molecule and to gain information about its vibrational frequency.

The outline of the paper is as follows. In section 2 the model for the CNT capacitively coupled to the molecule is described and its spectrum diagonalized. In section 3 a model for the coupled system is introduced and its Hamiltonian is exactly diagonalized by means of a canonical transformation. The setup for a transport experiment is then presented, tunneling rates in the sequential regime are evaluated and a master equation is set-up. Finally, linear charge and thermal conductances are obtained. Section 4 contains the results concerning the position-dependent coupling constant, linear conductance and thermopower. Finally, in section 5 we summarize our conclusions.

2. Nanotube, molecule and coupling

The device consists of a single-wall metallic CNT bounded in $x = 0$ and $L$, capacitively coupled to a molecule that vibrates around the position $x_0$. The system is schematically depicted.
Figure 1. Schematic rendering of the CNT coupled at $x_0$ to a molecule vibrating along its libration mode.

In the following we will concentrate on the libration modes of the molecule, since their excitation energy compares favorably with the energy scale at which transport experiments are performed.

The Hamiltonians of the decoupled CNT and vibrating molecule are respectively ($\hbar = 1$):

$$H^{(0)}_{\text{CNT}} = \sum_j \left[ \frac{E_j}{2} N_j^2 + \sum_{q>0} \omega_j(q) a_j^{\dagger} a_{j,q} \right],$$

$$H^{(0)}_{\text{mol}} = \frac{P^2}{2M} + U(R),$$

where $R = (X, Z)$ and $P = (P_0, P_z)$ and we neglect the motion of the molecule along the waist of the nanotube, i.e. we assume that the molecule fingerprint is larger than the CNT transverse dimension $D \ll L$. Here, $Z$ denotes a radial coordinate perpendicular to the CNT axis.

Equation (1) represents the bosonized Hamiltonian of the CNT within the LL language [7, 8, 10]. It is composed of four sectors $j \in \{c^+, c^-, s^+, s^-\}$ where $c^+$ ($s^+$) represent the total charge (spin) modes and $c^-$ ($s^-$) represent the relative charge (spin) ones. The first term represents the contribution of the CNT zero modes, with $N_j$ the number of extra electrons per sector with respect to a neutral reference situation with $N_0$ electrons. In the following, for definiteness, we assume $N_0$ to be a multiple of four and that each sector $j$ thus contains $N_0/4$ electrons. We have introduced $E_j = \pi v_j/4Lg_j$ with $v_j = v_F/g_j$ the propagation velocity of the mode $j$ and $g_j$ the LL interaction parameters, which capture the effects of short-range forward scattering among the electrons. One has $g_{c^+} = g \leq 1$ with $g = 1$ for non-interacting electrons. All other parameters $g_{j \neq c^+} = 1$ due to symmetries of the model [7]. The second term represents collective excitations of bosonic character, with spectrum $\omega_j(q) = v_jq$ with $q = \pi n_q/L$ the quantized momentum ($n_q > 0$ an integer) and canonical bosonic operators $a_{j,q}$.

The molecule sits in a potential well, which we assume separable $U(R) = U_X(X) + U_Z(Z)$. The shape of $U_X(X)$ and $U_Z(Z)$ is schematically depicted in figure 2. The molecule is located around the position $x_0$, corresponding to the minimum of $U_X(X)$. A rather shallow well is expected, which can be very well approximated by a harmonic potential $U_X(X) \sim \frac{M\omega_0^2}{2} (X - x_0)^2$. Concerning the $Z$ direction, the molecule occupies the minimum of a potential well constituted by a repulsive short-range part and an attractive long range tail. Such a well, located at a position $z_0$, is in general much narrower than the one that develops along the $X$ direction [56]. As a consequence, vibrations in the transverse $Z$ direction have typical frequencies $\omega_Z \gg \omega_0$. In this work, we concentrate on linear transport properties and low temperatures $k_B T \ll \omega_Z$, so that the motion in the $Z$ direction is effectively ‘frozen’ in the...
Figure 2. Schematic depiction of the potential wells where the molecule sits (a) along the nanotube and (b) in the radial direction. The blue curve in panel (a) represents the harmonic approximation assumed in this work. The shaded portion in panel (b) suggests the location of the CNT surface.

The ground state of \( U_Z(Z) \). Therefore, upon a redefinition of the zero of energies, the Hamiltonian of the molecule simplifies as

\[
H_{\text{mol}}^{(0)} = \frac{P_0^2}{2M} + \frac{M\omega_0^2}{2}(X-x_0)^2. \tag{3}
\]

The molecular vibrations around \( x_0 \) are thus described by a simple harmonic oscillator in equation (3), with \( M \) the molecule mass, \( X = x_0 + X_0 \) the fluctuating position of the molecule, and \( X_0 \) and \( P_0 \) the molecule displacement and momentum operators, respectively. Here, and in the following, we will consider the case of vibration frequencies \( \omega_0 < \omega_1 \) with

\[
\omega_1 = \frac{\pi v_F}{gL}. \tag{4}
\]

The molecule and the CNT are assumed to be electrostatically coupled via the term

\[
H_{\text{mix}} = \int_0^L dx \ V(x-x_0) \rho(x), \tag{5}
\]

where \( V(x) \) represents the coupling potential and \( \rho(x) \) the total CNT electron density. In this work, we neglect charge tunneling between the CNT and the molecule, which may be the subject of future investigations. We assume that the molecule is physisorbed to the CNT, neglecting chemisorption effects that may induce structural modifications of the local nature of chemical bonds [57, 58].

Here, \( V(x) \) represents the electrostatic potential induced on the CNT conduction electrons by the molecule charge cloud. As a model, we choose a finite-range screened potential

\[
V(x) = \frac{V_0}{2w} e^{-\frac{|x|}{w}} \tag{6}
\]

with \( V_0 > 0 \) describing the amplitude of the potential and \( w \) the interaction range. It must be stressed, however, that all the results presented in this paper do not depend qualitatively on the particular choice of \( V(x) \), as long as it is peaked with a width of the order \( w \). Assuming vibrations of small amplitude, we expand equation (5) to lowest order and obtain

\[
H_{\text{mix}} \approx \int_0^L dx \ V(x-x_0) \rho(x) - X_0 \int_0^L dx \ \rho(x) \partial_x V(x-x_0). \tag{7}
\]

The electron density can be decomposed as the sum of terms \( \rho(x) = \sum_{l=0}^{\infty} \rho^{(l)}(x) \), representing the long-wave term \( (l = 0) \) and spatially oscillating contributions with wavelengths...
\( \ell_i \approx (2k_F)^{-1} \) with \( k_F = \pi N_0/4L \) the CNT Fermi momentum. For \( l = 1 \) one has Friedel oscillations, due to finite-size effects [61]. Terms with \( l > 1 \) are induced for instance by electron–electron correlations, band curvature effects or scattering with impurities, which may lead to the formation of a Wigner molecule [16, 17, 19, 62]. In typical CNT sensors, one has \( N_0 \gg 1 \), with correspondingly short wavelengths: in particular one can already expect that the Friedel wavelength \( \ell_i \ll w \) for a typical value of \( N_0 \approx 100 \). In this case, the rapid oscillations of terms with \( l \geq 1 \) give a vanishing contribution in equation (7). We are assuming here that the molecule does not induce appreciable back-scattering on the CNT conduction electrons [59, 60]. These effects may be the subject of future investigations. Only the long-wave term of the electron density survives, which reads

\[
\rho(x) = \rho^{(0)}(x) = e^{\frac{N_{e+}}{L}} + \frac{e}{2\pi} [\partial_x \phi_{e+}(x) + x \to -x]
\]

with \( e \) the electron charge and

\[
\phi_j(x) = \sum_{q > 0} \sqrt{\frac{\pi}{qL}} \left\{ \sqrt{\frac{1}{g_j}} \cos(qx) A_{j,q}^{(\pm)} + i \sqrt{g} \sin(qx) A_{j,q}^{(-)} \right\} e^{-aq/2},
\]

LL field operators with \( A_{j,q}^{(\pm)} = a_{j,q} \pm a_{j,q}^\dagger \) and \( \alpha = k_F^{-1} \) a short-length cutoff. As is clear, the coupling only involves the total charge sector \( j = c+ \).

To proceed, we introduce \( \tilde{X}_\mu = i\sqrt{Lg/2\pi v_F \mu}(a_{+,\mu/L} - a_{+,\mu/L}^\dagger) \) with \( \mu \geq 1 \), and the canonically conjugated momenta \( \tilde{P}_\mu = \sqrt{\pi v_F \mu/2gL}(a_{+,\mu/L} + a_{+,\mu/L}^\dagger) \). The charge sector \( j = c+ \) of equation (1) becomes of \( \tilde{X}_\mu \) and \( \tilde{P}_\mu \)

\[
H^{(0)}_{c+} = \frac{E_{c+}}{2} N_{c+}^2 + \sum_{\mu \geq 1} \left( \frac{\tilde{P}_\mu^2}{2} + \omega_\mu^2 \tilde{X}_\mu^2 \right),
\]

where \( \omega_\mu = \pi \mu v_F / Lg \). Introducing \( \tilde{X}_0 = \sqrt{MX_0} \) and \( \tilde{P}_0 = P_0/\sqrt{M} \) the Hamiltonian of molecular vibrations becomes

\[
H^{(0)}_{\text{mol}} = \frac{\tilde{P}_0^2}{2} + \omega_0^2 \tilde{X}_0^2.
\]

The coupling in equation (7) can be decomposed into three terms \( H_{\text{mix}} = H^{(1)}_{\text{mix}} + H^{(2)}_{\text{mix}} + H^{(3)}_{\text{mix}} \) as

\[
H^{(1)}_{\text{mix}} = \gamma_1 N_{c+},
\]

\[
H^{(2)}_{\text{mix}} = \sum_{\mu \geq 1} \gamma_2(\mu) \tilde{X}_\mu,
\]

\[
H^{(3)}_{\text{mix}} = \sum_{\mu \geq 1} \gamma_3(\mu) \tilde{X}_0 \tilde{X}_\mu,
\]

where

\[
\gamma_1 = \xi \omega_0 \frac{L}{\ell_0} \mathcal{I}_1,
\]

\[
\gamma_2(\mu) = \xi \omega_0^2 \sqrt{2\eta^3} \frac{L}{\ell_0} \mathcal{I}_2(\mu),
\]
\[ \gamma_3(\mu) = -\pi \xi \omega_1^2 2\eta^2 I_3(\mu) \] (17)

and

\[ I_1 = \frac{1}{2w} \int_0^L \, dx \, e^{-\frac{|x-x_0|}{w}} , \] (18)

\[ I_2(\mu) = \frac{\mu e^{-\frac{\mu}{2w}}}{2\omega} \int_0^L \, dx \, e^{-\frac{|x-x_0|}{w}} \sin \left( \frac{\pi \mu x}{L} \right) , \] (19)

\[ I_3(\mu) = \frac{\mu^2 e^{-\frac{\mu}{2w}}}{w} \int_0^L \, dx \, e^{-\frac{|x-x_0|}{w}} \cos \left( \frac{\pi \mu x}{L} \right) . \] (20)

Here, we have introduced the dimensionless parameters

\[ \xi = \frac{eV_0}{L\omega_0} , \] (21)

\[ \eta = \frac{\omega_0}{\omega_1} \] (22)

with \( \ell_0 = (M\omega_0)^{-1/2} \) the characteristic oscillator length.

The terms in equations (12) and (13) can be promptly eliminated by means of a linear shift of the operators \( N \) and \( X \). The shift of \( N \) in equation (12) leads to an offset of the gate potential considered in transport. The linear shift of \( X \) produces a constant energy shift and hence its effects will be irrelevant on transport properties where only energy differences come into play. We can therefore discard terms in (12) and (13) and focus on equation (14), which couples the vibrational mode \( \tilde{X}_0 \) only to the plasmonic excitations \( \tilde{X}_\mu \). The bosonic part of equations (10), (11) and (14) constitute a quadratic form which can be diagonalized by means of a canonical transformation [10, 63]

\[ \tilde{P}_\mu = \sum_{v \geq 0} k_{\mu v} \tilde{P}_v, \quad \tilde{X}_\mu = \sum_{v \geq 0} k_{\mu v} \tilde{x}_v. \] (23)

The diagonalization procedure relies on the condition \( \omega_0 < \omega_1 \) [63], i.e. \( \eta < 1 \). This is satisfied if \( L < L^* \) with \( L^* = \pi \nu F / g \omega_0 \). For a typical value \( \omega_0 \approx 1 \) THz one obtains \( L^* \approx 2.5 \mu m \).

The diagonalized Hamiltonian is

\[ H_{\text{mol/CNT}} = \sum_{\mu \geq 0} \left( \tilde{p}_\mu^2 \frac{2}{2} + \Omega_\mu^2 \tilde{x}_\mu^2 \right) \] (24)

written in terms of the new collective normal modes \( \{ \tilde{x}_\mu, \tilde{p}_\mu \} \) with energy \( \Omega_\mu \), which exhibit a hybrid vibrational/plasmonic character. The coefficients \( k_{\mu v} \) are given by [63]

\[ k_{\mu v} = \gamma_3(\mu) \Omega_v - \omega_\mu^2 \left[ 1 + \sum_{\mu \geq 1} \frac{\gamma_3^2(\mu)}{\Omega_\mu^2 - \omega_\mu^2} \right]^{-1/2} \] (25)

while the eigenenergies \( \Omega_\mu \) are obtained solving the self-consistent equation

\[ \Omega_\mu^2 = \omega_0^2 + \sum_{v \geq 1} \frac{\gamma_\mu^2(v)}{\Omega_\mu^2 - v^2 \omega_1^2} . \] (26)
Figure 3. Setup of the proposed STM-CNT molecular sensor. The CNT is tunnel-coupled to a STM tip, which is able to scan the whole tube length, and to a lateral metallic contact. A back-gate, at potential $V_g$, is capacitively coupled to the CNT. The tip is kept at a temperature $T+\delta T$ while contacts are at a temperature $T$. See text for further details.

The condition
\[ \frac{1}{2\pi^2\xi^2\eta} \leq \sum_{\nu \geq 1} \frac{I^2_\nu}{\nu^2} \] ensures the positivity of the solutions of equation (26) preventing the Wentzel–Bardeen instability [63].

As a general feature, the mode with $\mu = 0$ is reminiscent of a vibrational mode dressed by a polaron cloud with energy $\Omega_0 < \omega_0$. As we will see, this polaron cloud has profound consequences on the transport properties of the system. All other modes with $\mu \geq 1$ are plasmon-like with a slightly increased energy $\mu \omega_1 < \Omega_\mu < (\mu + 1)\omega_1$ for $\mu \geq 1$.

For reasonable values of the system parameters (see section 4 for further details) $\xi = 0.1$, $\eta = 0.6$, $w = L/10$ and $\alpha = L/100$, one finds $\Omega_0 \approx 0.6\omega_0$ and $\Omega_\mu \approx \mu\omega_1$.

Due to the diagonalization, the operator $\phi_{\nu,+}(x)$ is also modified. In the low energy sector, we are only interested in the vibration-like excitations, with an energy of the order of $\Omega_0$. We can thus disregard the electronic collective excitations and approximate
\[ \phi_{\nu,+}(x) \approx \sum_{\nu \geq 1} k_{\nu,0} \left[ \sqrt{2g\omega_1} \sin \left( \frac{\pi \nu x}{L} \right) X_0 + \sqrt{\frac{2}{\nu^2 g\omega_1}} \cos \left( \frac{\pi \nu x}{L} \right) P_0 \right]. \] (28)

3. Scanning tunnel microscope tip coupling and transport properties

Let us now turn to a setup which allows the transport properties to be investigated. It is schematically depicted in figure 3. The CNT–molecule system is tunnel-coupled to a lateral metallic contact and a STM tip, labeled respectively by the index $\eta = D, S$, with tunneling amplitudes $\tau_\eta$. The tip scans the entire CNT length. An additional gate, capacitively coupled to the CNT, is kept at a potential $V_g$ and allows to tune the CNT chemical potential.

A promising tool to extract information about the spectrum of molecular excitations even in the linear regime is the thermopower. Suppose that the lateral contacts are kept at a
temperature \( T \) while the tip is placed at \( T + \delta T \), with \( \delta T \ll T \). As a consequence of the temperature gradient, electrons flow through the CNT–molecule system. The tip and the lateral leads are kept in an open-circuit configuration, which implies a steady current \( I = 0 \). As a result of the redistribution of electrons, a voltage drop \( \delta V \) between the tip and the contacts develops. Eventually, an equilibrium situation is reached. The thermopower \( S \) is defined as

\[
S = -\frac{\delta V}{\delta T} .
\]  

(29)

In the linear regime, the equilibrium condition

\[
I \approx G_V \delta V + G_T \delta T = 0
\]  

(30)

with

\[
G_V = \frac{\partial I}{\partial V}, \quad G_T = \frac{\partial I}{\partial T}
\]  

(31)

the charge and thermal linear conductances of the system, allows to obtain

\[
S = \frac{G_T}{G_V} .
\]  

(32)

We will consider the sequential tunneling regime, assuming that the typical tunneling rate through the STM vacuum barrier or the leads barrier is large with respect to the average rate of electrons flow. This is valid when the temperature \( T > \Gamma \), the average level broadening due to tunneling, and the system is not in the deep Coulomb blockade regime. However, it has been shown that for the low-temperature regime \( \Gamma < T < k_B^{-1} \omega_0 \), both elastic and inelastic cotunneling contributions to the thermopower have negligible effects even in the linear regime away from Coulomb oscillation resonances [38, 48].

A convenient tool to tackle the transport properties in the sequential regime is the master equation for the occupation probabilities of the CNT–molecule system states \( S \). As already stated, we are interested in energies smaller than \( \omega_1 \), thus retaining only the vibration-like excitations. The CNT–molecule Hamiltonian can thus be written as

\[
H_{\text{CNT–mol}} = \frac{E_{c+}}{2} (N_{c+} - N_g)^2 + \sum_{j \neq c} \frac{E_j}{2} N_j^2 + \frac{\tilde{p}_0^2}{2} + \Omega_0 \tilde{x}_0^2 .
\]  

(33)

Here we have included in the CNT–molecule Hamiltonian the effects of the gate kept at a potential \( V_g \), where \( N_g = C_g V_g/e \) and \( C_g \) the gate capacitance.

The contacts and STM tip are treated as non-interacting Fermi gases. The tunneling Hamiltonian which describes the connection between the CNT and the contacts is \( H_t = \sum_r H_t^{(r)} \) (\( r = S, D \)) with [10, 64, 65]

\[
H_t^{(S)} = \tau_S \sum_{a,s} \Psi_{a,s}^\dagger (x) \psi_{s,f} (0^+) + \text{h.c.} ,
\]  

(34)

\[
H_t^{(D)} = \tau_D \sum_{a,s,q} \Psi_{a,s}^\dagger (x_D) c_{s,q} + \text{h.c.} ,
\]  

(35)

where \( x_D = L \) is the position of the lateral contact. Here, \( \Psi_{a,s} \) is the field operator for right-movers in the CNT, with Dirac valley index \( \alpha \) and spin \( s \). It is given by [10]

\[
\psi_{a,s} (x) = \frac{J_{a,s}}{\sqrt{2\pi \alpha}} e^{-i\phi_{a,s}} e^{i\frac{\theta_{a,s} x}{4\alpha}} e^{i\frac{\phi_{a,s} x^2}{2\alpha}} ,
\]  

(36)
where $J_{α,s}$ is a Klein factor and

$$
Θ_{α,s} = θ_{c,+} + α θ_{−} + s θ_{z} + s α θ_{−},
$$

$$
N_{α,s} = N_{c,+} + α N_{−} + s N_{z} + s α N_{−},
$$

$$
Φ_{α,s}(x) = φ_{c,+}(x) + α φ_{−}(x) + s φ_{z}(x) + s α φ_{−}(x)
$$

with $[θ_{j}, N_{j}]=i δ_{j,j′}$. The operator $ψ_{s,F}(z)$ describes the forward propagating modes in the STM tip, with $z$ the vertical coordinate within the tip and $z=0^+$ the tip vertex. Finally, $c_{s,q}$ are standard Fermi operators describing electrons with spin $s$ and momentum $q$ in the lateral contact $η=D$.

Due to the spin-valley symmetry of a CNT, degeneracies occur in the spectrum of the Hamiltonian equation (33). In particular, we will consider in the following the resonance between states with $N_{c,+} = 4κ$ (filled shell, non-degenerate) and $N_{c,+} = 4κ+1$ electrons, which is fourfold degenerate [10]. We will label the CNT–molecule states as $S=|N_{c,+}, l⟩$ where $l$ is the vibrational quantum number, and keep track of the degeneracy via the factors $D_S$. We note here that even though our calculations have been performed for a CNT with a full fourfold degeneracy, the model can promptly take in account chirality effects leading to the emergence of a lower, twofold degeneracy due to the generality of the factors $D_S$. No qualitative modification of the results presented in the rest of the paper are expected in this case. The occupation probabilities $P_S$ of the system states are thus found, in the steady state, solving the master equation [66]

$$
−P_S ∑_{S′≠S} D_{S′} Γ_{S→S′}(x) + ∑_{S′≠S} P_{S′} D_S Γ_{S′→S}(x) = 0
$$

with the normalization condition $∑_S P_S = 1$. Here, the tunneling rates are

$$
Γ_{S→S′}(x) = Γ^{(D)}_{S→S′} + Γ^{(S)}_{S→S′}(x),
$$

where $x$ is the STM tip position along the CNT. The steady current can be conveniently evaluated on either the tip or the lateral contact. One finds

$$
I = e ∑_{l,l′} (P_{|[4κ,l⟩}|Γ^{(S)}_{|[4κ,l⟩→[4κ+l,l′]}) − P_{|[4κ+l,l′⟩}|Γ^{(S)}_{|[4κ,l⟩→[4κ+l,l′])}.\n$$

The tunneling rate for a transition between the initial state $|I⟩$ and the final state $|F⟩$ of the whole system—including the CNT, the STM tip and the lateral contact—is given by the Fermi golden rule

$$
Γ_{I→F} = 2π |⟨F|H_I|I⟩|^2 δ(E_F − E_I),
$$

where $E_I$, $E_F$ are the energies of the whole system in the initial and final state respectively. The calculation proceeds performing a trace of equation (43) over the degrees of freedom of the tip and of the lateral contact, assumed in thermal equilibrium, in contrast with the charge degree of freedom and the occupation number of the vibrational state which retain their full dynamics. We will omit here the details of this standard procedure and directly quote the final results [35], considering for simplicity only the case of tunneling in the CNT

$$
Γ^{(S)}_{|[4κ,l⟩→[4κ+l,l′]}) (x) = Γ^{(S)}_0 F_{II'}(x) f_S (Δ V + Ω_{II'} + e V / 2),
$$

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The final results transitions with different vibrational states. On the other hand, \( \lambda(x) \), diagonalization discussed in the previous section. work as results in the linear transport regime do not depend on the particular choice adopted.

The procedure is lengthy but straightforward \cite{54, 55}. Finally, \( f_\eta(E) = [1 + e^{E/k_BT_\eta}]^{-1} \) is the Fermi function for lead \( \eta \) at temperature \( T_\eta \) (\( T_\eta = T + \delta T \), \( T_D = T \)),

\[
\bar{\varepsilon} = E_{c+} \left( 4\kappa + \frac{1}{2} - N_g \right) + \frac{3}{8} \omega_1
\]

and \( \Omega_{l'} = \Omega_0 (l' - l) \). Note that in order to derive equations (44) and (45) we have assumed a symmetric voltage drop on both tunnel barriers. This choice is not restrictive for the present work as results in the linear transport regime do not depend on the particular choice adopted.

The position-dependent FC factors can be explicitly evaluated as

\[
F_{ll'}(x) = e^{-\bar{\lambda}^2(x)} \left[ \lambda(x) \right]^{2l'-l} \frac{L_{l'}}{L_{l-1}} \left| L_{l'}^{(l')} \right| \left( \lambda^2(x) \right)|^2
\]

with \( l_- = \min(l, l') \), \( l_+ = \max(l, l') \), \( L^2_p(x) \) the Laguerre polynomials and

\[
\lambda(x) = \sqrt{\frac{\omega_1}{\Omega_0} \left[ \sum_{\nu \geq 1} k_{\nu 0} \sin \left( \frac{\pi \nu x}{L} \right) \right]^2 + \frac{\Omega_0}{\omega_1} \left[ \sum_{\nu \geq 1} \frac{k_{\nu 0}}{\nu} \cos \left( \frac{\pi \nu x}{L} \right) \right]^2}
\]

a position-dependent CNT–molecule coupling parameter, whose explicit form depends on the diagonalization discussed in the previous section.

The coupling \( \lambda(x) \) determines the behavior of the tunneling rates and allows the possibility to trigger transitions between different molecular vibration state via the FC factors \( F_{ll'}(x) \). When \( \lambda(x) \ll 1 \), one has \( F_{ll'}(x) \approx \delta_{l,l'} \) and tunneling events are not able to trigger transitions among different vibrational states. On the other hand, \( F_{ll'}(x) \neq 0 \) for several different values of \( l \) and \( l' \) when \( \lambda(x) \neq 0 \). The larger \( \lambda(x) \), the wider is the jump \( |l' - l| \) allowed by the FC factors, while transitions with \( l \approx l' \) and/or small \( l, l' \) are strongly suppressed. Where \( \lambda(x) \) is sizeable, the transport properties of the CNT are then drastically influenced.

In the linear regime, the strategy is to expand and solve equation (40) to linear order in \( \delta V \) and \( \delta T \) and then plug the solution into the current expression (42), again retaining only the leading (linear) terms

\[
I \approx G_V \delta V + G_T \delta T.
\]

The procedure is lengthy but straightforward \cite{48, 67} and shall be omitted here. We just quote the final results

\[
G_V = G_0^{(V)} f(-\bar{\varepsilon}) \sum_{l,l'} e^{-\beta \Omega_{l'}} \left[ \bar{\varepsilon} + \Omega_{l'} - k_B T \log(4) \right] \chi_{l,l'}(x),
\]

\[
G_T = G_0^{(T)} f(-\bar{\varepsilon}) \sum_{l,l'} e^{-\beta \Omega_{l'}} \left[ \bar{\varepsilon} + \Omega_{l'} \right] f[\bar{\varepsilon} + \Omega_{l'} - k_B T \log(4)] \chi_{l,l'}(x).
\]
Here, we have introduced $G_0^{(V)} = \beta e^2\Gamma_0^{(D)}(1 - e^{-\beta \Omega_0})/2$, $G_0^{(T)} = \beta^2 e k_B \Gamma_0^{(D)}(1 - e^{-\beta \Omega_0})/2$, $\beta^{-1} = k_B T$, $f(E) = [1 + e^{\beta E}]^{-1}$ and

$$
\chi_{l,l'}(x) = \frac{4 A F_{l,l'}(x) F_{l,l'}(x_D)}{4 F_{l,l'}(x) + A F_{l,l'}(x_D)}
$$

(53)

with $A = \Gamma_0^{(D)} / \Gamma_0^{(S)}$ the barriers asymmetry ($A \gg 1$ for a typical STM setup). The logarithmic factors in equations (51) and (52) stem from the CNT spin and valley degeneracy and provide a shift of the peaks of $G_V$ and $G_T$ linear in temperature. We note here that the above results for $G_V$ and $G_T$ in the linear regime are identical to those which would have been obtained assuming the CNT and vibrational degrees of freedom fully relaxed [48].

4. Parameters and results

Before discussing our results, let us review the parameters upon which our model holds. The CNT–molecule coupling parameter $\lambda(x)$ in equation (49) is influenced by the dimensionless parameter $\eta = \omega_0 / \omega_1$ and to the dimensionless coupling strength $\xi$ defined in equation (21). For librational modes one can estimate a typical frequency of the order of 1–4 THz with $\omega_0 \approx 0.6–2.4$ meV, while for a weakly interacting CNT ($g \approx 1$) $\omega_1 \approx 2$ meV assuming $L \approx 1 \mu$m, which yields $\eta \approx 0.2$. For shorter CNTs, and/or for lower values of $g$ (stronger interactions), $\eta$ decreases accordingly. In general, the larger the mismatch between the molecule and plasmon frequency—and thus the smaller $\eta$—the weaker are the effects of the CNT–molecule coupling [10]. The interaction strength $\xi$ in turn depends on the electron–molecule interaction strength $V_0$, the CNT length and the molecule mass, as well as on its vibrational frequency. Typical values for $V_0$ are in the range 1–40 eV m [68]. For the CNT, we assume here an average length $L \approx 200$ nm and we consider fairly light molecules (such as NH$_3$) with average molar mass of about 20 g mol$^{-1}$. This allows to estimate $0.01 \leq \xi \leq 0.2$.

Estimates for the interaction range $w$ in equation (6) may be given on a phenomenological basis only. We expect it to be larger than the Luttinger cutoff length, thus satisfying $\alpha < w < L$. In the following, we will consider values in the range $w \approx L/10$.

The above estimates satisfy the condition in equation (27), ensuring the stability of the system and the validity of the proposed model.

Figure 4(a) shows the effective coupling parameters $\lambda(x)$ as a function of $x$, for different positions of the molecule attached to the CNT. As a general feature, we observe that $\lambda(x_D) \approx 0$ unless $x_0 \approx x_D$, i.e. when the molecule is very close to the drain contact (a rather peculiar situation). This means that, in general, tunneling events at the lateral contact will be rather inefficient in triggering molecular vibrations. On the other hand, the STM tip—being able to scan the CNT length—can excite oscillations in the molecule when it is located in proximity of the latter. Indeed, the curves in figure 4(a) always display a maximum of $\lambda(x)$ located at $x = x_0$. This already suggests that the STM tip can be a valuable tool to investigate the properties of the molecule. This will be confirmed by the results on the thermopower shown later in this section. The value of $\lambda(x_0)$ exhibits a slight increase as $x_0 \to 0$ (or $x_0 \to L$). This is due to the spatial behavior of the long-wave electron density: indeed one finds that in the parameters regime considered in this work, when $x_0$ deviates from the CNT center, $\lambda(x)$ is dominated by terms with $v \approx 1$ in equation (49). Inspecting equation (17) one observes that these terms are all large and in phase when $x_0$ is near the CNT borders.
Figure 4. Behavior of $\lambda(x)$ as a function of the position $x$ (units $L$) of the STM tip along the CNT, for: (a) different values of the molecule position $x_0/L$: 0.125 (red), 0.2 (green), 0.3 (blue), 0.5 (purple). Here, $\xi = 0.15$, $\eta = 0.25$ and $w = L/10$. (b) Different values of $\xi$: 0.01(red), 0.05 (green), 0.1 (blue), 0.15 (purple), 0.2 (cyan). Here, $x_0/L = 0.3$, $\eta = 0.25$ and $w = L/10$. (c) Different values of $\eta$: 0.05 (cyan), 0.2 (purple), 0.4 (blue), 0.6 (green), 0.8 (red). Here, $x_0/L = 0.3$, $\xi = 0.1$ and $w = L/10$. (d) Different values of $w/L$: 0.1 (red), 0.2 (green), 0.3 (blue), 0.4 (purple), 0.5 (cyan). Here, $x_0/L = 0.3$, $\xi = 0.1$, and $\eta = 0.1$. In all panels, $\alpha = L/30$ and $g = 1$. The arrows denote the direction of increasing parameters.

Given the relatively large range of variation of the different system parameters, it is worthwhile to investigate their effects on $\lambda(x)$. Figure 4(b) shows $\lambda(x)$ for different values of $\xi$. As it may be expected, since $\xi$ directly parameterizes the strength of the molecule–CNT coupling, $\lambda(x)$ increases (decreases) when $\xi$ increases (decreases). A similar behavior is observed when $\eta$ is varied—as shown in figure 4(c). The coupling between the molecule and the CNT is more efficient if $\eta$ increases, i.e. when the vibrational frequency and the plasmon frequency are closer and thus more resonant. Finally, figure 4(d) shows the dependence of $\lambda(x)$ on the width of the molecule–CNT interaction potential $w$: the width of the effective coupling closely follows $w$ with its maximum scaling as $w^{-1}$, in agreement with the behavior of $V(x)$ in equation (6).

Figure 5 shows the effects of Coulomb interactions on the coupling $\lambda(x)$. Clearly, as $g \to 0$ (from red to cyan curve) the coupling gets suppressed. This fact is due to the decrease of the parameter $\eta \propto g$. We want to stress here that additional effects induced by the presence of strong Coulomb interactions, such as the formation of a Wigner molecule in the CNT, are ignored since we assume the CNT to have a large number of particles $N_0$ with a corresponding Wigner wavelength shorter than the width $w$ of the molecule interaction potential, see section 2. The fact that the CNT–molecule coupling is larger for weakly interacting systems constitutes an advantage from the experimental point of view, due to the almost unavoidable presence of surrounding screening metalizations.
Figure 5. Behavior of $\lambda(x)$ as a function of the position $x$ (units $L$) of the STM tip along the CNT, for different values of the Luttinger interaction parameter $g =: 1$ (red, corresponding to $\eta = 0.7$), 0.8 (green, $\eta = 0.56$), 0.6 (blue, $\eta = 0.42$), 0.4 (purple, $\eta = 0.28$), 0.2 (cyan, $\eta = 0.14$). Here, $L = 875$ nm, $\omega_0 = 2$ Thz, $x_0 = 0.3L$, $\xi = 0.15$, and $w = L/10$, and $\alpha = L/30$. The arrows denote the direction of increasing $g$ and thus of decreasing interaction strength.

Figure 6. (a) Plot of $G_V$ (units $G_0^V$) as a function of $\bar{\epsilon}$ (units $\Omega_0$); (b) plot of $G_T$ (units $G_0^{(T)}$) as a function of $\bar{\epsilon}$ (units $\Omega_0$) and (c) Plot of $\bar{G} = \log [G_V/G_V(\bar{\epsilon} = 0)]$ as a function of $\bar{\epsilon}$ (units $\Omega_0$). Arrows denote the position of the exponentially suppressed vibrational sidebands induced by the coupling between the CNT and the molecule. (d) Plot of the conductance maximum $G_m(x)$ normalized to $G_0^V$ as a function of $x$ (units $L$) for different temperatures $T$ (units $\Omega_0/k_B$): 0.05 (red), 0.1 (green), 0.25 (blue), 0.5 (purple). Parameters for all panels: $\xi = 0.1$, $\eta = 0.6$, $w = L/10$, $A = 100$ and $\alpha = L/30$. In panels (a,b), $k_B T = 0.1\Omega_0$ and $x = x_0 = 0.3L$.

Let us now turn to the linear transport properties. Before investigating the thermopower $S$, it is useful to study the charge and thermal conductances. Figures 6(a) and (b) show the typical behavior of $G_V$ and $G_T$ as a function of the resonant energy $\bar{\epsilon}$, see equation (47). The linear charge conductance exhibits a peak centered around the main resonance value $\bar{\epsilon} = 0$, while the thermal conductance shows a kink centered in the same position. These features are
due to the contributions with \( l = l' \approx 0 \) in equations (51) and (52). Also the terms with \( l \neq l' \) and possibly \( l, l' \neq 0 \), due to the excitation of the molecule vibrational modes, contribute to the above quantities and lead in principle to satellite peaks red- and blue-shifted with respect to the main resonance, located around \( \tilde{\varepsilon} \approx n\Omega_0 \) \((n \text{ an integer})\). This would in principle allow direct extraction of the vibrational frequency of the molecule from a measurement of \( G_V \). These peaks, however, are not visible: in the regime \( k_B T \ll \Omega_0 \) they are exponentially suppressed, while at higher temperature they are subdued by the tails of the thermally broadened central peak. Figures 6(a) and (b) indeed show no detectable trace of such sidebands. Figure 6(c) shows a plot of

\[
\tilde{G} = \log \left[ \frac{G_V}{G_V(\tilde{\varepsilon} = 0)} \right].
\]  

(54)

For a single conductance peak, one would expect a featureless exponential decay of \( G_V \). However, the plot shows faint oscillations at the vibron resonance positions \( \tilde{\varepsilon} = n\Omega_0 \). Such oscillations are virtually undetectable in the linear plot of the conductance and extremely unlikely to be observed in experiment. Also \( G_T \) displays analogous features (not shown here).

Let us now analyze in more details the main peak of \( G_V \), concentrating on the low temperature regime \( k_B T \ll \Omega_0 \). Concentrating around \( \tilde{\varepsilon} \approx 0 \) and retaining only the terms \( l = l' \) in equation (51) one obtains

\[
G_V \approx \frac{G_0^{(V)}}{\cosh \left( \frac{\beta \tilde{\varepsilon}}{2} \right)} \cosh \left( \frac{\beta \tilde{\varepsilon} - \log(4)}{2} \right) \sum_l e^{-i\beta l\Omega_0} \frac{A F_0(x)}{A + 4 F_0(x)},
\]  

(55)

where we have exploited the fact that \( \lambda(x_D) \approx 0 \). The conductance exhibits a maximum for \( \tilde{\varepsilon} = 0 \) with the well-known \( T^{-1} \) power-law scaling through the factor \( G_0^{(V)} \). When \( A \ll 1 \) the conductance is essentially independent of the STM tip position, since conductance is dominated by the lateral conductance only. This case however is not very interesting from the point of view of a realistic STM setup, where \( A \gg 1 \). In this case, one can perform the summation in equation (55) and obtain an analytic expression for the space-dependent conductance maximum

\[
G_m(x) = \frac{8}{9} \frac{G_0^{(V)}}{1 - e^{-\beta\tilde{\varepsilon}_0}} \exp \left[ -\frac{\lambda^2(x)}{1 - e^{-\beta\tilde{\varepsilon}_0}} \right].
\]  

(56)

The above expression is especially simple for \( k_B T \ll \Omega_0 \) when one finds \( G_m(x) \approx (8/9)G_0^{(V)} e^{-\lambda^2(x)} \). A plot of \( G_m(x) \) is shown in figure 6(c) as a function of \( x \) for different temperatures. As expected by equation (56), it exhibits a dip in the location where the molecule sits. Therefore, measuring the maximum of \( G_V \) as a function of the STM position allows to extract \( \lambda(x) \) and ultimately reveals the position of the molecule along the CNT.

Finally, we turn to the thermopower \( S \), shown as a function of \( \tilde{\varepsilon} \) in figure 7(a). When the tip is away from the molecule, red line, it shows a featureless linear trend as a function of \( \tilde{\varepsilon} \), typical of its behavior around a Coulomb blockade oscillation [37]. We stress here that we are concentrating on a low-energy regime in which the electronic collective excitations of the CNT are effectively frozen out, leaving no signature on the thermopower \( S \). On the other hand, when the tip is located at \( x = x_0 \), blue curve, a non-monotonic behavior as a function of \( \tilde{\varepsilon} \) is shown. Each sawtooth-like dip is located at \( \tilde{\varepsilon} = n\Omega_0 \) \((n \text{ an integer})\) and signals the triggering of vibrational excitations in the molecule, in analogy to the behavior observed
in nano-electromechanical systems [48]. The thermopower $S$ is therefore able to detect the presence of a molecule attached to the CNT, by displaying vibrational sidebands at $\bar{\epsilon} = n\Omega_0$. We remind here that, usually, such vibrational sidebands are detected in the nonlinear transport regime. Since both $G_T$ and $G_V$ display the same exponential suppression for the vibrational sidebands, their ratio becomes insensitive to it. As a result, $S$ displays clear signatures of quantities not directly accessible in the direct measurements of the conductance [37]. In analogy with $G_V$, the visibility of this effect is strongly influenced by the asymmetry of tunnel barriers $A$, see figure 7(b). As $A$ decreases, the sidebands get weaker and eventually vanish altogether when $A \approx 1$. The STM setup, therefore, operates in the correct regime to exploit the information contained into $S$. Also thermal effects tend to smear out the above features, as shown in figure 7(c): in order to obtain the maximum contrast one needs $k_B T \ll \Omega_0$.

The thermopower, however, also encodes information about the position of the molecule. Figure 8(a) shows a colorscale map of $S$ as a function of the STM tip position $x$ and $\bar{\epsilon}$. Following the graph along vertical lines, one obtains the $S$ versus $\bar{\epsilon}$ plots discussed above. For $x$ away from $x_0$, an increase of $S$ as a function of $\bar{\epsilon}$ is observed, while features develop for $x \approx x_0$. Figure 6(b) shows curves of $S$ as a function of the tip position $x$ for the resonance conditions $\bar{\epsilon} = n\Omega_0$ ($n = 1, 2, 3$). Each of these curves exhibits a dip located at $x_0$, thus confirming that the thermopower is a tool able to detect the location of the attached molecule.

In order to be more quantitative, we study the dip of $S$ around $\bar{\epsilon} \approx \Omega_0$, considering for definiteness the low-temperature regime $k_B T \ll \Omega_0$. Only terms with $l^\prime = 0$ and $l = 0, 1$ must then be retained in equations (51) and (52). Neglecting the logarithmic factors, irrelevant at
small temperatures, one gets
\[ S \approx \frac{\Omega_0}{eT} \frac{2\chi_{0,0}(x)}{2\chi_{0,0}(x) + \chi_{1,0}(x)} \approx \frac{\Omega_0}{eT} \frac{2}{2 + \lambda^2(x)} \]  
(57)
for \( A \gg 1 \). The plot of this expression is shown in figure 8(b) as a dashed dot, in agreement with full numerics. Similar approximations can be obtained for the resonances at higher energy. Their expressions however are too involved to be reported here.

Thus, a measurement of \( S \) as the tip scans the CNT allows to extract \( \lambda(x) \) and confirms that thermopower is a powerful tool to extract information about the molecule and on its location.

5. Conclusions

In this paper we have considered the transport properties of a CNT capacitively coupled to a molecule vibrating along its librational modes. The CNT–molecule coupling has been diagonalized exactly, extracting the new eigenmodes of the system. Transport in the presence of an STM tip scanning the CNT length has been considered. Employing a master equation
approach in the sequential tunneling regime, analytic expressions for the linear charge and thermal conductances have been obtained, allowing to study the behavior of the thermopower. The transport properties depend on the tip position and are characterized by the appearance of a position-dependent coupling to the molecule, with a maximum peaked at its position.

The linear charge conductance of the system allows to extract information about the above position-dependent coupling. However, it is not a sensitive probe for the vibrational spectrum of the molecule. On the other hand, the thermopower shows features corresponding to resonances with the molecular vibrations, thus allowing to extract the molecular vibration frequency. These features also strongly depend on the position and are shown to be directly related to the effective CNT–molecule coupling, thus allowing to locate the molecule along the CNT.

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