

Ab-initio study of the optical properties of the Li-intercalated graphene and MoS₂

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Abstract Ab-initio calculations based on density functional theory have been performed to study the optical properties of the Li intercalated graphene and MoS₂. Comparative study of imaginary part of dielectric function for the Li doped, pristine graphene monolayer and their bulk counterparts has been done. The dielectric matrix has been calculated using the Quantum Espresso software package and its postprocessing code epsilon.x. The presented results show reliable qualitative description especially for computationally inexpensive calculation.

Keywords Graphene · Optical properties · MoS₂ · DFT

1 Introduction

In the past ten years the discovery of the graphene (Novoselov et al. 2004) and other 2D materials had started a completely new chapter in the material science. Graphene, a single atomic layer of carbon atoms arranged in a honeycomb lattice, has been attracting a remarkable attention for its unique properties (Zhang et al. 2005; Novoselov et al. 2007; Katsnelson et al. 2006; Kotov et al. 2012) ever since it was successfully isolated in 2004. Graphene's specific electronic structure and unique combination of the optical electronic properties have risen numerous investigations of its optoelectronic properties and possible applications in photonics, energy applications and detectors. Graphene electrical conductivity and visual transparency makes it excellent candidate for ITO replacement in touch

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screen technology. Graphitic films (films of various thicknesses, monolayer to ultrathin graphite) are explored for its possible applications in optoelectronics. Several studies have presented excellent performances of graphene films of 30Ω per square at 90 % transmittance for doped four layer CVD graphene (Bae et al. 2010) and $10 \text{ k}\Omega$ per square at 78 % transmittance in the visible, for large-scale liquid exfoliated graphene LBA films (Matković et al. 2016). It is known that optical transmittance of graphite increases upon metallization by intercalation with e.g caesium (Hennig 1965). This unusual property results from the unique band structure of the graphene layer; intercalation heavily dopes ultrathin graphite, shifting the Fermi level upward more than any other band engineering method (Hennig 1965; Khrapach et al. 2012; Wang et al. 2008; Efetov and Kim 2010) suppressing interband optical transitions due to Pauli blocking thus increasing transmittance of light in the visible range. Intercalation of atoms into layered materials is a well known method for providing new properties that are usually distinctly different from those of the pristine materials. Specially interesting is the intercalation of graphene with alkali metals (Wang et al. 2009; Kim et al. 2009; Reina et al. 2009; Buldum and Tetiker 2013; Profeta et al. 2012; Pešić et al. 2015). Graphene doped with Li is well-studied for energy storage applications such are Li-ion batteries and supercapacitors (Wang et al. 2009; Kim et al. 2009; Elias et al. 2009; Kim et al. 2008; Sekitani et al. 2008; Szczniak et al. 2014). Graphene intercalation is even more interesting knowing that doped graphene can be atomic thin superconductor (Profeta et al. 2012; Szczniak et al. 2014; Calandra and Mauri 2005; Pešić et al. 2014; Durajski 2015a; Margine and Giustino 2014; Si et al. 2013). Li doped graphene, since its very recent experimental realization (Ludbrook et al. 2015) has been drawing even more attention, first its theoretical prediction and afterwards its experimental realisation, has inspired search for other new 2D superconductors and their behaviour (Eom et al. 2006; Durajski 2015b; Penev et al. 2016). With all above considered, graphene doped with Li is interesting for many applications, from energy storage to optoelectronic and detail description of its optical properties is an important topic. Li doped graphitic materials are studied for optical properties, mostly in form of the ultrathin films (3–60 layers) (Bao et al. 2014), inspired by its recent experimental realization (Ludbrook et al. 2015), and we focus on graphene monolayer doped with Li, in a manner similar to intercalated graphite. Interest for application of other 2D materials in optoelectronics grown with experimental realisation of MoS_2 (Mak et al. 2010). The MoS_2 monolayer is a member of transitional metal dichalcogenides 2D materials family, and it has a hexagonal structure, like graphene, with the monoatomic Mo plane placed between two monoatomic S planes, and it displays some interesting electronic and photocatalytic properties (Sivek et al. 2013; Liu et al. 2010) Unlike the graphene, which does not have a band gap, a property essential for many optical applications, MoS_2 is direct-gap semiconductor (Mak et al. 2010) which opens possibilities for many optical applications. In this

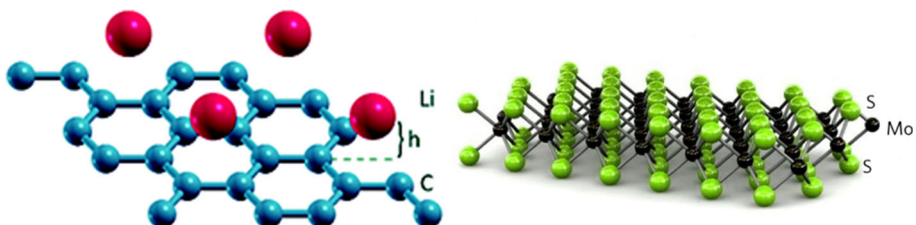


Fig. 1 Model of intercalated graphene and MoS_2

paper we study optical properties of graphene doped with lithium and MoS₂ (as shown in Fig. 1), in particular we discuss the imaginary part of dielectric function, using approaches based on DFT, implemented in the Quantum Espresso software package (Giannozzi 2009). We are interested in the study of the optical properties of this two materials using DFT as a computational inexpensive method for the qualitative description. First, we study MoS₂ and compare it with existing studies in order to approve this technique as sufficient for study and then we investigate graphene doped with Li and compare it with pristine graphene.

2 Computational details

For presented analysis, Quantum Espresso code (Giannozzi 2009), based on DFT, was used. The approach is based on an iterative solution of the Kohn–Sham equations of the DFT in a plane-wave basis set. The unit cell for Li-intercalated graphene was modeled in the $\sqrt{3} \times \sqrt{3}$ R60° in-plane unit cell, and consists of one adatom atom placed above the center of the carbon hexagon. The ionic positions in the cell are fully relaxed, in all calculations, to their minimum energy configuration using the Broyden–Fletcher–Goldfarb–Shanno (BFGS) algorithm. The hexagonal cell parameter c was set to $c = 12.5$ Å in order to simulate a two-dimensional system and to avoid an interaction due to periodicity. According to the DFT study (Ji et al. 2013) the favorable adsorption site, for the Li adatom on surface of the graphene, is above the center of the graphene hexagon called H-site. The norm-conserving pseudopotential (Perdew and Zunger 1981) and the plane wave kinetic energy cutoff of 65 Ry were used in the calculation of Li-intercalated graphene. The uniform k-point grid was composed of 4096 points in the first Brillouin zone. For MoS₂, GGA exchange–correlation functional, Perdew–Burke–Ernzerhof (PBE) (Krack 2005) was used for relaxation of the system. Also, similar as in graphene, to avoid periodicity effects, 20 Å vacuum between layers was added. The plane wave kinetic energy cutoff of 50 Ry was used and the uniform k-point grid was composed of 4096 points in the first Brillouin zone. Dielectric function $\epsilon(\omega)$ was calculated, in range 1–20 eV, within the framework of the random-phase approximation (RPA) (Brener 1975) based on DFT ground-state calculations, starting from eigenvectors and eigenvalues, implemented in Quantum Espresso code as `epsilon.x` post-processing utility. Matrix elements were accounted only for inter-band transitions that can cause an inaccuracy $\epsilon(\omega)$. RPA does not include the nonlocal part of the pseudo-potential and it is not able to include in the calculation the non-local field effects and excitonic effects. We are interested in the study of the optical properties of this two materials using DFT as a computational inexpensive method for the qualitative description. For more precise and detailed approach many-body theory and its methods are required (Bethe–Salpeter equation (BSE) and GW approximation).

3 Results

The imaginary part of the dielectric function of the MoS₂, pristine and Li-intercalated graphene is calculated (because it can be used to obtain the absorption spectra). The optical properties have been calculated in the energy range from 1 to 20 eV.

We calculate the dielectric function for the MoS₂ monolayer. The imaginary part of the dielectric function of MoS₂ for the **E** vector perpendicular to the c axis is presented in the

green color and \mathbf{E} parallel to the c axis is presented in the violet on the Fig. 2. Four distinct structures on the Fig. 2, at 1 (2.7 eV), 2 (3.7 eV), 3 (4.2 eV) and 4 (5.3 eV) can be connected to the interband transitions, marked on the inset of the electronic band structure, with 1, 2, 3 and 4 as well. All the interband transition depicted here are mainly due to the transition from the p valence bands of S to the d conduction bands of the Mo (Kumar and Ahluwalia 2012). The peak 1 is determined by the interband transitions from the valence bands I, II below the Fermi energy to the conduction bands I, II and III above the Fermi energy along ΓM and $K\Gamma$ direction. The peak 2 is due the interband transitions from the valence bands II below the Fermi energy to the conduction bands II and III above the Fermi energy along ΓM direction and near the M . The peak 3 exists due to the interband transitions from the valence bands III below the Fermi energy to the conduction bands II and III above the Fermi energy along $K\Gamma$ direction. Peak 4 is determined by the interband transitions from the valence bands IV below the Fermi energy to the conduction band I above the Fermi energy in the vicinity of the M high symmetry point. Our calculations are in agreement with the other similar DFT studies (Kumar and Ahluwalia 2012) and experimental research as well (Li et al. 2014) but for the more precise results an advance approach is needed (BSE). By concluding this, we proceed to imaginary part of the dielectric function of the pristinene and intercalated graphene. Results are presented on the Fig. 3. For the pristine graphene, there is a significant peak at small frequencies at 4 eV and another peak at 14 eV. The origin of these peak structures is $\pi \rightarrow \pi^*$ and $\sigma \rightarrow \sigma^*$ interband transition (Marinopoulos et al. 2004), respectively. Ellipsometry measurements show first peak is at 4.6 eV (Matković et al. 2012; Isić et al. 2011; Kostić et al. 2009) and it is connected with the van Hove singularity in graphenes density of states (the M point). The lower value compared to one derived from the experiment, could be due to neglecting of the interaction between graphene film and substrat and many-body interactions within the RPA calculation (Trevisanutto et al. 2010; Sedelnikova et al. 2011). There is also present singularity at zero frequency in (due to metallic property of studied system). Intercalation did not introduce the band gap so peaks are not shifted as it can be seen on the Fig. 3. The intensity of peaks obtained in this study cannot be discussed in proper way due to approximative nature of the used method. The variation in peak heights for the same material, can be observed in calculations based on various models (Bulusheva et al. 2016). We can discuss qualitatively, for peak at 4 eV, it is expected that, analogues to bulk graphite and bulk LiC_6 , due to the up-shift of the Fermi level, part of the π^* -like final bands in graphite fall below the Fermi level in LiC_6 and lead to a reduction of the peak

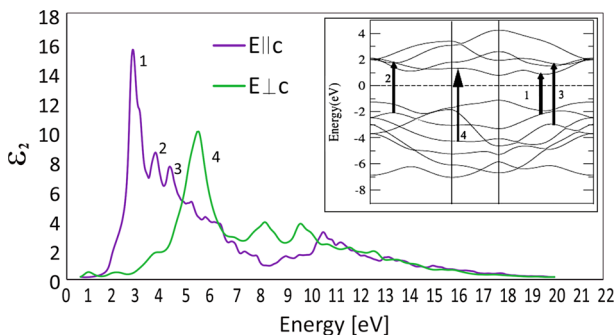
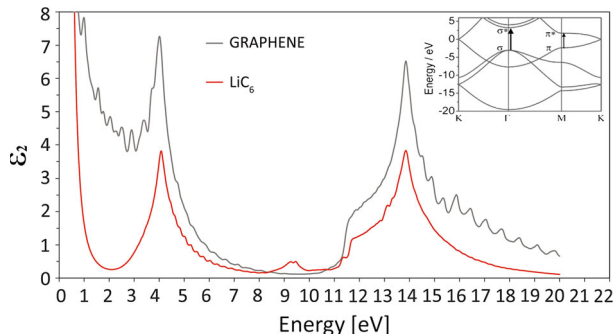


Fig. 2 The calculated imaginary part of the dielectric function for MoS_2

Fig. 3 The calculated imaginary part of the dielectric function for the pristine and intercalated graphene for the E vector perpendicular to the c axis



height (Chen and Rabii 1985). Similar is expected to happen in graphene and LiC_6 -monolayer. Similar effect is discussed in graphene monolayer doped with various amounts of B and N (Rani et al. 2014). Continuing analogy with LiC_6 bulk, for other peak a 14 eV, this structure also corresponds to transitions at graphite, however, due to zone folding, they correspond to contributions from different regions in the LiC_6 Brillouin zone (Chen and Rabii 1985; Eklund et al. 1986).

4 Conclusion

In this paper we have studied the optical properties i.e. the dielectric function of the MoS_2 as a monolayer transitional metal dichalcogenidemonolayer and the Li-intercalated graphene, as representative material for the alkali intercalated graphene and important material for energy and optoelectronic applications, using DFT techniques. We can conclude that the Li intercalation in monolayer graphene does not significantly affects the imaginary part of the dielectric function and hence the absorption spectra. Because of the similarity in there properties, in Li doped and pristine graphene, we can expect that they can be used in similar optic application. Experimental data for comparison are not yet available for LiC_6 but parallels with graphene and bulk LiC_6 can be drawn and discusses. Although used technique qualitatively well describes MoS_2 and LiC_6 , effects present in those materials due to the excitonic effects and interband transitions, demand detail and advanced approach (but computationally significantly more expensive, time-demanding and resource-consuming). In technical aspect we can conclude that DFT techniques can be used for study of the optical properties of these and similar 2D materials, and they provide the reliable and computationally non-expensive solution (even available for calculating on personal computer) for the satisfactory qualitative description.

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