The bulk is the limit

Coupled-cluster theory infrastructure in FHI-aims and how to accelerate convergence to the thermodynamic limit using PWs and NAOs

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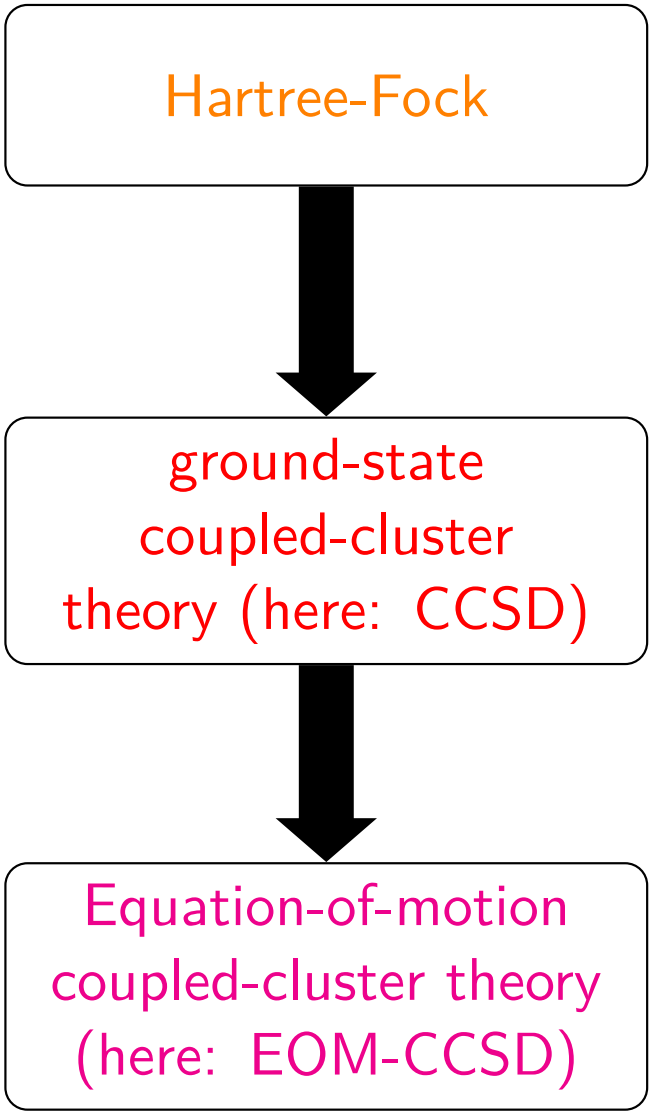
From Slater determinant to the correlated excited state



$$\hat{H}^{HF}\Phi_0 = E_0\Phi_0$$

$$\Psi_0^{CC} = e^{\hat{T}}\Phi_0$$

$$\hat{T} = \sum_{i,a} t_i^a a_a^\dagger a_i + \sum_{i,j,a,b} t_{ij}^{ab} a_a^\dagger a_b^\dagger a_j a_i + \ldots$$

$$\Psi_n^{CC} = \hat{R}_n^{EA/IP}\Psi_0^{CC}$$

$$\hat{R}_n^{EA} = \sum_a r^a a_a^\dagger + \sum_{i,a,b} r_i^{ab} a_a^\dagger a_b^\dagger a_i + \ldots$$

$$\hat{R}_n^{IP} = \sum_i r_i a_i + \sum_{i,j,a} r_{ij}^a a_a^\dagger a_j a_i + \ldots$$

From Slater determinant to the correlated excited state

Hartree-Fock

$\hat{H}^{HF}\Phi \quad E\Phi$

Why CC theory + FHI-aims?

- FHI-aims as all-electron code :
  No approx. of core electrons (no PPs or PAW ansatz)
- CC as a
  - reliable
  - systematically improvable
  - highly accurate
  - generally starting point dependence-free

  framework

$\Rightarrow$ Benchmarking state-of-the-art methods (e.g $G0W0$)

... Ψ

coupled-cluster theory
(here: EOM-CCSD)

$$\hat{R}_n^{IP} = \sum_i r_i a_i + \sum_{i,j,a} r_{ij}^a a_a^\dagger a_j a_i + \ldots$$

CC4S - Coupled Cluster (Theory) for Solids

- Open-source Quantum-chemistry package[1]
- Implements continuously growing range of correlated wave function methods[2]:
  - MP2
  - CCSD/CCSD(T)
  - RPA(+SOSEX)
  - (EE/IP/EA-)EOM-CCSD
  - CCSD(cT)[3]
- All methods available for materials and molecules

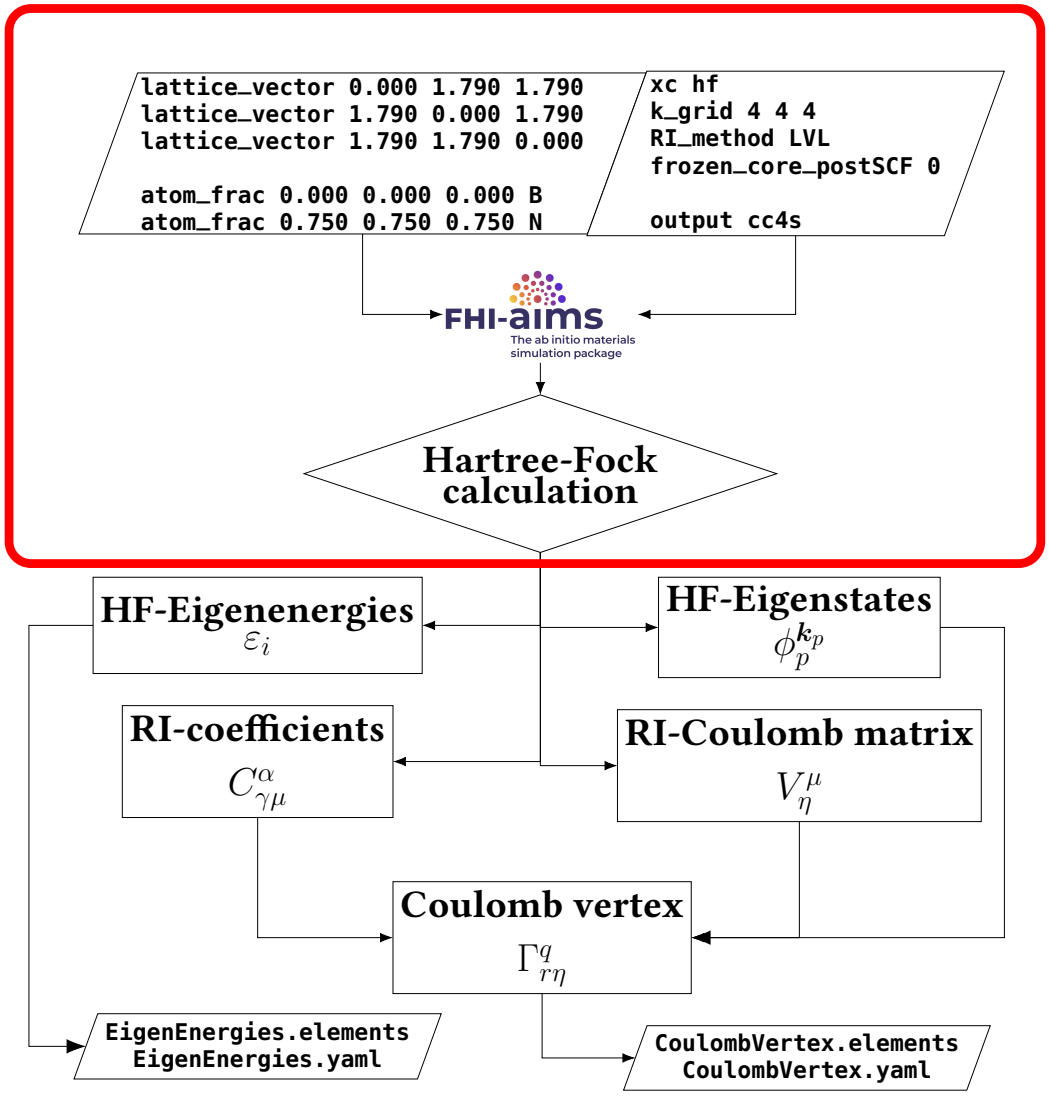
[1] https://github.com/cc4s/cc4s

[2] https://manuals.cc4s.org/user-manual/

[3] Masios et al. (2023). arXiv:2303.16957v3 (under review)

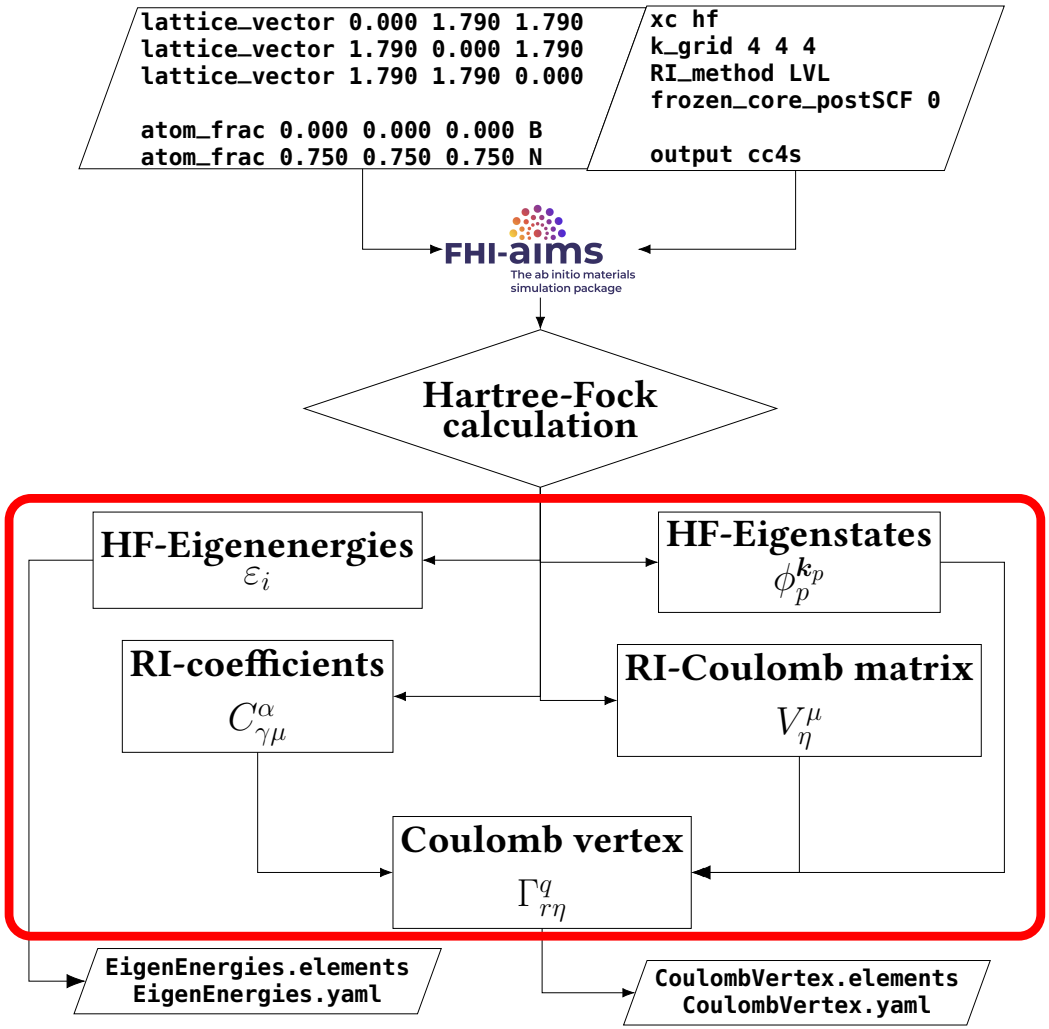
CC4S - Workflow

1. Use interfaced (periodic) HF/DFT-code to perform SCF calculation



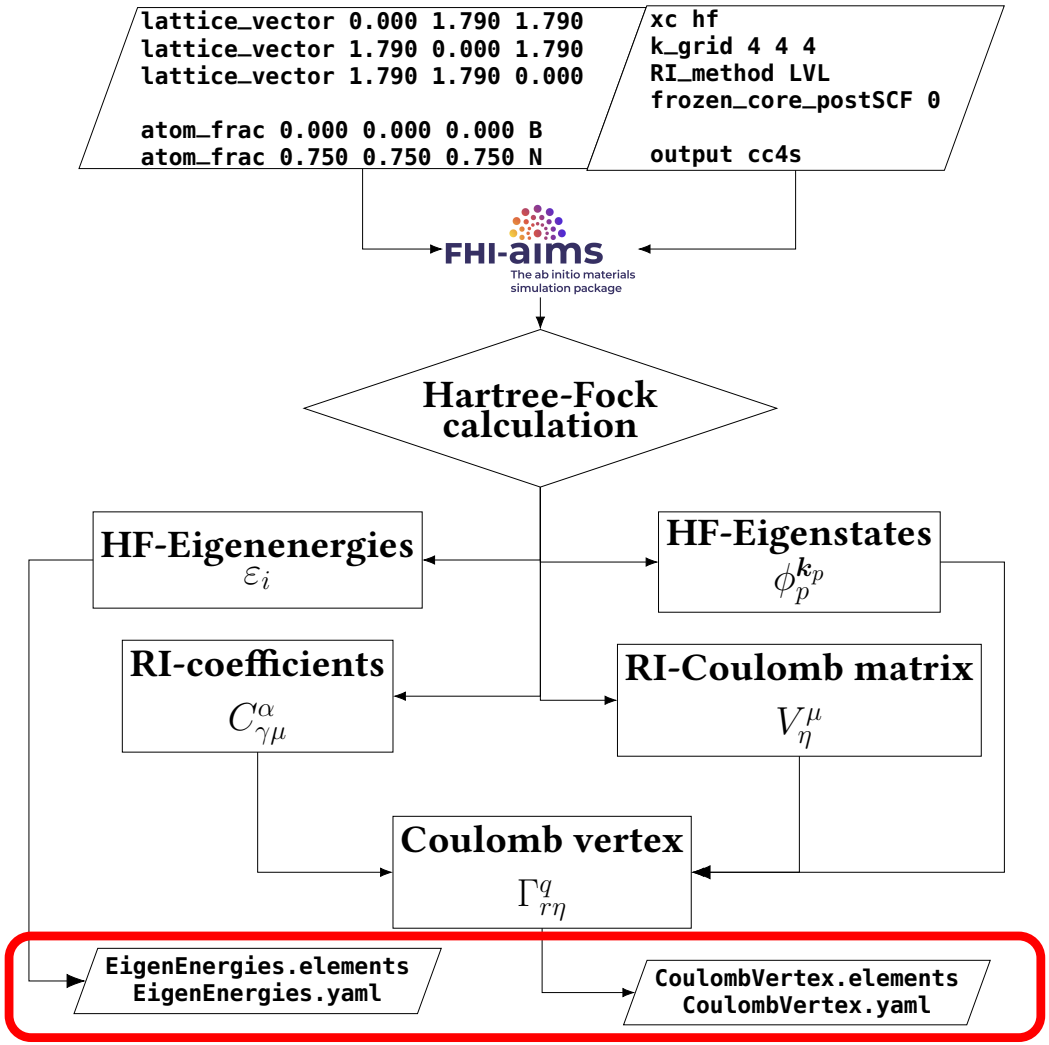
CC4S - Workflow

1. Use interfaced (periodic) HF/DFT-code to perform SCF calculation
2. Interface parses/calculates quantities relevant for CC4S

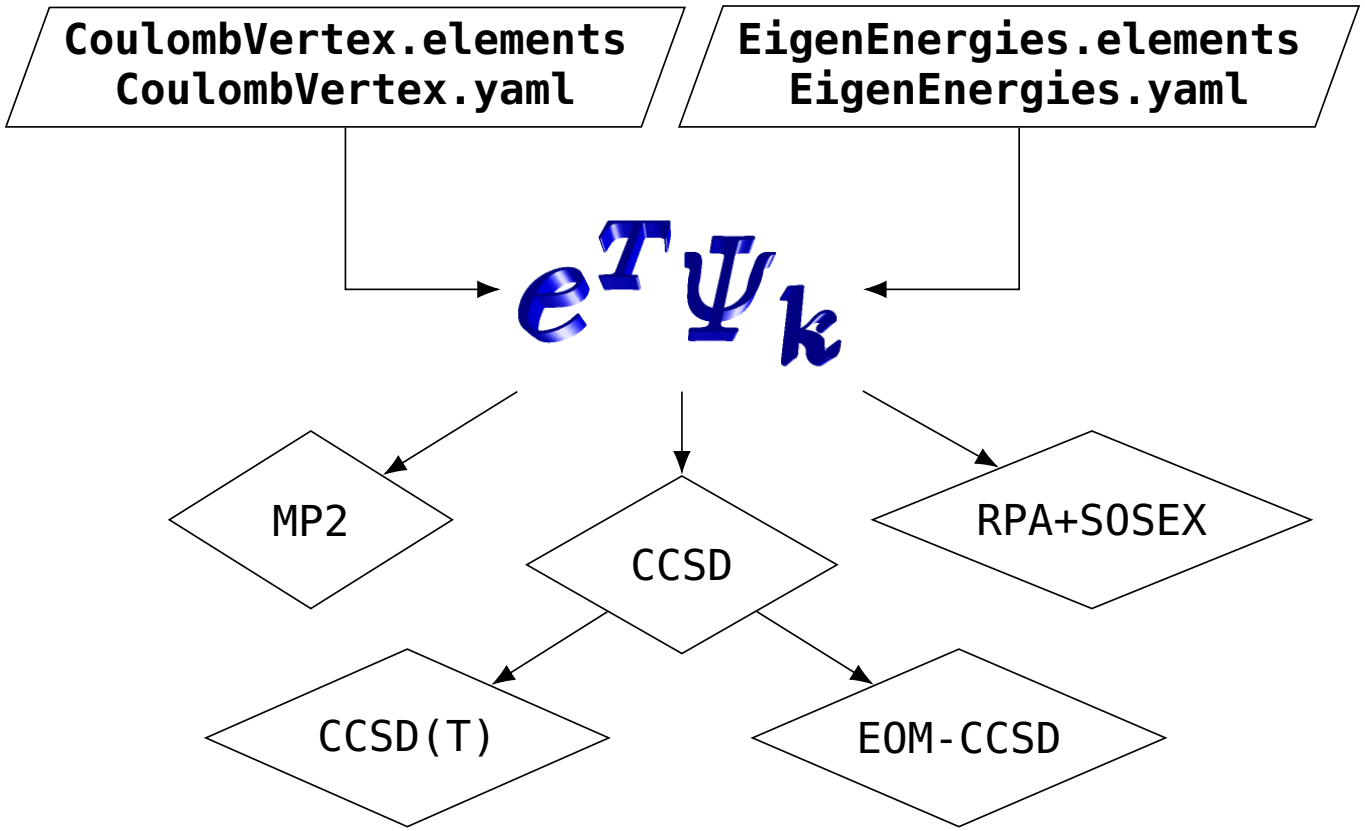


CC4S - Workflow

1. Use interfaced (periodic) HF/DFT-code to perform SCF calculation
2. Interface parses/calculates quantities relevant for CC4S
3. and writes them to files



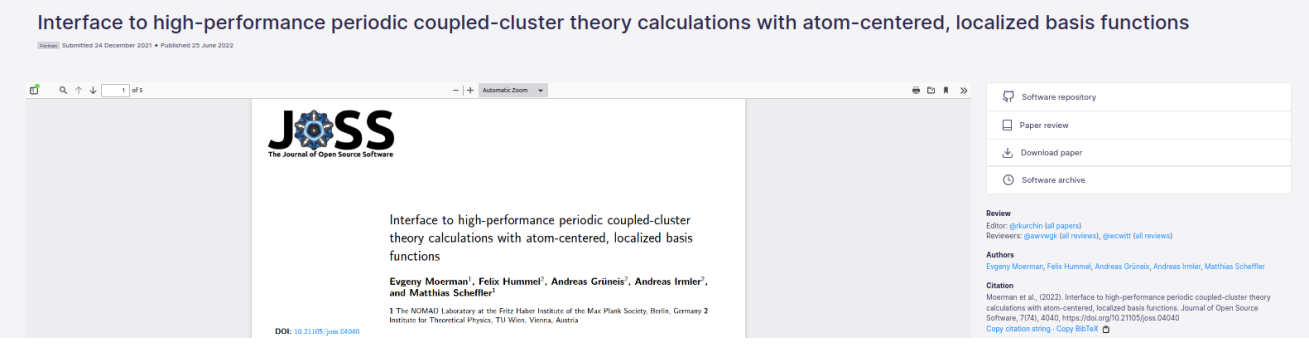
CC4S - Workflow



CC-aims

- CC-aims constitutes an interface between FHI-aims and CC4S
- It has been formulated in a very general manner, so that in principle any ab-initio code which
  - utilizes a localized atomic basis set and
  - employs a Resolution-of-Identity scheme for the representation of Coulomb integrals

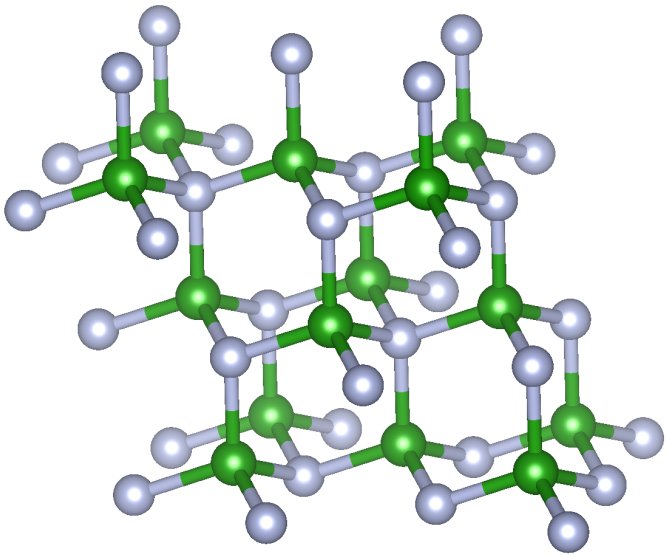
  can use it
- Completely open-source:
  `https://gitlab.com/moerman1/fhi-cc4s`



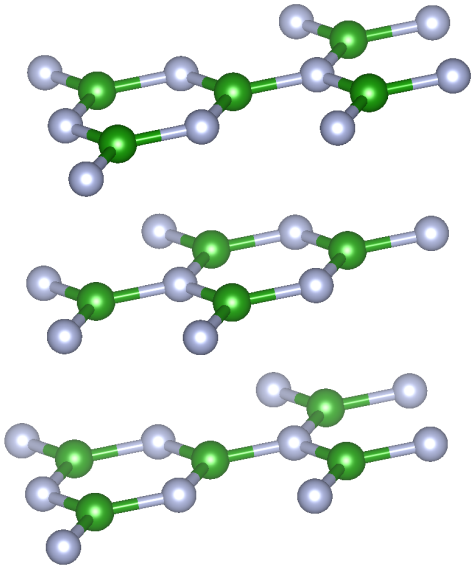
Moerman et al. (2022). J. Open Source Softw. 7 (74), 4040. `https://doi.org/10.21105/joss.04040`

Example application : stability of boron nitride phases

c-BN



r-BN



Experiment:

$$E(\text{c-BN}) - E(\text{r-BN}) = -82\, meV/atom^{(1)}$$
$$= -57\, meV/atom^{(2)}$$
$$= 4\, meV/atom^{(3)}$$

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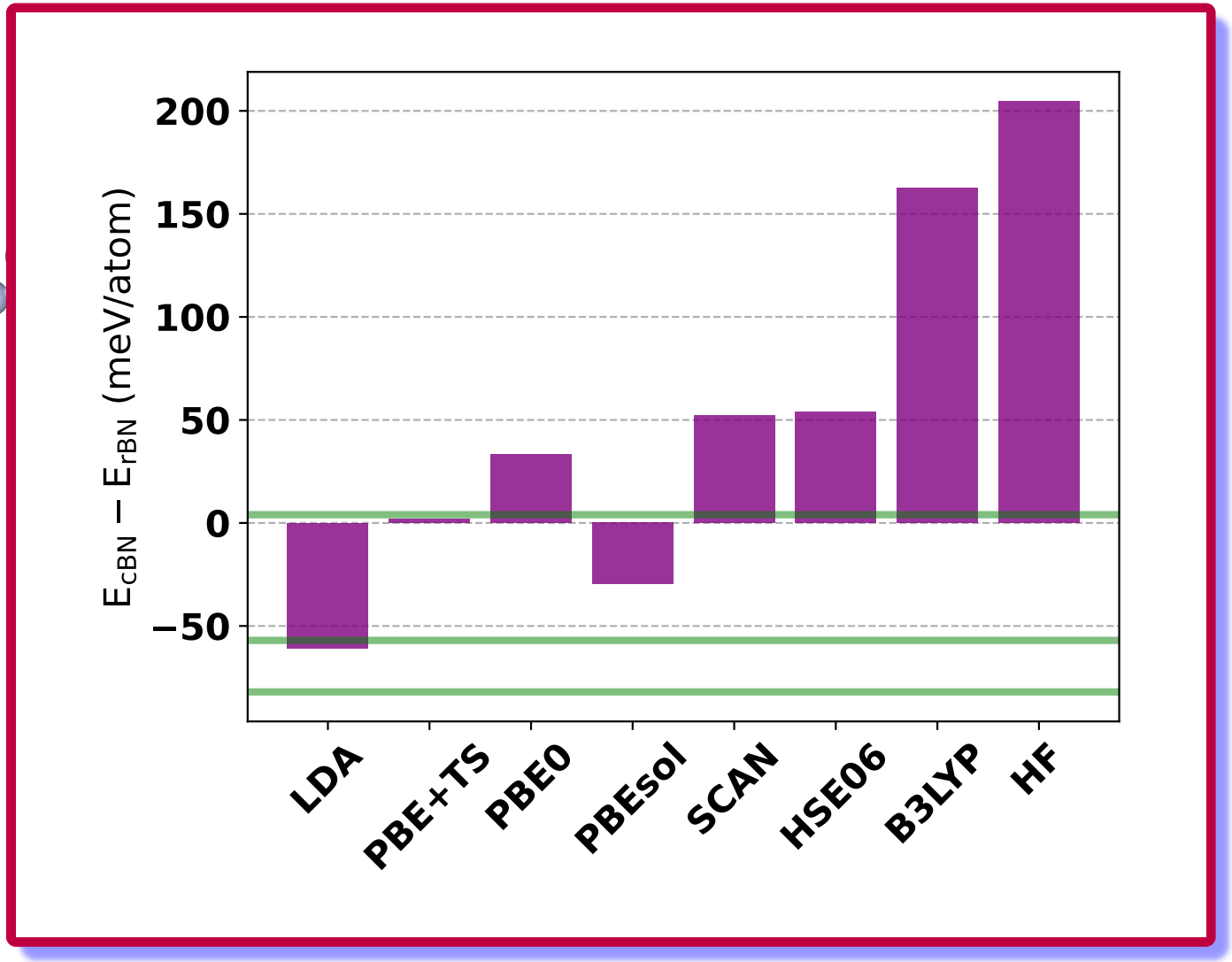
(1) V. L. Solozhenko (1995), High Pressure Res. 13, 199

(2) S. Jeong and K. Lee (2013), J. Nanosci. Nanotechnol. 13, 7766

(3) H. W. Day (2012), Am. Mineral. 97, 52

Example application : stability of boron nitride phases



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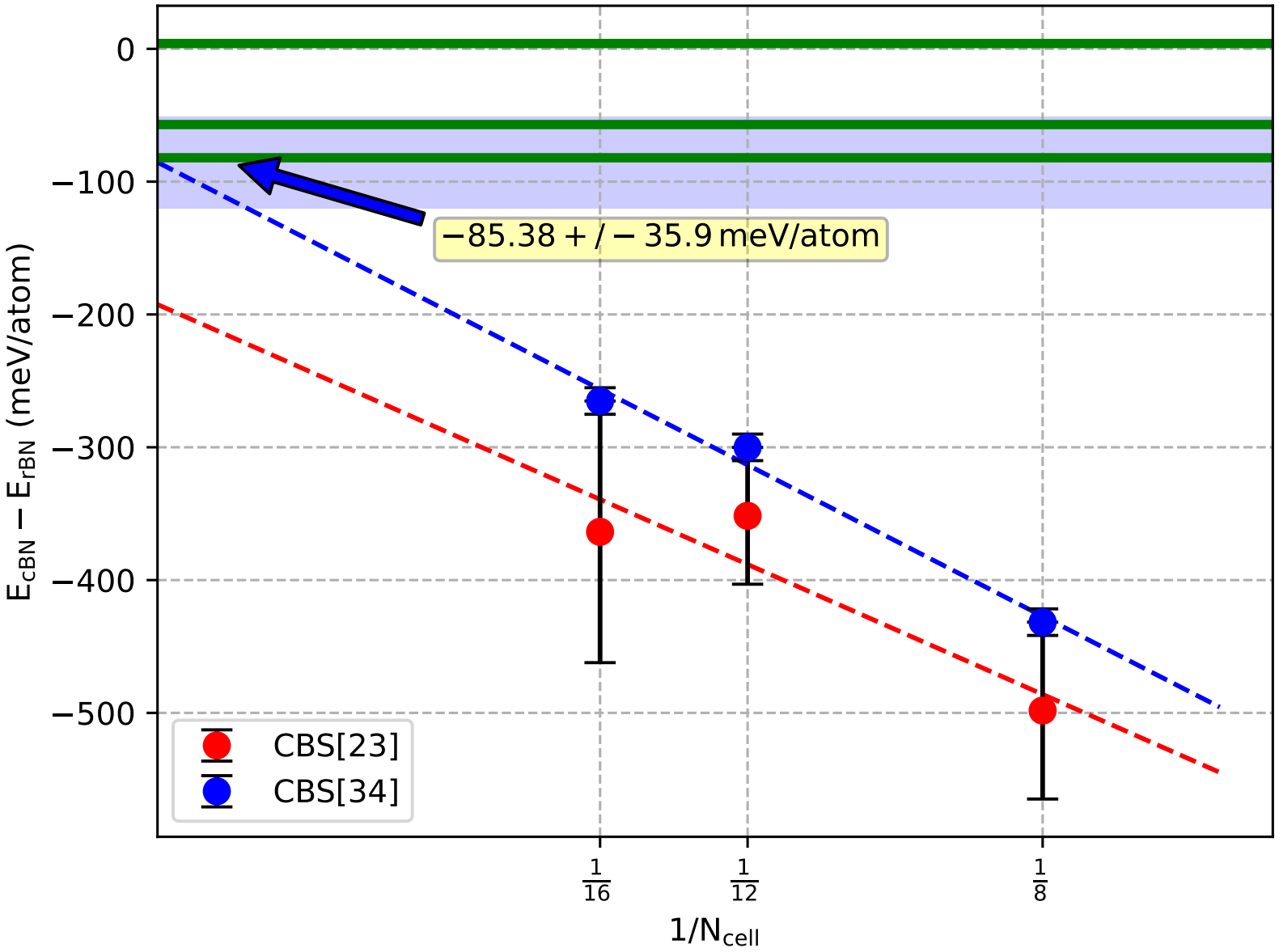
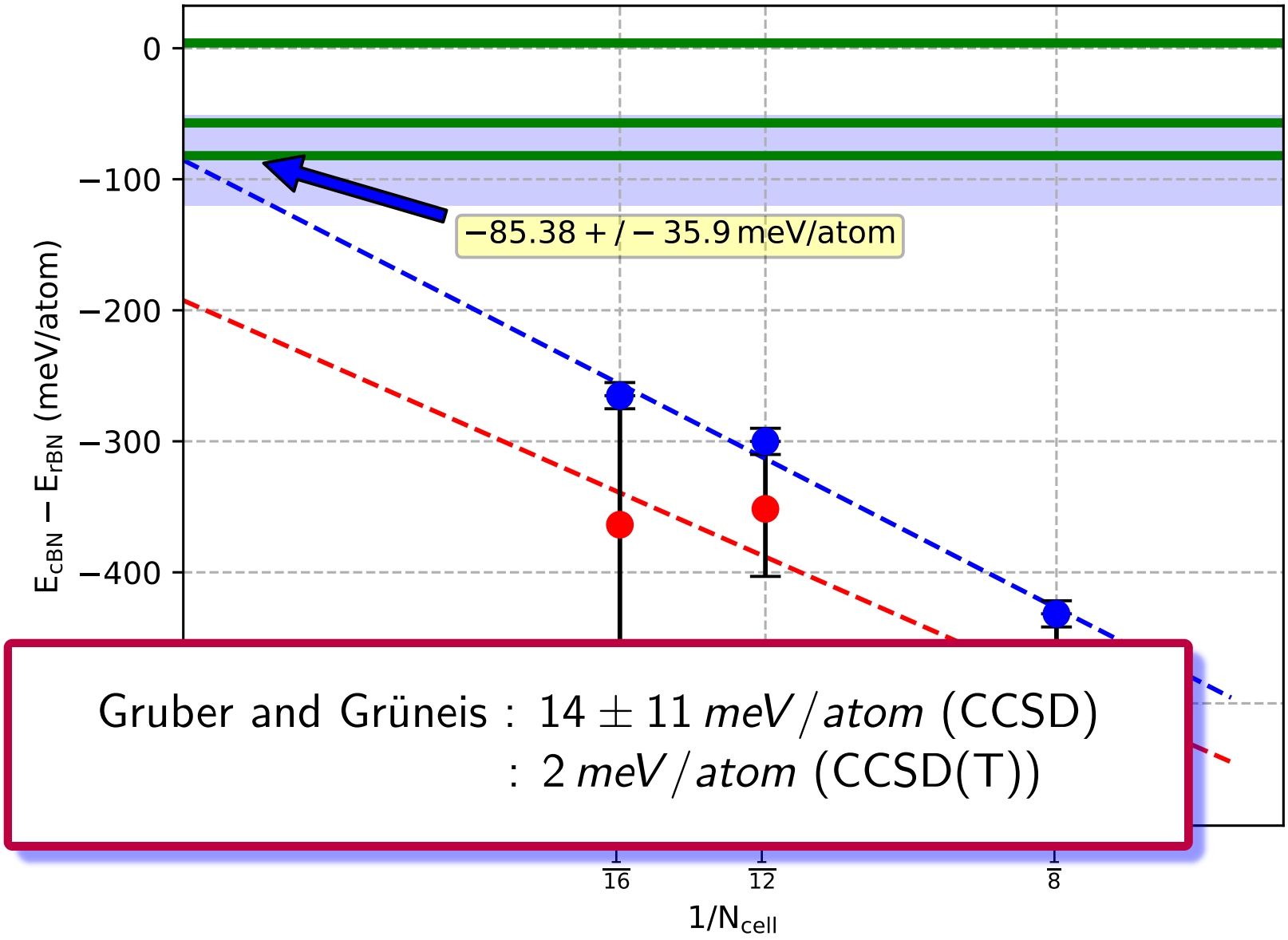
Results : stability of boron nitride phases

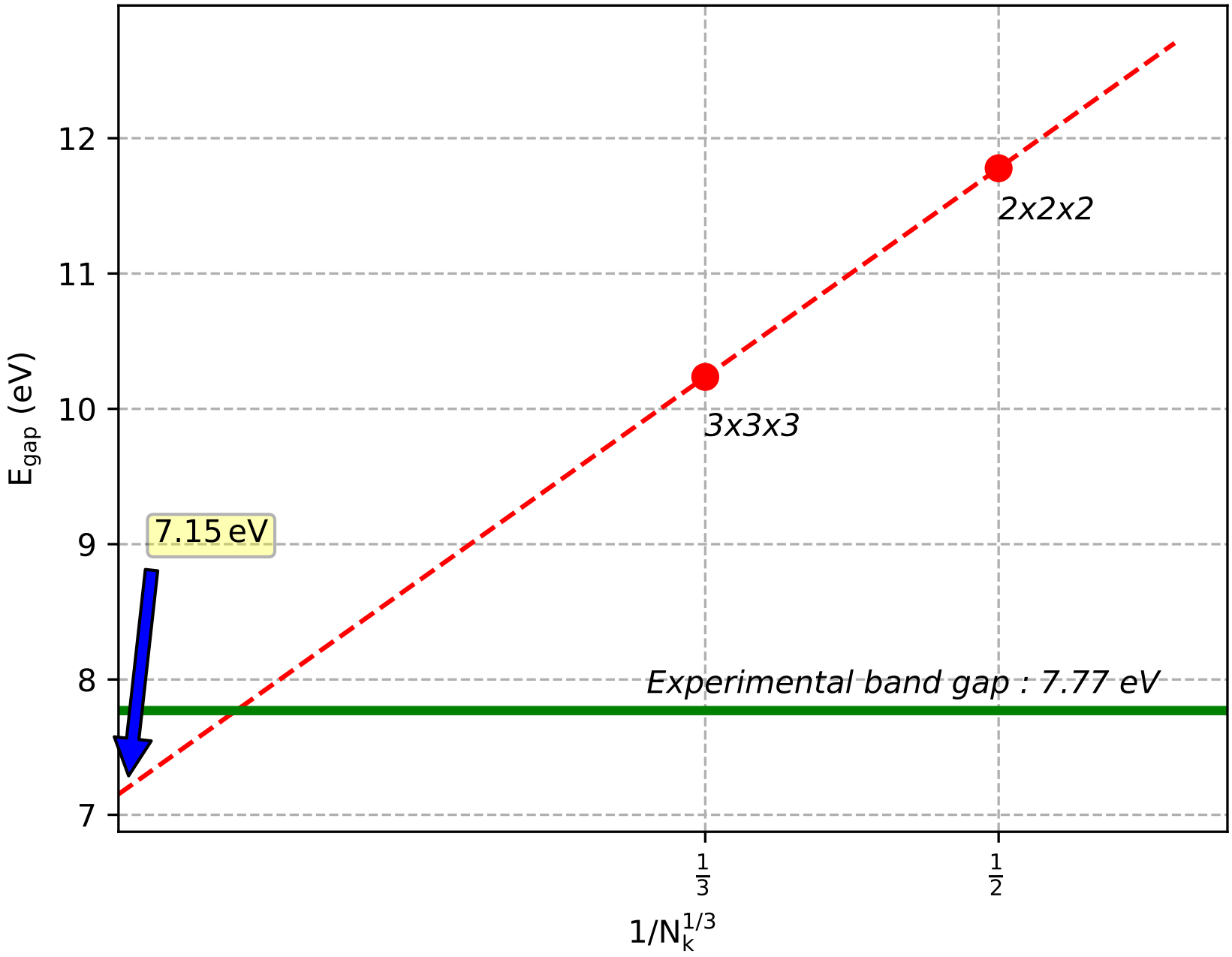


Results : stability of boron nitride phases

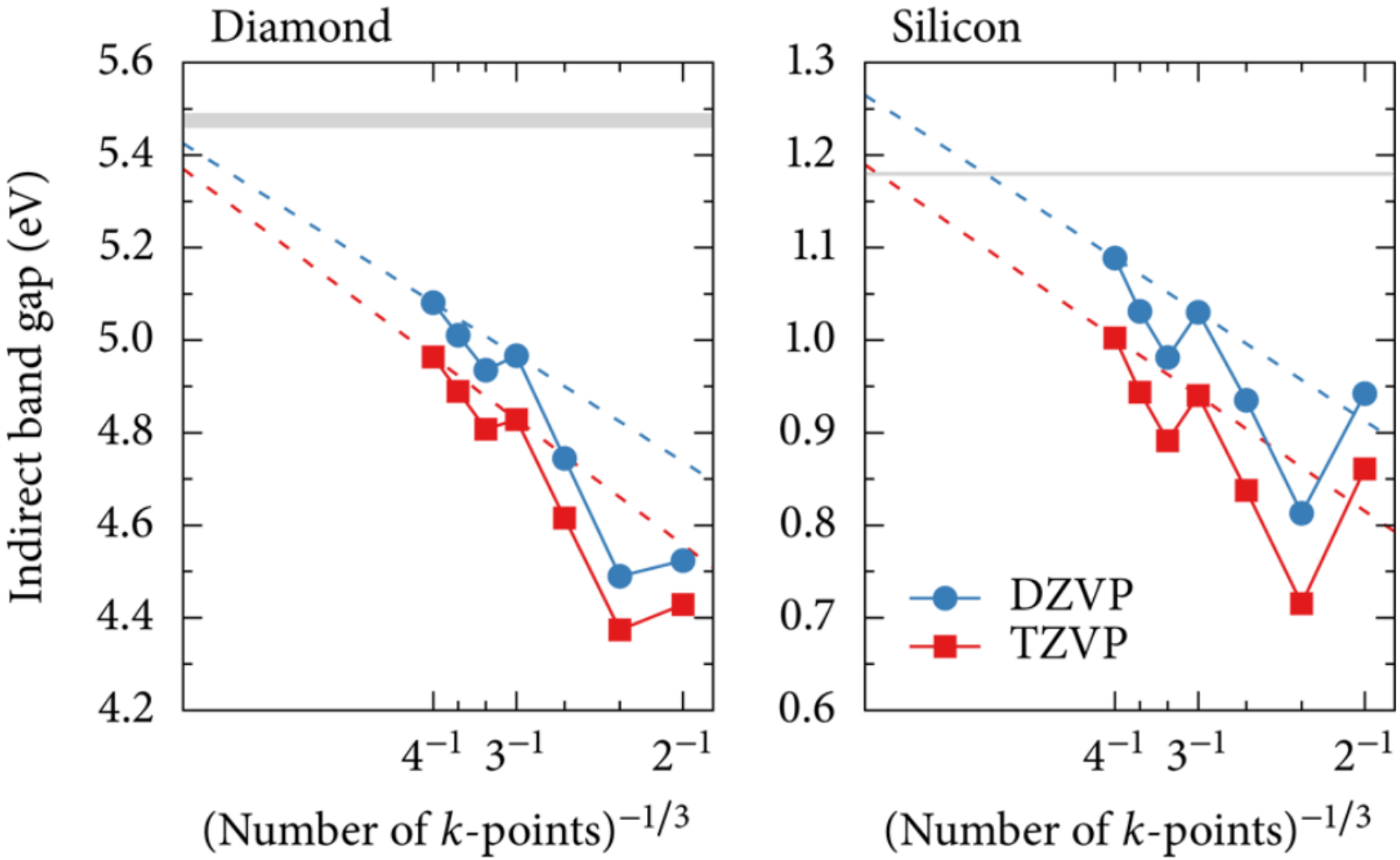


Gruber and Grüneis : $14 \pm 11\, meV/atom$ (CCSD)
: $2\, meV/atom$ (CCSD(T))

At the same time : MgO band gap from EOM-CC



Problem of the finite-size error of charged excitations



McClain et al. JCTC 13,3 (2017): 1209-1218

Problem of the finite-size error in CC theory

Problems with this approach:

- It is generally not obvious which extrapolation law must be applied ($\frac{1}{N_k}$, $\frac{1}{N_k^{1/3}}$, ...)
- Exceedingly expensive calculations need to be performed ($\geq$ 4x4x4 $\boldsymbol{k}$-grids)
- The extrapolation laws don't apply for too small/under-converged calculations.

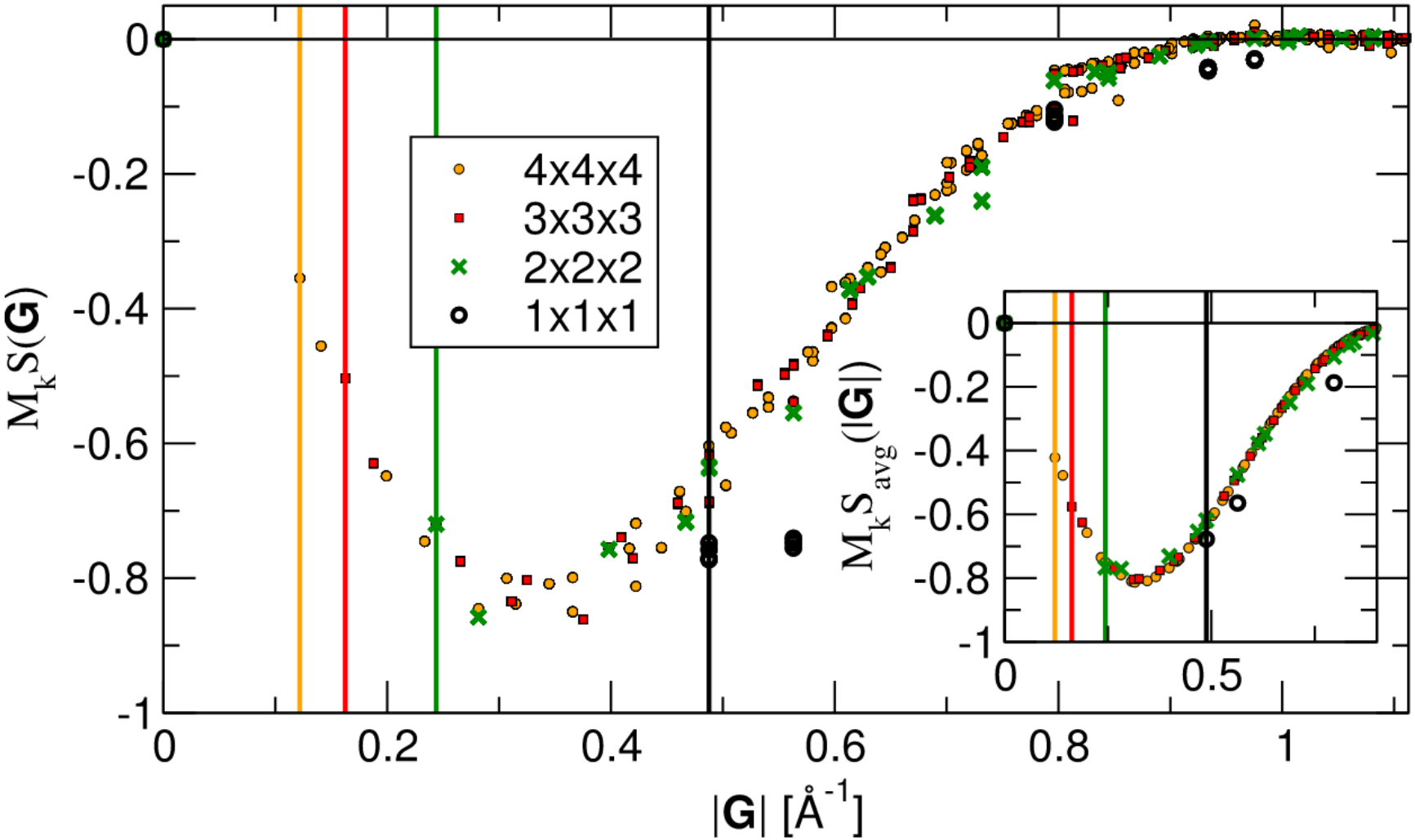
Structure factor-based finite-size correction

For the ground-state CC correlation energy E_{corr}, the (transition) structure factor $S(\boldsymbol{G})$ is introduced via

$$E_{corr} = \sum_{i,j,a,b} (t_{ij}^{ab} + t_i^a t_j^b)(2V_{ij}^{ab} - V_{ij}^{ba}) = \sum_{\boldsymbol{G}} V(\boldsymbol{G}) S(\boldsymbol{G})$$

- $\boldsymbol{G}$ being a grid in reciprocal space
- $V(\boldsymbol{G})$ being the Coulomb potential $\frac{4\pi}{\boldsymbol{G}^2}$ in reciprocal space

Structure factor-based finite-size correction



Liao and Grüneis JCP 145,14 (2016): 141102

How to estimate the finite-size error using the transition structure factor

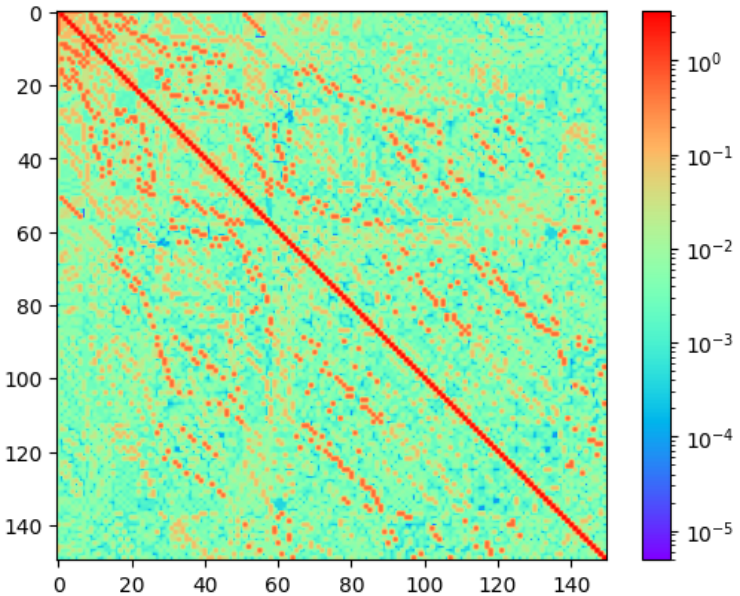
- Perform some relatively cheap (2x2x2-3x3x3) ground-state CC calculation
- Calculate the (incomplete) transition structure factor
- Perform quadratic interpolation to obtain missing $S(\boldsymbol{G})$ values near $\boldsymbol{G} = 0$
- Re-calculate $E_{corr} = \sum_{\boldsymbol{G}} S(\boldsymbol{G}) V(\boldsymbol{G})$ to obtain finite-size corrected correlation energy

BUT : Use of plane wave basis required !
Can we make it work for atom-centered basis functions?

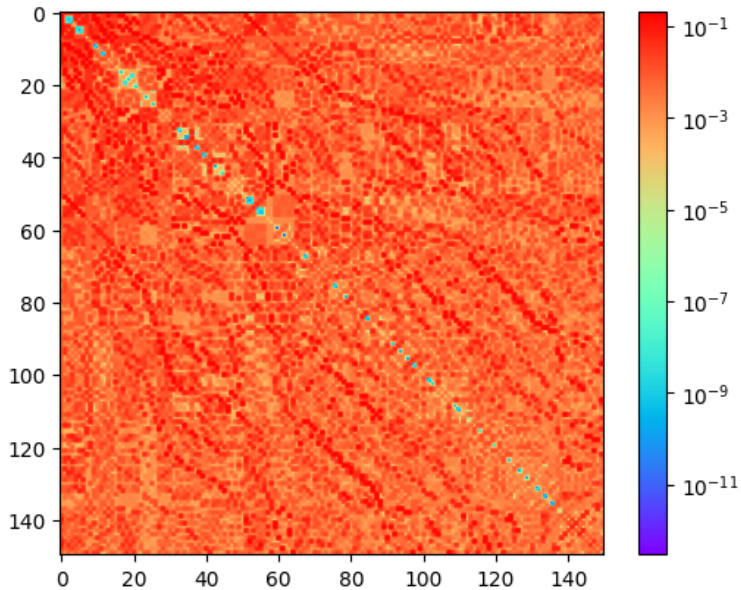
AO-PW basis transformation: How well does it work?

As a measure of quality let's look at the PW overlap $S^{PW}_{\boldsymbol{G},\boldsymbol{G'}}$ in the auxiliary basis representation:

$$S^{PW}_{\boldsymbol{G},\boldsymbol{G'}} = C^{*}_{\mu,\boldsymbol{G}} S_{\mu,\nu} C_{\nu,\boldsymbol{G'}} \stackrel{?}{=} \delta_{\boldsymbol{G},\boldsymbol{G'}} \quad \Longrightarrow \quad \underline{\underline{S}}^{PW} = \underline{\underline{C}}^{\dagger}\,\underline{\underline{S}}\,\underline{\underline{C}}$$



(a) $\Re(S^{PW}_{\boldsymbol{G},\boldsymbol{G'}})$

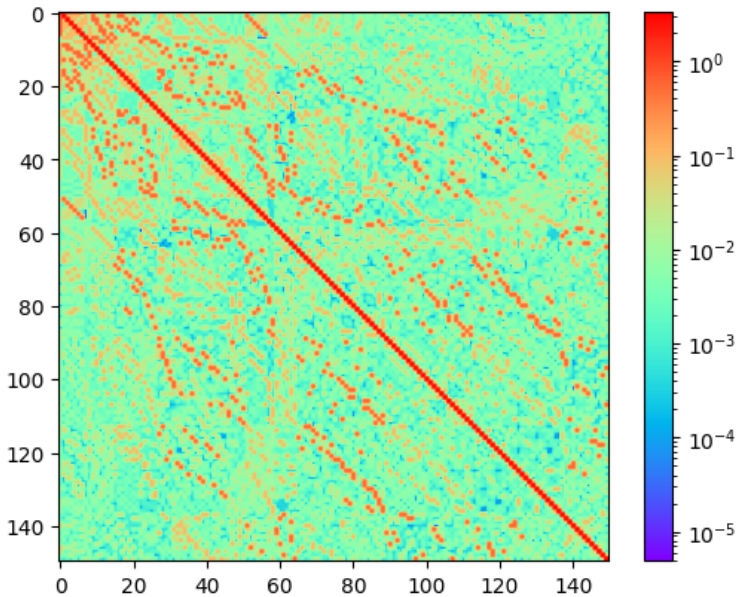


(b) $\Im(S^{PW}_{\boldsymbol{G},\boldsymbol{G'}})$

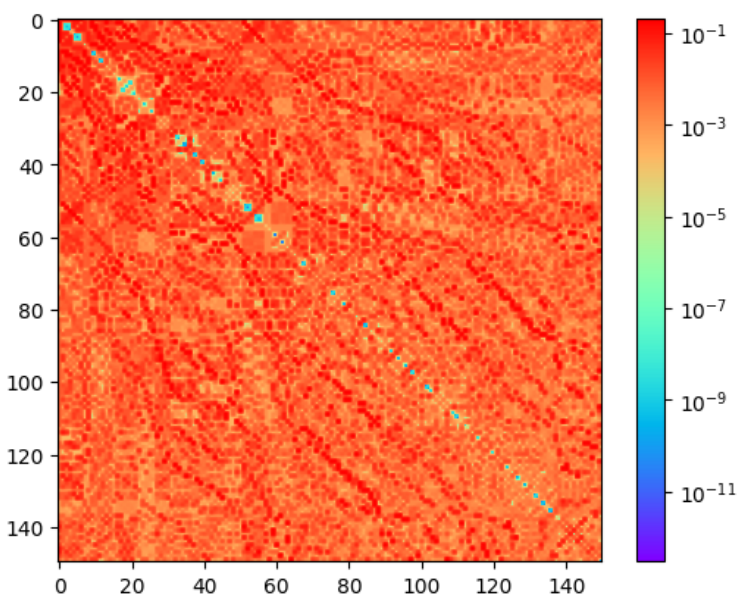
AO-PW basis transformation: How well does it work?

Not quite well:

- $S^{PW}_{\boldsymbol{G},\boldsymbol{G}'}$ is complex-valued
- $S^{PW}_{\boldsymbol{G},\boldsymbol{G}'}$ is not diagonally dominant for short $\boldsymbol{G}$-vectors



(c) $\Re(S^{PW}_{\boldsymbol{G},\boldsymbol{G}'})$



(d) $\Im(S^{PW}_{\boldsymbol{G},\boldsymbol{G}'})$

Reframing the structure factor ansatz : pair-energies

For a more efficient representation of products of states $\phi_p^*(\boldsymbol{r})\phi_q(\boldsymbol{r})$, an additional *auxiliary* basis $P_\mu(\boldsymbol{r})$ is often used

$$\phi_p^*(\boldsymbol{r})\phi_q(\boldsymbol{r}) = \sum_\mu C_{p,q}^\mu P_\mu(\boldsymbol{r})$$

Going from plane waves $e^{i\boldsymbol{G}\boldsymbol{r}}$ to the auxiliary basis $P_\mu(\boldsymbol{r})$:

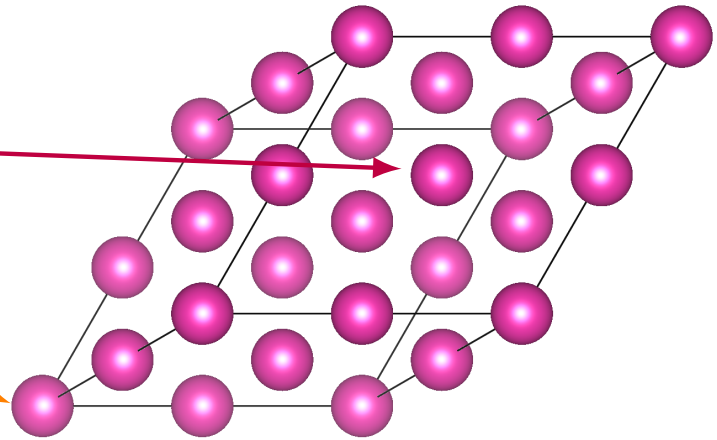
$$E_{corr} = \sum_{\boldsymbol{G}} S(\boldsymbol{G})V(\boldsymbol{G}) \quad \rightarrow \quad E_{corr} = \sum_{\mu\nu} S_\nu^\mu V_\mu^\nu$$

Instead of immediately summing over μ and ν, we can also compute the pair-energies:

$$E_{corr} = \sum_{\mu\nu} \epsilon_\nu^\mu \quad \text{with} \quad \epsilon_\nu^\mu = S_\nu^\mu V_\mu^\nu$$

Finite-size correction via pair-energies

$$E_{corr} = \sum_{\mu\nu} \epsilon_{\nu}^{\mu}$$



For each $\epsilon_{\mu\nu}$:

- $P_\mu(\boldsymbol{r} - \boldsymbol{\tau}_\mu)$ and $P_\nu(\boldsymbol{r} - \boldsymbol{\tau}_{nu})$ are localized on atoms at $\boldsymbol{\tau}_\mu$ and $\boldsymbol{\tau}_\nu$ with distance $\boldsymbol{\tau}_\mu - \boldsymbol{\tau}_\nu$
- $\epsilon_{\mu\nu}$ is contribution to the total correlation energy

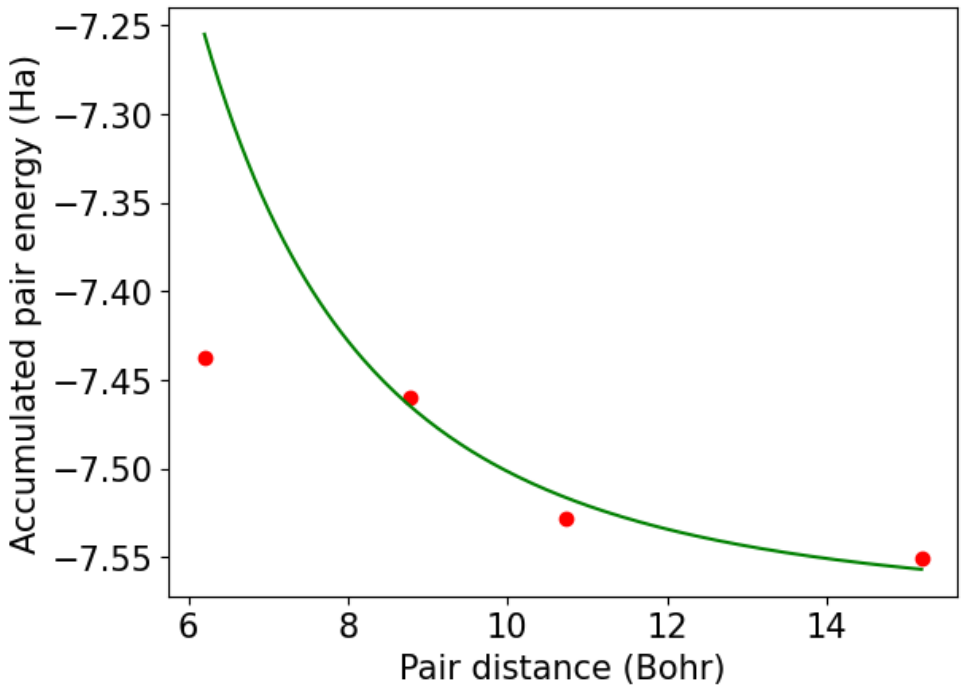
Interpretation of $\epsilon_{\mu\nu}$: Distance-resolved decomposition of correlation energy

New approach: Extrapolate $\epsilon_{\mu\nu}$ to $\boldsymbol{\tau}_\mu - \boldsymbol{\tau}_\nu \to \infty$

Finite-size correction via pair-energies

Benefits:

- Native, localized basis is used
- Long-range behavior of correlation is known (for ground-state : $1/r^3$)
- Very simple model



Current post-SCF obstacles in FHI-aims

However: For an efficient finite-size correction, the treatment of the long-range Coulomb potential needs to be consistent

Currently : Approximation of the long-range contribution to the Coulomb potential is inconsistent between SCF and post-SCF

This has detrimental consequences for post-SCF calculations:

- A NxNxN supercell-calculation does not yield the same result as a NxNxN $\boldsymbol{k}$-mesh
- Convergence to the thermodynamic limit is **not** always monotone

Current post-SCF obstacles in FHI-aims

However: For an efficient finite-size correction, the treatment of the long-range Coulomb potential needs to be consistent

Currently : Approximation of the long-range contribution to the

Work in progress:
Devise consistent scheme for post-SCF methods

- A NxNxN supercell-calculation does not yield the same result as a NxNxN $\boldsymbol{k}$-mesh
- Convergence to the thermodynamic limit is **not** always monotone

Summary and outlook

What has been done:

- Periodic and non-periodic CC calculations can be performed with FHI-aims (via the `CC-aims` interface)
- The EOM-CCSD algorithm has been implemented in `Cc4s` ($\rightarrow$ available for FHI-aims and VASP)
- A pair-energy based finite-size correction for atom-centered basis sets has been developed

What remains to be done:

- Fix long-range treatment of Coulomb potential for post-SCF methods in FHI-aims
- Benchmark pair-energy approach
- Extend functionalities of FHI-aims/`CC-aims`/`Cc4s` (natural orbitals, non-canonical CC theory, block-sparse $\boldsymbol{k}$-point treatment)

Ground-state coupled-cluster theory

Exponential ansatz

$$\Psi_0^{CC} = e^{\hat{T}}\Phi_0 \qquad \hat{T} = \sum_{i,a} t_i^a a_a^\dagger a_i + \sum_{i,j,a,b} t_{ij}^{ab} a_a^\dagger a_b^\dagger a_j a_i + \ldots$$

The amplitude equations

$$t_i^a\text{-equations} \quad \langle \Phi_i^a | e^{-\hat{T}} \hat{H} e^{\hat{T}} | \Phi_0 \rangle = 0$$

$$t_{ij}^{ab}\text{-equations} \quad \langle \Phi_{ij}^{ab} | e^{-\hat{T}} \hat{H} e^{\hat{T}} | \Phi_0 \rangle = 0$$

$$t_{ijk}^{abc}\text{-equations} \quad \langle \Phi_{ijk}^{abc} | e^{-\hat{T}} \hat{H} e^{\hat{T}} | \Phi_0 \rangle = 0$$

CC correlation energy

$$E_{\text{corr}} = \langle \Phi_0 | e^{-\hat{T}} \hat{H} e^{\hat{T}} | \Phi_0 \rangle = \sum_{i,j,a,b} (t_{ij}^{ab} + t_i^a t_j^b)(2V_{ij}^{ab} - V_{ij}^{ba})$$

Excited state coupled-cluster theory

Linear ansatz

$$\Psi_n^{CC} = \hat{R}_n^{EA/IP/EE}\Psi_0^{CC}$$

$$\hat{R}_n^{EA} = \sum_a r^a a_a^\dagger + \sum_{i,a,b} r_i^{ab} a_a^\dagger a_b^\dagger a_i + \ldots \quad \boldsymbol{R}^{EA} = (r^a, r_i^{ab}, \ldots)$$

$$\hat{R}_n^{IP} = \sum_i r_i a_i + \sum_{i,j,a} r_{ij}^a a_a^\dagger a_j a_i + \ldots \quad \boldsymbol{R}^{IP} = (r_i, r_{ij}^a, \ldots)$$

$$\hat{R}_n^{EE} = \sum_{i,a} r_i^a a_a^\dagger a_i + \sum_{i,j,a,b} r_{ij}^{ab} a_a^\dagger a_b^\dagger a_j a_i + \ldots \quad \boldsymbol{R}^{EE} = (r_i^a, r_{ij}^{ab}, \ldots)$$

$$\hat{H}\Psi_n = E_n\Psi_n \Rightarrow \hat{H}\hat{R}_n\Psi_0^{CC} = E_n\hat{R}_n\Psi_0^{CC} \Rightarrow \hat{H}\hat{R}_n e^{\hat{T}}\Phi_0 = E_n\hat{R}_n e^{\hat{T}}\Phi_0$$

$$\Rightarrow e^{-\hat{T}}\hat{H}\hat{R}_n e^{\hat{T}}\Phi_0 = e^{-\hat{T}}E_n\hat{R}_n e^{\hat{T}}\Phi_0$$

$$\overset{[\hat{R}_n,\hat{T}]=0}{\Rightarrow} (e^{-\hat{T}}\hat{H}e^{\hat{T}})\hat{R}_n\Phi_0 = E_n\hat{R}_n\Phi_0$$

Can we do the same for excited states?

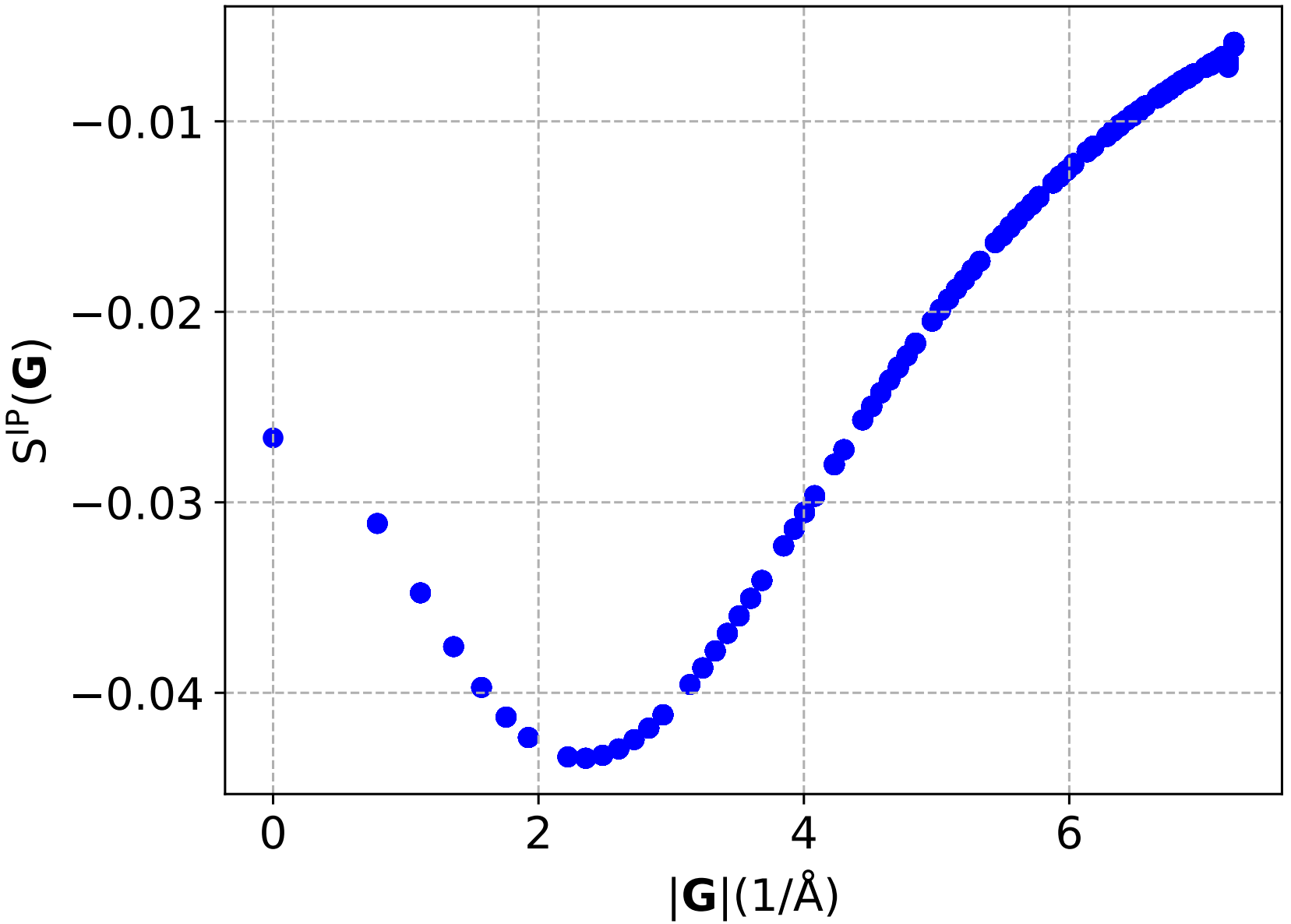
Similarly, let's define the EOM structure factor $S_n^{IP/EA}(\boldsymbol{G})$:

$$E_n^{IP/EA} = \sum_{\boldsymbol{G}} S_n^{IP/EA}(\boldsymbol{G}) V(\boldsymbol{G})$$

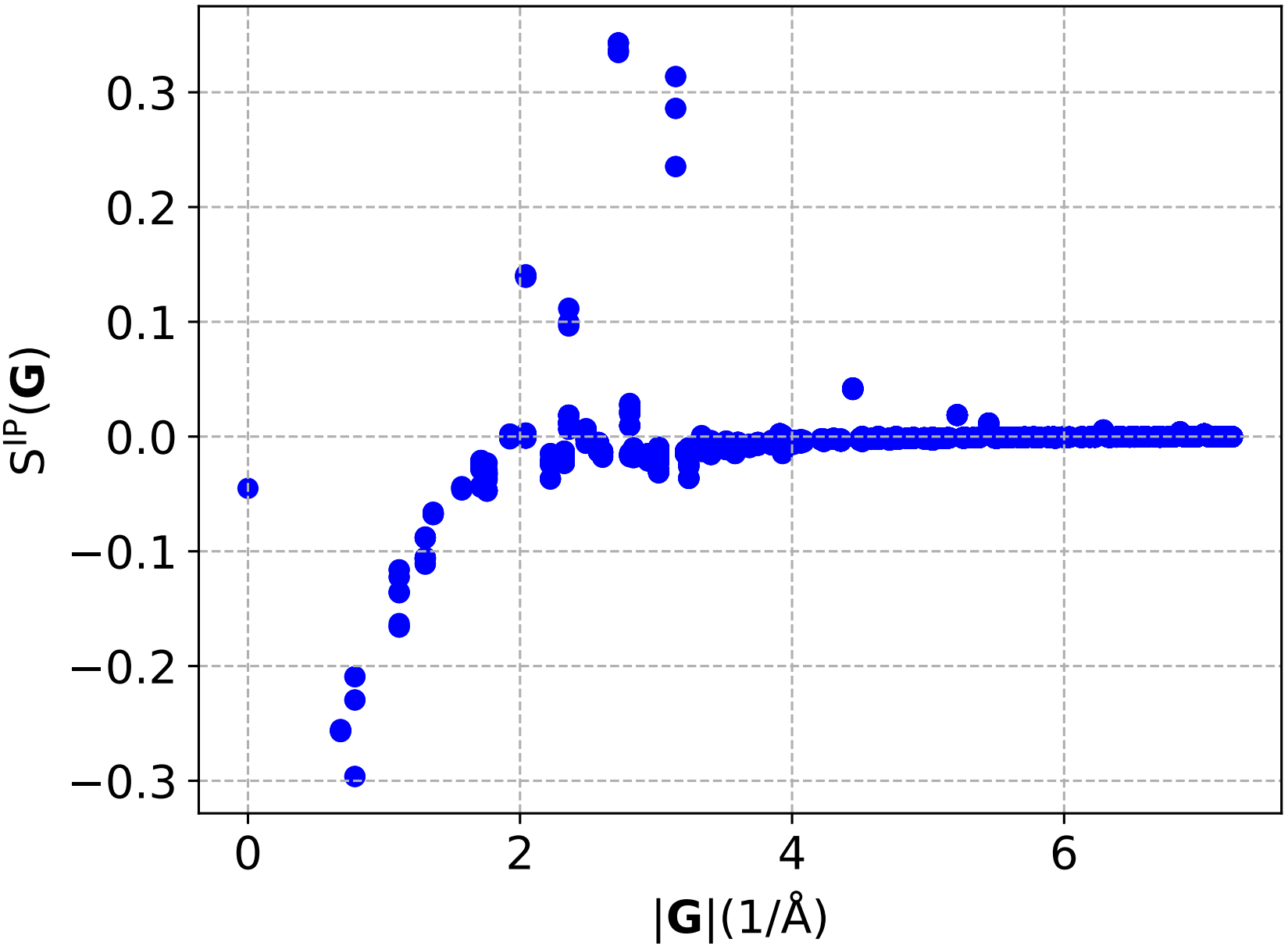
for the n-th ionization or electron capture.

How does the structure factor for an excited state looks like?

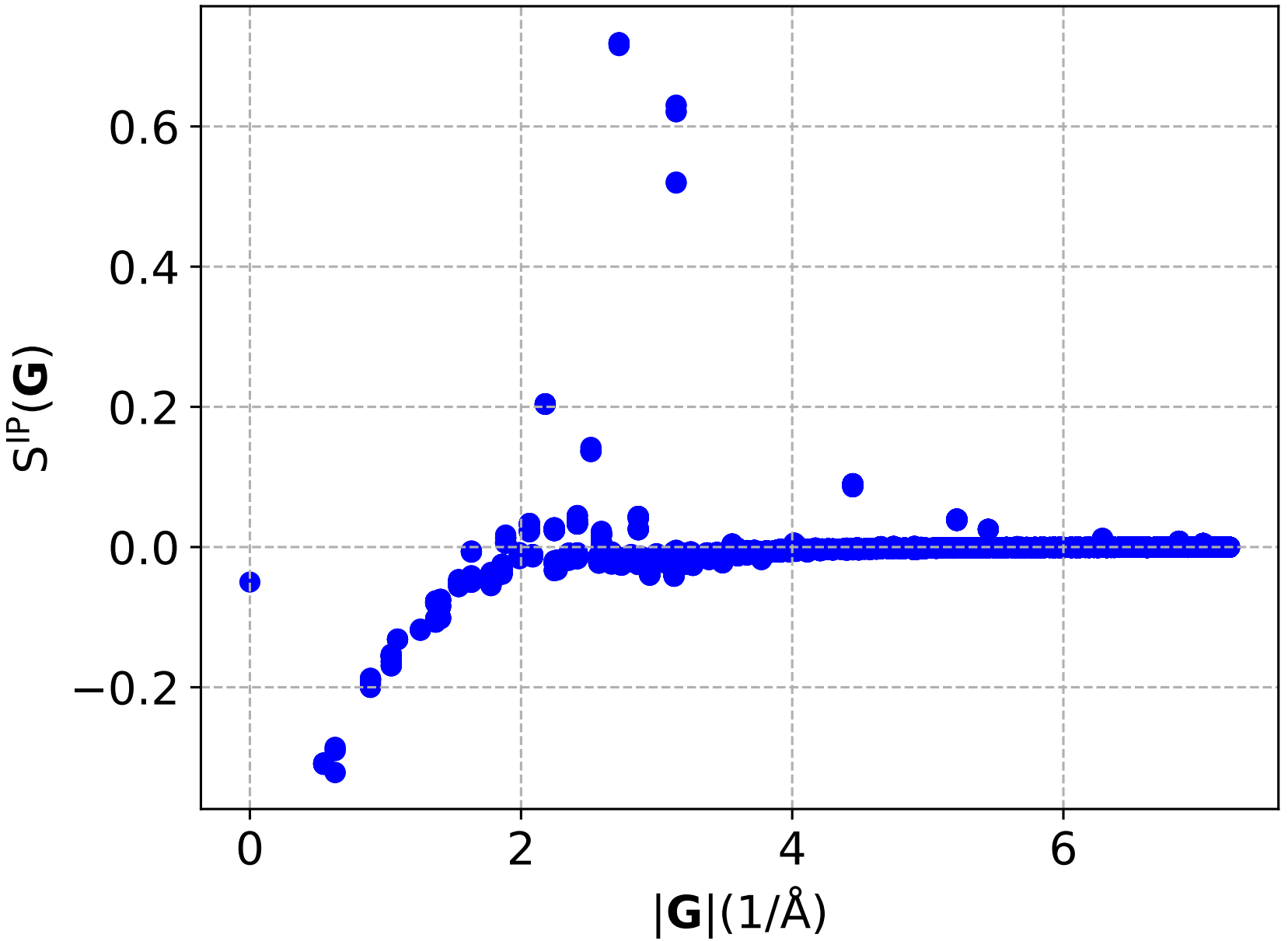
$S_1^{IP}(\boldsymbol{G})$ of a He-atom in a 8Åx8Åx8Å box



$S_1^{IP}(\boldsymbol{G})$ of LiH (4x4x4 $\boldsymbol{k}$-grid)



$S_1^{IP}(\boldsymbol{G})$ of LiH (5x5x5 $\boldsymbol{k}$-grid)



Initial findings

- $S_n^{IP/EA}(\boldsymbol{G}) \propto |\boldsymbol{G}|$ for small $|\boldsymbol{G}|$ (in CCSD $S(\boldsymbol{G}) \propto |\boldsymbol{G}|^2$)
- The finite-size error of IP/EA-EOM is proportional to $\frac{1}{N^{2/3}}$
- The correlation effects of a charged excitation have significantly longer range than ground-state correlation effects
- Interpolation of $S_n^{IP/EA}(\boldsymbol{G})$ to $\boldsymbol{G} = 0$ is not practical

Modeling the EOM structure factor explicitly

Can we find a model to fit the EOM structure factor?

Basic requirements of model $m(\boldsymbol{G})$:

- For small $|\boldsymbol{G}|$ (long-range) : $m(|\boldsymbol{G}|) \propto -|\boldsymbol{G}|$
- For large $|\boldsymbol{G}|$ (short-range) : $m(|\boldsymbol{G}|) \to 0$
- A minimum between both regions

In addition: By calculating $\left(\frac{\partial S}{\partial \boldsymbol{G}}\right)_{\boldsymbol{G}=\boldsymbol{0}}$ for the linear part, we can estimate the missing long-range contribution of $S(\boldsymbol{G})$.

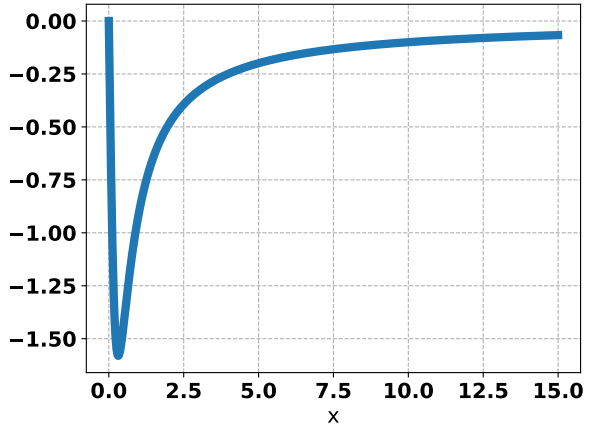
$\left(\frac{\partial S}{\partial \boldsymbol{G}}\right)_{\boldsymbol{G}=\boldsymbol{0}}$ can be approximated using the dipole matrix

$$\boldsymbol{d}_{p,q} = \langle \phi_p | \hat{\boldsymbol{r}} | \phi_q \rangle$$

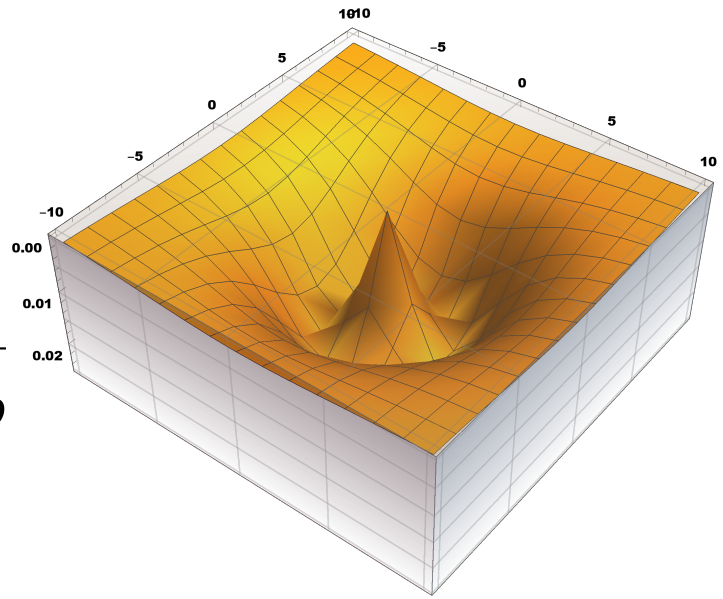
(comparable to "head" and "wing" of the macroscopic dielectric tensor routinely used in GW).

The modified Drude-Lorentz model

$$m(x) := -\frac{|x| - a}{(|x| - a)^2 + b}$$

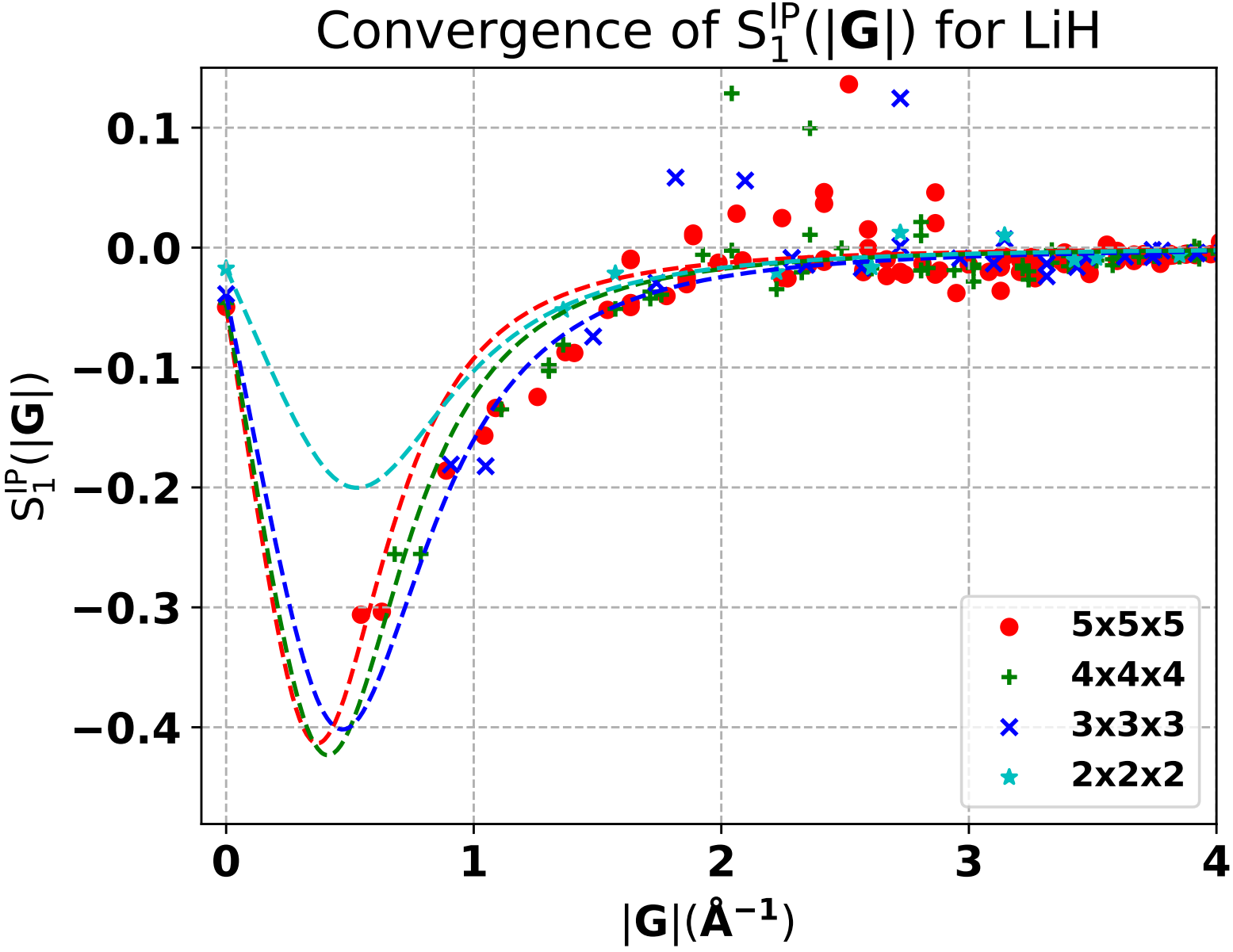


$$m(x_1, x_2, x_3) := -d\frac{\sqrt{c_1x_1^2 + c_2x_2^2 + c_3x_3^2} - a}{(\sqrt{c_1x_1^2 + c_2x_2^2 + c_3x_3^2} - a)^4 + b}$$

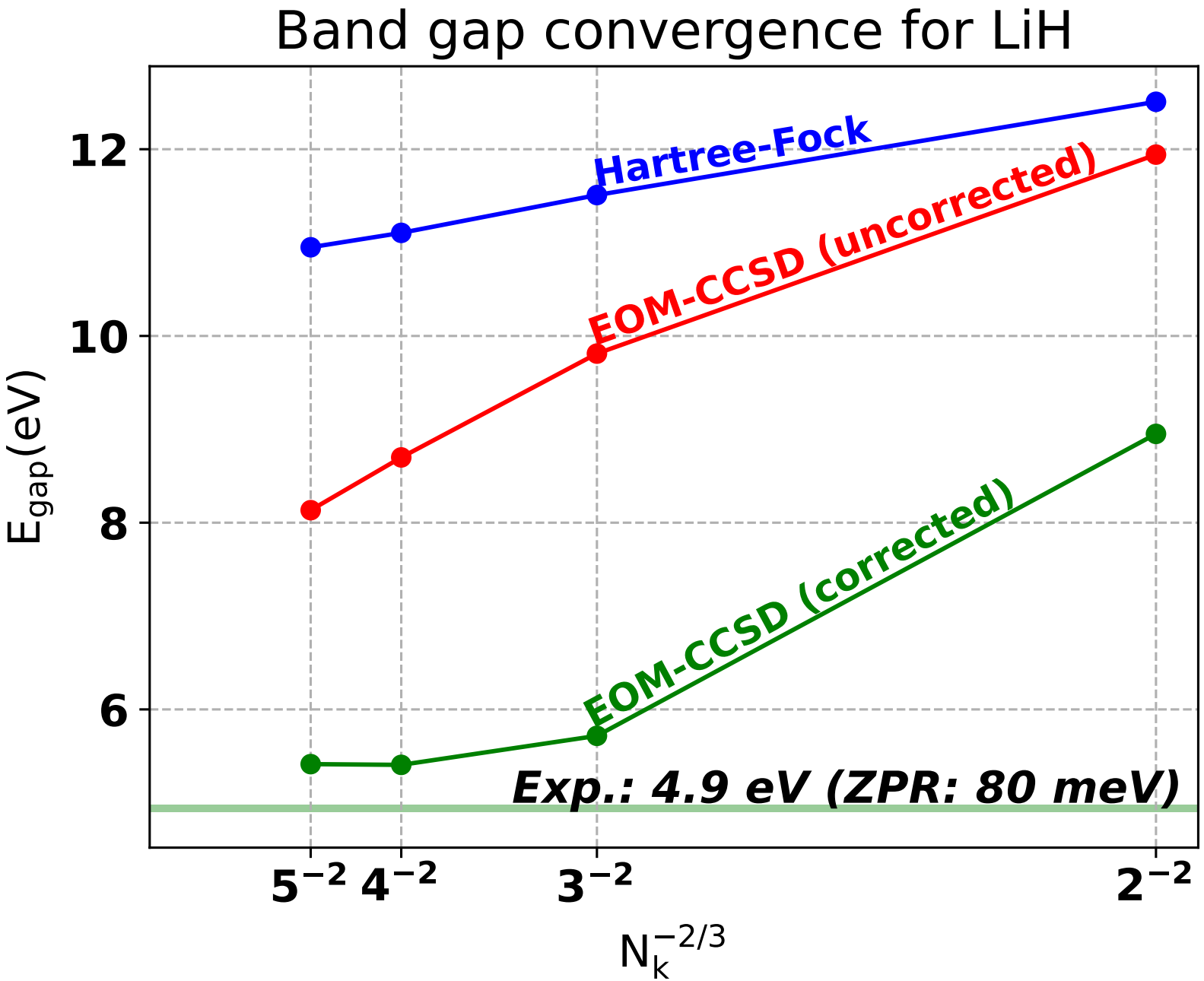


The modified Drude-Lorentz model

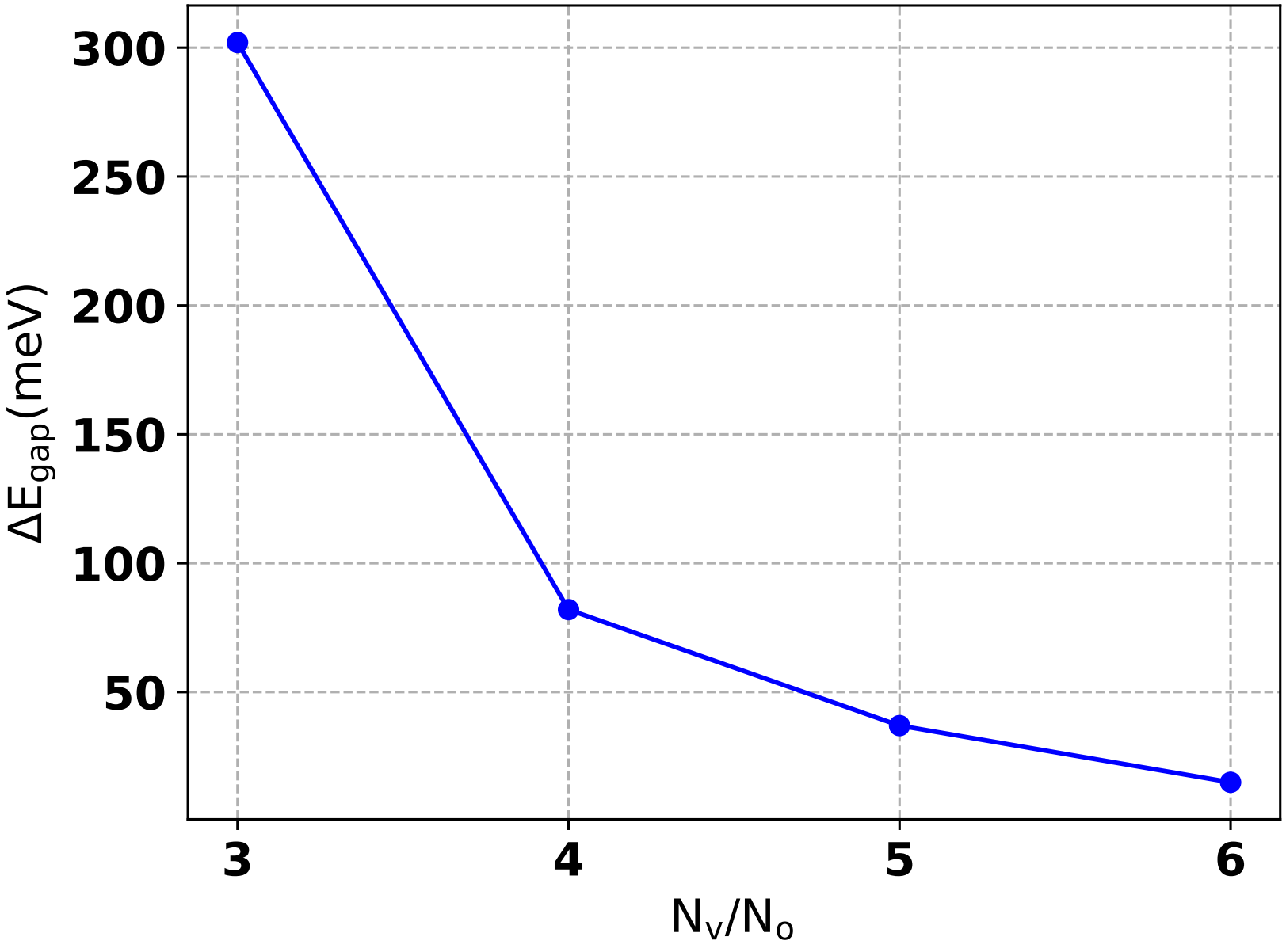
Simply perform constrained least-square fit of $S(\boldsymbol{G})$ using $m(\boldsymbol{G})$



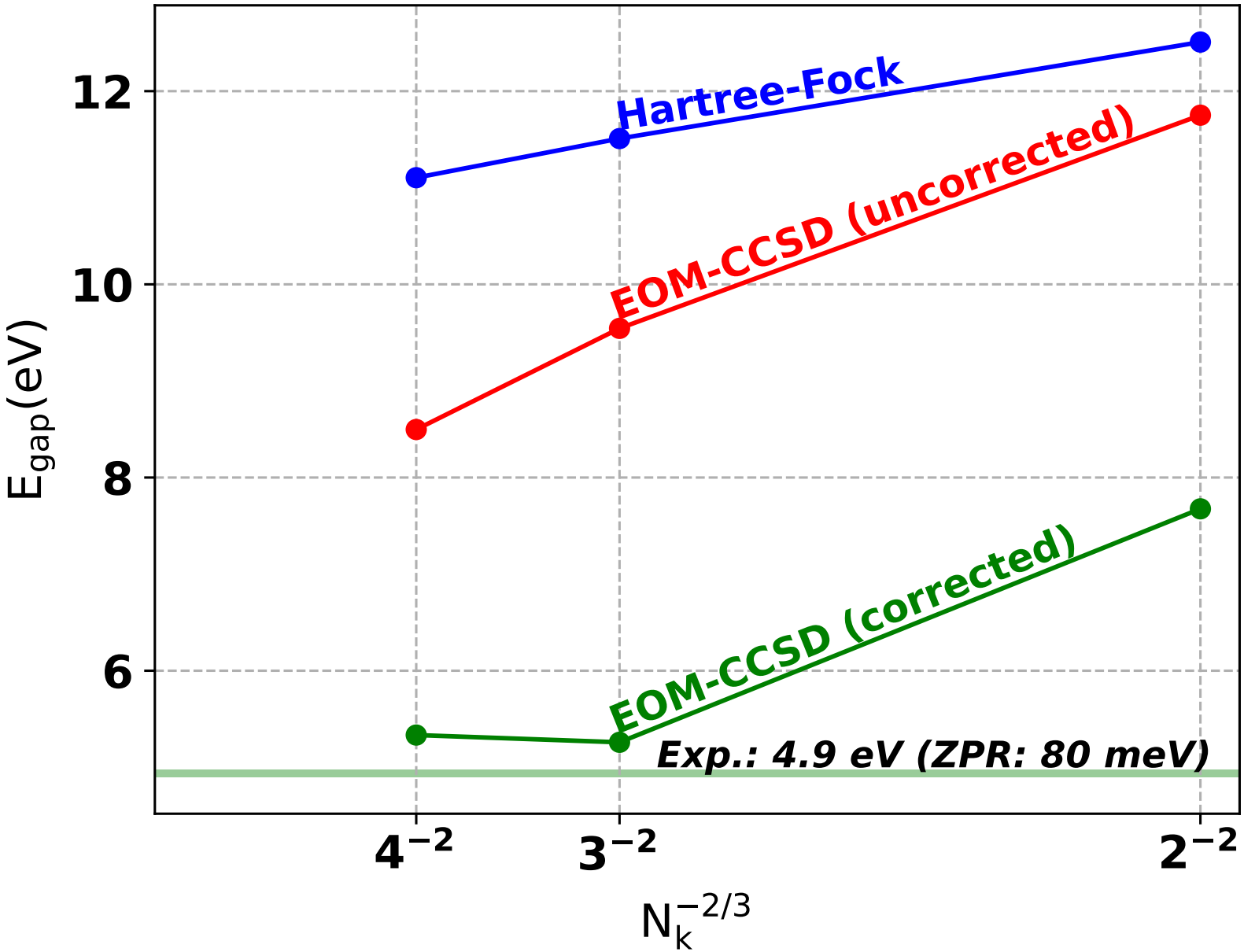
Initial results with a small basis ($N_v/N_o = 3$)



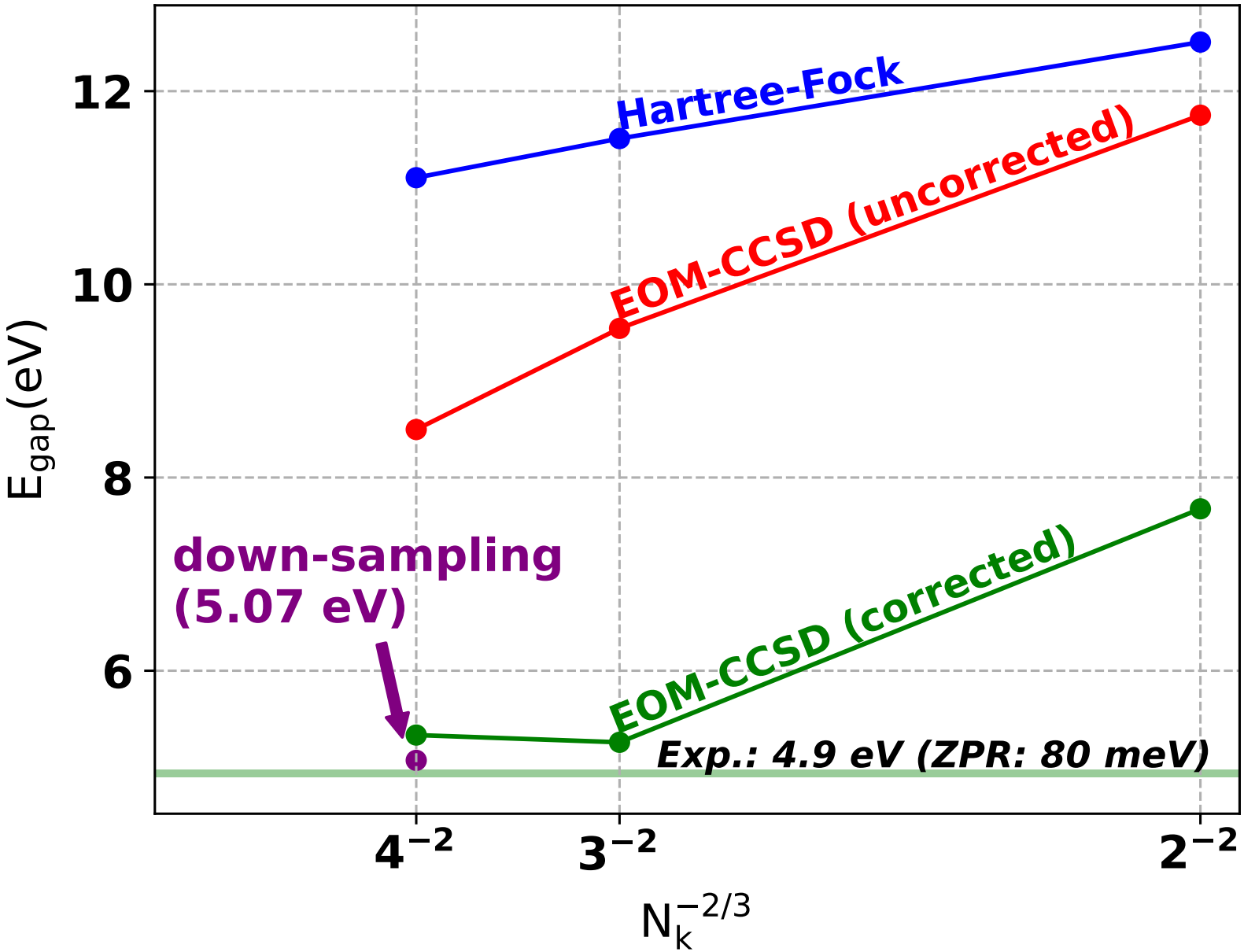
Basis set convergence



Final result with converged basis



Final result with converged basis



The final chapter: Coupled-cluster finite-size correction in FHI-aims

The current finite-size correction scheme (for CC and EOM-CC) is formulated in plane waves (PW), as

- structure factor $S(\boldsymbol{G})$ and Coulomb potential $V(\boldsymbol{G})$ are diagonal.
- PWs naturally provide a space ($\boldsymbol{G}$-space) in which interpolation of $S(\boldsymbol{G})$ is possible.

Problem: A localized, atom-centered basis does none of that.
Solution: Perform basis transformation before finite-size correction.

Example: Transforming the Coulomb potential

The real-space Coulomb potential $\frac{1}{|\boldsymbol{r}-\boldsymbol{r'}|}$ in FHI-aims is represented using an auxiliary basis $P_\mu(\boldsymbol{r})$:

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

In PWs, however, one can show that the Coulomb potential is

$$V_{\boldsymbol{G},\boldsymbol{G'}} = \int d\boldsymbol{r}\, d\boldsymbol{r'}\, \frac{e^{-i\boldsymbol{G}\boldsymbol{r}} e^{i\boldsymbol{G'}\boldsymbol{r'}}}{|\boldsymbol{r}-\boldsymbol{r'}|} = \frac{4\pi}{\boldsymbol{G}^2}\, \delta_{\boldsymbol{G},\boldsymbol{G'}}$$

We want to obtain an approximation of $V_{\boldsymbol{G},\boldsymbol{G'}}$ from our $V_{\mu,\nu}$:

$$V_{\boldsymbol{G},\boldsymbol{G'}} = \int d\boldsymbol{r}\, d\boldsymbol{r'}\, \frac{e^{-i\boldsymbol{G}\boldsymbol{r}} e^{i\boldsymbol{G'}\boldsymbol{r'}}}{|\boldsymbol{r}-\boldsymbol{r'}|} = \int d\boldsymbol{r}\, d\boldsymbol{r'}\, \frac{\sum_\mu C^*_{\mu,\boldsymbol{G}} P_\mu(\boldsymbol{r}) \sum_\nu C_{\nu,\boldsymbol{G'}} P_\nu(\boldsymbol{r'})}{|\boldsymbol{r}-\boldsymbol{r'}|}$$

$$= \sum_{\mu,\nu} C^*_{\mu,\boldsymbol{G}} V_{\mu,\nu} C_{\nu,\boldsymbol{G'}} = \underline{\underline{C}}^\dagger\, \underline{\underline{V}}\, \underline{\underline{C}}$$

Obtaining the transformation coefficients $C_{\mu,\boldsymbol{G}}$

As our atom-centered basis is not orthogonal, we need to take the overlap $S_{\mu\nu} = \int d\boldsymbol{r} P_\mu(\boldsymbol{r}) P_\nu(\boldsymbol{r})$ into account.

One can show that

$$C_{\mu,\boldsymbol{G}} = \sum_\nu (S^{-1})_{\mu,\nu} O_{\nu,\boldsymbol{G}} = \underline{\underline{S}}^{-1}\, \underline{\underline{O}}$$

,where

$$O_{\mu,\boldsymbol{G}} = \int d\boldsymbol{r}\, P_\mu(\boldsymbol{r}) e^{i\boldsymbol{G}\boldsymbol{r}} = \langle \mu | \boldsymbol{G} \rangle$$

A finite-size correction ansatz for localized basis sets

For a more efficient representation of products of states $\phi_p^*(\boldsymbol{r})\phi_q(\boldsymbol{r})$, an additional *auxiliary* basis $P_\mu(\boldsymbol{r})$ is often used

$$\phi_p^*(\boldsymbol{r})\phi_q(\boldsymbol{r}) = \sum_\mu C_{p,q}^\mu P_\mu(\boldsymbol{r})$$

With such a basis introduced, the structure factor can also be formulated using localized basis functions:

$$\begin{aligned} E_{corr} &= \sum_{\mu\nu} S_\nu^\mu V_\mu^\nu \\ &= \sum_{\mu\nu} \epsilon_{\mu\nu} \end{aligned}$$

Finite-size correction via pair-energies

$$E_{corr} = \sum_{\mu\nu} \epsilon_{\mu\nu}$$

For each $\epsilon_{\mu\nu}$:

- $P_\mu(\boldsymbol{r} - \boldsymbol{\tau}_\mu)$ and $P_\nu(\boldsymbol{r} - \boldsymbol{\tau}_{nu})$ are localized on atoms at $\boldsymbol{\tau}_\mu$ and $\boldsymbol{\tau}_\nu$ with distance $\boldsymbol{\tau}_\mu - \boldsymbol{\tau}_\nu$
- $\epsilon_{\mu\nu}$ is contribution to the total correlation energy

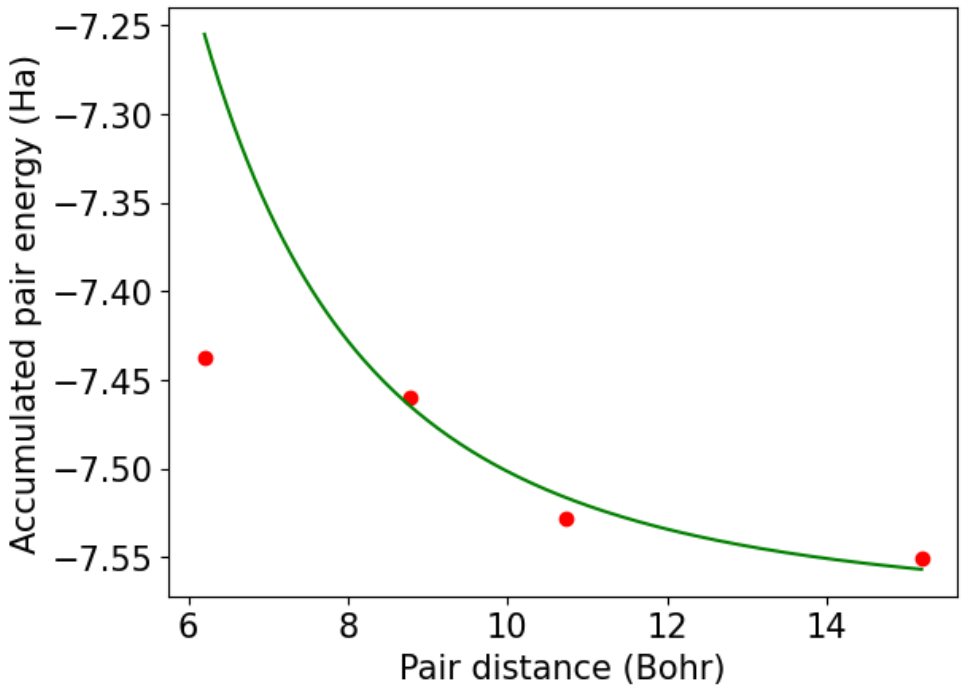
Interpretation of $\epsilon_{\mu\nu}$: Distance-resolved decomposition of correlation energy

New approach: Extrapolate $\epsilon_{\mu\nu}$ to $\boldsymbol{\tau}_\mu - \boldsymbol{\tau}_\nu \to \infty$

Finite-size correction via pair-energies

Benefits:

- Native, localized basis is used
- Long-range behavior of correlation is known (for ground-state : $1/r^3$)
- Very simple model



Derivative-based finite-size extrapolation

Basic idea: By calculating the first derivative $\left(\frac{\partial S}{\partial \boldsymbol{G}}\right)_{\boldsymbol{G}=\boldsymbol{0}}$, we can estimate the missing long-range contribution of $S(\boldsymbol{G})$.

$\Rightarrow$ It is not necessary to reach the minimum of $S(\boldsymbol{G})$.

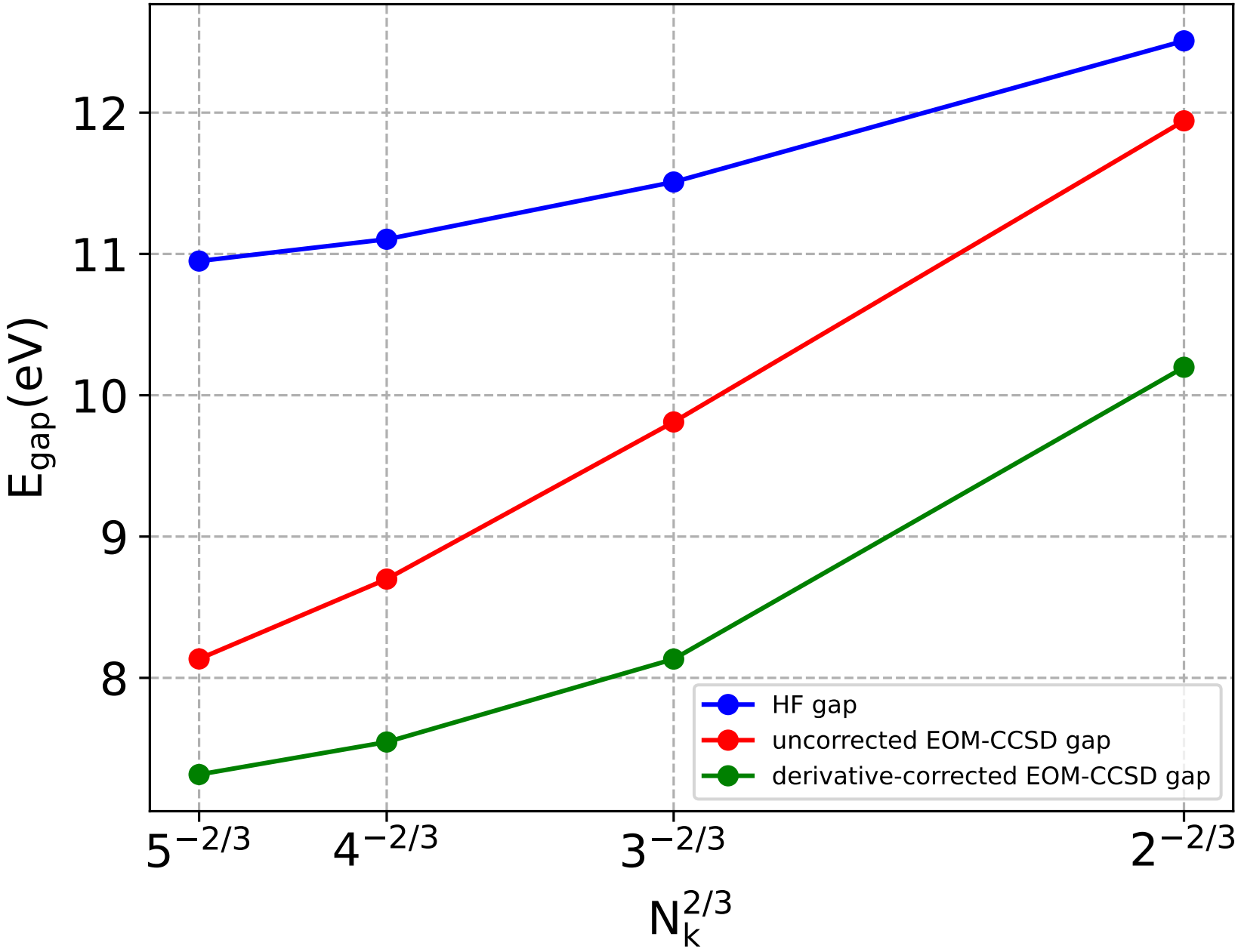
$\Rightarrow$ Smaller calculations can be sufficient to get a good estimate of the finite-size error.

$\left(\frac{\partial S}{\partial \boldsymbol{G}}\right)_{\boldsymbol{G}=\boldsymbol{0}}$ can be approximated using the dipole matrix

$$\boldsymbol{d}_{p,q} = \langle \phi_p | \hat{\boldsymbol{r}} | \phi_q \rangle$$

(comparable to "head" and "wing" of the macroscopic dielectric tensor routinely used in GW).

Derivative-based finite-size extrapolation for LiH



Derivative-based finite-size extrapolation for LiH

- Decent first attempt
- But still far away from the reference band gap of $\approx 5\,\mathrm{eV}$

A more refined treatment of the EOM structure factor is necessary