NOVEL-MATERIALS DISCOVERY GROUP

Fritz Haber Institute of the Max Planck Society

Exa-scaling Coupled Cluster in solids

Time-efficient, highly accurate calculations for Novel Materials Discovery

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September 28, 2020

$$|\Psi\rangle = e^{\hat{T}} |\Phi_0\rangle$$

Theoretical background - The CCSD Ansatz

- Post-SCF-method (HF or KS)
- Requires Φ_0^{KS} and virtual orbitals ϕ_a ($a \in \{N_{occ}+1, ..., N_{states}\}$)
- Ansatz of exact N-particle wave-function $|\Psi\rangle$:

$$\hat{H}|\Psi\rangle = E|\Psi\rangle$$

$$|\Psi\rangle = e^{\hat{T}}|\Phi_0^{KS}\rangle, \text{ where } \hat{T} = \hat{T}_1 + \hat{T}_2$$

$$\hat{T}_1 = \sum_{i,a} t_i^a \hat{a}_a^\dagger \hat{a}_i \text{ and } \hat{T}_2 = \sum_{i,j,a,b} t_{ij}^{ab} \hat{a}_a^\dagger \hat{a}_b^\dagger \hat{a}_j \hat{a}_i$$

$$|\Psi\rangle = \left(1 + (\hat{T}_1 + \hat{T}_2) + \frac{1}{2}(\hat{T}_1 + \hat{T}_2)^2 + ...\right)|\Phi_0^{KS}\rangle$$

$$= |\Phi_0^{KS}\rangle + \sum_{i,a} t_i^a |\Phi_i^a\rangle + \sum_{i,j,a,b} t_{ij}^{ab} |\Phi_{ij}^{ab}\rangle + \sum_{i,j,a,b} t_i^a t_j^b |\Phi_{ij}^{ab}\rangle + ...$$

Theoretical background - The CCSD equations

- Goal: Find optimal amplitudes t_i^a and t_{ij}^{ab}
- Obtain equations by projecting onto ground state and excited determinants:
  - $\langle \Phi_0 | e^{-\hat{T}} \hat{H} e^{\hat{T}} | \Phi_0 \rangle = E$
  - $\langle \Phi_i^a | e^{-\hat{T}} \hat{H} e^{\hat{T}} | \Phi_0 \rangle = 0$
  - $\langle \Phi_{ij}^{ab} | e^{-\hat{T}} \hat{H} e^{\hat{T}} | \Phi_0 \rangle = 0$
- Solve non-variational, non-linear equations iteratively

$$E_{CCSD}^c = \langle \Phi_0 | e^{-\hat{T}} \hat{H} e^{\hat{T}} | \Phi_0 \rangle - E_0^{HF/KS} = 2 f_i^a t_a^i + (2 v_{ab}^{ij} - v_{ba}^{ij}) \tau_{ij}^{ab}$$

$$\tau_{ij}^{ab} = t_{ij}^{ab} + t_i^a t_j^b$$

$$f_i^a = \langle \phi_i | \hat{f}^{HF} | \phi_a \rangle$$

$$v_{ij}^{ab} = \langle \phi_i \phi_j | \phi_a \phi_b \rangle - \langle \phi_i \phi_j | \phi_b \phi_a \rangle$$

Theoretical background - The CCSD equations

The t_1-equation:

$$
\begin{aligned}
& f_i^a - 2f_b^j t_j^a t_i^b + h_b^a t_i^b - h_i^j t_j^a + h_b^j (2t_{ji}^{ba} - t_{ij}^{ba} + t_i^b t_j^a) + \\
& (2v_{bi}^{ja} - v_{ib}^{ja}) t_j^b + (2v_{bc}^{ja} - v_{cb}^{ja}) \tau_{ji}^{bc} - (2v_{bi}^{jk} - v_{bi}^{kj}) \tau_{jk}^{ba} = 0 \\
& h_j^i = f_j^i + (2v_{ab}^{ik} - v_{ba}^{ik}) \tau_{jk}^{ab} \\
& h_a^c = f_a^c + (2v_{ab}^{ik} - v_{ab}^{ki}) \tau_{ik}^{cb} \\
& h_a^i = f_a^i + (2v_{ab}^{ik} - v_{ba}^{ik}) t_k^b \\
& \tau_{ij}^{ab} = t_{ij}^{ab} + t_i^a t_j^b \\
& f_i^a = \langle \phi_i | \hat{f}^{HF} | \phi_a \rangle \\
& v_{ij}^{ab} = \langle \phi_i \phi_j | \phi_a \phi_b \rangle - \langle \phi_i \phi_j | \phi_b \phi_a \rangle
\end{aligned}
$$

The t_2-equation has 35 terms...[1]

[1] For a more in-depth discussion of the Coupled Cluster theory see the review by Crawford and Schaefer (2000)

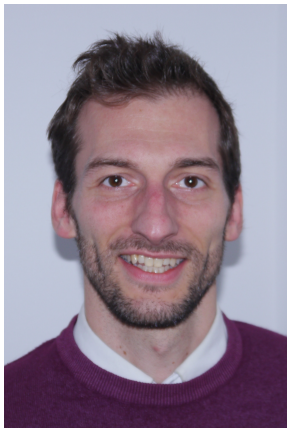
Why Coupled Cluster?

DFT	CC
xc-functional needs to be chosen	Blackbox method
Non-systematic approximation of correlation	In principle exact (given enough resources)
No way of systematically improving functional	Systematic improvement of approximation by including higher excitations
Scaling N^3	Scaling $\geq N^6$(CCSD)

CC4S - Coupled Cluster For Solids

- Code developed by Felix Hummel and Andreas Grüneis (TU Wien)
- CCSD calculation of periodic systems
- Requires input: eigenvalues, hamiltonian and reduced representation of 4-center-2-electron-integrals ($\Gamma^{s}_{q\mu}$)

(a) Andreas Grüneis

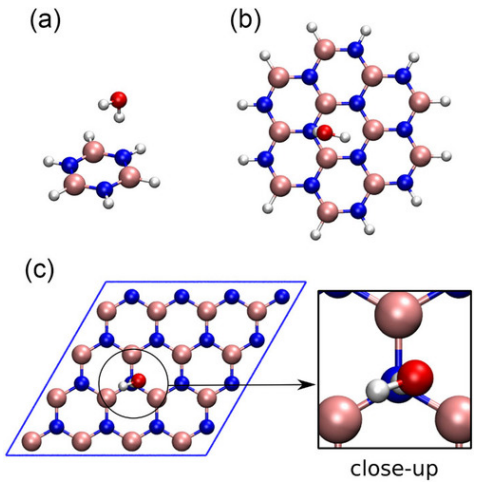


(b) Felix Hummel

(c) Andreas Irmler

Goals

- Develop interface between FHI-aims and CC4S
- Find performance bottlenecks in CC4S
- Develop standalone, highly parallelizable CCSD implementation as library (**CC4S-X + CTF-X**) based on CC4S
- Benchmark interface and library wrt. scaling and accuracy for larger systems (∼30-50 atoms)
- Investigate further possibilities to decrease size scaling
- Calculate band structures using Equation-of-motion Coupled Cluster (EOM-CCSD)



Current stage - The coulomb vertex in CC4S

- CC4S requires 4-center-2-electron-integrals
  $V_{pq}^{rs} = \int d\boldsymbol{r} d\boldsymbol{r'} \phi_p^*(\boldsymbol{r}) \phi_q^*(\boldsymbol{r'}) \frac{1}{|\boldsymbol{r} - \boldsymbol{r'}|} \phi_r(\boldsymbol{r}) \phi_s(\boldsymbol{r'})$
- Instead of transferring the entire 4-dimensional array, use 3-dimensional Coulomb-Vertex[2] $\Gamma_p^r(\boldsymbol{G}) = \sqrt{\frac{4\pi}{\boldsymbol{G}^2}} \int d\boldsymbol{r} e^{i\boldsymbol{G}\boldsymbol{r}} \phi_p^*(\boldsymbol{r}) \phi_r(\boldsymbol{r})$
- It can be shown that

$$V_{pq}^{rs} = \frac{1}{(2\pi)^3} \int d\boldsymbol{G}\, \Gamma_p^r(\boldsymbol{G}) \Gamma_q^s(\boldsymbol{G}) \overset{\text{disc.}}{=} \sum_{\boldsymbol{G}} \Gamma_p^{*r\boldsymbol{G}} \Gamma_{q\boldsymbol{G}}^s$$

This applies to plane waves, but what to do for localized orbitals?

[1] Hummel, Tsatsoulis, Grüneis (2017)

Current stage - The coulomb vertex in FHI-aims

$$V_{pq}^{rs} = \sum_{\boldsymbol{G}} \Gamma_{p}^{*r\boldsymbol{G}} \Gamma_{q\boldsymbol{G}}^{s} \qquad \phi_i(\boldsymbol{r})\phi_j(\boldsymbol{r}) = \sum_{\nu} C_{ij}^{\nu} P_{\nu}(\boldsymbol{r})$$

- Find quantity, which contracted with its hermitian adjoint yields V_{pq}^{rs}
- The RI-coefficients (denoted by C_{ij}^{ν}) used in FHI-aims replace the role of the reciprocal grid points $\boldsymbol{G}$
- It can be shown:

$$\Gamma_{q\mu}^{s} = \sum_{\nu,i,j} (V^{\frac{1}{2}})_{\mu\nu} C_{ij}^{\nu} c_i^{*s} c_j^{q}$$

auxiliary coulomb matrix $V_{\mu\nu} = \int d\boldsymbol{r} d\boldsymbol{r}' \frac{P_{\mu}(\boldsymbol{r}) P_{\nu}(\boldsymbol{r}')}{|\boldsymbol{r} - \boldsymbol{r}'|}$

KS solution matrix c_j^{q}

RI-coefficients C_{ij}^{ν}

Outlook

- First Scalapack-based interface implemented last week (on branch: MPI-parallelize_CC4S_interface)
- Testing interface on h-BN sheet
- Calculation of H_2O-adsorption energy with different
  - basis set sizes
  - numbers of cpus (scaling plots)