

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

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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

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)

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

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

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

- Build-in size-extensivity
- Coefficient equations are nonlinear
- Have to be solved in an 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

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

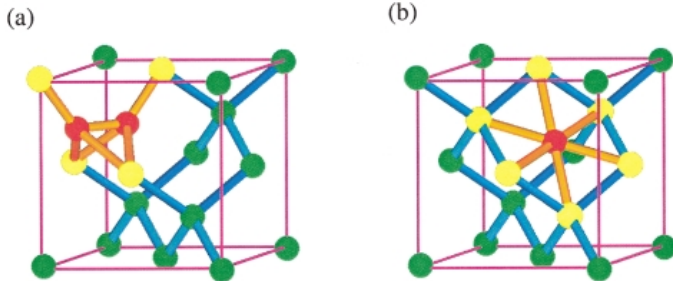


Figure: (a) The split-110 (X) and (b) hexagonal (H) interstitial defects [10].

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

The T Cell

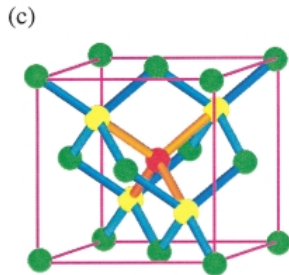


Figure: (c) The tetrahedral (T) interstitial defect [10].

- 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_{bulk}
- 2 Energy of the interstitial cell E_{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

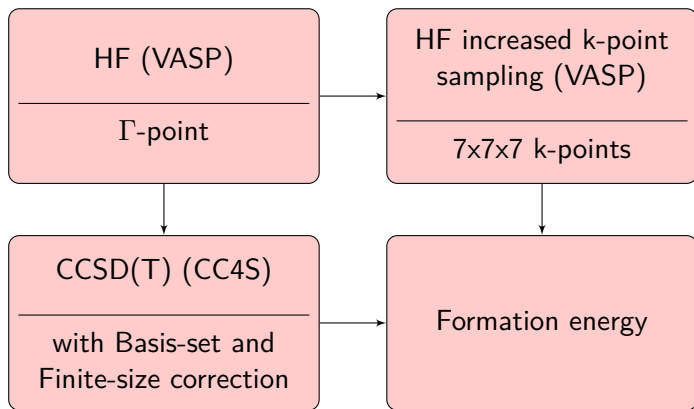


Figure: Schematic representation of the workflow

Finite Size 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]

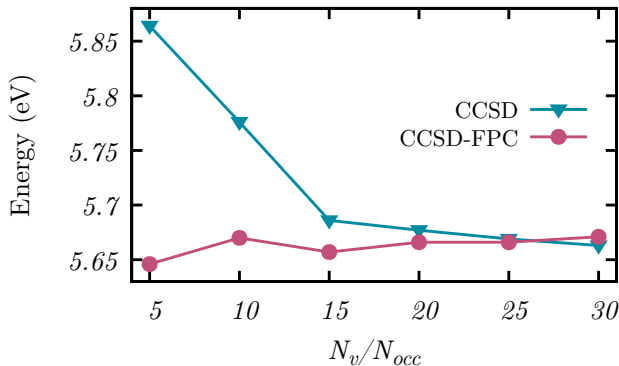


Figure: CCSD formation energy of the X interstitial. At the Γ -point

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

Outlook

- Coupled Cluster is one of the most accurate Wavefunction theories in Quantum Chemistry
- + Can be used for systems with ≈ 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

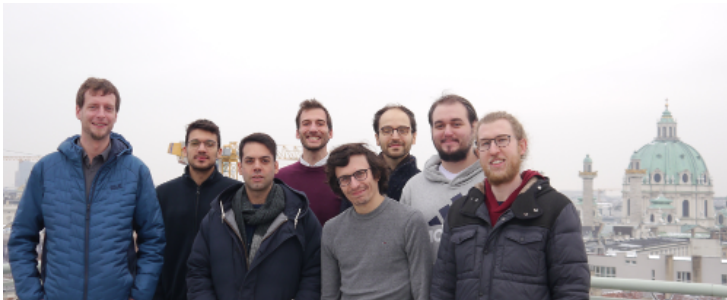


Figure: Adreas Grüneis, Nikolaos Masios, Theodoros Tsatsoulis, Felix Hummel, Andreas Irmler, Alejandro Gallo, Faruk Salihbegovic, Tobias Schäfer



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