A New Method for Bandstructure Calculation and Its Application to Edge Termination Effects in Graphene

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Understanding the impact of surface terminations on the electronic properties of materials is crucial for designing tailored electronic and optoelectronic applications. In this study, we employ a recently developed real-space bandstructure calculation method—"A Method of Calculating Bandstructure in Real-Space with Application to All-Electron and Full Potential" [1]—to investigate the absolute band energies of graphene with three different passivations: hydrogen (H), fluorine (F), and hydroxyl (OH). Unlike conventional k-space methods, which rely on infinitely periodic boundary conditions and are unable to determine absolute band energies, this novel approach enables direct computation of band energies relative to the vacuum level by considering the potential of an extended finite system. The method leverages the combined contributions of nuclear and electron-electron interaction potentials, effectively eliminating the divergence of long-range effects and allowing for the extraction of a converged net potential within the unit cell. After obtaining the net potential from an extended finite system through self-consistent calculations, the band structure can be determined non-self-consistently using Bloch-periodic boundary conditions within the unit cell, enabling the identification of core, valence, and conduction bands.

The starting point is the Density Functional Theory (DFT) and Kohn-Sham one-electron equation described by v-representability to project in real space the one-electron wavefunction as follows:

$$-\frac{1}{2}\nabla^2\phi(r)+V_{nuclei}(r)\phi(r)+V_{hxc}(r)\phi(r)=\varepsilon\phi(r), \tag{1}$$

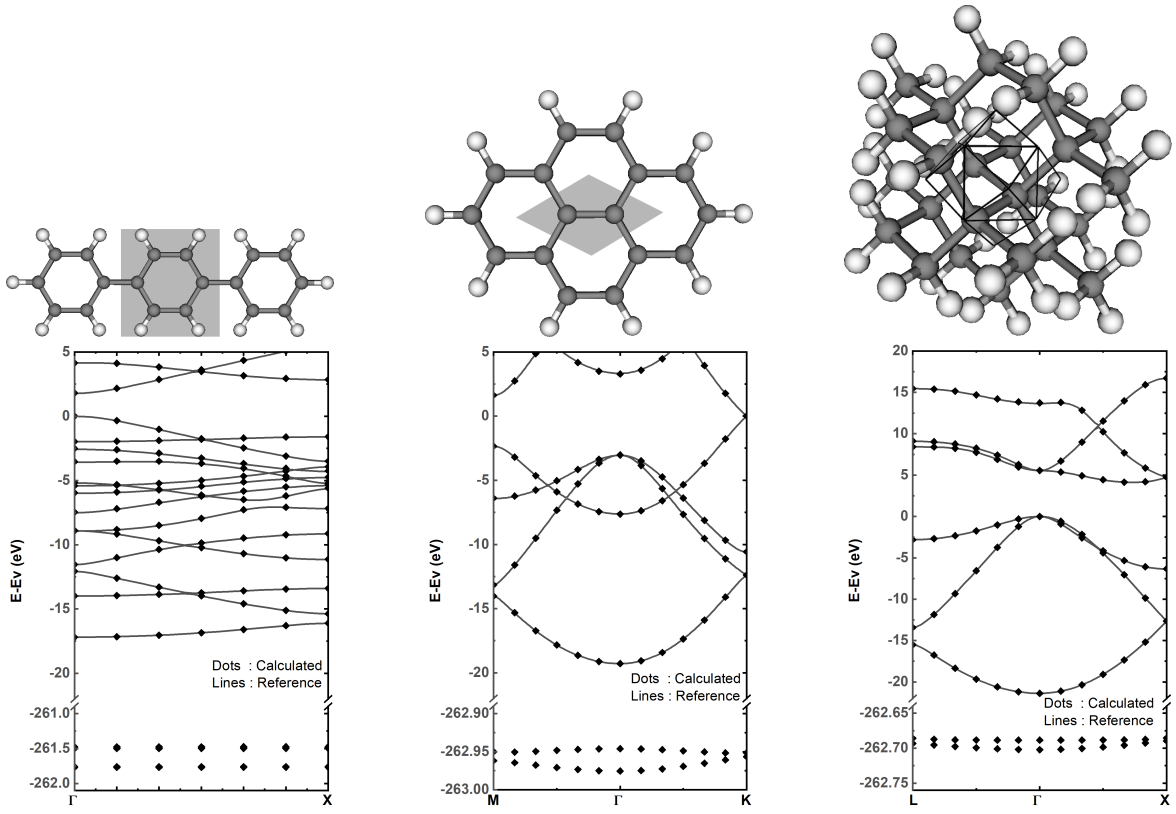
where V_{hxc} is the Hartree, Exchange and Correlation terms. In the case of infinitely repeated unit cells model, the nuclear potential $V_{nuclei}(r)$ is composed of an infinitely large number of potentials $V_{nuclei}(R_j-r)$ associated with atom j at position R_j. Therefore, in this model, because of the effect of long-range Coulomb potentials, $V_{nuclei}(r)$ term becomes infinitely large. However, in real situations, electrons are never really experiencing this infinitely large potential, and the potential energy felt by one electron can be better expressed by combining V_{nuclei} and V_{hxc} in equation (1) based on each unit-cell, as follows:

$$-\frac{1}{2}\nabla^2\phi(r)+\sum_{m}^{adjacent}\left\{\sum_{n}\left[V^n_{nuclei}(R_{m,n}-r)+V^n_{hxc}(R_{m,n}-r)\right]\right\}\phi(r)=\varepsilon\phi(r), \tag{2}$$

Using the aforementioned method, the band structure of any 1D, 2D, or 3D material can be computed, with examples illustrated in Fig. (1). We further investigated three distinct edge terminations of graphene, revealing that these terminations induce shifts in its absolute band energies shown in Fig. (2), with variations of up to approximately 0.7 eV among the studied cases. This work represents the first computational comparison and analysis of passivation effects on graphene's absolute band energies, highlighting the effectiveness of this method in accurately capturing such effects.

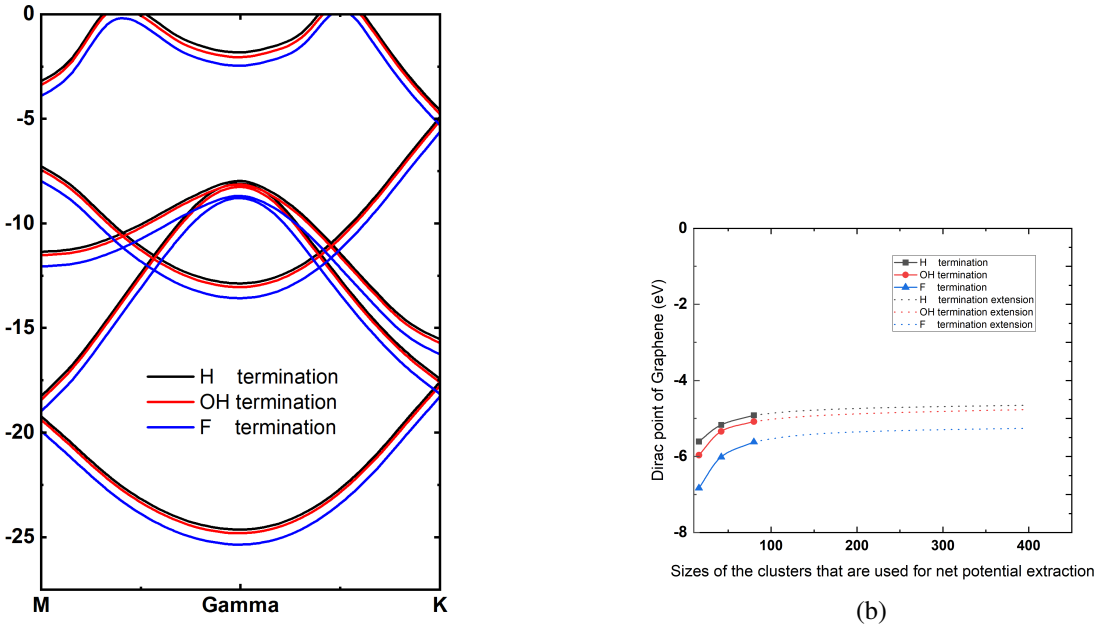
References

[1] Dongming Li, James Kestyn and Eric Polizzi, *A method of calculating bandstructure in real-space with application to all-electron and full potential*, Computer Physics Communications **295**, 109014 (2024).



(a) (b) (c)

Fig. 1: Bandstructure calculations for 1D PPP (a), 2D Graphene (b) and 3D carbon Diamond (c). Our results for valence and conduction bands are compared with references obtained by k-space pseudopotential calculations. Core bands are also presented. The figures on top represent the finite systems that are used to extract the net potentials in their corresponding unit-cells. (Extracted from [1])



(a) (b)

Fig. 2: (a) Bandstructures of Graphene with -H, -OH and -F edge terminations at the LDA-1/2 density funcitonal physical model (energy level is given in eV), (b) Absolute Dirac Point extrapolation