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Periodic DFTB for supported clusters : Implementation and application to benzene dimers deposited on graphene

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Abstract: The interest for properties of clusters deposited on surfaces has grown in the recent years. In this framework the Density Functional based Tight Binding (DFTB) method appears as a promising tool due to its ability to treat extended systems at the quantum level with a low computational cost. We report the implementation of periodic boundary conditions for DFTB within the deMonNano code with *k*-points formalism and corrections for intermolecular interactions. The quality of the DFTB calculations is evaluated by comparison with dispersion-corrected DFT calculations. Optimized lattice properties for a graphene sheet and graphite bulk are in agreement with reference data. The deposition of both benzene monomer and dimers on graphene are investigated and the observed trends are similar at the DFT and DFTB levels. Moreover, interaction energies are of similar orders of magnitude for these two levels of calculation. This study has evidenced the high stability of a structure made of two benzene molecules deposited close to each other on the graphene sheet. This work demonstrates the ability of the new implementation to investigate surface deposited molecular clusters properties.

Keywords: Periodic DFTB; Benzene dimers; Graphene

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0. Introduction

The modelling of functional extended surfaces has grown in past decades to investigate, for fundamental and engineering purposes, a large number of phenomena or applications such as e.g. deposition [1], growth and migration [2], 2D assembly [3], catalysis [4], electrocatalysis [5], photocatalysis [6], molecular electronics [7], depollution [8], sensing [9]... Many of these studies have focused on deposited clusters, i.e. finite aggregations of basis elements (atoms or molecules) adsorbed on surfaces. Indeed, the physico-chemical properties of a cluster are distinct from the ones of both the single entities and the infinite cluster (bulk) and strongly depend on the size and structure of the cluster [10]. Understanding and controlling the structuration of deposited clusters could thus allow a precise tuning of their properties.

The theoretical study of clusters deposited on extended surfaces is very challenging due to the size of the space of structural and electronic configurations to be explored and to the high level of computational methods that has to be implemented. Indeed, the a priori unknown nature of the interactions between the cluster building blocks and between the cluster and the surface (with potential charge transfers at the cluster-surface interface) prevents the use of empirical force fields in favor of methods in which the electronic structure is explicitly considered. The very high computational cost of *ab initio* and Density Functional Theory (DFT) methods prohibiting their use for the study of such systems, particularly when dealing with global optimisation or finite-temperature molecular dynamics, one strategy consists in implementing in a periodic formulation approximate quantum mechanical methods. Among them, DFTB is an approximated DFT schemes with a much lower computational cost enabled by the use of

parameterised integrals in a minimal valence basis set [11–14]. There have been several implementations of DFTB within periodic conditions in various codes [15–21], allowing to compute structural, mechanical and electronic properties. In the present work, we report a new implementation of the DFTB scheme for periodic systems within the deMonNano code [22] combined with corrections to describe long range intermolecular interactions.

The model system chosen for assessing the performance of this implementation consists in benzene dimers deposited on a graphene surface. This system is relevant in an astrophysical context as it can be seen as a simple model of Polycyclic Aromatic Hydrocarbons (PAH) clusters adsorbed on large carbonaceous grains or on very large PAHs. Indeed, despite PAHs are expected to be ubiquitous in the interstellar medium [23] and their clusters have been proposed to play a significant role in the interstellar physics and chemistry [24], the structural and energetic property changes induced by their deposition on a surface remain to a large extent unknown. The second motivation for selecting this benchmark system is that a reasonable description of the benzene dimers potential energy surface is challenging even with *ab initio* schemes [25], making it a system of choice to address the quality our approach. This is due to the fine equilibrium between Pauli repulsion, dispersion and coulomb interaction, which drives the competition between parallel and T-shaped structures. In the past, we have shown that the combination of DFTB with empirical dispersion and atomic charges corrections allowed for a proper description of such systems [26].

In this paper, the periodic formulation of DFTB which has been implemented in deMonNano is presented in section 1, with a special focus on the originality of the present scheme with respect to other periodic implementations i.e. its combination with the WMull charge correction approach. Computational details are given in section 2 and the applications to graphene, graphite and benzene monomer and dimers deposited on graphene are discussed in section 3. Finally a conclusion is given in section 4.

1. Methods

1.1. DFTB

The Density Functional based Tight-Binding method (DFTB) can be derived from DFT from several approximations [11,13,14,16,27].

The first one relies on expression of molecular orbitals (MOs) $\phi_i(\mathbf{r})$ as linear combinations of atomic orbital (LCAO)-type basis sets using minimal valence bases χ_μ .

$$\phi_i(\mathbf{r}) = \sum_{\mu} c_{i\mu} \chi_{\mu}(\mathbf{r}) \quad (1)$$

A Taylor expansion of the DFT energy is done as a function of the electronic density, the real density ρ of the system minimizing the Kohn-Sham energy being searched as a perturbation with respect to a reference density ρ_0 ($\rho = \rho_0 + \delta\rho$):

$$E[\rho(r)] = E[\rho_0(\mathbf{r})] + \int \frac{\delta E[\rho(\mathbf{r})]}{\delta \rho(\mathbf{r})} \Big|_{\rho_0} \delta \rho(\mathbf{r}) + \frac{1}{2} \int \int \frac{\delta^2 E[\rho(\mathbf{r})]}{\delta \rho(\mathbf{r}) \delta \rho(\mathbf{r}')} \Big|_{\rho_0} \delta \rho(\mathbf{r}) \delta \rho(\mathbf{r}') + \dots + \frac{1}{p!} \int \int \dots \int \frac{\delta^p E[\rho(\mathbf{r})]}{\delta \rho(\mathbf{r}) \delta \rho(\mathbf{r}') \dots \delta \rho(\mathbf{r}^{(p)})} \Big|_{\rho_0} \delta \rho(\mathbf{r}) \delta \rho(\mathbf{r}') \dots \delta \rho(\mathbf{r}^{(p)}) \quad (2)$$

In the original version, also known as the non self-consistent DFTB (sometimes referred to as zeroth-order DFTB or simply DFTB [11,12]), only the zeroth and first order terms of the Taylor expansion are retained. In the DFTB2 scheme [27], also known as self-consistent charge (SCC) DFTB, and in the DFTB3 scheme [28], the second and third order terms are also taken into account, respectively.

At the DFTB0 level, the potential energy reads :

$$E^{DFTB0} = \sum_{\alpha < \beta} E_{rep}(\mathbf{r}_{\alpha\beta}) + \sum_{i\mu\nu} n_i c_{i\mu} c_{i\nu} H_{\mu\nu}^0 \quad (3)$$

74 with $E_{rep}(\mathbf{r}_{\alpha\beta})$ a repulsive contribution between atoms α and β , n_i the occupation of
 75 the orbital i and $H_{\mu\nu}^0$ the matrix elements associated to the Kohn Sham operator at the
 76 reference density expressed in the atomic basis. Its matrix elements, as well as those
 77 of the atomic overlap matrix S , can be parameterized as only one- or two-body terms.
 78 This is allowed by the definition of the reference density as a superposition of atomic
 79 densities $\rho_0 = \rho_0^\alpha + \rho_0^\beta + \rho_0^\gamma + \dots$ and the reduction of integrals to one- or two-center
 80 terms :

- 81 • $H_{\mu,\nu \in \alpha}^0(\rho_0) \approx H_{\mu\nu}^0(\rho_0^\alpha) \approx \delta_{\mu\nu} \epsilon_{\mu\alpha}$; the atomic orbital energies of the isolated atom α
- 82 • $H_{\mu \in \alpha, \nu \in \beta}^0(\rho_0) \approx H_{\mu\nu}^0(\rho_0^\alpha + \rho_0^\beta)$ which only depends on the distance between the two
 83 corresponding atomic centers : $H_{\mu \in \alpha, \nu \in \beta}^0(\mathbf{r}_\alpha - \mathbf{r}_\beta)$

Focusing from now on the SCC-DFTB level[27], the previous energy expression becomes :

$$E^{SCC-DFTB} = E^{DFTB0} + \frac{1}{2} \sum_{\alpha\beta} \gamma_{\alpha\beta} q_\alpha q_\beta \quad (4)$$

The last term corresponds to the second-order contribution and depends on the electronic density fluctuation $\delta\rho$ represented by atomic charges q_α . $\gamma_{\alpha\beta}$ is a matrix whose diagonal terms are equal to the atomic Hubbard parameters and off-diagonal terms contain the $1/R$ coulomb interaction between atomic charges and an exchange-correlation energy contribution:

$$\gamma_{\alpha\beta} = \int \int \left(\frac{1}{|\mathbf{r} - \mathbf{r}'|} + \left. \frac{\delta^2 E_{xc}}{\delta\rho(\mathbf{r})\delta\rho(\mathbf{r}')} \right|_{\rho_0} \right) F_0^\alpha(\mathbf{r} - \mathbf{r}_\alpha) F_0^\beta(\mathbf{r}' - \mathbf{r}_\beta) d\mathbf{r} d\mathbf{r}' \quad (5)$$

84 where F_0^α is the normalised spatial extension for the excess/default of electrons around
 85 atom α with respect to the neutral atom, assumed here to have no angular dependence.

Since the second-order term contains atomic charges, this introduces a term depending on the charges $H^1(q)$ into the TB operator.

$$(H^0 + H^1(q))C_i = \epsilon_i S C_i \quad (6)$$

with

$$H_{\mu\nu}^1 = \frac{1}{2} S_{\mu\nu} \sum_{\xi} q_\xi (\gamma_{\alpha\xi} + \gamma_{\beta\xi})$$

86 where μ and ν belong to atoms α and β , respectively. As the charges depend on the MO
 87 coefficients $c_{i\mu}$, the new secular equation must be solved self-consistently with respect to
 88 atomic charges, at the origin of the method's name self-consistent-charge (SCC-)DFTB.

In the standard SCC-DFTB version [27], the atomic charges are computed from the density matrix P and the atomic basis overlap S matrix within the Mulliken approximation.

$$q_\alpha = \sum_{\mu \in \alpha} \sum_{\nu} P_{\mu\nu} S_{\mu\nu} \quad (7)$$

with

$$P_{\mu\nu} = \sum_{i\mu} n_i c_{i\mu} c_{i\nu}$$

In previous works, we have shown that atomic charges can be improved by taking into account the bond polarisation, adapting the Charge Model class IV scheme for DFTB [26,29]. This approach, which requires the calculation of Mayer's bond order, is computationally expensive and hardly transferable to a periodic implementation. To

circumvent this bottleneck, we have recently introduced a simpler scheme, named in the following WMull for Weighted Mulliken charges [30], to correct atomic charges with the following expression

$$q_\alpha = \sum_{\mu \in \alpha} \sum_{\nu} P_{\mu\nu} S_{\mu\nu} (1 + t_{\alpha\beta}) \quad (8)$$

$t_{\alpha\beta} = -t_{\beta\alpha}$ is an empirical parameter accounting for a non-symmetric repartition of the electrons between different atomic types, the Mulliken symmetric repartition being recovered for $t_{\alpha\beta} = 0$. The second order contribution to the Kohn Sham operator matrix is modified as follows :

$$H_{\mu\nu}^1 = \frac{1}{2} S_{\mu\nu} \sum_{\xi} q_{\xi} (\gamma_{\alpha\xi} (1 + t_{\alpha\beta}) + \gamma_{\beta\xi} (1 - t_{\alpha\beta})) \quad (9)$$

89 We have shown that this simple scheme provides similar results to those obtained with
90 the Charge Model approach to model clusters of PAHs [31] and water [32].

91 1.2. DFTB for periodic systems

92 The former implementation of periodic DFTB within deMonNano was restricted to
93 the Γ -point approximation only [22]. In the present implementation, the electronic prob-
94 lem is searched self consistently after defining a set of \mathbf{k} -points in the reciprocal space. A
95 step of the self-consistent scheme consists in solving separately the secular equations
96 for each \mathbf{k} -point to obtain the molecular orbitals $\phi_i^{\mathbf{k}}$. Molecular orbitals obtained for all
97 \mathbf{k} -point are then used to build the total electronic density, the latter being used as an
98 input for the next self-consistent step.

99

For a given \mathbf{k} -point, the molecular orbitals $\phi_i^{\mathbf{k}}$ must full-fill the Bloch-Theorem, that is

$$\hat{T}_{\mathbf{R}} \phi_i^{\mathbf{k}} = e^{i\mathbf{k}\mathbf{R}} \phi_i^{\mathbf{k}}(\mathbf{r}) \quad (10)$$

where $\hat{T}_{\mathbf{R}}$ is the operator associated to a translation of \mathbf{R} , where \mathbf{R} is a vector connecting two unit cells. This is achieved by expanding the MOs on an basis of Bloch functions built from the real space atomic orbitals.

$$\phi_i^{\mathbf{k}}(\mathbf{r}) = \sum_{\mathbf{k}} c_{i\mu}^{\mathbf{k}} \chi_{\mu}^{\mathbf{k}}(\mathbf{r})$$

with

$$\chi_{\mu}^{\mathbf{k}}(\mathbf{r}) = \frac{1}{\sqrt{N}} \sum_{\mathbf{N}} e^{i\mathbf{k}\mathbf{R}_{\mathbf{N}}} \chi_{\mu}(\mathbf{r} - \mathbf{R}_{\mathbf{N}}) \quad (11)$$

where the infinite sum relies on all the possible translation from the main unit cell to any of the other ones. The overlap and Kohn Sham operator matrices expressed in this basis can be written from their real-space equivalent making use of the following transformation :

$$H_{\mu\nu}^{\mathbf{k}} = \sum_{\mathbf{N}} e^{i\mathbf{k}\mathbf{R}_{\mathbf{N}}} H_{\mu\nu}(\mathbf{r}_{\alpha} - \mathbf{r}_{\beta} - \mathbf{R}_{\mathbf{N}}) = \sum_{\mathbf{N}} e^{i\mathbf{k}\mathbf{R}_{\mathbf{N}}} (H_{\mu\nu}^0(\mathbf{r}_{\alpha} - \mathbf{r}_{\beta} - \mathbf{R}_{\mathbf{N}}) + H_{\mu\nu}^1(\mathbf{r}_{\alpha} - \mathbf{r}_{\beta} - \mathbf{R}_{\mathbf{N}}))$$

and

$$S_{\mu\nu}^{\mathbf{k}} = \sum_{\mathbf{N}} e^{i\mathbf{k}\mathbf{R}_{\mathbf{N}}} S_{\mu\nu}(\mathbf{r}_{\alpha} - \mathbf{r}_{\beta} - \mathbf{R}_{\mathbf{N}}) \quad (12)$$

100 where μ and ν belong to atoms α and β , respectively.

In the previous expressions, the matrix elements of H^0 and S are easily obtained from the DFTB Slater Koster tables and rapidly vanish for large values of $\mathbf{R}_{\mathbf{N}}$. The first

order contribution to $H_{\mu\nu}$ is also short range with respect to $(\mathbf{r}_\alpha - \mathbf{r}_\beta - \mathbf{R}_N)$ but contains an infinite long range coulomb sum :

$$H_{\mu\nu}^{1,\mathbf{k}}(\mathbf{r}_\alpha - \mathbf{r}_\beta - \mathbf{R}_N) = \frac{1}{2} S_{\mu\nu}(\mathbf{r}_\alpha - \mathbf{r}_\beta - \mathbf{R}_N) \sum_{\xi} \sum_N q_{\xi} (\gamma_{\alpha\xi}(\mathbf{r}_\alpha - \mathbf{r}_{\xi} - \mathbf{R}_N) + \gamma_{\beta\xi}(\mathbf{r}_\beta - \mathbf{r}_{\xi} - \mathbf{R}_N)) \quad (13)$$

In practice, this infinite sum is replaced by an Ewald summation. The secular equation is solved for each \mathbf{k} -point :

$$H^{\mathbf{k}} C_i^{\mathbf{k}} = \epsilon_i^{\mathbf{k}} S^{\mathbf{k}} C_i^{\mathbf{k}} \quad (14)$$

101 The eigenvalues $\epsilon_i^{\mathbf{k}}$ resulting from all the \mathbf{k} -point secular equations are then sorted
102 in ascending order to drive the determination of $n_i^{\mathbf{k}}$, the orbital occupation number
103 following either a canonical occupation or a Fermi distribution.

The density matrix can therefore be computed for each \mathbf{k} -point

$$P_{\mu\nu}(\mathbf{k}) = \sum_i n_i^{\mathbf{k}} c_{i\mu}^{\mathbf{k}*} c_{i\nu}^{\mathbf{k}} \quad (15)$$

104 We follow the approach of reference [15], which consists in building the real space
105 density matrix and computing atomic charges in the real space. The real space density
106 matrix is obtained by summing over the \mathbf{k} -points :

$$P_{\mu\nu}(\mathbf{R}_N) = \sum_{\mathbf{k}} P_{\mu\nu}(\mathbf{k}) e^{-i\mathbf{k}\mathbf{R}_N} \quad (16)$$

and Mulliken charges are then computed as follows :

$$q_\alpha = \sum_{R_N} P_{\mu\nu}(\mathbf{R}_N) S_{\mu\nu}(\mathbf{r}_\alpha - \mathbf{r}_\beta - \mathbf{R}_N) \quad (17)$$

107 and used as inputs for the next SCC cycle.

The simple WMull correction to Mulliken charges can be generalised to the periodic equations replacing equation 17 and 13 by

$$q_\alpha = \sum_{R_N} P_{\mu\nu}(\mathbf{R}_N) S_{\mu\nu}(\mathbf{r}_\alpha - \mathbf{r}_\beta - \mathbf{R}_N) (1 + t_{\alpha\beta}) \quad (18)$$

108 and

$$H_{\mu\nu}^{1,\mathbf{k}}(\mathbf{r}_\alpha - \mathbf{r}_\beta - \mathbf{R}_N) = \frac{1}{2} S_{\mu\nu}(\mathbf{r}_\alpha - \mathbf{r}_\beta - \mathbf{R}_N) \sum_{\xi} \sum_N q_{\xi} (\gamma_{\alpha\xi}(\mathbf{r}_\alpha - \mathbf{r}_{\xi} - \mathbf{R}_N) (1 + t_{\alpha\beta}) + \gamma_{\beta\xi}(\mathbf{r}_\beta - \mathbf{r}_{\xi} - \mathbf{R}_N) (1 - t_{\alpha\beta}))$$

109 2. Computational details

110 2.1. DFTB calculations

Different DFTB parameters are available in the literature (cf. website www.dftb.org), depending on the choices made during the parameterization procedure such as the DFT functional, the basis sets type (Gaussian, Lorentzian) used to generate the atomic orbitals, the confinement imposed on these orbitals, the reference data used to compute the repulsive contribution E_{rep} and, for the second and third order DFTB, the values of the atomic Hubbard parameters and their derivatives. In this work, we are working with the BIO DFTB set of parameters [27] provided within the deMonNano code (equivalent to the mio parameters from the website www.dftb.org).

Dispersion interaction corrections can be introduced in the DFTB Hamiltonian using an empirical diatomic formulae. Two types of corrections are available in the deMonNano code and will be tested in the next section. The first one (hereafter labelled D1) is a

Lennard Jones type potential with short range corrections introduced by Zhechkov *et al.* [33]. The second one (hereafter labelled D2 [26]) is given by

$$E_{\text{disp}} = - \sum_N \sum_{\alpha, \beta} f_{\text{damp}}(|\mathbf{r}_\alpha - \mathbf{r}_\beta - \mathbf{R}_N|) \frac{C_{AB}^6}{|\mathbf{r}_\alpha - \mathbf{r}_\beta - \mathbf{R}_N|^6} \quad (19)$$

111 where f_{damp} is a damping function screening the short range contribution and $C_{\alpha\beta}^6$
 112 an empirical parameter (see [26] for details). In both cases, only the van der Waals
 113 contributions larger than 10^{-5} Hartree are taken into account, in order to limit the
 114 number N of boxes involved in the sum.

115 When calculations are performed with the WMull scheme, a value of $t_{CH} = 0.245$ has
 116 been determined to provide the atomic charges for the benzene molecule in agreement
 117 with reference calculations (see tables and discussion in reference [26]).

118 Regarding convergency criterions, we have used a tolerance of 10^{-8} for the atomic
 119 charges during the SCC process and 5.10^{-6} Hartree/Bohr for the largest gradient for
 120 local optimizations.

121 2.2. DFT calculations

122 Dispersion corrected DFT calculations were performed under periodic boundary
 123 conditions using the Vienna *ab initio* simulation package (VASP [34–36]) together with
 124 PAW pseudopotentials [37,38] and the DFT-D3 semiempirical dispersion-corrected func-
 125 tional in its zero-damping formalism [39]. This functional has been chosen as it has been
 126 reported as a relevant choice for studies involving graphene [40]. A conjugate-gradient
 127 algorithm was used to relax the ions and the convergence criterion was set up so that
 128 the maximum atomic force was less than $0.01 \text{ eV } \text{\AA}^{-1}$, all atoms being allowed to relax
 129 unconstrained. To avoid interactions between the benzene monomers/dimers and their
 130 periodic images, a cubic box measuring 50\AA on a side was used for isolated systems.
 131 For supported ones, the calculations were performed on a $29.92 \text{\AA} \times 34.55 \text{\AA}$ graphene
 132 surface (these values having been calculated on the basis of the graphene equilibrium
 133 lattice parameter reported in section 3.1) containing 392 carbon atoms placed in a 50
 134 \AA high simulation box to avoid any interaction between the adsorbed molecule and
 135 the underside of the graphene sheet of the upper periodic box. Since the size of the
 136 supercell was large enough, the Brillouin zone sampling in reciprocal space restricted
 137 to the Γ -point was sufficient to ensure good convergence of the total energy, except
 138 for the calculations aiming at determining the equilibrium parameters of the graphite
 139 bulk which required a $1 \times 1 \times 5$ k-points grid. A plane-wave kinetic energy cut-off of 450
 140 eV was employed. For dealing with the partial occupancies around the Fermi level, a
 141 Methfessel-Paxton smearing was used with $\sigma = 0.2 \text{ eV}$ [41].

142

143 3. Results and discussion

144 In this section, we discuss the results of the DFTB calculations. All details about
 145 the dispersion-corrected DFT calculation performed to evaluate the quality of the DFTB
 146 calculations are given in the previous section, so that the computational details reported
 147 below only concern the DFTB calculations.

148 3.1. Graphene and Graphite

149 In order to model graphene, we have first optimized the lattice parameter, working
 150 with a periodic box containing 392 atoms ($\sim 30 \text{\AA} \times 35 \text{\AA} \times 50 \text{\AA}$). For such a large simulation
 151 box, the Γ -point approximation remains valid as the energy varies by less than $3.4 \cdot 10^{-4}$
 152 eV/atom (0.0008%) when going from one to three k-points in the x and y directions, and
 153 by less than $1.3 \cdot 10^{-4}$ eV/atom (0.0003%) when going from three to five k-points. The
 154 equilibrium C-C bond length determined with one or three k-points in x and y directions
 155 are the same at the precision of 10^{-3}\AA . Values of $1.430 \pm 0.001 \text{\AA}$ and $1.46 \pm 0.001 \text{\AA}$ were

156 obtained with the DFTB-D1 and DFTB-D2 methods, respectively (see Table 1). These
 157 values are slightly larger than the value of 1.421 Å previously reported by Zhechkov *et al.*
 158 using the Γ -point approximation and a smaller unit cell [33]. The DFTB-D2 values gives
 159 the best agreement with the C-C bond length obtained at the DFT-D3 level (1.425 ± 0.001
 160 Å) as well as with the experimental values (1.42 Å).

161 The graphite bulk has been modeled by including two layers of the previously
 162 defined graphene sheet in the periodic box. In order to determine the appropriate
 163 number of k-points in the z direction (perpendicular to the graphene planes), we have
 164 performed single point energy calculations for an interlayer distance of 3.5 Å, chosen
 165 because it corresponds to the DFT-D3 one (3.488 Å, see Table 1), with one k-point in
 166 the x and y directions. The total energy varies by $2 \cdot 10^{-4}$ eV/atom (0.0004%) when the
 167 number of k-points is increased from one to three in the z direction, and then remains
 168 constant for calculations performed with five, seven and nine k-points in the z-direction.
 169 We have thus determined the equilibrium parameters of the graphite bulk with three
 170 k-points in the z directions (Table 1). Using either one or three k-points in the x and
 171 y directions led to the same results at the target precision of 0.001 Å. The DFTB-D1
 172 and DFTB-D2 C-C bond length are reduced by 0.001 Å with respect to their values in
 173 the graphene sheet, a trend also observed at the DFT-D3 level. The DFTB-D1 interlayer
 174 equilibrium distance (3.383 ± 0.001 Å) is in agreement with both the value of reference
 175 [33] with a four layers model in the Γ -point approximation (3.38 Å) and the experimental
 176 data (3.356 Å). The interlayer distance is reduced to 3.131 ± 0.001 Å at the DFTB-D2 level.
 177 With respect to theoretical references (DFT-D3, RPA and QMC) and experimental values,
 178 we can conclude that the DFTB-D1 method gives better quality results for the graphite
 179 interlayer distances, while the the DFTB-D2 method prevails for the C-C bond length.

Table 1. Graphene and Graphite structural data (in Å). *In these computational studies the d_{C-C} distance was fixed to the one determined experimentally. ** Differences between the two DFTB-D1 calculations are detailed in the text.

Methods	$d_{C-C}^{Graphene}$	$d_{C-C}^{Graphite}$	$d_{interlayer}^{Graphite}$
DFTB-D1**	1.430 ± 0.001	1.429 ± 0.001	3.383 ± 0.001
DFTB-D2	1.426 ± 0.001	1.425 ± 0.001	3.131 ± 0.001
DFTB-D1**	1.421 [33]	1.421 [33]	3.38 [33]
DFT-D3	1.425 ± 0.001	1.424 ± 0.001	3.488 ± 0.001
RPA		1.42* [42]	3.34* [42]
QMC		1.42* [43]	3.426* [43]
Expt	1.42 [44]	1.422 [45,46]	3.356 [45,46]

180 3.2. Benzene supported on Graphene

181 We performed local structural optimisation for systems consisting of an isolated
 182 benzene molecule deposited on top of a graphene monolayer. On the basis of the
 183 results obtained in section 3.2, the calculations have been performed in the Γ -point
 184 approximation, the initial structures corresponding to a benzene molecule deposited in
 185 the proper orientation on the optimized graphene layer. Four different configurations
 186 have been probed, labelled a_1, a_2, a_3, a_4 , which can be visualised in Figure 1. The three
 187 first ones correspond to the structures labelled a_1, a_2, a_3 in reference [47]; hollow, bridge,
 188 top in reference [48] and AA, SP and AB in reference [49]. The last structure a_4 was
 189 named top-rot in reference [48] and also studied in reference [50].

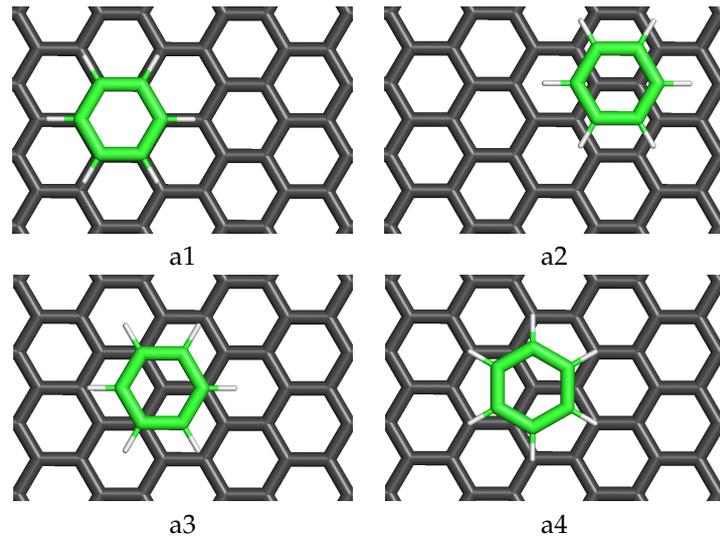


Figure 1. Isolated benzene molecule deposited on graphene.

Table 2. Binding energies of benzene on graphene in eV. The experimental binding energy of a benzene molecule on a graphite surface is -0.50 ± 0.08 eV [51].

Method	a1	a2	a3	a4
DFTB-D1	-0.639	-0.652	-0.654	-0.651
DFTB-D2	-0.439	-0.448	-0.447	-0.451
DFT-D3	-0.428	-0.450	-0.453	-0.450
LDA [47]	-0.16	-0.23	-0.24	
ω B97X-D [49]			-0.47	
optB86b-vdw [50]				-0.5
vdW-DF1 [48]			-0.49	
vdW-DF2 [48]			-0.43	
Expt. Saturated Adsorption Enthalpy [50]				-0.5

190 DFTB-D1 and DFTB-D2 results agree on the main trends, also present at the DFT-D3
 191 level : three almost degenerated structures, namely a_2 , a_3 and a_4 , and the a_1 structure
 192 being less stable by about 0.012(DFTB-D2)/0.015(DFTB-D1)/0.025(DFT-D3) eV (see Table
 193 2). The absolute binding energies provided by the DFTB-D2 scheme are in very good
 194 agreement with DFT results (apart from LDA) and experimental measurements. The
 195 DFTB-D1 scheme gives poorer results, with an overestimation of the binding energies of
 196 about 35% (~ 0.2 eV).

197 Regarding the z-separation between the benzene monomer and the graphene sheet (see
 198 table 3), DFTB-D1 and DFTB-D2 clearly underestimate the benzene-graphene distance by
 199 ~ 0.35 Å. However, it should be noted that z-separations calculated with the dispersion
 200 corrected DFT functionals also significantly differ from each other by up to 0.25Å.

Table 3. Z-separation of Benzene on Graphene (in Å).

Method	a1	a2	a3	a4
DFTB-D1	3.152	3.133	3.130	3.138
DFTB-D2	3.080	3.073	3.081	3.054
DFT-D3	3.465	3.382	3.358	3.415
ω B97X-D [49]	3.36	3.30	3.35	
vdW-DF1 [48]			3.6	
vdW-DF2 [48]			3.5	

201 3.3. Benzene dimers in vacuum

202 Reproducing the benzene dimer potential energy surface is a challenging task for
 203 DFT schemes, due to the fine competition between the various contributions to the total
 204 energy. This is even more true for approximated schemes like the DFTB method. Briefly,
 205 three characteristic structural families can be identified, namely sandwich (S), parallel-
 206 displaced (PD) and T-shaped (T), each one presenting several minima. In this work, the
 207 sandwich eclipsed (SE) structure has been selected to represent the sandwich family. The
 208 PD family is represented by the isomer shown in Figure 2 as it was previously reported
 209 to be the most stable of this family at the DFTB level. Two additional structures were
 210 considered to account for the T-shaped family, namely the T and Csoa isomers (corre-
 211 sponding to T4 and Csoa in reference [26]), which only differ by a slight displacement of
 212 the top benzene from a symmetric position toward a position over a carbon atom. These
 213 two structures were previously reported to be degenerated as their energies differ by less
 214 than 10^{-3} eV at the DFTB level and the present DFT-D3 calculations show a difference
 215 of $8 \cdot 10^{-3}$ eV in favor of the Csoa isomer.

216
 217 The binding energies for the different optimized structures are reported in Table 4
 218 for both the DFTB, DFT-D3 and *ab initio* reference calculations (CCSD(T) and SAPT). In
 219 the case of the T-shaped family, only one of the two studied isomers could be located on
 220 the DFTB potential energy surfaces, namely Csoa with the DFTB-D1 method and T with
 221 the DFTB-D2 one. DFT-D3 and *ab initio* reference calculations agree on the fact that T-
 222 shaped and PD structures are close in energy and by far more stable than the SE structure.
 223 This ordering is not reproduced at the DFTB-D1 nor at the DFTB-D2 level, i.e. for the
 224 two dispersion corrections investigated in the absence of atomic charge corrections,
 225 because the SE structure is found to be almost degenerated with the PD structure and
 226 the T-shaped isomer is found to be the less stable one in both cases. Introducing the
 227 WMull charge correction detailed in section 1 with the D1 dispersion (DFTB-D1-WMull)
 228 makes the PD structure the most stable but the T-shaped structure remains the less stable.
 229 Finally, the DFTB-D2-WMull method provides a correct picture with the T-shaped and
 230 PD isomers being close in energy and more stable than the SE isomer. In addition, the
 231 binding energies are of the same order as those of the reference calculations.

Table 4. Binding energies for benzene dimer bz_2 in eV.

Method	T-shaped	PD	SE
DFTB-D1	Csoa -0.126	-0.194	-0.192
DFTB-D1-WMull	Csoa -0.140	-0.162	-0.148
DFTB-D2	T -0.099	-0.135	-0.132
DFTB-D2-WMull	T -0.113	-0.104	-0.086
DFT-D3	Csoa -0.146	-0.152	-0.106
	T -0.138		
CCSD(T) [25]	Csoa -0.12	-0.12	-0.07
SAPT [25]	Csoa -0.12	-0.12	-0.08

232 3.4. Benzene dimers supported on Graphene

233 It appeared from the previous sections that the DFTB-D2-WMull methods is the
 234 best choice for modelling at the DFTB level both an isolated benzene molecule deposited
 235 on a graphene layer and a benzene dimer in vacuum. This level of theory has thus been
 236 chosen to conduct the calculations aiming at investigating the deposition of a benzene
 237 dimer on a graphene sheet. Among the possible adsorption modes of a benzene molecule
 238 on a graphene monolayer, we selected the a_4 one as it was found to be the most stable at
 239 this level of theory (see section 3.2) and added a second benzene unit to form T, PD or
 240 SE configurations. The optimised structures, obtained in the Γ -point approximation, are
 241 shown in Figure 2.

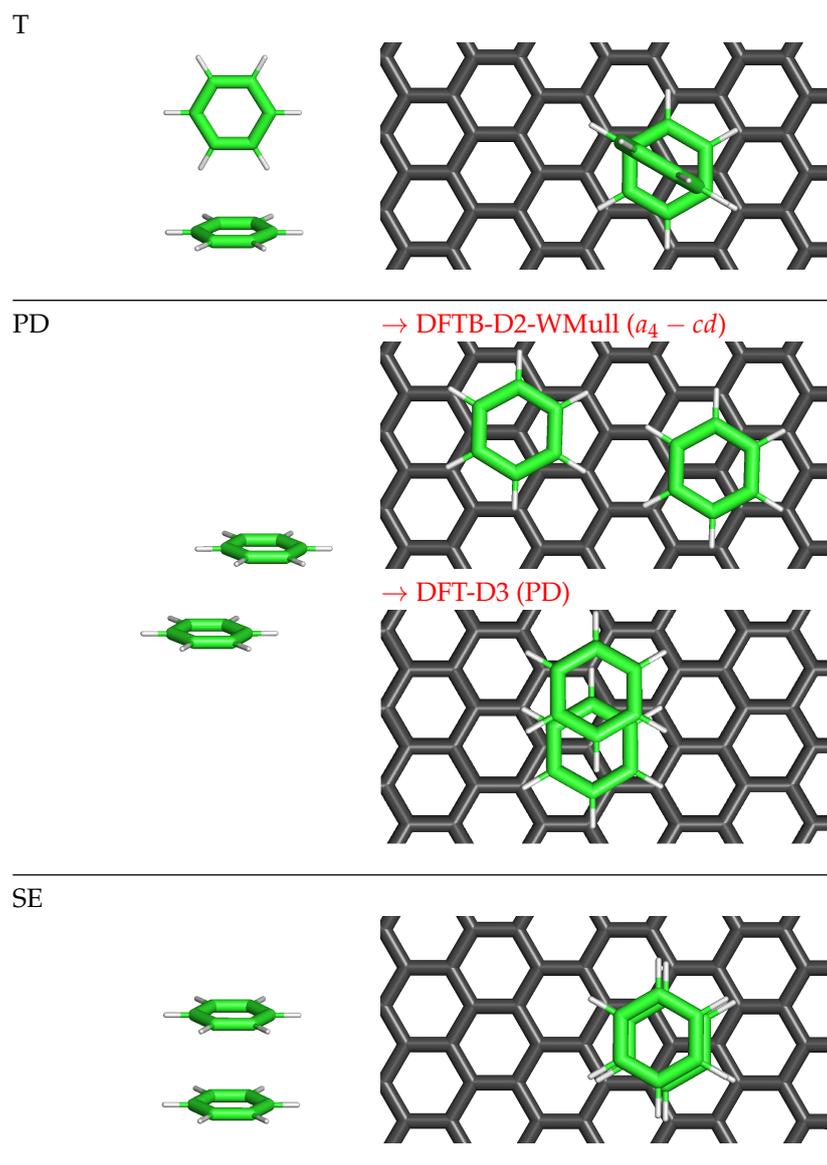


Figure 2. Benzene dimers bz_2 in vacuum and deposited on graphene

242 It can be seen that T and SE structures were preserved during the optimisation. On
 243 the opposite, the deposited PD dimer was stable at the DFT-D3 level only and led to a
 244 dissociated configuration at the DFTB-D2-WMull level in which the two benzene units
 245 are close to each other, both exhibiting a a_4 adsorption configuration on the graphene
 246 sheet. This configuration is hereafter named $a_4 - cd$ (close deposition on a_4 adsorption
 247 sites). In this latter, the hydrogen atom of each benzene molecule is pointing in-between
 248 two hydrogen atoms of the other benzene unit. Such a configuration limits the coulomb
 249 repulsion between the positively charged hydrogen atoms while preserving some attrac-
 250 tive dispersion interactions.

251

Table 5. Binding energy of benzene dimers bz_2 on graphene in eV. * No value is reported at the DFTB-D2-WMull level for PD as the optimisation led to the $a_4 - cd$ structure.

Dissociation ref.	DFTB-D2-WMull				DFT-D3			
	T	PD*	$a_4 - cd$	SE	T	PD	$a_4 - cd$	SE
graphene + 2bz	-0.586	↳	-0.929	-0.573	-0.605	-0.624	-0.938	-0.583
graphene + bz_2	-0.473	↳	-	-0.487	-0.467	-0.473	-	-0.478
graphene@bz + bz	-0.135	↳	-0.478	-0.122	-0.156	-0.175	-0.489	-0.134
graphene@2bz	0.316	↳	-0.027	0.329	0.294	0.275	-0.039	0.316

252 The binding energies associated to the optimized structures are reported in Table
253 5 making use of various choices for the potential energy zeroth reference. In the first
254 line (graphene + 2bz), the reference energy is the sum of the energies for an optimized
255 graphene monolayer and two isolated benzene molecules. It appears that, at the DFT
256 and DFTB levels, the most stable configuration relies on the dissociation of the benzene
257 dimer to form the $a_4 - cd$ structure. The energetic difference between the T-shaped
258 structure and the less stable SE dimer is twice smaller (0.013 eV vs 0.027 eV at the DFTB
259 level and 0.022 eV vs 0.052 eV at the DFT level) when the dimer is deposited with respect
260 to the gas phase condition. This is probably due to the interaction between the graphene
261 surface and the benzene molecule that is furthest from the surface, which is favored in
262 the sandwich configuration. In the second line (graphene + bz_2), the reference energy
263 is that of an isolated graphene sheet plus that of the optimized dimer in its T, PD or SE
264 form, respectively. The gained energy for the non-dissociating dimers (T and SE) are
265 similar (~ 0.46 - 0.49 eV, for DFT and DFTB values), only very slightly above the binding
266 energy of a single benzene with graphene (0.45 eV for DFT and DFTB values). In the
267 third line (graphene@bz + bz), the reference energy is that of a benzene deposited on
268 a graphene sheet plus that of an isolated benzene. It differs from the isolated dimers
269 by 0.022 eV for the T-shaped structure and 0.036 eV for the SE structure at the DFTB
270 level and 0.018 eV and 0.028 eV at the DFT level. The larger value obtained for the
271 SE dimer can be, again, related to the expected larger interaction energy between the
272 graphene sheet and the second further benzene unit in the SE configuration. The last
273 line (graphene@2bz) compares the binding energies with the one of a system where two
274 benzene molecules would be deposited in a_4 configurations without interaction between
275 them. This configuration appears to be more stable than those corresponding to the
276 deposition of a T-shaped or SE dimer. The negative sign obtained for the $a_4 - cd$ structure
277 shows that the latter is the most stable investigated configuration as it maximizes the
278 interaction between each benzene molecule and the graphene surface while maintaining
279 some stabilizing intermolecular interactions between the two benzene units. Again, this
280 conclusion holds at both the DFT and DFTB levels. It should also be noted that the
281 values of the interaction energies are of similar order for these two levels of calculation.

282 4. Conclusions

283 In the present paper, we have reported a new implementation of periodic boundary
284 conditions in the DFTB code deMonNano, as only the Γ -point approximation was
285 available in the previous version of the code. An originality of our scheme is the
286 inclusion of atomic charge corrections which improves the description of intermolecular
287 coulomb interactions. It allows to recover a reasonable description of molecular clusters,
288 as shown in the particular case of benzene dimers in this work. Dispersion corrections are
289 also mandatory for a proper description of such interactions and we have benchmarked
290 two empirical correction schemes. One of them gives the best C-C bond distance in
291 graphene and graphite whereas the second one provides the best interlayer distance in
292 graphite, according to previous reference calculations and experiments, as well as with
293 new DFT calculations performed with the DFT-D3 dispersion corrected functional.

294 Benzene monomer and dimers have been optimized at the DFTB and DFT levels,
295 providing the following similar trends. For the deposition of a single benzene monomer

296 on a graphene sheet, the adsorption of the benzene centered on top of graphene carbon
297 atom or C-C bond leads to almost degenerated structures, by far more stable than
298 the superimposition of the benzene on top of a graphene aromatic cycle. The most
299 stable one at the DFTB level has been selected to build initial conditions for benzene
300 dimers deposition on graphene. The structural energy gap between the most stable
301 T-shaped dimer and less stable Sandwich-like dimer is divided by two when the cluster
302 is supported on graphene. The supported Parallel-Displaced structure appeared to be
303 not stable at the DFTB level, leading to a structure where the two benzene are deposited
304 close to each other on the graphene surface. This structure is the most stable one of
305 our calculations at DFT and DFTB levels, also more stable than the deposition of two
306 benzene monomer at infinite distance, which is not the case of the deposited sandwich or
307 T-shaped dimers. As a conclusion, we have shown the ability of the new implementation
308 to characterize properties of molecular clusters deposited on surfaces.

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