Adsorption on 2D Materials

Arian Afshar
Faranak Ghadirian

Isfahan University of Technology
Advisor : Prof. Hashemi Far
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1 Introduction

2D materials are types of materials, that are made of one layer of atoms, like Graphene, silicene. These types of materials have applications in labs as well as industry. There has been a extreme usage of 2D materials in the making of sensors and catalysts. In this project we analysed adsorption of molecules like H_2O and CO_2 on Graphene and silicene.

We used Materials Studio which is a comprehensive software suite developed by Dassault Systèmes BIOVIA for materials modeling and simulation. It provides a wide range of tools and capabilities for studying the properties, behavior, and performance of materials at the atomic and molecular levels.

2 Theory

We begin by stating that the Born-Oppenheimer approximation is used throughout calculations. writing the Schrödinger equation for H_2 molecule we have :

$$\hat{H}\Psi(\vec{r_1},\vec{r_2}) = E\Psi(\vec{r_1},\vec{r_2})$$

$$\hat{H} = -\frac{\nabla_1^2}{2} - \frac{\nabla_2^2}{2} + \frac{1}{|\vec{r_1}-\vec{r_2}|} - \frac{1}{|\vec{r_1}-\vec{R_A}|}\frac{1}{|\vec{r_1}-\vec{R_B}|} - \frac{1}{|\vec{r_2}-\vec{R_A}|} - \frac{1}{|\vec{r_2}-\vec{R_B}|}$$

the third term in the hamiltonian relates to the coupling of two electrons and A and B denote each of the porotons.

For many body systems we can write :

$$\hat{H} = \sum_i \frac{-\nabla_i^2}{2} + \sum_{i>j} \frac{1}{|\vec{r_i}-\vec{r_j}|} + \sum_{i,\alpha} \frac{-Z_\alpha}{|\vec{r_i}-\vec{R_\alpha}|} + \sum_{\alpha>\beta} \frac{Z_\alpha Z_\beta}{|\vec{R_\alpha}-\vec{R_\beta}|} + \sum_\alpha \frac{\nabla_\alpha^2}{2M_\alpha}$$

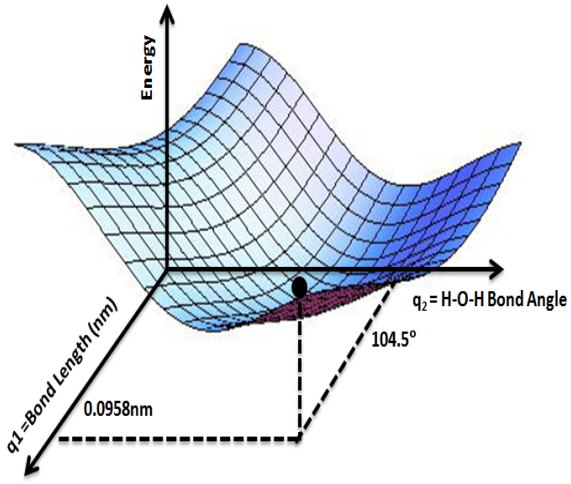
The first two terms relate to the electrons and the thrid terms is about electron-nucleus and the last two terms are due to the nucleus.

Born-Oppenhimer approximation elaborates on the idea that the dyanamics of electron is independent of the dynamics of nucleus. So we will have :

$$\left\{ \hat{H}_e = \sum_i \frac{-\nabla_i^2}{2} + \sum_{i>j} \frac{1}{|\vec{r_i}-\vec{r_j}|} + \sum_{i,\alpha} \frac{-Z_\alpha}{|\vec{r_i}-\vec{R_\alpha}|} \right\} \Psi_e(\vec{r_i}) = E(R_\alpha)\Psi_e(\vec{r_i}) \quad (1)$$

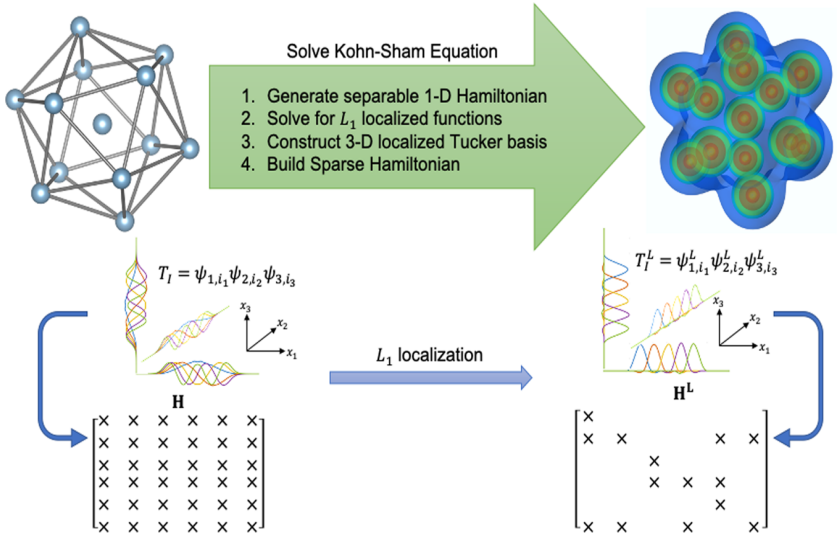
Here we negelcted the terms that involved only the nucleus.

This equation leads to a concept called Born-Oppenheimer surface.



Using this concept we can calculate forces and somehow relate this to the geometry of our system.

These equations are not easy to solve, hence people found a better way to deal with this problem called the Kohn-Sham calculations.



people replaced the electron coupling to a continious potential as follows :

$$\hat{H}_e = \sum_i \frac{-\nabla_i^2}{2} + \sum_{i>j} \frac{1}{|\vec{r_i} - \vec{r_j}|} + \sum_{i,\alpha} \frac{-Z_\alpha}{|\vec{r_i} - \vec{R_\alpha}|} \tag{2}$$

$$\int \frac{n(\vec{r'})\mathrm{d}r\mathrm{d}r'}{|\vec{r'}-\vec{r}|} + V_{XC} \tag{3}$$

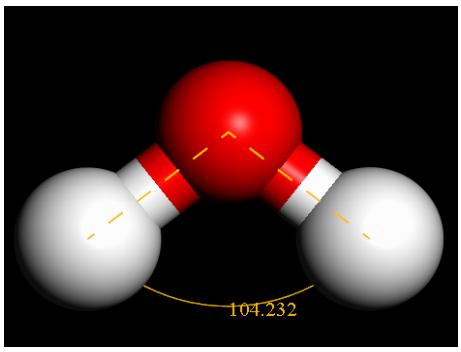
the V_{XC} part is due to quantum effects of electron-electron interaction.
By solving Kohn-Sham equations we are able to understand the electron structure and a lot more about materials.

3 Presentation

We started by making H_2O and CO_2 molecules, and then doing a geometry optimization on them using SCF method and GGA-PBE approximations. results were as follows :

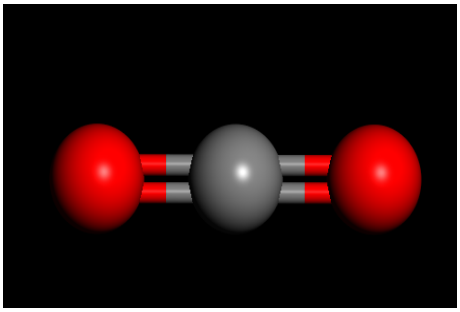
3.1 H_2O

we first drew two Hydrogen molecules and attached them to an Oxygen at an arbitrary angle, then Materials Studio did a Geometry Optimization and the angle turned out to be 104.232° which is acceptable



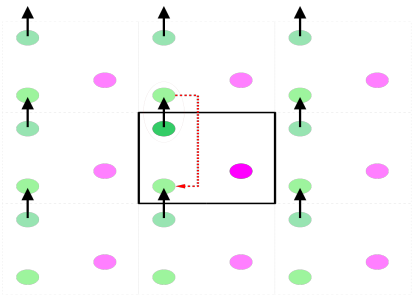
These calculations are quite CPU intensive. This run alone took about 20-30 mins to be completed.

3.2 CO_2



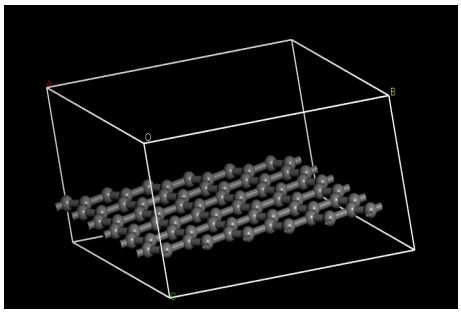
we did the exact same process for the CO2

Then we made a sheet of Graphene and Silicene by using preiodic Boundary conditions.



3.3 Graphene

As said before we used periodic boundary conditions. In addition since Drawing carbon atoms and bounds in Graphene configuration is difficult to do by hand and there is no Graphene in Materials Studio Library, we downloaded the structure then did a geometry optimization. The results were as follows :



Furthermore we simulated a physical adsorption by adjusting the distance between molecules and the sheet and did a geometry optimization to find the optimum geometry of the interaction and calculate the adsorption energy. The results were as follows :

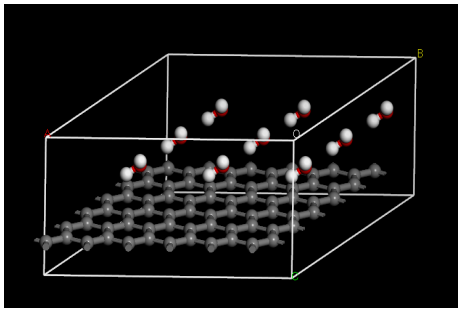


Figure 1: H_2O on graphene

it is axiomatic that adsorption energy for two subtances like A& B is in the form of

$$E_{ads} = (E_A + E_B) - E_{A-B} \tag{4}$$

For this configuration we calculated that

$$1261.39 + 471.88 - 1733.93 \approx -0.66 \text{ ev} \tag{5}$$

which is a chemical bond

we also did the exact same thing with CO_2 molecules.

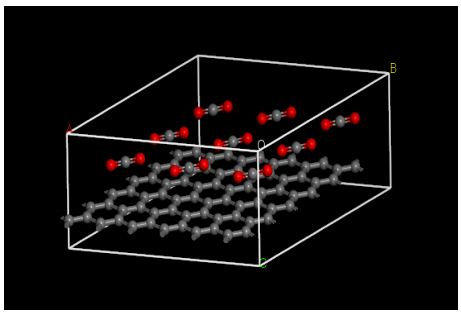
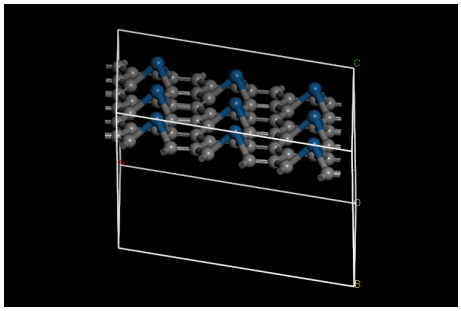


Figure 2: CO_2 on graphene

For this configuration we calculated that

$$1037.01 + 1261.39 - 2298.99 \approx -0.59 \text{ ev} \tag{6}$$

We also doped Pt on graphene and adsorped H_2O on it.



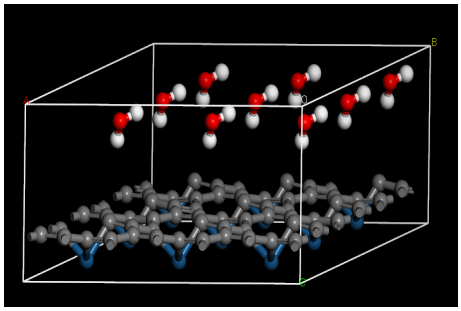


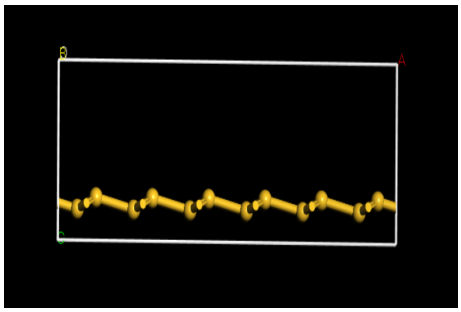
Figure 3: H_2O on doped graphene

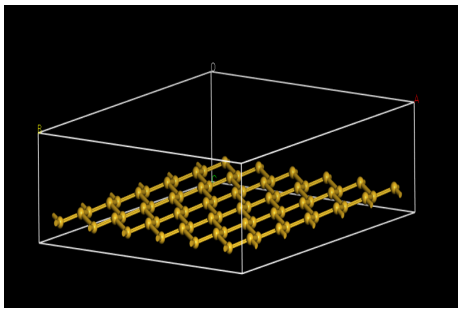
For this configuration we calculated that

$$14148.11 + 471.88 - 14621.09 \approx -1.11 \text{ ev} \tag{7}$$

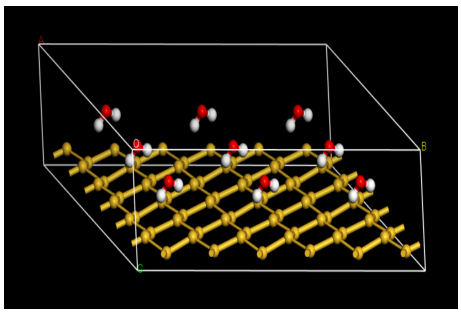
3.4 Silicene

Silicine is a two-dimensional allotrope of silicon, similar to graphene for carbon. It would consist of a single layer of silicon atoms arranged in a hexagonal lattice structure.





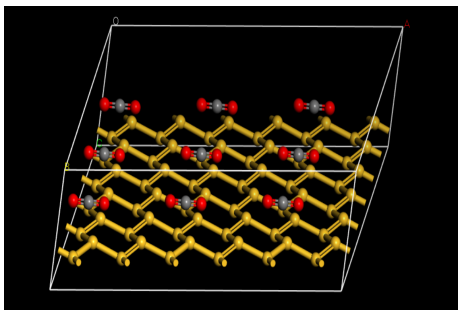
We did the exact same thing with Silicene as well and results are as follows:



For this configuration we calculated that

$$1358.51 + 471.88 - 1830.79 \approx -0.40 \text{ ev} \tag{8}$$

and for CO_2 we have :



For this configuration we calculated that

$$1037.01 + 1358.51 - 2395.77 \approx -0.25 \text{ ev} \tag{9}$$

4 Conclusion

In this study, we investigated the adsorption properties of water and carbon dioxide on two-dimensional materials, specifically silicene and graphene. Our results indicated that graphene exhibited higher adsorption energies, indicating a stronger adsorption capability compared to silicene. However, an interesting finding emerged when graphene was doped with Pt. The adsorption energy increased significantly, surpassing the already high levels observed for pristine graphene. This suggests that graphene, upon Pt doping, exhibited an even stronger adsorption capacity for water and carbon dioxide. These findings highlight the potential of graphene and its doped variants for enhanced adsorption applications, providing valuable insights for the development of advanced materials in areas such as environmental remediation and gas separation.

APPENDIX

A Method used to solve Kohn-Sham equation