# Solitonics with polyacetylenes - Supporting Information

Daniel Hernangómez-Pérez,[1,*] Suman Gunasekaran,[2] Latha Venkataraman,[2,3] and Ferdinand Evers[1,†]
[1]*Institute of Theoretical Physics, University of Regensburg, 93040 Regensburg, Germany*
[2]*Department of Chemistry, Columbia University, New York, New York 10027, United States*
[3]*Department of Applied Physics, Columbia University, New York, New York 10027, United States*

## I. METHODS

For our *ab-initio* calculations we use the FHI-aims package[1], which implements the Kohn-Sham formulation of density functional theory using an all-electron localized basis set. As exchange-correlation functional, we employ the hybrid functional B3LYP[2] and include scalar relativistic corrections to the kinetic energy of all atoms at the zeroth-order regular approximation (ZORA) level. We use the optimized basis set "light" (roughly equivalent to "double zeta" quality). The ground-state is obtained using rather strict convergence criteria in the self-consistency field (SCF) cycle for the difference in the particle density ($10^{-5}$), sum of the Kohn-Sham eigenvalues ($10^{-4}$ eV), total energy ($10^{-8}$ eV) and energy gradients ($10^{-5}$ eV/Å) between successive SCF iterations. For comparison, standard settings are $10^{-4}$ for the particle density, $10^{-3}$ eV for the sum of the Kohn-Sham eigenvalues, $10^{-6}$ eV for the total energy and $10^{-4}$ eV/Å for the energy gradients between successive SCF iterations. The geometry optimizations are performed using the enhanced Broyden-Fletcher-Shanno-Goldfarb optimization algorithm. Molecular structures are considered to be relaxed only if the value of the components of the residual forces per atom drop below the threshold value of $10^{-3}$ eV/Å.

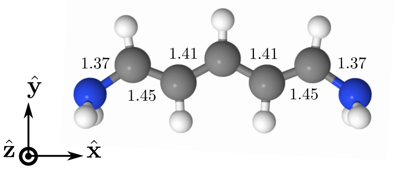

FIG. 1. Geometry of the neutral wire with $L = 7$ "sites", corresponding to five carbon and two nitrogen atoms; bond lengths (in Å) are given as obtained from a DFT-based geometry optimization (with B3LYP functional). Weak bond-length alternation (BLA) is discernible, switching sign at the center atom; for longer wires it gradually evolves into a domain wall, *i.e.*, the soliton. Nomenclature: coordinate system with the molecular backbone located in the $x{-}y$ plane.

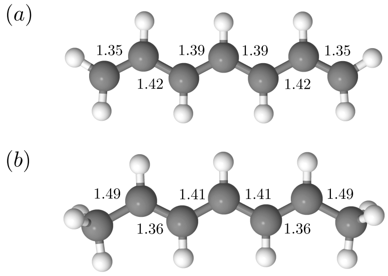

FIG. 2. Geometry of neutral wires with $L = 7$ "sites" with (a) symmetric $CH_2$-$CH_2$ terminal groups (b) symmetric $CH_3$-$CH_3$ terminal groups. Bond lengths (in Å) are given as obtained from a DFT-based geometry optimization (with B3LYP functional). Weaker BLA is obtained in both mirror-symmetric chains, switching sign at the center atom; only if mirror-symmetry would be broken strong BLA would manifest in the wire center enforced by the single bond of *i.e.* a terminal methyl group.

## II. BOND-LENGTH ALTERNATION IN POLYACETYLENE-BASED MOLECULES

The domain-wall state will gradually evolve with increasing length of the molecule and is fully developed only at $N \gtrsim N_c$. In the example, Fig. 1 , a very short wire with $L = 7$ sites is shown to illustrate the mirror symmetry together with an early stage of BLA. For comparison, we also show analogue mirror-symmetric wires, *i.e.* $CH_2$ and $CH_3$ terminal groups, in Fig. 2 presenting nascent domain walls located at the center of the wire. In the long wire limit, this proto domain-wall evolves into the full topological domain-wall state independently of the end groups choosen for the wire, see Fig. 4. We observe that, for the case of $CH_2$ terminal end groups, the domain-wall state interpolates in the opposite way between the two BLA phases as compared to $NH_2$ and $CH_3$ terminal groups. In other words, odd $CH_2$-$CH_2$ wires host an antisoliton as compared to $NH_2$-$NH_2$ and $CH_3$-$CH_3$ wires. At the Kohn-Sham level, this difference manifests in the fact that the topological domain-wall associated to the anti-soliton populates the opposite sublattice, see Fig. 3.

## III. "READ OUT" VIA POLARIZATION MEASUREMENT

### A. Phenomenology of induced polarization

A physical observable that allows for experimental monitoring of the domain-wall position is the induced polarization $\delta\mathbf{p}(V) = e\int d\mathbf{r}\,\delta\rho(\mathbf{r},V)\mathbf{r}$, where $\delta\rho(\mathbf{r},V)$ denotes the change in the charge density induced by applying the electric field

---

[*] e-mail:daniel.hernangomez@ur.de
[†] e-mail:ferdinand.evers.de

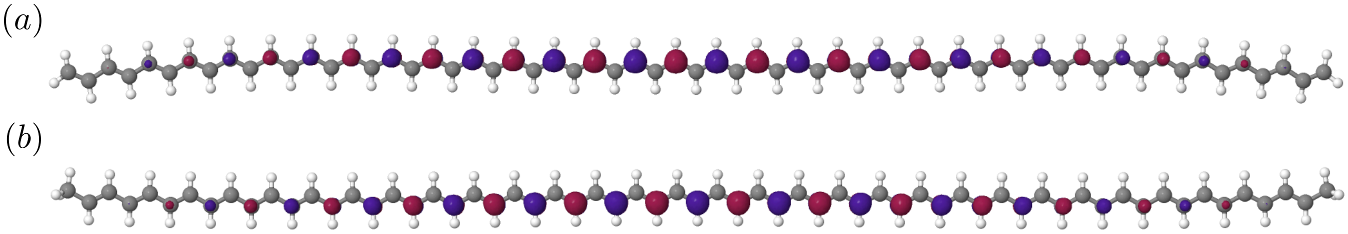

FIG. 3. Kohn-Sham orbital that forms the topological domain-wall along wires with $L = 63$ "sites" and terminal end groups (a) $CH_2$ (b) $CH_3$.

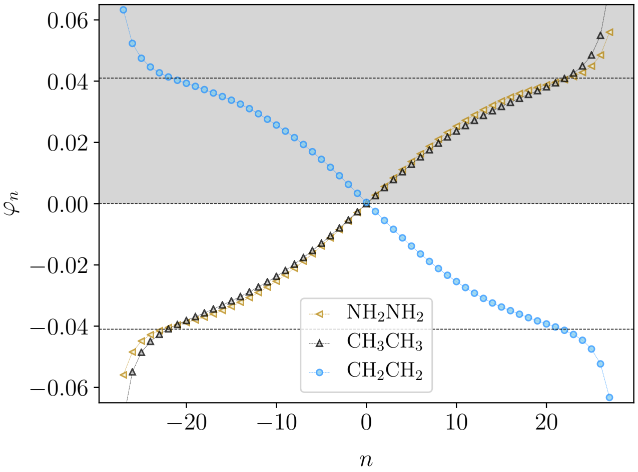

FIG. 4. Order parameter plotted along different wires with $L = 113$ "sites" and three different terminal end groups ($NH_2$-$NH_2$, dark yellow; $CH_2$-$CH_2$ light blue dots and $CH_3$-$CH_3$, black triangles).

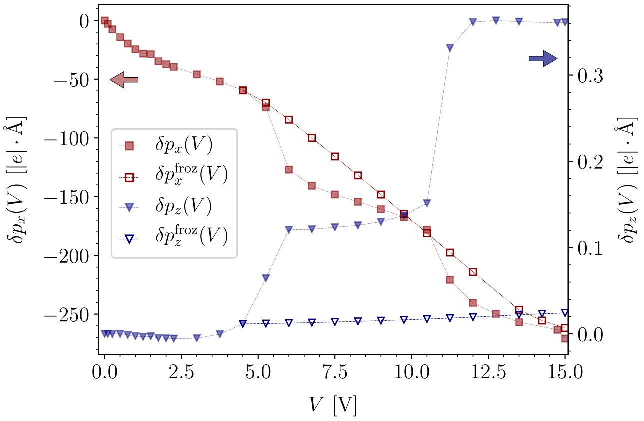

FIG. 5. Evolution of the induced dipole moment - longitudinal to the wire (full squares, left axis); and transverse (full triangles, right axis) - with increasing voltage $V$ at excess charge $Q = |e|$. Open symbols indicate the evolution if the molecular geometry is frozen at $V \gtrsim 5$V. The absence of the step for open symbol traces indicates that the step is indeed a manifestation of the soliton - anti-soliton pair creation.

characterized by the voltage drop $V$. Our results for the evolution of the polarization with increasing $V$ are displayed in Fig. 5. In the regime of small voltages, the soliton moving towards the edge largely determines the longitudinal polarizability of the molecule, $\alpha = \mathrm{d}[\delta p_x(V)]/\mathrm{d}V|_{V=0}$; the numerical value is proportional to the (inverse) curvature of the confinement potential (*i.e.* force constant) and therefore very sensitive to the wire length $L$. Equating the restoring force and the voltage induced force yields a parametrical estimate of $\alpha \sim -q_{\mathrm{sol}}^2/2\kappa L_{\mathrm{uc}}$, where $q_{\mathrm{sol}}$ denotes the charge carried by the soliton, $\kappa$ the curvature seen in the inset of Fig. 2(c) in the main paper and $L_{\mathrm{uc}}$ the length of the molecule given in the number of unit cells. For $L$=113 "sites" wire, we find that $\alpha = -29 \pm 2\ |e| \cdot \text{Å}/V$, which corresponds to $-6.7 \pm 0.3$ $[10^{-20}$ esu].

At slightly larger voltages outside the linear regime the soliton arrives near one of the edges of the wire and the induced polarization saturates reaching a value $\delta p_x(V) \simeq -|e|(n/2 - \xi)a$, where $a = 2.46$ Å is the length of the unit cell. For the wire here considered, $n = 55$ and $\xi \simeq 14$, so we expect a saturation value around $\delta p_x^{\mathrm{sat}} \simeq -35|e| \cdot$ Å, reasonably consistent with Fig. 5.

### B. Sanity check: effect of geometry relaxation on induced polarization

In order to assess the impact of the molecular geometry (*i.e.* electron-phonon coupling) on the step formation seen in Fig. 5 we perform the following sanity check: we fix the geometry of the nuclei right before the first step-like feature in the induced electrical polarization $\delta p_{x,z}$ occurs; then we monitor $\delta p_{x,z}$ for larger voltages at a frozen geometry. The resulting traces are shown in Fig. 5, with open symbols. If the nuclei cannot react to the shift of the electronic charge, the step-like features are indeed no longer present. From total energy calculations, the energy reduction by pair-nucleation can be estimated to be $\gtrsim 0.25$ eV, qualitatively consistent with previous estimations[3].

## IV. ELECTRICAL READOUT OF THE POSITION OF A SINGLE SOLITON

Fig. 6 displays the transmission of the polymethine wire for several different positions of the topological domain-wall.

The transmission function is estimated from a parametrized tight-binding calculation using the Meir-Wingreen formula[4]

$$T(E) = \mathrm{Tr}\left[\hat{\Gamma}_{\mathrm{S}}\hat{G}\hat{\Gamma}_{\mathrm{D}}\hat{G}^{\dagger}\right], \tag{1}$$

for a 1D chain with $N = 113$ sites. The Green's function of the coupled molecular system, $\hat{G} := \hat{G}(E)$, is given by

$$\hat{G}(E) = \left[E\,1\!\!1 - \hat{H}_0 - \hat{\Sigma}_{\mathrm{S}}(E) - \hat{\Sigma}_{\mathrm{D}}(E)\right]^{-1}, \tag{2}$$

with $\hat{H}_0$ being the tight-binding Hamiltonian of the molecular wire and $\hat{\Sigma}_\alpha(E)$ the self-energy of the source and drain contacts, $\alpha$=S,D. We denote by $\hat{\Gamma}_\alpha := \hat{\Gamma}_\alpha(E) = i[\hat{\Sigma}_\alpha(E) - \hat{\Sigma}^{\dagger}_\alpha(E)]$ the anti-Hermitian part of the corresponding self-energy.

The Hamiltonian of the molecular wire has the form of

$$\hat{H}_0 = \sum_{j=1}^{N} \varepsilon_j \hat{c}^{\dagger}_j \hat{c}_j + \sum_{j=1}^{N=1} t_j \left[\hat{c}^{\dagger}_{j+1}\hat{c}_j + \mathrm{H.c.}\right], \tag{3}$$

with $\hat{c}^{\dagger}_j$ (resp. $\hat{c}_j$) the creation (resp. annihilation) operators, $t_j$ the hopping amplitudes and $\varepsilon_j$ the on-site energies. We set the on-site energy of the carbon atoms to $\varepsilon = -2.8$ eV and the on-site energy of the nitrogen caps to $\varepsilon = 1.2$ eV. The set of hopping amplitudes $\{t_j\}_{j=1}^{N}$ is chosen so as to reproduce a particular pattern of single ($s$) and double ($d$) bonds, see *e.g.* Fig. 1 in the main text. For instance, if the soliton is located in the center of the wire, we connect two finite wires of the same length with opposite hopping patterns, *i.e.* $t_s, t_d, t_s, t_d, \ldots$ and $t_d, t_s, t_d, t_s, \ldots$. A topological defect is then described by two consecutive bonds of the same type. Choosing different lengths for the two segments to be connected, we effectively move the soliton along the 1D wire. The value of the hopping parameters is chosen to be $t_s = 2.833$ eV, $t_d = 3.446$ eV so that we reproduce the energy gap, $\Delta \simeq 1.226$ eV and $\pi$-bandwidth $b = 12.558$ eV obtained from a *ab-initio* band structure calculation (not shown here) with the B3LYP functional (which amount to $\Delta = 1.229$ eV and $b = 12.56$ eV respectively).

For each reservoir, the self-energy has been calculated in the usual way using the decimation technique[5]. We assume a 1D linear (not conjugated) semi-infinite chain with averaged hopping amplitude $[t = (t_s + t_d)/2]$ and no onsite-energy. The number of iterations in the decimation procedure

$$\hat{\Sigma}_i(E) = |t|^2 g_i(E), \tag{4}$$

$$g_{i+1} = [E + i\eta_{\mathrm{dec}} + \hat{\Sigma}_i(E)]^{-1}, \tag{5}$$

with initialization $\Sigma_0(E) = 0$ and $\eta_{\mathrm{dec}} = 0.01t$ is chosen to be large enough to ensure numerical convergence of the self-energy and the corresponding surface Green's function, $g_i(E)$. For simplicity, we assume the source and drain to be the symmetric. Asymmetric coupling will not change qualitatively our results, only affecting to the maximum value of the conductance when the domain-wall is located at the center of the wire.

As can be seen from Fig. 6, when the soliton is located in the center of the wire, the mid-gap state produces a unit transmission at Fermi energy because the coupling to the leads is symmetric. Moving the topological defect away from the center, the transmission at the Fermi energy decreases strongly and non-linearly. If the soliton moves further away to the center and close to one of the edges, the conductance drops even further by several orders of magnitude as one would expect for a simple gapped system.

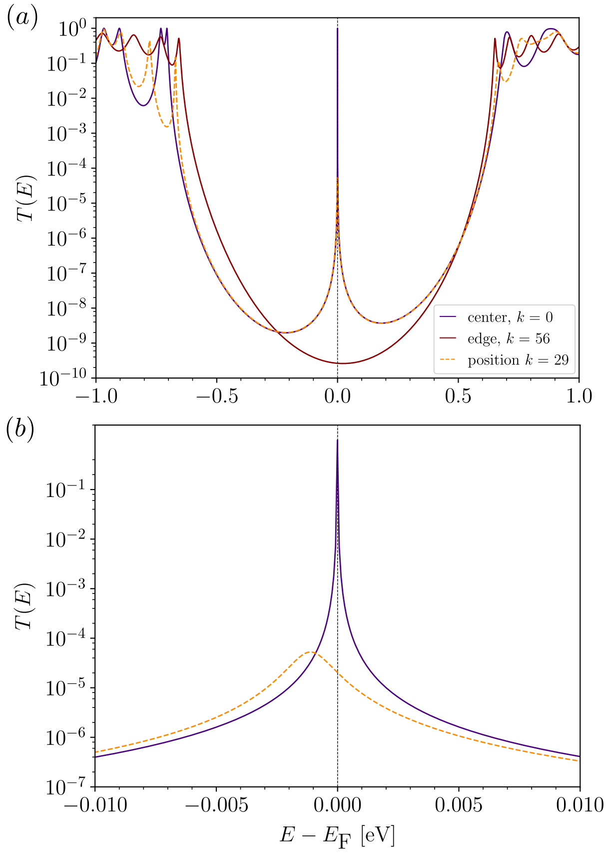

FIG. 6. Signatures of the domain wall in the zero bias conductance, $G$ (expressed in units of the conductance quantum, $2e^2/\hbar$). (a) Transmission function $T(E)$ obtained using Eq. (1) with $G = T(E_{\mathrm{Fermi}})$. The soliton is located at the center of the wire (continuous violet line); at the edge of the wire (continuous red line) and at the atomic position $k = 29$ (roughly in between the center and the edge; dashed yellow line). (b) Zoom of the transmission function in a smaller energy range (closer to the Fermi energy) to highlight the continuous flow when the topological domain-wall is moved away from the center of the wire.

[1] V. Blum, R. Gehrke, F. Hanke, P. Havu, V. Havu, X. Ren, K. Reuter, and M. Scheffler, "*Ab initio* molecular simulations with numeric atom-centered orbitals," Comput. Phys. Comm. **180**, 2175–2196 (2009).

[2] S. H. Vosko, L. Wilk, and M. Nusair, "Accurate spin-dependent electron liquid correlation energies for local spin density calculations: a critical analysis," Canadian Journal of Physics **58**, 1200–1211 (1980), https://doi.org/10.1139/p80-159.

[3] S. Kivelson, "Soliton model of polyacetylene," in Solitons, Modern Problems in Condensed Matter Sciences, edited by S. E. Trullinger, V. E. Zakharov, and V. L. Pokrovsky (Elsevier Science Ltd, 1986) 1st ed.

[4] Y. Meir and N. S. Wingreen, "Landauer formula for the current through an interacting electron region," Phys. Rev. Lett. **68**, 2512–2515 (1992).

[5] J. C. Cuevas and E. Scheer, Molecular Electronics, 2nd ed. (World Scientific, 2010) https://www.worldscientific.com/doi/pdf/10.1142/7434.