

Study of interaction between Li and graphene patch using first-principles method

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An investigation into the interactions between Li and graphene patch (C₄₈H₁₈) was performed using first-principles calculations including B3LYP/6-31G(d) and ROHF/6-31G(d) levels of theory. These calculations determined two adsorption configurations, named bound and unbound configuration, which correspond to different separation distances between Li and graphene patch. The results show that when Li is adsorbed, the site on top of the hexagon (H position) is the most stable position. The 2s valence electrons of Li are partially transferred to graphene patch and the binding energy is -1.43eV at the H position for the bound configuration using the B3LYP method. This study indicates that it is more suitable on this scale to use the B3LYP method to deal with the interactions between adsorbed Li atom and graphene patch.

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1. Introduction

Graphene is a new carbon nanomaterials that has garnered much attention from both experimental and theoretical researchers [1-3]. And the composite of graphene and metal, in particular alkali metal, has great utility in hydrogen storage materials, high performance batteries, quantum computers, superconductors and for applications in electronics industries because of its novel electronic structure and mechanical characteristics [4-10]. Because of the diversity of its potential applications, examination of the structure and characteristics of the composite formed from graphene and alkali metal is important. Current research has focused on their interactions, the stable adsorption configuration, adsorption energy, the electronic structure and properties between alkali metal atoms and graphene [11-13].

A typical example of graphene and alkali metal composite is graphene and lithium (Li). The graphene composite has an important application in the fabrication of embedded lithium battery materials [14, 15]. Therefore, studies to investigate of the adsorption of Li on graphene are very helpful to understand the interactions characteristic between other alkali metals and graphene [13, 16-19].

Recently, studies from both experimental and theoretical researchers have been published on the interactions between Li and graphene [5, 19-23]. For example, Chan *et al.* [5] studied the adsorption energy, geometry, dipole moment and work function of different metal adatoms using first-principles density-functional

theory. However, these results conflicted with a previous study that examined the microscopic bonding mechanism, charge transfer and the interaction between metal adatoms and graphene [24-26]. For instance, both investigations determined divergent binding energies and equilibrium distances between Li and graphene using different density functional theory (DFT) methods. Specifically for the binding energies, the reported values range from 1.10eV using the generalized gradient approximation (GGA) algorithm to 1.68eV using the local spin density approximation (LSDA) algorithm [22]. In addition, there is also debate on the charge transfer and adsorption distances, which are important areas of investigation for studies pertaining to the between alkali metals and graphene [19, 21, 22, 27]. The mechanism of interaction in the composite system has not been completely elucidated, and the studies have been complicated by the use of different methods to study the system of graphene and Li. Thus, there is still much to be learned about the properties of graphene and Li composites. A particularly important research issue is to determine the electronic properties of the graphene and Li system.

In the present work, we study the interactions between Li and graphene patch by characterizing the adsorption behavior of Li using Hartree-Fock (HF) and density functional theory (DFT). The graphene patch can be characterized as four rows of linear polyacenes containing four rings (C₄₈H₁₈), and is designated as “4a4z”, based on the number of rings in the armchair and zigzag edge structures. We focus on the structure, binding energy and charge transfer between Li and graphene patch in this

system. Based on HF and DFT, we obtain two adsorption configurations (bound and unbound) which correspond to different degrees of separation between Li and graphene patch. We determined that the site on top of the hexagon is the most stabilized position when Li is adsorbed and charge transfer occurs from Li to graphene patch.

2. Calculation details

Geometric optimization of the Li and graphene patch systems were performed at the B3LYP/6-31G(d) and ROHF/6-31G(d) levels of theory using Q-Chem software [28]. In the ROHF/6-31G(d) level, we ran spin-restricted open shell calculations (ROHF) to avoid spin contamination which is found in unrestricted Hartree-Fock (UHF) calculations. Using the B3LYP/6-31G(d) calculation, spin contamination is negligible because the value of $\langle S^2 \rangle$ differs from $s(s+1)$ by less than 10%. To study the interactions between Li and graphene patch, Li located at different positions on graphene patch, as shown in Fig.1. The graphene patch displays zigzag and arm-chair edge structures of similar length and can be observed as four rows of linear polyacenes containing four rings. The chemical formula $C_{48}H_{18}$, is designated as “4a4z” based on the number of rings in the armchair and zigzag edges. H, M, and T represent the Li adsorption on top of the hexagon, on the middle of the bond and on top of a C atom, respectively.

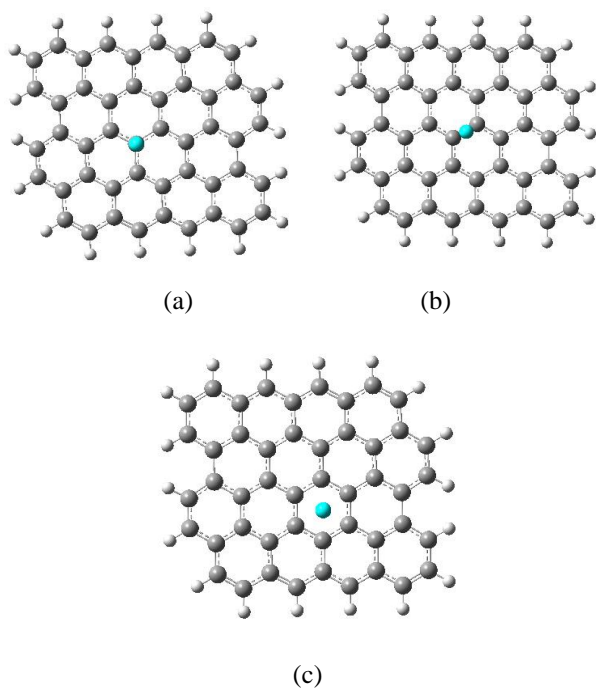


Fig. 1. The structure of Li with graphene patch. (a) T position (b) M position (c) H position. The blue atom is Lithium, grey atom is Carbon, and light grey atom is Hydrogen.

3. Results and discussion

3.1 Optimization

The interactions between Li metal and graphene patch were studied using the first-principles method at the level of DFT and HF. The corresponding results are shown in Table 1. Based on the data in Table 1, we obtained two configurations (bound and unbound) corresponding to different separation distances of Li on graphene patch after geometric optimization. The bound configuration corresponded to short distances (1.75Å~2.07Å) between Li and graphene patch, and the unbound configuration corresponded to longer distances (3.91Å~5.33Å). For the bound configuration, charge transfer occurred, however, it did not occur in the unbound case between Li and graphene patch.

Table 1. The equilibrium distance d , energy E and the charges q of the Li and graphene patch system using B3LYP/6-31G(d) and ROHF/6-31G(d) methods.

Position	Method	d (Å)	E (Hartree)	q (e)
T	B3LYP/6-31(d)	1.75 ^a	-1847.743682	0.431
		4.04 ^b	-1847.698472	-0.023
	ROHF/6-31(d)	1.83 ^a	-1835.857287	0.559
		5.33 ^b	-1835.848126	-0.005
M	B3LYP/6-31(d)	2.00 ^a	-1847.733491	0.557
		4.44 ^b	-1847.698437	0.016
	ROHF/6-31(d)	2.07 ^a	-1835.842008	0.662
		5.29 ^b	-1835.848139	-0.005
H	B3LYP/6-31(d)	1.75 ^a	-1847.743642	0.431
		3.91 ^b	-1847.698471	-0.027
	ROHF/6-31(d)	1.83 ^a	-1835.857295	0.560
		5.01 ^b	-1835.848123	-0.006

a. bound configuration

b. unbound configuration

For the bound configuration, the Li atom congruently stabilized at the H position with approximately the same equilibrium distance ($d=1.75$ Å at B3LYP/6-31G(d) and $d=1.83$ Å at ROHF/6-31G(d)) and energy when it initially bound to the T and H positions. At the M position, Li converges at the initial M position with a longer distance ($d=2.00$ Å at B3LYP/6-31G(d) and $d=2.07$ Å at ROHF/6-31G(d)) and increased energy ($E=-1847.733491$ Hartree at B3LYP/6-31G(d) and $E=-1835.842008$ Hartree at ROHF/6-31G(d)) compared to those at the H position in the bound configuration.

After optimization, Li atom located at its initial T and H positions with approximately the same equilibrium

distances ($d=3.91\text{ \AA}$ 、 4.04 \AA at B3LYP/6-31G(d) and $d=5.01\text{ \AA}$ 、 5.33 \AA at ROHF/6-31G(d)) and energy in the unbound configuration. What need points out is that the unbound configuration could not be obtained when Li atom was located at a distance of 4 \AA from graphene patch at the M position prior to optimization by B3LYP/6-31G(d), and it converted into the bound configuration at a distance of 2 \AA and energy of $-1847.733491\text{ Hartree}$. When the initial distance between Li and graphene patch at the M position was further increased, the unbound configuration was obtained with an equilibrium distance of 4.44 \AA and increased energy, compared to either the T or H positions calculated using the B3LYP/6-31G(d) method. Utilizing the ROHF method, we obtained an equilibrium distance ($d=5.29\text{ \AA}$) similar to the T/H positions with slightly decreased energy ($-1835.848139\text{ Hartree}$) than these positions.

In total, these results using B3LYP/6-31G(d) method suggest that the system is the most stabilized when Li is adsorbed at the H position in the bound configuration, which is well in agreement with the previous experimental and theoretical reports [29-31]. As reported in the literature, the equilibrium distance for Li in the bound configuration is mainly in range from 1.64 to 2.36 \AA [27, 31-35]. For example, Khanta *et al.* [27] reported a distance of 1.64 \AA between the Li atom and the graphene plane above the center of a hexagon of carbon atoms using LDA calculations. Zhu and Lu [34] determined a distance range of 1.71 – 1.75 \AA between Li and different graphene models quantified using B3LYP calculations. Cabria *et al.* [35] reported an equilibrium distance of 1.86 – 1.91 \AA using GGA and 1.80 – 2.36 \AA quantified by LDA. The obtained distances in the bound configuration about 1.75 \AA using B3LYP and 1.83 \AA determined with ROHF in our studies are consistent with these previous reports. In contrast, the distance in the unbound configuration we obtained using both B3LYP/6-31G(d) and ROHF/6-31G(d) methods was shorter compared with Baker's study, in which the distance that the authors calculated was longer than 5 \AA quantified using both HF and DFT methods [36].

Table 2. The differences in energy between unbound and bound configurations (unbound-bound).

Position	Method	$E(\text{eV})$
T	B3LYP/6-31(d)	1.23
	ROHF/6-31(d)	0.25
M	B3LYP/6-31(d)	0.95
	ROHF/6-31(d)	-0.17
H	B3LYP/6-31(d)	1.23
	ROHF/6-31(d)	0.25

The differences in energy between unbound and bound configuration (unbound-bound) are presented in

Table 2. These data demonstrate that the energy in the bound configuration was lower compared to the unbound case at every position regardless of whether B3LYP/6-31G(d) or ROHF/6-31G(d) method was used, except in the case of the M position calculated using the ROHF/6-31G(d) method. In this case, the obtained energy of the unbound configuration was lower than that of the bound configuration with a difference of 0.17 eV . A similar result was observed in the Baker's study [36].

3.2 Charge transfer

It is important to investigate the charge transfer between Li and graphene patch, as it can provide insight into the electronic transport properties of graphene. Other studies have also paid attentions to this question. We calculated the interaction and charge transfer between Li and graphene patch. According to Baker's data [36], the charge transfer can be evaluated using the spin density on Li. When the spin density of Li is approximate 0, it named as ionic configuration (the electron of Li transferred to graphene patch). When the spin density on Li is approximate 1, it named as nonionic configuration. Additionally, the Mulliken charge is often used to describe charge transfer because Mulliken charge population analysis can reveal the charge distribution and bonding strength of molecular or atomic clusters.

By our calculations, the obtained bound and unbound configurations correspond to the reported ionic and nonionic configurations. The charge transfer exists in the bound configuration between Li and graphene patch. The calculated Mulliken charge was determined to be $0.431e$ and $0.560e$ using the B3LYP and HF methods at the H position. This shows us that charge transfer from Li to graphene patch in the most stable H position. For the M position, the Mulliken charges are $0.557e$ and $0.662e$ calculated using B3LYP and HF methods, respectively. Zhu and Lu [34] reported that the Mulliken charge varies from $0.40e$ to $0.44e$ in different graphene models based on B3LYP calculations. Ji *et al.* [31] obtained $0.399e$ based on PW91 result. Our B3LYP result of $0.431e$ at the H position is in good agreement with these previous results. In contrast, the Mulliken charge at the M position was higher than that reported by other studies. Charge transfer did not occur in the unbound configuration, since the electron of Li did not transfer to graphene patch.

3.3 Binding energy

The binding energy (E_b) of Li and graphene system is defined as

$$E_b = E_{\text{Li_gra}} - E_{\text{gra}} - E_{\text{Li}}$$

Where $E_{\text{Li_gra}}$, E_{gra} and E_{Li} represent the total energy of the Li-graphene patch system, graphene patch and Li,

respectively. For three positions calculated using the B3LYP and HF methods, the binding energies E_b are all negative, as shown in Table 3, which suggests that the Li atom adsorbs stably on graphene patch. As we know, the smaller binding energy indicates that as more heat is released in the adsorption process, the system becomes more stable. The E_b of H position is the smallest binding energy, regardless of which method was used to determine the bound and unbound configurations, which suggests that the H position is the most stable adsorption position. The corresponding binding energy $E_{b1} = -1.43\text{eV}$ at the H position for the bound configuration using the B3LYP method is in agreement with the reference's data of -1.6eV [27] and -1.1eV [37]. At the M position, the binding energy ($E_{b2} = -1.15\text{eV}$) is the greatest and the interactions are weaker between Li and the surrounding C atoms determined using the B3LYP method, which indicates unstable adsorption. The E_{b1} is -0.62eV using the HF method at the H position for bounded state, which demonstrates an obvious difference with that calculated using the B3LYP method.

In total, we think that calculation of binding energy for this system is more suitable on this scale using B3LYP method.

Table 3. Binding energy for bound configuration (E_{b1}) and unbound configuration (E_{b2}).

Position	Method	E_{b1}	E_{b2}
T	B3LYP/6-31(d)	-1.43	-0.20
	ROHF/6-31(d)	-0.62	-0.37
M	B3LYP/6-31(d)	-1.15	-0.20
	ROHF/6-31(d)	-0.20	-0.37
H	B3LYP/6-31(d)	-1.43	-0.20
	ROHF/6-31(d)	-0.62	-0.37

4. Conclusions

In summary, the interactions between Li and graphene patch were investigated using first-principles calculations. The calculations showed that there are two adsorption configurations (bound and unbound) corresponding to different separation distances between Li and graphene patch. For bound configurations, the system is the most stabilized when Li is adsorbed at the H position, and Mulliken population analysis results indicate that charge transfer occurs from Li to graphene patch. The binding energy is -1.43eV at the H position for the bound configuration determined using the B3LYP method.

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