Harnessing Large-Scale Quantum Calculations for Predicting Material and Chemical Properties

Anshuman Kumar

Ph.D., Materials Science and Engineering
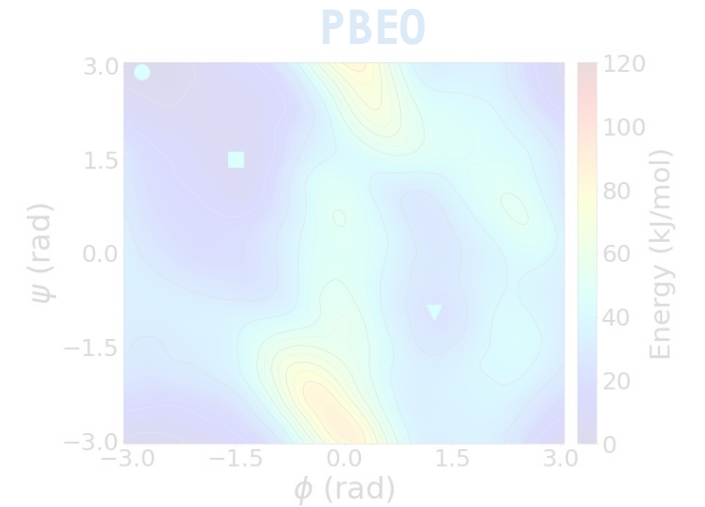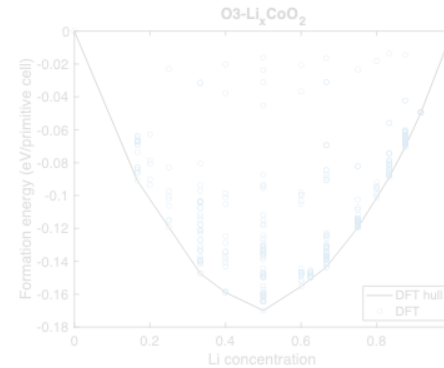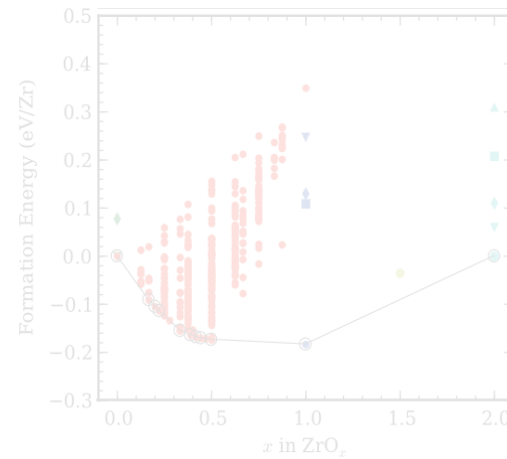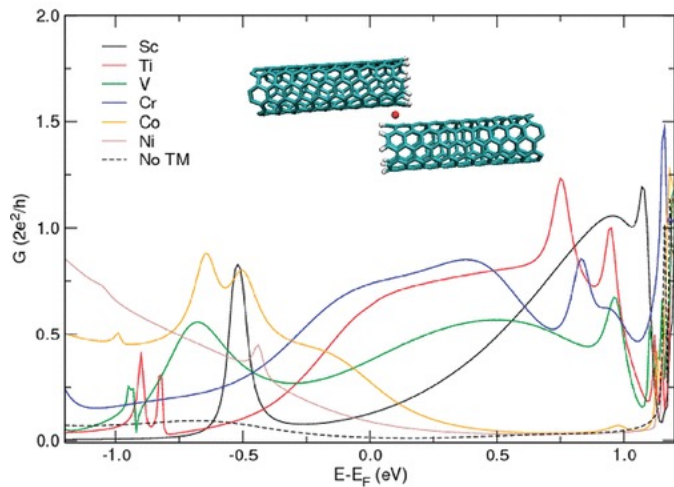*University of California Riverside*

November 08, 2023

Contents

- Background and Motivation

- Project Description and Objectives

- DFT and DFTB

- Results

- Conclusion

- Publications

Background and Motivation

Puchala, B., & van der Ven, A. (2013). *Physical Review B, 88*(9), 094108
Huran, A. W., et al. (2020).*Physica Status Solidi, 14*(6), 2881–2888
Sevgen, E., et al. (2018)*Journal of Chemical Theory and Computation, 14*(6), 2881–2888

Li, Y. & Marzari, N., et al. (2011).*ACS Nano, 9726-9736*
Teichert, G., et al. (2021).*arXiv preprint, 2104*(08318)

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Research Projects

Calculate the transport properties of Carbon Nanotubes

Efficient calculation of formation energies and convex hull

Large scale Metadynamics calculations

DFT+NEGF

DFTB+CASM

GPU-DFTB

❖ Dopant atoms vs inter/intra conductivity

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Intratube

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DFT Introduction (brief)

Born-Oppenheimer Approximation

$$\Psi_{total}(\vec{r}, \vec{R}) = \Psi_{el}(\vec{r}, \vec{R}) \, \Psi_N(\vec{R})$$ [1]

Electronic Schrodinger Equation

$$\widehat{H}_{el} \Psi_{el}(\vec{r}, \vec{R}) = E_{el} \Psi_{el}(\vec{r}, \vec{R})$$ [2]

DFT Introduction (brief)

$$E[n] = T[n] + E_{ext}[n] + E_H[n] + E_{xc}[n] \qquad [3]$$

$$T = \sum_i \int \psi_i^* \nabla^2 \psi_i dr \qquad E_{ext} = \int V_{ext}(\vec{r}) n(\vec{r}) d^3 r \qquad E_H = \frac{1}{2} \iint \frac{n(\vec{r})n(\vec{r}')}{|\vec{r} - \vec{r}'|} d^3 r d^3 r'$$

$$\left[-\frac{\hbar^2}{2m} \nabla^2 + V_{ext}[n](\vec{r}) + V_H[n](\vec{r}) + V_{XC}[n](\vec{r}) \right] \psi_i(\vec{r}) = \epsilon_i \psi_i(\vec{r}) \qquad [4]$$

$$V_H(\vec{r}) = \int \frac{n(\vec{r}')}{|\vec{r} - \vec{r}'|} d^3 r' \qquad V_{xc}(\vec{r}) = \frac{\delta E_{XC}[n]}{\delta n(\vec{r})}$$

$$n(\vec{r}) = \sum_i^N |\psi_i(\vec{r})|^2$$

Self Consistent Field (SCF) Procedure

Guess for the wavefunction or density

$$\psi_i(\vec{r}) \; ; \; n_{in}(\vec{r})$$

Calculate Effective Potential

$$V_{eff}(\vec{r}) = V_{ext}(\vec{r}) + V_H[n] + V_{XC}[n]$$

Solve KS Equations

$$\left[-\frac{\hbar^2}{2m}\nabla^2 + V_{eff}(\vec{r})\right]\psi_i(\vec{r}) = \epsilon_i\psi_i(\vec{r})$$

Compute Electron Density

$$n_{out}(\vec{r}) = \sum_i^N |\psi_i(\vec{r})|^2$$

$$R = |n_{out}(\vec{r}) - n_{in}(\vec{r})|$$

NO

$R < tolerance$

YES

Energy, density, wavefunctions
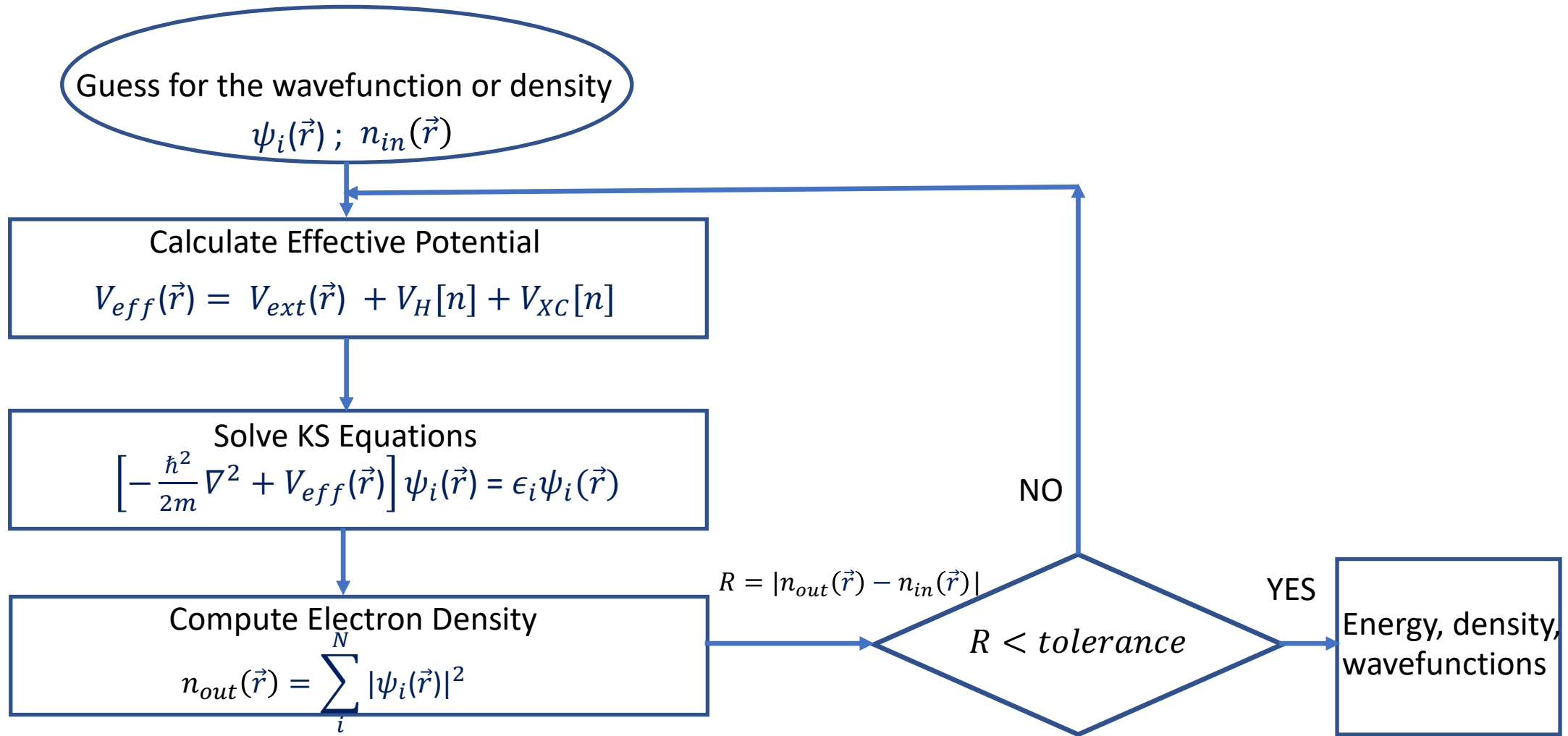
Research Statement

Can we enhance transport in aligned CNT?

Chen, M., Li, W., **Kumar, A.**, Li, G., Itkis, M., Wong, B., & Bekyarova, E. (2019). Covalent Atomic Bridges Enable Unidirectional Enhancement of Electronic Transport in Aligned Carbon Nanotubes. *ACS Applied Materials & Interfaces, 11*(21), 19315–19323

Transport properties of doped CNT

current flow with Li and Cr atoms in CNT

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Transmission

Cr

Li

Intertube: Cr shows enhanced transmission
Intratube: Li shows enhanced transmission

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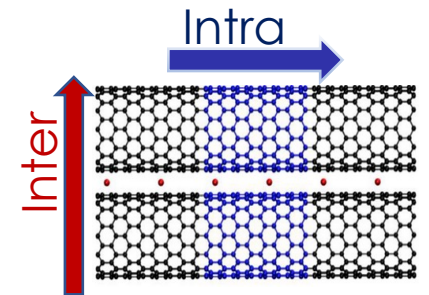
Density of States

High DOS with Cr doping

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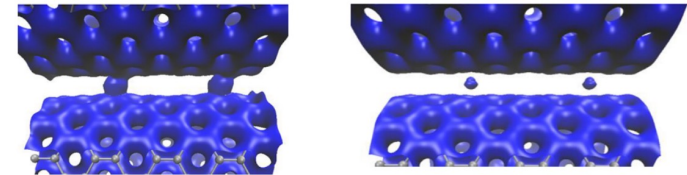
Conductance

$$G = \frac{2e^2}{h} \int_{-\infty}^{\infty} T(E) \left\{ -\frac{\partial f(E)}{\partial E} \right\} dE$$

	SWNT + Cr (S)	SWNT + Li (S)
Intra	1.75×10^{-5}	1.52×10^{-4}
Inter	2.05×10^{-5}	1.75×10^{-7}

Charge Analysis

- Li transfers 0.175 e$^-$ to SWNT

- For Cr charge transfer is negligible (0.091 e$^-$)

Electron Density

Cr

Li

Intratube

Intertube
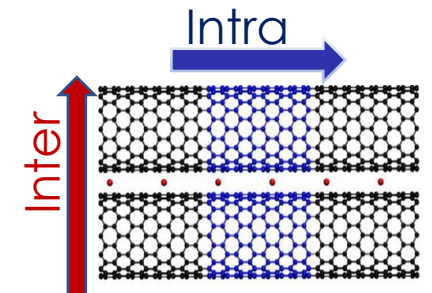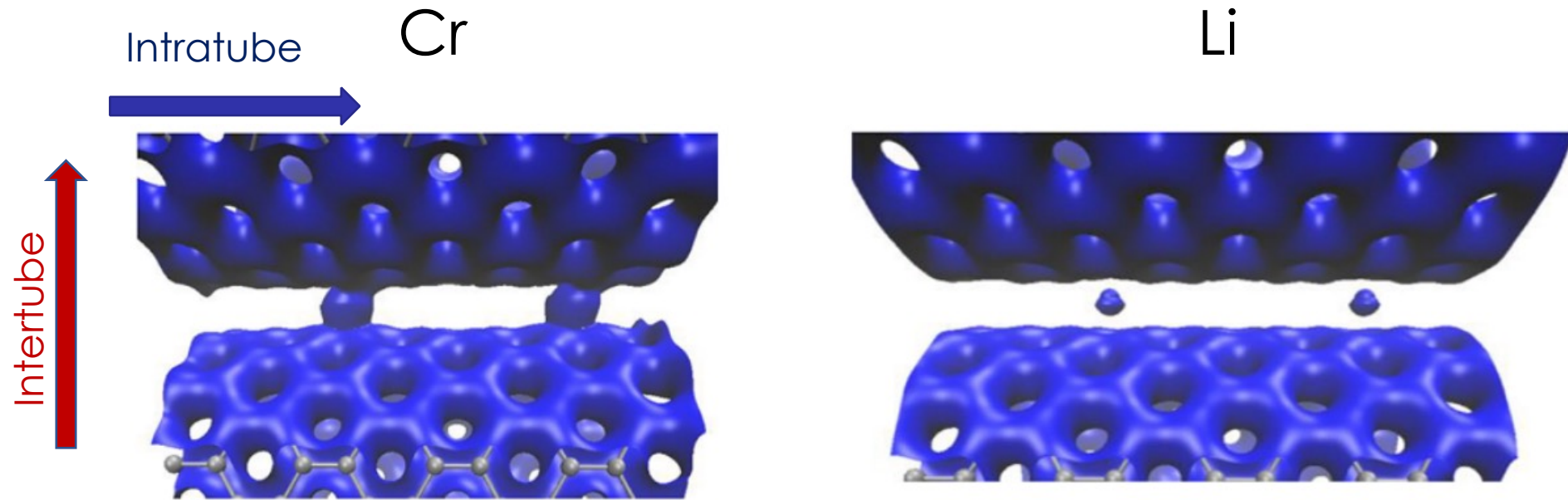
Cr orbitals hybridization forms conducting channel

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NEGF (brief)

Lead1 Device Lead2

$$\left[E\mathbb{I} - \mathbf{H}_D - \Sigma^R\right]\mathbf{G}^R = \mathbb{I}$$

$$T(E) = Tr\left[\boldsymbol{\Gamma}_L \mathbf{G}^R \boldsymbol{\Gamma}_R \mathbf{G}^A\right] \qquad \mathbf{G}^A = \mathbf{G}^{R\dagger}$$

$$\boldsymbol{\Gamma} = i\left(\Sigma^R - \Sigma^A\right) \qquad \Sigma^A = \Sigma^{R\dagger}$$

$$G = \frac{2e^2}{h}\int_{-\infty}^{\infty} T(E)\left\{-\frac{\partial f(E)}{\partial E}\right\}dE$$
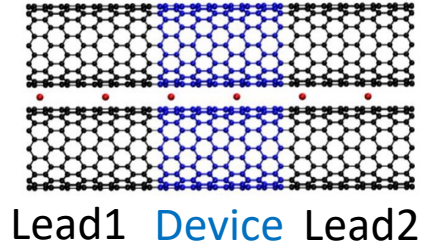
Perform DFT with PBC to obtain device Hamiltonian and self-energy

Chen, M., Li, W., **Kumar, A.**, Li, G., Itkis, M., Wong, B., & Bekyarova, E. (2019). Covalent Atomic Bridges Enable Unidirectional Enhancement of Electronic Transport in Aligned Carbon Nanotubes. *ACS Applied Materials & Interfaces, 11*(21), 19315–19323

FHI-aims

Left Lead   Device   Right Lead
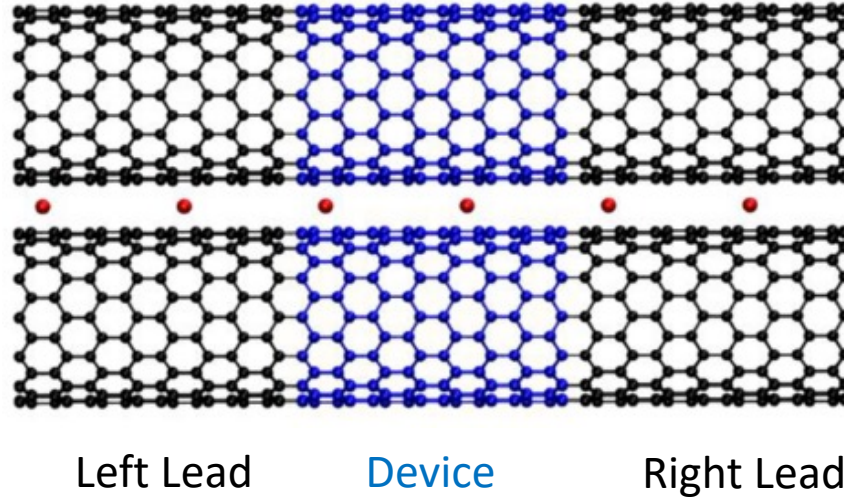
- All-electron, full-potential code, uses numeric atom-centered basis
- Enables accurate treatment of all electrons in the same footing without relying on pseudopotentials
- Geometry relaxation (force tol. = 10^{-4} eV/A)
- DFT to fetch self energy
- Input geometry for Transport calculations (left lead + device + right lead)
- Device Hamiltonian and self energies used in T(E)
- PBE with vdW interaction

Chen, M., Li, W., **Kumar, A.**, Li, G., Itkis, M., Wong, B., & Bekyarova, E. (2019). Covalent Atomic Bridges Enable Unidirectional Enhancement of Electronic Transport in Aligned Carbon Nanotubes. *ACS Applied Materials & Interfaces, 11*(21), 19315–19323

Key Findings

- dopants affects directional transport in SWCNTs

- Covalent bond formed by Cr increases the Intertube conductivity

- Li mostly affects the conductivity along the CNT

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DFTB

Why DFTB ?

- DFT good for small systems.

- Classical methods *does not consider quantum nature of chemical systems*.

- DFTB extremely fast for large systems

- Parameterized DFT with atom-centered basis functions

Kumar, A., Ali, Z. A., & Wong, B. M. (2023). Efficient Predictions of Formation Energies and Convex Hulls from Density Functional Tight Binding Calculations. *Journal of Materials Science & Technology, 141,* 236–244
Kumar, A. et al (2023). GPU-Enhanced DFTB Metadynamics for efficiently Predicting Free Energies of Biochemical Systems. *Molecules, 28,* 1277–1297
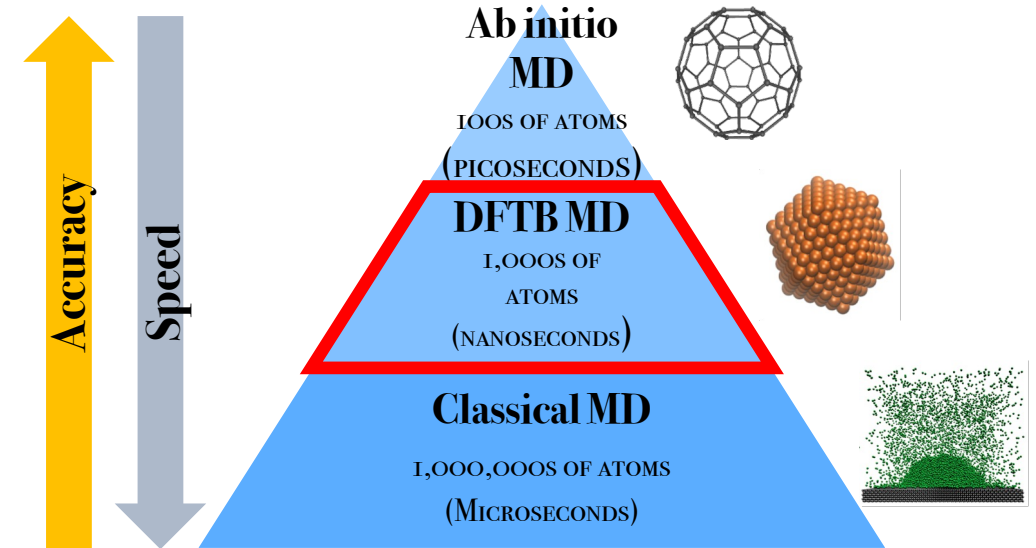
Why DFTB?

- DFTB 1-2 orders of magnitude faster than DFT

DFTB+CASM

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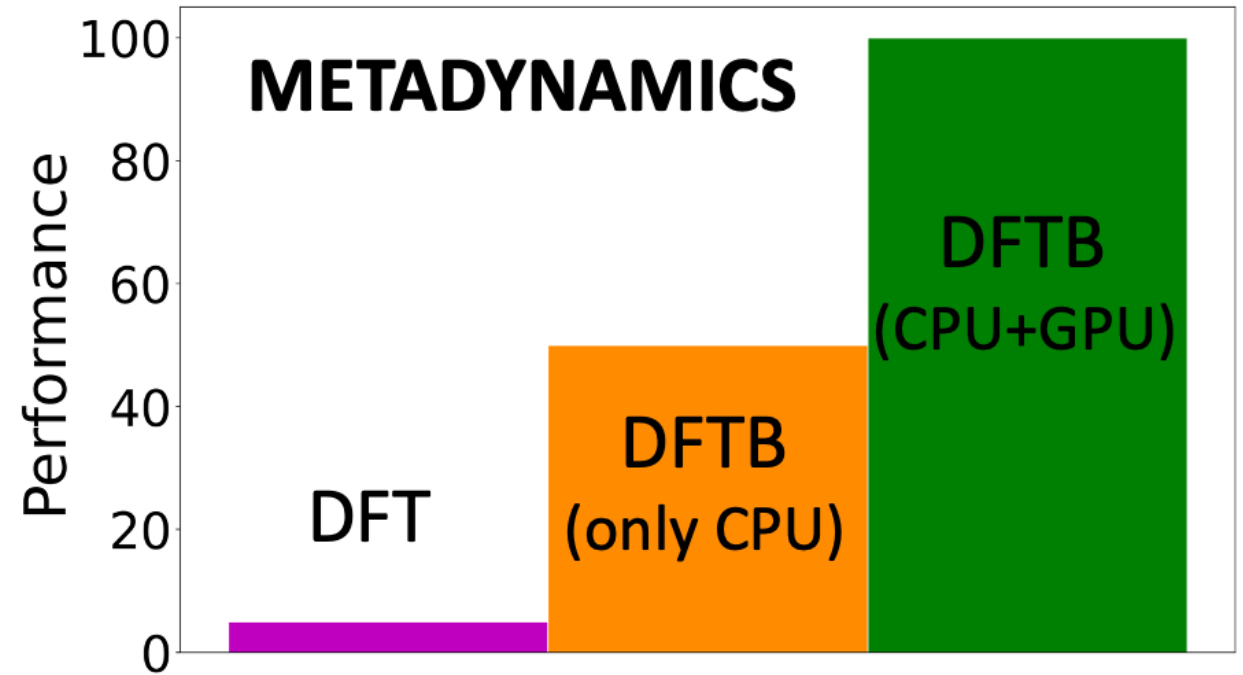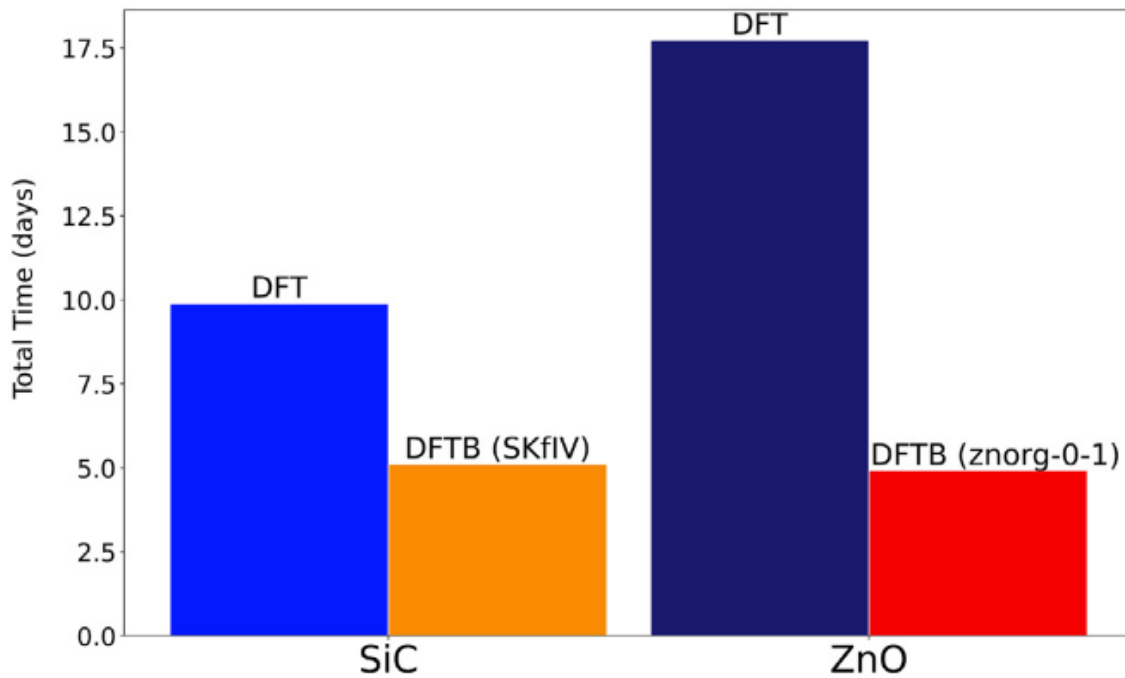
DFTB Theory (brief)

$$E_{DFTB} = \sum_i^{occ} \langle \phi_i | \hat{H}_0 | \phi_i \rangle \; + \; \frac{1}{2} \sum_{\alpha,\beta}^{N} \gamma_{\alpha\beta} \Delta q_\alpha \Delta q_\beta \; + \; E_{rep}$$

Non-SCC H (Parameterized)

Long-range electrostatic interactions

Short-range repulsion

$\hat{H}_0$ **parametrized to** account for core and valence electrons

$\gamma_{\alpha\beta}$ depends on charge fluctuation and separation of atoms

E_{rep} approximates many–body effects (e.g., exchange – correlation)

$$\hat{H}_{DFTB} = \langle \phi_\mu | \hat{H}_0 | \phi_\nu \rangle + \frac{1}{2} S_{\mu\nu} \sum_X (\gamma_{\alpha X} + \gamma_{\beta X}) \Delta q_X$$

$$\hat{H}_0 = -\frac{1}{2}\nabla^2 + \nu_{eff}[\rho^\alpha(\boldsymbol{r})] + \nu_{eff}[\rho^\beta(\boldsymbol{r})]$$

- Hamiltonian solved self-consistently

- Hamiltonian and overlap matrix elements are pretabulated

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Kumar, A., Ali, Z. A., & Wong, B. M. (2023). Efficient Predictions of Formation Energies and Convex Hulls from Density Functional Tight Binding Calculations. *Journal of Materials Science & Technology, 141,* 236–244
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Research Statement

Can we find stable structures of alloys *efficiently?*

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Research Statement

ZnO and SiC unit cell

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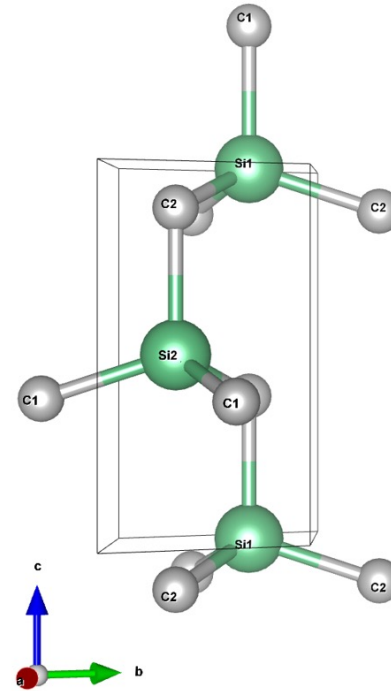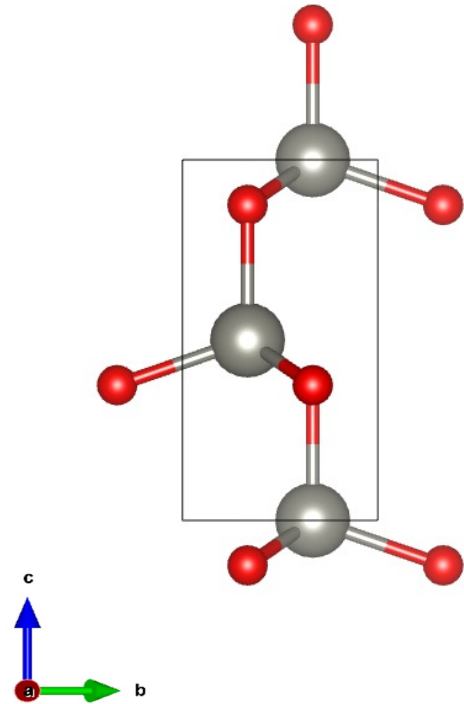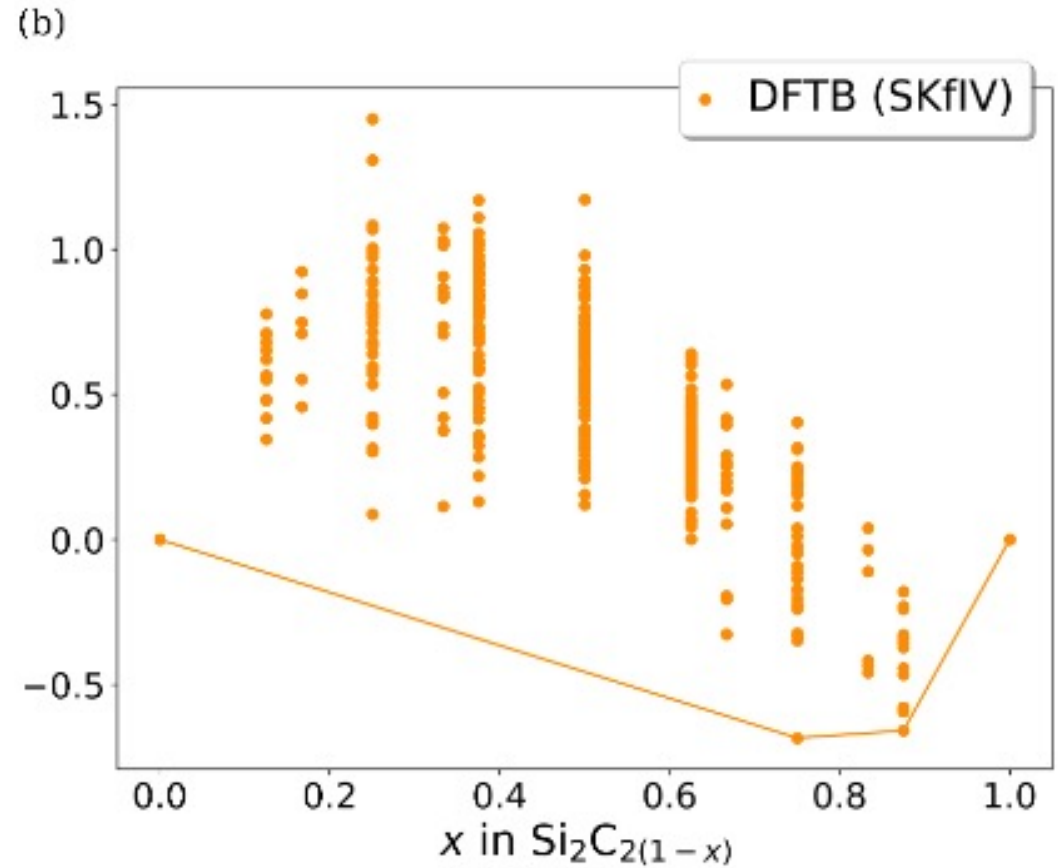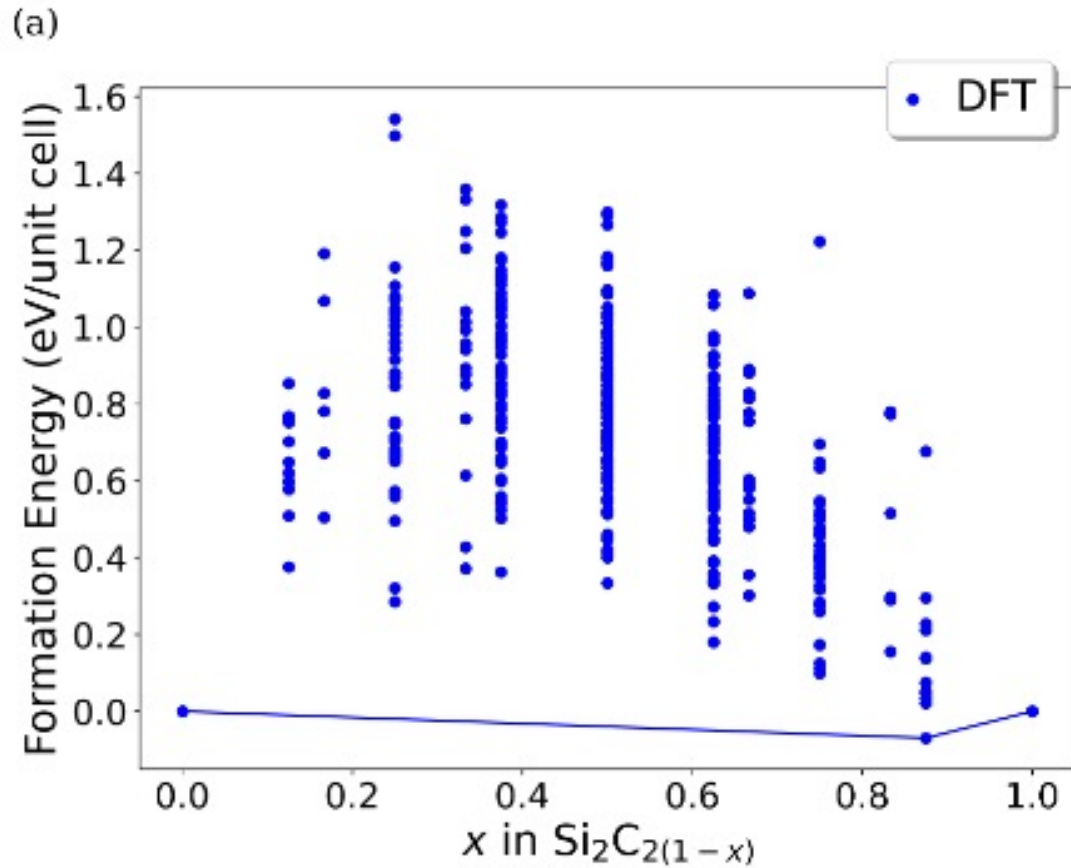
CASM+DFTB
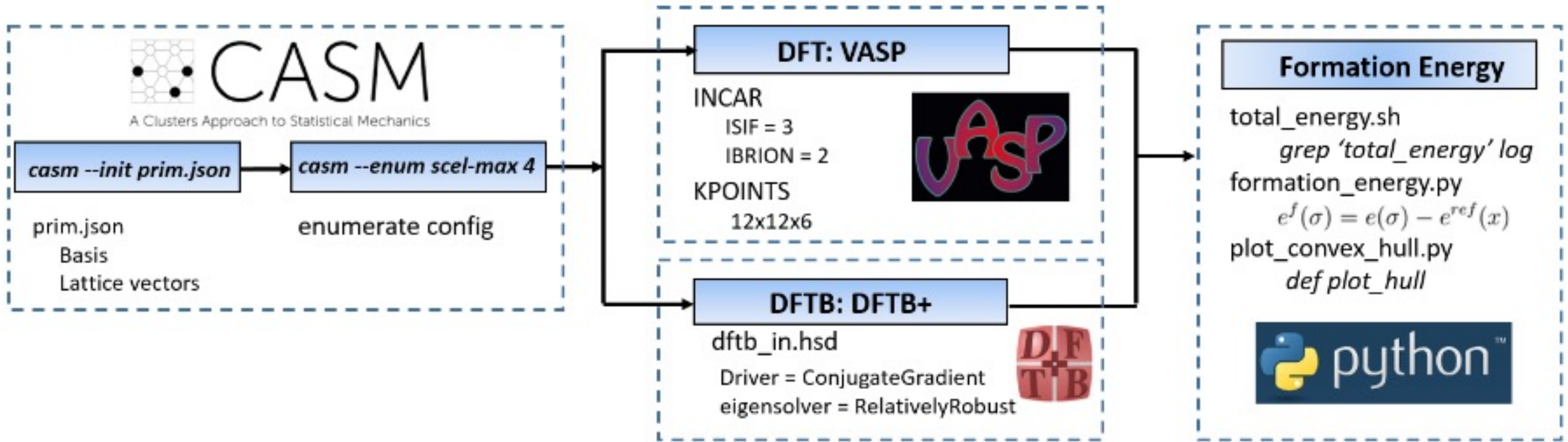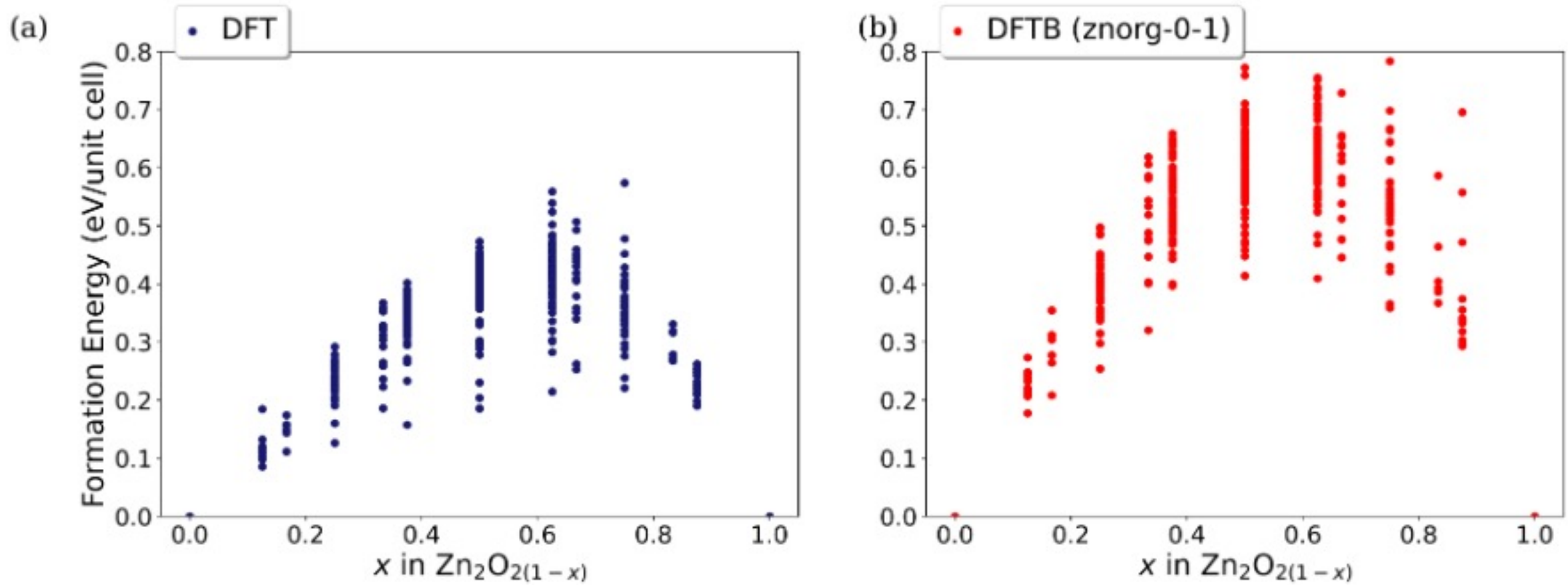

CASM: cluster approach of statistical mechanics

Results: Convex Hull

- SiC shows convex hull; minima lying nearly the same concentration

Kumar, A., Ali, Z. A., & Wong, B. M. (2023). Efficient Predictions of Formation Energies and Convex Hulls from Density Functional Tight Binding Calculations. *Journal of Materials Science & Technology, 141*, 236–244

Convex Hull

(a) DFT — Formation Energy (eV/unit cell) vs x in $Zn_2O_{2(1-x)}$

(b) DFTB (znorg-0-1) — vs x in $Zn_2O_{2(1-x)}$

- DFT and DFTB gives similar results

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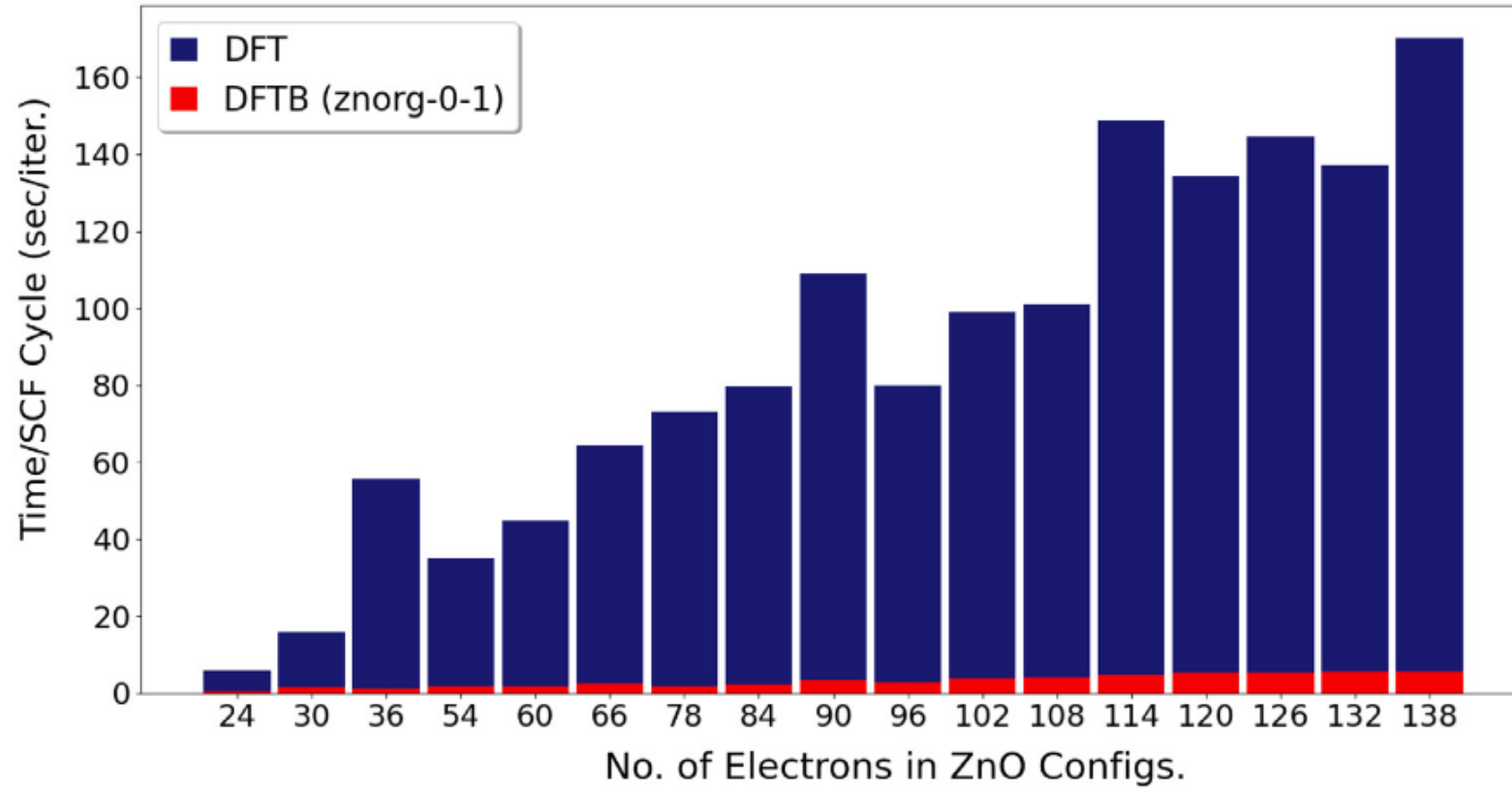
DFTB Efficiency

- Time/SCF very less for DFTB

DFTB Efficiency
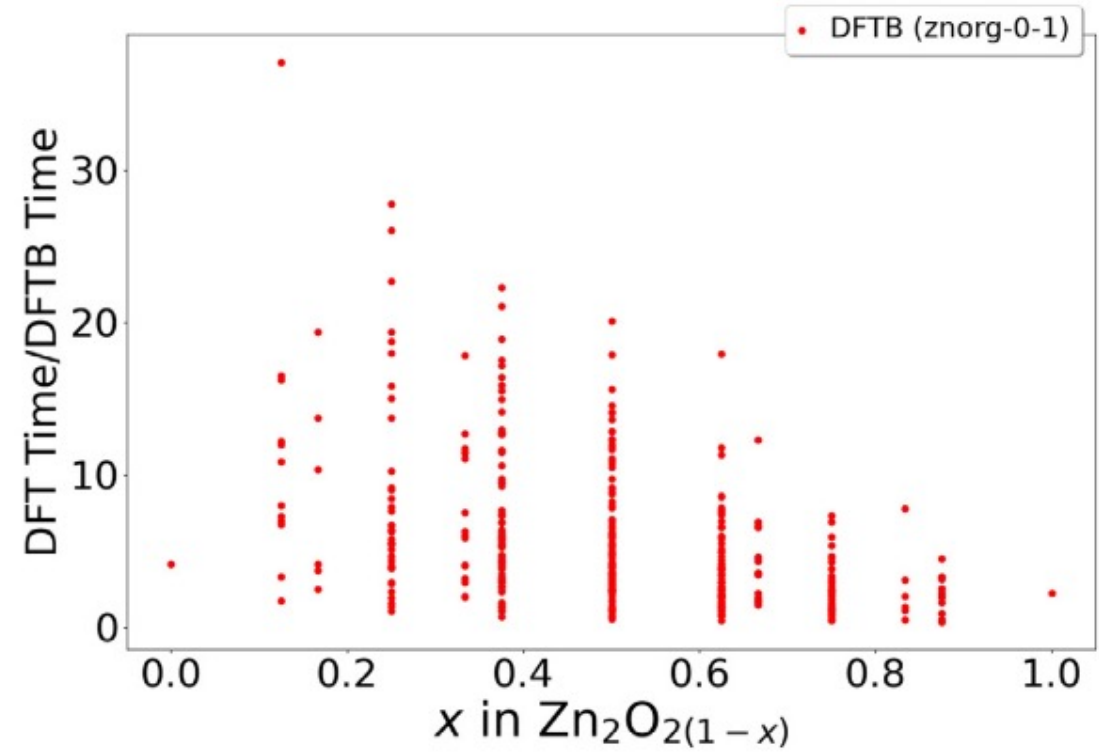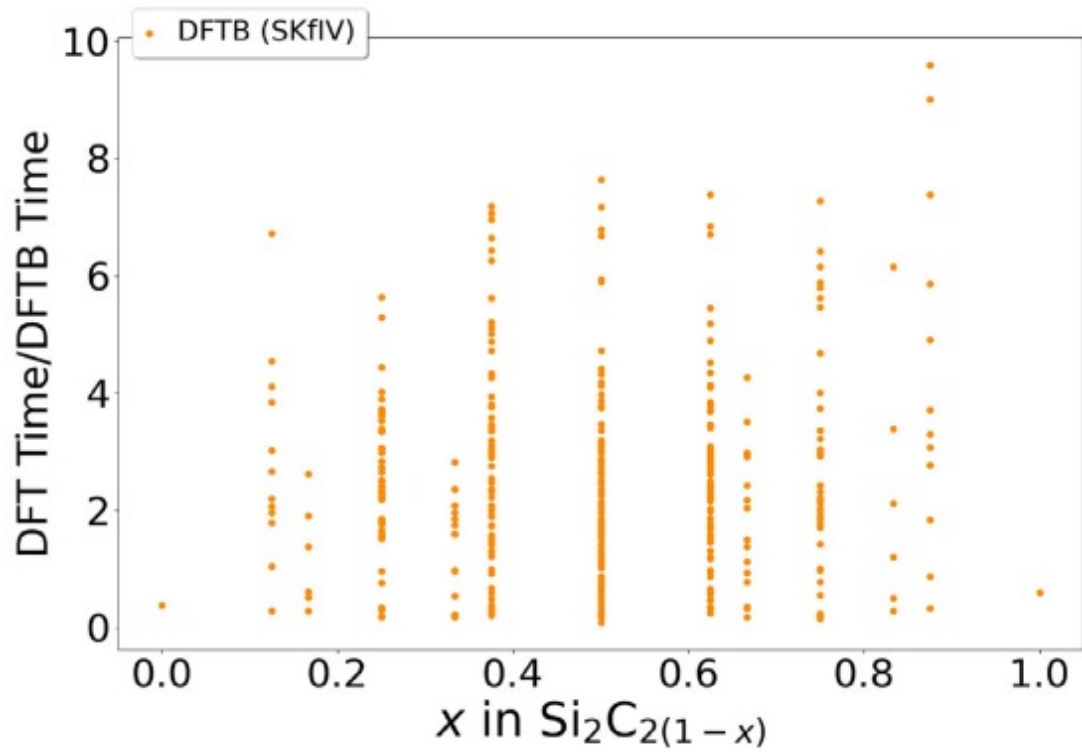
- DFTB with ZnO is more efficient

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DFTB Efficiency

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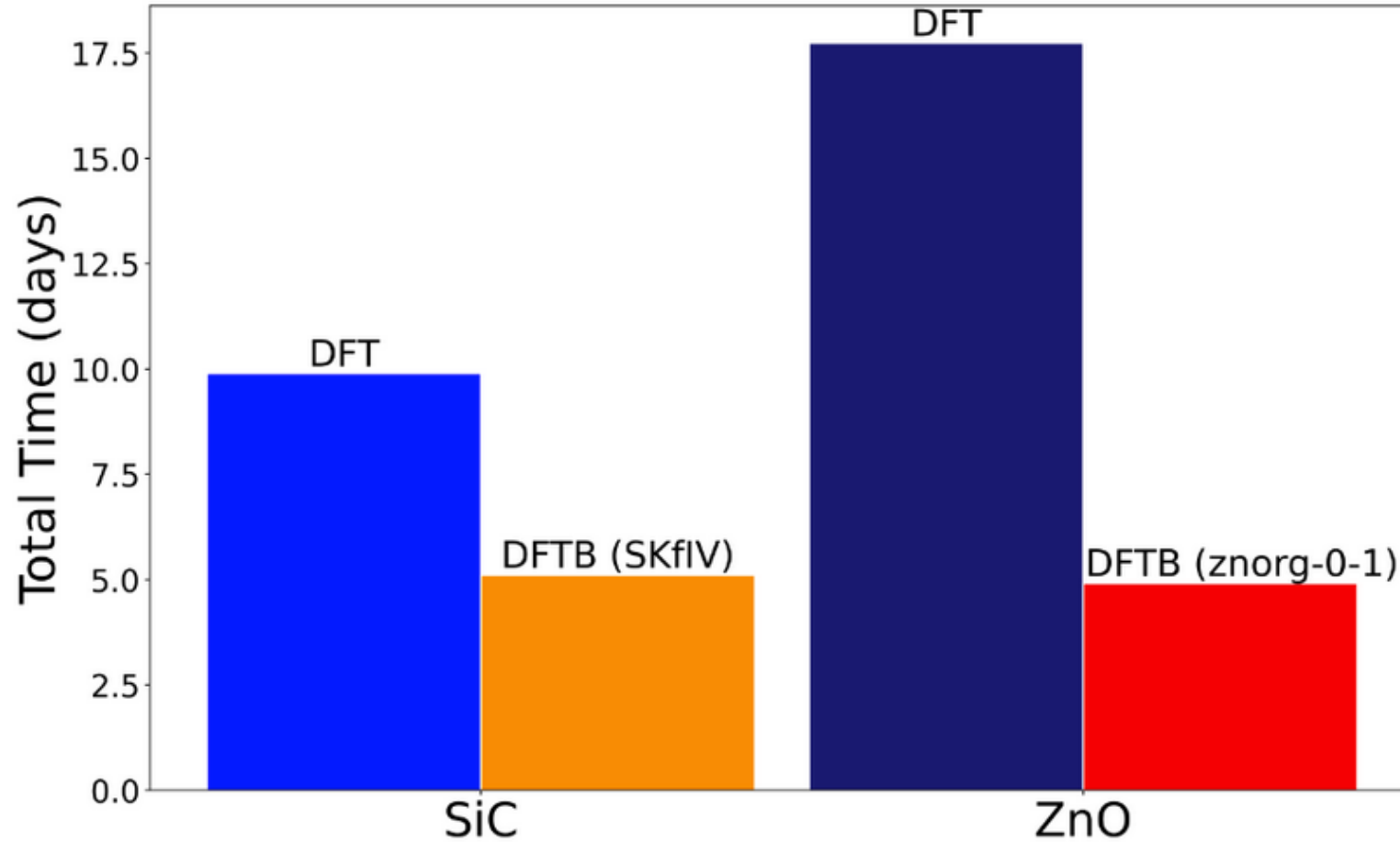
Key Takeaways

- Integrated DFTB with CASM

- DFTB as an efficient tool for screening

Research Question

Can we accelerate ab initio Metadynamics?

Kumar, A. et al (2023). GPU-Enhanced DFTB Metadynamics for efficiently Predicting Free Energies of Biochemical Systems. *Molecules, 28*, 1277–1297

Metadynamics- Motivation

- Molecular Dynamics and rare events

- Chemical Reactions and conformation changes can take longer

  - Protein/RNA folding (µs-s); reaction pathways (ns)
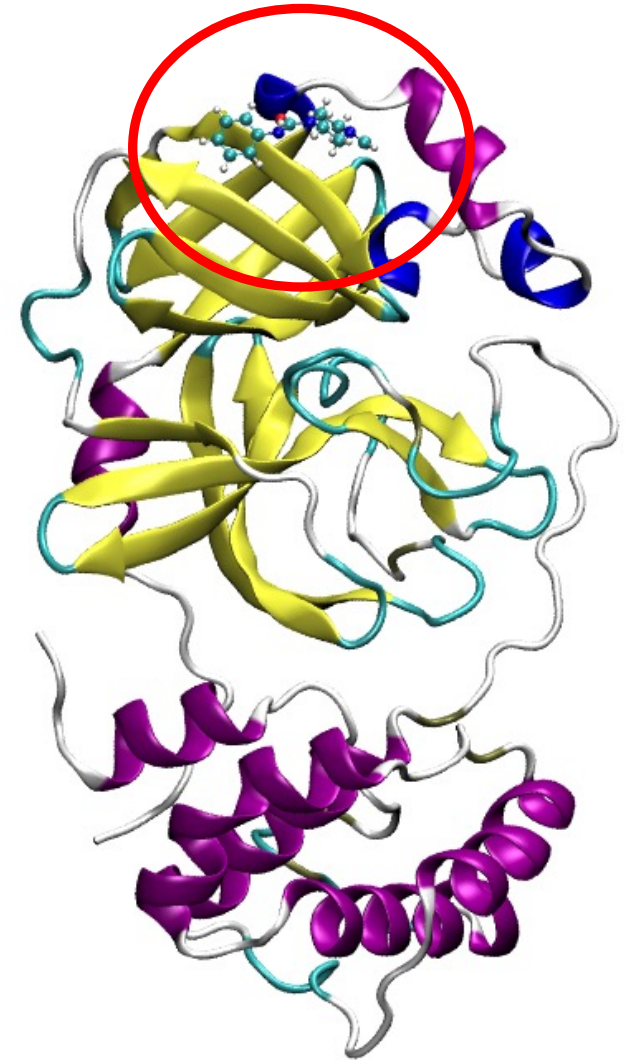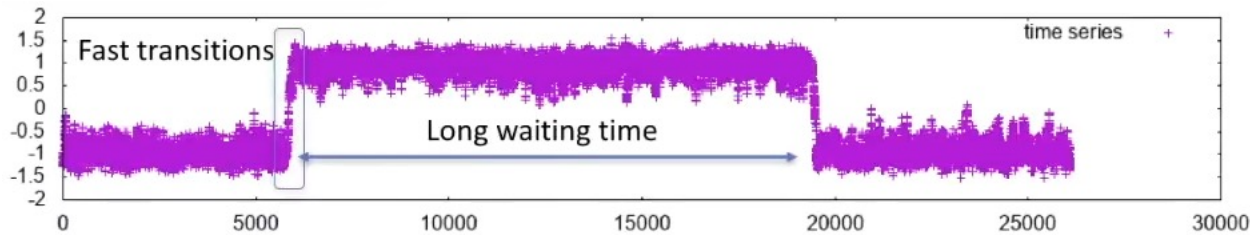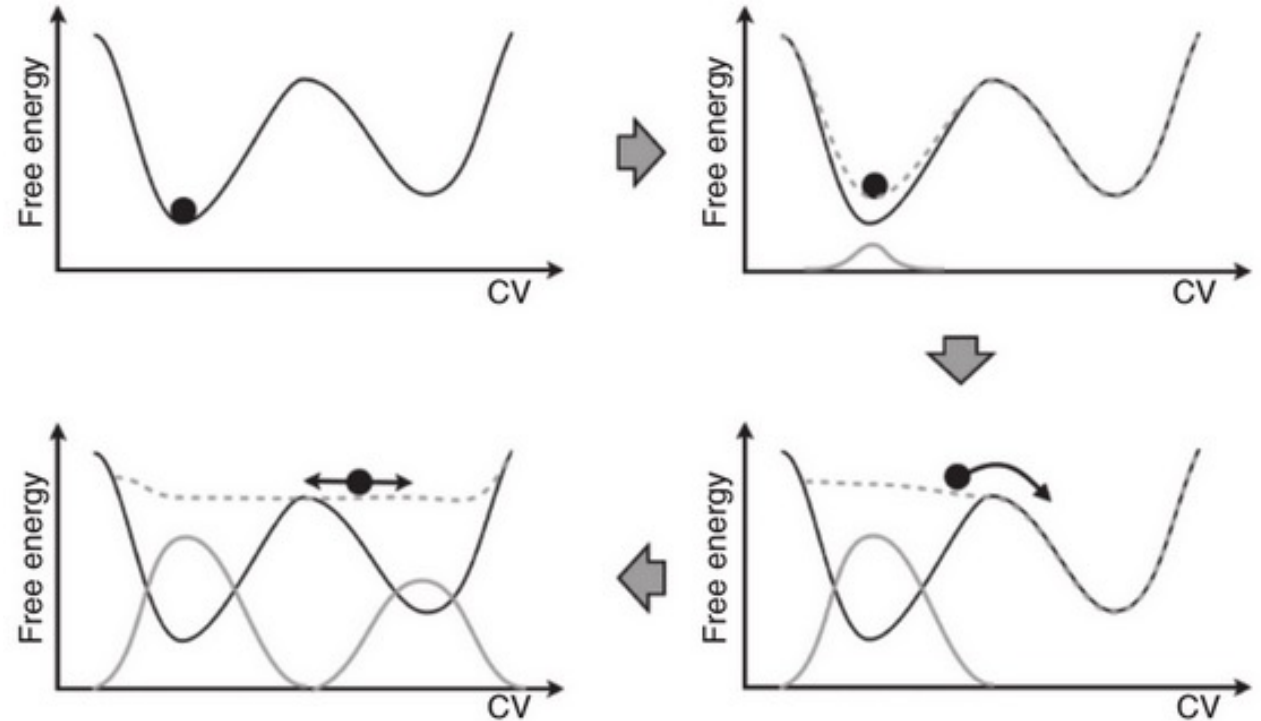
Methods for Faster Molecular Dynamics

- Enhanced Sampling technique: Metadynamics

- DFTB instead of DFT

- Use accelerated hardware: GPUs

Metadynamics (brief)

- Collective Variables (CV) for analyzing and biasing MD simulations
  - Function of atomic coordinates
    - Distances, angles, RMSD

- Biasing to accelerate events

- Analyze the MD simulations

$$V_B = \sum_{t'=\tau, 2\tau, \ldots}^{t} \omega e^{-V(s,t')} \exp\left[\frac{-[s - s(t')]^2}{2\sigma^2}\right]$$

$$V(s, t \to \infty) = -F(s) + C$$

DFTB+GPU

Solve the eigenvalue by diagonalizing the Hamiltonian

$$\widehat{H}\psi = \mathrm{E}\psi$$

$$P^{-1}AP = \begin{bmatrix} \lambda_1 & & & \\ & \lambda_2 & & \\ & & \ddots & \\ & & & \lambda_n \end{bmatrix}$$

Matrix with eigenvalues on diagonal

3 Eigensolvers in DFTB+

- QR
- DivideAndConquer
- RelativelyRobust

MAGMA

GPU-ACCELERATED MICROSOFT AZURE

Allec, S. I., Sun, Y., Sun, J., Chang, C. A., & Wong, B. M. (2019). Journal of Chemical Theory and Computation, 15(5), 2807–2815.

MAGMA

- Linear algebra library like LAPACK
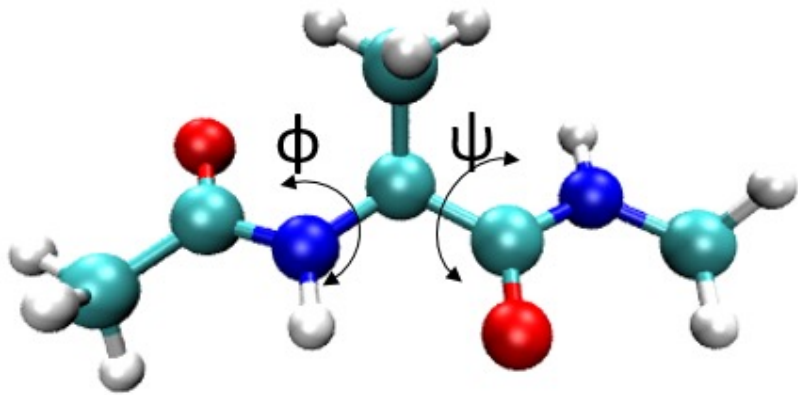- Used for hybrid "multi-core + GPU" architecture

Implementation in DFTB+

LAPACK routine DSYGVD ➡ MAGMA_DSYGVD

> DSYGVD computes all the eigenvalues, and optionally, the eigenvectors
> of a real generalized symmetric-definite eigenproblem, of the form
> A*x=(lambda)*B*x, A*Bx=(lambda)*x, or B*A*x=(lambda)*x. Here A and
> B are assumed to be symmetric and B is also positive definite.
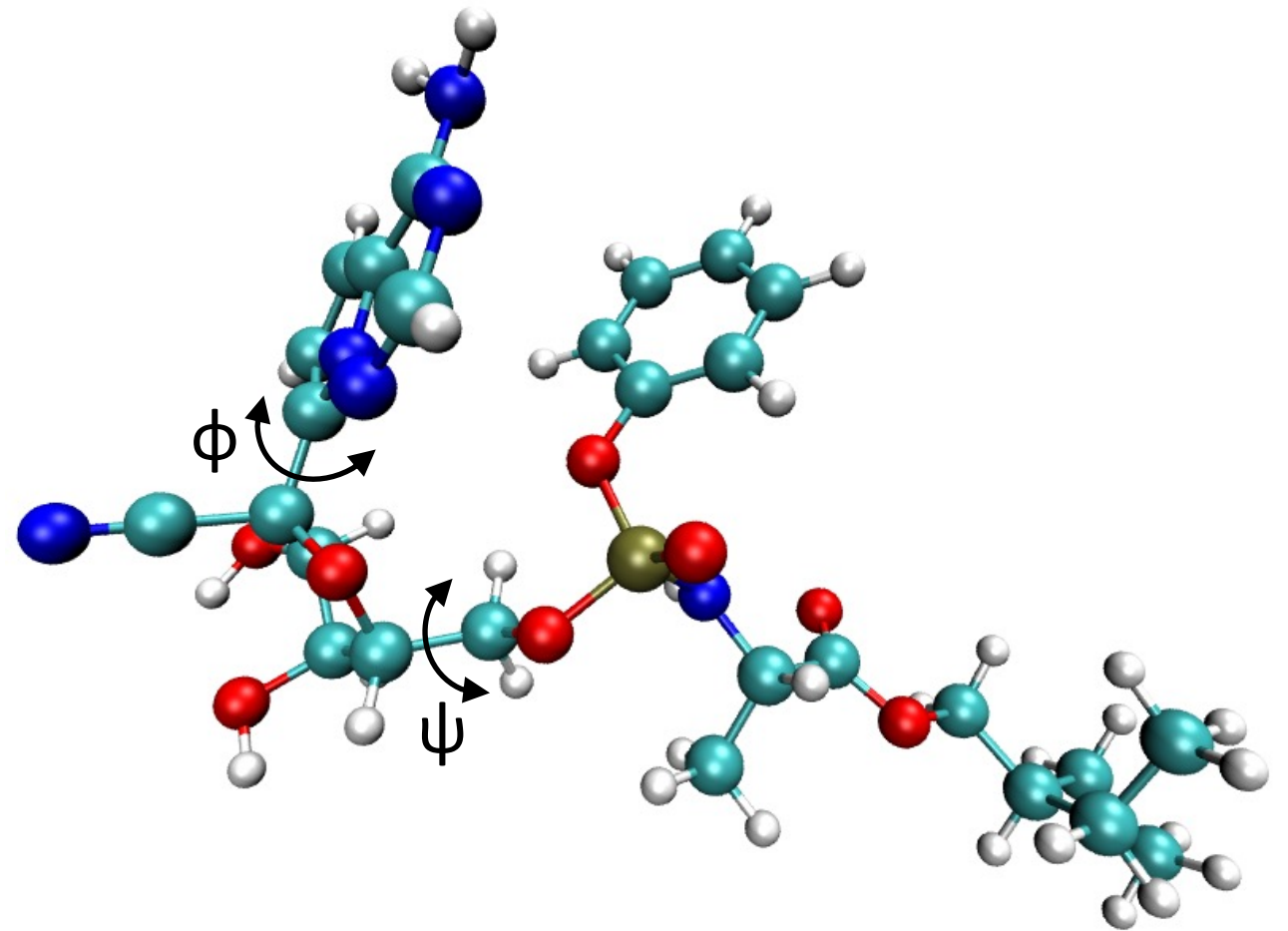> If eigenvectors are desired, it uses a divide and conquer algorithm.

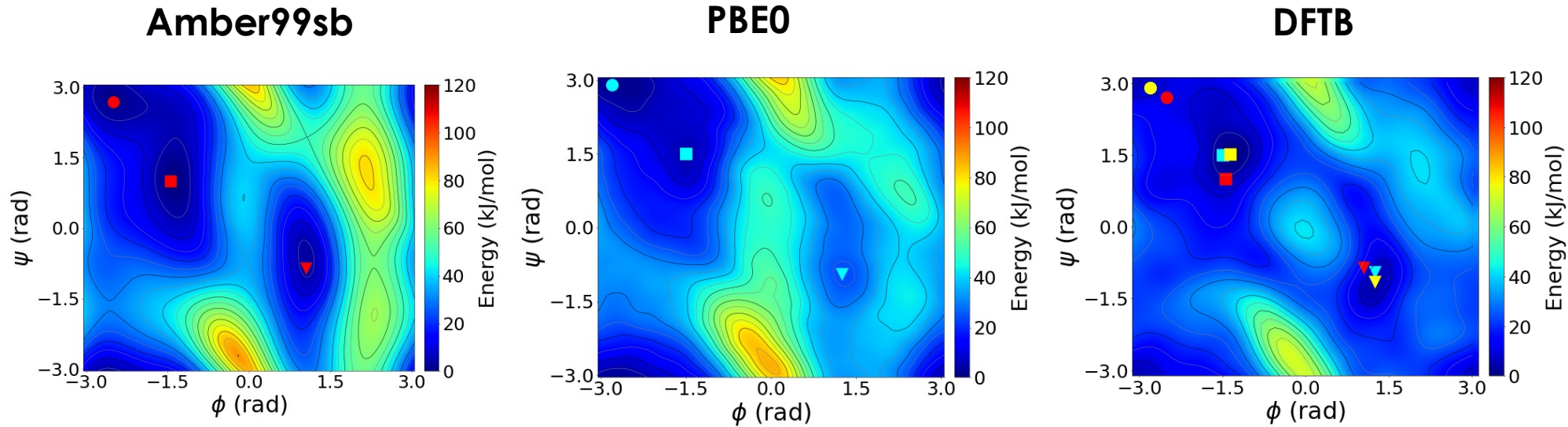- Use GPU to accelerate matrix-vector product

Alanine dipeptide (ADP)

Remdesivir

DFTB Accuracy

Free Energy Surface of ADP

Amber99sb **PBE0** **DFTB**

- DFTB and PBE0 predicts metastable structure at nearly the same locations

- DFTB ~ **18 hours**; PBE0 ~**32 days**

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Sevgen, E.; Giberti, F.; Sidky, H.; Whitmer, J. K.; Galli, G.; Gygi, F.; de Pablo, J. J. *Journal of Chemical Theory and Computation* **2018**,14, 2881–288

DFTB Accuracy
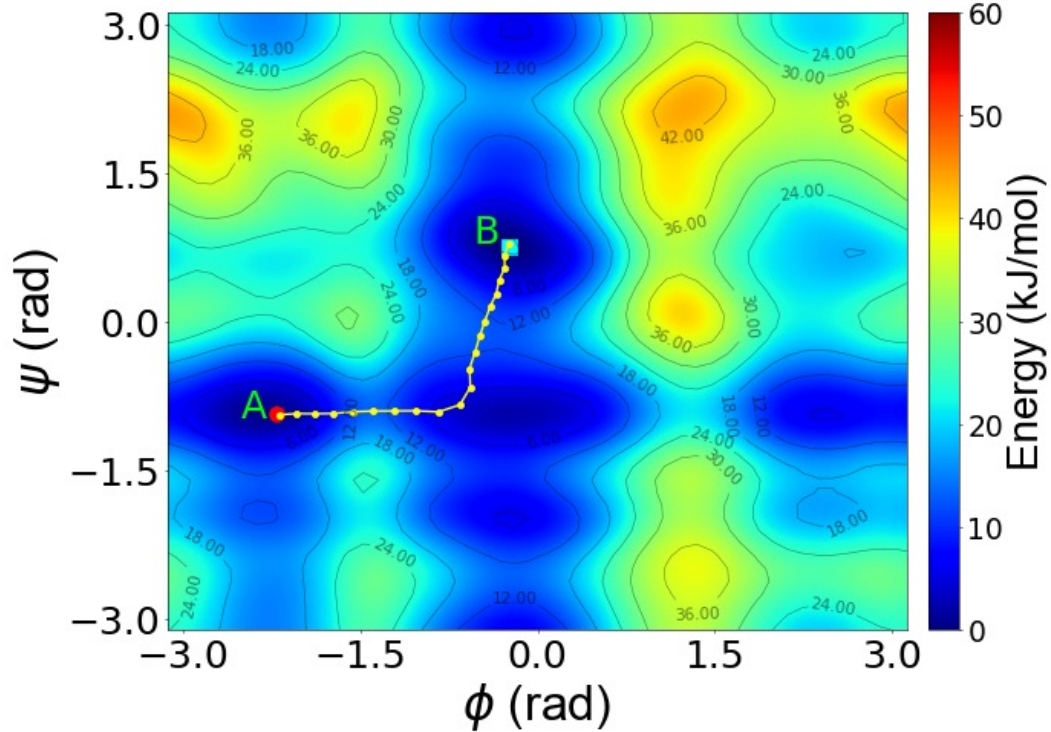
- DFTB and Amber-ff19sb predicts different minima

- DFT hybrid calculations shows energy of C < A

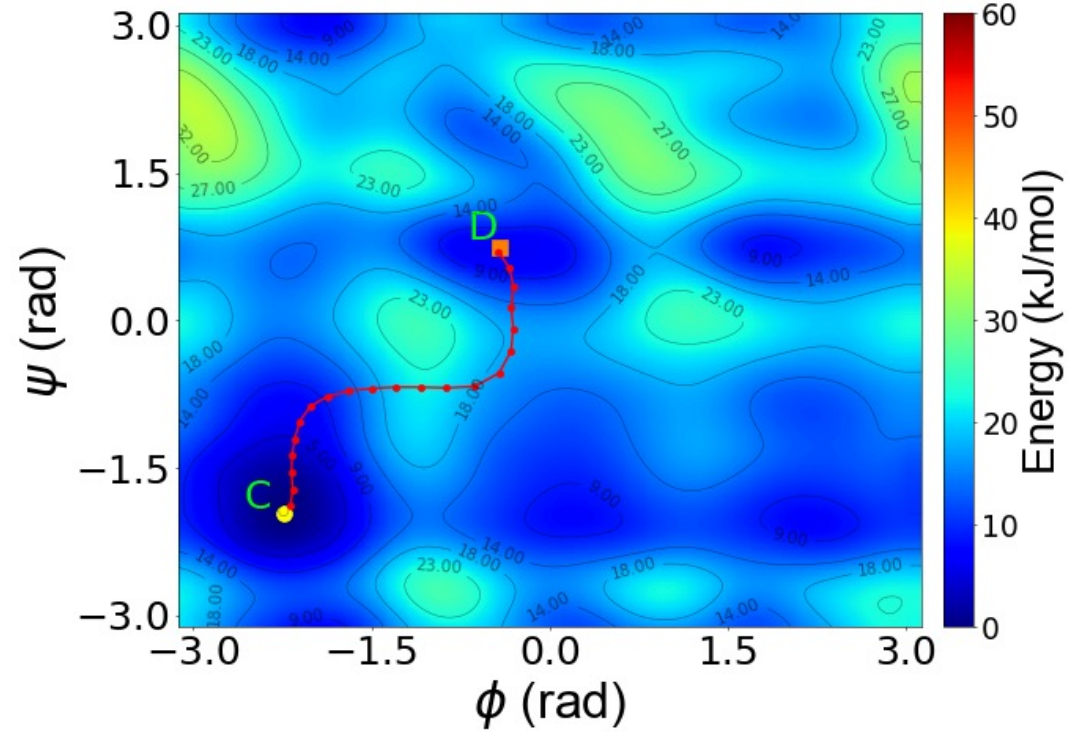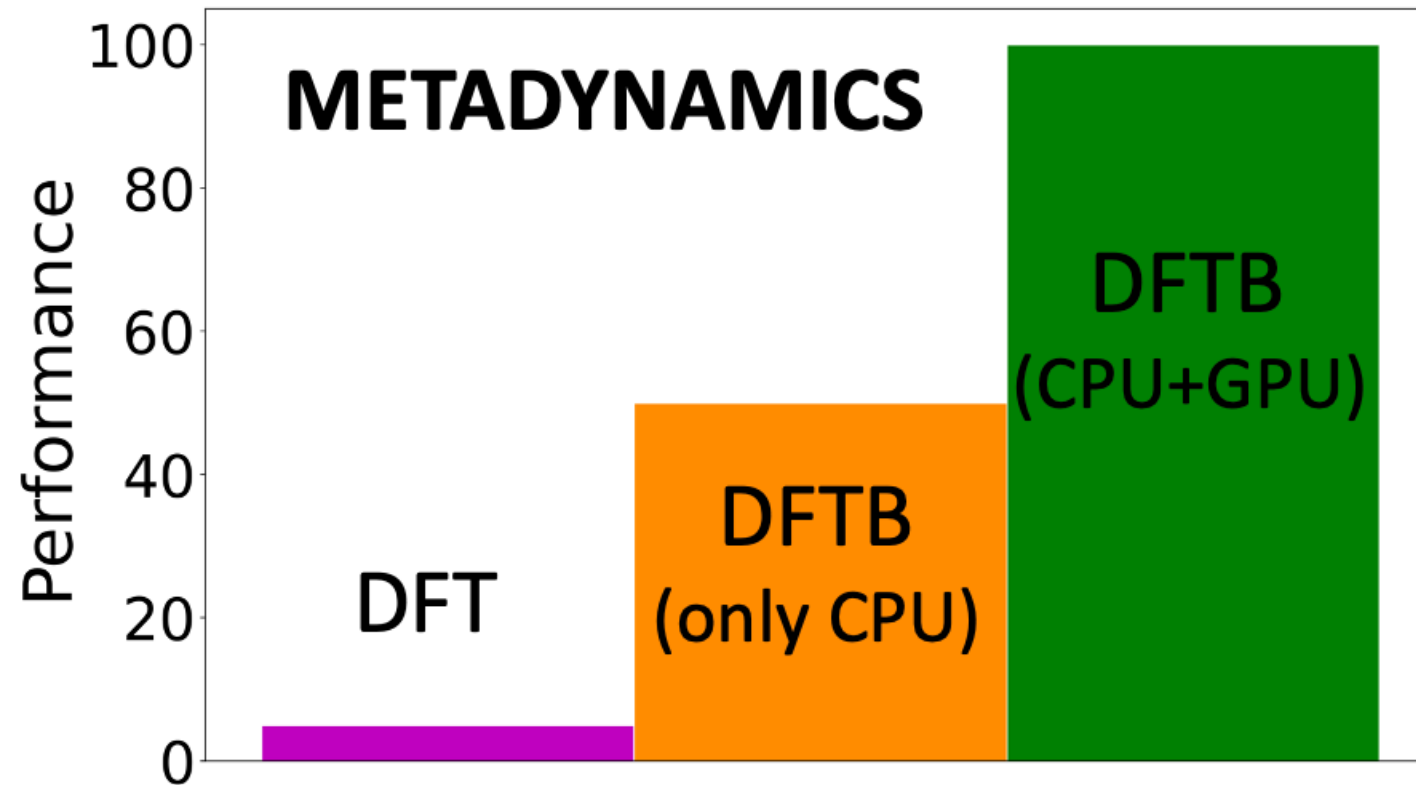# Results: DFTB Efficiency

- DFTB is 2 orders of magnitude faster than DFT

Kumar, A. et al (2023). GPU-Enhanced DFTB Metadynamics for efficiently Predicting Free Energies of Biochemical Systems. *Molecules, 28*, 1277–1297

Key Takeaways

- DFTB is more accurate than classical calculations

- GPU+DFTB is 2 orders of magnitude faster than DFT

Kumar, A. et al (2023). GPU-Enhanced DFTB Metadynamics for efficiently Predicting Free Energies of Biochemical Systems. *Molecules, 28*, 1277–1297.

Conclusion

- Used DFT to characterize transport properties of doped CNT

- Interfaced CASM with DFTB for accelerated calculation of convex hull and formation energies

- Extended GPU-DFTB for obtaining quantum free energy surfaces and transition path

- GPU-DFTB is powerful tool for material science, physics, and chemistry.

List of Publications

1. Chen, M., Li, W., **Kumar, A.**, Li, G., Itkis, M., Wong, B., & Bekyarova, E. (2019). Covalent Atomic Bridges Enable Unidirectional Enhancement of Electronic Transport in Aligned Carbon Nanotubes. *ACS Applied Materials & Interfaces*, *11*(21), 19315–19323.

2. **Kumar, A**., Ali, Z. A., & Wong, B. M. (2023). Efficient Predictions of Formation Energies and Convex Hulls from Density Functional Tight Binding Calculations. *Journal of Materials Science & Technology*, *141*, 236–244

3. **Kumar, A.** et al (2023). GPU-Enhanced DFTB Metadynamics for Efficiently Predicting Free Energies of Biochemical Systems. *Molecules*, *28*, 1277–1297.

4. **Kumar, A**., Schweitzer-Stenner, R., & Wong, B. M. (2019). A new interpretation of the structure and solvent dependence of the far UV circular dichroism spectrum of short oligopeptides. *Chemical Communications*, *55*(40), 5701–5704

5. **Kumar, A.**, Toal, S., DiGuiseppi, D., Schweitzer-Stenner, R., & Wong, B. (2020). Water-Mediated Electronic Structure of Oligopeptides Probed by Their UV Circular Dichroism, Absorption Spectra, and Time-Dependent DFT Calculations. *The Journal of Physical Chemistry B*, *124*(13), 2579–2590.

6. **Kumar, A.**, Wang, X., Shelton, C. R., & Wong, B. M. (2020). Harnessing deep neural networks to solve inverse problems in quantum dynamics: machine-learned predictions of time-dependent optimal control fields. *Phys. Chem. Chem. Phys.*, *22*(40), 22889–22899.

7. Xu, L., **Kumar, A.**, & Wong, B. M. (2018). Linear polarizabilities and second hyperpolarizabilities of streptocyanines: Results from broken-Symmetry DFT and new CCSD(T) benchmarks. *Journal of Computational Chemistry*, *39*(28), 2350–2359

8. Kwon., H., **Kumar, A.,** & Wong, B. M. (2023). Electron/Hole Mobilities of Periodic DNA and Nucelobase Structures from Large-Scale DFTB Calculations, *The Journal of Physical Chemistry B*, *2023.*

9. Wang, X., Okyay, M. S., **Kumar, A.**, and Wong, B. M. (2023). Accelerating quantum optimal control of multi-qubit systems with symmetry-based Hamiltonian transformations. *AVS Quantum Science, 5 (4)*.

10. Raza, A., Hong, C., Wang, X., **Kumar, A.**, Shelton, C. R., & Wong, B. M. (2021). NIC-CAGE: An open-source software package for predicting optimal control fields in photo-excited chemical systems. *Computer Physics Communications*, *258*, 107541.

11. Joo, Y., Huang, L., Eedugurala, N., London, A. E., **Kumar, A**., Wong, B. M., Boudouris, B. W., & Azoulay, J. D. (2018). Thermoelectric Performance of an Open-Shell Donor–Acceptor Conjugated Polymer Doped with a Radical-Containing Small Molecule. *Macromolecules, 51(10), 3886–3894*.

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