

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 [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]

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)

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

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

- 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

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?

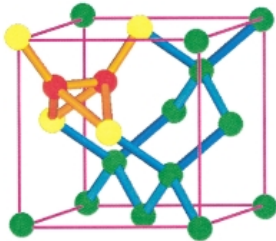
Doing the CCSD(T) calculation

- 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 $N_v \rightarrow \infty$

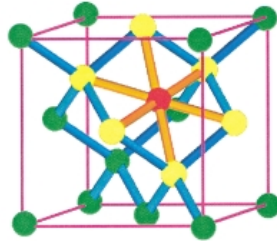
In both cases we need extrapolation and correction schemes

The X and H Cells

(a)



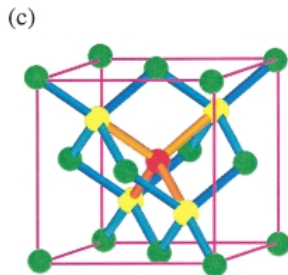
(b)



(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].

- 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?

Give the formula for the formation energy Maybe a promo about error cancelation

Workflow leading us to CCSD(T) energies

give the workflow chart leading to the CC results

Finite size correction Correction

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

Basis Set Correction

give the plot

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. 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.

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>.

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>.