Electronic Supplementary Information file for "Hydrogen-dimer lines and electron waveguides in graphene"

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Structural properties of hydrogen dimer lines

We focus here on some structural properties of the n-superlattice structures described in the main text, as obtained by geometry optimizations at the Density Functional Theory level, employing the Perdew-Burke-Ernzerhof (PBE) functional[1, 2] to handle exchange and correlation effects. In these calculations, as mentioned in the main text, core-electrons were described by separable norm-conserving pseudopotentials[3] with a partial core correction[4], and a set of numerical atomic orbitals with compact support of double- ζ plus polarization quality was used to expand the wavefunction, as implemented in SIESTA[5]. The rectangular graphene unit cell with lattice vectors $a'_1 = a_1 + a_2$ and $a'_2 = a_2 - a_1$ [where $a_1 = a_0(\frac{\sqrt{3}}{2}, -\frac{1}{2}), a_2 = a_0(\frac{\sqrt{3}}{2}, +\frac{1}{2})$ are primitive lattice vectors of graphene and a_0 its lattice constant] was used as a reference to generate $1 \times n$ supercells containing $4 \times n$ carbon atoms and 2 hydrogen atoms each, and a consistent sampling of the Brillouin zone (BZ) was achieved with a Monkhorst-Pack scheme[6] using a $50 \times 50\sqrt{3}/n$ k-point mesh on the surface plane. A large vacuum layer 21 Å large was introduced along the surface normal, and a simple one-k point sampling of the BZ along this direction was employed, as usual.

Two different situations were considered – namely single- and bi- layer graphene – which are representative of free-standing graphene and of a graphene sheet which is supported on an insulating substrate, respectively. Fig.1, for example, shows the n = 10 SL structures in free-standing and "supported" graphene. In both cases, we performed two different structural optimizations, with or without relaxation of the cell parameters, to mimic two different physical situations, *i.e.* the infinitely extended superlattice structures and a hydrogen dimer guide embedded in pristine graphene, respectively. Ionic relaxations and cell optimizations used stringent thresholds on the maximum component of the atomic forces (0.005 eV/Å) and on the maximum component of the stress tensor (0.1 MPa),

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Figure 1: Transport channels defined by parallel hydrogen dimer lines placed at a distance of $10 a_0 \approx 2.46$ nm, on single- and bi- layer graphene (left and right panel, respectively). Black and white balls for carbon and hydrogen atoms, respectively.



Figure 2: Interlayer potential in AB-stacked bilayer graphene, as computed with the bare PBE functional using a double- ζ plus polarization set of atom-centered orbitals. Black and red symbols for uncorrected and conterpoise-corrected *ab initio* results, lines are spline interpolations of the data to guide the eyes. The vertical bar marks the experimental equilibrium interlayer spacing in graphite.

together with a 500 Ry mesh cutoff for the real space integrations. The latter value is sufficiently large to make negligible any egg-box effect.

Notice that, with the above set-up, interaction in graphene bilayer is only representative of the true interlayer potential, since the latter necessarily requires taking into account the van der Waals dispersion contributions which are absent by construction in any semi-local exchange-correlation functional. Our results, though, are considerably more reliable than those obtained with the pure PBE functional in conjunction with plane-waves or real grids, since the Basis Set Superposition Error (BSSE) partially compensates for the lack of dispersion forces, at least at short range. The BSSE is a known problem which plagues calculations using atom-centered basis sets and leads to an overestimation of the binding energies due to the uneven description of the single-particle space that a geometrydependent basis necessarily provides. Typically, one needs to corrected for the BSSE, for instance following the *a posteriori* counterpoise correction (CP) scheme of Boys and Bernardi[7], but here we exploit such an error to obtain a realistic description of the system without additional computational cost¹. This is shown in Fig. 2 where we report the interlayer interaction potential (per C atom) in AB-stacked graphene bilayer, as obtained by both CP-corrected and uncorrected calculations. While the first give the results expected for a semi-local functional, the second agree well with empirically corrected DFT or vdW-inclusive DFT functionals[8] –both for the position of the minimum and the depth of the potential well– and thus represent a simple surrogate for more sophisticated approaches, at least for the present system.

The results of the calculations on the n-superlattices are reported in Figs. 3 and 4 for single layer graphene and in Fig. 5 for bilayer graphene. In such figures the height profile of the carbon skeleton is shown across the channels, starting and ending with the sp^3 carbon atoms which bind the hydrogen atoms. As is evident from these figures, binding of hydrogen atoms determines a sizable curvature of the graphene sheet which extends for a quite a large distance from the line position. For narrow ribbons (e.g. $n \leq 10$ in the single layer case shown in Fig.3) such bending involves the whole structure and gives it an approximate parabolic shape, with constant curvature across the channel. Wider channels, on the other hand, develop a flat region in their middle which resembles pristine graphene, but keep a sizable curvature close to the hydrogen dimer lines, which is similar to the one found for the

 $^{^{1}}$ Inclusion of semi-empirical corrections, though computational cheap by themselves, would force us to considerably enlarge the basis set in order to minimize the BSSE.



Figure 3: Height profile of the carbon skeleton in the n-SL structures for n = 3 - 20, along a direction perperdicular to the hydrogen dimer lines, as results from full structural relaxation not including optimization of the cell parameters, vertically shifted for comparison. Symbols denote the position of the carbon atoms, and lines are spline interpolations of the data. The leftmost and rightmost symbols are for the sp^3 C atoms binding hydrogen. (Vertical displacements use a scale which is four times larger than horizontal one).

narrower structures.

Cell optimization has little effect on this behavior and only affects the curvature of the most constrained structures. Similarly for the interaction with an underlying substrate (here an additional graphene layer), which has the effect of anticipating the appearance of the flat region, which in this case occurs for $n \approx 7$.

Fig. 6 (left panel) shows the behaviour of the curvature of the graphene sheet close to the hydrogen lines, as a function of n, for the different situations considered, along with curves $\sim 1/n^{\alpha}$ fitted to the small n data (*i.e.* for n smaller than the value which signals the appearance of the flat region). The optimal value of α is close to 1 for free-standing graphene, but increases above 2 when graphene is supported as a consequence of the interaction with the substrate (see caption to Fig. 6).

Finally, Fig. 6 (right panel) shows the relative variation of the channel width which results, for both singleand bi-layer graphene, when allowing the cell parameters to vary. As is evident from that figure, cell relaxation has minor effect on the structures. Interestingly, for small n, free standing graphene exploits a lattice compression ($\leq 1.4\%$) to attain a curvature smaller than the one found with fixed cell parameters.

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Figure 4: Same results as in Fig. 3 for selected SL structures as indicated, when structural relaxation includes optimization of the cell parameters.



Figure 5: Same results as in Fig. 3 for n-SL structures in graphene bilayer (only the layer which binds hydrogen atoms is shown). Results of full structural relaxation with (right panel) and without (left panel) optimization of cell parameters.



Figure 6: Left: curvature of the graphene sheet in the neighborhoods of the dimer lines, as a function of the superlattice size. Symbols in grey, orange, green and cyan for single- and bi- layer graphene, without and with cell optimization, respectively. Lines are non-linear curve fitting to the data, $\xi = A_0 + A_1/n^{\alpha}$, using the smallest n values. The optimal α values are 1.32, 1.13, 1.58 and 2.24, respectively. Right: relative variation of the channel widths a_n as result from cell optimization in single- and bi-layer graphene (color coding as in the left panel).

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