

# 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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Conclusão

# 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 [3]
- Finite Size Corrections (CCSD) [2]
- Basis set extrapolation techniques [4]
- Embedding and orbital compatisation schemes [6]
- Molecule surface interactions [7]
- Excited states of defects [1]

# 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?

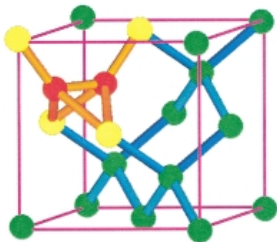
# Doing the CCSD(T) calculation

- 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  $N_v \rightarrow \infty$

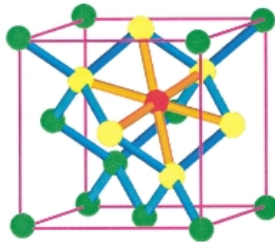
In both cases we need extrapolation and correction schemes

# The X and H Cells

(a)



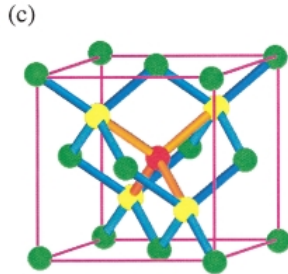
(b)



(a) The split-110 (X) and (b) hexagonal (H) interstitial defects [5].

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

# The T Cell



(c) The tetrahedral (T) interstitial defect [5].

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

# How to calculate the Formation energy?

Give the formula for the formation energy



# Workflow leading us to CCSD(T) energies

give the workflow chart leading to the CC results

# Basis Set Correction

give the plot

# Finite size correction Correction

differentiate the defect concentration the gamma point correction (finite size correction) and the twist averaging

# Results

give the final table and discuss it

Modelo	Acurácia
SVM	0.88
$k$ -NN	0.80
Naive Bayes	0.83
MLP	0.95

Exemplo de Tabela

# Listagem

Listagem de itens com *itemize*:

- Item 1
- Item 2
- Item 3

Listagem de itens com *enumerate*:

- ① Item 1
- ② Item 2
- ③ Item 3

Lorem ipsum dolor sit amet, consectetur adipiscing elit. Etiam eget ligula eu lectus lobortis condimentum. Aliquam nonummy auctor massa.

## Bloco

Pellentesque habitant morbi tristique senectus et netus et malesuada fames ac turpis egestas. Nulla at risus.

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## Distribuição Normal

$$f(x) = \frac{1}{\sigma\sqrt{2\pi}} e^{-\frac{1}{2}\left(\frac{x-\mu}{\sigma}\right)^2}$$

## Transformada de Fourier Discreta

$$X(\omega) = \sum_{n=0}^{L-1} x_n e^{-i\omega n}, \quad x \in \mathbb{R}^L$$



# Algoritmos

Algoritmo *Selection Sort*, que ordena um vetor  $x \in \mathbb{R}^N$  em tempo  $\mathcal{O}(N^2)$ :

```
for  $i \in [0, \dots, N - 1]$  do  
     $m \leftarrow i$   
    for  $j \in [i + 1, \dots, N - 1]$  do  
        if  $x_j < x_m$  then  
             $m \leftarrow j$   
        end if  
    end for  
    if  $x_i \neq x_m$  then  
         $a \leftarrow x_i$   
         $x_i \leftarrow x_m$   
         $x_m \leftarrow a$   
    end if  
end for
```

# Código-fonte

Código-fonte do algoritmo *Selection Sort* em Python:

```
lista = [3,2,1]
for i in range(len(lista)):
    menor = i
    for j in range(i+1,len(lista)):
        if lista[j] < lista[menor]:
            menor = j
    if lista[i] != lista[menor]:
        aux = lista[i]
        lista[i] = lista[menor]
        lista[menor] = aux
print(lista)
```

Utilize “fragile” ao invés de “plain” ao definir um *frame* que contém um *verbatim*

Obrigado!

- [1] Alejandro Gallo et al. “A periodic equation-of-motion coupled-cluster implementation applied to F-centers in alkaline earth oxides”. In: *The Journal of Chemical Physics* 154.6 (Feb. 2021), p. 064106. ISSN: 0021-9606. DOI: 10.1063/5.0035425. eprint: [https://pubs.aip.org/aip/jcp/article-pdf/doi/10.1063/5.0035425/15584304/064106\\\_1\\\_online.pdf](https://pubs.aip.org/aip/jcp/article-pdf/doi/10.1063/5.0035425/15584304/064106\_1\_online.pdf). URL: <https://doi.org/10.1063/5.0035425>.
- [2] Thomas Gruber et al. “Applying the Coupled-Cluster Ansatz to Solids and Surfaces in the Thermodynamic Limit”. In: *Phys. Rev. X* 8 (2 2018), p. 021043. DOI: 10.1103/PhysRevX.8.021043. URL: <https://link.aps.org/doi/10.1103/PhysRevX.8.021043>.
- [3] Felix Hummel, Theodoros Tsatsoulis, and Andreas Grüneis. “Low rank factorization of the Coulomb integrals for periodic coupled cluster theory”. In: *The Journal of Chemical Physics* 146.12 (Mar. 2017), p. 124105. ISSN: 0021-9606. DOI: 10.1063/1.4977994. eprint: [https://pubs.aip.org/aip/jcp/article-pdf/doi/10.1063/1.4977994/1481241/124105\\\_1\\\_online.pdf](https://pubs.aip.org/aip/jcp/article-pdf/doi/10.1063/1.4977994/1481241/124105\_1\_online.pdf).

1063/1.4977994/15525179/124105\\_1\\_online.pdf. URL:  
<https://doi.org/10.1063/1.4977994>.

- [4] Andreas Irmmler et al. “Duality of Ring and Ladder Diagrams and Its Importance for Many-Electron Perturbation Theories”. In: *Phys. Rev. Lett.* 123 (15 2019), p. 156401. DOI: 10.1103/PhysRevLett.123.156401. URL: <https://link.aps.org/doi/10.1103/PhysRevLett.123.156401>.
- [5] W.-K. Leung et al. “Calculations of Silicon Self-Interstitial Defects”. In: *Phys. Rev. Lett.* 83 (12 1999), pp. 2351–2354. DOI: 10.1103/PhysRevLett.83.2351. URL: <https://link.aps.org/doi/10.1103/PhysRevLett.83.2351>.
- [6] Tobias Schäfer et al. “Surface science using coupled cluster theory via local Wannier functions and in-RPA-embedding: The case of water on graphitic carbon nitride”. In: *The Journal of Chemical Physics* 155.24 (Dec. 2021), p. 244103. ISSN: 0021-9606. DOI: 10.1063/5.0074936. eprint: <https://pubs.aip.org/aip/jcp/article-pdf/doi/10.>

1063/5.0074936/14838228/244103\\_1\\_online.pdf. URL:  
<https://doi.org/10.1063/5.0074936>.

- [7] Theodoros Tsatsoulis. *Periodic quantum chemical methods for molecule-surface interactions*. 2020. URL:  
<https://repositum.tuwien.at/handle/20.500.12708/15241>.