



Using the transition structure factor to reach the thermodynamic limit faster in periodic coupled cluster theory

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1 Abstract

Given the large role metals play in applications like catalysis and surface chemistry, there is a current need for efficient calculations using high-accuracy wavefunction-based methods. For method like coupled cluster, however, these calculations are expensive to run due to the large finite size errors associated with simulating a metal with a periodic finite supercell. Here I will present on our twist angle selection method called "structure factor twist averaging" that we developed to help address this cost. Typically, twist angles are used to change the occupation of orbitals, which breaks degeneracy and produces a different energy at each new twist angle. Averaging over a set of twist angles can reduce finite size error and produces a more balanced description of the system but is expensive to run. Our method uses a property of the solids called the transition structure factor to select the one twist angle that reproduces the average system and contains the smallest amount of finite size errors. Given the direct relationship the transition structure factor has with the energy, we find that it is an effective way to select our special twist angle. I will demonstrate the effectiveness of this method for a range of system sizes and basis sets using a model system. I will also show how our method performs with real systems by applying it to a range of solids.

2 Transition structure factor in coupled cluster and solids

The transition structure factor is a new non-observable property in solids that has a direct relationship to the correlation energy

Density map of the correlation in the system

Convergence of S_G mirrors the convergence of the correlation energy

Derived from the coupled cluster correlation energy expression [1]:

$$E_{corr} = \frac{1}{4} \sum_{ijab} v_{ijab} t_{ijab}$$

$$E_{corr} = \int_{k_1} \int_{k_2} \int_G S_G v_G dG$$

$$S_G \propto G^2$$

$$\Delta E_{corr} = \int_{small G} S_G v_G dG \quad \Delta E_{corr} \propto \frac{1}{N}$$

$$= \sum_G v_G S_G, \text{ where } v_G = \frac{4\pi}{G^2}$$

$$S_G \propto \sum_{ijab} t_{ijab} \delta(k_i - k_a - G) \delta(k_j - k_b + G)$$

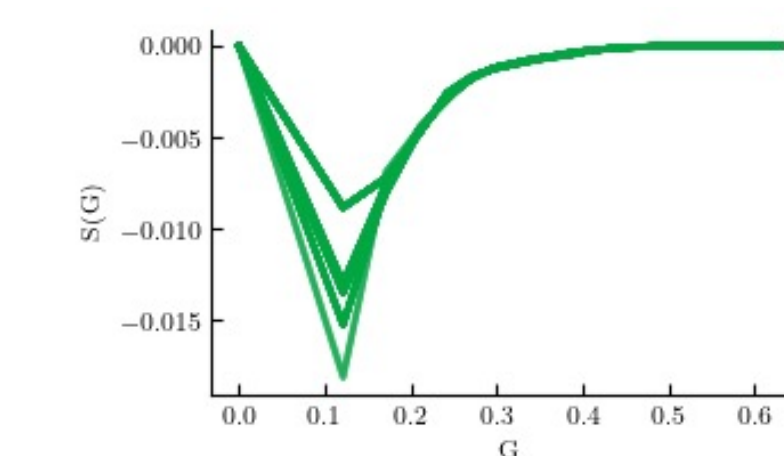
S_G goes to 0 as correlation goes to 0

The transition structure factor can be used to evaluate the convergence rates of the FSE in solids

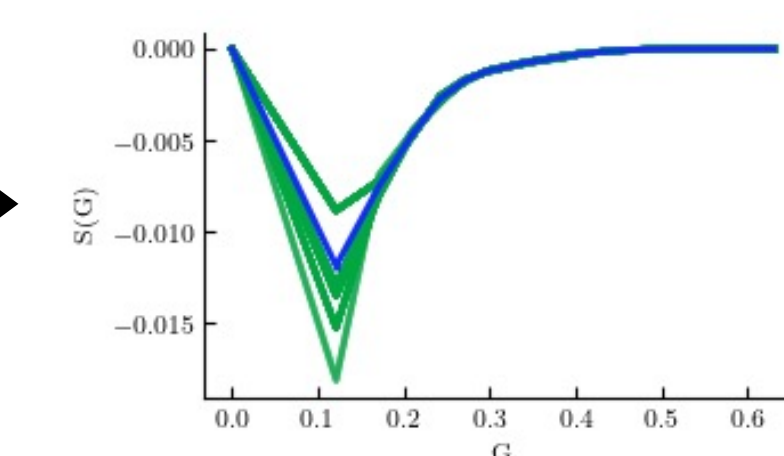


3 Structure factor twist averaging (sFTA)

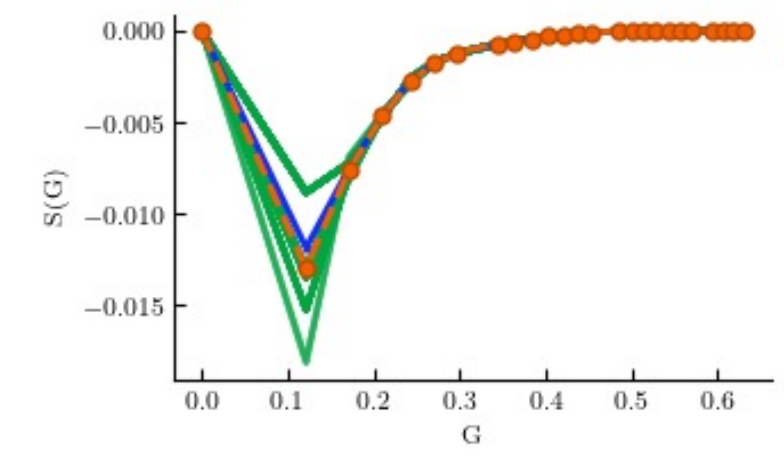
sFTA looks at the transition structure to select a special twist angle that reproduces the twist averaged energy. [2] This is done using the following steps:



1. Run 100 twist angles using MP2 and gather the structure factors



2. Find the averaged structure factor

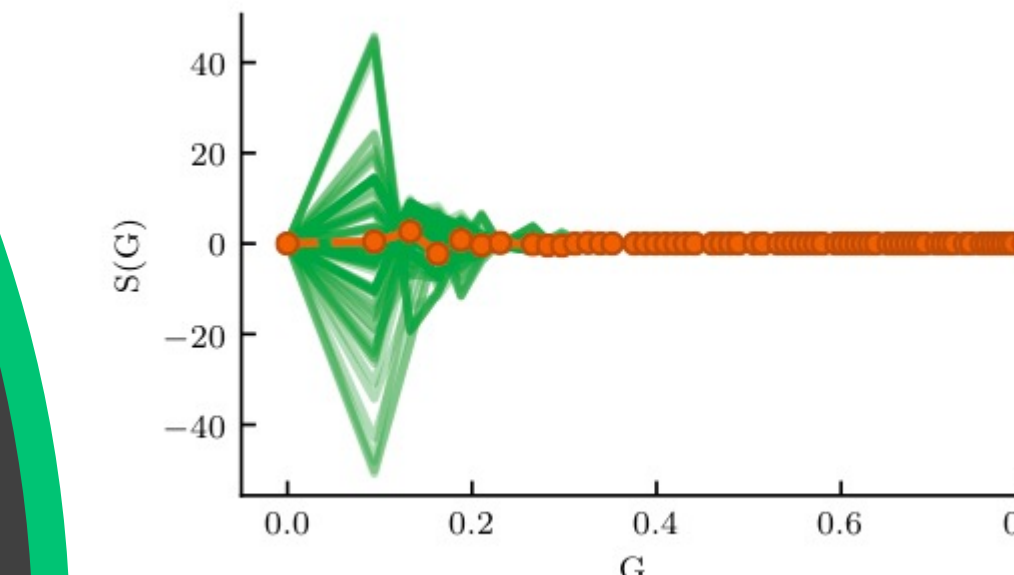


3. Select the twist angle most like the averaged S(G)

The special twist angle will have the structure factor with the smallest residual difference, r , to the average structure factor:

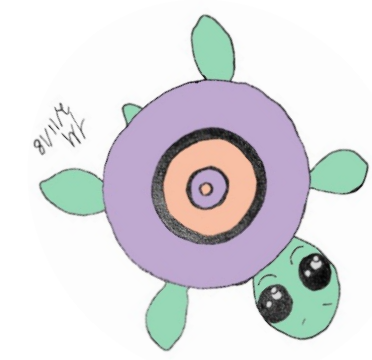
$$r = \sum_G |\bar{S}(G) - S_{k_s}(G)|^2$$

The special twist angle is used to run a CCSD calculation, cutting down the cost of getting the TA-CCSD energy from N_s CCSD calculations to 1 CCSD calculation.



A difference plot to the average shows that the sFTA-CCSD structure factor can reproduce the TA-CCSD structure factor for Na-bcc

Presenter



Tina Mihm

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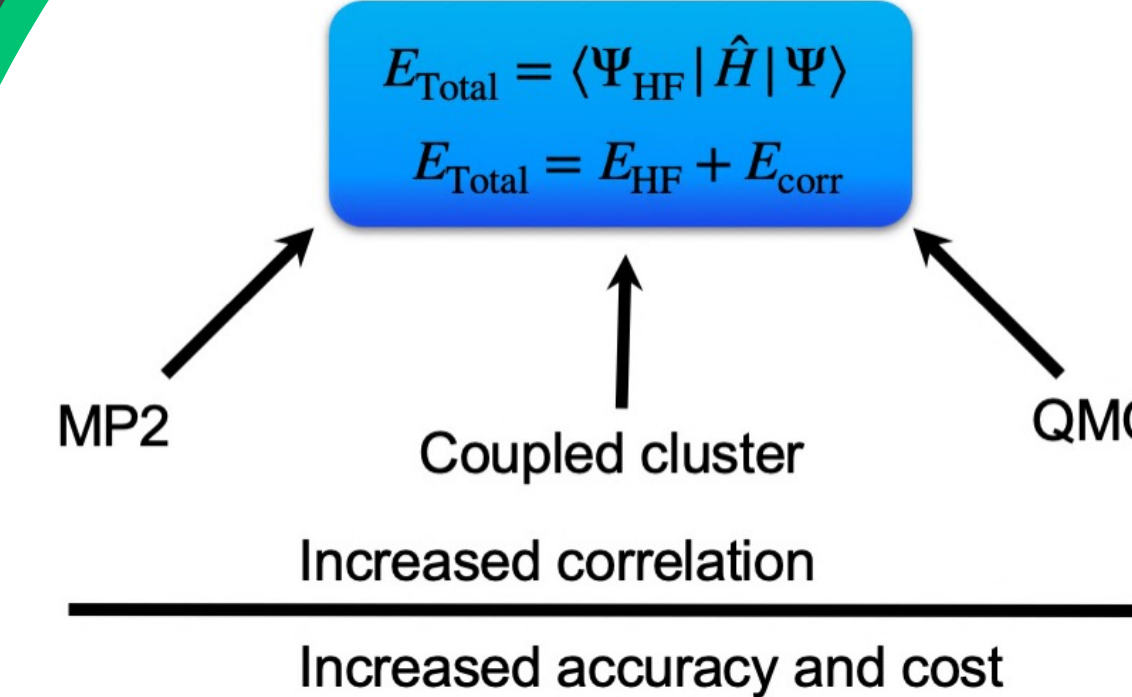
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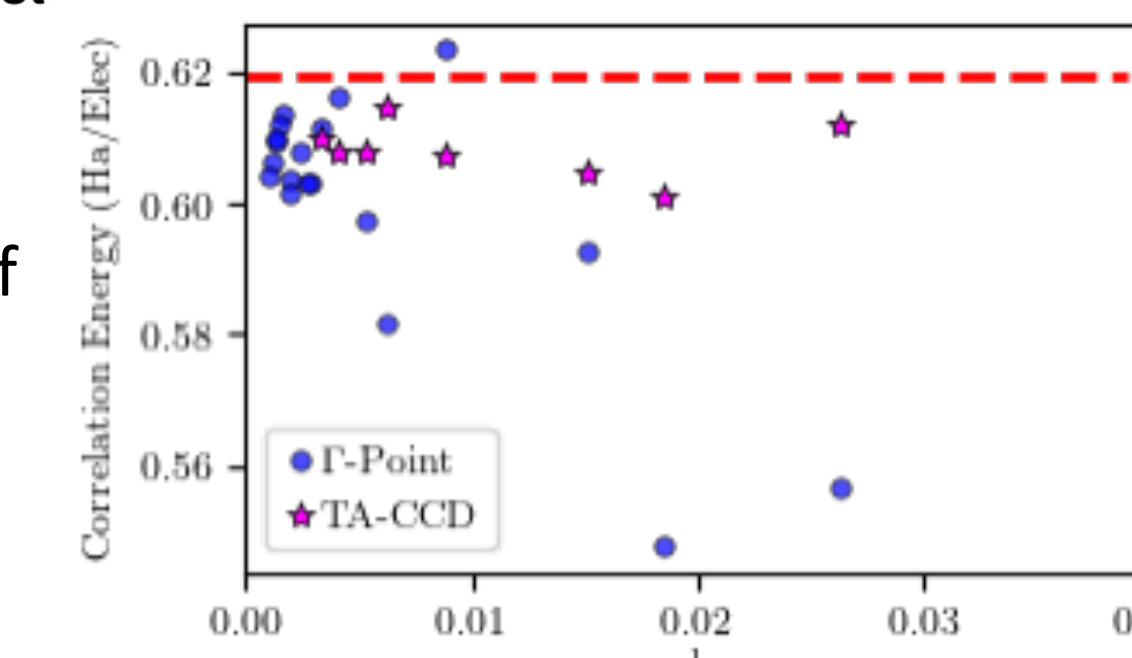
Many-Body Problem in Metals

Our research is currently focused on the finite sized effects that occur in solids.



Many-body methods have been gaining in popularity in material science due to improved accuracy over methods such as DFT

Currently, the largest source of error comes from the finite size effects found in solids

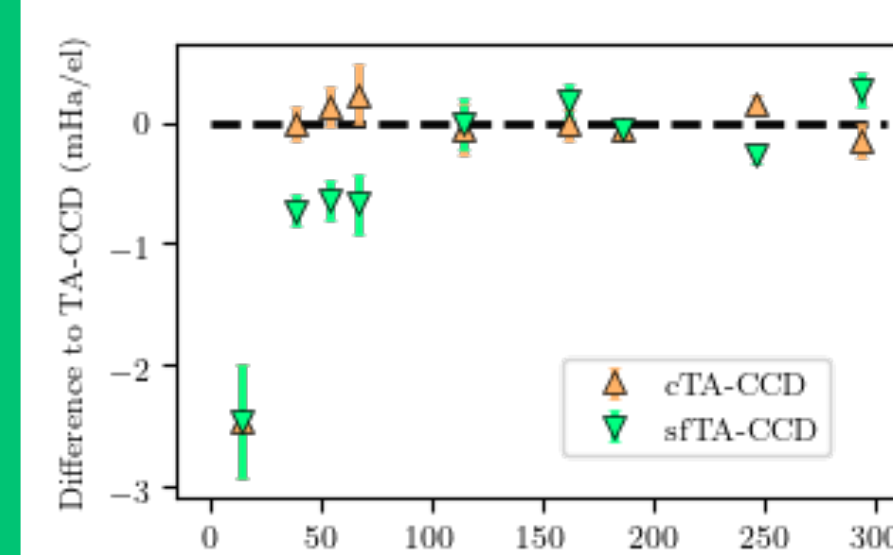


Twist averaging can reduce these errors, but is costly to run

4 Validating the sFTA method

We tested the efficiency of our new sFTA method using the uniform electron gas (UEG).

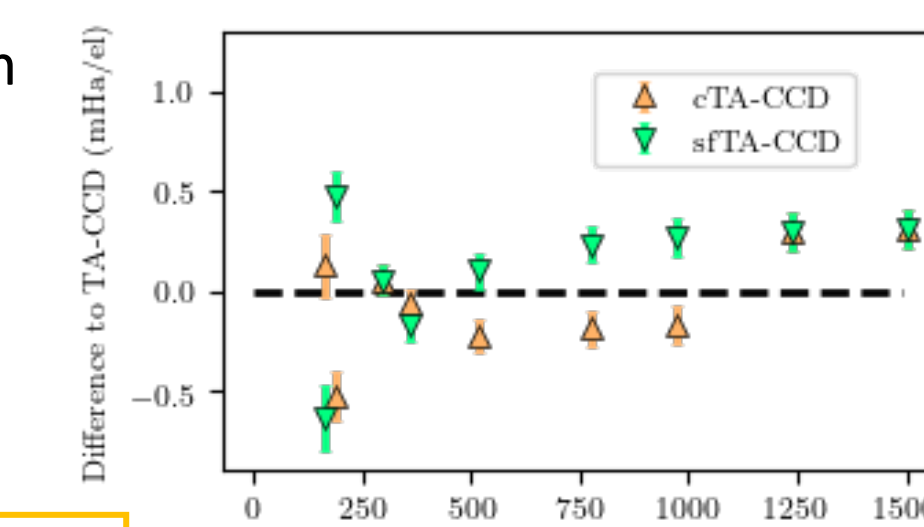
The results are compared to our previous method for the UEG called "connectivity twist averaging" (cTA). [3]



We get the same comparison with sFTA-CCD and TA-CCD as we saw with cTA-CCD

MAE (mHa/el):
cTA: 0.4(2)
sFTA: 0.6(2)

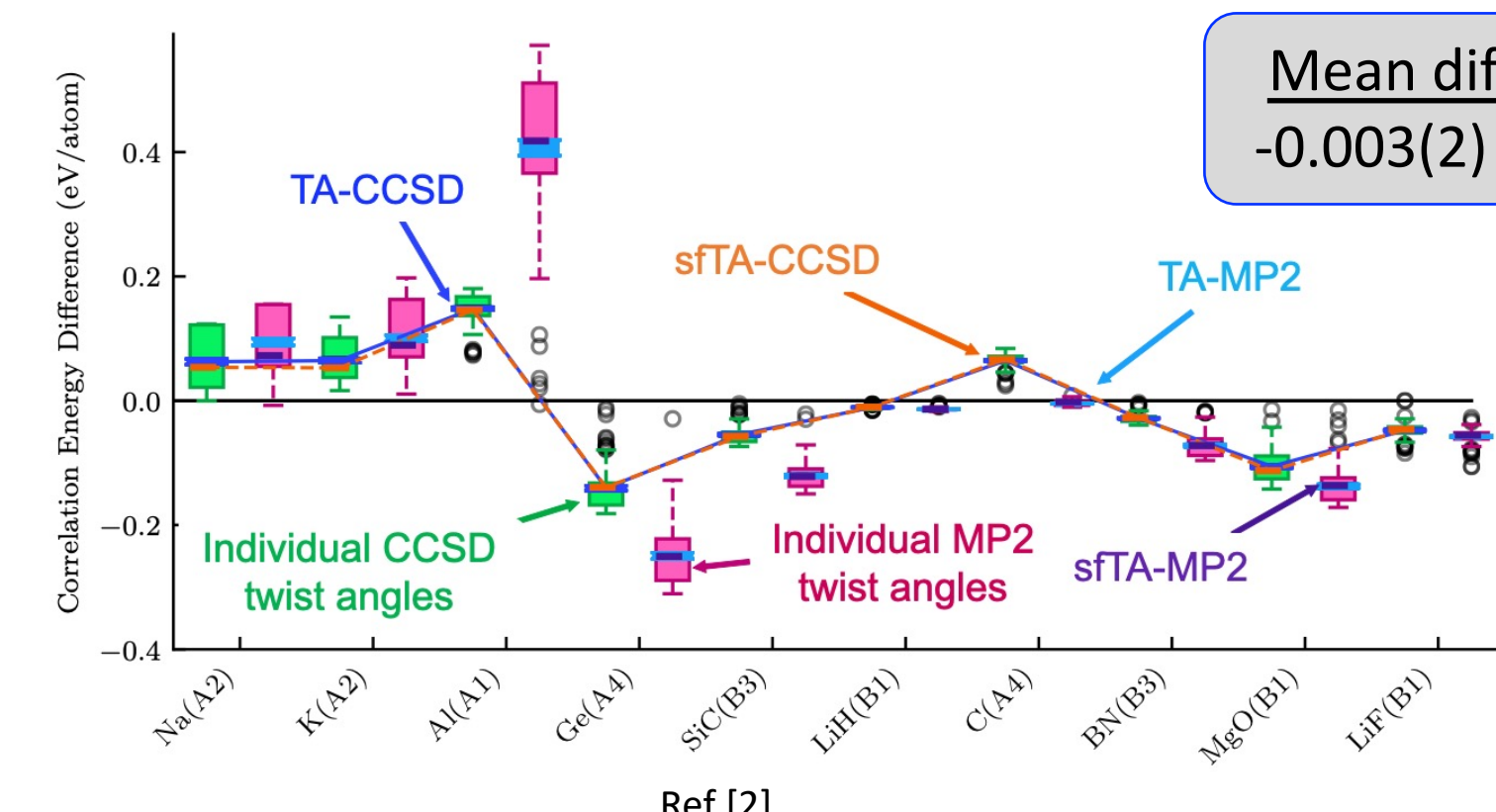
This is consistent across system size and basis set range



MAE (mHa/el):
cTA: 0.2(1)
sFTA: 0.3(1)

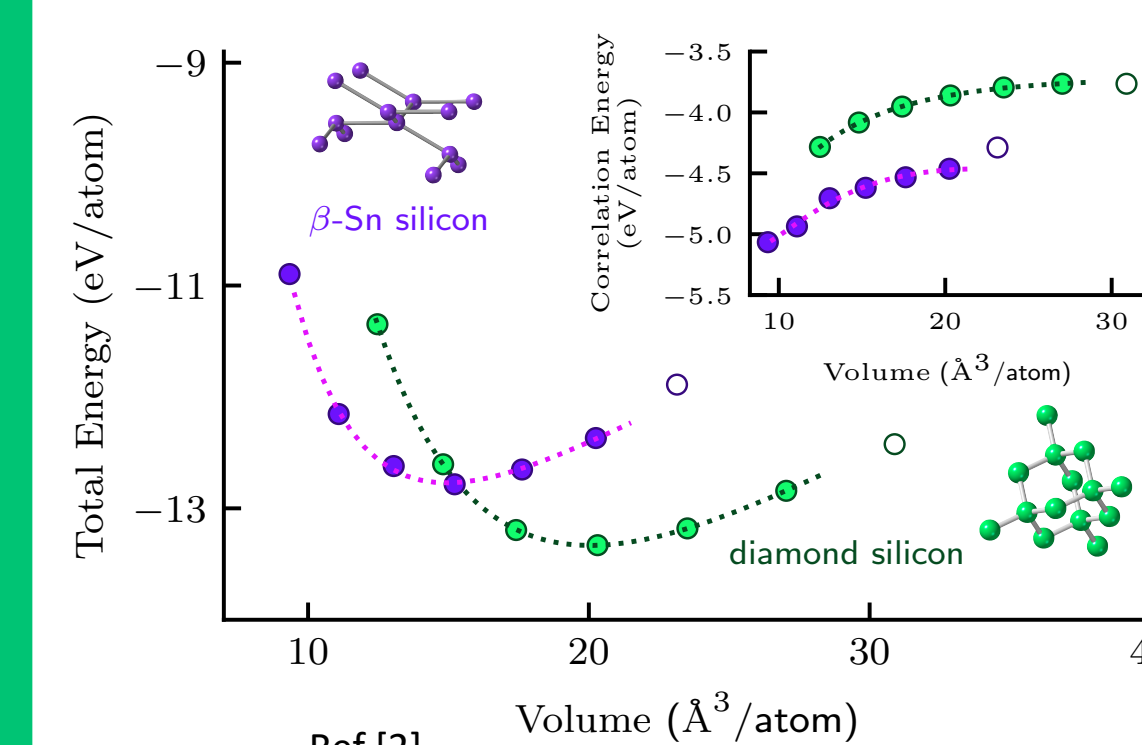
Note: the HF eigenvalues were not averaged for our cTA-CCD energies

With real solids, we show that we can reproduce TA-CCSD across a range of metals, semiconductors and insulators



Mean difference:
-0.003(2) eV/atom

5 Using sFTA-CCSD on Energy-Volume curves



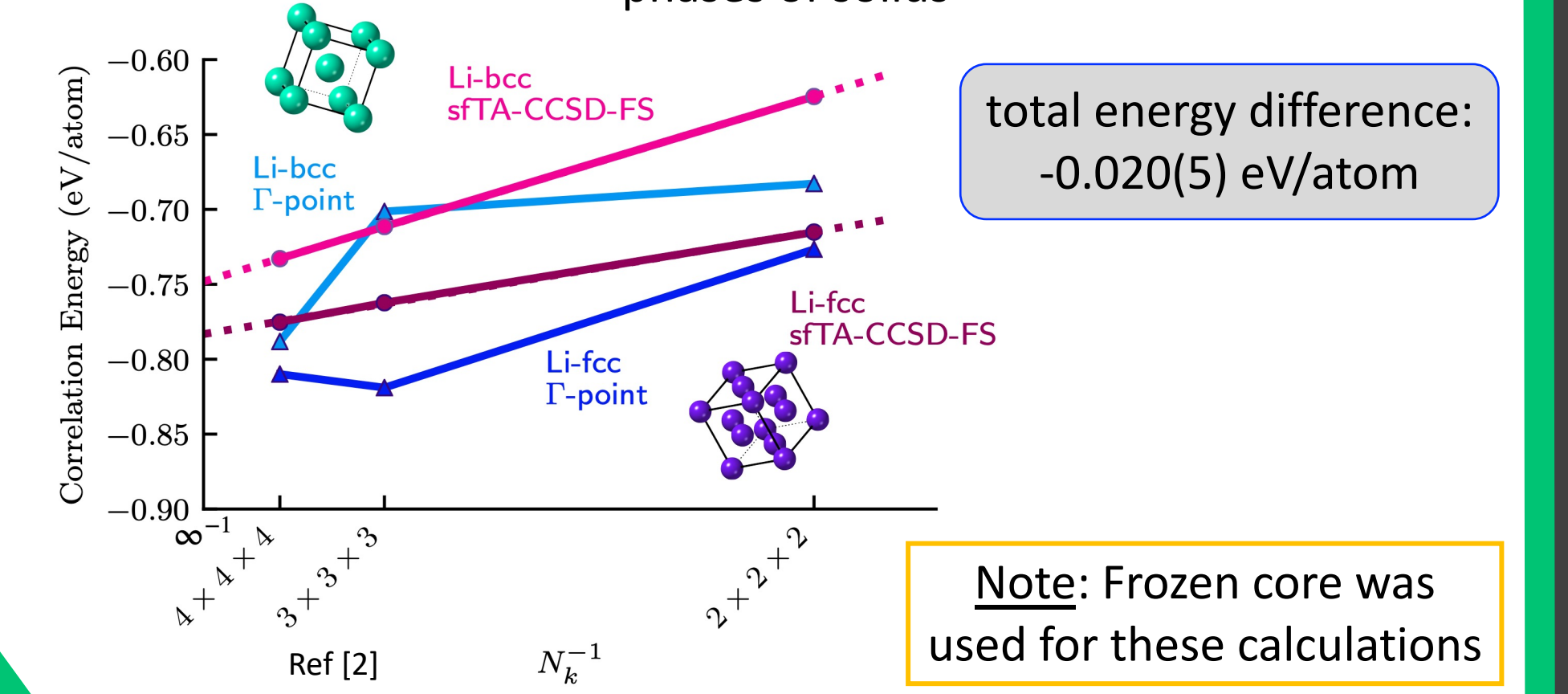
We can use our sFTA method to get CCSD energy for applications such as calculating the equation-of-State for two phases of Si

sFTA-CCSD-FS reproduces DMC P_t , but not the energy difference, ΔE

Property	HF	sFTA-CCSD-FS	sFTA-DCSD-FS	Expt.	DMC [4]	DMC+EMP-pp [5]	AFQMC [6]
ΔE (eV/atom)	1.302	0.562	0.494	—	0.505	0.329	0.365
P_t (GPa)	52.96	17.37	15.26	—	17.8	13.16	13.9
P_t incl. vib. corrections (GPa)	51.66	16.07	13.96	11.3 - 12.5	16.5	12.2	12.6

6 Using sFTA-CCSD on energy differences between phases

We can use our sFTA method to get CCSD energy differences between phases of solids



total energy difference: -0.020(5) eV/atom

Note: Frozen core was used for these calculations

We can see that the FSE in the two phases are reduced for the sFTA-CCSD energies, indicated by the smoother convergence to the TDL for both phases.

7 Future Directions

1. Using sFTA to predict energies for adsorption reactions with metal surfaces using H_2 adsorbed onto an Al surface to test
2. Fitting the transition structure factor with machine learning to generate a finite size correction for CCSD calculations. [7]