Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Supporting Information for: Ab initio modelling of spin relaxation lengths in disordered graphene nanoribbons

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The problem of a disordered system

The treatment applied to a disordered system is similar to that of a single defect.[1,2] Indeed, we could use the same equations to obtain the electronic transport properties of any 1-D device if one knows its Hamiltonian H_S. In other words, we define the Green's function for the scattering region as

$$G_S^R(E,L) = \left[E \times S_S - H_S(L) - \Sigma_L(E) - \Sigma_R(E)\right]^{-1}, \tag{1}$$

from there, the transmission probability can be calculated using the Landauer-Büttiker formula

$$T(E) = Tr[\Gamma_L G_S^{R\dagger} \Gamma_R G_S^R] \ , \tag{2}$$

however, a disordered problem requires the inversion of a Hamiltonian with hundreds of thousands of degrees of freedom. In particular, if we are dealing with a localized basis within the density functional theory, the number of orbitals per site quickly renders the problem intractable.

An alternative treatment assumes that the large 1-D device—the disordered system—is constructed of a number of different building blocks, as schematically shown in Figure S1. These two sets of building blocks are represented by different box sizes and colors (green and red), where the on-site Hamiltonians H_i correspond to the i-th block and the terms $V_{i,j}$ correspond to the coupling between the two adjacent blocks (we assume that each layer only couples to the adjacent ones). In our particular case, these blocks are a set of single defect scattering regions (Fig. S1) and pristine units. Furthermore, the scattering region H_S is attached to two electrodes represented by the left (right) self energies Σ_L and Σ_R.

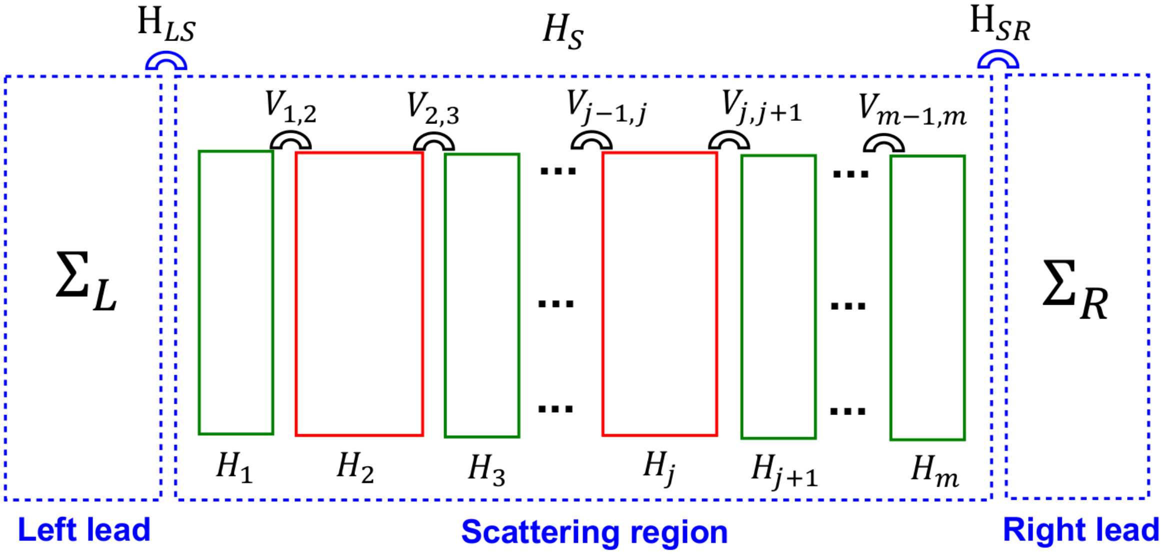

Figure S1: Schematic representation of a problem of multiple defects transport at nano-scale. The device was built on two different set of blocks (red and green) and each block is described by H_i and by the coupling V_{ij}.

In order to visualize the procedure we write down the full Hamiltonian for the central region

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

We notice that H_S is clearly block-diagonal. It is important to point out that, whenever a localized basis set is used, this structure can always be obtained by appropriately reordering the orbitals.

The complete Green's function equation for our disordered system is given by

$$\begin{pmatrix} \bar{H}_1 - \Sigma_L & \bar{V}_{1,2} & 0 & \cdots & 0 & \cdots & 0 & 0 \\ \bar{V}_{2,1} & \bar{H}_2 & \bar{V}_{2,3} & \cdots & 0 & \cdots & 0 & 0 \\ 0 & \bar{V}_{3,2} & \bar{H}_3 & \ddots & \vdots & 0 & \cdots & 0 \\ \vdots & \vdots & \ddots & \ddots & \bar{V}_{j-1,j} & 0 & \vdots & \vdots \\ 0 & 0 & \cdots & \bar{V}_{j,j-1} & \bar{H}_j & \bar{V}_{j,j+1} & \cdots & 0 \\ \vdots & \vdots & 0 & 0 & \bar{V}_{j+1,j} & \ddots & \ddots & \vdots \\ 0 & 0 & 0 & \cdots & \vdots & \ddots & \bar{H}_{m-1} & \bar{V}_{m-1,m} \\ 0 & 0 & 0 & \cdots & 0 & \cdots & \bar{V}_{m,m-1} & \bar{H}_m - \Sigma_R \end{pmatrix} \times$$

$$
\begin{pmatrix}
G_1 & G_{1,2} & G_{1,3} & \cdots & G_{1,j} & \cdots & G_{1,m-1} & G_{1,m} \\
G_{2,1} & G_2 & G_{2,3} & \cdots & G_{2,j} & \cdots & G_{2,m-1} & G_{2,m} \\
G_{3,1} & G_{3,2} & G_3 & \ddots & \vdots & G_{3,j} & \cdots & G_{3,m} \\
\vdots & \vdots & \ddots & \ddots & G_{j-1,j} & G_{j-1,j+1} & \vdots & \vdots \\
G_{j,1} & G_{j,2} & \cdots & G_{j,j-1} & G_j & G_{j,j+1} & \cdots & G_{j,m} \\
\vdots & \vdots & G_{j+1,3} & G_{j+1,j-1} & G_{j+1,j} & \ddots & \ddots & \vdots \\
G_{m-1,1} & G_{m-1,2} & G_{m-1,3} & \cdots & \vdots & \ddots & G_{m-1} & G_{m-1,m} \\
G_{m,1} & G_{m,2} & G_{m,3} & \cdots & G_{m,j} & \cdots & G_{m,m-1} & G_m
\end{pmatrix}
$$

$$
= \begin{pmatrix}
I & 0 & 0 & \cdots & 0 & \cdots & 0 & 0 \\
0 & I & 0 & \cdots & 0 & \cdots & 0 & 0 \\
0 & 0 & I & \ddots & \vdots & 0 & \cdots & 0 \\
\vdots & \vdots & \ddots & \ddots & 0 & 0 & \vdots & \vdots \\
0 & 0 & \cdots & 0 & I & 0 & \cdots & 0 \\
\vdots & \vdots & 0 & 0 & 0 & \ddots & \ddots & \vdots \\
0 & 0 & 0 & \cdots & \vdots & \ddots & I & 0 \\
0 & 0 & 0 & \cdots & 0 & \cdots & 0 & I
\end{pmatrix}, \tag{4}
$$

where $\bar{H}_i = [ES_i - H_i]$ and $\bar{V}_{i,j} = [ES_{i,j} - H_{i,j}]$.

Given the one-dimensional strucutre of the system, the self-energies, and consequently the matrices $\Gamma_{L/R}$, only couple to the leftmost or rightmost blocks, *i.e.*

$$\Gamma_L = \begin{pmatrix} \Gamma_L & 0 & 0 & \cdots & 0 & \cdots & 0 & 0 \\ 0 & 0 & 0 & \cdots & 0 & \cdots & 0 & 0 \\ 0 & 0 & 0 & \ddots & \vdots & 0 & \cdots & 0 \\ \vdots & \vdots & \ddots & \ddots & 0 & 0 & \vdots & \vdots \\ 0 & 0 & \cdots & 0 & 0 & 0 & \cdots & 0 \\ \vdots & \vdots & 0 & 0 & 0 & \ddots & \ddots & \vdots \\ 0 & 0 & 0 & \cdots & \vdots & \ddots & 0 & 0 \\ 0 & 0 & 0 & \cdots & 0 & \cdots & 0 & 0 \end{pmatrix}, \tag{5}$$

and

$$\Gamma_R = \begin{pmatrix} 0 & 0 & 0 & \cdots & 0 & \cdots & 0 & 0 \\ 0 & 0 & 0 & \cdots & 0 & \cdots & 0 & 0 \\ 0 & 0 & 0 & \ddots & \vdots & 0 & \cdots & 0 \\ \vdots & \vdots & \ddots & \ddots & 0 & 0 & \vdots & \vdots \\ 0 & 0 & \cdots & 0 & 0 & 0 & \cdots & 0 \\ \vdots & \vdots & 0 & 0 & 0 & \ddots & \ddots & \vdots \\ 0 & 0 & 0 & \cdots & \vdots & \ddots & 0 & 0 \\ 0 & 0 & 0 & \cdots & 0 & \cdots & 0 & \Gamma_R \end{pmatrix}. \tag{6}$$

Here $\Gamma_{L/R}(E) = i[\Sigma_{L/R}(E) - \Sigma_{L/R}(E)^\dagger]$ are the coupling matrices that represent the rates at which electrons are scattered into (or out of) the ribbon. Moreover, one can notice that the blocks of interest to calculate transport properties are those that effectively couple both electrodes. Thus, in terms of Green's function we only need to calculate the element $G_{1,m}$ for a complete description of transport properties. Hence, the transmission coefficient for a disordered system is given by

$$T(E) = Tr[\Gamma_L G_{1,m}^\dagger \Gamma_R G_{1,m}]. \tag{7}$$

While the Hamiltonian is clearly block-tridiagonal, the Green's function is, in general a dense matrix. Nonetheless, since we are dealing with a large number of blocks randomly distributed and due to the tridiagonal nature of H_S, we could apply the so-called decimation[3] technique- which is a particular case of a Gaussian elimination procedure. In that sense, this is an exact procedure whose efficiency arises from the structure of the Hamiltonian, and the fact that only a block of the Green's function is required.

Thus, the decimation procedure comprises a Gaussian elimination starting from the second line (block) all the way to the $(m-1)-th$ line recursively. We notice this by writing the Green's functions equations for each of the blocks G_{im},

$$\begin{aligned} \left[\bar{H}_1 - \Sigma_L\right] G_{1,m} + \bar{V}_{1,2} G_{2,m} &= 0 \quad \mathrm{i} = 1 & (8) \\ \bar{V}_{m,m-1} G_{m-1,m} + \left[\bar{H}_m - \Sigma_R\right] G_{m,m} &= I \quad i = m & (9) \\ \bar{V}_{i,i-1} G_{i-1,m} + \bar{H}_i G_{i,m} + \bar{V}_{i,i+1} G_{i+1,m} &= 0 \quad 1 < i < m. & (10) \end{aligned}$$

For the case $i = 2$ equation can be recast to isolate G_{2m},

$$G_{2,m} = -\bar{H}_2^{-1}\left[\bar{V}_{2,1} G_{1,m} + \bar{V}_{2,3} G_{3,m}\right] \tag{11}$$

and substituted in equations 8 and 9 for (i=3),

$$\begin{aligned} \left[\bar{H}_1 - \bar{V}_{1,2}\bar{H}_2^{-1}\bar{V}_{2,1} - \Sigma_L\right] G_{1m} - \bar{V}_{1,2}\bar{H}_2^{-1}\bar{V}_{2,3} G_{3,m} &= 0 & (12) \\ -\bar{V}_{2,3}\bar{H}_2^{-1}\bar{V}_{21} G_1 m + \left[\bar{H}_3 - \bar{V}_{3,2}\bar{H}_2^{-1}\bar{V}_{2,3}\right] G_{3m} - \bar{V}_{3,4} G_{4,m} &= 0. & (13) \end{aligned}$$

If we redefine the couplings and the Hamiltonians,

$$\begin{aligned} \left[\bar{H}_1^1\right] &\equiv \bar{H}_1 - \bar{V}_{12}\bar{H}_2^{-1}\bar{V}_{2,1} & (14) \\ \left[\bar{V}_{1,3}^1\right] &\equiv -\bar{V}_{1,2}\bar{H}_2^{-1}\bar{V}_{2,3} & (15) \\ \left[\bar{H}_3^1\right] &\equiv \bar{H}_3 - \bar{V}_{3,2}\bar{H}_2^{-1}\bar{V}_{2,3}, & (16) \end{aligned}$$

one obtains a new set of equivalent Green's functions equations. After applying the procedure $(m-2)$ times recursively, the reduced Green's function becomes

$$\begin{pmatrix} H_{1,1}^{eff} - \Sigma_L & H_{1,m}^{eff} \\ H_{m,1}^{eff} & H_{m,m}^{eff} - \Sigma_R \end{pmatrix} \begin{pmatrix} G_{1,1} & G_{1,m} \\ G_{m,1} & G_{m,m} \end{pmatrix} = \begin{pmatrix} I & 0 \\ 0 & I \end{pmatrix}, \tag{17}$$

where

$$\begin{aligned} H_{1,1}^{eff} &= \bar{H}_1^{m-2} = \bar{H}_1 - \textstyle\sum_{i=1}^{m-2} \bar{V}_{1,i+1}^{i-1} \left[\bar{H}_{i+1}^{i-1}\right]^{-1} \bar{V}_{i+1,1}^{i-1}, \\ H_{m,m}^{eff} &= \bar{H}_m^{m-2} = \bar{H}_m - \bar{V}_{m,m-1}^{0} \left[\bar{H}_{m-1}^{m-3}\right]^{-1} \bar{V}_{m-1,m}^{0}, \\ H_{1,m}^{eff} &= \bar{V}_{1,m}^{m-2} = -\bar{V}_{1,m-1}^{m-3} \left[H_{m-1}^{m-3}\right]^{-1} \bar{V}_{m-1,m}^{0}, \end{aligned} \tag{18}$$

Although, for a non-collinear spin system, a similar expansion of matrices in the spin space has been done, here, we do not include such equations as they are analogous.

Equivalence between Green's function elements obtained by decimation and full Hamiltonian: the case of a 3x3 matrix

Decimation Green's function

Consider the block-tridiagonal, one-orbital-per-site Hamiltonian,

$$H_{\mathrm{S}} = \begin{pmatrix} H_1 & V_{1,2} & 0 \\ V_{2,1} & H_2 & V_{2,3} \\ 0 & V_{3,2} & H_3 \end{pmatrix}, \tag{19}$$

described in an orthogonal basis set, $S_{i,j} = \delta_{i,j}$.

The corresponding Green's function is given by:

$$G = (\varepsilon I - H_s - \Sigma_L - \Sigma_R)^{-1}\,. \tag{20}$$

Explicitly the full Green's function corresponding to the 3x3 Hamiltonian H_s, is given by

$$G = \begin{pmatrix} \varepsilon - H_1 - \Sigma_L & -V_{1,2} & 0 \\ -V_{2,1} & \varepsilon - H_2 & -V_{2,3} \\ 0 & -V_{3,2} & \varepsilon - H_3 - \Sigma_R \end{pmatrix}^{-1} . \tag{21}$$

We first adopt the decimation procedure to reduce the 3x3 problem into an equivalent 2x2 one using the procedure described in section 1. To this purpose we write down the explicit Green's function equation,

$$\begin{pmatrix} \varepsilon - H_1 - \Sigma_L & -V_{1,2} & 0 \\ -V_{2,1} & \varepsilon - H_2 & -V_{2,3} \\ 0 & -V_{3,2} & \varepsilon - H_3 - \Sigma_R \end{pmatrix} \begin{pmatrix} g_1 & g_{1,2} & g_{1,3} \\ g_{2,1} & g_2 & g_{2,3} \\ g_{3,1} & g_{3,2} & g_3 \end{pmatrix} = I \tag{22}$$

Using equations (12) and (13), the decimation procedure for this simple case yields a 2x2 equivalent Green's function problem,

$$\begin{pmatrix} \varepsilon - H_1 + \frac{V_{1,2}V_{2,1}}{H_2-\varepsilon} - \Sigma_L & -\frac{V_{1,2}V_{2,3}}{H_2-\varepsilon} \\ -\frac{V_{2,1}V_{3,2}}{H_2-\varepsilon} & \varepsilon - H_3 + \frac{V_{3,2}V_{2,3}}{H_2-\varepsilon} - \Sigma_R \end{pmatrix} \begin{pmatrix} g_1 & g_{1,3} \\ g_{3,1} & g_3 \end{pmatrix} = \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}, \tag{23}$$

and the associated Green's function of the reduced Hamiltonian is given by:

$$\tilde{G}(\varepsilon) = \frac{1}{\Delta} \begin{pmatrix} (\varepsilon - H_3 - \Sigma_R)(\varepsilon - H_2) - V_{3,2}V_{2,3} & V_{1,2}V_{2,3} \\ V_{2,1}V_{3,2} & (\varepsilon - H_1 - \Sigma_L)(\varepsilon - H_2) - V_{1,2}V_{2,1} \end{pmatrix} . \tag{24}$$

where

$$\Delta = (\varepsilon - \Sigma_R - H_3)\,(\varepsilon - H_2)(\varepsilon - \Sigma_L - H_1) \tag{25}$$

$$- V_{2,3}V_{3,2}(\epsilon - \Sigma_L - H_1) - V_{1,2}V_{2,1}\,(\varepsilon - \Sigma_R - H_3) \tag{26}$$

Full Hamiltonian Green's function

After explicitly computing the full matrix inversion one obtains

$$\mathrm{G}(\varepsilon) = \tfrac{1}{\Delta}\begin{pmatrix} (\varepsilon - H_3 - \Sigma_R)(\varepsilon - H_2) - V_{3,2}V_{2,3} & -V_{1,2}(\varepsilon - H_3 - \Sigma_R) & V_{2,1}V_{3,2} \\ -V_{2,1}(\varepsilon - H_3 - \Sigma_R) & (\varepsilon - H_1 - \Sigma_L)(\varepsilon - H_3 - \Sigma_R) & -(\varepsilon - H_1 - \Sigma_L)V_{2,3} \\ V_{1,2}V_{3,2} & -V_{3,2}(\varepsilon - H_1 - \Sigma_L) & (\varepsilon - H_1 - \Sigma_L)(\varepsilon - H_2) - V_{1,2}V_{2,1} \end{pmatrix}^{-1} \tag{27}$$

By comparing equation (25) and equation (27) one can clearly see that the matrix elements $\tilde{G}(\varepsilon)_{1,2} = G(\varepsilon)_{1,3}$. This clearly indicates that the reduction of a full Hamiltonian by decimation method, is an exact procedure that only take advantage of the block-tridiagonal nature of operators.

Concentration in a disordered system

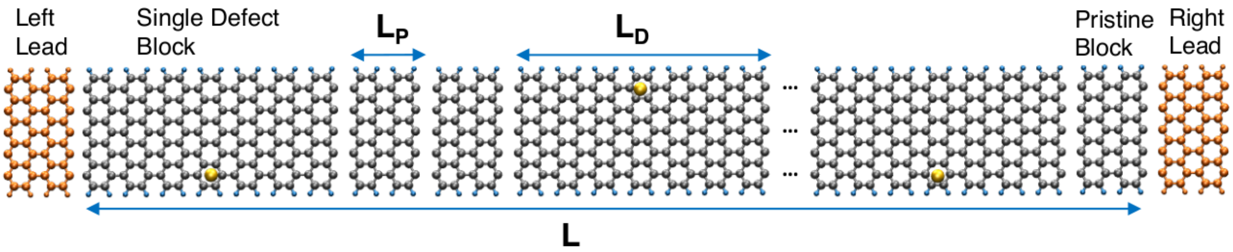

Figure S2: Schematic representation of a disordered system. Here, single defect blocks are randomly separated by pristine blocks. L is the length of the device, L_D is the length of the single defect block and L_P is the length of the pristine block.

The equation employed to compute the concentration of Ni adatoms in a disordered system is given by

$$[Ni] = \frac{N_D.A_{Ni}}{N_D.(A_C.n_C^D + A_H.n_H^D) + (N_T - N_D)(A_C.n_C^P + A_H.n_H^P)}, \tag{28}$$

where N_D: total number of defects,

N_T: total number of blocks,

n_C^D: number of carbon atoms in the defect block,

n_H^D: number of hydrogen atoms in the defect block,

n_C^P: number of carbon atoms in the pristine block (electrode block),

n_H^P: number of hydrogen atoms in the pristine block, and

A_E: atomic mass of atom E (E: C, H, Ni).

A typical assembly of a disordered system studied in this work is shown in Figure S2. The number of atoms treated with this approach range from 5855 to 93680. The length of the device is calculated with

$$L = N_D.L_D + (N_T - N_D)(L_P), \tag{29}$$

where L_D and L_P are the lengths for, both the single defect and pristine blocks, respectively.

Convergence of conductance with respect to the number of realizations

Conductance results shown in the manuscript have been averaged up to 100 individual conductance files, i.e, 100 realizations. Therefore, we guarantee that conductance converge to specific value.

Figure S3 clearly shows the typical convergence of polarization as a function of the number of realizations for energy E_2.

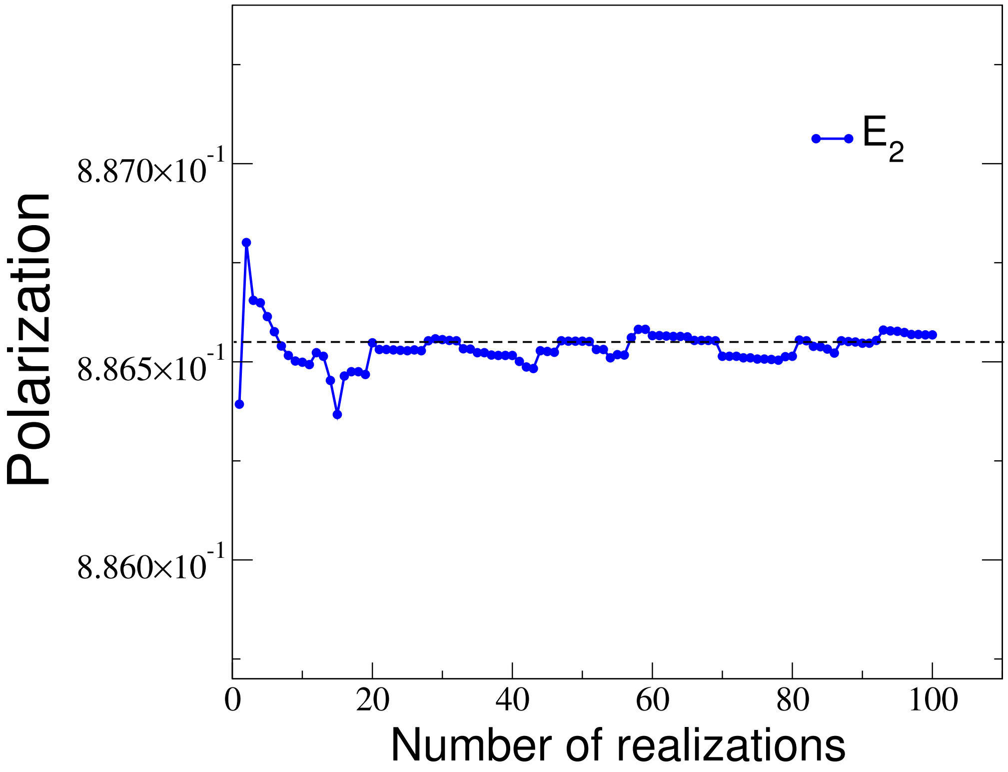

Figure S3: Typical polarization convergence as a function of the number of realizations for E_2. The dashed line is a guide for the eyes.

References

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