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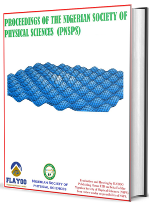

First-principles analysis of electric field, spin–orbit coupling and lithium adsorption in graphene

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ABSTRACT

This study presents a first-principles examination of the effects of external electric fields (EEFs) on ion transport and adsorption processes in graphene. The Perdew–Burke–Ernzerhof (PBE) and local modified Becke–Johnson (lmBJ) exchange–correlation functionals, as implemented in WIEN2k, were used to investigate a 4×4 monolayer graphene supercell and lithium adsorption on graphene under electric fields ranging from 0.5 to 5 V/Å. The results indicate that the external electric field and spin–orbit coupling (SOC) modify the electronic structure of graphene, with lmBJ enhancing bandgap resolution. Lithium adsorption generated localised states, improved charge transfer and tuned the energy gap as the external field varied. The findings suggest that controlled electric fields can alter graphene's electronic properties, supporting possible developments in nanoelectronics and energy storage.

Keywords: Graphene, Lithium adsorption, Electric field, Density functional theory.

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1. INTRODUCTION

Graphene, a two-dimensional material composed of a single sheet of carbon atoms arranged in a hexagonal honeycomb lattice, is a semimetal with a zero bandgap at the Dirac cone. It has received considerable interest because of its outstanding electrical, mechanical and chemical properties [1–3]. However, its use in nanoelectronics, sensing and energy-storage devices is restricted by its zero-bandgap nature and weak intrinsic interactions [4].

External electric fields (EEFs), chemical doping, defect engineering and spin–orbit coupling (SOC) are among the methods that have been investigated to modify the electronic structure of graphene [5, 6]. Lithium adsorption has attracted significant attention because of its importance in lithium-ion batteries and its capacity to facilitate charge transfer and electronic reconstruction in graphene-based systems [7–9].

In addition, perpendicular electric fields can change the charge distribution, adsorption energetics and band alignment in two-dimensional materials [10, 11]. However, conventional generalised gradient approximation (GGA) functionals, such as PBE, often underestimate subtle bandgap changes, motivating the use of more advanced exchange–correlation potentials, such as lmBJ, to improve electronic-structure resolution [4, 12].

An EEF, SOC and lithium adsorption each affect the electronic structure of graphene through distinct mechanisms: EEF modi-

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fies band alignment and charge distribution, SOC introduces spin splitting near the Dirac point, and lithium adsorption induces n-type doping by charge transfer to graphene. These effects collectively influence the bandgap, making graphene sheets suitable for nanoelectronics and energy-storage applications [5, 7, 9, 11, 13].

This study presents a unified first-principles analysis of the effects of electric field, SOC and lithium adsorption on graphene, revealing their combined influences on the band structure, density of states and adsorption stability.

2. COMPUTATIONAL DETAILS

Calculations were performed using the full-potential linearised augmented plane wave plus local orbitals (FP-LAPW + lo) method of density functional theory (DFT), as implemented in the WIEN2k package. The GGA, specifically the Perdew–Burke–Ernzerhof (PBE) and local modified Becke–Johnson (lmBJ) functionals, was used to account for exchange–correlation effects. SOC was included specifically in the bandgap calculations for pristine graphene under external electric fields (Section 3.1 and Figure 2); SOC was not applied in the lithium adsorption calculations.

A 4×4×1 graphene supercell containing 32 carbon atoms was used to model pristine graphene. A vacuum spacing of 15 Å was introduced perpendicular to the graphene plane to avoid spurious interactions between periodic images. The product of R_{MT} and K_{MAX} gave the cutoff parameter RK_{MAX}, where R_{MT} denotes the smallest muffin-tin radius of the atoms and K_{MAX} is the maximum value of the reciprocal-lattice vectors used in the plane-wave expansion. For this calculation, the cutoff parameter RK_{MAX} was set to 5.5, which is consistent with typical values reported for carbon-based systems in FP-LAPW calculations and ensures a balance between computational accuracy and efficiency [15]. The reciprocal lattice of graphene is a triangular lattice, resulting in a hexagonal Brillouin zone. A 7 × 7 × 1 k-point mesh in the irreducible part of the first Brillouin zone was used for the calculation. To ensure high computational accuracy, self-consistent convergence criteria of 10^{-6} Ry for energy and 1.0 mRy/Bohr for force were used. Based on this method, the electronic structure was analysed.

An external electric field was applied along the z-direction via a zigzag potential. The graphene sheet was centred at $z = 0.25$, ensuring that the periodic kinks of the sawtooth potential were in the vacuum region, away from the atomic sites. The field strength defined by `EFIELD` directly corresponds to an electric-field value expressed in V/Å, allowing systematic variation in the external perturbation applied to the system. The actual physical electric-field strength (EF), in volts per angstrom (V/Å), was related to the WIEN2k input parameter (`EFIELD`) by

$$\mathrm{EF}\,(\mathrm{V}\,\text{Å}^{-1}) = \frac{2\times\mathrm{EFIELD}}{c}\times\frac{13.6}{0.529177}. \tag{1}$$

Here, EF is the physical electric field in volts per angstrom, `EFIELD` is the input field in Rydbergs (Ry), c is the lattice constant along the z-direction in Bohr, 13.6 is the conversion factor from Rydberg to electron volts (eV) and 0.529177 is the Bohr radius in angstroms (Å) [14, 15]. Equation (1) was used to determine the corresponding value of `EFIELD` for a desired electric-field strength in V/Å.

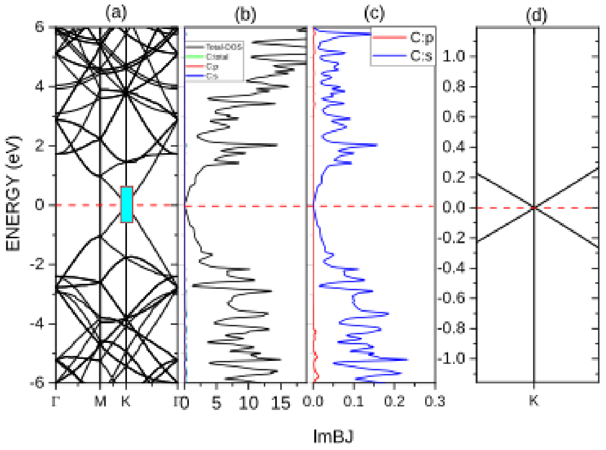

Figure 1. (a) Band structure, (b) density of states (DOS), (c) partial density of states (PDOS) and (d) zoomed view of the Dirac point of pristine graphene calculated using the lmBJ functional, with the Fermi level at 0 eV, confirming its semimetallic nature.

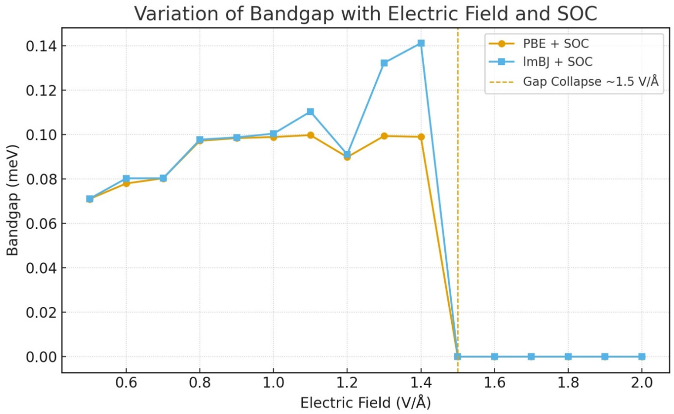

Figure 2. Bandgap variation with electric field for graphene with spin–orbit coupling using PBE and lmBJ.

Adsorption studies were conducted by placing Li atoms on several high-symmetry sites of the graphene sheet: hollow (H), bridge (B) and top (T). For each configuration, full structural relaxation was performed. The adsorption energy was evaluated using

$$E_{\mathrm{ads}} = E_{\mathrm{ion/graphene}} - E_{\mathrm{graphene}} - E_{\mathrm{ion}}, \tag{2}$$

where $E_{\mathrm{ion/graphene}}$ is the total energy of the adsorbed system, E_{graphene} is the total energy of pristine graphene and E_{ion} is the total energy of the ion [9, 16–19].

3. RESULTS AND DISCUSSION

3.1. PRISTINE GRAPHENE UNDER EXTERNAL ELECTRIC FIELD AND SPIN–ORBIT COUPLING

For pristine graphene, both PBE and lmBJ calculations confirmed preservation of the Dirac cone at the K-point in the absence of external perturbations, maintaining a zero bandgap, as shown in Figure 1 for lmBJ. When an electric field was applied, small bandgap openings (< 0.15 meV) were observed in a narrow range of fields. At higher field strengths, the gap closes, as also observed in Ref. [20].

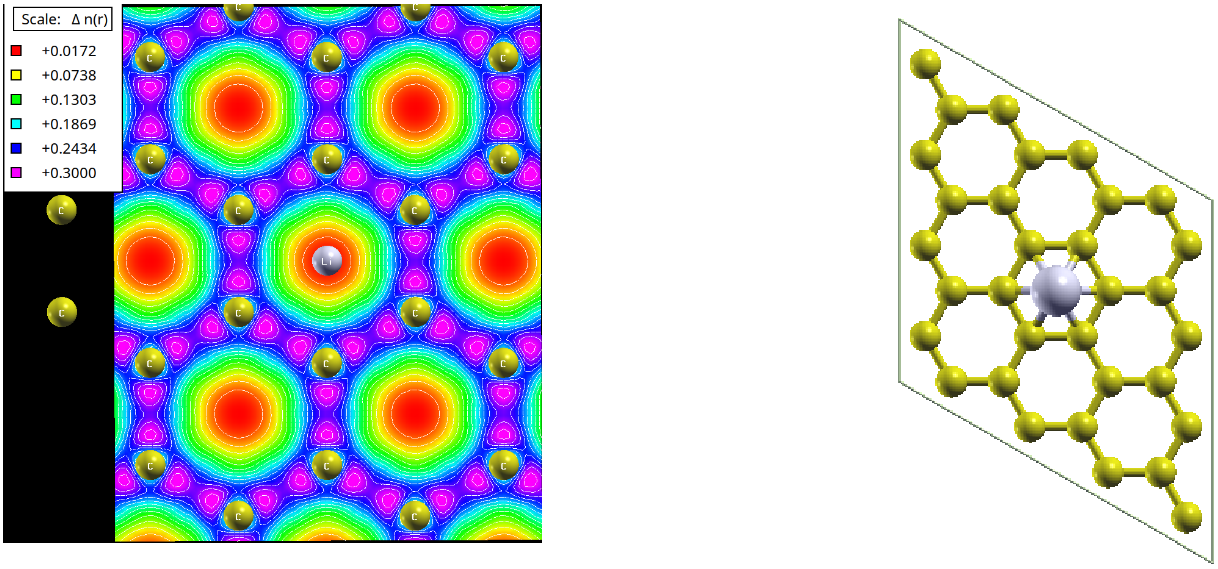

Figure 3. Optimised structure and electron-density distribution of a lithium adatom on graphene.

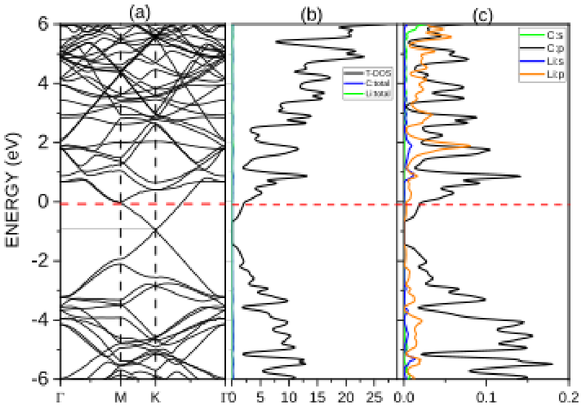

Figure 4. (a) Band structure, (b) total density of states (T-DOS) and (c) partial density of states (P-DOS) of a lithium adatom on pristine graphene using the PBE functional.

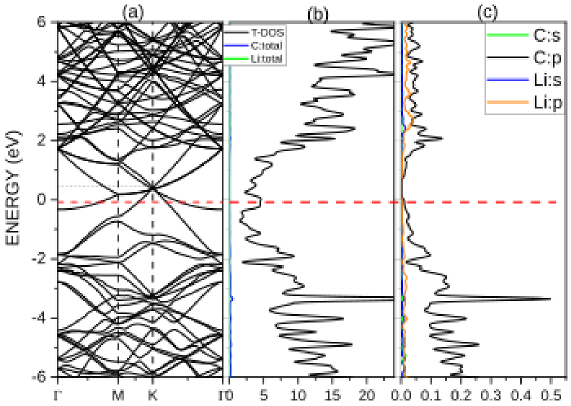

Figure 5. (a) Band structure, (b) total density of states (T-DOS) and (c) partial density of states (P-DOS) of lithium-adsorbed graphene under an electric field of 3.0 V/Å using lmBJ.

The addition of SOC slightly increases the bandgap, which is consistent with the weak intrinsic spin–orbit interaction of graphene [6]. However, the lmBJ functional exhibits improved sensitivity to these subtle modifications compared with PBE, particularly near the Dirac point. Figure 2 shows the bandgap variation with electric field for graphene with SOC using PBE and lmBJ. The results confirm that pristine graphene exhibits only minimal bandgap tunability under the combined electric field and SOC, with lmBJ offering a more sensitive prediction of these subtle electronic modifications.

3.2. LITHIUM ADSORPTION ON GRAPHENE

The results indicate that the Li adatom preferentially occupies the hollow site, which exhibits the lowest total energy and therefore represents the most stable adsorption site. Lithium adsorption at the hollow site leads to significant charge transfer from Li to the graphene π system, resulting in n-type doping and an upward shift of the Fermi level [7, 9]. Figure 3 shows the optimised structure and electron-density distribution of a lithium adatom at a hollow site on a graphene sheet.

The calculated adsorption energies fall within the reported GGA range of −1.07 to −1.56 eV, with lmBJ yielding slightly weaker binding owing to its reduced tendency for overbinding [13, 21].

As shown in Figures 4(a) and 4(b), the PBE-calculated band structure and total DOS exhibit a clear upward shift of the Fermi level, signalling n-type doping due to charge transfer from Li to graphene. The Dirac cone is distorted. Figure 4(c), which shows the PDOS, further confirms hybridisation between the Li 2p orbitals and the C 2p states, particularly just above the Fermi level.

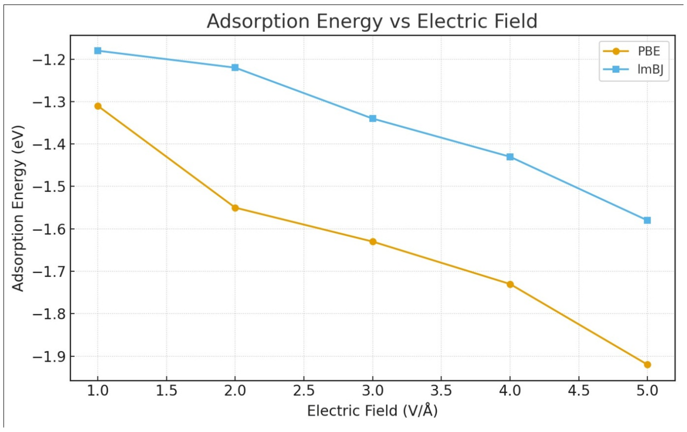

Figure 6. Effect of electric field on adsorption energy of graphene using PBE and lmBJ potentials.

3.3. ELECTRIC-FIELD EFFECT ON LITHIUM-ADSORBED GRAPHENE

As the electric field increases from 1 to 5 V/Å, the electronic structure of lithium-adsorbed graphene undergoes a clear transition from semimetallic to metallic behaviour. At lower fields, a pseudogap with a low density of states at the Fermi level is observed, while higher fields induce band crossings and increased DOS at E_F.

As the field increases to 3 V/Å, as shown in Figure 5, the bandgap begins to close, with bands approaching the Fermi level, and the adsorption energy is −1.34 eV. Figure 6 represents the variation in adsorption energies as the electric field increased using both PBE and lmBJ. Importantly, the adsorption energy becomes more negative with increasing electric-field strength, indicating enhanced lithium stability on the graphene surface. This trend highlights the role of electric fields in strengthening ion–surface interactions and facilitating charge redistribution [10, 12]. Physically, the applied EEF polarises the Li–graphene interface, increasing the electrostatic attraction between the positively charged Li adatom and the negatively polarised graphene layer. The enhanced charge redistribution, as reflected in the increased DOS at the Fermi level (Figure 5), confirms stronger orbital hybridisation between Li 2p and C 2p states at higher fields, which drives stabilisation of the adsorbed state.

4. CONCLUSION

This first-principles study demonstrates that, while pristine graphene exhibits limited bandgap tunability under an electric field and SOC, lithium adsorption fundamentally alters its electronic structure. The combined application of external electric fields and advanced exchange–correlation functionals reveals enhanced adsorption stability, strong orbital hybridisation and controllable metallic transitions. These findings provide a theoretical foundation for designing graphene-based electronic and energy-storage devices through electric-field and ion-adsorption engineering.

DATA AVAILABILITY

The data will be available on request from the corresponding author.

DECLARATION OF COMPETING INTEREST

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this manuscript.

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