GPU-Enhanced DFTB Approaches for Probing Multi-component Alloys

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June 08, 2021

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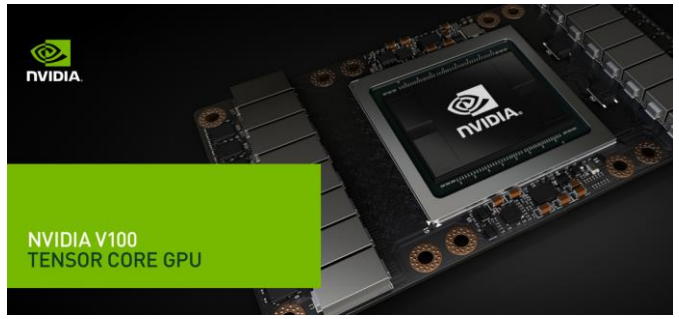
Project Description and Objectives

- **Purpose:** Incorporate GPU into DFTB to *accelerate calculations of multi-component alloys*
- Alignment to Fossil Energy objectives:
  GPU-enhanced DFTB enables *fast/accurate predictions of complex, structural materials used in fossil energy power plants*



- **Current Methods in the Field**
  - **Classical force-field based theory:** can handle large systems but poorly describe the electronic level of details in materials/alloys
  - **Density functional theory (DFT):** efficiently captures the quantum-mechanical nature of alloys but cannot handle large sizes relevant to alloys
  - **Density functional tight binding (DFTB):** can probe large systems at quantum level, significantly faster than DFT

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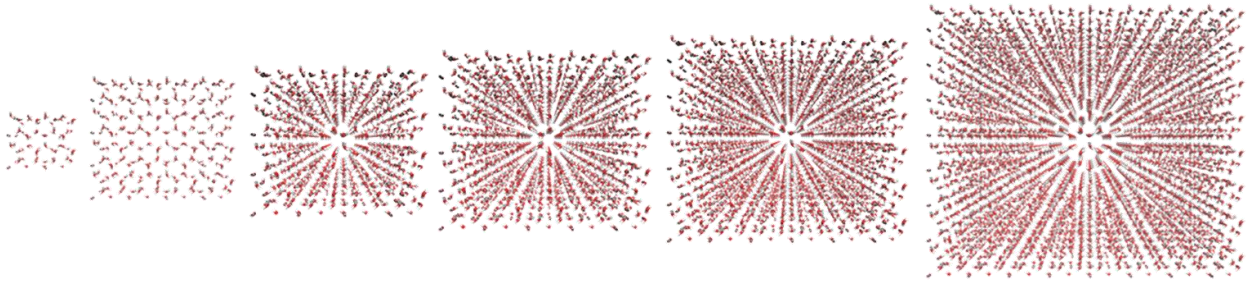
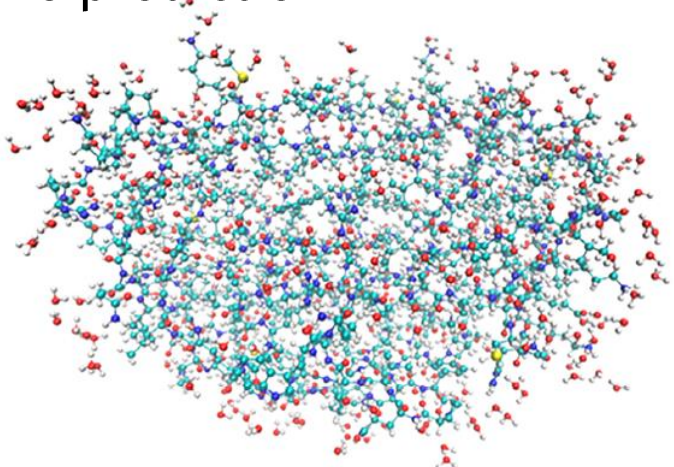
Project Description and Objectives

- Current Status of project
  - Successfully incorporated GPUs into DFTB for extremely fast calculations of large systems
  - Successfully parameterized DFTB and used in crystal structure prediction



up to 15,000 atoms!



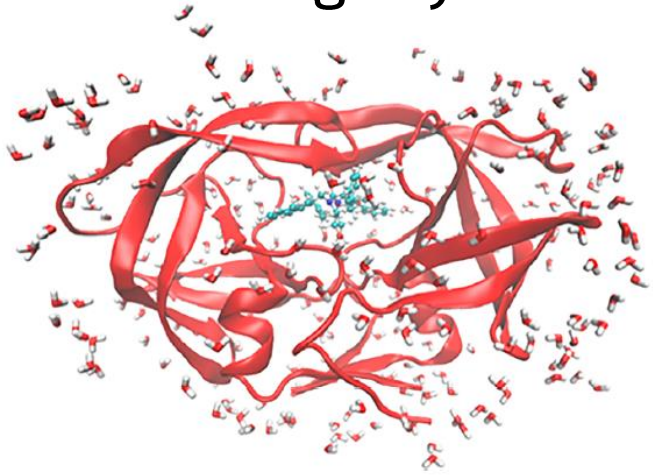
around 5,000 atoms

  - Project on-track to meet deliverables: goals/objectives have not changed

Phase 1: GPU parallelization done; **Phase 2:** DFTB parameterization done

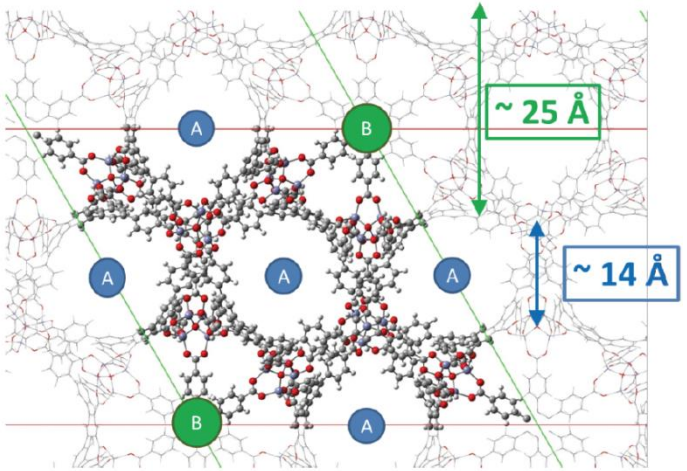
Why Use DFTB for Alloys?

- *Density Functional Tight Binding (DFTB):* parameterized DFT with atomic-centered basis functions
- DFTB *extremely fast* for large systems



S. Allec, Y. Sun, J. Sun, C.A. Change, B.M. Wong
Journal of Chemical Theory and Computation, 15, 2807-2815 (2019)

~ 5,000 atoms in unit cell



K. Leong, M.E. Foster, B.M. Wong
J. Mater. Chem. A **2**, 3389 (2014)

> 1,000 atoms in unit cell
(geometry optimizations ~ minutes)

- Implemented GPU-enhanced DFTB in this project to accelerate dynamics calculations of alloys

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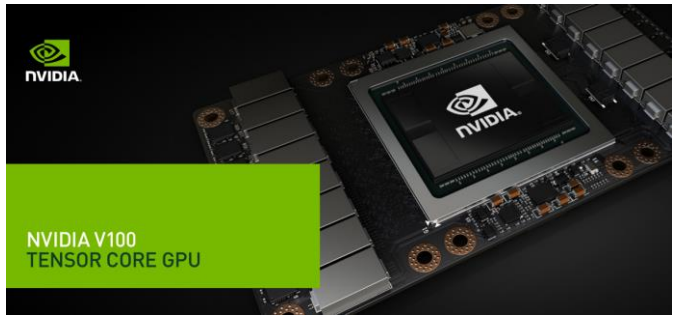
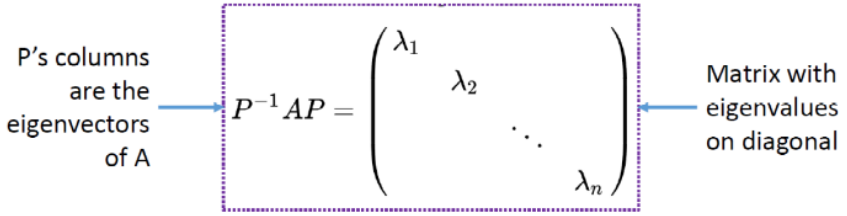
GPU Implementation

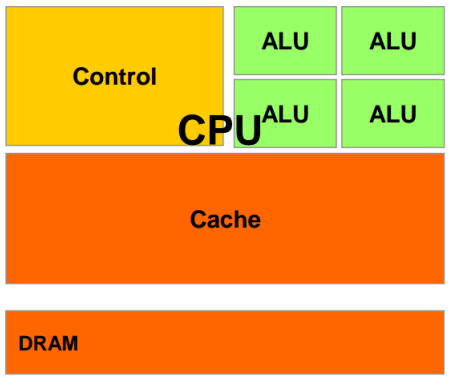
$$\hat{H}\Psi = E\Psi$$

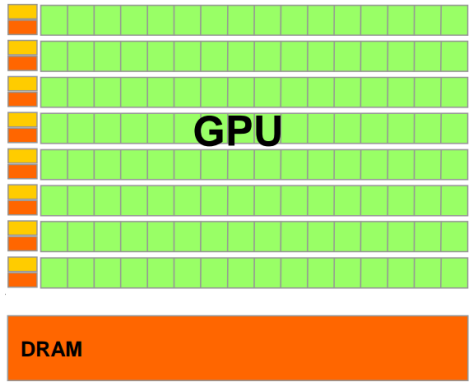


Solves the eigenvalue problem by diagonalizing the Hamiltonian



•3 eigensolvers in DFTB+:
- QR
- DivideAndConquer
- RelativelyRobust





•Several Cores
•Low Latency
•Good for serial processing
•Can do handful of operations at once

•Many Cores
•High Throughput
•Good for parallel processing
•Can do thousands of operations at once

MAGMA

- Linear algebra library similar to LAPACK
- Used for hybrid "Multi-core +GPU" architectures.

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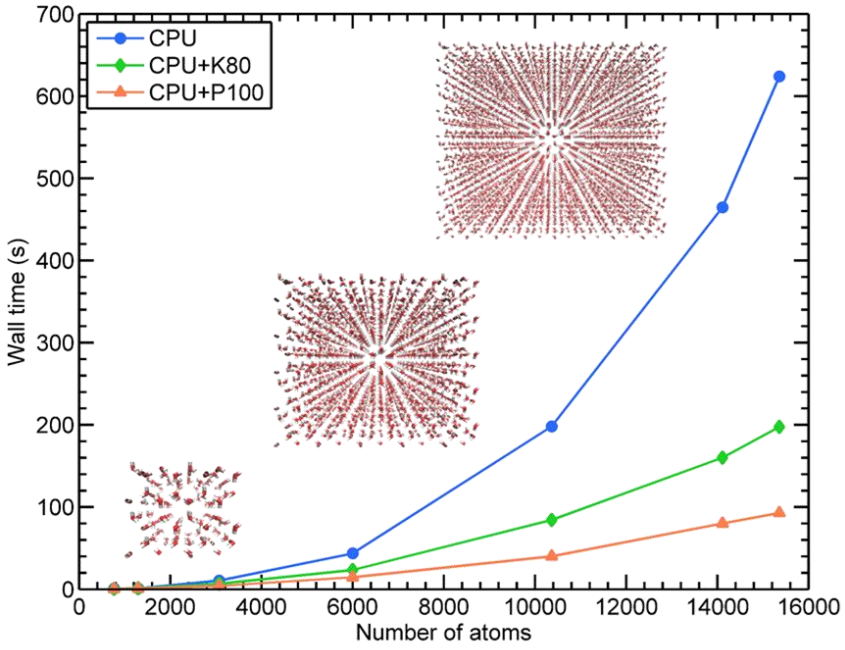
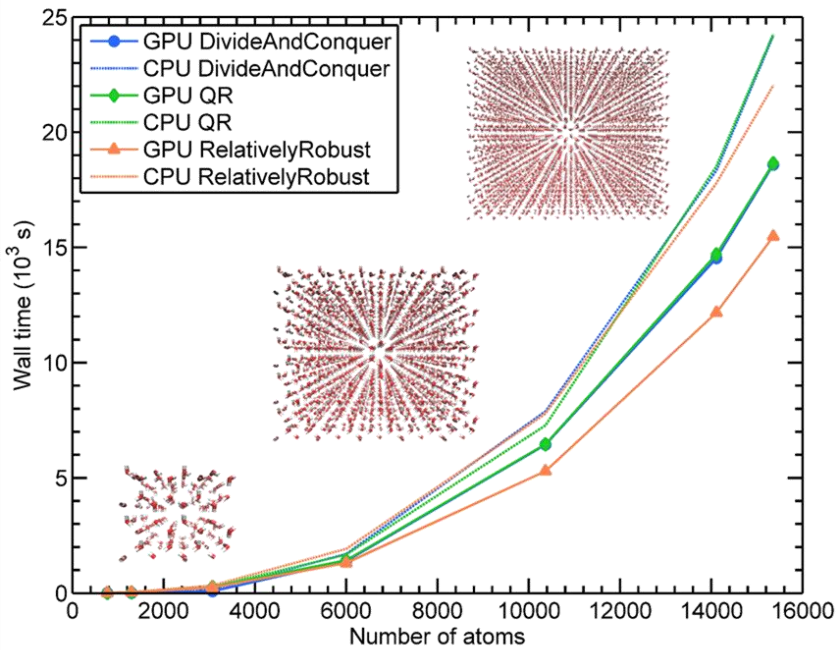
Results of Phase 1: GPU Acceleration

- Performed CPU/GPU benchmarks on large systems (~15,000 atoms!)
- Different algorithms scale with varying performance
- Relatively Robust has the best performance on GPU
- Large complex systems (i.e. alloys) can be modelled



CPUs vs GPUs



algorithm comparison

Allec, S. I.; Sun, Y.; Sun, J.; Chang, C.-e. A.; Wong, B. M., Heterogeneous CPU+GPU-Enabled Simulations for DFTB Molecular Dynamics of Large Chemical and Biological Systems. *Journal of Chemical Theory and Computation* **2019,** *15* (5), 2807-2815.

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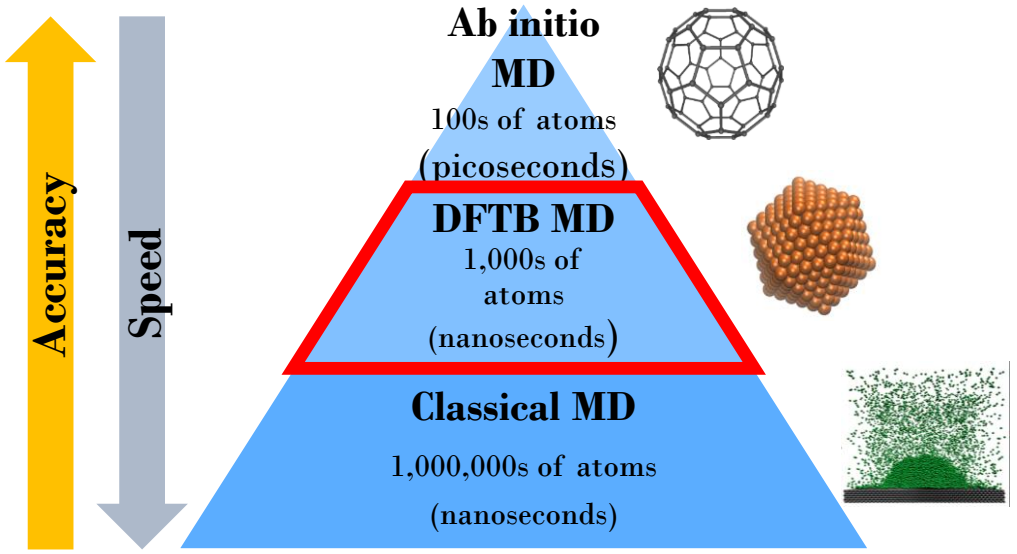
GPU-enabled DFTB

- Why use DFTB ?
  - DFT good for small systems
  - Classical methods do not consider quantum nature of chemical/material systems.
  - DFTB merges reliability of DFT with computational efficiency of tight binding
  - Slater-Koster files used instead of DFT functionals



Challenges

- DFTB limited by set of parameters for elements in periodic table (Slater – Koster files)

Goal

- Create Slater – Koster files for missing element pairs
- Use DFTB to calculate phases/properties of multi-component alloys

GPU-enabled DFTB

DFTB THEORY

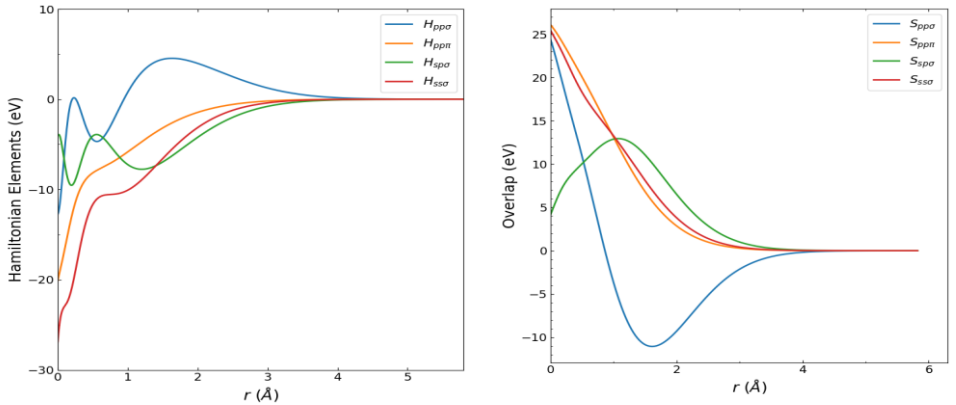
$$E_{\mathrm{DFTB}} = \sum_{i}^{occ} \langle \phi_i | H_0 | \phi_i \rangle + \frac{1}{2} \sum_{\alpha,\beta}^{N} \gamma_{\alpha\beta} \Delta q_\alpha \Delta q_\beta + E_{rep}$$

non-SCC H (**parametrized**)

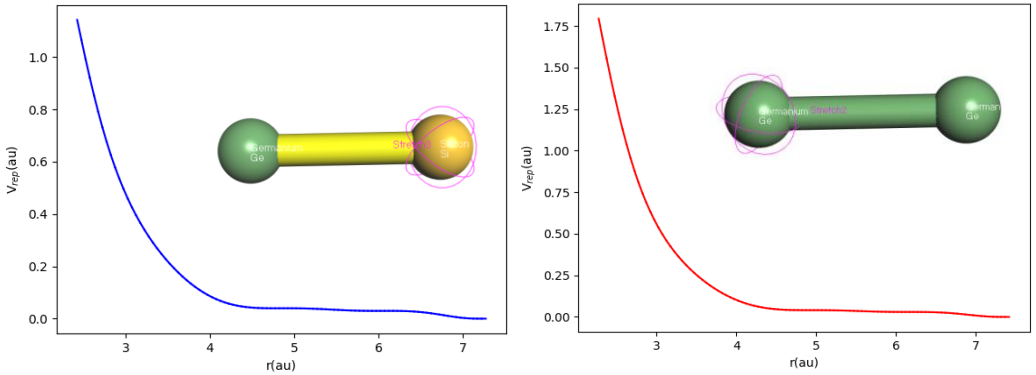
Long-range electrostatic interactions

Short-range repulsion

- E_{rep} lumps together many-body effects (e.g., exchange-correlation)
- H_0 and overlap *matrix elements parametrized beforehand* from DFT calculations



Hamiltonian (H) and Overlap (S) from Ge-Ge Slater-Koster files.



Repulsive Potentials for Ge-Si and Ge-Ge

$$H_{\mu\nu}(\boldsymbol{r}) = \langle \phi_\mu(\boldsymbol{r}) | H_0 | \phi_\nu(\boldsymbol{r} - \boldsymbol{r_o}) \rangle \,,\; S_{\mu\nu}(\boldsymbol{r}) = \langle \phi_\mu(\boldsymbol{r}) | \phi_\nu(\boldsymbol{r} - \boldsymbol{r_o}) \rangle$$

$$H_0 = -\frac{1}{2}\nabla^2 + v_{eff}[\rho^a(\boldsymbol{r})] + v_{eff}[\rho^b(\boldsymbol{r} - \boldsymbol{r_o})]$$

$$E_{rep} = E^{tot}_{DFT} - E^{tot}_{DFTB,bare} = \sum_{i<j}^{pairs} U_{type(ij)}(r_{ij})$$

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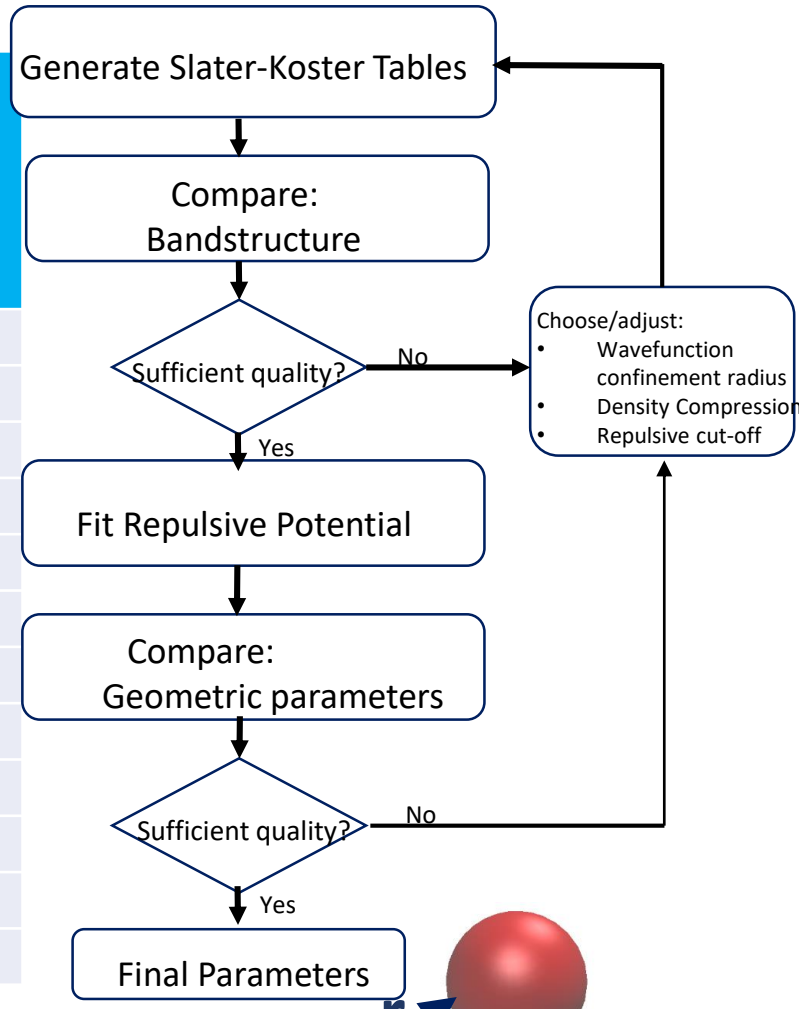
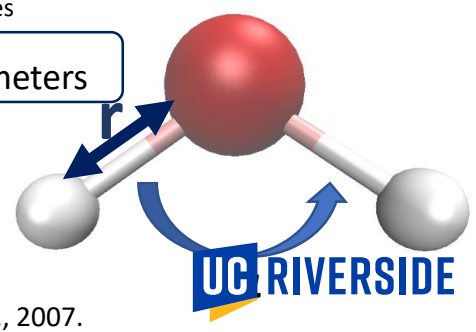
Results of Phase 2 : DFTB Parameterization

Compound	Multiplicity	Parameter*	DFT	DFTB	Δ(DFTB-DFT)	Δ(DFTB-DFT)%
FeH_2	3	r	1.54	1.503	-0.037	-2.40
		α	102.365	110.34	7.975	7.79
	5	r	1.66	1.58	-0.08	-4.82
		α	177.3	179.9	2.6	1.47
FeO	1	r	1.54	1.6	0.06	3.90
	3	r	1.58	1.68	0.1	6.33
	5	r	1.61	1.75	0.14	8.70
$Fe(CH3)_2$	1	r	1.92	1.89	-0.03	-1.56
		α	117.7	125.71	8.01	6.81
	3	r	1.94	2.13	0.19	9.79
	5	r	2.05	1.96	-0.09	-4.39





*r in Angstrom, α in degrees

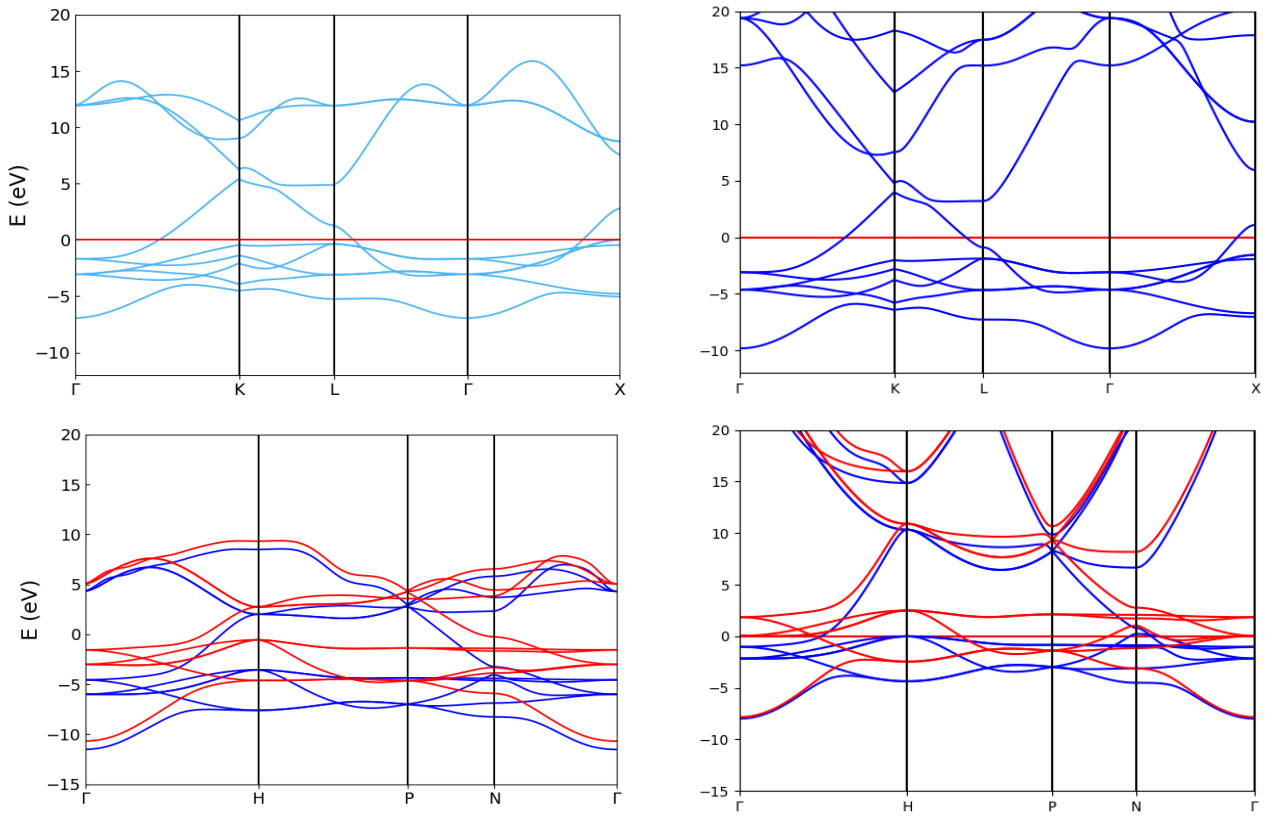
Accelrys Software Inc., *Discovery Studio Modeling Environment, Release 8.0* , San Diego: Accelrys Software Inc., 2007.

Results of Phase 2 : DFTB Parameterization

Bandstructures

Au (FCC)

Fe (BCC)



Using DFTB

Using DFT(pbe)

- Valence and conduction bands calculated via DFTB and DFT, show almost the same dispersion/delocalization

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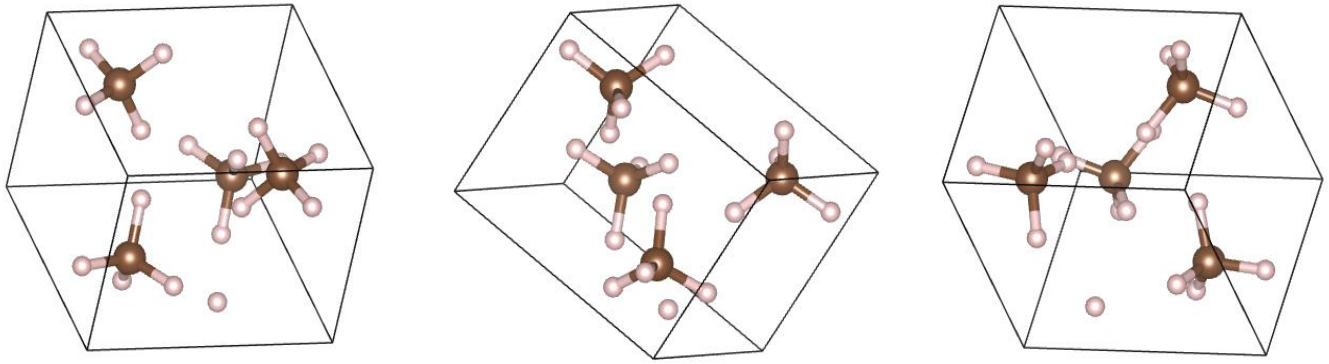
Results of Phase 3 : Crystal Structure Prediction

Constrained Evolutionary Scheme for Structure Prediction of Molecular Crystal (CH_4)

- Variable-cell structure prediction of CH_4 with cell size containing 4 formula units at 20 GPa (4 molecules/unit cell).
- Use USPEX's evolutionary structure prediction algorithm to investigate possible structures of Methane (at T=0, P=20 GPa).

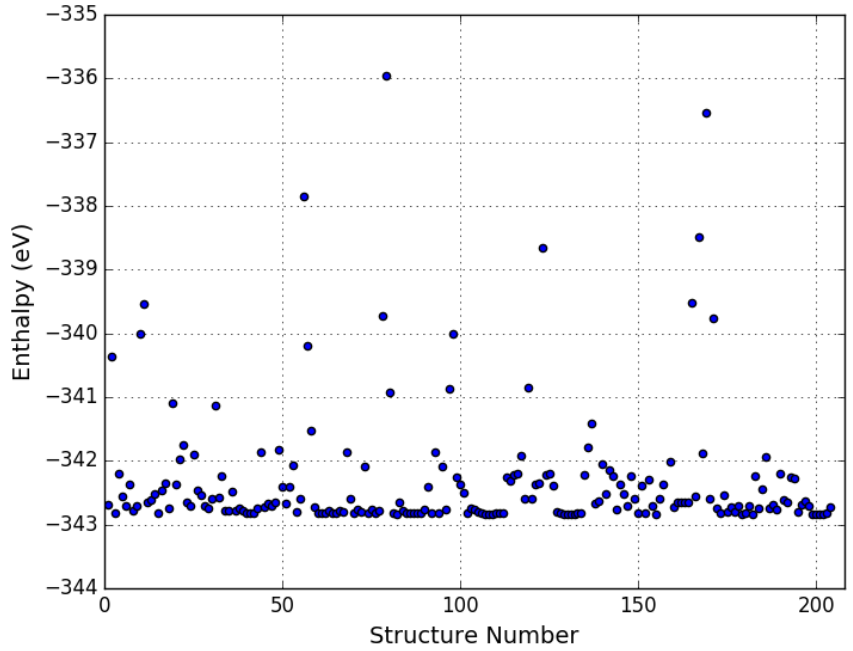
METHOD:

- Initial population of 20 structures and part of new generations are produced using space-group symmetry combined with random cell parameters and, random positions and orientation of molecular units.
- Structure relaxation via GPU enabled DFTB3 (3ob-3-1 parameters) with Lennard-Jones potential.
- Every subsequent generation is produced from the best 60% of the previous generation.
- New population/structures created via variation operators (heredity, lattice mutation, soft mutation, permutation)
- Ran till 9 generations, 204 total structures were ranked based on enthalpy.

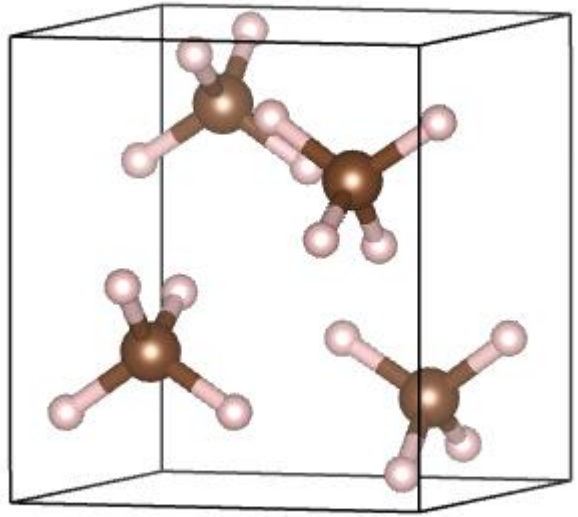


A few crystal structures of CH_4 produced using space group symmetry during the 1st generation in USPEX

Results of Phase 3 : Crystal Structure Prediction



Enthalpy for distinct structures of CH_4 during various stages (generation) in the evolutionary algorithm



Molecular crystal structure of CH_4 as predicted by GPU-DFTB at 20 GPa

- Calculated enthalpy on distinct configurations of CH_4 .
- In each generations distinct structures of CH_4 are generated via variation operators.
- At pressure 20 GPa, the low enthalpy structures are all made of well-separated CH_4 molecules.
- Each CH_4 molecule forms a slightly distorted tetrahedron with C-H distance about 1.06-1.08 A^o and H-C-H angles in the range 108.70^o – 110.4^o.
- At low pressure methane keeps its molecular state.

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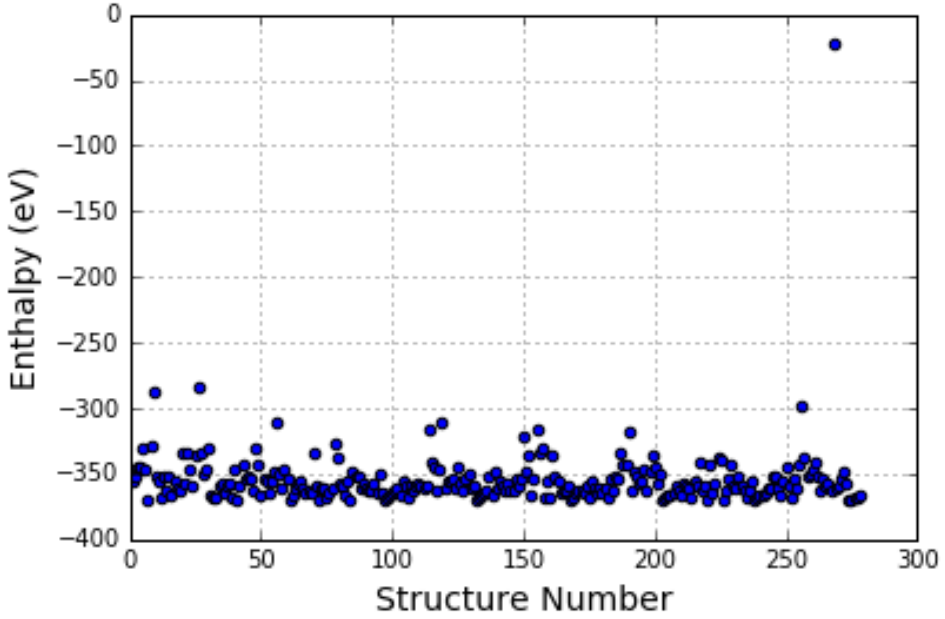
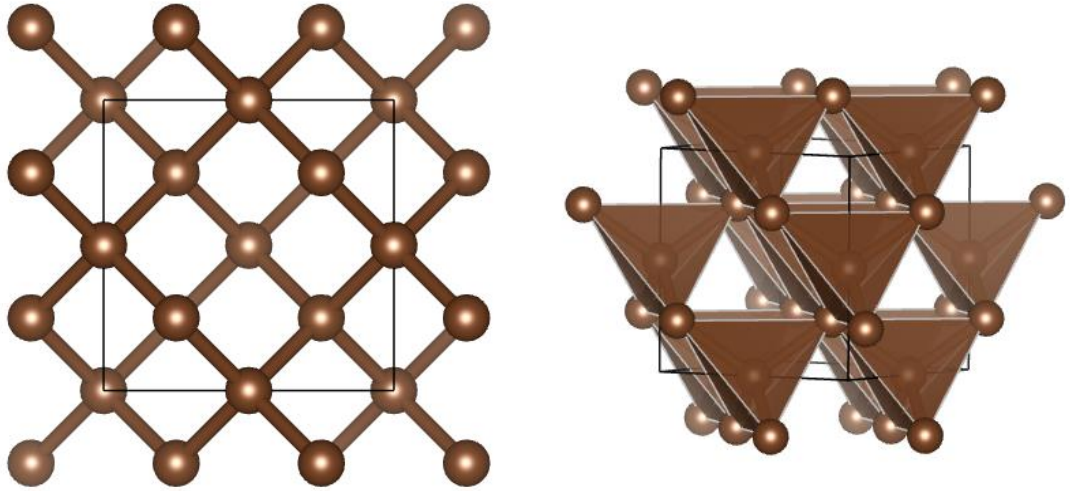
Results of Phase 3 : Crystal Structure Prediction



Enthalpy for distinct structures of C during various stages(generation) in the evolutionary algorithm



Diamond crystal structure of C as predicted by GPU-DFTB

- Enthalpy on distinct configurations of C .
- In each generations distinct structures of C are generated via variation operators.
- Diamond crystal structure is predicted for C, and the energy difference between graphite and diamond seems to be overestimated by DFTB.
- Future goal include exploring crystal structures of Fe, Ni, Al alloys at different temperature and pressure.

Preparing Project for Next Steps

- **Market Benefits/Assessment**
  - **Current market gap:** existing simulation tools (i.e. MD/DFT) not capable of predicting dynamics of large alloy systems
  - **Benefits:** project goals directly translate to understanding (1) structural deformation in complex alloys & (2) reactive processes in these complex systems

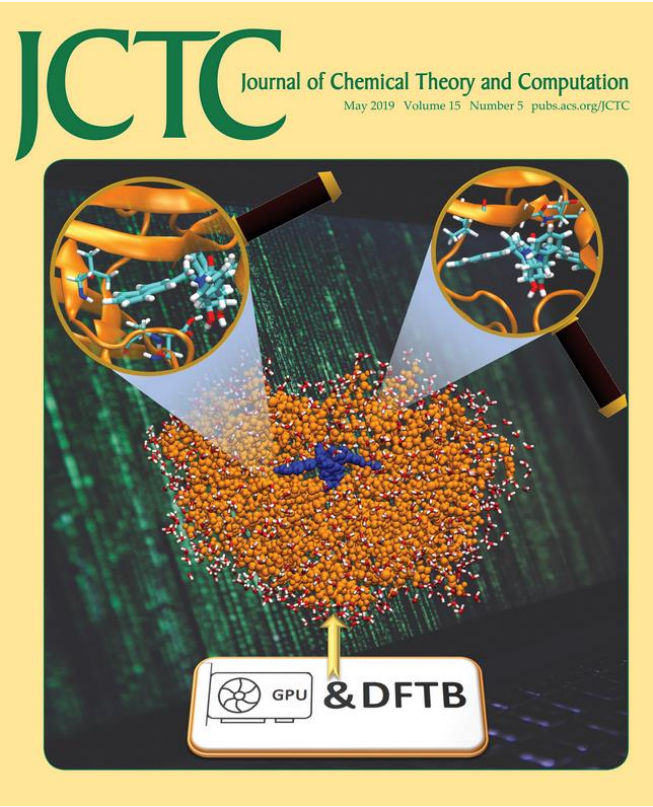
- **Technology-to-Market Path**
  - **Technology transfer is high:** many technologies depend on structural materials, including furnaces and structural composites in buildings
  - **New research:** first demonstration of accelerating DFTB with GPUs for large systems

Concluding Remarks

- Applicability to Fossil Energy and alignment to strategic goals
  - GPU-enhanced DFTB enables fast predictions of complex, structural materials used in fossil energy power plants
  - **Better than Classical methods & orders of magnitude faster than DFT**

- **Next step**: incorporate GPU-DFTB for obtaining phase diagrams of alloy systems

- **First demonstration** of accelerating DFTB-based dynamics with GPUs for large systems
  - Published in *Journal of Chemical Theory & Computation* (IF: 5.4)
  - **Featured as cover for the May 14, 2019 issue**



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Acknowledgement and Disclaimer

This material is based upon work supported by the Department of Energy Award Number DE-FE0030582.

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