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Implementation
of a Tight-Binding Model
for Carbon-Hydrogen compounds

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Abstract

We implement a tight-binding model for the electronic structure and the total adiabatic energy of hydro-carbon compounds. The C++ code implements periodic boundary conditions, and can perform geometry optimization by means of the simplex method. We check for the correctness of the implementation by evaluating the relaxed structures and molecular levels of a few simple molecules such as H_2, CH_4, C_2H_4. We then apply the method to several hydrocarbons with less than thirty atoms, to hydrogenized graphene flakes, and to graphane. We find that the adopted tight-binding parameterization can fail in preventing multiple bonds on the same hydrogen atom, thereby leading to unphysical equilibrium structures.

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Contents

1 Introduction

Hydrocarbons are present in nature in several forms and with a broad range of molecular structures. The study of those compounds is important for man in this stage of history, because of their main role as fossil fuels. In the bargain, in the near future hydrocarbon structures such as graphane could become very important for electronics as novel semiconductor materials. Graphane is a hydrogenized graphene predicted theoretically on 2003 and produced in 2009 [1] by reversible hydrogenetion of graphene.

We study these hydro-carbon compounds by means of a tight binding model, to be introduced in the next section. For every studied molecule we report its relaxed shape obtained by minimizing the total adiabatic energy, plus its electronic properties. In the present work we reproduce the results of previous studies done with the same or similar methods and we find and discuss unsuspected problems with enstablished parametrization.

2 The Tight Binding model

The tight-binding (TB) model is a useful technique for solving the problem of the adiabatic motion of the electrons in the field provided by the nuclei. The TB is not an ab-initio method. Its most remarkable feature of it is the providing of a fair accuracy, needed to describe complex systems at a low computational cost, more efficient than ab-initio methods, but far more expensive than empirical ones. We apply the TB model to the electronic states of crystalline solid Bloch function. The positions of the atoms are

$$R_{jl} = d_j + R_l \,, \tag{1}$$

where $R_l = n_1 a_1 + n_2 a_2 + n_3 a_3$, with n_i integer numbers and a_i are the primitive vectors and d_j are the basis vectors locating the N_b atoms in each unit cell.The total Hamiltonian is defined by :

$$H_{tot} = T_e + T_n + U_{ee} + U_{nn} + U_{ne} \,. \tag{2}$$

With the Born-Oppeneimer approximation we ignore the nuclear kinetic term and the nuclear wave function too, so we can write the electronic Hamiltonian as:

$$H_e = T_e + U_{ee} + U_{en} + U_{nn} = \sum_i \frac{p_i^2}{2m} + \frac{1}{2} \sum_{i \neq j} \frac{e^2}{r_i - r_j} + \frac{1}{2} \sum_{ik \neq jl} \frac{Z_i Z_j e^2}{R_{ik} - R_{jl}} - \sum_{ijl} \frac{Z_j e^2}{r_i - R_{jl}} \,. \tag{3}$$

In the spirit of the one-electron picture the many-body problem is further reduced to the problem of one electron moving in an average field U_{ave} due to the other electrons

and the ions. We write now the reduced one-electron Hamiltonian as

$$h_e = \frac{p^2}{2m_e} + U_{ave}. \tag{4}$$

The corrisponding Schroedinger equation is

$$h_e\phi(r) = \varepsilon\phi(r), \tag{5}$$

where ε is the one electron band energy. We define ΔU_{ave} the part in the potential U_{ave} that does not involve the considered atom and we write the matrix elements:

$$\langle\phi_n(r)|\Delta U_{ave}|\phi_m(r)\rangle = C_{nm}(R), \tag{6}$$

where n is a collective index (α, l, j), and α is a shorthand for a full set of atomic quantum numbers defining an orbital. We can define the overlap integrals as

$$S_{\alpha'(j'l'),\alpha(jl)} = \langle\phi_{\alpha'j'l'}(r)|\phi_{\alpha jl}(r)\rangle. \tag{7}$$

So we can write the tight-binding secular problem:

$$\sum_n \left(E_{nm}^{atom} S_{nm} + C_{nm}(R)\right) B_n(R) = \varepsilon \sum_n S_{nm} B_n(R). \tag{8}$$

The Hamiltonian and the wave function $\phi(r)$ exhibit important symmetries. h_e is invariant under lattice traslations R_l. According to the Bloch's theorem the wave functions ϕ_{nk} is:

$$\phi_{nk}(r) = \phi_{nk}(r + R_{jl})e^{-ikR_{jl}}. \tag{9}$$

The idea of the TB method is to expand the crystalline wave function on a basis of atomic orbitals. We construct the following symmetric combination:

$$\Phi_{\alpha jk}^{Bloch}(r) = \frac{1}{\sqrt{N_{Bvk}}}\sum_l e^{ikR_l}\phi_\alpha(r - R_l - d_j) = \frac{1}{\sqrt{N_{Bvk}}}\sum_l e^{ikR_l}\phi_{\alpha jl}(r). \tag{10}$$

The electronic orbitals, i.e. the eigenfunctions of Eq. (4) are then expanded as linear combination of the state of Eq. (10):

$$\phi_{nk}(r) = \frac{1}{\sqrt{N_b}}\sum_{\alpha j} B_{n\alpha j}\Phi_{\alpha jk}^{Bloch}. \tag{11}$$

The full electronic eigenfunction is then a Slater determinant of the energy states of type (11) solving Eq. (4). The matrix equation is obtained doing the bra-ket product of Eq. (5) with the $\langle\Phi_{\alpha jk}^{Bloch}|$ to have:

$$\langle\Phi_{\alpha jk}^{Bloch}|h_e|\phi_{nk}\rangle = \int \Phi_{\alpha jk}^*(r)\varepsilon_n(k)\phi_{nk}(r)dr. \tag{12}$$

Although the equation developed to here are quite simple, the computational cost of the calculation of the integrals is high so the TB model is not so efficient for large time simulation. So some approximation are usually employed.
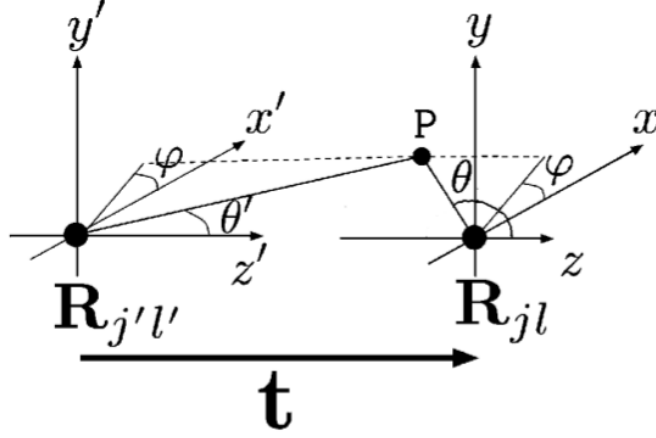
Figure 1

2.1 The Lowdin Orbitals

We can remove the non-orthogonality problem by introducing a new set of orthogonalized orbitals and then we can write the matrix form of the Schroedinger equation:

$$hB_n(k) = \varepsilon_{nk}SB_n(k),$$ (13)

where $B_n(k)$ are the coefficients of the orbitals combination. With this method we obtain a a simplified secular problem that is free from overlap contribution. The wave function is given by:

$$\psi_\nu(k,r) = \frac{1}{\sqrt{N_c}}\sum_{\alpha j}C_{\nu\alpha j}(k)\phi_{\alpha jk}(r).$$ (14)

For each wave vector k the solution of the Schroedinger equation requires a standard diagonalization of the Hamiltonian h_e matrix. For the 1-electron problem, different values of k do not mix together.

2.2 The two-center approximation

In this section we regard the form of the Hamiltonian to simplify the computational cost of the calculus of the overlap integrals. In fact we consider the average potential U_{ave} as a sum of spherical contributions located at all lattice sites. We can rewrite the one-electron Hamiltonian as:

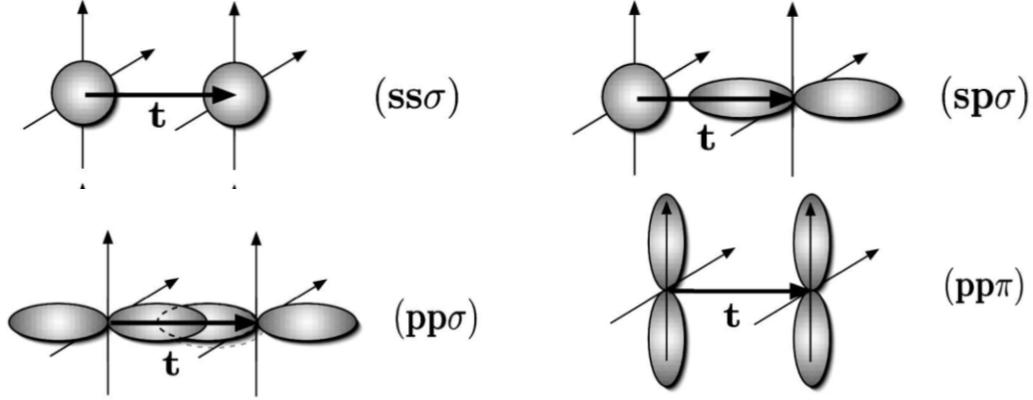$$h(r) = \frac{p^2}{2m_e} + \sum_{j''l''}V_{j''l''}(r).$$ (15)

Figure 2: Scheme of the form and of possible types of overlaps for s and p atomic orbitals.

When we write explicitly the matrix element we obtain

$$h_{\alpha'(j'l'),\alpha(jl)} = \langle \phi_{\alpha'j'l'}(r)|\frac{p^2}{2m_e} + U_{ave}(r)|\phi_{\alpha jl}\rangle = \langle \phi_{\alpha'j'l'}(r)|\frac{p^2}{2m} + \sum_{(j''l'')} U_{j''l''}|\phi_{\alpha jl}\rangle.$$

(16)

The two center approximation consist in neglecting the terms in the $\sum_{j''l''}$ with $(j''l'')$ non coinciding with either $(j'l')$ or (jl). The approximation is good due the smallness of the neglected three-center integrals.

The first direct consequence of the two center approximation is that we can formally treat the matrix elements as if we had a sort of "diatomic molecule" system. Following the Slater-Koster [2] approach we introduce the vector $t = R_{(j'l')} - R_{(jl)} = d_{j'} + R_{l'} - d_j - R_l$ joining the two selected atoms. We introduce the director cosines of the vector t:

$$c_i = t_i/|t|, \quad i = (x, y, z).$$

This geometrical construction is represented in figure 1. The matrix element consist so in the product of a radial integral and a function of the director cosines. These overlaps are sketched in Fig. 2.

2.3 The Parametrization for Carbon and Hydrogen

In this section we report the semi-empirical form of the adopted TB model. The total adiabatic potential is the sum of a contribution E_{bs} of the electrons described with the TB formalism plus a repulsive term U_{rep}, which is completely empirical. E_{bs} is the sum of the one-electron energy of the occupied states:

$$E_{bs} = 2\int_{BZ} \sum_{n}^{occup} \varepsilon_n(k)dk,$$

(17)

Parameter	C-C	H-H	H-C
ε_s[eV]	−2.990	−4.74946	
ε_p[eV]	3.710		
$V_{ss\sigma}$[eV]	−5.000	−0.441	−6.52263
$V_{sp\sigma}$[eV]	4.700		6.81127
$V_{ps\sigma}$[eV]	−4.700		
$V_{pp\sigma}$[eV]	5.500		
$V_{pp\pi}$[eV]	−1.550		
ϕ_0[eV]	8.18555	0.0546	9.1175
r_0[Å]	1.536329	2.1393	1.10168
r_c[Å]	2.18	0.7103	0.0522159
r_{cut}[Å]	2.6	1.22	1.85
n	2.0	0.4495	0.234238
n_c	6.5	1.565	0.434526
d_0[Å]	1.64	2.301	0.785648
d_c[Å]	2.1052	0.3561	0.14
d_{cut}[Å]	2.6	1.22	1.85
m	3.30304	1.02	0.709795
m_c	8.6655	0.8458	0.867909

Table 1: The bond parameters, ε_s ε_p are the on site energy, the other terms are referred to Eq. (19), (20).

where the state energies $\varepsilon_n(k)$ are obtained solving Eq. (5) at each k-point in the Brillouin zone, and the factor 2 accounts for the spin degeneracy. We adopt the parametrization proposed by Volpe *et al* [4] as a extension of the work by Xu *et al* [3] that introduces the interaction between the carbon 2s and 2p and the hydrogen 1s orbitals. This work adopt the standard Goodwin-Skinner and Pettifor [2] scaling function for the radial integrals, in the form:

$$s(r) = \left(\frac{r_0}{r}\right)^n \exp\left(n\left[-\left(\frac{r}{r_c}\right)^{n_c} + \left(\frac{r_0}{r_c}\right)^{n_c}\right]\right). \tag{18}$$

This kind of function is taken to multiply all of the fixed matrix elements in Table 1 to obtain distance-dependent energy overlap:

$$h_{\alpha\alpha'}(r) = V_{\alpha\alpha'}\left(\frac{r_0}{r}\right)^n \exp\left(n\left[-\left(\frac{r}{r_c}\right)^{n_c} + \left(\frac{r_0}{r_c}\right)^{n_c}\right]\right). \tag{19}$$

Effective coordination		Repulsive functional	
α	1.35Å	a_0	12.62 eV
β	-0.5	b_0	1.84716
γ	10Å^{-1}	b_1	-1.9428
		c_0	0.03335 eV^{-1}
		c_1	0.1227 eV^{-1}

Table 2: Numerical values of the parameters in the effective coordination number function z, Eq. (23), and the repulsive functional $F(x,z)$, Eq. (24)

With different numerical parameters (see Table 1) a similar distance dependecy is taken for the 2-body dependency in the repulsive energy between atoms.

$$\phi_{jj'}(r) = \phi_{jj'}^{(0)} \left(\frac{d_0}{r}\right)^m \exp\left(m\left[-\left(\frac{r}{d_c}\right)^{m_c} + \left(\frac{d_0}{d_c}\right)^{m_c}\right]\right). \tag{20}$$

All interactions are truncated at a short-range cut-off r_{cut}. A total quantity ϕ_i is obtained as

$$\phi_i = \sum_j \phi_{ij}. \tag{21}$$

The total repulsive energy is given by two different contributions: one is the sum from the work of Xu *et al*, and involves only the homoatomic interactions. This part is:

$$E_{rep} = \sum_j f[\sum_{j'} \phi(R_{jj'})], \tag{22}$$

where f is a 8-degree polynomial [5]. The second part was proposed by Volpe *et al* [4] to describe the C-H interaction. They propose to evaluate for each hydrogen the quantity:

$$z_i = \sum_j [1 + e^{\gamma(r_{ij}-\alpha)}]^\beta, \tag{23}$$

where the sum runs over all carbon atoms within the cut-off. The contribution of the H atom to E_{rep} is given by a polynomial $F = F(z,\phi)$ of the form:

$$F(z,\phi) = a_0 + (b_0 + zb_1)\phi + (c_0 + zc_1)\phi^2, \tag{24}$$

where $z = z_i$ of Eq. (23), $\phi = \phi_i$ is the repulsive function of Eq. (21), and the total repulsive energy is

$$E_{rep} = E_{rep}^{homo} + \sum_i F(z_i, \phi_i). \tag{25}$$

The parameters are reported in table 2.

2.4 Implementation

We acquired and modified a pre-existing C++ code for the computation of the TB bands and total energy for structures composed only by carbon atoms, given their atomic positions. The original code could then relax the atomic positions to achieve a minimum of the total adiabatic energy. The main implementation of this minimization was given by a standard conjugate gradients module. In addition a simplex routine is available. The relaxation based on the simplex method is slower than the one based on gradients, but it has the advantage that it does not require us to program and test all formulas involving gradients. We added the hydrogen-hydrogen and the hydrogen-carbon interaction following Ref [4]. With those modification the program acquired the functionality to calculate equilibrium distance and shape of hydrogen-containing molecules and solids.

2.5 Protocol

To obtain a stable structure, represented by a local minimum of the total adiabatic potential, we follow the protocol that we define now:

- we create an *xyz* file with the approximate atomic coordinates.

- we run the TB program with options as:

  - the type of boundary conditions applied to the supercell (none for a molecule, 1d for linear, 2d for a planar structure) and the corresponding *k*-points sampling;

  - the number of *k*-points used to sample the bands, if relevant.

- we run the minimization with the simplex method.

At the end of the minimization, the code outputs the relaxed structure, its energy and its electronic structure. When the relaxed structure is available, we can evaluate the band structure by selecting an appropriate path in *k*-space. In such a case, the total energy is not available. The total energy can be used to estimate the formation energy, given by the simple formula

$$E_{for} = E_{tot} - n_{\mathrm{C}}E_{\mathrm{C}} - n_{\mathrm{H}}E_{\mathrm{H}} \, , \tag{26}$$

where n_C and n_H are the number of carbon and hydrogen atoms and E_C, E_H are the free-atom energy values. Another quantity of interest is the gap between the highest occupied molecular level (HOMO) and the lowest unoccupied molecular level (LUMO).
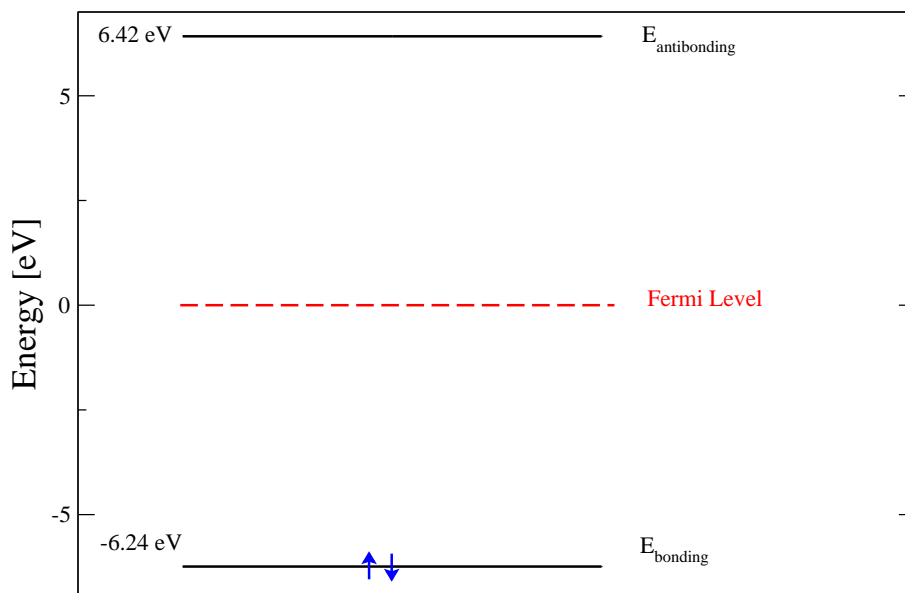
Figure 3: Energy levels of the H_2 molecule.

3 Results

To start, we test the program on a few simple molecules such as H_2, H_3, and single bond C-H. The test with the H_2 molecule yields the following results: the bonding-antibonding gap is 12.48 eV. The equilibrium distance is 0.66 Å instead of the established value of 0.74 Å [6]. The electronic structure of H_2 is reported in Fig. 3 In the case of the single bond C-H we find an equilibrium distance of 1.04 Å while the reference value is 1.09 Å.

3.1 Organic Compounds

The molecules which we focus on in the first part of this project are simple organic compound. First of all we study the geometrical and spectral shape of saturated alkene molecules, which involve only single bonds. Each carbon atom has sp^3 hybridization, and it forms 4 bonds.

The simplest alkene is methane, CH_4, see Fig. 4a. It has a regular tetrahedral geometrical shape which reflects in the degeneracy of its energy levels, see figure 5. The TB calculation indeed finds the correct symmetry and the electronic level degeneracy, in particular a threefold degenerate HOMO. Other hydrocarbons including ethane and the ones shown in figure 4 have sp^3 hybridization. However, their symmetry is lower and therefore the level degeneracy is less important.

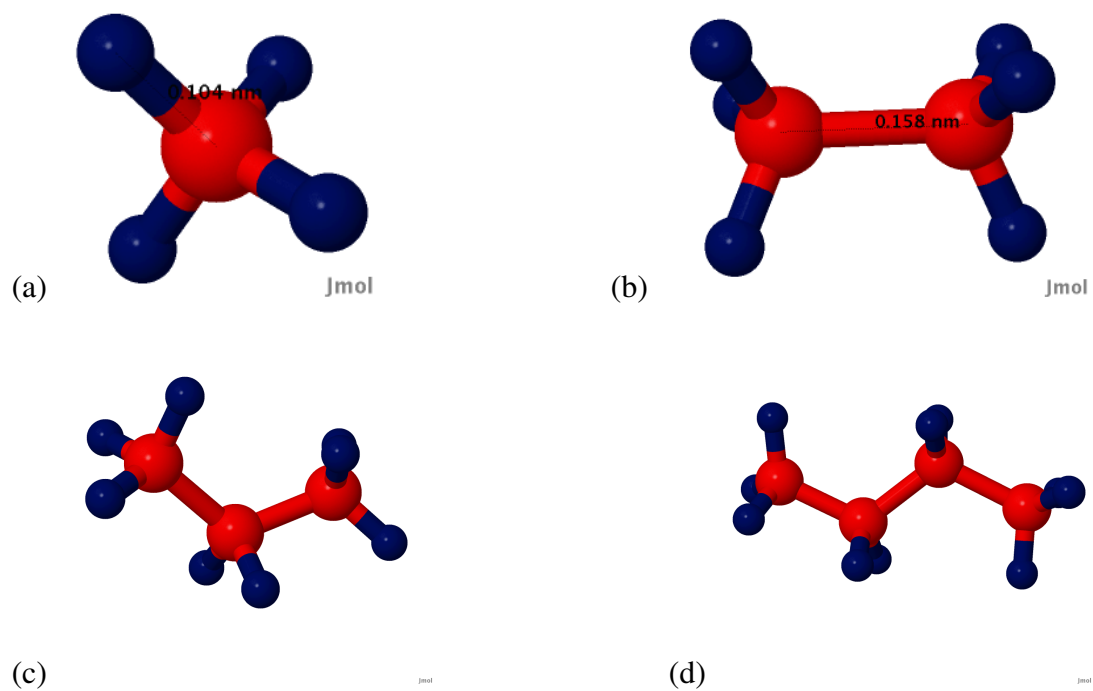Table 3 reports the formation energies and electronic gaps for studied alkane

Figure 4: the relaxed structures for (a) methane CH_4 (b) ethane C_2H_6 (c) propane C_3H_8 (d) butane C_4H_{10}.
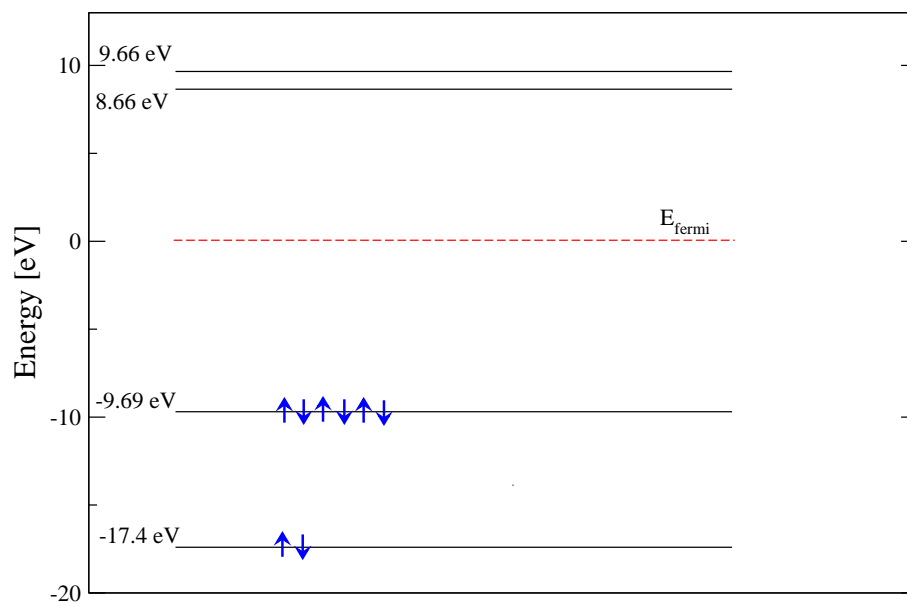

Figure 5: Energy levels of methane; the second and third level are both threefold degenerate.

Alkane	E_{for} [eV]	ΔE_{gap} [eV]
Methane CH_4	-20.76	18.64
Ethane C_2H_6	-32.55	12.50
Propane C_3H_8	-45.95	12.07
Butane C_4H_{10}	-58.90	10.38

Table 3: For comparison, the formation energy and the HOMO-LUMO gap for a number of the alkenes of increasing chain length. .

compounds. We regard the molecular bonds-length to characterize the type of bond between carbons; from the literature [6] the C-C bond length is 1.53 Å, the double C=C bond is 1.34 Å, and the triple C≡C is 1.20 Å. The simulated ethane has C-C single bond's lenght of 1.58 Å .

3.2 Carbynes

Next, we consider carbynes, namely unsaturated sp carbon chains with hydrogens only at their ends. The simplest example is ethene (C_2H_4). Such carbynes with two hydrogen atoms at each end of the chain present double C=C bonds. The double bonds are stronger than the single bonds of alkanes; in the case of ethene the double bond's length results of 1.36 Å. The carbynes with a single hydrogen at each end of the chain, e.g. acetylene (HCCH), have alternating single and triple bonds, provided that the number of carbon is even. The single bond between the triple ones result of 1.362 Å, similar to the referenced value is 1.378 Å . With two hydrogen atoms at each end of the chain we observe that, if the number of carbons is odd the CH_2 group at the two ends relax to orthogonal planes, while if the number is even, the molecule is planar, see Fig. 6.

We tested the torsional energy of an odd-n carbyne namely propadiene $H_2C=C=CH_2$. Starting from the fully relaxed configurations we rotate rigidly the hydrogens at one end and evaluate the total energy of the molecule. The minimum is at $90°$ torsional angle. The barrier at the flat configuration amounts to 1.4 eV.

3.3 Aromatic Compounds

To investigate the model capability to describe sp^2-hybridized compounds, we simulate a few aromatic compounds. The resonating nature of the aromatic bonds is usually accounted for fairly by TB model.

Here we study benzene (C_6H_6), naphthalene ($C_{10}H_8$) and anthracene ($C_{14}H_{10}$) (see Figure 8). We also consider bigger circular compound such as coronene, and for
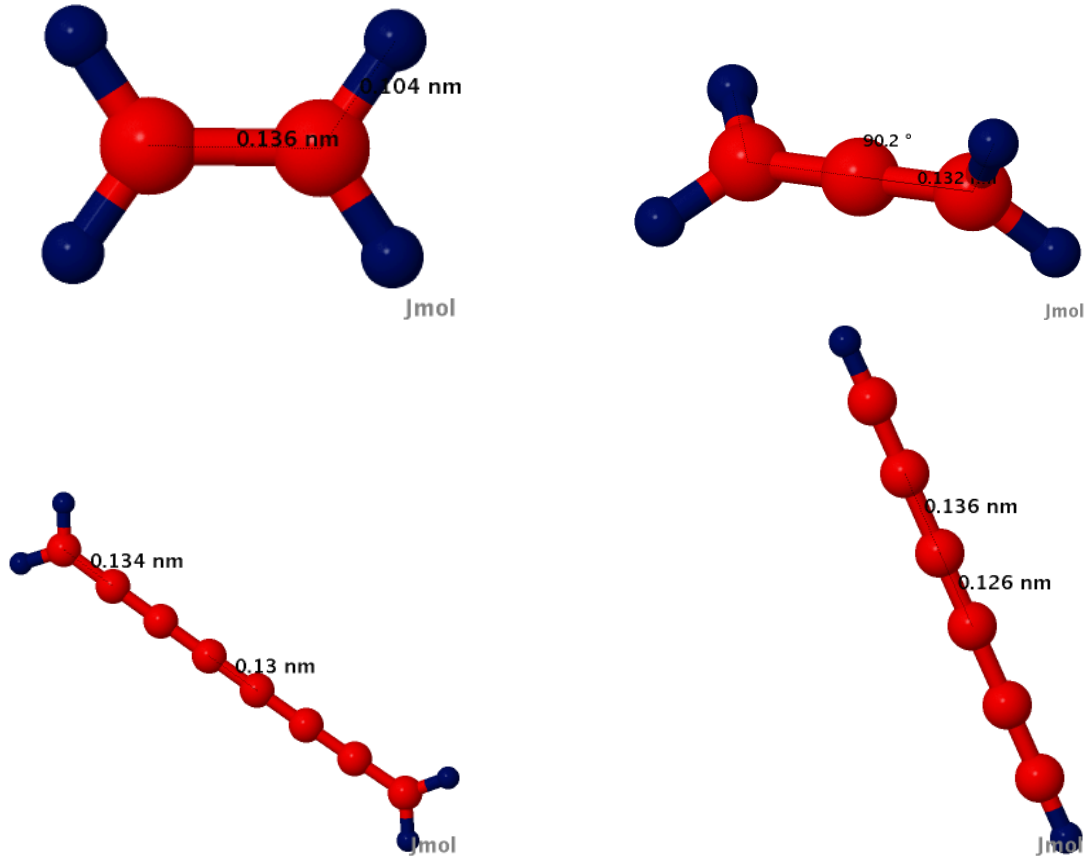
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Figure 6: The relaxed configurations of a few sp carbon chains with H-terminated ends.

comparison we also consider its hydrogen-free version, a little round flake of graphene. We also carried out a similar simulation for C_{54} and its hydrogenated version. The evident effect of hydrogenation (Figures 9, 10) is a broadening of the gap between the HOMO and the LUMO. It is effectively what we expect, because the hydrogen atoms saturate the free metallic bonds.

3.4 Graphene and Graphane

Graphene is a 2D crystal, composed only by carbon atoms, arranged in an honeycomb structure. To describe it we write the graphene primitive lattice vectors that define the unit cell:

$$\vec{a}_1 = a\,(1,0)\ , \tag{27}$$

$$\vec{a}_2 = a\left(\frac{1}{2}, \frac{\sqrt{3}}{2}\right). \tag{28}$$

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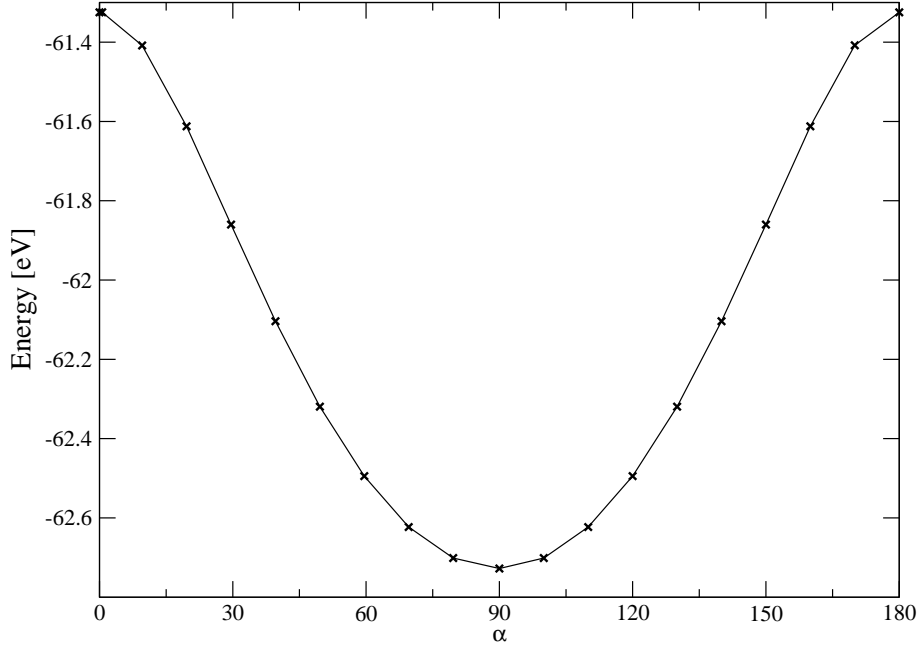
Figure 7: The total adiabatic energy as a function of the torsional angle

Those lattice vectors have length $|\vec{a}_1| = |\vec{a}_2| = \sqrt{3}a_{CC} = a = 2.46126$ Å where a_{CC} is the C-C spacing of 1.421 Å [7], see figure 11. The basis vectors where the atoms are placed are $\vec{0}$ and $\frac{1}{3}(\vec{a}_1 + \vec{a}_2)$.

Its hydrogenated counterpart, graphane, is based on the same hexagonal lattice periodicity, with 2 carbons and 2 hydrogen atoms per unit cell. Since the C atoms are sp^3 hybridized, the C atomic positions are shifted vertically, as described in table 5. We compare the band structure of graphene with the bands of graphane. In calculations based on a 80×80 k-points grid, we evaluate the relaxed energy as a function of the lattice spacing, and obtain $a = 2.564$ Å, see figure 12. In correspondence to this minimum, we have the C-H bond length named $z_{CH} = 1.05$ Å, see table 5.

To draw the bands, the code calculates the energy along the k-point path passing through Γ M K of figure 11b. The C-C bond length increases from $d_{C-C} = 1.421$ Å of graphene to $d_{C-C} = 1.56$ Å (single bond) in graphane, corresponding to $z_1 = 0.19$ Å. A larger cell for graphane was also obtained theoretically by the DFT study of Flores *et al.* [8]; but this is in contrast to the experimental finding by Elias *et al.* [1].

In the TB model the gap of graphane amounts to 6.0 eV. We note also that all bands are separate and do not overlap.
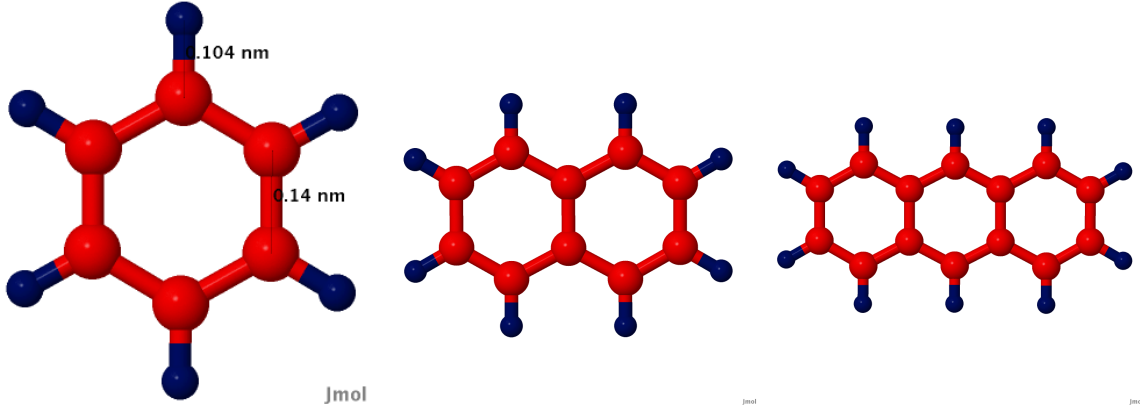
Figure 8: The relaxed structures of (left to right): benzene (C_6H_6), naphthalene ($C_{10}H_8$) and anthracene ($C_{14}H_{10}$).

	E_{for} [eV]	ΔE_{gap} [eV]
C_6H_6	-58.07	4.13
$C_{10}H_8$	-91.77	2.67
$C_{14}H_{10}$	-125.37	1.85
C_{24}	-149.33	1.17
$C_{24}H_{12}$	-203.00	2.28
C_{54}	-349.78	0.09
$C_{54}H_{18}$	-434.18	1.16

Table 4: The formation energy and the HOMO-LUMO gap of a few aromatic compounds.

4   Discussion and Conclusion

In this thesis we implement a program based on the parametrization introduced by Volpe and Cleri for hydrogen-carbon compounds. During our study, we discovered a seriously unphysical behavior of this parameterization. We come now to discuss these problems. When we start off minimizations from configurations characterized by atomic coordinations near to the expected geometric shape, the results are usually fine. However, if we start off at configurations which involve hydrogen coordination greater than unity, the code converges to unphysical configurations characterized by strong multiple H coordination and a large (several eV) energy gain. This problem is especially evident when the physical H-C≡C-H and unphysical configurations of H_2C_2 are considered in figure 16. The unphysical losange shape is predicted to lie 5.4 eV lower in energy than the correct linear configuration. Similar extra-stable unphysi-
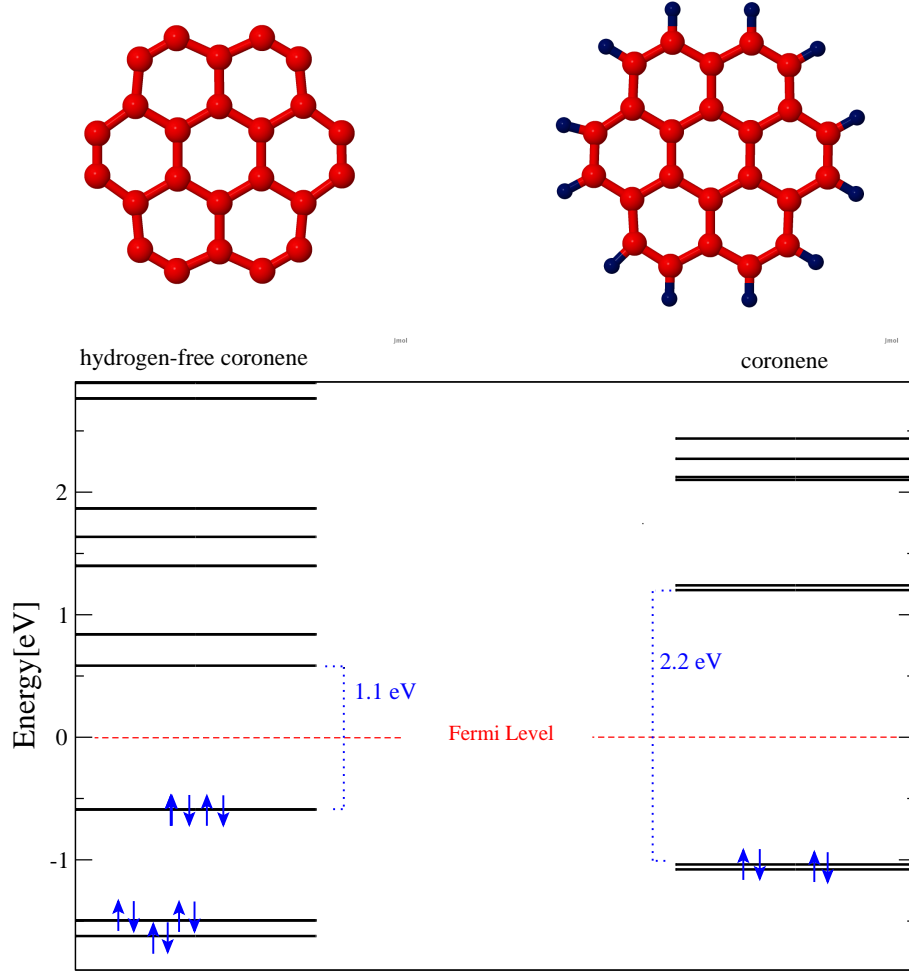
Figure 9: Comparison between hydrogen-free coronene C_{24} (Left) and coronene $C_{24}H_{12}$ (Right)

	x	y	z
$C_{(1)}$	0	0	$-z_1$
$C_{(2)}$	$\frac{a}{2}$	$\frac{\sqrt{3}a}{6}$	z_1
$H_{(1)}$	0	0	$-z_1 - z_{CH}$
$H_{(2)}$	$\frac{a}{2}$	$\frac{\sqrt{3}a}{6}$	$z_1 + z_{CH}$

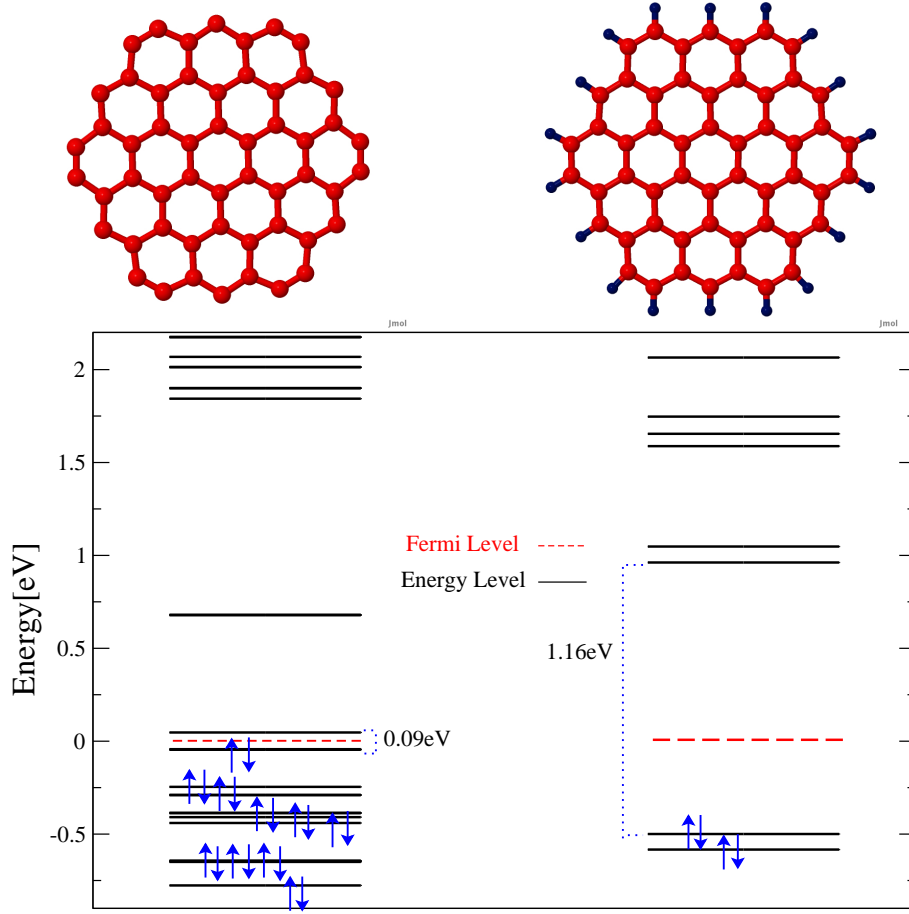Table 5: The atomic relaxed positions in the unit cell of graphane, where a is the lattice spacing, and $z_1 = \frac{1}{2}\sqrt{d_{C-C}^2 - \frac{a^2}{3}}$.

Figure 10: 54 carbon atoms graphene sheet C_{54} (Left) and boundary saturated $C_{54}H_{18}$ (Right)

cal twofold-coordinated hydrogen atoms can be found only when studying $C_{24}H_{12}$, $C_{54}H_{18}$, graphene, etc.

This problem can be traced to the repulsive energy Eq. (24) which relies on a negative coefficient b_1, see table 2. Its negative value indeed favors multiple bonds involving a simple hydrogen. This is very surprising, in view of the statement by Volpe and Cleri that "the effect of the function z is to smear out a too rapid variation in the local coordination, and the resulting variation of charge density x, when several C atoms are close to an H atom". This parameterization needs therefore full reconsideration, in order to fix this unphysical behavior, without upsetting its correct features.
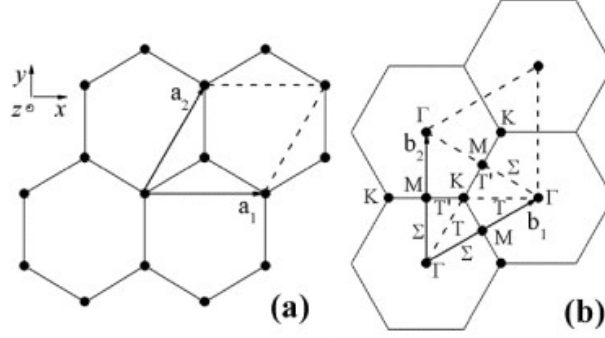
Figure 11: (a) the unit cell of the graphene crystal and (b) the corresponding cell in the reciprocal space (Brillouin zone)
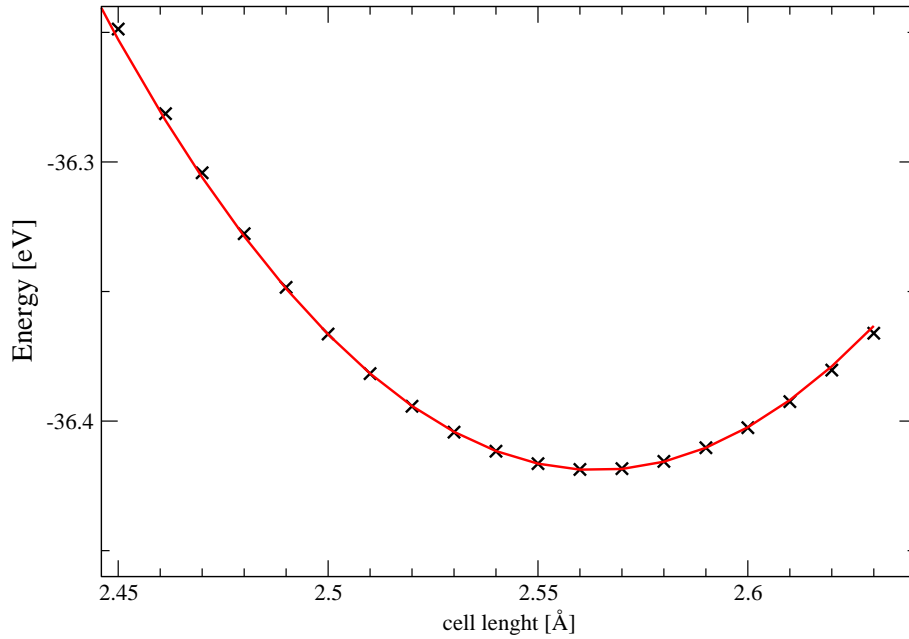

Figure 12: The total energy of graphane, computed with the TB model and a 80×80 k-points grid, as a function of the hexagonal lattice parameter a. Solid line: a parabolic fit of the data in $2.55 - 2.57$ Å interval.

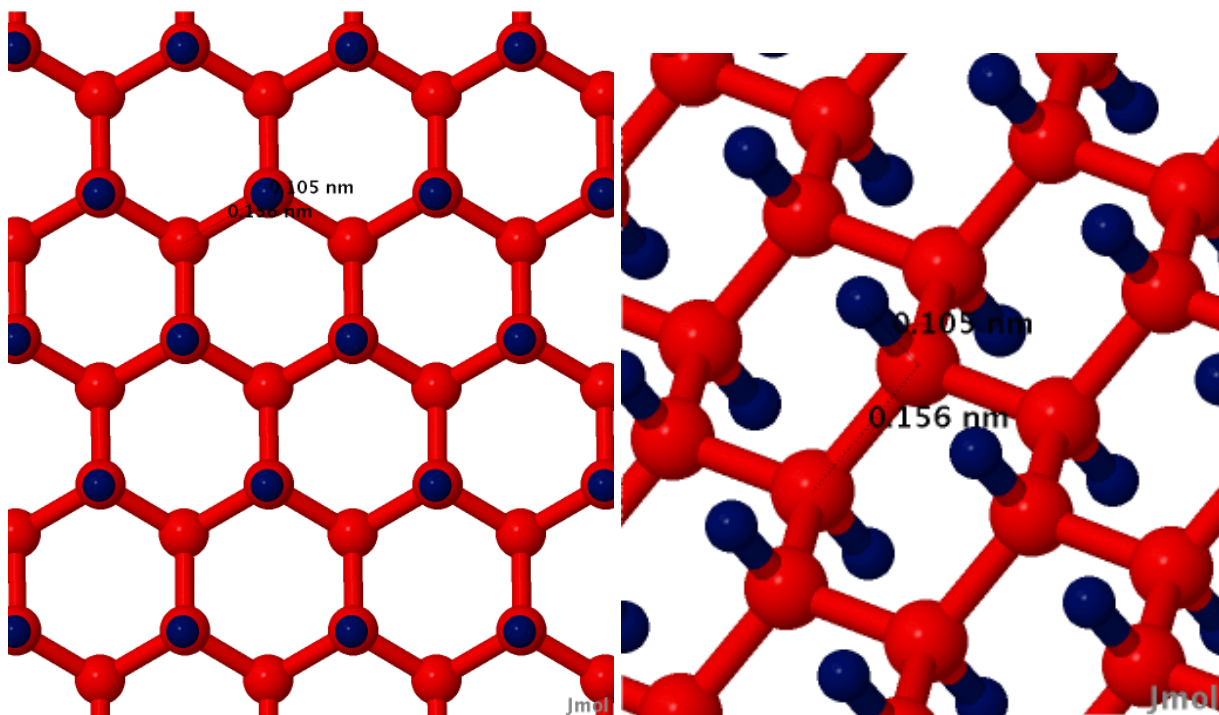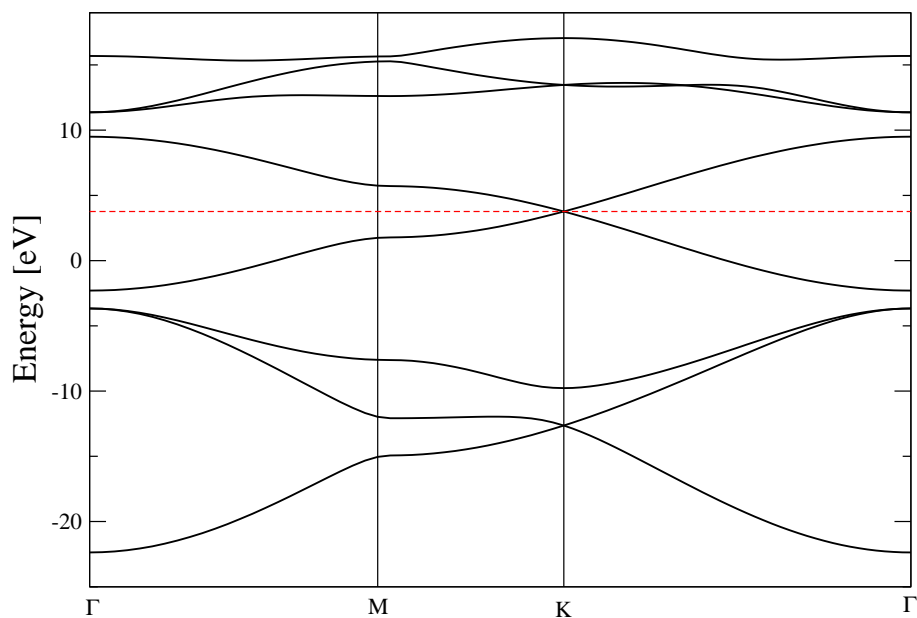Figure 13: The structure of graphane; left: top view. Right: oblique view.

Figure 14: The electronic band structure of graphene. The dashed line marks the Fermi level.
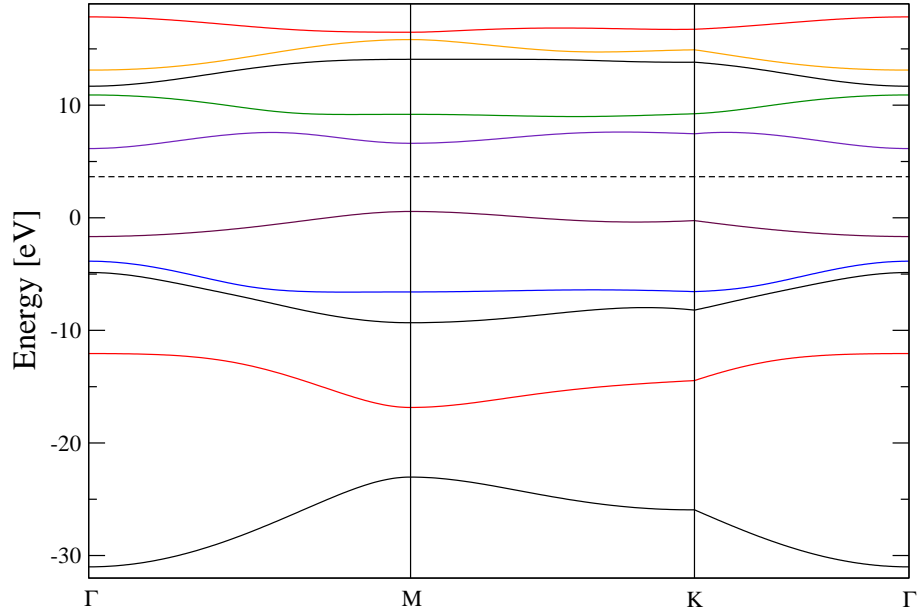
Figure 15: The electronic band structure of graphane. The dashed line marks the Fermi level.
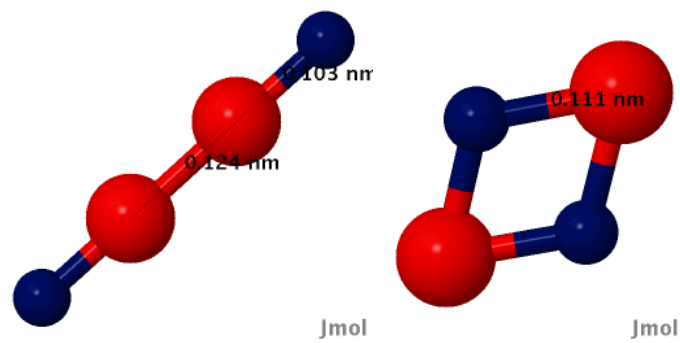

Figure 16: Left: the physical linear configuration of acetylene, characterized by $E_{for} = -15.38$ eV. Right: the unphysical global minimum of the Volpe-Cleri adiabatic potential, characterized by $E_{for} = -20.78$ eV, as much as 5.4 eV more stable.
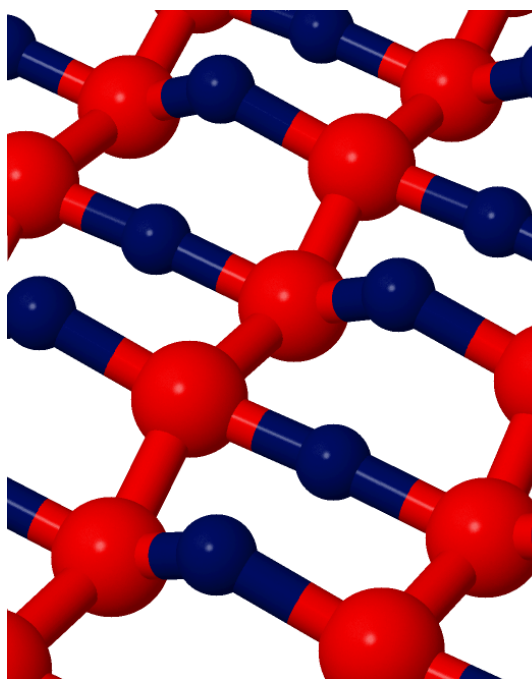
Figure 17: Unphysical graphane, with twofold- coordinated H. This struc-
ture is predicted 37.60 eV more stable than the correct one of Fig. 13 by
Volpe and Cleri's parameterization [4]

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