

# Complexes of Li, Na and Mg with 2D Allotropies of Second and Third Period. A Theoretical Study

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# Complexes of Li, Na and Mg with 2D allotropies of second and third period.

## A theoretical study

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**Keywords:** nanoflakes; inorganic analogues of haeckelites; lithium, sodium and magnesium; DFT.

**Abstract:** Complexes of Li, Na and Mg with graphene, silicene, phosphorene nanoflakes (NFs) and their 2D allotropies have been studied at dispersion corrected TPSS/def-TZVP level of theory. The energy partition analysis of the complexes revealed that for most of the complexes exchange and correlation energies represent dominant contributions to the binding with strong charge transfer from metal atom to a NF. The exceptions are Mg complexes of graphene and phosphorene NFs where binding is due to dispersion and correlation terms. This difference is also reflected in large Mg-NF distances suggesting weak intermolecular interactions in these complexes. The calculated activation energies for metal hopping are easily achievable at room temperatures for carbon and silicon allotropies. However, they are significantly higher for phosphorus allotropies reaching almost 18 kcal/mol. There is a reasonably good correlation between the activation energies for hopping and binding energies for graphene, silicene and phosphorene NFs. Such correlation is not observed however for graphene, silicene and phosphorene 2D allotropies.

## Introduction

Although 2D materials have become a mainstream in materials chemistry, only after graphene discovery in 2004, [1] the first 2D material, molybdenum disulfide was obtained and studied, back to 1986.[2] 2D materials fill the gap between 1D and 3D materials possessing valuable properties for applications especially in micro- and optoelectronics.[3] Graphene discovery pushed forward an extensive search for 2D allotropies of other elements. Following the graphene discovery, 2D

allotropies of boron, phosphorus, silicon and germanium have been obtained too.[4–9] Although all 2D allotropies share the same topology, possessing honeycomb structure, their physical structural and chemical properties are very different. Thus, graphene and borophene are plane due to  $sp^2$  hybridization common for 2<sup>nd</sup> row elements, while Si, P and Ge honeycomb allotropies have buckled geometry. The electronic properties of the allotropies change too from metallic for borophene to semiconductor for phosphorene. Although honeycomb allotropies are the most stable 2D allotropies for all these elements, they are not the only possible ones. Thus, carbon allotropies consisting of fused azulene rings known as “haeckelites”[10] (Fig. 1) are dynamically stable and occur naturally as Stone –Wales defects in graphene.[11] Moreover, it has been recently demonstrated theoretically, that silicon, phosphorus and germanium, but not boron are also capable of forming stable 2D allotropies of “haeckelite” topology.[12] Moreover, inorganic haeckelites were found to be relatively more stable than honeycomb structures compared to the corresponding carbon counterparts. It has been found that haeckelites have much higher affinity to Li atoms than graphene which make them promising anode materials for Li-ion batteries.[13] Although Li-ion [14] batteries have second highest possible theoretical energy densities after proton batteries, lithium is expensive and chemically very active. Possible alternative to Li – ion batteries are Na- and Mg-ion batteries. [15, 16] Sodium is much cheaper than Li, although more chemically active and offering lower theoretical energy density. Magnesium, on the other hand is not only much more accessible than Li, it also more environmentally stable and offers higher energy density than Na. Haeckelites, including new inorganic systems are potentially interesting anode materials for Li-ion, Na-ion and Mg-ion batteries, therefore, the understanding of the interaction nature between 2D systems and metal atoms is of great importance. The aim of this manuscript is to study the interaction nature of Li, Na and Mg atoms with organic and inorganic haeckelites and to compare the results with these for honeycomb allotropies. Moreover, the mobility of metal atoms along 2D surfaces has also been explored.

### **Computational details**

2D allotropies were modeled as passivated by hydrogen atoms nanoflakes (NFs) containing 96 heavy atoms (Fig. 2) All calculations were carried out using gradient corrected meta TPSS functional in combination with triple zeta quality def-TZVP basis set.[17, 18] Grimme D3bj dispersion correction was applied in all cases.[19] TPSS functional offers a reasonable tradeoff between speed and

accuracy.[17] Frequency calculations were run for all structures to ensure that minimum or transition state was found. All calculations were carried out using TURBOMOLE 7.5 code.[20] To obtain deeper insight into the interaction nature between a NF and metal atom, energy decomposition analysis (EDA) was used.[21] The total interaction energy ( $E_{int}$ ) was partitioned in physically meaningful contributions.

$$E_{int}=E_{el}+E_{ex}+E_{orb}+E_{corr}+E_{disp}$$

where  $E_{el}$  is electrostatic interaction,  $E_{ex}$  is exchange interaction,  $E_{orb}$  is the orbital relaxation energy,  $E_{corr}$  is the correlation energy and  $E_{disp}$  is the dispersion energy. In our analysis we neglected  $E_{orb}$  term since in all cases it was smaller than 0.001 kcal/mol.

Metallic complexes with honeycomb NFs are denoted as **X-Me**, where **X** stands for the element symbol of the NF and **Me** – for metal atom type. In case of haeckelite allotropies, the metal complexes are marked as **HX5-Me** or **HX7-Me** where **X** stands for the element, **Me** – for the metal atom type and **5** or **7** is the complexation site: pentagon or heptagon.

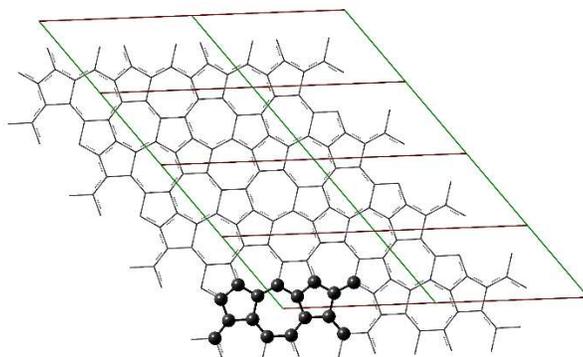


Fig. 1 Haeckelite topology.

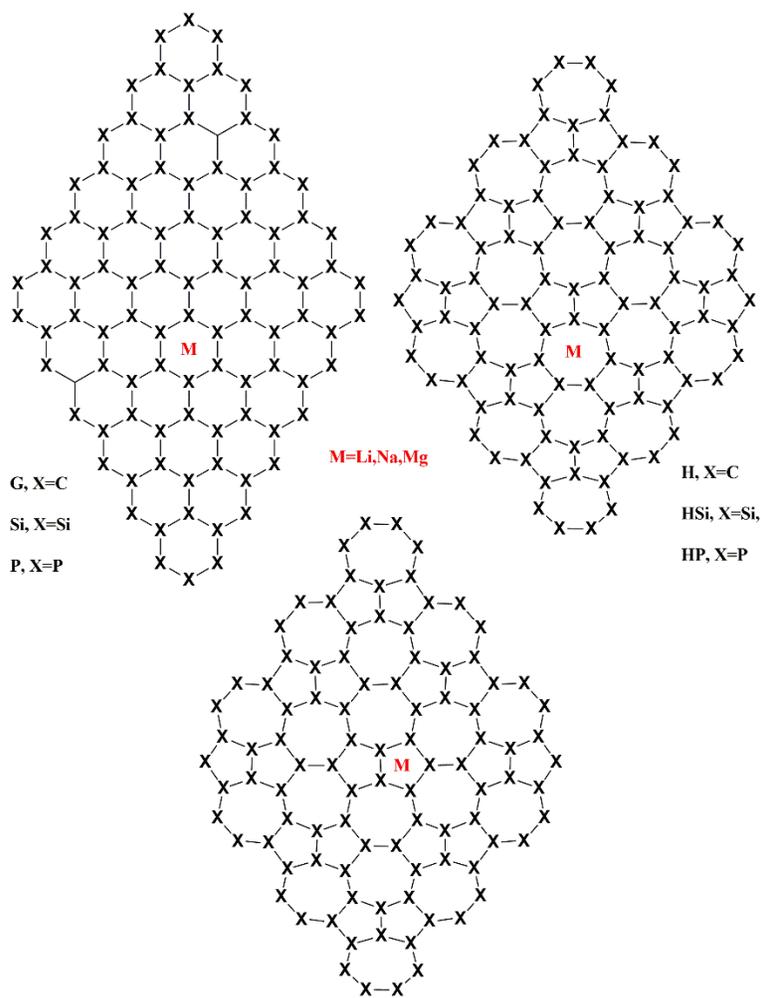


Fig.2 Topologies of studied NF complexes with Li, Na and Mg.

## Results and Discussion.

### Geometry

Fig. 2 depicts the topology of studied metal complexes. In almost all cases the metal atom is in the center and slightly above the polygon. The exception is **HSi5** complexes where in stable structure the metal atom interacts with two pentagons at once. Corresponding optimized geometries are shown in the Fig.3. Optimized Cartesian coordinates of the complexes are in supporting information.

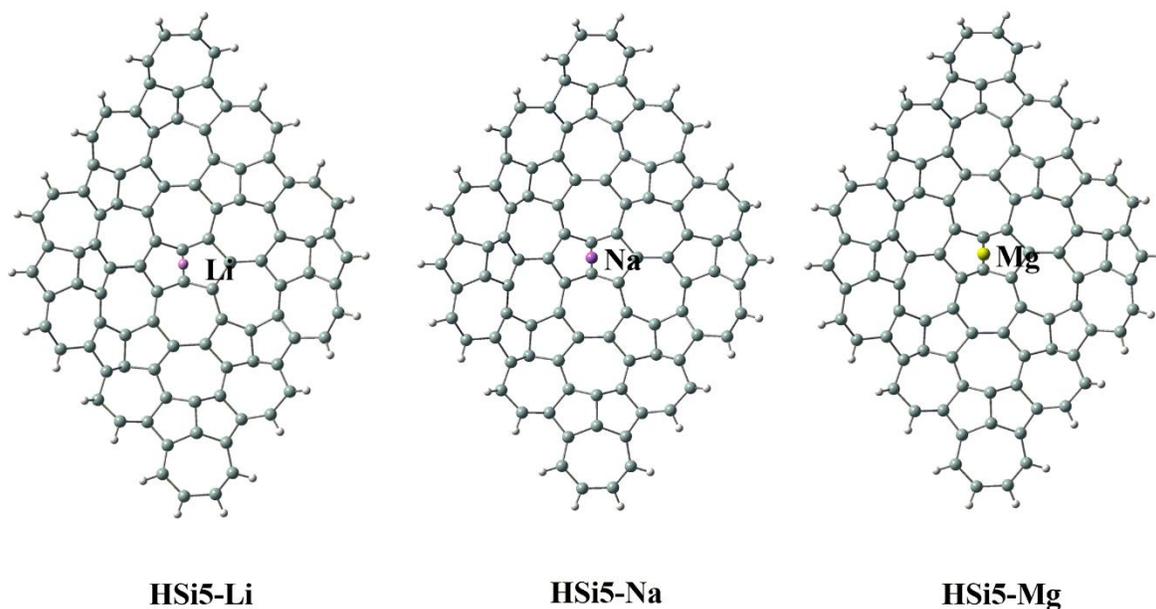


Fig.3. Optimized geometries of **HSi5-Me** complexes

Fig.4 shows shortest distances in complexes between the metal and the NF atoms. For Li and Na there is a clear correlation of shortest distances with both valence radii of metal atoms and these of NF atoms. Thus, the largest distances are detected for **Si-Na**, **HSi5-Na** and **HSi7-Na** complexes in accordance with valence radii of Na and Si which are the biggest among the metal atoms and the NF atoms, respectively. However, complexes with magnesium do not follow this trend, especially in the case of **G-Mg** complex with the longest distance out of all complexes. We will discuss this exception latter. Studied NFs have 5-, 6- and 7- member rings as complexation sites and the complexation preference depends on the metal atom size and the complex shape. For nearly plane **H** and **Si** systems, metal-NF distance in complexes increases with the atom size. The situation becomes more complex for **HSi**, **P** and **HP** NFs which are not plane, the correlation between the atom size and the atom distance is lost for these complexes. The analysis of the interaction nature is helpful for these cases.

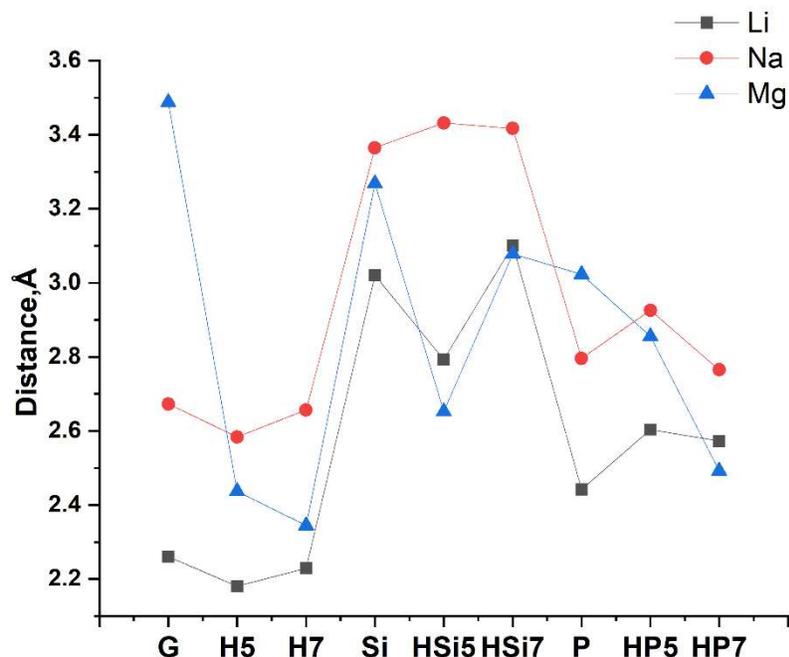


Fig.4 Shortest distances between metal and NF atoms in metal complexes.

### *Interaction energies*

Fig.5, 6, 7, 8 and 9 show the total binding energies and their components for studied complexes: electrostatic, exchange, correlation and dispersion, respectively. As seen from the Fig.5, for all complexes Mg shows the lowest binding energies except for **HP7-Mg** system, while Li binding energies are the highest. Graphene shows smallest affinity to all types of metal atoms while the binding energies for silicene and phosphorene or for their allotropies are notably higher. The lowest binding energy is detected for **G-Mg** complexes. Inspecting the different terms to the binding energy for **G-Mg** complex, it was found that the dispersion and correlation are the most important binding contributions, electrostatic and exchange interaction are very low in comparison to other systems suggesting mostly weak intermolecular interaction in this complex. Natural charge of Mg atom is essentially 0 (Fig.10) and electronic configuration of Mg is  $3S^2$ , similar to that in Mg atom. On the other hand, haeckelite **H** shows much better affinity to Mg atom, the most important binding contributions comes from exchange and correlation interactions suggesting chemical bonding between **H** and Mg, dispersion becomes less important in this case. Mg natural charge in **H5-Mg**

and **H7-Mg** complexes are between 0.9 and 1.0 while natural electron configuration of Mg atom becomes  $3S^1$ , implying total electron transfer from Mg to haeckelite. Such a big difference between two isomeric carbon NFs is due to higher aromatic stabilization of benzene fragments of graphene compared to haeckelites resulting in lower electron affinity of graphene NF compared to haeckelite ones. [12] In case of Li and Na there is a complete electron transfer from metal atom to the NF for all complexes. For haeckelite carbon allotropies the binding energies of **H** complexes are higher compared to graphene. The difference is due to lower electrostatic repulsion and more negative exchange interactions in case of haeckelite. Correlation and dispersion barely affect resulting binding energies. Similar trends for binding energies can be observed for silicon allotropies, however, binding energies are higher compared to carbon counterparts and increase in the order  $Mg < Na < Li$ . Higher binding energies for silicone haeckelite allotropy compared to silicene are due to better relation between electrostatic repulsion, exchange attraction and better correlation stabilization for the formers. Dispersion does not play important role there. The electrostatic repulsion in all silicone containing NF-metal complexes decreases in the order  $Mg > Na > Li$ , thus explaining the relative stability of the complexes for different metals. Other contributions are less important. It is interesting to note (Fig.10), that for Mg complexes of silicone haeckelite allotropy and especially for **HSi5-Mg** one, the natural charge of Mg atom is 1.4 – the second highest out of all complexes which corresponds to natural electron configuration of Mg atom  $3S^{0.56}$ . In case of **Si-Mg** complex, the natural charge at Mg atom is only 0.7. This is due to almost 1 eV higher electron affinity of **HSi** compared to silicene.[12]

Binding energy for complexes with phosphorene NFs and phosphorene allotropy follows the trend found for other complexes  $Li > Na > Mg$  for all except for **HP7-Me** systems where the highest binding energy was found for Mg, while Li and Na have almost the same binding energies. This anomaly can be explained analyzing charges and geometry. As seen the shortest **Mg-P** bond is about 0.5 Å shorter in **HP7-Mg** compared to **P-Mg** and **HP5-Mg**, and the second shortest Mg-P distance in **HP7-Mg** is 2.54 Å, still 0.4 Å shorter compared to the shortest Mg-P distance in **P-Mg** and **HP5-Mg** complexes. This suggests that in **HP7-Mg** complex Mg atom forms two polar bond with different P atoms which is further conformed by high positive natural charge of 1.4 at Mg, compared to 0.52 and 0.63 in **P-Mg** and **HP5-Mg**, respectively. Natural electron configuration of Mg in **HP7-Mg** is  $3S^{0.54}$ , showing that two valence electrons of Mg participate in the formation of chemical bonding resulting in highest binding energy out of all complexes. Large seven membered ring in **HP** promotes interaction of Mg atom with two phosphorus at the same time. EDA shows that for phosphorus containing NFs,

Li and Na have similar electrostatic repulsion components, exchange and correlation energies. Dispersion interaction is higher for Na due to higher polarizability compared to Li. The most important binding contributions come from exchange and correlation energies. Mg complexes are different. The contribution to the binding energy depends on the complex type. For **P-Mg** complex the most important binding terms are correlation and dispersion, indication of mostly intermolecular interactions, while for **HP5-Mg** and **HP7-Mg** exchange and correlation attraction dominate in the binding. Considering the most important binding terms and distances between Mg and P atoms in **P-Mg**, **HP5-Mg** and **HP7-Mg** complexes it can be concluded that unlike **HP5-Mg** and **HP7-Mg**, where there is a covalent interaction between the NF and Mg atom, in **P-Mg** these interactions are mostly intermolecular. In **P-Mg** complex the contributions from electrostatic and exchange interactions are very small compared to **HP5-Mg** and **HP7-Mg** while P-Mg distance in **P-Mg** is large, larger than the sum of covalent radii of Mg and P.

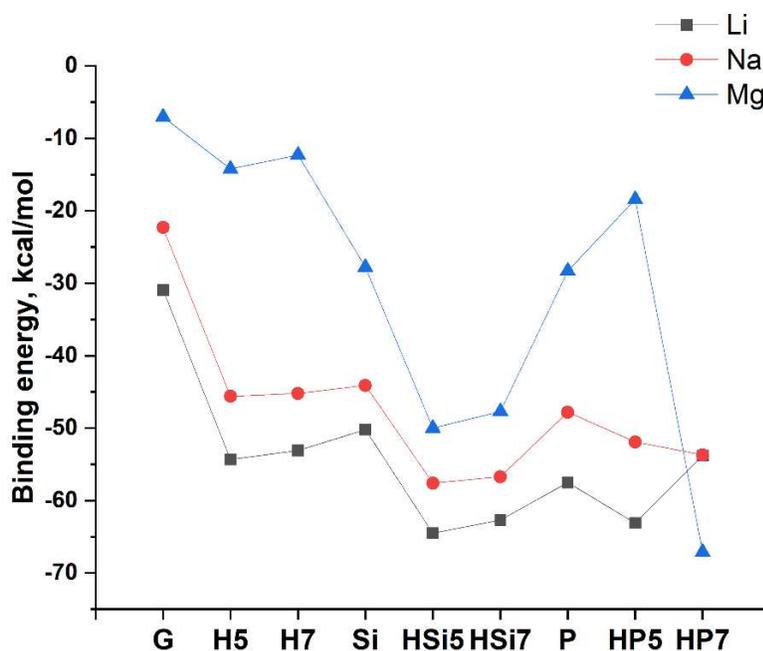


Fig.5 Total binding energies in studied complexes.

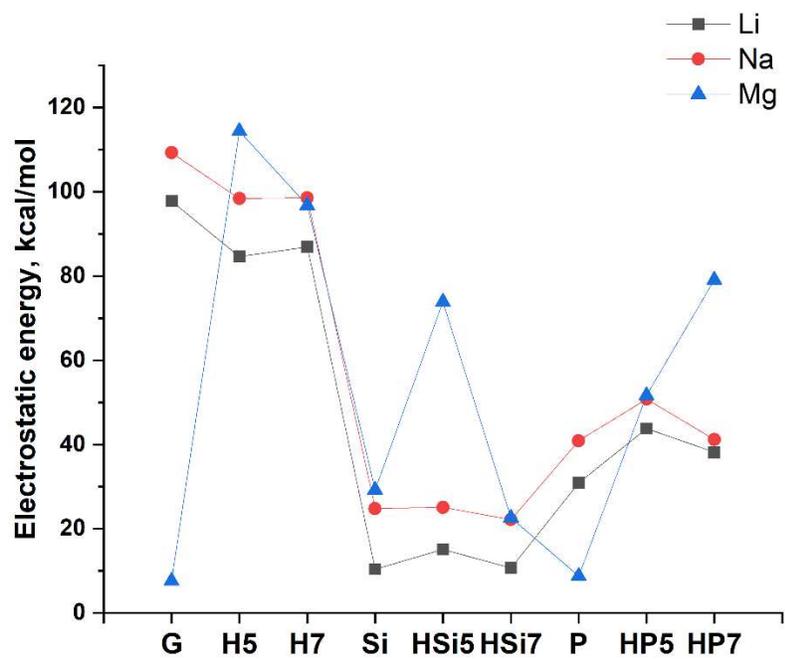


Fig.6 Electrostatic interaction in studied complexes.

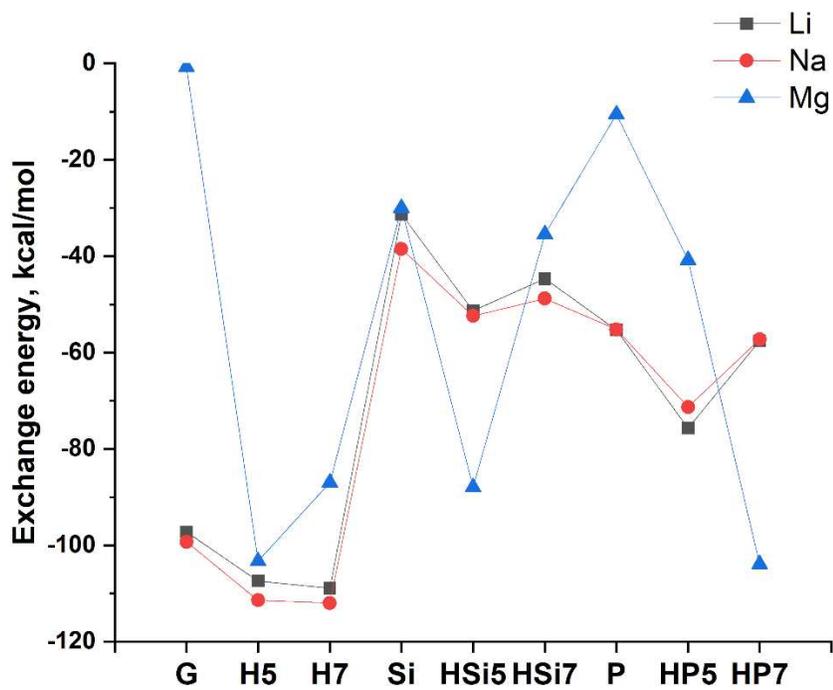


Fig.7 Exchange interaction in studied complexes.

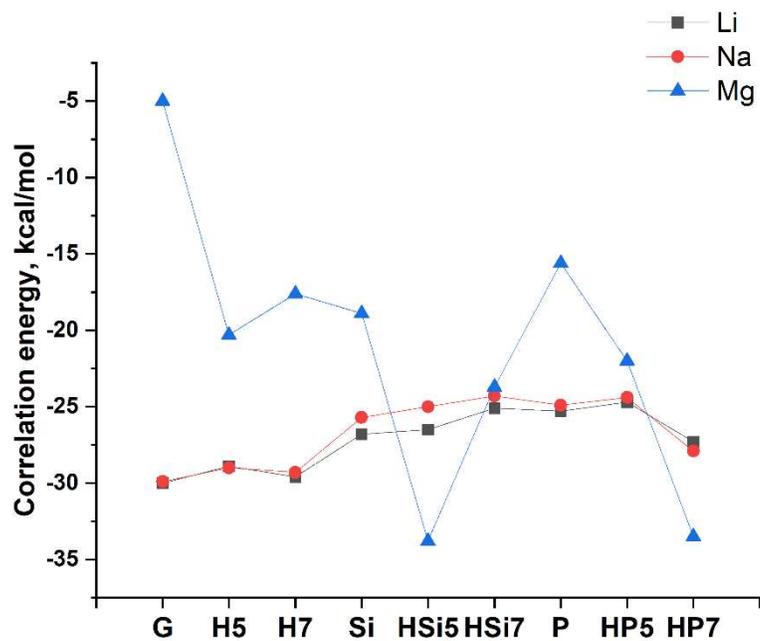


Fig.8 Correlation interaction in studied complexes.

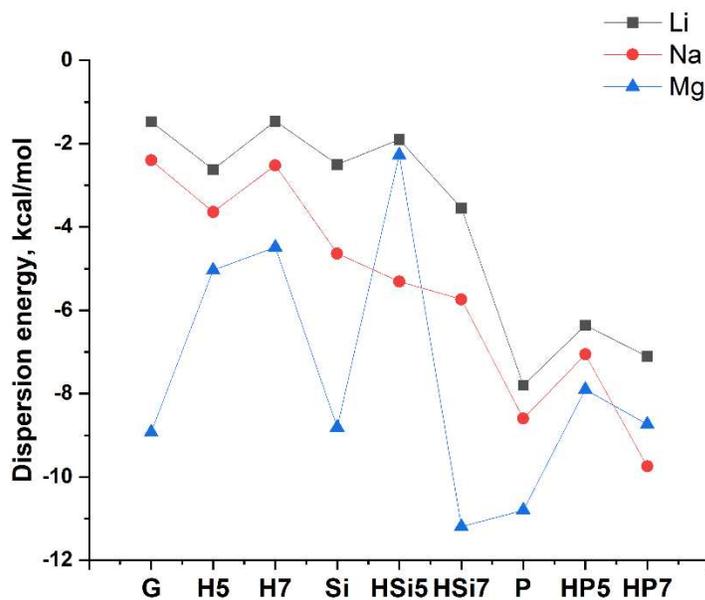


Fig. 9 Dispersion interaction in studied complexes

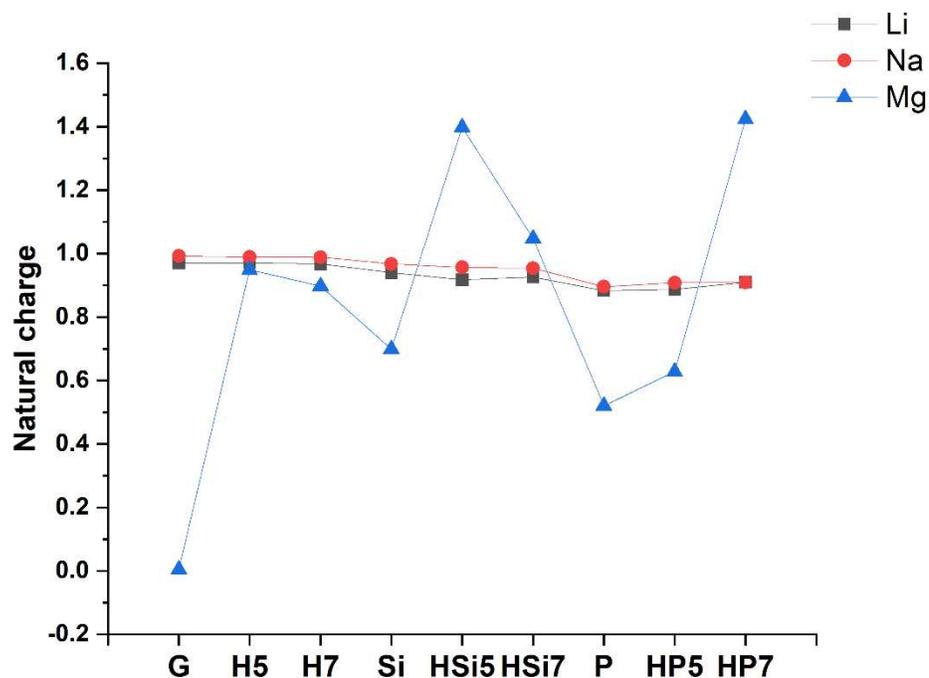


Fig. 10 Natural charges of metal atoms in studied complexes

### ***Activation energies for hopping***

Fig. 11 and 12 show calculated activation energies for metal atoms diffusion along the NFs. In case of hexagonal allotropies: graphene, silicene and phosphorene, (Fig.11) the activation energies for hopping increase in this direction being the lowest for graphene and highest for phosphorene. As seen from the Fig 13, there is a certain correlation between the binding and activation energies with R-squared of 0.38. The highest activation energies correspond to **P-Li**, having the highest binding energy. The lowest activation energy was calculated for **G-Mg**, this complex shows the lowest binding energy too. The highest activation energies are for Li while the smallest are for Mg, except for phosphorene where the lowest activation energy is for Na.

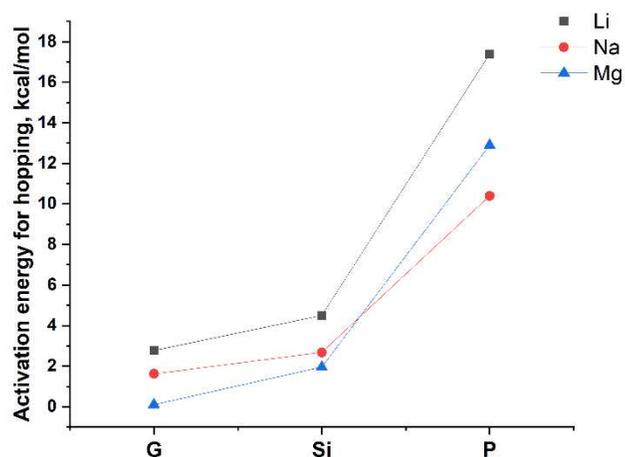


Fig.11 Activation energies for metal hopping in complexes of graphene (**G**), silicene (**Si**) and phosphorene (**P**)

In case of haeckelite allotropies of carbon, silicon and phosphorus there are 3 different ways of hopping for metal atoms: heptagon-heptagon (7-7), pentagon-pentagon (5-5) and heptagon-pentagon (7-5 or 5-7). 5-5 Transitions states (TSs) were detected only for Li atom and only for carbon and phosphorus allotropies. For other metals and systems, the structure of TS corresponds to a minimum. This is related to the larger sizes of Na and Mg atoms compared to Li and small size of pentagon ring where Na and Mg atoms can form a complex with two pentagons at the same time as shown in Fig.3. Hopping activation energies for carbon and silicon allotropies are close to these of graphene and silicene being in the range between 0.2 and 6 kcal/ mol, all easily assessable at room temperature. The activation energies vary greatly for **HP** system from almost 17 kcal/mol for Na (5-7) to 0.5 kcal /mol for Li (5-5), however they are generally lower than these estimated for phosphorene.

The estimation of average activation energies of metal atoms among all studied NF type, Mg shows the lowest average activation energy of 4.15 kcal/mol, Na – 5.70 and Li – the highest 6.13 kcal/mol.

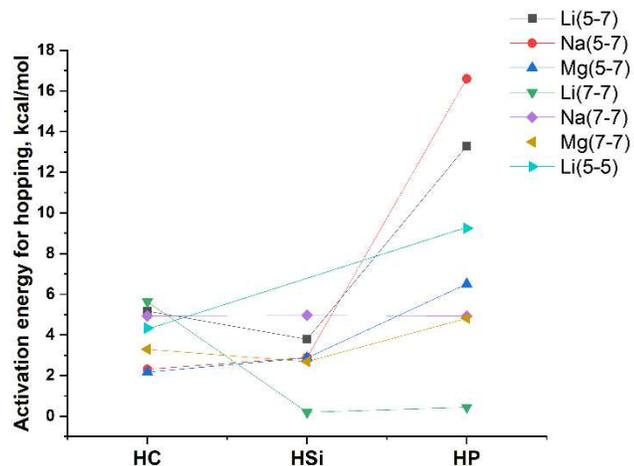


Fig.12 Activation energies for metal hopping in complexes of H, HSi and HP allotropies.

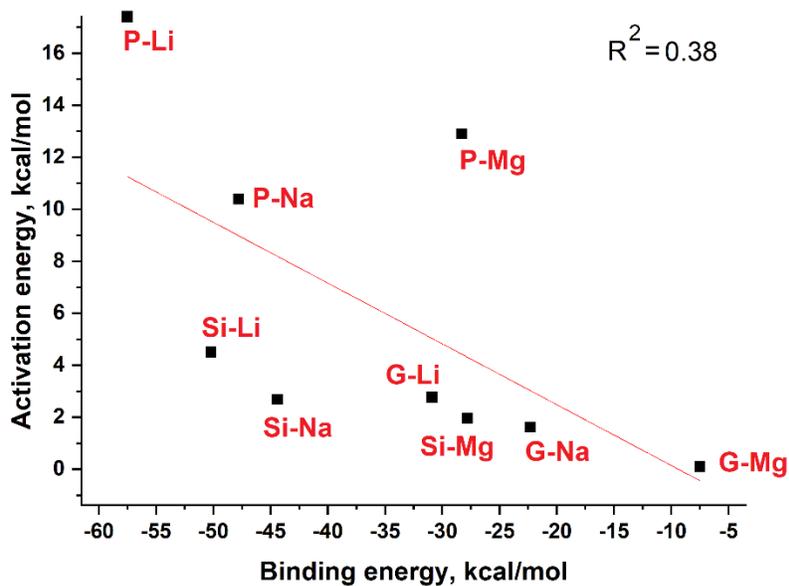


Fig 13 Binding vs activation energies of metal hopping for graphene, silicene and phosphorene NFs.

As can be seen, the average activation energies of metal atom migrations do not vary much with metal nature, however, the average activation energies for different NF types do vary (Fig 14). The lowest average activation energies were calculated for graphene NFs, while the highest one was detected for phosphorene. The average activation energies for hackelites and its silicon analogue

differ by only 2 kcal/mol from these for graphene and silicene, while **HP** allotropy shows noticeably lower hopping activation energies compared to phosphorene. A combination of graphene and Mg leads to the lowest activation energy of hopping while **P-Li** have the highest activation energy.

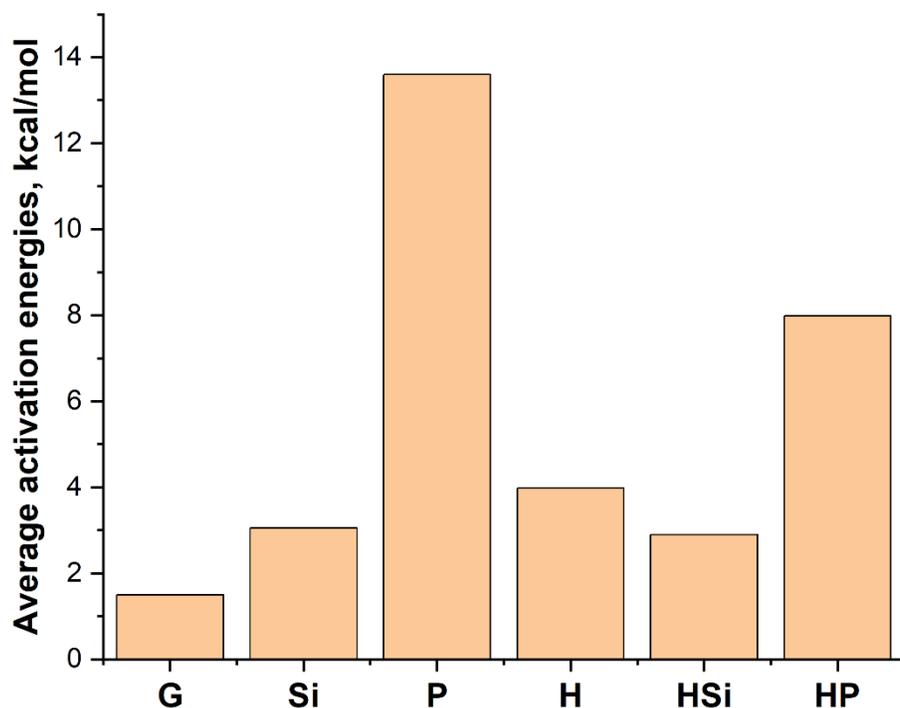


Fig. 14 Average activation energies for hopping for different NF types for all studied metals.

## Conclusions

Complexes formed by Mg are quite different from these formed by Na and Li. In the latter case there is always a complete electron transfer from metal atom to a NF and the most important contribution to the binding energy comes from exchange and correlation stabilization. Binding of Mg to a NF depends strongly on the NF type, ranging from **G-Mg** complex where there is no charge transfer from Mg to NF with dispersion being the most important contribution to binding, to **HP7-Mg** complex showing the highest binding energy out of all studied complexes where Mg transfers almost 1.5 electrons to the NF. In this case the most important contributions to the binding are from

exchange and correlation. The Mg – NF distance is 1 Å shorter for the latter complex. Generally, the binding energies increase in the order Mg<Na<Li for all types of NFs with exchange and correlation contributing to binding, being the most important. Dispersion is only important for **G-Mg** complex. Haeckelite allotropies for carbon and silicon show higher binding energies compared to graphene and silicene, unlike phosphorus allotropies where there is no clear difference between phosphorene and **HP** allotropy which could be related to weak *p* electron coupling between phosphorus atoms in these systems. The activation energies for hopping are easily achievable at room temperatures for carbon and silicon allotropies. However, they are significantly higher for phosphorene and **HP** allotropies achieving almost 18 kcal/mol. There is a reasonably good correlation between the activation and binding energies for graphene, silicene and phosphorene NFs. Such correlation is not observed however for **HC**, **HSi** and **HP** allotropies.

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### **Declarations**

#### **Finding**

PAPIIT (IN201219/31)

CONACyT (Grant 251684)

DGAPA of the UNAM under postdoctoral fellowship Grant No. CJIC/CTIC/4732/2020.

#### **Conflicts of interest/Competing interests.**

We declare no conflicts of interests.

#### **Availability of data and material**

Not applicable

### **Code availability**

TURBOMOLE V7.5 2020, a development of University of Karlsruhe and Forschungszentrum Karlsruhe GmbH, 1989-2007, TURBOMOLE GmbH, since 2007; available from <https://www.turbomole.org>

### **Authors' contributions**

Cesar Gabriel Vera de la Garza – a PhD student - performed EDA analysis

Wilmer Esteban Vallejo Narváez – a postdoctoral fellow – transition state search, and partial manuscript writing.

Luis Daniel Solís Rodríguez – an undergraduate student – routine optimizations of complexes

Seguei Fomine – group leader, the manuscript idea and writing.

## References

1. Novoselov KS, A K Geim, S V Morozov, et al (2004) Electric Field Effect in Atomically Thin Carbon Films. *Science* 306:666–669. <https://doi.org/10.1126/science.1102896>
2. Joensen P, Frindt RF, Morrison SR (1986) Single-layer MoS<sub>2</sub>. *Materials Research Bulletin* 21:457–461. [https://doi.org/10.1016/0025-5408\(86\)90011-5](https://doi.org/10.1016/0025-5408(86)90011-5)
3. Chang H, Wu H (2013) Graphene-Based Nanomaterials: Synthesis, Properties, and Optical and Optoelectronic Applications. *Advanced Functional Materials* 23:. <https://doi.org/10.1002/adfm.201202460>
4. Aufray B, Kara A, Vizzini S, et al (2010) Graphene-like silicon nanoribbons on Ag(110): A possible formation of silicene. *Applied Physics Letters* 96:. <https://doi.org/10.1063/1.3419932>
5. Lalmi B, Oughaddou H, Enriquez H, et al (2010) Epitaxial growth of a silicene sheet. *Applied Physics Letters* 97:. <https://doi.org/10.1063/1.3524215>
6. Castellanos-Gomez A (2015) Black Phosphorus: Narrow Gap, Wide Applications. *The Journal of Physical Chemistry Letters* 6:. <https://doi.org/10.1021/acs.jpcllett.5b01686>
7. Dávila ME, Xian L, Cahangirov S, et al (2014) Germanene: a novel two-dimensional germanium allotrope akin to graphene and silicene. *New Journal of Physics* 16:. <https://doi.org/10.1088/1367-2630/16/9/095002>
8. Mannix AJ, Zhou X-F, Kiraly B, et al (2015) Synthesis of borophenes: Anisotropic, two-dimensional boron polymorphs. *Science* 350:. <https://doi.org/10.1126/science.aad1080>
9. Feng B, Zhang J, Zhong Q, et al (2016) Experimental realization of two-dimensional boron sheets. *Nature Chemistry* 8:. <https://doi.org/10.1038/nchem.2491>
10. Enyashin AN, Ivanovskii AL (2011) Graphene allotropes. *physica status solidi (b)* 248:1879–1883. <https://doi.org/10.1002/pssb.201046583>
11. Chuvilin A, Meyer JC, Algara-Siller G, Kaiser U (2009) From graphene constrictions to single carbon chains. *New Journal of Physics* 11:083019. <https://doi.org/10.1088/1367-2630/11/8/083019>
12. de la Garza CGV, Narváez WEV, Rodríguez LDS, Fomine S (2021) Novel 2D allotropic forms and nanoflakes of silicon, phosphorus, and germanium: a computational study. *Journal of Molecular Modeling* 27:142. <https://doi.org/10.1007/s00894-021-04775-4>
13. Mpourmpakis G, Froudakis GE, Tylianakis E (2006) Haeckelites: A promising anode material for lithium batteries application. An *ab initio* and molecular dynamics theoretical study. *Applied Physics Letters* 89:. <https://doi.org/10.1063/1.2403922>
14. Xu Y, Wu X, Ji X (2021) The Renaissance of Proton Batteries. *Small Structures* 2:. <https://doi.org/10.1002/sstr.202000113>

15. Slater MD, Kim D, Lee E, Johnson CS (2013) Sodium-Ion Batteries. *Advanced Functional Materials* 23:.. <https://doi.org/10.1002/adfm.201200691>
16. Aurbach D, Lu Z, Schechter A, et al (2000) Prototype systems for rechargeable magnesium batteries. *Nature* 407:.. <https://doi.org/10.1038/35037553>
17. Tao J, Perdew JP, Staroverov VN, Scuseria GE (2003) Climbing the Density Functional Ladder: Nonempirical Meta-Generalized Gradient Approximation Designed for Molecules and Solids. *Physical Review Letters* 91:.. <https://doi.org/10.1103/PhysRevLett.91.146401>
18. Schäfer A, Huber C, Ahlrichs R (1994) Fully optimized contracted Gaussian basis sets of triple zeta valence quality for atoms Li to Kr. *The Journal of Chemical Physics* 100:.. <https://doi.org/10.1063/1.467146>
19. Grimme S, Ehrlich S, Goerigk L (2011) Effect of the damping function in dispersion corrected density functional theory. *Journal of Computational Chemistry* 32:.. <https://doi.org/10.1002/jcc.21759>
20. TURBOMOLE V7.5 2020, a development of University of Karlsruhe and Forschungszentrum Karlsruhe GmbH, 1989-2007, TURBOMOLE GmbH, since 2007; available from <https://www.turbomole.org>.
21. Su P, Li H (2009) Energy decomposition analysis of covalent bonds and intermolecular interactions. *The Journal of Chemical Physics* 131:.. <https://doi.org/10.1063/1.3159673>