Density functional calculation of graphene monolayer for detecting carcinogenic heavy metals in water

by

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Abstract

The thesis discusses the ability of graphene monolayer for the possible detection of carcinogenic heavy metals like Arsenic (As), Cadmium (Cd), Chromium (Cr), Mercury (Hg), and Lead (Pb) present in water as the most common pollutants. These highly toxic and nonbiodegradable carcinogenic chemicals are responsible for various allergies and intractable diseases. The density functional theory (DFT) has been used to perform the calculations of electronic properties to understand the response of graphene towards heavy metals both in a vacuum and aqueous environments. DFT calculations have been done using the Gaussian 16 software package. The geometries of each calculated compound, either as graphene or complex (heavy metal and adsorbed graphene) have been optimized via B3LYP with the basis set of def2SVP. A 4 x 5 graphene (defined as a graphene with 4 carbon atoms time 5 carbon atoms) has been modeled and optimized, as well as other compounds. Energetics of heavy metal and water molecules with pristine graphene in both vacuum and aqueous environments are studied by the variations in binding distances and binding energies. The energetics study reveals that As and Cr show adsorption on the surface with higher binding energies and smaller binding distances in comparison with the other three carcinogenic heavy metals. To further understand the possible detection capability of graphene monolayer calculations of the density of states (DOS), the highest occupied molecular orbital (HOMO), and the lowest unoccupied molecular orbital (LUMO) were performed. The energy difference between occupied orbitals and virtual orbitals shown on DOS profiles are HOMO and LUMO energy gaps. The calculations show that As, Pb or Cr with graphene has lower HOMO and LUMO energy gap than pristine graphene in vacuum. As, Pb, Cd or Cr with graphene in water has a lower energy gap than pristine graphene. Lower HOMO and LUMO energy gap leads to an increase in the charge transfer, which may contribute to the absorption behaviors of heavy metals on graphene indicating a potential candidate for the detection of heavy metals. Cd only confirms its feasibility for detection in a water environment. The binding energies of Cr are -20.78 eV and -16.18 eV in vacuum and water, respectively. The HOMO and LUMO energy gaps are 0.87 eV and 0.99 eV in vacuum and water, respectively. In comparison with the other four carcinogenic heavy metals, the graphene monolayer shows better detection capability with Cr in both vacuum and aqueous environments.

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Contents

Ał	ostrac	et	i			
Ac	knov	vledgements	iii			
1	Intr	oduction	1			
	1.1	Discovery of graphene	1			
	1.2	Structural properties of graphene	2			
	1.3	Electronic properties of graphene	4			
	1.4	Objectives	7			
2	Met	hodology	9			
	2.1	Computational details	9			
3	Res	ults and Discussion	11			
	3.1	Energetics of heavy metals with pristine graphene in vacuum	11			
	3.2 Electronic properties of heavy metals with pristine graphene in vacuum					
	3.3	Energetics of heavy metals with pristine graphene in aqueous environ-				
		ment	18			
	3.4	Electronic properties of heavy metals with pristine graphene in aqueous environment	20			
4	Con	clusions	26			
5	Bibl	iography	28			

List of Tables

3.1	Binding energy $E_{binding}$, binding distance d of heavy metal from	
	graphene sheet	11
3.2	Comparison of HOMO and LUMO energy gap of graphene after the	
	adsorption of As, Cd, Cr, Hg, Pb in vacuum.	17
3.3	Comparison of HOMO and LUMO energy gap of graphene after the	
	adsorption of As, Cd, Cr, Hg and Pb in water environment	21

List of Figures

1.1	Optimized structures of graphene monolayer. Top is the side view of graphene, below is the top view of graphene	2
1.2	(a) Atomic structure of a carbon atom. (b) Energy levels of outer electrons in carbon atoms. (c) The formation of sp2 hybrids. (d) The crystal lattice of graphene, where A and B are carbon atoms belonging to different sub-lattices, a_1 and a_2 are unit-cell vectors. (e) σ bond and π bond formed by sp^2 hybridization [9].	3
1.3	Honeycomb lattice and its Brillouin zone. Left:lattice structure of graphene, made out of two interpenetrating triangular lattice unit vectors, and i=1,2,3 are the nearest- neighbor vectors). Right: corresponding Brillouin zone. The Dirac cones are located at the K and K' points [12].	5
1.4	Electronic dispersion in the honeycomb lattice. Left: energy spectrum (in units of t) for finite values of t and t', with $t = 2.7eV$ and t'=0.2t. Right: zoom in of the energy bands close to one of the Dirac points [12].	6
3.1	Optimized structures of (a) As, (b) Cd, (c) Cr, (d) Hg, (e) Pb, adsorbed graphene	12
3.2	Binding energy of (a) As, (b) Cd, (c) Cr, (d) Hg, (e) Pb, adsorbed graphene.	13
3.3	HOMO (1) and LUMO (2) of graphene after adsorption of (a) As, (b) Cd, (c) Cr, (d) Hg, (e) Pb. The depicted molecular orbitals were obtained using B3LYP DFT with the basis set of def2-SVP.	14
3.4	Comparison of DOS Profile of graphene after the adsorption of (a) As, (b) Cd, (c) Cr, (d) Hg, (e) Pb, and (f) graphene before the adsorption in	
3.5	The corresponding DOS of graphene after the adsorption of As, Cd, Cr, Hg, Ph in vacuum (smooth lines).	16 17
3.6	Comparison of HOMO and LUMO gap energies (eV) before and after the adsorption of As. Cd. Cr. Hg and Pb.	18
3.7	Optimized structures of (a) As, (b) Cd, (c) Cr, (d) Hg, (e) Pb, adsorbed graphene in water environment.	19
3.8	Comparison of binding energy of graphene after the adsorption of As, Cd, Cr, Hg, Pb	20
3.9	Comparison of binding energy of graphene after the adsorption of As, Cd, Cr, Hg, Pb	22

3.10	Comparison of DOS Profile of graphene after the adsorption of (a)As,	
	(b)Cd, (c)Cr, (d) Hg, (e)Pb in water environment. (f) DOS Profile of	
	pristine graphene in water environment	23
3.11	The corresponding DOS of graphene after the adsorption of As, Cd, Cr,	
	Hg and Pb in water environment (smooth lines).	24
3.12	Comparison of HOMO and LUMO energy gap of graphene after the	
	adsorption of As, Cd, Cr, Hg and Pb in water environment	25

Chapter 1

Introduction

1.1 Discovery of graphene

Graphene is a distinct allotrope of carbon. Graphene can be obtained by exfoliating from bonded sheets down to one layer. The discovery of graphene has created a great sensation in physics, chemistry, material science, and related areas. Single layer graphene was explored by P.R. Wallace in 1947. He also pointed out the electronic properties of graphite. Hanns-Peter Boehm, Ralph Setton, Eberhard Stump introduced the term graphene in 1986, they referred graphene to as carbon in its order crystalline form, and they also referred to the suffix-ene as polycyclic aromatic hydrocarbons that can form hexagonal and ring structures [1].

In 2004, a paper was first produced and identified by the group of Andre Geim and Konstantin Novoselov. They isolated single-layer graphene by pulling graphene layers from graphite and transferring them onto thin silicon dioxide on a silicon wafer, this process is called either micromechanical cleavage or the Scotch tape technique [2]. The graphene electrically and interacted with silicon dioxide, it provides a nearly neutral charge on the graphene layer. Silicon wafer beneath the silicon dioxide can vary the charge density in the graphene over a wide range by applying the electrodes to silicon wafer. High-throughput visual recognition of graphene on a proper substrate can contrast small but noticeable optical changes [3].

Quantum electrodynamics has provided a clear understanding of the theory of condensed matter, it reveals phenomena that the charge carriers in graphene (a single atomic layer of carbon) mimic relativistic particles with zero rest mass governed by Dirac's equation [4]. The Quantum Hall effect can be observed because the electrons are confined in two-dimensional graphene. It has the existence of a non-zero Berry's phase of the electron wave function because of the exceptional topology of the graphene band structure [5]. The effect was reported by Geim's group and by Zhang, and Geim's group published a paper announcing the achievement of graphene in Science magazine, entitled "Electric field effect in atomically thin carbon films." This paper is now the most highly cited paper in material physics [6]. Nobel Prize in Physics was awarded to Prof. A.K. Geim and K.Novoselov in 2010 for their research on graphene.

1.2 Structural properties of graphene

Graphene has two sp^2 bonded carbon atoms, which make its structure look like a honeycomb crystal as seen in Figure 1.1 [7].



Figure 1.1: Optimized structures of graphene monolayer. Top is the side view of graphene, below is the top view of graphene

Graphene can be wrapped up to form other graphitic materials such as fullerenes, carbon nanotubes and thin graphene films as a single atomic plane of carbon [8]. Carbon is the sixth element in the periodic table with a ground-state electronic configuration of $1s^22s^22Px^12Pyy^12Pz^0$ as shown in Figure 1.2(b)[9]. The nucleus of a carbon atom is surrounded by six electrons as shown in Figure 1.2(a), the energy level of 2Pz has no electron though it is the same energy level as 2Px and 2Py. These electrons are valence electrons, and they can form three types of hybridization, sp, sp^2 and sp^3 in Figure 1.2(c). These carbon atoms form a layer of honey comb planar structure by sharing sp^2 electrons with their three neighboring carbon atoms in Figure 1.2(d). The stability of the planar ring depends on the resonance and delocalization of the electrons [9].



Figure 1.2: (a) Atomic structure of a carbon atom. (b) Energy levels of outer electrons in carbon atoms. (c) The formation of sp2 hybrids. (d) The crystal lattice of graphene, where A and B are carbon atoms belonging to different sub-lattices, a_1 and a_2 are unit-cell vectors. (e) σ bond and π bond formed by sp^2 hybridization [9].

There is an out of plane π bond which made up by 2Pz orbitals in sp^2 hybridization of two neighboring carbon atoms. Meanwhile, an in-plane σ bond is formed by the 2s, 2Px and 2Pyhybridized orbitals [9]. As a result, it gives stronger sp^3 hybridized bonds. Two dimensional (2D) graphene sheet consists of convalently bonded carbon atoms, forming the basis of both 3D graphite and 1D carbon materials [10]. In monolayer graphene, the elastic properties include intrinsic breaking strength of membranes. The nonlinear elastic force interprets displacement behaviours of graphene membranes, and yields second and third order elastic stiffness. These quantities correspond to Young's modulus of E = 1.0 TPa and an intrinsic tensile strength of 130 GPa [10]. These structural properties prove that graphene is the strongest material ever measured. Half-filled π band forms the conduction band and valence band with zero band gap and permits free moving electrons. Also, half π band provides a weak van der waals interaction between adjacent graphene layers in multi-layer graphene [9].

1.3 Electronic properties of graphene

Graphene is a thin single atomic layer of two dimensional closely packed honeycomb carbon lattice, and its derivatives have attracted much attention in many fields of physics, chemistry and medicine due to its unique physicochemical properties. They are high surface area, excellent electrical conductivity, remarkable biocompatibility and ease of surface functionalization and these proprieties provide great potentials in the applications of graphene based electronic devices [11]. In a review by Castro Neto [12], the structure of monolayer graphene can be seen as a triangular lattice with a basis of two atoms per unit cell, as seen in Figure 1.3. Two primitive lattice vectors are written as:

$$\overrightarrow{a_1} = \frac{a}{2}(3,\sqrt{3}) \text{ and } \overrightarrow{a_2} = \frac{a}{2}(3,\sqrt{3}). \tag{1.1}$$

where $a = \sqrt{3}a_0 = \sqrt{3} \times 1.42 = 2.46$ Å is the lattice constant, which is the distance between unite cells. The reciprocal-lattice vectors are given by [12]:

$$\overrightarrow{b}_1 = \frac{2\pi}{3a}(1,\sqrt{3}) \text{ and } \overrightarrow{b}_2 = \frac{2\pi}{3a}(1,-\sqrt{3}).$$
 (1.2)

There are the two points K and K' at the corners of graphene Brillouin zone (BZ) which are of particular importance for the physics of grphene. These Dirac points in momentum space are at the positions:

$$\overrightarrow{K} = \left(\frac{2\pi}{3a}, \frac{2\pi}{3\sqrt{3}a}\right) and \overrightarrow{K'} = \left(\frac{2\pi}{3a}, \left(-\frac{2\pi}{3\sqrt{3}a}\right)\right).$$
(1.3)

The three nearest neighbor vectors in real space are:

$$\overrightarrow{\delta_1} = \frac{a}{2}(1,\sqrt{3})\overrightarrow{\delta_2} = \frac{a}{2}(1,-\sqrt{3})\overrightarrow{\delta_3} = -\frac{a}{2}(1,0).$$
(1.4)

and the other six second-nearest neighbors are located at

$$\overrightarrow{\delta_1'} = \pm \overrightarrow{a_1}, \overrightarrow{\delta_2'} = \pm \overrightarrow{a_2}, \overrightarrow{\delta_3'} = \pm \overrightarrow{a_2} - \overrightarrow{a_1}.$$
(1.5)



Figure 1.3: Honeycomb lattice and its Brillouin zone. Left:lattice structure of graphene, made out of two interpenetrating triangular lattice unit vectors, and i=1,2,3 are the nearest-neighbor vectors). Right: corresponding Brillouin zone. The Dirac cones are located at the K and K' points [12].

Electrons can hop to both nearest and next nearest neighbor atoms and it can be considered by the tight-binding Hamiltonian function for electrons in graphene:

$$H = -t \sum_{\langle i,j \rangle,\sigma} (a^{+}_{\sigma,i}b_{\sigma,j} + H.c.) - t' \sum_{\langle \langle i,j \rangle \rangle,\sigma} (a^{+}_{\sigma,i}a_{\sigma,j} + b^{+}_{\sigma,i}b_{\sigma,j} + H.c.).$$
(1.6)

where $a_{\sigma,i}^+$ creates an electron of spin σ , $t \ (\approx 2.8 \text{ eV})$ is the nearest neighbor hopping energy, and t' is the next nearest neighbor hopping energy. The energy bands derived from the Hamiltonian have the form [13]:

$$E_{\pm}(\overrightarrow{k}) = \pm \sqrt{3 + f(\overrightarrow{k})} - t'f(\overrightarrow{k}).$$
(1.7)

$$f(\overrightarrow{k}) = 2\cos(\sqrt{3}k_ya) + 4\cos(\frac{\sqrt{3}}{2}k_ya)\cos(\frac{3}{2}k_xa).$$
(1.8)



Figure 1.4: Electronic dispersion in the honeycomb lattice. Left: energy spectrum (in units of t) for finite values of t and t', with t = 2.7 eV and t'=0.2t. Right: zoom in of the energy bands close to one of the Dirac points [12].

where the \pm sign applies to the upper π band and the lower π band. The energy *E* is zero when t' = 0, the electron spectrum is symmetric around zero, as shown in the figure 1.4. For finite values of t', the electron symmetry is broken and it becomes asymmetric. In figure 1.4, there is a picture of full band of graphene with a zoom in the band structure close too one of the Dirac points which are also K and K' point in the Brillouin zone [12]. The simulated band structure of graphene is symmetric, which means that the hopping of electrons between the two sub-lattices in the structure of monolayer graphene leads to the formation of two energy bands which are upper and lower bands. The hopping of electrons intersect at points where E is zero. The Fermi level also locates at these points which are referred as Dirac Points [9]. The conduction and valence bands can be compared with tight-binding model in the experiments, and density functional theory (DFT) can be employed to describe the band structure of graphene [13].

1.4 Objectives

About 71 percent of the earth's surface is covered with water, it includes ocean water, rivers, glaciers, groundwater, inland seas, etc. The earth has abundant water, but only a small percent-age (about 0.3 percent) is usable by humans. Where much of the 99.7 percent that is usable is unattainable. The majority of freshwater is located underground as soil moisture and in aquifers and nearly 65 percent of drinkable water is in glaciers. To protect the water and control pollution, various environmental policies have been made worldwide, and researchers are putting their best efforts into developing efficient technologies for water purification [14,15].

Heavy metals differ widely in their chemical properties and can be used extensively in electronics and machines of everyday life. They are able to enter into the aquatic and food chains of humans and animals from many sources. Some of the causes of environmental pollution in the world are heavy heavy metal use. Heavy metals like Arsenic (As), Cadmium (Cd), Chromium (Cr) Mercury (Hg), and Lead (Pb) are among the most common pollutants found in wastewater. They are highly toxic and non-biodegradable carcinogenic chemicals, responsible for various allergies and intractable diseases [17]. These five elements have been selected for further discussion in this study. They are also listed as chemicals of major public health concern by World Health Organization (WHO) because they can present unique toxicological profiles, and with long biological half-lifetimes for these five metals, toxicity occurs at what is traditionally considered as low environmental concentrations [18].

To monitor water quality during purification, well-designed sensors are highly needed. Well-designed sensors can monitor water quality and identify contaminates in order to effectively control pollution, and hence manage water resources. These sensors are expensive and require frequent maintenance. The limitations make the sensors inadequate for continuous water sensing applications [16]. In recent years, many researchers have proven graphene and its derivatives can be very promising materials for sensing applications. In many research papers, graphene and derivatives are suitable materials for the preconcentration pollutants due to their excellent sorption ability [18]. There is a review on the use of carbon nanotubes and graphene for the removal of heavy metals from water, where, Xu [19] has summarized and discussed that the functionalized derivatives of carbon nanotubes and graphene with high surface area and adsorption sites are proposed to remove heavy metals. In a report by Wang [20], it has been reported that graphene oxides (GO) were investigated by using batch techniques, which indicates that the binding of Pb on GO is mainly attributed to the COOH groups, and GO may be suitable materials for the preconcentration of heavy metal ions from a large volume of aqueous solutions. While in a report by Ananthanarayanan [21], it has been demonstrated that graphene quantum dots (GQDs) is a material promising a wide range spectrum of applications in bio-imaging, optical and electronic sensors, and its sensing ability toward charged Fe atom. Shetepliuk [22] reported the strong sensitivity of graphene towards charged Cd, Hg, Pb atoms by analyzing the variations in optical properties of graphene. However, recent reports lack the in-depth study of chemiresistive type graphene-based metal detectors, especially on density functional theory (DFT) based sensitivity analysis.

This study will discuss an attempt to investigate the possible use of graphene monolayer to detect toward Arsenic (As), Cadmium (Cd), Chromium (Cr) Mercury (Hg), and Lead (Pb) by analyzing electronic properties in both vacuum and aqueous environments. The significant variations in band distance, banding energy, density of states (DOS) profile, HOMO and LUMO profiles of graphene monolayer due to interaction of heavy metals have been analyzed to understand the suitability of graphene monolayer as a sensor for carcinogenic heavy metals.

Chapter 2

Methodology

2.1 Computational details

Density Functional Theory (DFT) is a computational quantum mechanical modeling method used in physics, chemistry, and materials science to investigate electronic properties. DFT calculations have been done using the Gaussian 16 software package. The geometries of each calculated compound, either as graphene or complex (heavy metal adsorbed graphene) have been optimized via B3LYP with the basis set of def2-SVP. Density functional theory has become the standard computational method based on its superior performance in numerous energy assessments of small molecules like-charged heavy metals. Based on its superior performance in numerous energy assessments of small molecules, B3LYP is the most widely used functional. B3LYP reproduces the geometries of smaller and larger compounds very well, such as metal cations and graphene containing more than one carbon atom [23]. As such, B3LYP for calculations is useful and appropriate for the simulation of graphene monolayer.

This thesis research models the interaction between the different metal cations and the graphene by adopting the B3LYP functional and the split valence def2-SVP basis set. The interacting cations are optimized without any constraints, while the positions of the graphene atoms are kept frozen. This approach is computationally demanding in order to verifying the effect of the interaction atom-by-atom on the graphene surface [24]. In this study, the graphene monolayer surface is represented by a lattice built up of 20 carbon atoms shown in Figure 1.1.

Following the optimization, each structure was subjected to vibrational analysis at the same level of theory. A 4 x 5 graphene has been modeled and optimized, as well as other compounds

(cation and pristine graphene). The interaction of heavy metals and graphene sheet has been comprehended by computing the binding free energy using [25]:

$$E_{Binding} = E_{Complex} - (E_{Graphene} + E_{cation}), \tag{2.1}$$

where $E_{Binding}$, $E_{Complex}$, $E_{Graphene}$, and E_{cation} are the free binding energy, the total energies of the system containing adsorbate (cation) and graphene sheet, the energy of graphene sheet, and the energy of cation, respectively.

Solvent effects (in water) are analyzed using the continuum solvation model based on the charge density (SMD). In addition, visualization of molecular structures and molecular orbitals is carried out via GaussView 6 software package. The density of state (DOS) calculation has been used via Gaussum software package.

Chapter 3

Results and Discussion

3.1 Energetics of heavy metals with pristine graphene in vacuum

The graphene sheet of 4 x 5 (defined as 4 carbon atoms times 5 carbon atoms) has been modeled and relaxed, with an isolated cation located above pristine graphene, to understand the interaction between the carcinogenic heavy metal and the pristine graphene. The optimized geometries with binding distance (defined as the minimum distance between the sheet and the adsorbent) between the atom and pristine graphene sheet are illustrated in Figure 3.1. The binding energy and binding distance for different heavy metal are summarized in Table 3.1. The binding energies for heavy metals have been plotted in Figure 3.2. The negative binding free energy indicates that the reaction is stable, hence graphene monolayer is able to operate at a normal room temperature without requiring external energy.

The binding energy $E_{binding}$ and binding distance d of the systems have been calculated and summarized in Figure 3.3. The results reveal that As and Cr elements are adsorbed on graphene

	In Vacuum		In Water Environment	
Adsorbent	$E_{binding}(eV)$	dÅ	$E_{binding}(eV)$	d (Å)
As	-17.43	2.11	-14.99	2.15
Pb	-13.56	3.00	-13.28	2.70
Hg	-13.87	3.48	-13.35	3.50
Cd	-12.76	4.21	-13.28	4.10
Cr	-20.78	1.62	-16.18	1.58

Table 3.1: Binding energy E_{binding}, binding distance d of heavy metal from graphene sheet.



Figure 3.1: Optimized structures of (a) As, (b) Cd, (c) Cr, (d) Hg, (e) Pb, adsorbed graphene



Figure 3.2: Binding energy of (a) As, (b) Cd, (c) Cr, (d) Hg, (e) Pb, adsorbed graphene.

sheets with higher binding energy and smaller binding distance, whereas Cd, Hg, and Pb are adsorbed on graphene sheets with lower binding energy and large banding distances.

3.2 Electronic properties of heavy metals with pristine graphene in vacuum

To further understand the possible detection capability of graphene monolayer, the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) energies are important quantum mechanical parameters in evaluating a wide range of electronic interactions [26]. The HOMO and LUMO profiles of the graphene after adsorption of heavy metals have been calculated and visualized in Figure 3.6.

To further validate the above-mentioned HOMO LUMO profiles, the density of states (DOS) has also been calculated before and after the adsorption of heavy metal, shown in Figure 3.4. The DOS result shows the full spectrum of graphene before and after the adsorption. The DOS result shows nonbonding, bonding, and anti-bonding interactions. The positive



Figure 3.3: HOMO (1) and LUMO (2) of graphene after adsorption of (a) As, (b) Cd, (c) Cr, (d) Hg, (e) Pb. The depicted molecular orbitals were obtained using B3LYP DFT with the basis set of def2-SVP.

values of DOS indicate the bonding interactions while the negative values indicate the antibonding interactions and zero values indicate the nonbonding interactions [27]. In Figure 3.5 which was plotted and smoothed by using MATLAB. The DOS profiles from energy -25 eV and 0 eV, the range includes the energy HOMO and LUMO energy gap. The DOS curves show that overlapping population in the molecular orbital, the purple line indicates the pristine graphene in vacuum. The graph exhibits the orbital characteristics of different heavy metals on a graphene sheet. In Figure 3.5, we present the variation of DOS for the studied compounds. Graphene has the highest density of states in the range of -15 eV to -10 eV, but graphene sheets

after adsorption of heavy metals shifts from the location of pristine graphene. In the graph 3.5, graphene sheets after the adsorption of As and Cr shift more in the comparison with the other three heavy metals [28]. From this analysis, we can predict that As and Cr can be the most chemically active due to the energy variations from pristine graphene.

In every profile of DOS, there are one green line and one red line, corresponding to the occupied orbitals and virtual orbitals, respectively. The difference between occupied orbitals and virtual orbitals are HOMO-LUMO gap shown in Table 3.2. In order to evaluate the orbital energy level behaviors of the compounds, the highest occupied MO (HOMO), and the lowest unoccupied MO (LOMO) have been performed. The values of the HOMO LUMO gap energies were shown in Figure 3.6. The HOMO LUMO gap energy of graphene is 1.45 eV, and the theoretical calculations show that the HOMO LUMO gap energy of As, Pb, or Cr is less than that of pristine graphene. It can be seen in Figure 3.6 that adsorption of Hg does not change the energies or distributions of the HOMO and the LUMO of graphene. However, the HOMO and LUMO energy gap decrease to 0.61 eV, 0.80 eV, and 0.87 eV when As, Pb, or Cr cation and graphene transfer charges more easily comparing with other two heavy metals in a vacuum, which may contribute to their distinct absorption behaviors on graphene.



Figure 3.4: Comparison of DOS Profile of graphene after the adsorption of (a) As, (b) Cd, (c) Cr, (d) Hg, (e) Pb, and (f) graphene before the adsorption in vacuum.



Figure 3.5: The corresponding DOS of graphene after the adsorption of As, Cd, Cr, Hg, Pb in vacuum (smooth lines).

	LUMO (eV)	HOMO (eV)	HOMO-LUMO gap (eV)
Graphene	-4.88±0.01	-6.33±0.02	1.44±0.03
As	-17.83±0.02	-18.44±0.01	0.61±0.03
Pb	-8.64±0.01	-9.44±0.01	0.61±0.02
Hg	-8.97±0.01	-10.56±0.01	1.59±0.02
Cd	-8.66±0.01	-10.48±0.01	1.82±0.02
Cr	-20.19±0.01	-21.06±0.01	0.87±0.02

Table 3.2: Comparison of HOMO and LUMO energy gap of graphene after the adsorption of As, Cd, Cr, Hg, Pb in vacuum.



Figure 3.6: Comparison of HOMO and LUMO gap energies (eV) before and after the adsorption of As, Cd, Cr, Hg and Pb.

3.3 Energetics of heavy metals with pristine graphene in aqueous environment

The optimized geometries of heavy metal adsorbed graphene in an aqueous environment are shown in Figure 3.7. The values of binding energies and binding distances for different heavy metals have been summarized in Table 3.1. The computed binding energy of the heavy metals in the presence of water molecules is shown in Figure 3.8. The results reveal that the strongest binding energy is between the graphene sheet and Cr (-16.18ev) and the weakest binding energy is between graphene and Cd (-13.27ev). the binding energy between the heavy metal and pristine graphene has improved for Cd while weakening for As and Cr due to the presence of water molecules. The binding energy and binding distance confirm that the heavy metal acts as a donor for both vacuum and water environments. Both environments depict the strong interaction of Cr with pristine graphene by analyzing the energy between heavy metal

and pristine graphene.



Figure 3.7: Optimized structures of (a) As, (b) Cd, (c) Cr, (d) Hg, (e) Pb, adsorbed graphene in water environment.



Figure 3.8: Comparison of binding energy of graphene after the adsorption of As, Cd, Cr, Hg, Pb.

3.4 Electronic properties of heavy metals with pristine graphene in aqueous environment

The DOS, HOMO, LUMO, and energy gap profiles have been calculated and visualized to understand the sensitivity of graphene sheets toward heavy metals in an aqueous environment. The HOMO and LUMO geometries are shown in Figure 3.9. The electronic absorption spectrum corresponds to the transition of molecular orbital of the title of the compound. The DOS profile changes because graphene adsorbs different heavy metals as shown in Figure 3.10. The variations are caused by the electronic differences between different heavy metals. In order to smooth the DOS Profiles, MATLAB11 program has been used to obtain Figure 3.11 by applying the appropriate procedure to smooth the curves of the DOS profiles from energy -25 eV and 0 eV, the range includes the energy HOMO and LUMO energy gap. The DOS curves show that overlapping population in the molecular orbital, the purple line indicates the graphene. The graph exhibits the orbital characteristics of different heavy metals on a graphene sheet. The variations of DOS for the studied compounds are shown in Figure 3.5. Graphene has a high density of states in the range of -15 eV to -10 eV, but graphene sheets after adsorption

3.4 Electronic properties of heavy metals with pristine graphene in aqueous environment

	LUMO (eV)	HOMO (eV)	HOMO-LUMO
			gap (eV)
Graphene	-4.48 ±0.01	-6.11±0.01	1.63±0.02
As	-5.92±0.01	-6.82±0.02	0.90±0.03
Pb	-3.47±0.01	-4.58±0.01	1.10±0.02
Hg	-4.32±0.01	-5.91±0.01	1.60±0.02
Cd	-4.32±0.01	-4.83±0.01	0.52±0.02
Cr	-6.17±0.01	-7.16±0.01	0.10±0.02

Table 3.3: Comparison of HOMO and LUMO energy gap of graphene after the adsorption of As, Cd, Cr, Hg and Pb in water environment.

of heavy metals shifts their location. Graphene after the adsorption of Cd has the highest density of states in the range and may have the highest chemical activity. However, the graphene after the adsorption of Cd has shifted less in the range of -10 eV to -15 eV in the comparison with graphene after the adsorption of As. In the graph 3.5, the curve of graphene sheets after the adsorption of As and Cr have shifted more from the curve of pristine graphene in the comparison with the other three heavy metals curves[28]. From this analysis, we can predict that graphene sheets after the adsorption of As, Cr, and Cd can be the most chemically active due to the energy variation from pristine graphene.

In every profile of DOS, there are one green line and one red line, indicating occupied orbitals and virtual orbitals, respectively. The energy difference between occupied orbitals and virtual orbitals is HOMO LUMO gap. The values of energies HOMO LUMO gaps have been calculated and summarized in Table 3.3. And in the Figure 3.12, where As, Cd and Cr show higher LUMO and HOMO energies than graphene, but the energy gaps become to 0.90 eV, 0.51 eV, and 0.99 eV after adsorption on graphene. The interactions of the orbitals of As, Cd or Cr cation and graphene make the charge transfer increase in water environment, which may contribute to their distinct absorption behavior on graphene [27]. Hg adsorbed graphene has similar gap energy to graphene, which is around 1.60 eV. The HOMO LUMO energy gap does not change due to Hg, it indicates that graphene may not be a good candidate for detecting Hg in a water environment.



Figure 3.9: Comparison of binding energy of graphene after the adsorption of As, Cd, Cr, Hg, Pb.



Figure 3.10: Comparison of DOS Profile of graphene after the adsorption of (a)As, (b)Cd, (c)Cr, (d) Hg, (e)Pb in water environment. (f) DOS Profile of pristine graphene in water environment



Figure 3.11: The corresponding DOS of graphene after the adsorption of As, Cd, Cr, Hg and Pb in water environment (smooth lines).



Figure 3.12: Comparison of HOMO and LUMO energy gap of graphene after the adsorption of As, Cd, Cr, Hg and Pb in water environment.

Chapter 4

Conclusions

DFT calculations of graphene monolayer adsorbed with different heavy metal elements in vacuum and aqueous environments have been performed using the Gaussian 16 software package. The geometries of each calculated compound, either as graphene or complex (heavy metal adsorbed graphene) have been optimized via B3LYP with the basis set of def2- SVP. Following the optimization, each structure was subjected to vibrational analysis at the same level of theory. A 4 x 5 graphene has been modeled and optimized, as well as graphene after adsorption of carcinogenic heavy metals like As, Cd, Cr, Hg, and Pb. Pristine graphene and graphene after the adsorption of heavy metals have been modeled and investigated in both vacuum and aqueous environments. The energy reveals that the As and Cr show adsorption on the surface of pristine graphene, confirming their strong interactions with graphene. The density of state (DOS) shows the occupied orbitals and virtual orbitals. The DOS profiles change due to different heavy metals towards the graphene monolayer. Graphene after the adsorption of heavy metal has the higher density of states and may have the higher chemical activity. The DOS smooth curves of graphene sheets after the adsorption of As and Cr shift more from the location of pristine graphene curves in both vacuum and water environments. From this analysis, we can predict that As and Cr can be the most chemically active due to the energy distance variations. The variation gap between the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) from the DOS profile, before and after the adsorption of heavy metals confirms the detecting capabilities of graphene for As, Cr, and Pb in both vacuum and water environments. Cd only confirms the feasibility for detection in water environment. The binding energies of Cr are -20.78 eV and -16.18 eV in vacuum and water, the HOMO LUMO energy gaps are 0.87 eV 0.99 eV in vacuum and water. In comparison with the other four carcinogenic heavy metals, it is concluded that the graphene monolayer has a better detecting ability for Cr in both vacuum and aqueous environments.

Chapter 5

Bibliography

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