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Original Research

Density Functional Theory Investigation of Lead Adsorption by a Graphene Layer

Parastoo Bayat[1], Mohammad Yousefi[2,✉]

[1]*Department of Chemistry, Yadegar-e Imam Khomeini (RAH) Shahr-e Rey Branch, Islamic Azad University, Tehran, Iran*

[2]*Department of Chemistry, Faculty of Pharmaceutical Chemistry, Tehran Medical Sciences, Islamic Azad University, Tehran, Iran*

✉*Corresponding Author*: M. Yousefi; *Email*: myousefi50@hotmail.com; *ORCID*: 0000-0002-5609-2640

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Abstract: According to the importance of heavy metal pollutants removal from environment, this work was performed to adsorb lead (Pb) metal by means of a model of graphene (Gr) layer. To approach this goal, density functional theory (DFT) calculations were performed to obtain the optimized 3D molecular structures besides evaluating the electronic features. The adsorption of Pb atomic substance was investigated in this work, and the results indicated its appropriate adsorption by the Gr layer. Moreover, examining the electronic molecular orbital features also indicated that the Gr model could work as a sensor for detection of the existence of Pb in addition to the capability of its adsorption and removal. As a consequence, the investigated model system of this work could be proposed for working in dual functions of detection and removal for Pb from the environment.

Keywords: Graphene; Lead; Pollutant; Adsorption; DFT; Molecular orbital.

Introduction

From the early days of nanostructures innovation, their surface area have been always seen as an important feature for participating in adsorption processes with other substances [1-3]. After a while, the innovation of graphene introduced a carbon monolayer with plenty of surface area for adsorbing other substances [4-6]. In this regard, numerous works have been done to this time to develop such features for adsorption processes of different purposes for pollutants removal up to drug delivery systems [7-9]. Moreover, the sensing function of nanostructures has been another important feature for these novel materials to work as sensors of existences of specified substances in the environment [10]. To this aim, careful recognition of adsorption processes could help to achieve more insights about the nature of such materials and their applications for various specified purposes [11]. Heavy metals are those abundant pollutant substances in the industrial environments with serous harmful impacts on the human health system [12]. Such pollutants are almost available in all phases of gases, liquids, and solids in the environment and careful dealing

with them for their detection and removal is indeed a must [13]. One of the expected benefits of applications of nanostructures is their capability for adsorbing such heavy metals to work in pollution treatment issues [14].

Within this work, a mode graphene (Gr) was investigated for adsorbing lead (Pb) heavy metal in order to see details of such system for Pb-based pollutant removal. Because of the abundant of Pb in most of industrial environments, the Pb metal was investigated to be adsorbed by the Gr model based on the achievements of earlier work [15-17]. Quantum calculations were performed to obtain the optimized 3D structures and their electronic features for interpreting the models systems. The models systems and obtained results of this work were exhibited in Table 1 and Figures 1-3.

Materials and Methods

The materials of this work were molecular model of Gr and atomic Pb (Figure 1) for investigating the adsorption processes to see details of such mechanism by means of performing density functional theory (DFT) calculations. First, the singular model of Gr was optimized to obtain the minimized energy structure. Next, adsorption of Pb at the surface of Gr was investigated by performing additional optimization calculations to obtain the Pb@Gr complex model. In this step, the stabilized model of Pb@Gr complex was obtained and the adsorption energy (AE) was measured. To evaluate the electronic features, frontier molecular orbitals including the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) were calculated to measure their energy levels and energy gap (EG) distances. Moreover, chemical hardness (CH) and chemical softness (CS) were evaluated for interpreting the reactivity tendency of the models. All the quantitative results were summarized in Table 1. The HOMO-LUMO distribution patterns were also exhibited in Figure 2 in addition to visualizing the electrostatic potential (ESP) surfaces. To show benefit of such model system for sensing functions, diagrams of density of states (DOS) were also evaluated for the models systems (Figure 3). All calculations of this work were done by employing the B3LYP/6-31G*/LANL2DZ level of DFT as implemented in the Gaussian program [18]. It is worth to mention that performing quantum calculations could provide insightful information at the smallest levels of molecules and atoms to describe the models systems for developing further applications especially for those complicated nano-systems [19-21].

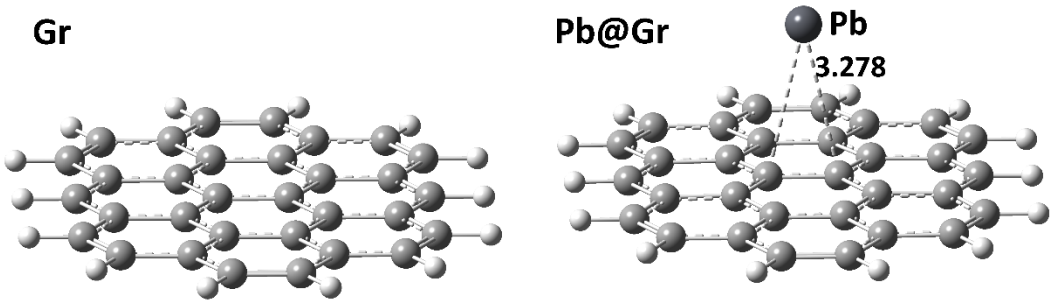

Figure 1: The optimized models systems of singular Gr and Pb@Gr complex. Pb…C distance was shown.

Table 1: Evaluated quantitative results for the models.*

Models	AE	HOMO	LUMO	EG	CH	CS
Gr	n/a	-4.941	-2.012	2.929	1.464	0.683
Pb@Gr	-0.629	-2.921	-2.204	0.717	0.358	2.789

*The models were shown in Figure 1. All values are in eV, CS is in eV^{-1}.

Results and Discussion

The main goal of this work was to investigate adsorption of Pb by a Gr layer to approach the information about details of function the Gr layer for applications in Pb-based pollutant sensing and removal. As shown in Figure 1, the models of this work were atomic Pb, molecular Gr, and the complex of Pb@Gr system indicating the adsorbed system. In this regard, performing DFT calculations yielded the optimized structures of both of singular and complex states. The layered structure of Gr was obtained first, and the adsorption process was examined next to approach the goal of this work. The results of optimization calculations indicated that the Pb atom was placed at a distance of 3.278 Å from the closest C atom of the Gr layer, in which a value of -0.629 eV was calculated for the adsorption strength (AE) as listed in Table 1. It could be supposed as a type of physical interaction of Pb at the Gr surface. Accordingly, the values of HOMO and LUMO and related parameters were changed, in which the levels of HOMO and LUMO were moved to a closer energy distance together In the Pg@Gr model in comparison with the singular Gr model. In this regards, the sensing function of Gr for Pb could be supposed. The variation of each of CH and CS values could also indicated the impacts of adsorbed Pb at the surface of Gr layer. To explore more features of the models, the visualized HOMO and LUMO distribution patterns and ESP surfaces of Figure 2 and DOS diagrams of Figure 3 could help.

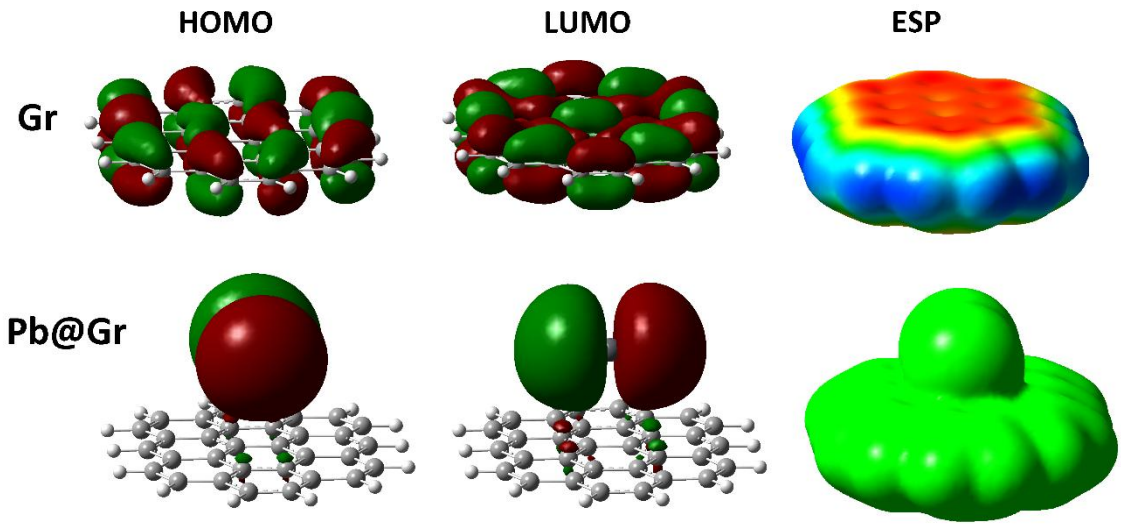

Figure 2: The HOMO-LUMO distribution patterns and ESP surfaces of singular Gr and Pb@Gr complex.

Based on the visualized achievements of Figure 2, variation of HOMO and LUMO were significant from the singular Gr model to the Pb@Gr complex. In this regard, the models were described by complete distributions of patterns at whole surfaces of Gr in the singular model, whereas such patterns were moved all to the adsorbed Pb atom in the Pb@Gr complex. This achievement is very important in order to show the major role of adsorbed Pb for putting significant impacts on the electronic features of the Gr layer model. Accordingly, the ESP surfaces indicated the model size of Gr was appropriate for participating in Pb adsorption process, in which the red color region (negative charge) of Gr was placed in the middle of layer providing an active site of adsorption of metal atom. Subsequently, the ESP surface of Pb@Gr model showed neutralization of whole system by existence of the Pb atom. As a result, the adsorption hypothesis was approved here to have such Pb@Gr complex model besides the variations of electronic features. Furthermore, variations of electronic features could help the Gr model to work in sensing function.

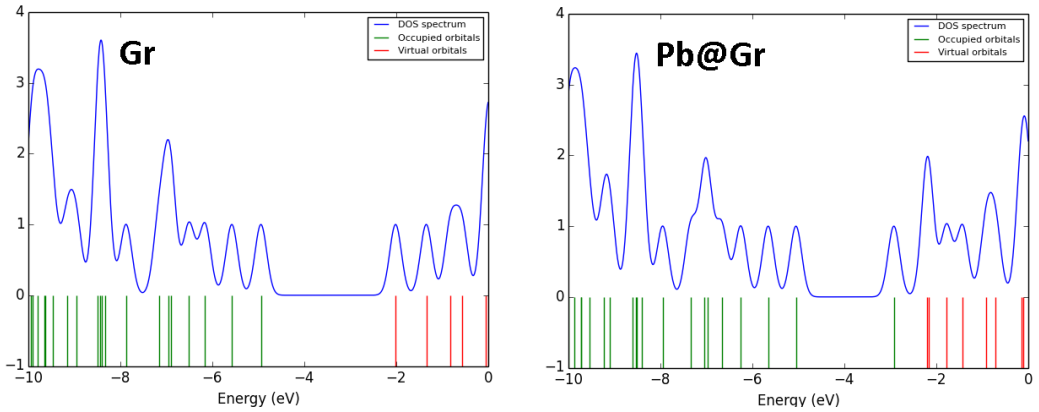

Figure 3: The illustrated DOS diagrams of singular Gr and Pb@Gr complex.

To show the sensing function of Gr model, the illustrated diagrams of DOS of singular and complex models (Figure 3) could show such benefit of electronic monitoring for the investigated system. The adsorption of Pb at the Gr surface could be taken place for two reasons of sensing and removal, in which the terms of energies and visualized features both approved such benefit of Gr layer for adsorption of Pb atom. Consequently, such model system could be proposed for further investigation in the treating fields of pollution issues.

Conclusion

Within this work, the hypothesis of Pb adsorption by a Gr layer was investigated in order to approach sensing and removal functions towards treating the pollutant issues. The required information of this work were obtained by performing DFT calculations. In this regard, the singular model of Gr was obtained in a layered model with appropriate surface for participating in interaction with the Pb atom. Nest, the complex of Pb@Gr was explored by performing additional optimization calculations to investigate the Pb adsorption by the Gr layer. The results indicated that such complex model could be achieved regarding the evaluation of energy values and related visualized representations of frontier molecular orbitals featuers and ESP surfaces. Moreover, the illustrated diagrams of DOS indicated the benefit of such model systems for working in sensing functions besides the expected role of removal by the adsorption process. As a consequence, the investigated model of Pb@Gr complex could be proposed for performing further investigations related to the pollutants issues.

Disclosure Statement

The author(s) did not report any potential conflict of interest.

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