

# Calculating the Silicon Self-interstitials Formation Energies Using Periodic Coupled Cluster Theory

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# Presentation

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Andreas Grüneis Group: What do we do?

Introduction to Quantum Chemistry

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Outlook

# Andreas Grüneis Group: What do we do?

- Developing, implementing and applying Quantum Chemical methods to solid state systems.
- CCSD, CCSD(T), EOM-CCSD.
- Tensor Decompositions [7]
- Finite Size Corrections (CCSD) [6]
- Basis set extrapolation techniques [8]
- Embedding and orbital compatisation schemes [13]
- Molecule surface interactions [14]
- Excited states of defects [5]

Homemade coupled cluster program for solids (cc4s)

# A Quick Introduction to Quantum Chemistry

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## Second Quantisation Formalism

An orbital  $\varphi_a(\mathbf{r})$  is written as a operator acting on a vacuum

$$\varphi_a(\mathbf{r}) = \langle \mathbf{r} | \hat{c}_a^\dagger | 0 \rangle$$

The electron that is associated with the orbital  $\varphi_a(\mathbf{r})$  is now associated with the creation operator  $\hat{c}_a^\dagger$ .

# More Electrons: Slater Determinants

Two electron Slater determinant

$$\Psi(\mathbf{r}_1, \mathbf{r}_2) = \begin{vmatrix} \varphi_a(\mathbf{r}_1) & \varphi_a(\mathbf{r}_2) \\ \varphi_b(\mathbf{r}_1) & \varphi_b(\mathbf{r}_2) \end{vmatrix} = \varphi_a(\mathbf{r}_1)\varphi_b(\mathbf{r}_2) - \varphi_b(\mathbf{r}_1)\varphi_a(\mathbf{r}_2)$$

Or in second quantisation

$$|\Psi\rangle = \hat{c}_b^\dagger \hat{c}_a^\dagger |0\rangle, \quad \Psi(\mathbf{r}_1, \mathbf{r}_2) = \langle \mathbf{r}_1 \mathbf{r}_2 | \Psi \rangle$$

- The antisymmetry of the Slater determinant is encoded in the algebra of the operators  $\hat{c}_n^\dagger$ .
- Slater determinant with N electrons:

$$|\Psi\rangle = \hat{c}_1^\dagger \hat{c}_2^\dagger \hat{c}_3^\dagger \dots \hat{c}_N^\dagger |0\rangle$$

# The Electronic Structure Problem

Hamiltonian: clamped-nuclei approximation

$$\hat{\mathcal{H}} = -\frac{1}{2} \sum_i \nabla_i^2 - \sum_{iN} \frac{Z}{|\vec{R}_N - \vec{r}_i|} + \frac{1}{2} \sum_{i \neq j} \frac{1}{|\vec{r}_i - \vec{r}_j|}.$$

$\vec{R}_N$  are constant vectors describing the position of the nuclei.

In Second Quantisation

$$\hat{\mathcal{H}} = \sum_{p,q} h_q^p \hat{c}_p^\dagger \hat{c}_q + \sum_{p,q,r,s} \frac{1}{4} V_{rs}^{pq} \hat{c}_p^\dagger \hat{c}_q^\dagger \hat{c}_r \hat{c}_s$$



# Solving the Hamiltonian

We want to solve the time independent Schrödinger equation

$$\hat{\mathcal{H}}(\mathbf{r})\Psi_n(\mathbf{r}) = E_n\Psi_n(\mathbf{r}),$$

- Hilbert space of the all possible one body orbitals (Hartree-Fock)
- Hilbert space of all possible Slater determinants (Post Hartree-Fock)

First step Hartree-Fock Find the minimum by variation of orbitals in a single Slater determinant

$$E_{\text{HF}} = \min_{\{\varphi_i\}} \langle \varphi_1 \dots \varphi_N | \hat{\mathcal{H}} | \varphi_1 \dots \varphi_N \rangle$$

- Upperbound to the Groundstate
- A single Slater-Determinant
- Only Exchange Correlation
- No static or dynamic Correlation

## Exact Solution: linear combination of Slater determinants

$$|\Psi\rangle = \sum_k C_k |\Phi_k\rangle$$

The Orbitals generate a basis of Slater determinants

Simple Example **Helium**

- One body Hilbert space

$$\{\chi_k\} = \{\varphi_{100}, \varphi_{200}, \varphi_{210}, \dots\}$$

- Many body Hilbert space

$$\{\Phi_k\} = \{|\varphi_{100}, \varphi_{100}\rangle, |\varphi_{100}, \varphi_{200}\rangle, \dots\}$$

# Basis Set Functions

In practice we have to choose a basis set of functions to represent our orbitals

$$\varphi_i(\mathbf{r}) = \sum_n C_n^i \chi_n(\mathbf{r})$$

## Bloch's Theorem

$$\psi_{\vec{k}}(\vec{r}) = u_{\vec{k}}(\vec{r}) e^{i\vec{k}\vec{r}}.$$

We work with plane-waves.

$$\chi_{\vec{k}}(\vec{r}) = e^{i\vec{k}\vec{r}}.$$

# A Quick Introduction to Coupled Cluster Theory

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# Configuration Interactions: CI

We want to find the Coefficients  $C_k$

$$|\Psi\rangle = \sum_k C_k |\Phi_k\rangle$$

Starting with the Hartre-Fock determinant

$$|\text{HF}\rangle = |\varphi_1 \dots \varphi_N\rangle = \hat{c}_1^\dagger \dots \hat{c}_N^\dagger |0\rangle$$

We can define the level of excitation of a Slater determinant

# Excited Slater determinants

All possible singles excitations

$$|\Psi_{\text{singles}}\rangle = \sum_{ai} C_i^a |\Phi_i^a\rangle = \sum_{ai} C_i^a \hat{c}_a^\dagger \hat{c}_i |\text{HF}\rangle$$

All possible doubles excitations

$$|\Psi_{\text{doubles}}\rangle = \sum_{abij} C_{ij}^{ab} |\Phi_{ij}^{ab}\rangle = \sum_{abij} C_{ij}^{ab} \hat{c}_a^\dagger \hat{c}_b^\dagger \hat{c}_j \hat{c}_i |\text{HF}\rangle$$

$\vdots$

$$|\Psi\rangle = |\Psi_{\text{singles}}\rangle + |\Psi_{\text{doubles}}\rangle + |\Psi_{\text{triples}}\rangle + \dots$$

# Coupled Cluster Theory

- Among the most successful theories in quantum chemistry
- Exponential ansatz

$$|\Psi_{CC}\rangle = e^{\hat{T}}|\text{HF}\rangle$$

- The cluster operator creates all excitations

$$\hat{T} = \underbrace{\sum_{ai} t_i^a \hat{c}_a^\dagger \hat{c}_i}_{\hat{T}_1} + \underbrace{\sum_{abij} t_{ij}^{ab} \hat{c}_a^\dagger \hat{c}_b^\dagger \hat{c}_j \hat{c}_i}_{\hat{T}_2} + \dots$$

- by truncating the  $\hat{T}$  operator at  $\hat{T}_2$  we do CCSD



- With the Cluster operator

$$\hat{T} = \hat{T}_1 + \hat{T}_2$$

- CCSD includes excitations up to N-th order

$$e^{\hat{T}} = \left( 1 + \underbrace{\hat{T}_1 + \hat{T}_2 + \frac{1}{2!}\hat{T}_1^2}_{\text{CISD}} + \frac{1}{2!} \left( \underbrace{\hat{T}_2^2}_{\text{quad.}} + \underbrace{\hat{T}_1\hat{T}_2 + \hat{T}_2\hat{T}_1}_{\text{triples}} \right) + \dots \right)$$

- Exact two electron correlation
- Coefficient equations are nonlinear
- Have to be solved in a iterative way

# CCSD(T) Theory

- CCSD theory scales as  $O(N^6)$  - doable
- CCSDT theory scales as  $O(N^8)$  - too expensive
- Incorporating some of the triples correlation in a perturbative way
- CCSD(T) scales as  $O(N^7)$
- CCSD(T) gives consistently highly accurate results for a large set of molecules

CCSD(T) is the golden standard of quantum chemistry

# Application to the Si Self-Interstitials

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# Motivation

- Silicon is important in the industry
  - Transistors requires near-atomic accuracy
  - A single trapping center alters the electronic properties
- Silicon Self-Diffusion some experimental data available
  - Migration Barrier
  - Formation Energy
- We have big computers
- Why not use CCSD(T), to calculate the formation energy?

# Doing the CCSD(T) calculation

- Periodic supercell approach - VASP
- Double Trouble
  - Finite size Convergence  $N_k \rightarrow \infty$ 
    - Finite size errors due to finite K-point sampling
    - Finite size errors due to defect concentration
  - Basis-set Convergence  $N_v \rightarrow \infty$

In both cases we need extrapolation and correction schemes

# The X and H Cells

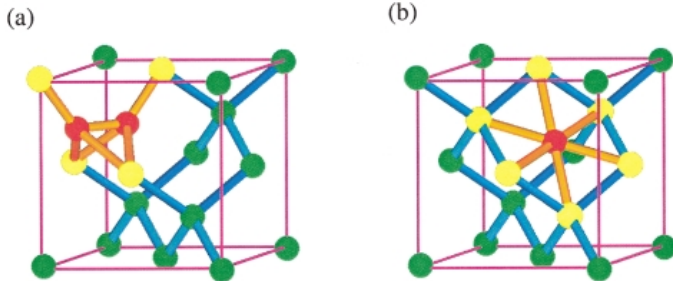


Figure: (a) The split-110 (X) and (b) hexagonal (H) interstitial defects [10].

- Defect atoms are red
- Their nearest neighbors are yellow
- The bonds between them are orange

# The T Cell

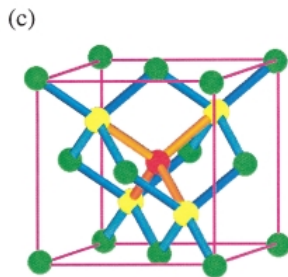


Figure: (c) The tetrahedral (T) interstitial defect [10].

- For benchmarking reasons two more interstitials are added
- the vacancy (V) and the DFT-PBE hexagonal (C3V)

All cells are relaxed using DFT-PBE

# How to calculate the Formation energy?

- 1 Energy of the Pristine cell  $E_{\text{bulk}}$
- 2 Energy of the interstitial cell  $E_{\text{int}}$

## Formation Energy

$$E_f = E_{\text{int}} - \frac{N_{\text{int}}}{N_{\text{bulk}}} E_{\text{bulk}}$$

Energies can be calculated at any level of theory



# Workflow leading us to the converged CCSD(T) energies

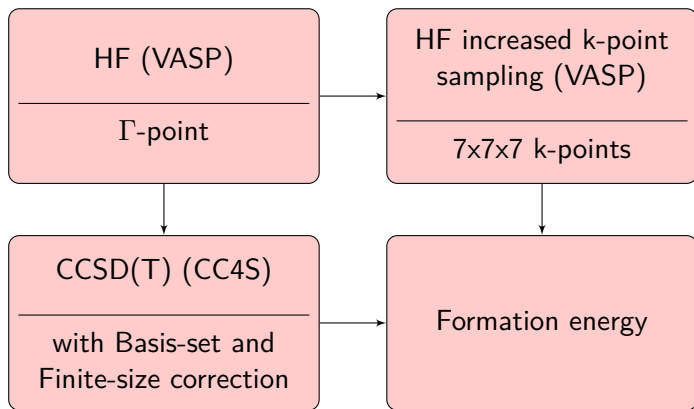


Figure: Schematic representation of the workflow

# Finite Size Incompleteness Error

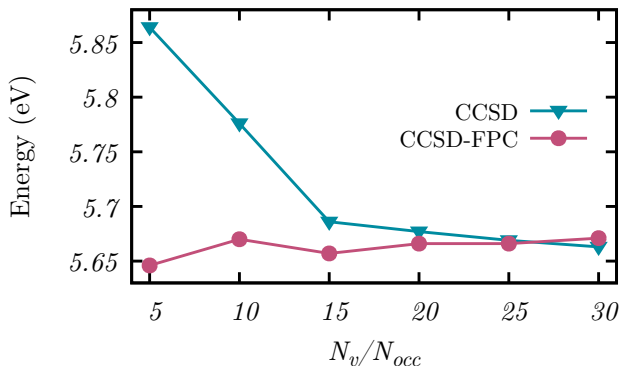
Due to the periodic supercell approach, we are always having a defined defect concentration

- Finite size error due to periodic images  $\rightarrow$  bigger cell
- Finite size error due finite number of kpoints
  - in the case of HF  $\rightarrow$  increase kpoints
  - in the case of CCSD(T)  $\rightarrow$  finite size correction[6]
- Correction is done on one k-point  $\rightarrow$  twist averaging
  - Calculate the CCSD(T) correction at random k-points
  - Take a look at the average and standard deviation

# Basis Set Incompleteness Error

The Basis set incompleteness error comes mostly from the electron-electron cusp

- Pair-specific cusp correction in cc4s, focal-point correction (FPC)[8]



**Figure:** CCSD formation energy of the X interstitial. A  $\Gamma$ -centered cubic mesh was used.

# Results

**Table:** Computed and converged HF, CCSD and CCSD(T) formation energies including all reported corrections, compared to QMC [11], RPA [9], PBE [9], LDA [12, 1],  $G_0W_0$  [12] and HSE [1] from the literature and also experimental data [4, 3, 2, 16, 15].

| Cell | HF    | CCSD  | CCSD(T) | QMC | QMC (nobf) | $G_0W_0$ | RPA  | RPA (216) | HSE  | PBE  | LDA  | Exp.      |
|------|-------|-------|---------|-----|------------|----------|------|-----------|------|------|------|-----------|
| X    | 7.930 | 5.295 | 4.535   | 4.4 | 4.9        | 4.46     | 4.27 | 4.2       | 4.46 | 3.56 | 3.29 |           |
| H    | 8.162 | 5.559 | 4.810   | 4.7 | 4.9        | 4.4      | 4.45 | 4.33      | 4.82 | 3.74 | 3.4  | 4.2 - 4.7 |
| T    | 9.954 | 7.127 | 6.316   | 5.1 | 5.2        |          | 4.53 | 4.93      | 4.92 | 3.66 | 3.56 |           |

- X and H look good
- T does not look good
  - Multiconfigurational character?

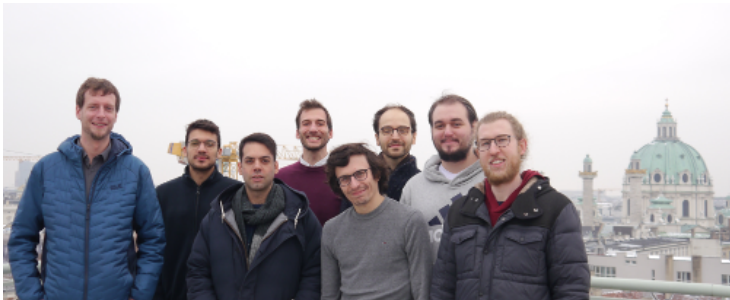
# Outlook

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- Coupled Cluster is one of the most accurate Wavefunction theories in Quantum Chemistry
- + Can be used for systems with  $\approx 50$  atoms
- + ab initio - no parameters
- + size extensivity - perfect for solid state physics
- only applicable to weakly correlated systems
- gets expensive fast - CCSD(T)  $O(N^7)$

# Thank you!

## Thank you



**Figure:** Adreas Grüneis, Nikolaos Masios, Theodoros Tsatsoulis, Felix Hummel, Andreas Irmler, Alejandro Gallo, Faruk Salihbegovic, Tobias Schäfer



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