Understanding hydrodesulfurization at the atomic level: a computational science approach applied to catalysis

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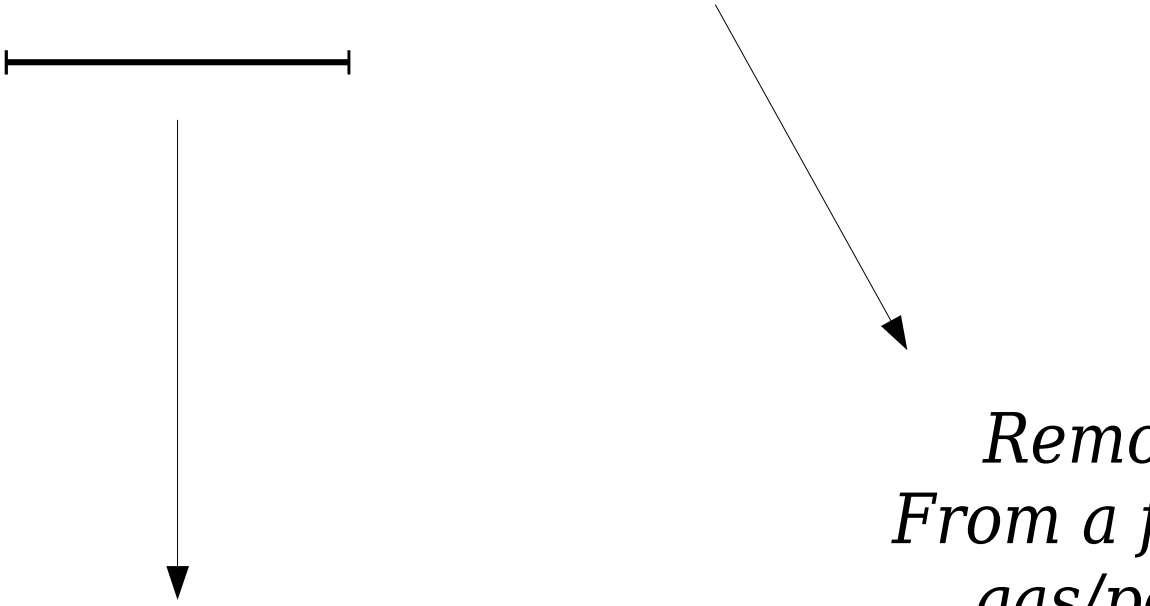
Introduction

About the research project

Flue-gas desulfurization

Hydrodesulfurization

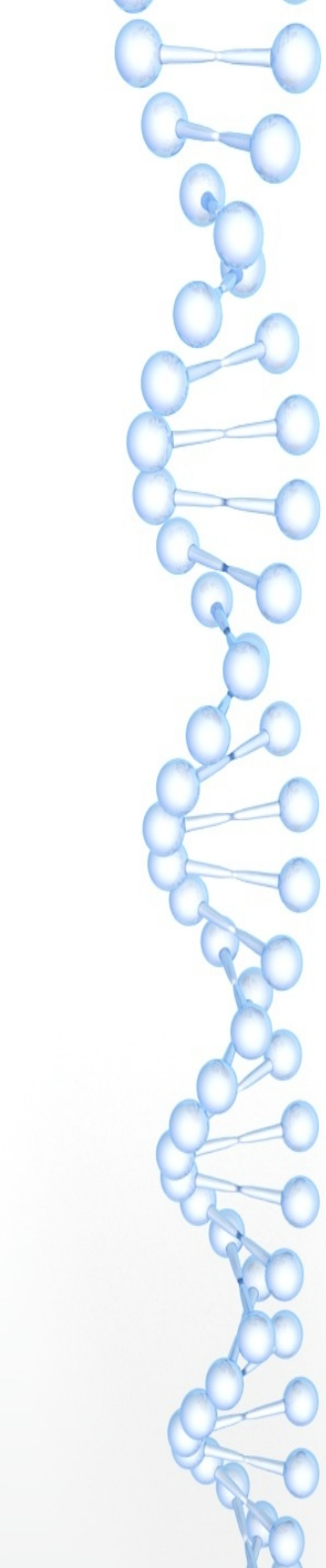
Hydrodesulfurization



Remove sulfur From a fuel (natural gas/petroleum)

Hydrogen sulfide (H_2S)

Hydrodesulfurization



$$\underline{1.}\ MoS_2 + H_2 \rightarrow MoS_2^{(S\text{-}Vac.)} + H_2S$$

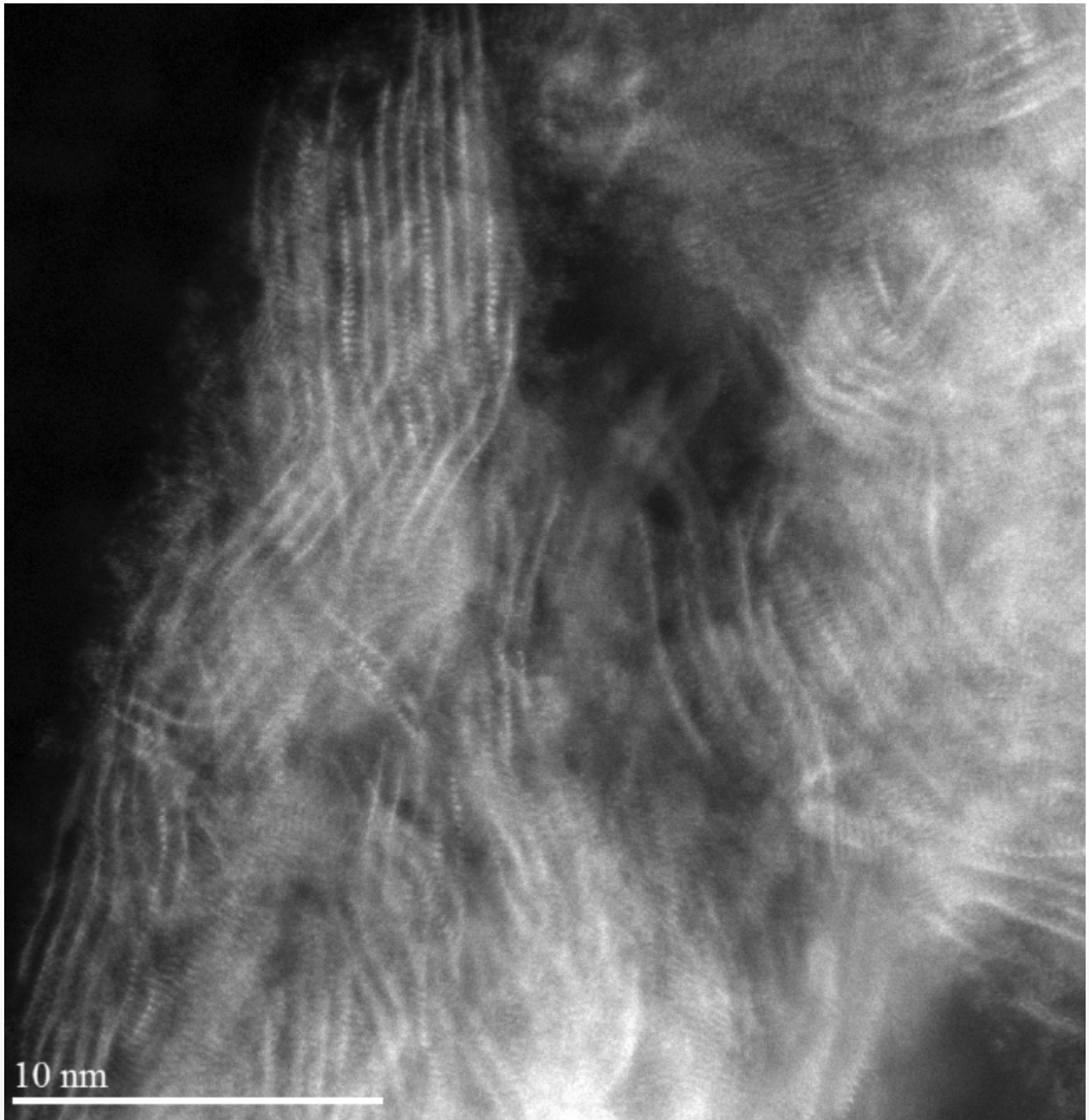
$$\underline{2.}\ MoS_2^{(S\text{-}Vac.)} + C_4H_4S + 3H_2 \rightarrow MoS_2 + C_4H_{10}$$

HRTEM images

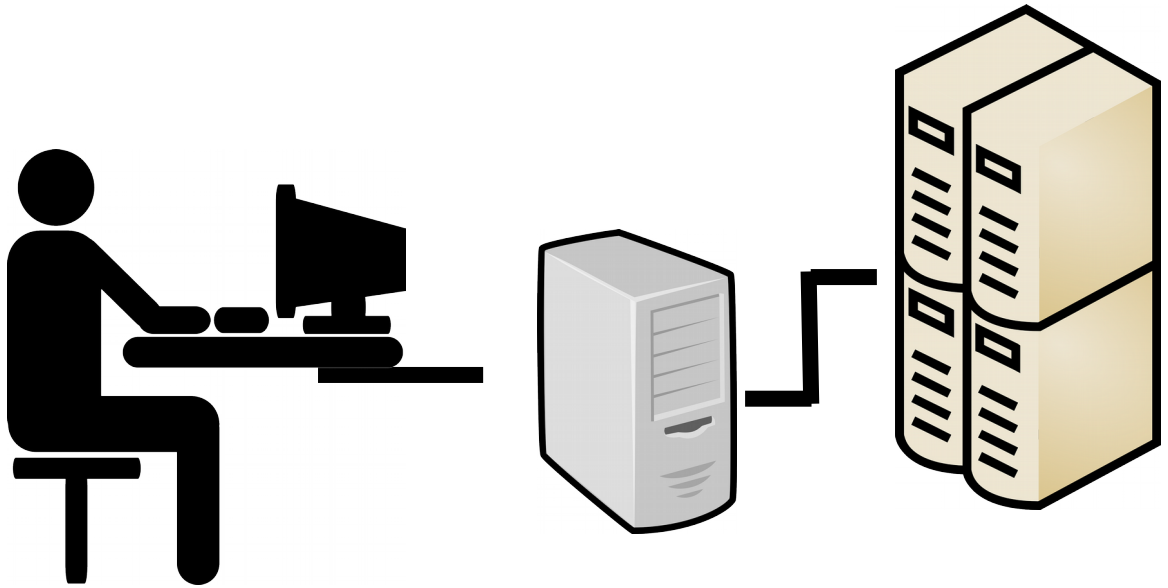
Miguel José Yacamán
University of Texas at San Antonio, USA

https://en.wikipedia.org/wiki/Miguel_José_Yacamán

HRTEM images



Computer simulations



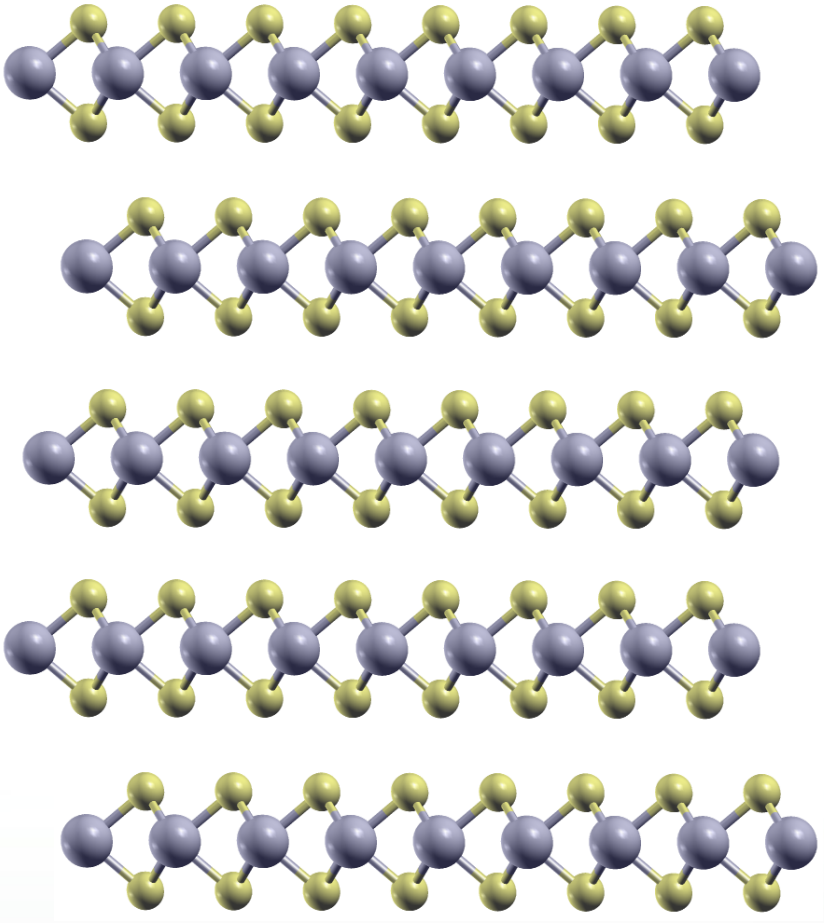
Classical:

Lammps - Reax

Quantum calculations:

Quantum Espresso: PBE(GGA) / Hybrid (HSE)

2D Van Der Waals solids

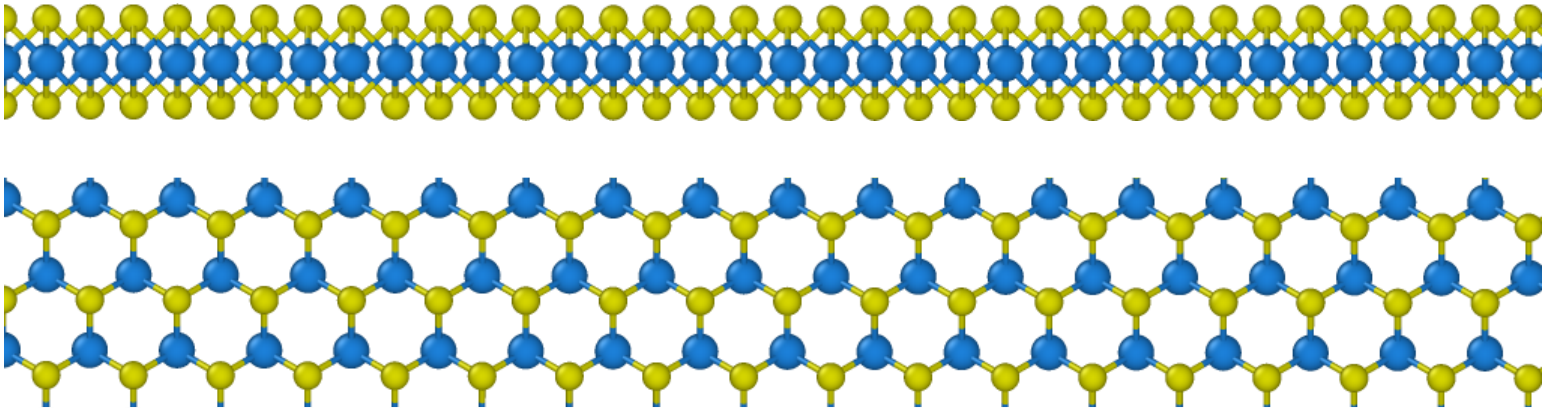


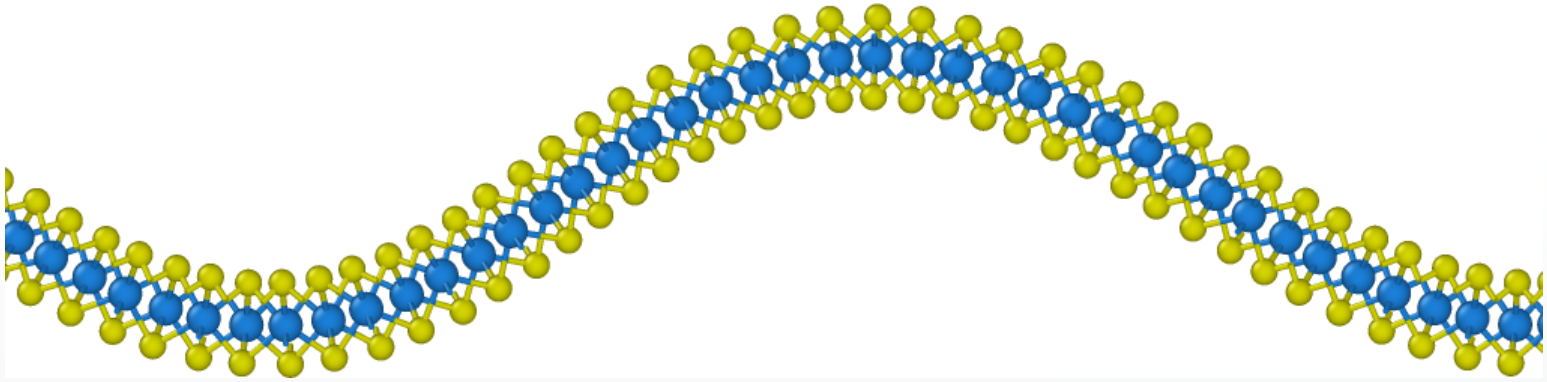
Weak interaction:

Van Der Waals interactions

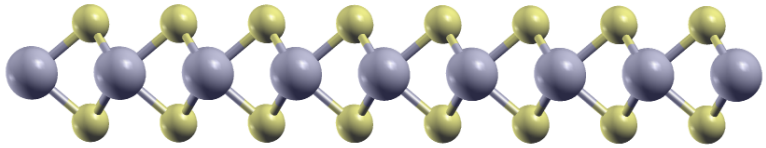
Strong covalent/ionic bonds

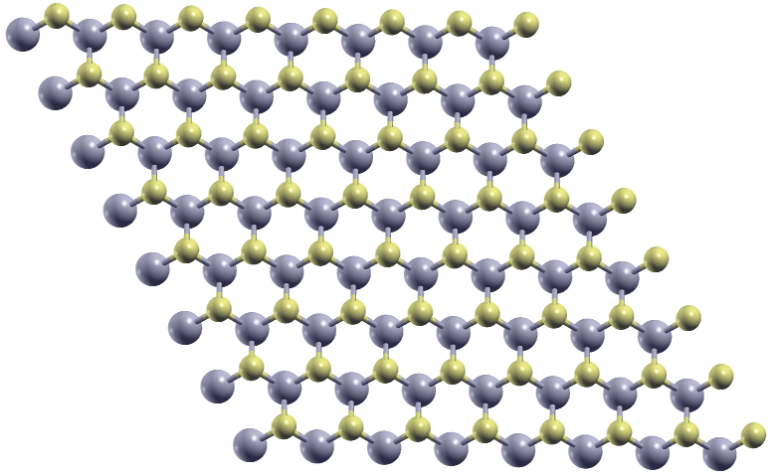
Planar MoS_2 layers

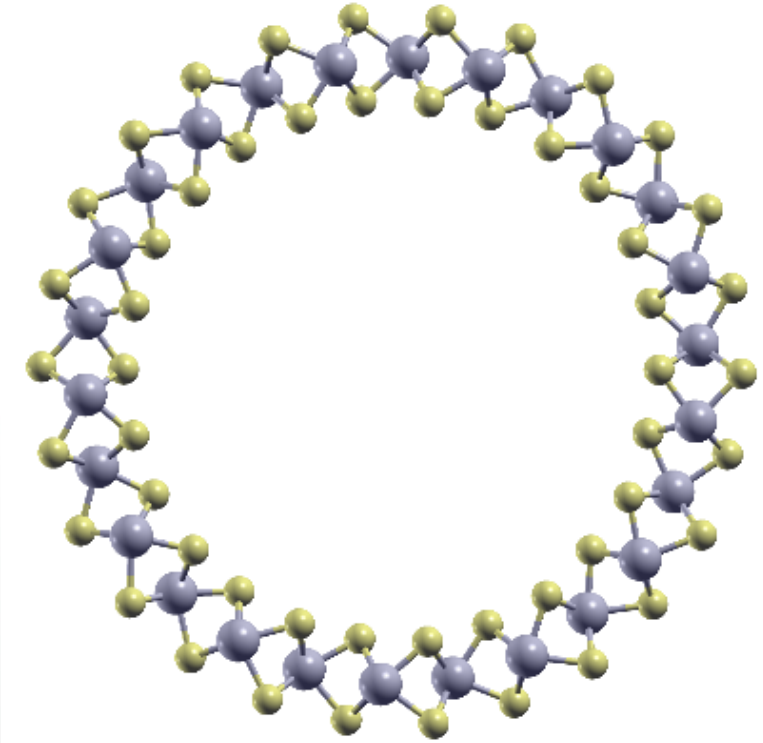


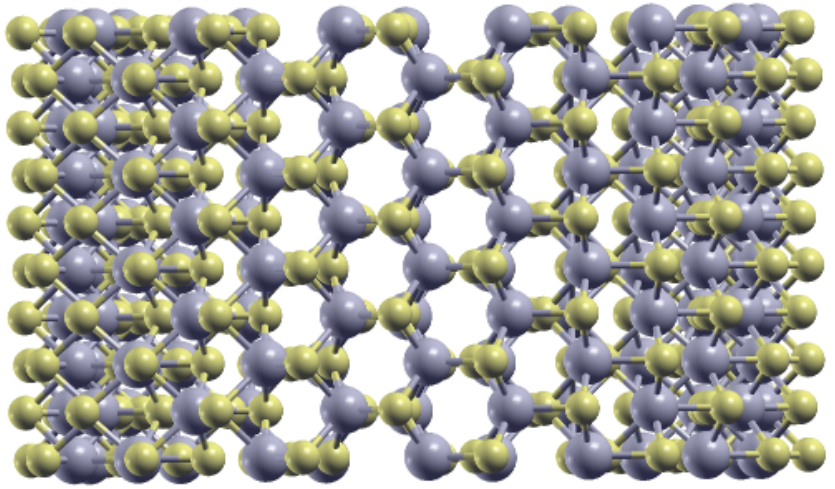


Planar MoS_2 layers

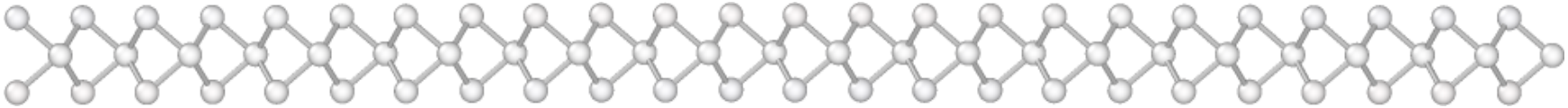


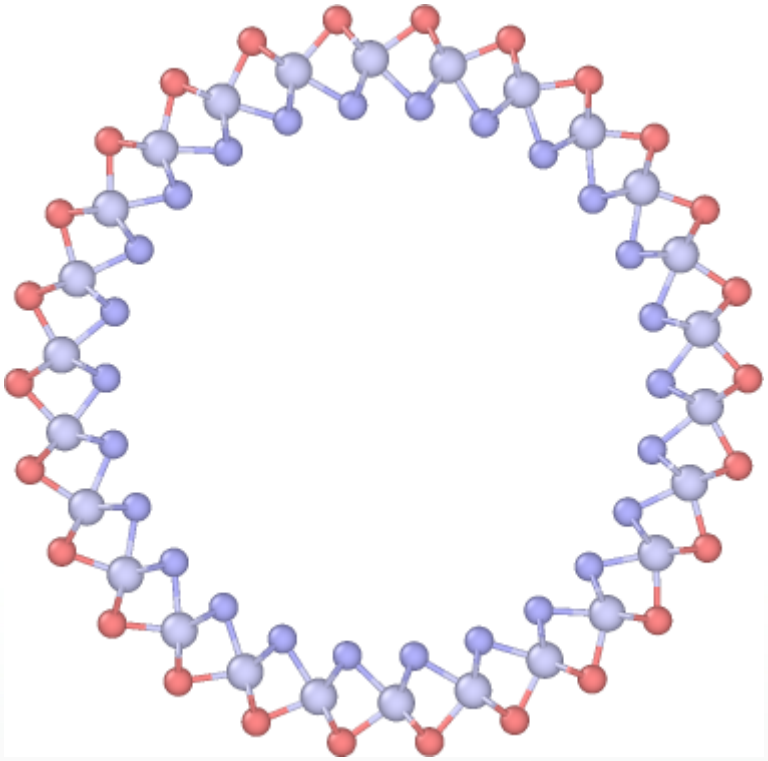


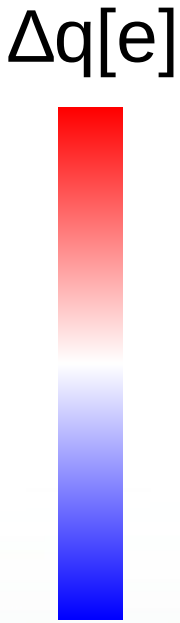




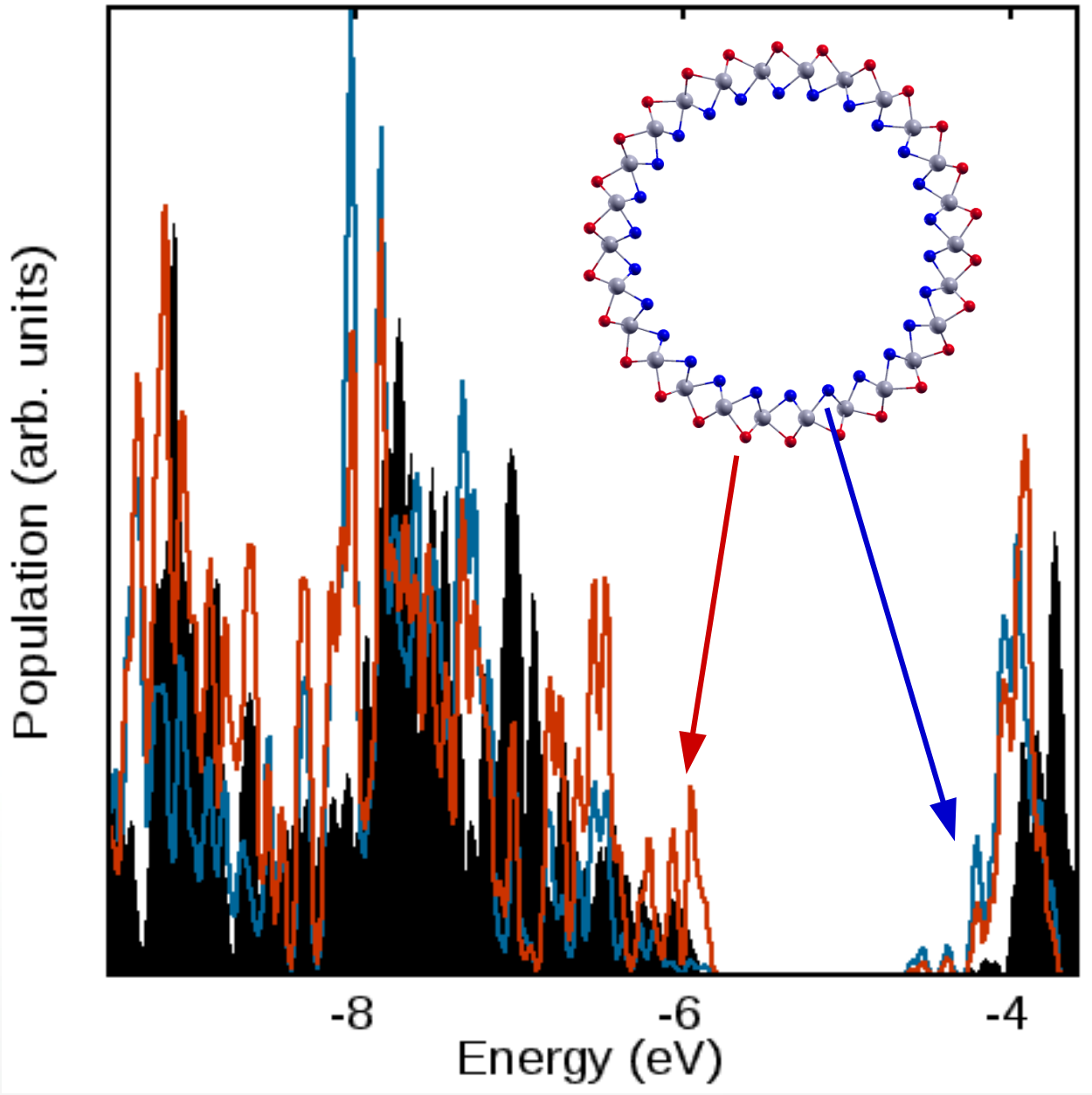
Curved MoS_2 layers



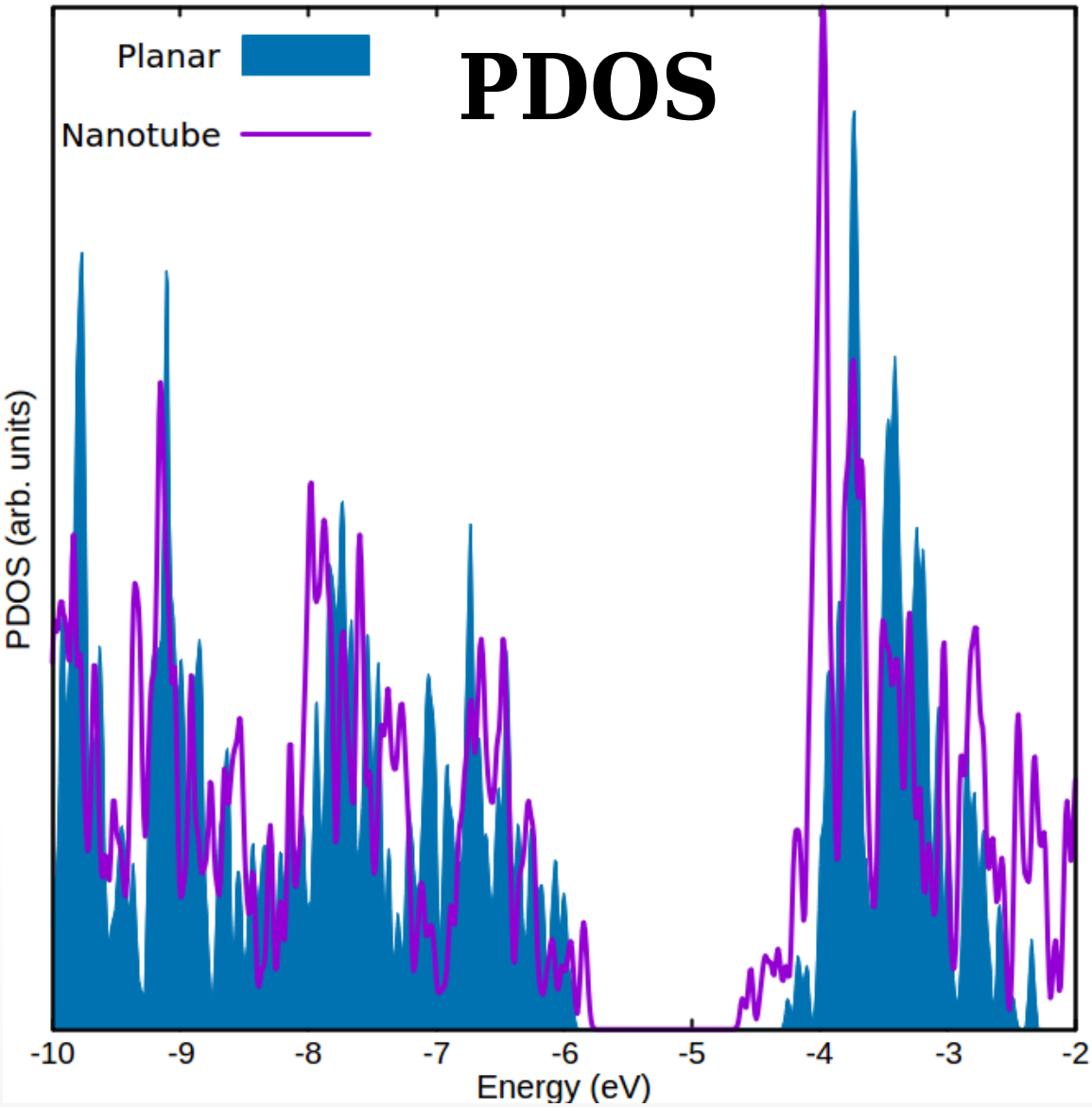




Curved MoS_2 layers



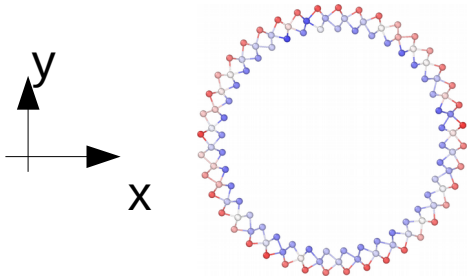
Curved MoS_2 layers



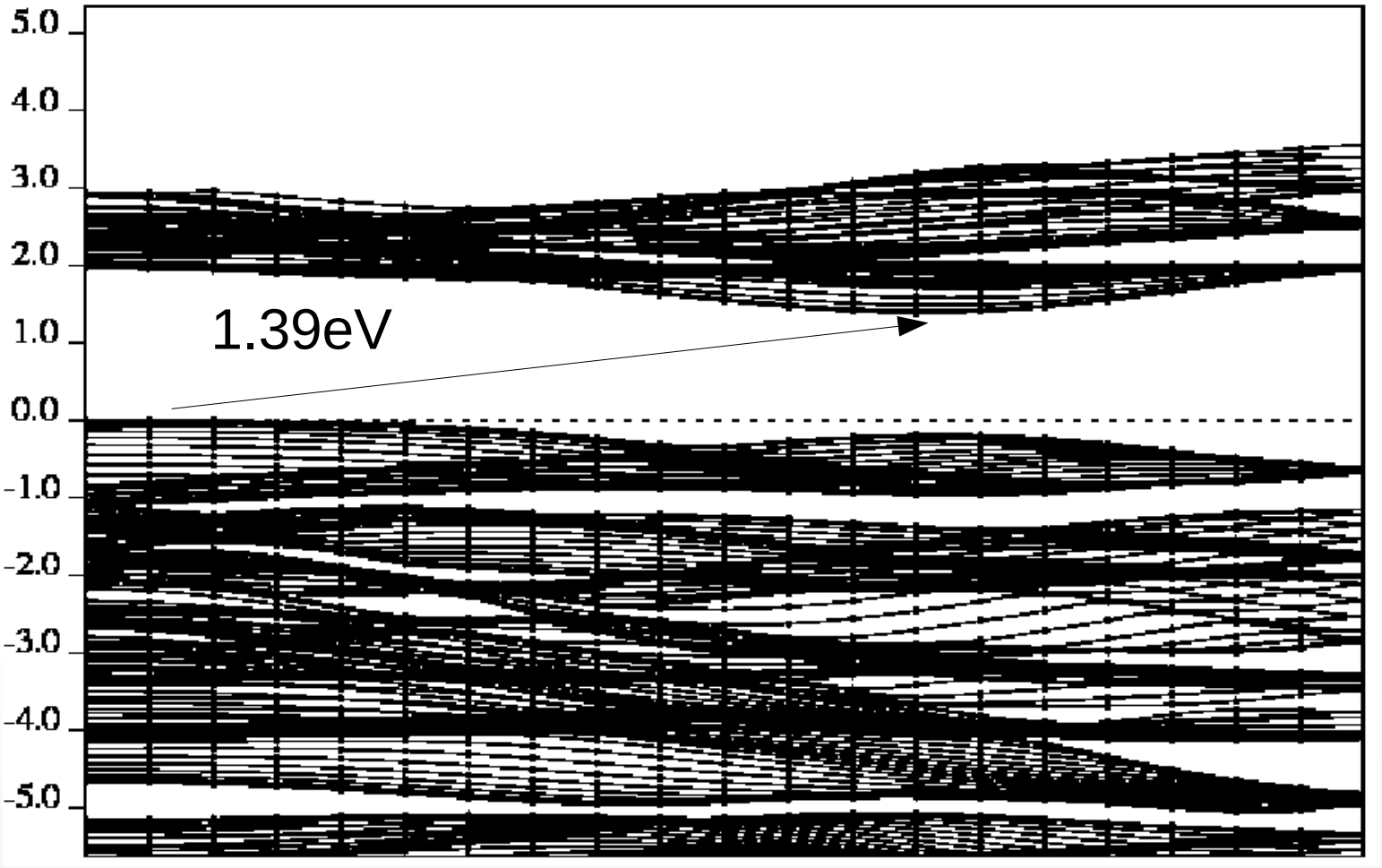
HUMO-LUMO gap

1.66eV
1.18eV

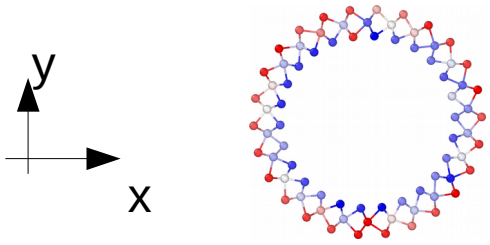
Curved MoS_2 layers



k_z: Γ → X
(nanotube direction)



Curved MoS_2 layers



k_z: Γ → X
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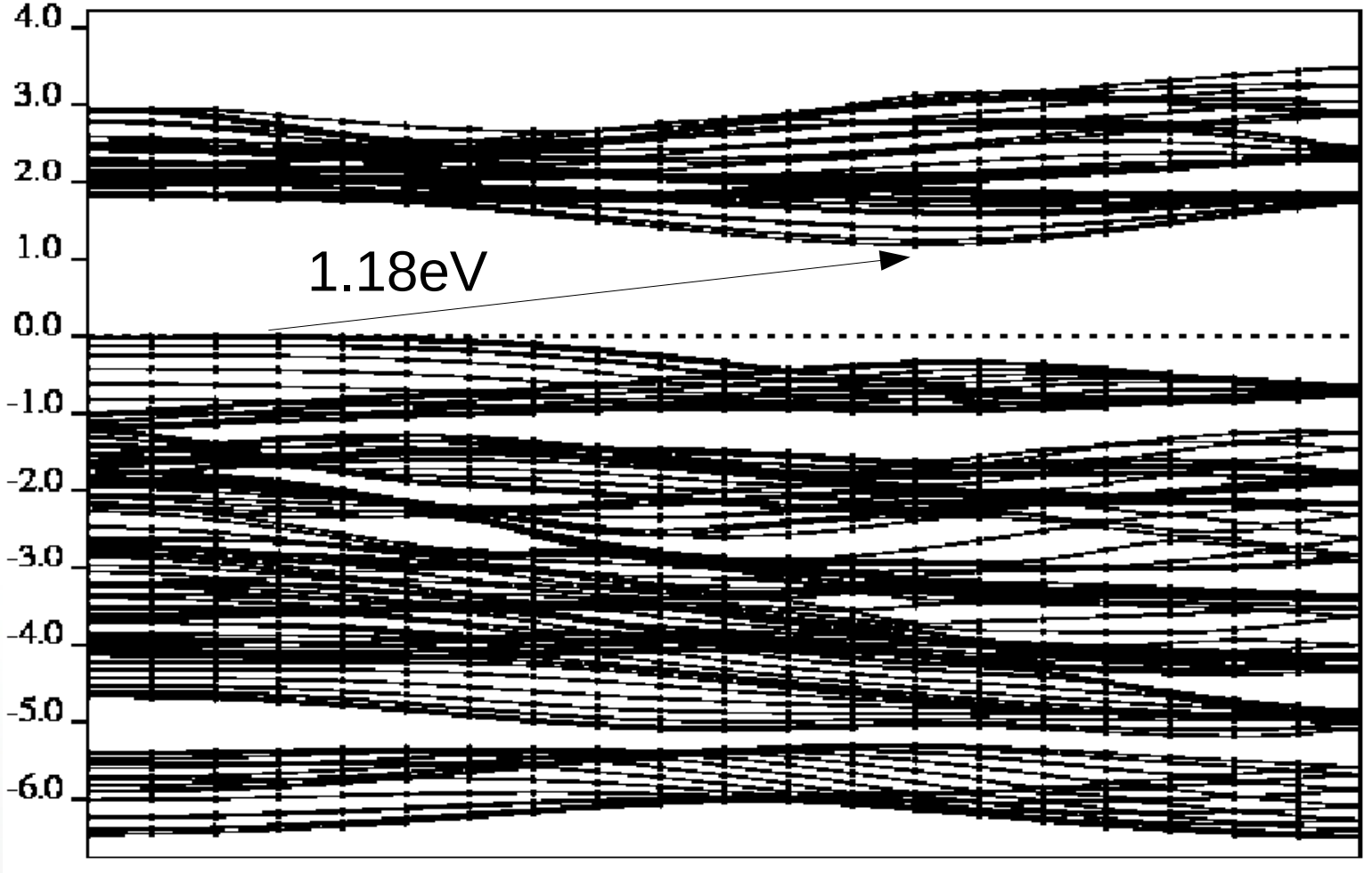
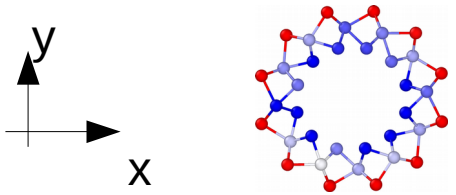


Curved MoS_2 layers



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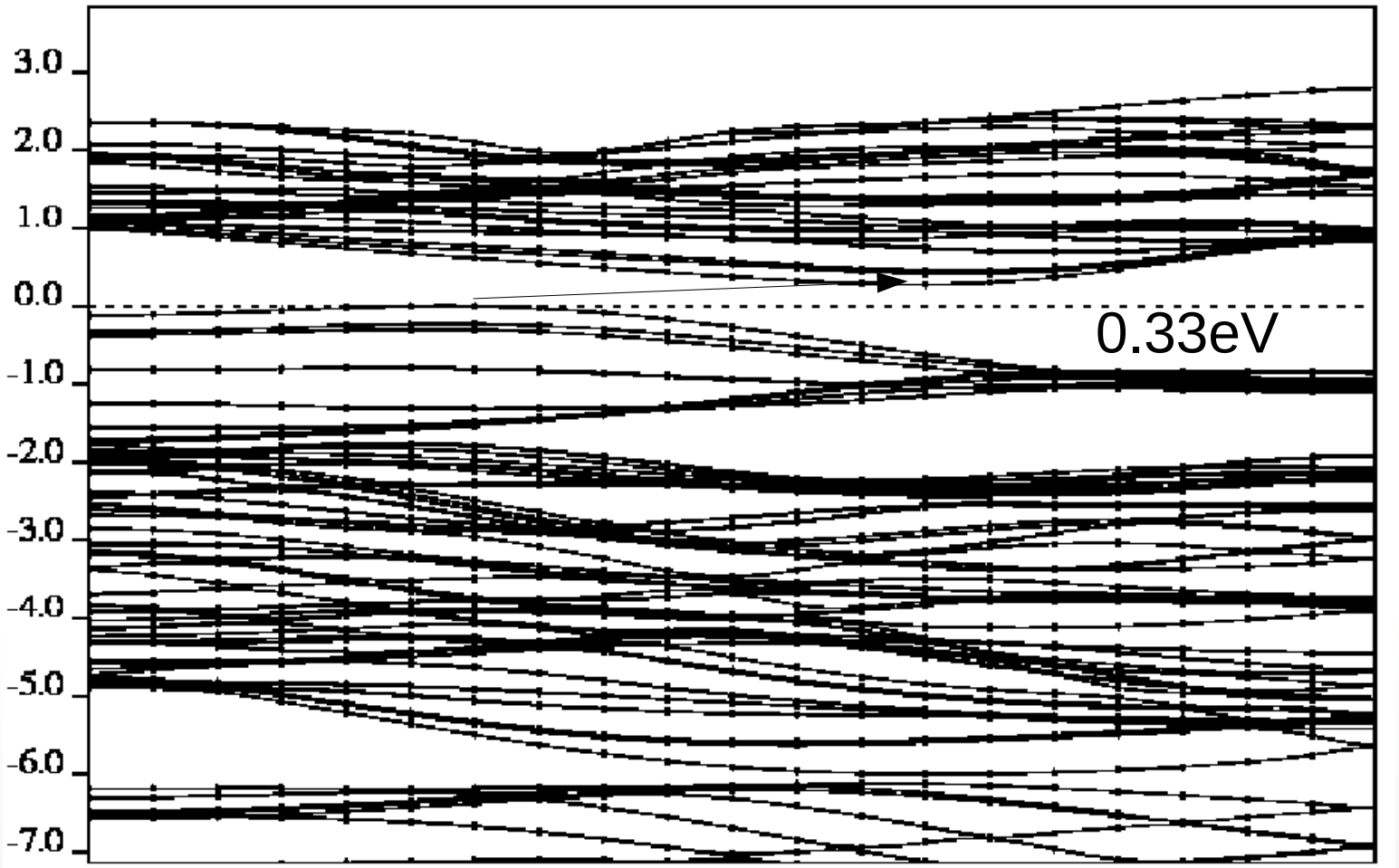
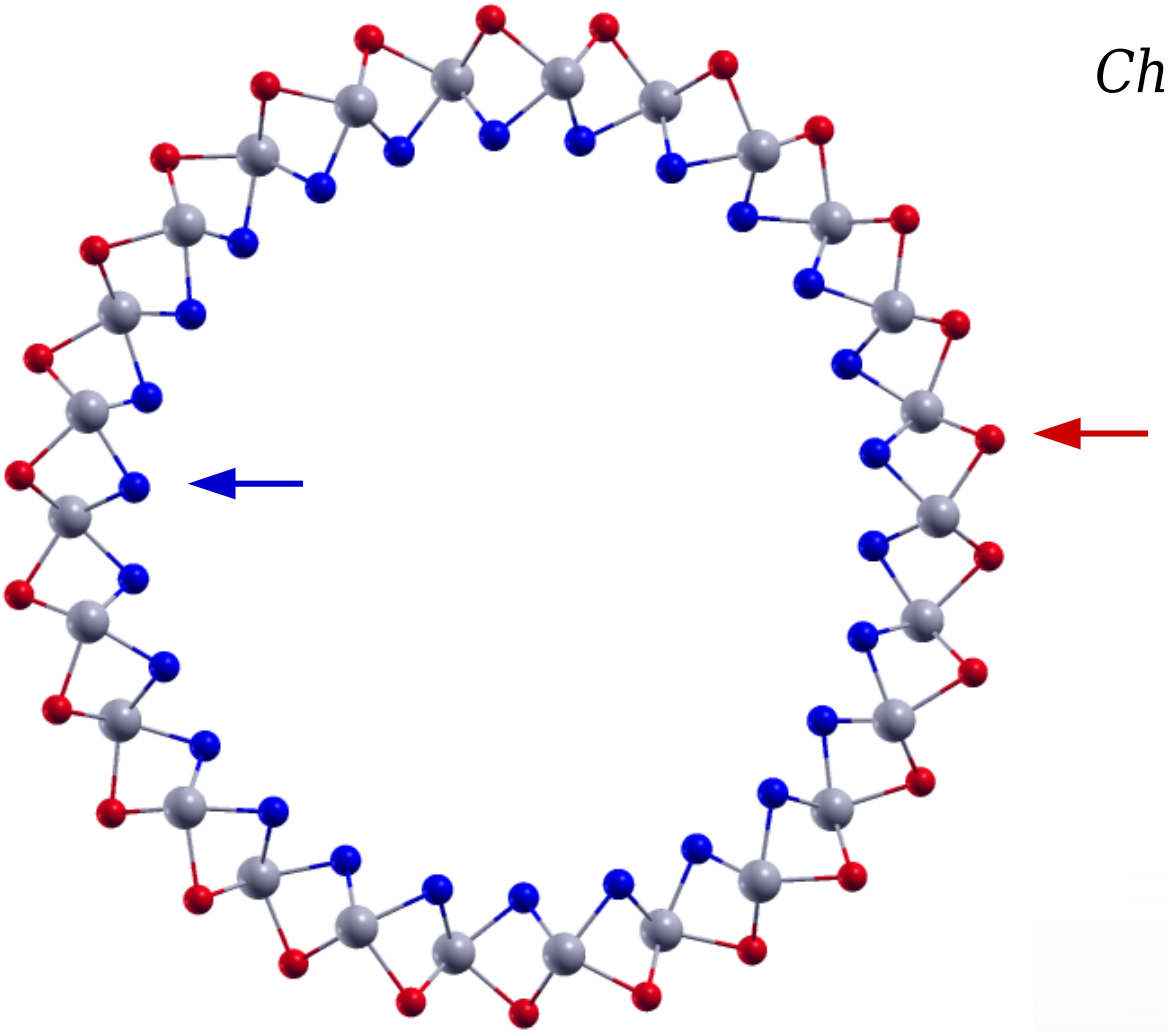


S-vacancies



Chemical potential for S: H_2S

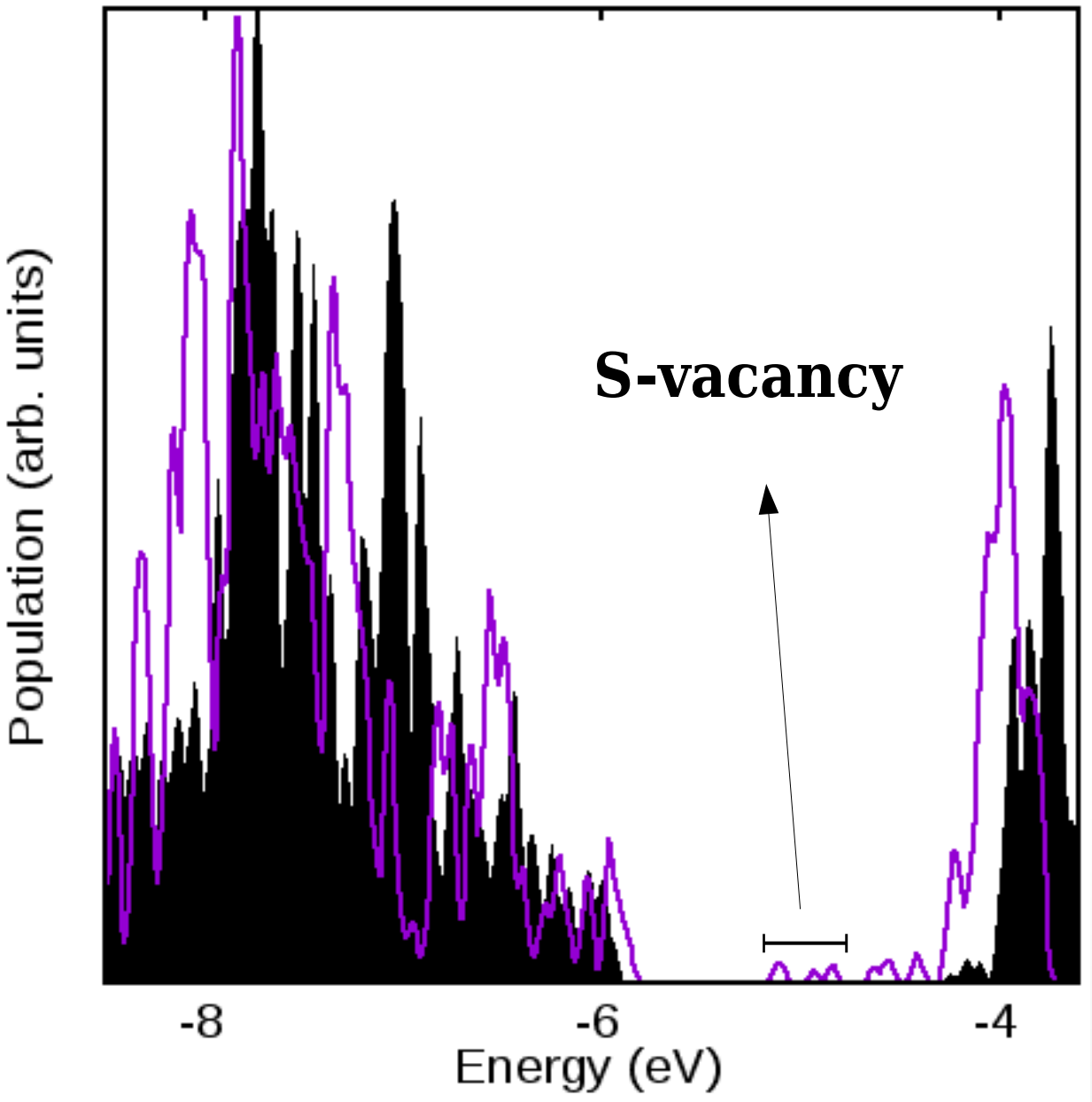
S-vacancy Formation energy

Planar → 2.34eV

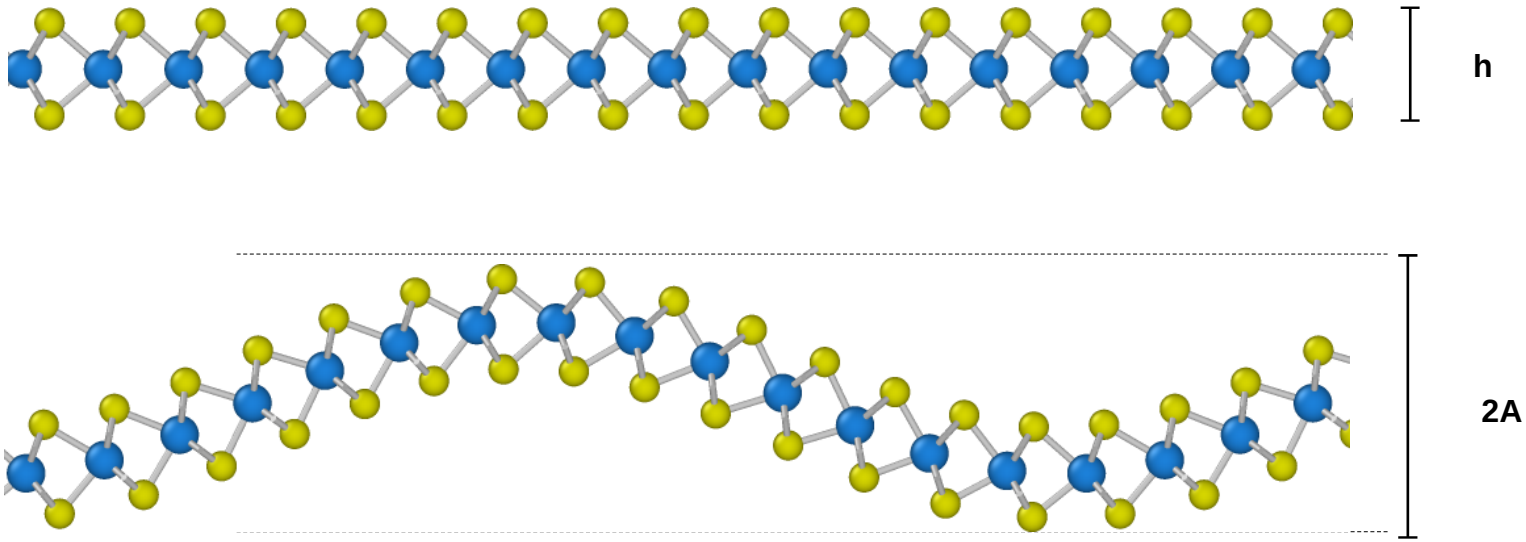
Inside → 1.63eV

Outside → 3.91eV

S-vacancies



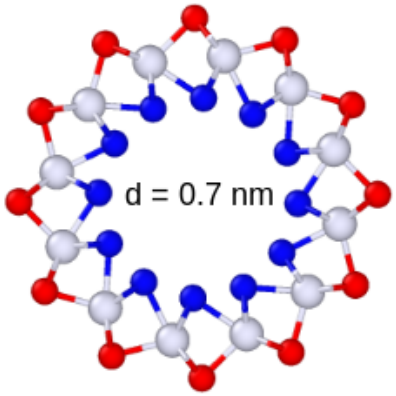
Reax validation



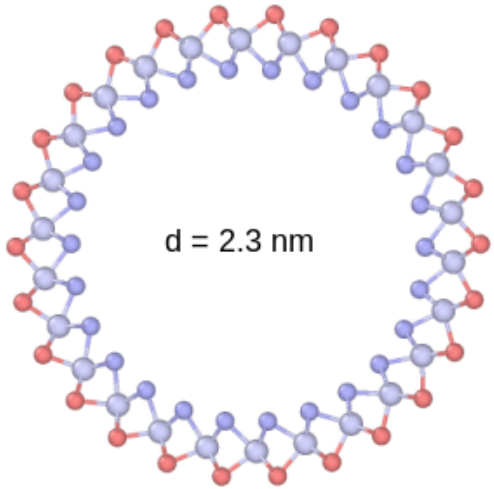
(12x1x1) L_{eq}	d_{MoS} [Å]	d_{MoMo} [Å]	h [Å]	A (comp. 10%) [Å]
ReaxFF	2.42	3.19	3.14	7.81
DFT	2.41±0.02	3.18±0.01	3.13±0.01	7.87

Reax validation

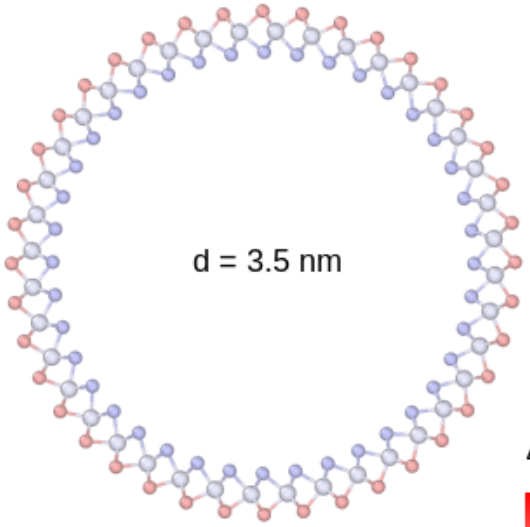
ReaxFF



(6x1x1)

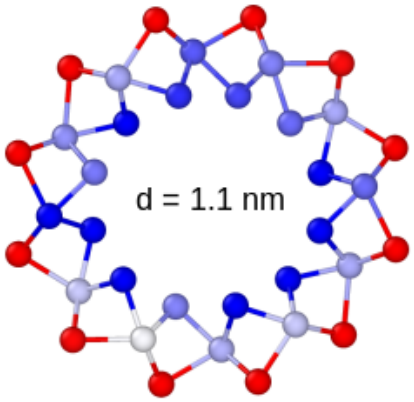


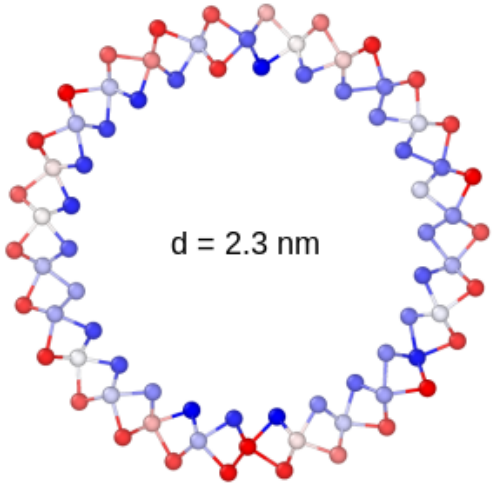
(13x1x1)

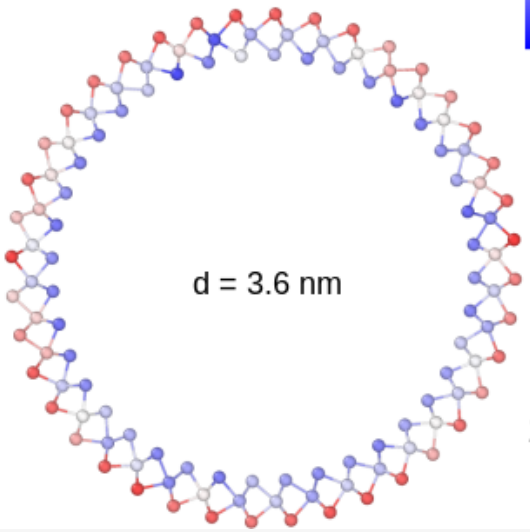


(20x1x1)

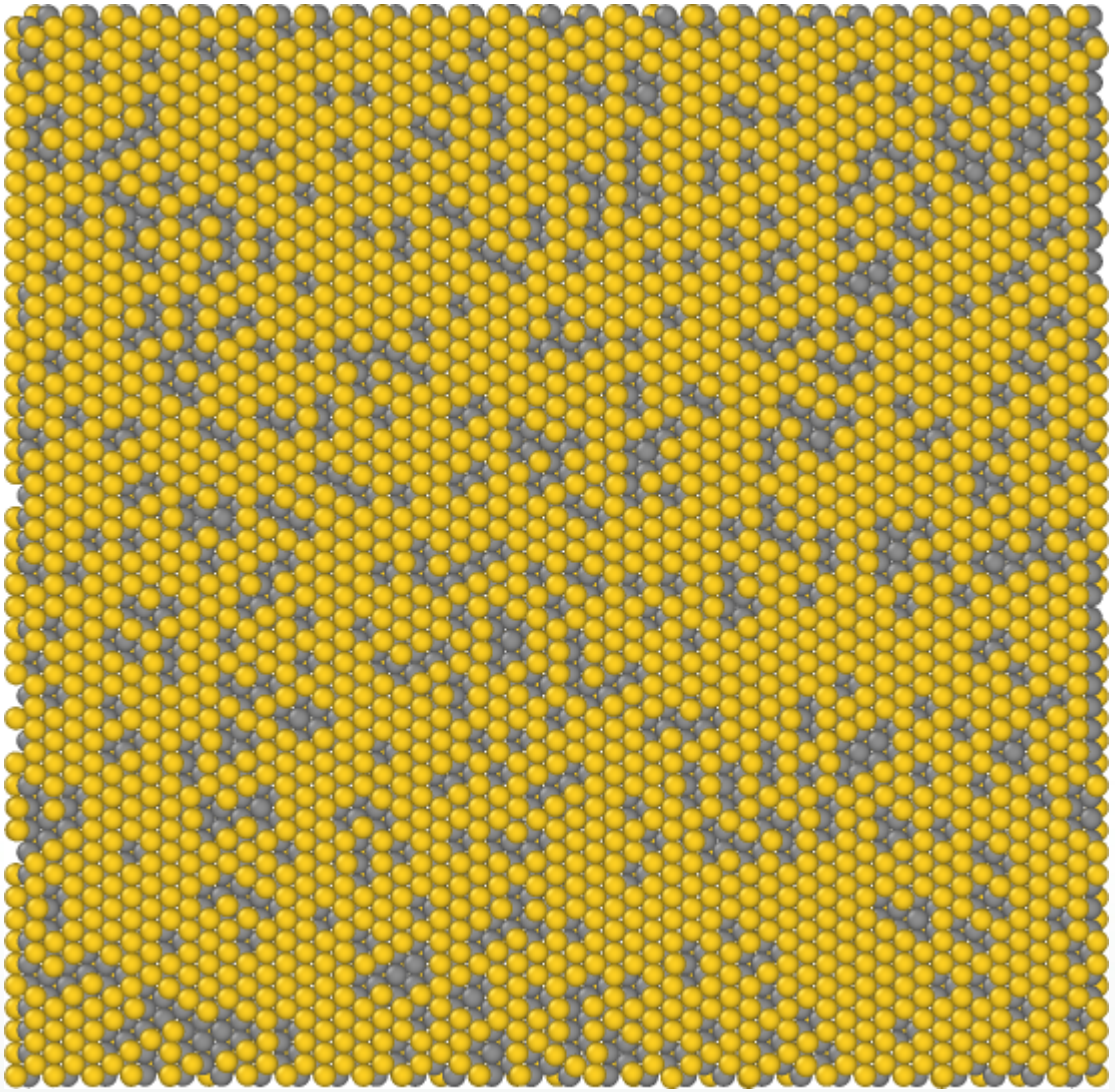
DFT





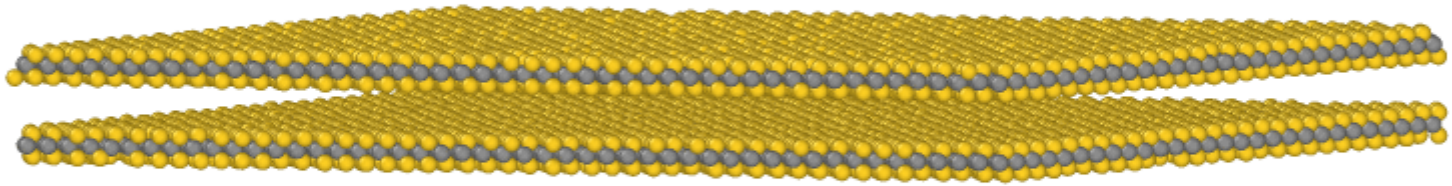


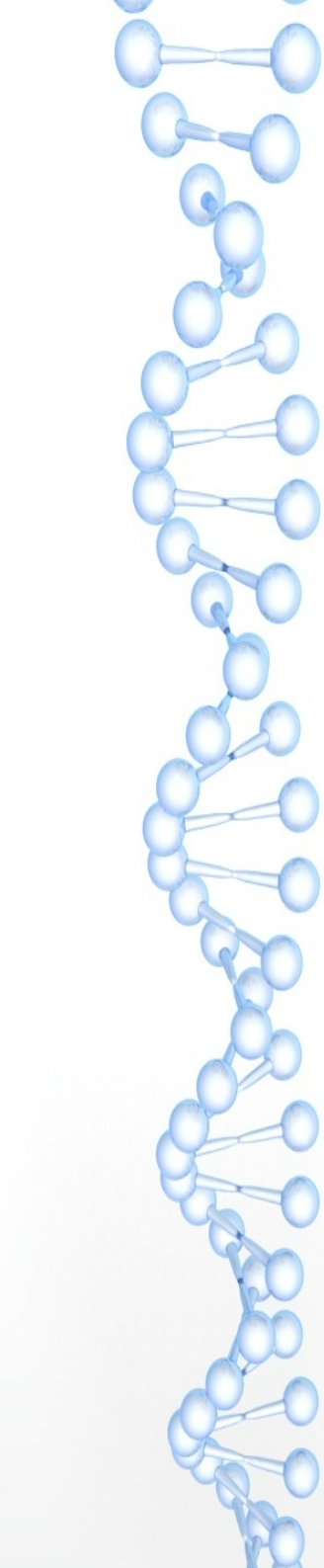
Vacancy → Curved structures



NPT at
700K

Vacancy → Curved structures





Ongoing work

Quantify vacancy/curvature relation

Influence of additional layers:

Van der Waals interactions

Acknowledgments