Ab-Initio Investigation of Lithium Intercalation and Diffusion in Bilayer Graphene for Neuromorphic Applications

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Motivation

Neuromorphic computing
Conventional computers suffer from the **von Neumann bottleneck**, where separated memory and processing cause high energy use and limited throughput. Neuromorphic architectures address this by **co-locating memory and computation** through **artificial synapses**.

Device: ECRAM synapses
Electrochemical random-access memory (ECRAM) uses **ionic intercalation in a channel material** to modulate conductance, enabling **analog synaptic weights**.

Material: Li-intercalated bilayer graphene
In bilayer graphene ECRAM, **Li intercalates between graphene layers**, changing carrier density and enabling **programmable conductance states**.

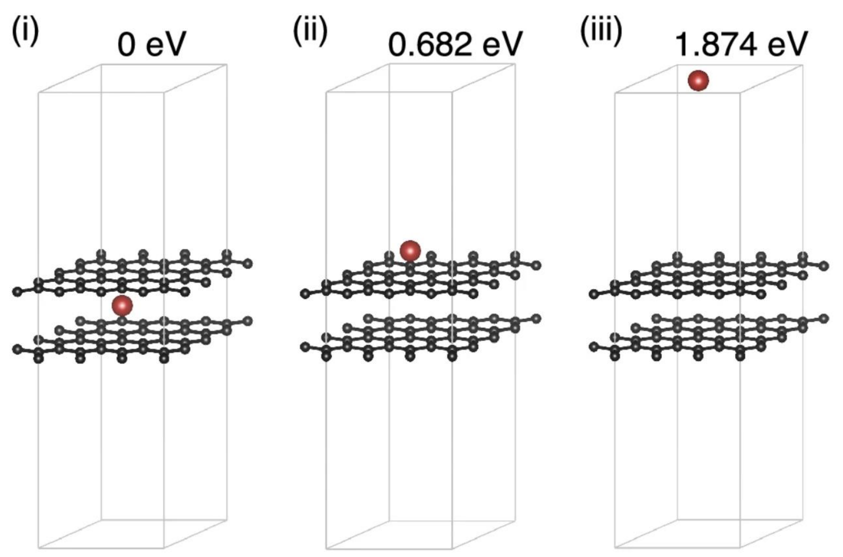
Research Goal
Use **ab-initio calculations** to understand **Li intercalation mechanisms** [1] **and diffusion timescales**, providing a theoretical basis for **designing Li intercalated graphene-based neuromorphic devices**.

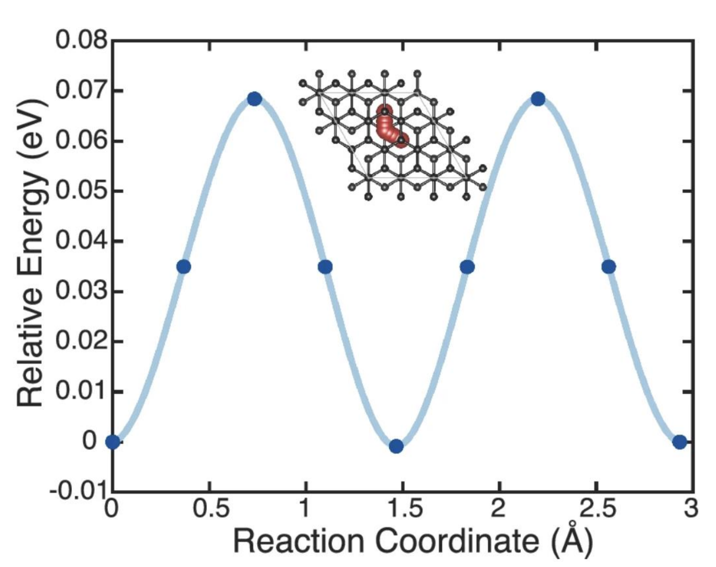
Li Intercalation is Energetically Favorable for ECRAM

DFT total-energy calculations show **Li strongly prefers the interlayer region of AB-stacked bilayer graphene**.

Interlayer Li has the lowest energy (**0 eV**) compared with **surface adsorption (+0.68 eV)** and **vacuum (+1.87 eV)**.

NEB calculations show a **very low diffusion barrier (~0.07 eV)** between neighboring intercalation sites. This enables **rapid in-plane Li diffusion**, allowing fast conductance modulation in the device channel.





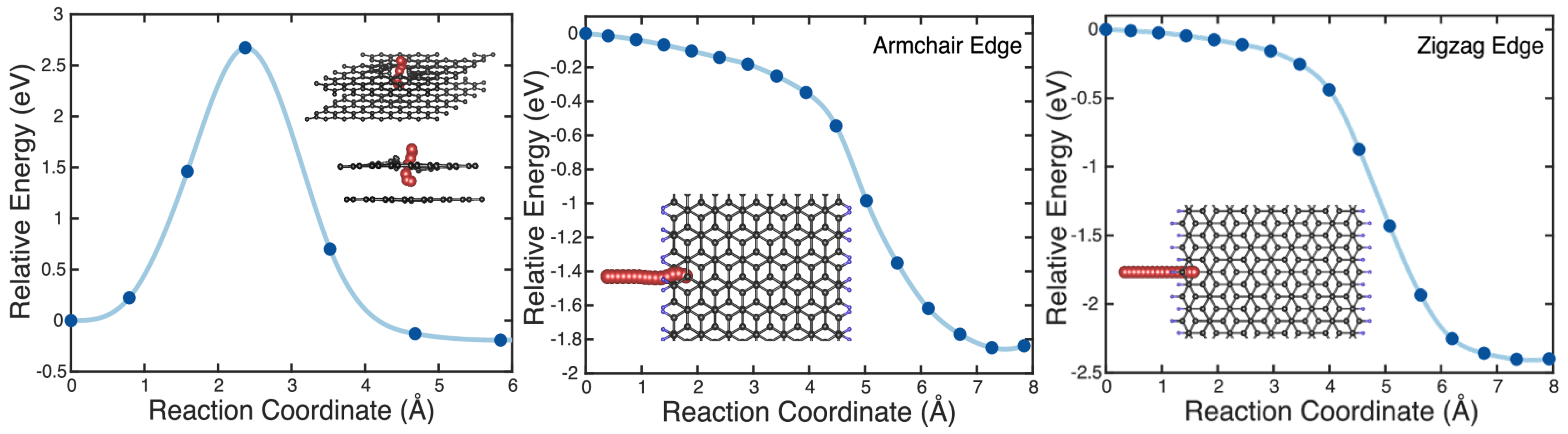
Li Intercalation Mechanisms

To understand Li insertion into the bilayer interlayer, **CI-NEB calculations** were performed for three pathways:

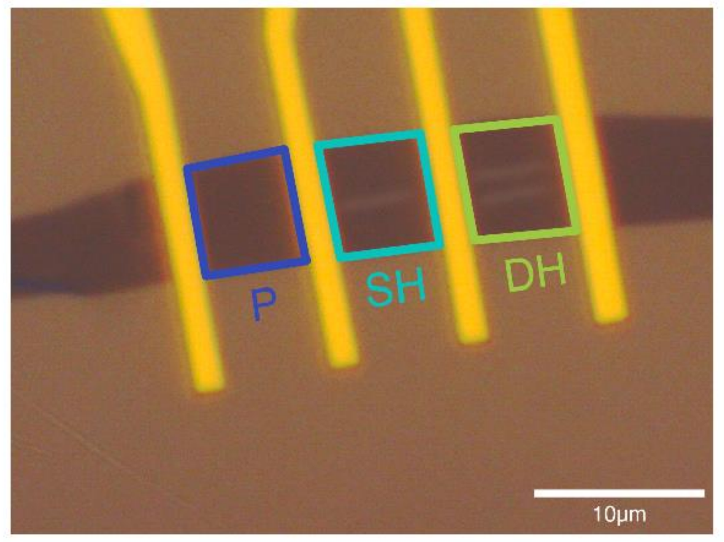
- insertion through a **1C vacancy** in the top layer
- insertion from **H-terminated zigzag edges**
- insertion from **H-terminated armchair edges**

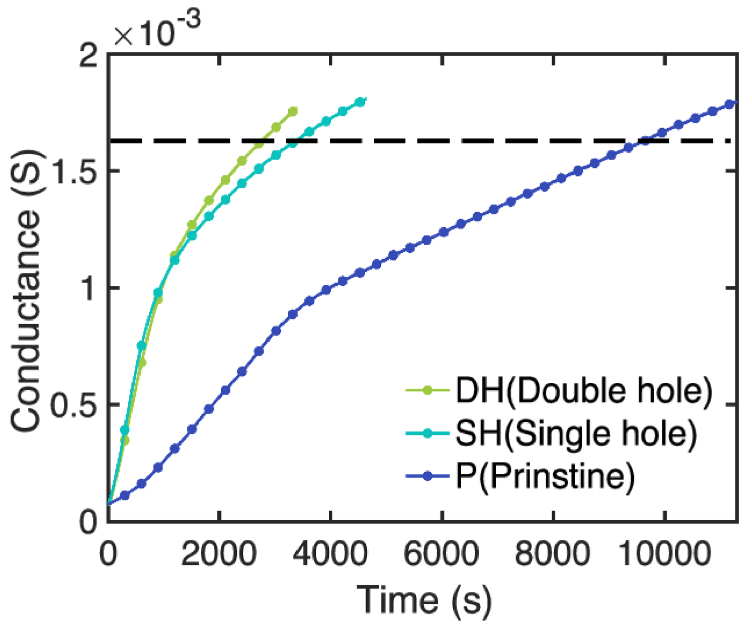
Vacancy-assisted insertion shows a **large barrier (~2.7 eV)**, indicating Li penetration through basal-plane defects is **energetically unlikely**.

In contrast, both **edge insertion is barrierless**, showing that **Li enters primarily through graphene edges**.



Experimental results from **University of Pittsburgh collaborators** [1] support the edge-insertion mechanism. Devices with **etched holes**, which increase exposed edges, exhibit **much faster conductance modulation**, consistent with **edge-driven Li intercalation** predicted by ab-initio calculations.





Ab-initio Calculation of Diffusion Constant

The Li **diffusion coefficient** D in AB-stacked bilayer graphene can be computed fully from first principles:

$$D = \frac{n_p}{2d} l^2 \Gamma,\ \Gamma = \nu e^{-\frac{E_a}{k_B T}}$$

where n_p is the number of equivalent diffusion pathways, l is the hop distance, d is the dimensionality of diffusion. The jump frequency Γ depends on the diffusion barrier E_a and the **attempt frequency** ν, which can be computed from the vibrational free energies [2,3]:

$$\nu = \frac{k_B T}{h} e^{\frac{F_{IS}^{vib} - F_{TS}^{vib}}{k_B T}},\ F^{vib} = \sum_i k_B T ln\left(2 sinh \frac{h\nu_i}{2 k_B T}\right)$$

where F_{TS}^{vib} and F_{IS}^{vib} are the vibrational free energies of the initial and transition states of the diffusion, and ν_i are the normal mode frequencies.

(AB, C18-Li-C18)	$d_{interlayer}$ in Å	ν in Hz	D in cm^2/s
With dispersion (DFT-D3)	3.83	8.75e+11	6.8459e-06
Without dispersion	4.09	1.94e+12	4.6602e-05

Our results show **dispersion corrections** significantly affects Li diffusion by:
- **reducing graphene interlayer spacing**
- **increasing diffusion barriers**
- **modifying the vibrational spectrum**
- **reducing the predicted diffusion constant**

Phonon calculations also show **attempt frequencies ~10^{12} s^{-1}**, lower than the commonly assumed **10^{13} s^{-1}**.

The predicted Li diffusion coefficient is approximately in good agreement with experimentally reported values of ~10^{-6} to 10^{-5} cm^2/s [4].

Future Work, Acknowledgments, and References

- Explore additional **Li intercalation pathways**
- Study effects of **charge states and Li concentration**

Supported by the NSF Future of Semiconductors (FuSe) Program, Award 2328815.
Experimental collaborators (University of Pittsburgh):
Yuzhi He, Feng Xiong, Shahin Hashemkhani, Rajkumar Chinnakonda Kubendran
Undergraduate Researcher: Keya Joy

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