Confinement effects and why carbon nanotubes bundles can work as gas sensors †

Rodrigo G Amorim^{*a}, A. Fazzio^{b‡}, Antônio J.R. da Silva^{b,c‡} and Alexandre R. Rocha^{a,d}

Received Xth XXXXXXXXXX 20XX, Accepted Xth XXXXXXXX 20XX First published on the web Xth XXXXXXXXX 200X DOI: 10.1039/b000000x

In this supporting material we provide detailed information on the energetics and final arrangement of the different adsorption sites considered in this study. This is done to justify the configurations shown in figure 1c-d of the main manuscript. Furthermore we also present a more detailed overview of the Molecular Dynamics simulation and transport calculations per-

formed on different snapshots in order to justify our results for the disordered case.

1 Supporting Information

In this supporting material we provide detailed information on the energetics and final arrangement of the different adsorption sites considered in this study. This is done to justify the configurations shown in figure 1c-d of the main manuscript.

Furthermore we also present a more detailed overview of the Molecular Dynamics simulation and transport calculations performed on different snapshots in order to justify our results for the disordered case.

1.1 Energetics and stability of adsorbed molecules on isolated CNTs

The question of stability in SWCNT was investigated in detail for two molecules, namely *CO* and *NH*₃. For a complete understanding of the adsorption process we studied three possible positions of the molecules on the carbon nanotube hexagonal matrix. In figure S1 we show schematically three position labeled by I, II and III corresponding to top (T), hollow (H) and bridge (B) sites on the tube, respectively. Furthermore, for *CO* molecules three possible orientations (as we can see in the figure S1(a-c)) were considered. We shall call them *CO* (a), *OC* (b) and axial (c) orientation.For the *NH*₃ molecules, two orientations were considered; the nitrogen atom is pointing either away (e) or towards (d) the nanotube as we can be seen in the figure S1(d-e). All calculations were performed

† Electronic Supplementary Information (ESI) available: [details of any supplementary information available should be included here]. See DOI: 10.1039/b000000x/

^c Laboratório Nacional de Luz Síncrotron, Campinas, São Paulo, Brazil.

^d Instituto de Física Teórica, Universidade Estadual Paulista, São Paulo, SP, Brazil; E-mail: reilya@ift.unesp.br



Fig. S1 Schematic positions of the molecular gas (*CO* and NH_3) considered adsorved in the SWCNT. Was considered three different places and three (two) orientations for *CO* (NH_3).

using *ab initio* density functional theory 1,2 as described in the main text.^{*}

The energy differences using as a reference the most stable configuration of each molecule are shown in the table S1. For carbon monoxide the *IIb* configuration is the most stable structure and the one considered in the manuscript. For ammonia the most stable stucture is the *IId* as can seen in the table S1. We note that the energy difference between the different positions/orientations lies in the range 0.03 - 0.06 eV for the perpendicular configurations in *CO* whereas it is much higher for the axial orientation of the molecule (~ 0.2 eV). For ammonia they vary between 0.03 eV and 0.06 eV.

^a Centro de Ciência Naturais e Humanas, Universidade Federal do ABC, Santo André, SP, Brazil.

^b Instituto de Física, Universidade de São Paulo, São Paulo, SP, Brazil.

^{*} The electronic structure calculations are based on density functional theory as implemented in the SIESTA package³ with the inclusion of a parametrized disperson-corrected atom-centered potential (DCACP)^{4,5} which accounts for van der Waals (vdW) interactions. In our DFT simulations we used the Generalized Gradient Approximation (GGA) within the Perdue-Burke-Ernzerhof (PBE) proposal⁶ to treat the exchange-correlation potential, a double-*ζ* polarized basis set (DZP) and standard norm-conserving pseudopotentials⁷.

Table S1 Relative energies (given in eV) of relaxed SWCNT with adsorbed CO and NH_3 molecules in different configurations. The structural indexing follows Figure S1.

CO	a	b	с	NH ₃	d	e
Ι	0.031	0.055	-	Ι	0.027	-
Π	0.028	0.000	0.192	Π	0.000	0.055
ш	-	-	0.214	III	0.034	-

In the table S2 we show the distances between the molecules and the isolated SWCNT. We note that in all cases studied the distance between the molecules and the nanotube is in the same range. From these results we can infer that the main type of interaction between molecule and nanotube is of the van der Waals type, and no chemical bond is formed.

Table S2 Distances given in Å of relaxed SWCNT with adsorbed molecular gas CO and NH_3 .

CO	a	b	с	NH ₃	d	e
Ι	2.95	3.32	-	Ι	3.23	-
Π	3.168	3.26	3.13	Π	3.37	3.14
III	-	-	3.12	III	3.30	-

1.2 Electronic Transport Properties in Bundles

For our transport calculations we use the non-equilibrium Green's function formalism^{8–11}. Within this framework we initially divide a one-dimensional system into three different parts following the procedure first put forward by Caroli *et al.*¹². These three parts consist of two semi-infinite charge reservoirs to the left and to the right of a central scattering region. In the specific case of this work we are interested in the electronic transport properties of either isolated nanotubes or CNTs in bundles containing molecules adsorbed on the tube walls. Figure 1a, c and d of the manuscript depict the central scattering region used in our calculations. In all cases the electrodes are made up of a semi-infinite repetition of a unit cell of the pristine system (denoted here as the principal layer (PL)) to either the left or the right of the scattering region.

The main quantity that characterizes our system is then the Green's function for the scattering region which can be written down as

$$G_{S}(E,V) = [E \times S_{S} - H_{S}[\rho] - \Sigma_{L}(E,V) - \Sigma_{R}(E,V)]^{-1} ,$$
⁽¹⁾

where S_S and H_S are finite operators for the overlap and the Hamiltonian of the central scattering region whereas $\Sigma_{L/R}$ are

the so called self-energies which account for the effect of the electrodes onto the central region. These will be described in detail in section 1.3. Here we assume that the Hamiltonian is a functional of the charge density ρ and depends indirectly on the external bias *V*.

From the knowledge of the Green's function and the coupling of the scattering region to the charge reservoirs it is possible to calculate the transmission coefficients

$$T(E) = \Gamma_{\rm L}(E, V) G_S(E, V) \Gamma_{\rm R}(E, V) G_S^{\dagger}(E, V)$$
(2)

where the coupling matrices are given by

$$\Gamma_{\alpha} = i \left[\Sigma_{\alpha} - \Sigma_{\alpha}^{\dagger} \right] \tag{3}$$

with $\alpha \equiv \{L, R\}$. Subsequently the current can be calculated

$$I(V) = \frac{e^2}{h} \int dE \ T(E,V) \left[f(E,\mu_{\rm L}) - f(E,\mu_{\rm R}) \right] , \quad (4)$$

where the chemical potentials $\mu_{L/R}$ for the left and right electrodes are given by

$$\mu_{\rm L} = E_F + \frac{V}{2} \tag{5}$$

$$\mu_{\rm R} = E_F - \frac{V}{2} . \qquad (6)$$

Finally, in the linear regime, the differential conductance is given by

$$g = \lim_{V \to 0} \frac{dI}{dV} \,. \tag{7}$$

In principle, the theory described above could be used to calculate the electronic transport properties of any onedimensional device provided the Hamiltonian H_S is know. As it was mentioned in the manuscript this Hamiltonian is chosen to be the Kohn-Sham Hamiltonian coming from density functional theory^{1,2}. The combination DFT+NEGF has been successfully applied to a variety of problems in nanoscale systems^{9,10,13,14}.



Fig. S2 Schematic representation of a system consisting of *m* building blocks. Each segment is described by a Hamiltonian H_i and by the coupling $V_{ij} = V_{ij}\delta_{ij\pm 1}$ between building blocks.

Nonetheless, the system we are dealing with here entails two additional difficulties. The first is the fact that the device is, in principle, a disordered three-dimensional system (in the case of the bundle). In order to circumvent this problem we enlarge the unit cell in the transverse direction while including periodic boundary conditions. This way one increases the possible arrangements of sites in the case of low concentration of molecules. With the enlarged cell (shown in Figure 1a of the manuscript) we perform our calculations -in the single molecule case - with 720 carbon atoms (plus one molecule adsorbed onto the tube walls on either of the eight binding sites). This turns our three dimensional problem into a wide onedimensional one, where the electronic transport occurs along the tube's axial direction.

Secondly, for a description of a large number os molecules randomly distributed along the bundle one must consider a system with tens of thousands of atoms (in our case approximately 50,000) using an atomistic description. We solve this problem using the recursive Green's fuction method $^{15-20}$ whereby we use the short-range interaction between different degrees of freedom (all orbitals within each atom) to our advantage . In figure S2 we present a schematic representation of a general one-dimensional device. It was divided into different segments each of which is denoted by a Hamiltonian H_i and the coupling between adjacent segments V_{ij} .[†] We note here that the on-site Hamiltonians H_i are not necessarily the same for every *i*. They can be, for instance, pristine regions or segments containing molecules in different relative positions.

Therefore the Hamiltonian for the scattering region can be written in block-tridiagonal form, *i. e.*,

$$H_{\rm S} = \begin{pmatrix} H_1 & V_{1,2} & 0 & 0 & 0 & \cdots & 0 \\ V_{2,1} & H_2 & V_{2,3} & \cdots & 0 & \cdots & 0 \\ 0 & V_{3,2} & \ddots & V_{j-1,j} & 0 & \cdots & 0 \\ \vdots & \vdots & V_{j,j-1} & H_j & V_{j,j+1} & \cdots & \vdots \\ 0 & 0 & 0 & V_{j+1,j} & \ddots & \ddots & 0 \\ \vdots & \vdots & \vdots & \vdots & \ddots & H_{m-1} & V_{m-1,m} \\ 0 & 0 & 0 & 0 & 0 & V_{m,m-1} & H_m \end{pmatrix}$$
(8)

In the case of a non-orthogonal basis set the Overlap matrix can be written in analogous form.

This way equation 1 for the specific problem of a long onedimensional system is simply

$\begin{pmatrix} \bar{H}_1 - \Sigma_L \\ \bar{V}_{2,1} \end{pmatrix}$	$ar{V}_{1,2} \ ar{H}_2$	$0 \ ar{V}_{2,3}$	0	0 0		0 \ 0)	
0	$\bar{V}_{3,2}$	••.	$\bar{V}_{j-1,j}$	0		0		
÷	÷	$\bar{V}_{j,j-1}$	\bar{H}_j	$\bar{V}_{j,j+1}$	•••	÷	$\mathscr{G} = I$.	(9)
0	0	0	$\bar{V}_{j+1,j}$	•.	·	0		
: 0	: 0	: 0	: 0	· 0	$ar{H}_{m-1}$ $ar{V}_{m,m-1}$	$ar{V}_{m-1,m}$ $ar{H}_m - \Sigma_{ m R}$	J	

For simplicity we have introduced the bar operators in such a way that the on-site and the off-site matrix elements are

$$\bar{H}_i = [ES_i - H_i] \tag{10}$$

$$\bar{V}_{i,j} = [ES_{i,j} - H_{i,j}],$$
 (12)

respectively.

While the Hamiltonian H_S is clearly block-tridiagonal the same cannot be said about the Green's function which is generally a dense matrix,

[†]For non-adjacent segments the coupling is considered to be zero. The segments can be chosen in such a way that this condition is always satisfied.

$$\mathscr{G} = \begin{pmatrix} \mathscr{G}_{1} & \mathscr{G}_{1,2} & \mathscr{G}_{1,3} & \cdots & \mathscr{G}_{1,j} & \cdots & \mathscr{G}_{1,m-1} & \mathscr{G}_{1,m} \\ \mathscr{G}_{2,1} & \mathscr{G}_{2} & \mathscr{G}_{2,3} & \cdots & \mathscr{G}_{2,j} & \cdots & \mathscr{G}_{2,m-1} & \mathscr{G}_{2,m} \\ \\ \mathscr{G}_{3,1} & \mathscr{G}_{3,2} & \mathscr{G}_{3} & \ddots & \vdots & \mathscr{G}_{3,j+1} & \cdots & \mathscr{G}_{3,m} \\ \vdots & \vdots & \ddots & \ddots & \mathscr{G}_{j-1,j} & \mathscr{G}_{j-1,j+1} & \vdots & \vdots \\ \\ \mathscr{G}_{j,1} & \mathscr{G}_{j,2} & \cdots & \mathscr{G}_{j,j-1} & \mathscr{G}_{j} & \mathscr{G}_{j,j+1} & \cdots & \mathscr{G}_{j,m} \\ \vdots & \vdots & \mathscr{G}_{j+1,3} & \mathscr{G}_{j+1,j-1} & \mathscr{G}_{j+1,j} & \ddots & \ddots & \vdots \\ \\ \mathscr{G}_{m-1,1} & \mathscr{G}_{m-1,2} & \mathscr{G}_{m-1,3} & \cdots & \vdots & \ddots & \mathscr{G}_{m-1} & \mathscr{G}_{m-1,m} \\ \\ \mathscr{G}_{m,1} & \mathscr{G}_{m,2} & \mathscr{G}_{m,3} & \cdots & \mathscr{G}_{m,j} & \cdots & \mathscr{G}_{m,m-1} & \mathscr{G}_{m} \end{pmatrix} \right).$$
(13)

However, if one looks at the coupling matrices Γ_L and Γ_R , it can be noted that the only terms that differ from zero are the first and last diagonal blocks for the left and right electrodes

$$\Gamma_{\rm L} = \begin{pmatrix} i \begin{bmatrix} \Sigma_{\rm L} - \Sigma_{\rm L}^{\dagger} \end{bmatrix} & 0 & 0 & 0 & 0 & \cdots & 0 \\ 0 & 0 & 0 & \cdots & \cdots & \cdots & 0 \\ 0 & 0 & \ddots & 0 & 0 & \cdots & 0 \\ \vdots & \vdots & 0 & 0 & 0 & \cdots & \vdots \\ 0 & 0 & 0 & 0 & \ddots & \ddots & 0 \\ \vdots & \vdots & \vdots & \vdots & \ddots & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 \end{pmatrix},$$
(14)

and

$$\Gamma_{R} = \begin{pmatrix} 0 & 0 & 0 & 0 & 0 & \cdots & 0 \\ 0 & 0 & 0 & \cdots & 0 & \cdots & 0 \\ 0 & 0 & \ddots & 0 & 0 & \cdots & 0 \\ \vdots & \vdots & 0 & 0 & 0 & \cdots & \vdots \\ 0 & 0 & 0 & 0 & \ddots & \ddots & 0 \\ \vdots & \vdots & \vdots & \vdots & \ddots & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & i \left[\Sigma_{R} - \Sigma_{R}^{\dagger} \right] \end{pmatrix} .$$
(15)

Consequently, with a little algebra it is possible to show that the total transmission (equation 2) can be reduced to

$$T(E) = Tr \left[\Gamma_{\rm L} \mathscr{G}_{1m} \Gamma_{\rm R} \mathscr{G}_{1m}^{\dagger} \right] \,. \tag{16}$$

In other words, of all the elements of the Green's function, the only ones that are of real interest for the electronic transport properties are the ones that effectively couple the left electrode (segment of index 1) to the right electrode (segment of index m) - the two extremes of the scattering region.

Thus, ideally, one would only need to calculate the block $\mathscr{G}_{1,m}$ of the Green's function to calculate the full electronic

transport properties of the system. The way to solve this problem is to recursively remove the degrees of freedom in the central scattering region $^{17,19-21}$. Due to the tridiagonal nature of the total Hamiltonian, we can perform a procedure known as decimation 22 which in many aspects is similar to Gaussian elimination.



Fig. S3 Schematic representation of the decimation procedure for a Hamiltonian consisting of *m* building blocks written in tridiagonal form.

A schematic representation of this procedure is shown in figure S3. One can see that after each renormalization step the

building blocks immediately to the right and to the left and the coupling are the only terms that differ while all the other elements are left unchanged. Furthermore, we perform the decimation procedure for the next step using the result of the previous one.

We start off with the original Green's function equation for the full system



The terms in blue denote segments along the diagonal and terms in red correspond to the coupling of that building block with the rest of the device. After the first decimation step (superscript index equal to 1) the terms $V_{1,2}$ and H_2 are removed resulting in the effective Hamiltonian with matrix elements

$$\bar{H}_{1}^{1} = \bar{H}_{1} - \bar{V}_{1,2} \left[\bar{H}_{2} \right]^{-1} \bar{V}_{2,1} , \qquad (18)$$

$$\bar{H}_{3}^{1} = \bar{H}_{3} - \bar{V}_{3,2} [\bar{H}_{2}]^{-1} \bar{V}_{2,3} , \qquad (19)$$

$$\bar{V}_{1,3}^1 = 0 - \bar{V}_{1,2} [\bar{H}_2]^{-1} \bar{V}_{2,3} .$$
 (20)

All the remaining terms are left unchanged. This way equation 17 is reduced to



The procedure can be repeated m-2 times until the right electrode is reached. At the (m-3)-th step the reduced Green's function has the following reduced shape

$$\begin{pmatrix} \mathfrak{A}_{1}^{(m-3)} - \Sigma_{L} & \mathfrak{f}_{1,m-1}^{(m-3)} & 0\\ \mathfrak{f}_{1,m-1}^{(m-3)} & \mathfrak{f}_{m-1}^{(m-3)} & \mathfrak{f}_{m-1,m}\\ \mathfrak{f}_{m,m-1} & \mathfrak{f}_{m-1}^{(m-3)} & \mathfrak{f}_{m-1,m}\\ 0 & \mathfrak{f}_{m,m-1} & \mathfrak{K}_{m} - \Sigma_{R} \end{pmatrix} \times \begin{pmatrix} \mathfrak{G}_{1} & \mathfrak{G}_{1,m-1} & \mathfrak{G}_{1,m}\\ \mathfrak{G}_{m-1,1} & \mathfrak{G}_{m-1} & \mathfrak{G}_{m-1,m}\\ \mathfrak{G}_{m,1} & \mathfrak{G}_{m,m-1} & \mathfrak{G}_{m} \end{pmatrix} = \begin{pmatrix} I & 0 & 0\\ 0 & I & 0\\ 0 & 0 & I \end{pmatrix},$$
(22)

and finally after the last step one reaches

$$\begin{pmatrix} H_{1,1}^{\text{eff}} - \Sigma_{L} & H_{1,m}^{\text{eff}} \\ H_{m,1}^{\text{eff}} & H_{m,m}^{\text{eff}} - \Sigma_{R} \end{pmatrix} \begin{pmatrix} \mathscr{G}_{1,1} & \mathscr{G}_{1,m} \\ \mathscr{G}_{m,1} & \mathscr{G}_{m,m} \end{pmatrix} = \begin{pmatrix} I & 0 \\ 0 & I \end{pmatrix}.$$
(23)

Thus, one has obtained a Green's function equation for the two renormalized electrodes coupled via an effective scattering potential. This effective Hamiltonian satisfies the same

1-10 | 5

Green's function equation for our initial device.[‡] Each term in this effective Hamiltonian is give by

$$H_{1,1}^{\text{eff}} = \bar{H}_1^{m-2} = \bar{H}_1 - \sum_{i=1}^{m-2} \bar{V}_{1,i+1}^{i-1} \left[\bar{H}_{i+1}^{i-1} \right]^{-1} \bar{V}_{i+1,1}^{i-1}$$
(24)

$$H_{m,m}^{\text{eff}} = \bar{H}_m^{m-2} = \bar{H}_m - \bar{V}_{m,m-1}^0 \left[\bar{H}_{m-1}^{m-3} \right]^{-1} \bar{V}_{m-1,m}^0$$
(25)

$$H_{1,m}^{\text{eff}} = \bar{V}_{1,m}^{m-2} = -\bar{V}_{1,m-1}^{m-3} \left[H_{m-1}^{m-3} \right]^{-1} \bar{V}_{m-1,m}^{0}$$
(26)

Finally, to simplify our problem we assume that the coupling between to different segments is always equal to the coupling of the pristine GNRB, in other words,

$$\bar{V}_{i,i+1} = \begin{array}{c} M' - N \\ N \end{array} \begin{bmatrix} 0 & 0 \\ \bar{V}_0 & 0 \end{bmatrix} , \qquad (27)$$

where N is the dimension of the defect-free system with coupling between principal layers equal to \bar{V}_0 , and M and M' are the dimensions of the two adjacent building blocks.

After performing this procedure we are able to calculate the transmission coefficients using equation 16 and subsequently the differential conductance g.

Our calculations were performed on nanotubes approximately 180 nm in length containing more than 50,000 atoms. As mentioned previously this is accomplished by randomly assembling segments of nanotube bundles (either with or without molecules). Each segment was obtained by a separate DFT calculation. Considering the disordered nature of the system we performed, for each concentration of molecules, no less than 50 realizations, *i. e.*, considering a fixed number of molecules adsorbed onto the tubes we randomly select the arrangement of building blocks and calculate the conductance. This procedure was then repeated at least 50 times and an average was calculated. The results are shown in figure 4 of the manuscript.

1.3 Leads self-energies

The Green's function for the entire open system is given by

$$\begin{pmatrix} \mathcal{E}\mathscr{S}_{L} - \mathscr{H}_{L} & \mathcal{E}\mathscr{S}_{L}S - \mathscr{H}_{LS} & 0\\ \mathcal{E}\mathscr{S}_{SL} - \mathscr{H}_{SL} & \mathcal{E}S_{S} - \mathcal{H}_{S} & \mathcal{E}\mathscr{S}_{S}R - \mathscr{H}_{SR}\\ 0 & \mathcal{E}\mathscr{S}_{RS} - \mathscr{H}_{RS} & \mathcal{E}\mathscr{S}_{R} - \mathscr{H}_{R} \end{pmatrix} \mathscr{G} = \mathscr{I} ,$$
(28)

with

$$\mathcal{G} = \begin{pmatrix} \mathcal{G}_{L} & \mathcal{G}_{RS} & \mathcal{G}_{LR} \\ \mathcal{G}_{LS} & G_{S} & \mathcal{G}_{SR} \\ \mathcal{G}_{RL} & \mathcal{G}_{RS} & \mathcal{G}_{R} \end{pmatrix} , \qquad (29)$$

where we have partitioned the Green's functions \mathscr{G} into the infinite blocks describing the left- and right-hand side leads \mathscr{G}_{L} and \mathscr{G}_{R} , those describing the interaction between the leads and scattering region \mathscr{G}_{LS} , \mathscr{G}_{RS} , the direct scattering between the leads \mathscr{G}_{LR} , and the finite block describing the extended molecule G_{S} . We have also introduced the matrices \mathscr{H}_{L} , \mathscr{H}_{R} , \mathscr{H}_{LS} , \mathscr{H}_{RS} and their corresponding overlap matrix blocks, indicating respectively the left- and right-hand-side leads Hamiltonian and the coupling matrix between the leads and the scattering region; H_{S} is an $N \times N$ matrix.

Here we consider that our electrodes are formed by a periodic structure described by an "on-site" Hamiltonian H_0 and a coupling H_1 between adjacent cells. The infinite matrices, \mathscr{H}_L and \mathscr{H}_R describe the leads and have the following blockdiagonal form

$$\mathscr{H}_{\rm L} = \begin{pmatrix} \ddots & \ddots & \ddots & \ddots & \vdots \\ 0 & H_{-1} & H_0 & H_1 & 0 \\ \dots & 0 & H_{-1} & H_0 & H_1 \\ \dots & \dots & 0 & H_{-1} & H_0 \end{pmatrix}, \quad (30)$$

with similar expressions for \mathcal{H}_R and the overlap \mathscr{S} matrix counterparts. In contrast the coupling matrices between the leads and the extended molecule are infinite-dimensional matrices whose elements are all zero except for a rectangular block coupling the last unit cell of the leads and the scattering region. For example we have

$$\mathscr{H}_{\mathrm{LS}} = \left(\begin{array}{c} \vdots \\ 0 \\ H_{\mathrm{LS}} \end{array}\right). \tag{31}$$

The crucial step in solving equation (28) is to write down the corresponding equation for the Green's function involving the scattering region and the last unit cell (the surface) of the left and right leads and then evaluate the retarded Green function for the scattering region G_S . This can be done by assuming that the potential drop occurs entirely across the extended molecule and there are no changes to the electronic structure of the charge reservoirs arising from neither the coupling to the molecule nor through the external bias. Bearing that in mind we can focus solely on the scattering region and treat the effect of electrodes in terms of an effective interaction.

This can be achieved by eliminating the degrees of freedom of the electrodes one by one from deep into the leads all the way to the interface with the scatterer. Effectively, one can renormalise the total Hamiltonian using a procedure that can be shown to be exact²². The final expression for G_S has the form already presented in equation 1, where the self-energies are given by

$$\Sigma_{\rm L}^{\rm R}(E) = (\varepsilon^+ S_{\rm SL} - H_{\rm SL}) g_{\rm L}^{0\rm R}(E) (\varepsilon^+ S_{\rm LS} - H_{\rm LS})$$
(32)

[‡] A similar procedure can in fact be used in a dense system. In that case, however, all coupling terms must be taken into consideration and thus there is no computational gain in this procedure and it becomes identical to a Gaussian elimination procedure.

and

$$\Sigma_{\rm R}^{\rm R}(E) = (\varepsilon^+ S_{\rm SR} - H_{\rm SR}) g_{\rm R}^{\rm 0R}(E) \left(\varepsilon^+ S_{\rm RS} - H_{\rm RS}\right).$$
(33)

Here $g_{\rm L}^{0\rm R}$ and $g_{\rm R}^{0\rm R}$ are the retarded *surface* Green function of the leads, i.e. the leads retarded Green functions evaluated at the unit cell neighbouring the extended molecule when this one is decoupled from the leads. Formally $g_{\rm L}^{0\rm R}$ ($g_{\rm R}^{0\rm R}$) corresponds to the right lower (left higher) block of the retarded Green's function for the whole left-hand side (right-hand side) semi-infinite lead. These are simply

 $\mathscr{G}_{\mathrm{L}}^{\mathrm{OR}}(E) = [\varepsilon^{+} \mathscr{S}_{\mathrm{L}} - \mathscr{H}_{\mathrm{L}}]^{-1}$

and

 $\mathscr{G}_{\mathbf{R}}^{0\mathbf{R}}(E) = [\varepsilon^{+}\mathscr{S}_{\mathbf{R}} - \mathscr{H}_{\mathbf{R}}]^{-1}.$ Note that \mathscr{G}_L^{0R} (\mathscr{G}_R^{0R}) is not the same as \mathscr{G}_L^R (\mathscr{G}_R^R) defined in equation (29). In fact the former are the Green functions for the semi-infinite leads in isolation, while the latter are the same quantities for the leads attached to the scattering region. Importantly one does not need to solve equations (34) and (35) for calculating the leads surface Green functions and a closed form avoiding the inversion of infinite matrices can be provided²². From equations (32) and (33) it is clear that the problem is reduced to that of computing the retarded surface Green functions for the left- $(g_{\rm L}^{0\rm R})$ and right-hand side $(g_{\rm R}^{0\rm R})$ lead respectively. This does not require any self-consistent procedure since the Hamiltonian is known and it is equal to that of the bulk leads plus a rigid shift of the on-site energies. However the calculation should be repeated several times since the Σ 's are energy dependent. Therefore it is crucial to have a stable algorithm.

There are a number of techniques in the literature to calculate the surface Green functions of a semi-infinite system. These range from recursive methods^{8?} to semi-analytical constructions²². The latter method gives us a prescription for calculating the retarded surface Green function exactly considering only the knowledge of the Hamiltonian (and overlap matrix) of an infinite periodic system and by considerign appropriate boundary conditions for the Green's function.

The main idea is to construct the Green function for an infinite system as a summation of Bloch states with both real and imaginary wave-vectors, and then to apply the appropriate boundary conditions to obtain the Green function for a semiinfinite lead.

As shown in equation 30 the Hamiltonian and the overlap matrices are arranged in a tridiagonal block form, having respectively H_0 and S_0 on the diagonal, and H_1 and S_1 as the first off-diagonal blocks (see figure S4)). Since we are dealing with an infinite periodic quasi-one-dimensional system, the Schrödinger equation can be solved for Bloch states

$$\psi_z = n_k^{1/2} e^{ikz} \phi_k \tag{36}$$



Fig. S4 Infinite periodic system used as current/voltage probe and schematic diagram of the Hamiltonian. H_0 and S_0 are the matrices describing the Hamiltonian and the overlap within a unit cell, while H_1 and S_1 are the same quantities calculated between two adjacent unit cells. The arrow indicates the direction of transport (here along the z axis).

and reads

(34)

(35)

$$\left[K_0 + K_1 e^{ik} + K_{-1} e^{-ik}\right]\phi_k = 0 , \qquad (37)$$

where $z = a_0 j$ with j integer and a_0 the separation between principal layers, k is the wave-vector along the direction of transport (in units of π/a_0), ϕ_k is a N-dimensional column vector and n_k a normalisation factor. Here we introduce the $N \times N$ matrices

$$K_0 = H_0 - ES_0 \,, \tag{38}$$

$$K_1 = H_1 - ES_1 \,, \tag{39}$$

$$K_{-1} = H_{-1} - ES_{-1} \,. \tag{40}$$

Since the Green's functions are constructed at a given energy our task is to compute k(E) (both real and complex) instead of E(k) as conventionally done in band theory. A numerically efficient method to solve the "inverse" secular equation k = k(E) is to map it onto an equivalent eigenvalue problem. It is simple to demonstrate²² that the eigenvalues of the following $2N \times 2N$ non-Hermitian matrix

$$M = \begin{pmatrix} -K_1^{-1}K_0 & -K_1^{-1}K_{-1} \\ I_N & 0 \end{pmatrix}$$
(41)

for a given energy E are $e^{ik(E)}$ and that the upper N components of the eigenvectors are the vectors ϕ_k .

Finally, the knowledge of k and $\{\phi_k\}$ is sufficient to construct the retarded Green function for the doubly-infinite system, which has the form²²

$$G_{zz'} = \begin{cases} \sum_{l}^{N} \phi_{k_{l}} e^{ik_{l}(z-z')} \tilde{\phi}_{k_{l}}^{\dagger} V^{-1} & z \ge z' \\ \sum_{l}^{N} \phi_{\bar{k}_{l}} e^{i\bar{k}_{l}(z-z')} \tilde{\phi}_{\bar{k}_{l}}^{\dagger} V^{-1} & z \le z' \end{cases}, \quad (42)$$

where the summation runs over both real and imaginary k_l . In equation (42) k_l (\bar{k}_l) are chosen to be the right-moving or right-decaying (left-moving or left-decaying) Bloch states, i.e. those with either positive group velocity or having k-vector with positive imaginary part (negative group velocity or negative imaginary part). $\{\phi_{k_l}\}$ are the corresponding vectors, and V is defined in reference²². Finally $\{\tilde{\phi}_{k_l}\}$ is just the dual of $\{\phi_{k_l}\}$ obtained from

$$\tilde{\phi}_{k,}^{\dagger}\phi_{k_{m}} = \delta_{lm} \tag{43}$$

$$\tilde{\phi}_{\bar{k}_l}^{\dagger}\phi_{\bar{k}_m} = \delta_{lm} \tag{44}$$

(45)

In the case of a non-orthogonal basis set the same expression is still valid if V is now defined as follows

$$V = \sum_{l}^{N} \left(H_{1}^{\dagger} - ES_{1}^{\dagger} \right) \left[\phi_{k_{l}} e^{-ik_{l}} \phi_{k_{l}}^{\dagger} - \phi_{\bar{k}_{l}} e^{-i\bar{k}_{l}} \phi_{\bar{k}_{l}}^{\dagger} \right].$$
(46)

Finally the surface Green functions for a semi-infinite system can be obtained from those of the doubly-infinite one by an appropriate choice of boundary conditions. For instance if we subtract the term

$$\Delta_{z}\left(z'-z_{0}\right) = \sum_{l,h}^{N} \phi_{\bar{k}_{h}} e^{i\bar{k}_{h}(z-z_{0})} \phi_{\bar{k}_{h}}^{\dagger} \phi_{k_{l}} e^{ik_{l}\left(z_{0}-z'\right)} \phi_{k_{l}}^{\dagger} V^{-1} , \quad (47)$$

from $G_{zz'}$ of equation (42) we obtain a new retarded Green function vanishing at $z = z_0$. Note that $\Delta_z (z' - z_0)$ is a linear combination of eigenvectors (wavefunctions) and therefore does not alter the causality of G.

In this way we obtain the final expression for the retarded surface Green functions of both the left- and right-hand side lead

$$g_{\rm L}^{0} = \left[I_{\rm N} - \sum_{l,h} \phi_{\bar{k}_{h}} e^{-i\bar{k}_{h}} \phi_{\bar{k}_{h}}^{\dagger} \phi_{k_{l}} e^{ik_{l}} \phi_{k_{l}}^{\dagger} \right] V^{-1}, \quad (48)$$

$$g_{\rm R}^{0} = \left[I_{\rm N} - \sum_{l,h} \phi_{k_h} e^{ik_h} \phi_{k_h}^{\dagger} \phi_{\bar{k}_l} e^{-i\bar{k}_l} \phi_{\bar{k}_l}^{\dagger} \right] V^{-1}.$$
(49)

Once these operators have been calculated it is easy to obtain the self-energies from equations 32 and 33. These need to be computed at the beginning of the calculation only for a given energy mesh.

1.4 Molecular Dynamics and transport in CNT bundles: single molecule case

We performed a Quantum Molecular Dynamics (QMD) simulation implemented in SIESTA code using the NVT canonical ensable with Nose-Hoover thermostat^{23,24}. One thousand steps were considered to reach thermal equilibrium and after ten thousands steps of molecular dynamics were performed (5 ps with 0.5 fs time step). The temperature used this simulation was 300 K. The main question addressed here is how the temperature can affect the postion of the molecule, and futhermore, whether these variations in position can alter the transport properties. Firstly we observed that, in both cases, the molecules flow freely along the tube, but not along of the transverse direction.

Figure S5 shows four different snapshots of our molecular dynamics simulation. As one can see, the molecule freely rotates inside the channel formed between the nanotubes in the bundle. From each of these configurations we performed NEGF+DFT calculations^{8–11} to determine the electronic transport properties. The results are presented in figure S5(a-d) for carbon monoxide and figure S5(e-h) for ammonia.

From the graphs it is possible conclude that, although there are significant changes in molecular orientation the transmittance, in all cases shown, are not altered. In essence, this justifies the assumptions made in the main text where we use only one configuration for our calculations of the disordered system.

References

- 1 P. Hohenberg and W. Kohn, Phys. Rev, 1964, 136, B864.
- 2 W. Kohn and L. J. Sham, Phys. Rev., 1965, 140, A1133.
- 3 E. Artacho, D. Sánchez-Portal, P. Ordejón, A. García and J. M. Soler, *Phys. Stat. Sol. (b)*, 1999, **215**, 809.
- 4 O. A. von Lilienfeld, I. Tavernelli, U. Rothlisberger and D. Sebastiani, *Phys. Rev. Lett.*, 2004, **93**, 153004.
- 5 M. P. Lima, A. Fazzio and A. J. R. da Silva, *Phys. Rev. B*, 2009, **79**, 153401.
- 6 J. P. Perdew, K. Burke and M. Ernzerhof, *Phys. Rev. Lett.*, 1996, 77, 3865– 3868.
- 7 N. Troullier and J. L. Martins, Phys. Rev. B, 1991, 43, 1993-2006.
- 8 S. Datta, *Electronic Transport in Mesoscopic Systems*, Cambridge University Press, Cambridge, 1st edn, 1995, pp. 57–67 e 86–88.
- 9 M. Brandbyge, J.-L. Mozos, P. Ordejn, J. Taylor and K. Stokbro, *Phys. Rev. B*, 2002, **65**, 165401.
- 10 A. R. Rocha, V. M. García-Suárez, S. Bailey, C. Lambert, J. Ferrer and S. Sanvito, *Phys. Rev. B*, 2006, **73**, 085414.
- 11 F. D. Novais, A. J. R. da Silva and A. Fazzio, *Brazilian Journal of Physics*, 2006, 36, 799.
- 12 C. Caroli, R. Combescot, P. Nozieres and D. Saint-James, J. Phys. C, 1971, 4, 916.
- 13 A. R. Rocha, V. M. García-Suárez, S. W. Bailey, C. J. Lambert, J. Ferrer and S. Sanvito, *Nature Materials*, 2005, 4, 335.
- 14 T. B. Martins, R. H. Miwa, A. J. R. da Silva and A. Fazzio, *Physical Review Letters*, 2007, 98, 196803.
- 15 C. Gómez-Navarro, P. J. de Pablo, J. Gómez-Herrero, B. Biel, F. J. Garcia-Vidal, A. Rubio and F. Flores, *Nature Mat.*, 2005, 4, 534.
- 16 R. Avriller, S. Roche, F. Triozon, X. Blase and S. Latil, Modern Physics Letters B, 2007, 21, 1955.
- 17 T. Markussen, R. Rurali, M. Brandbyge and A.-P. Jauho, *Phys. Rev. B*, 2006, **74**, 245313.
- 18 C. G. Rocha, A. Wall, A. R. Rocha and M. S. Ferreira, J. Phys. C: Cond. Matt., 2007, 19, 346201.
- 19 A. R. Rocha, M. Rossi, A. J. R. da Silva and A. Fazzio, *Phys. Rev. Lett.*, 2008, **100**, 176803.



Fig. S5 Transmittance in fuction of the energy for four QMD configurations in both molecular gas cases. The QMD snapshot was showed in detail for each gas where we can see the gas evolution in time. For a to d we show the transmittance of CO gas and from e to h we show the NH_3 .

- 20 A. R. Rocha, M. Rossi, A. , Fazzio and A. J. R. da Silva, *J. Phys. D*, 2010, **43**, 374002.
- 21 T. Markussen, R. Rurali, A.-P. Jauho and M. Brandbyge, *Physical Review Letters*, 2007, **99**, 076803.
- 22 S. Sanvito, C. J. Lambert, J. H. Jefferson and A. M. Bratkovsky, Phys.

Rev. B, 1999, 59, 11936.

- 23 S. Nose, J.Chem.Phys., 1984, **81**, 511.
- 24 W. Hoover, Phys. Rev. A, 1985, 31, 1695.