Recursive open boundary and interfaces method for material property predictions

James Charles[1], Sabre Kais[2,3], Tillmann Kubis[1,4,5,6]

[1] *School of Electrical and Computer Engineering, Purdue University, West Lafayette, IN, USA*

[2]*Department of Physics and Astronomy, Purdue University, West Lafayette, IN, USA*

[3]*Department of Chemistry, Purdue University, West Lafayette, IN, USA*

[4]*Network for Computational Nanotechnology, Purdue University, West Lafayette, IN, USA*

[5]*Purdue Center for Predictive Materials and Devices, West Lafayette, IN, USA*

[6]*Purdue Institute of Inflammation, Immunology and Infectious Disease, West Lafayette, IN, USA*

tkubis@purdue.edu

Simulations are essential to accelerate the discovery of new materials and to gain full understanding of known ones. Although hard to realize experimentally, periodic boundary conditions are omnipresent in material simulations. We introduce ROBIN (recursive open boundary and interfaces) [1], the first method allowing open boundary conditions in material and interface modeling. The computational costs are limited to solving quantum properties in a focus area which allows explicitly discretizing millions of atoms in real space and to consider virtually any type of environment (be it periodic, regular, or random). Figure 1 verifies the local density of states resulting of an all-real space ROBIN calculation of pristine graphene against analytical results. The impact of the periodicity assumption is assessed in detail with silicon dopants in graphene. Graphene was confirmed to produce a band gap with periodic substitution of 3% carbon with silicon in agreement with published periodic boundary condition calculations [2]. Instead, 3% randomly distributed silicon in graphene only shifts the energy spectrum. The predicted shift agrees quantitatively with published experimental data [2]. The shift is a linear function of the Si concentration (see Fig. 3) in agreement with the small linear response a few-percent Si perturbation should yield.

The ROBIN method allows to consider the interface between graphene alloyed with 3% randomly and 3% periodically distributed Si. Figure 4 shows the significant density of states difference these only stoichiometrically identical systems show.

In summary, we show that assuming periodicity elevates a small perturbation of a periodic cell into a strong impact on the material property prediction. Periodic boundary conditions can be applied on truly periodic systems only. More general systems should apply an open boundary method for reliable predictions.

[1] Charles J. et al., ACS Materials Lett. **2**, 247 (2020)

[2] Zhang, S. J. et al., Nanoscale **8**, 226 (2015)

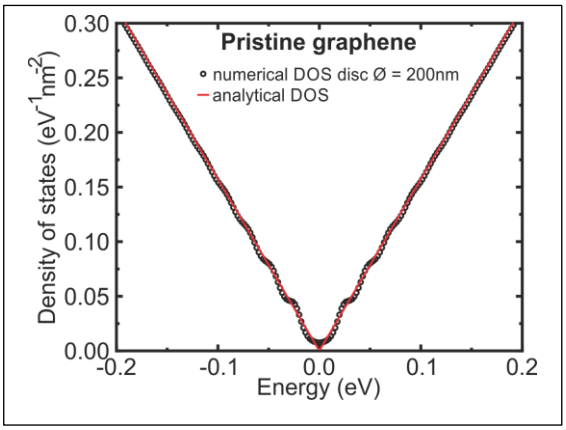

Fig.1: Verification of the ROBIN method against analytical results: The numerical density of states resulting of the ROBIN method (symbols) of graphene discs agree better with the analytical density of states (line) with larger discretized disc diameter.

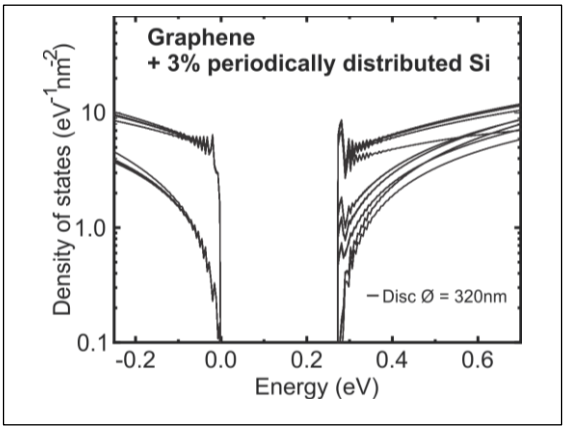

Fig.2: The density of states of graphene with 3% periodically distributed silicon solved with the ROBIN method reproduces the 0.28eV band gap of Ref.19 when the on-site energy of Si is chosen as 4.75eV. The 282 individual atoms considered in the DOS-solution area fall into 9 distinct groups of DOS lines – corresponding to the 9 different chemical atom environments in the graphene + 3% Si unitcell.

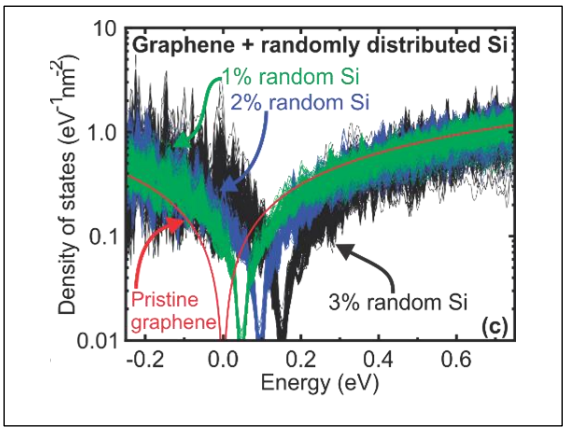

Fig.3: The DOS solved in the ROBIN method of randomly distributed Si atoms in graphene does not show a bandgap. Instead, increasing Si content shifts the DOS to higher energies by about 47meV per Si-percentage (i.e. about 1% of the assumed onsite energy difference of carbon and silicon atoms). This value is in quantitative agreement with the experimental observations in Ref.2

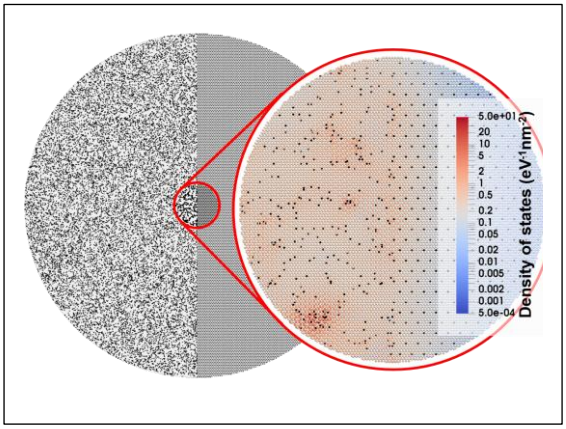

Fig.4: (left) 200nm disc of graphene (carbon atoms are white) with 3% Si atoms (black) distributed randomly on the left, and periodically on the right half of the disc. (right) Electronic density of states of the center 25 nm of the 200nm graphene disc solved with open boundary conditions at 10meV above the Dirac point of pristine graphene. Carbon atoms are colored according to the electronic DOS, silicon atoms are black. The electronic DOS shows domain formation in the left half and electronic tunneling into the right half of the disc.

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