Affordable and highly accurate coupled-cluster level band gaps

A structure factor-based finite-size correction for equation-of-motion coupled-cluster theory

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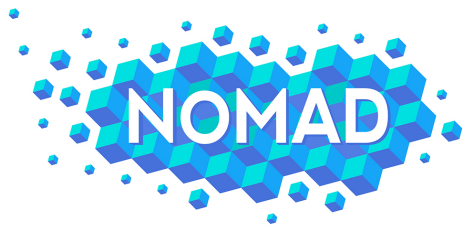
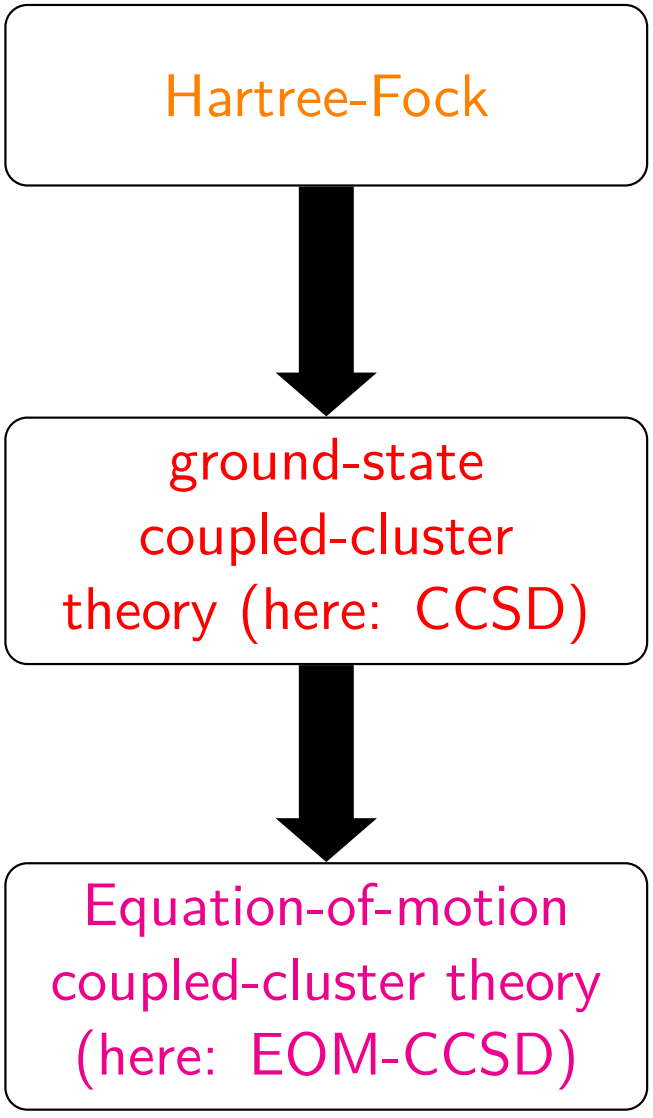


Excited states in coupled-cluster theory



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

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

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

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

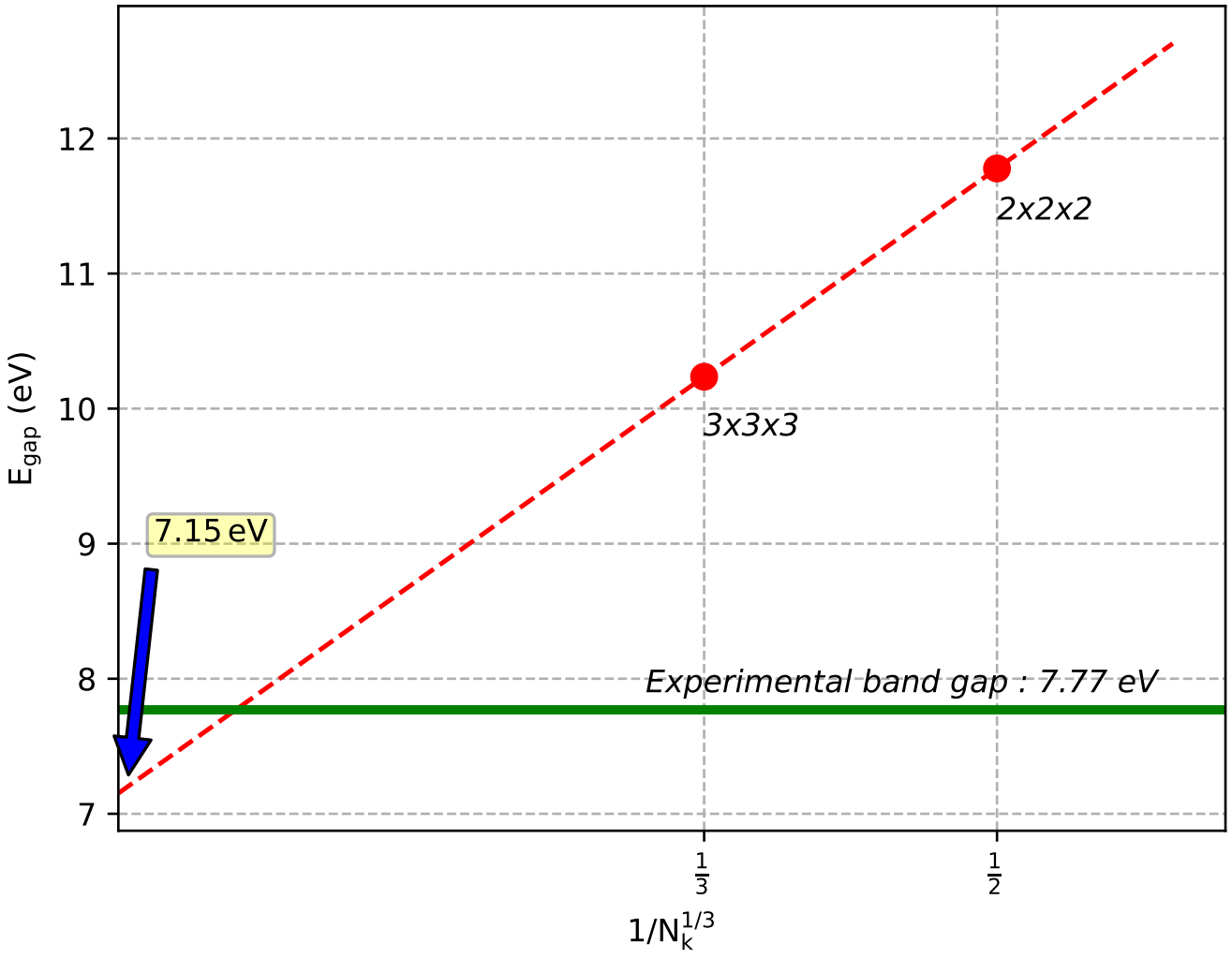
$$\hat{R}_n^{EA} = \sum_a r^a a_a^\dagger + \sum_{i,a,b} r_i^{ab} a_a^\dagger a_b^\dagger a_i + \ldots$$

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

Problem of the finite-size error of charged excitations

The naive approach

- Perform calculations of increasing supercell/ $\boldsymbol{k}$-grid size
- Extrapolate using some law



Problem of the finite-size error of charged excitations

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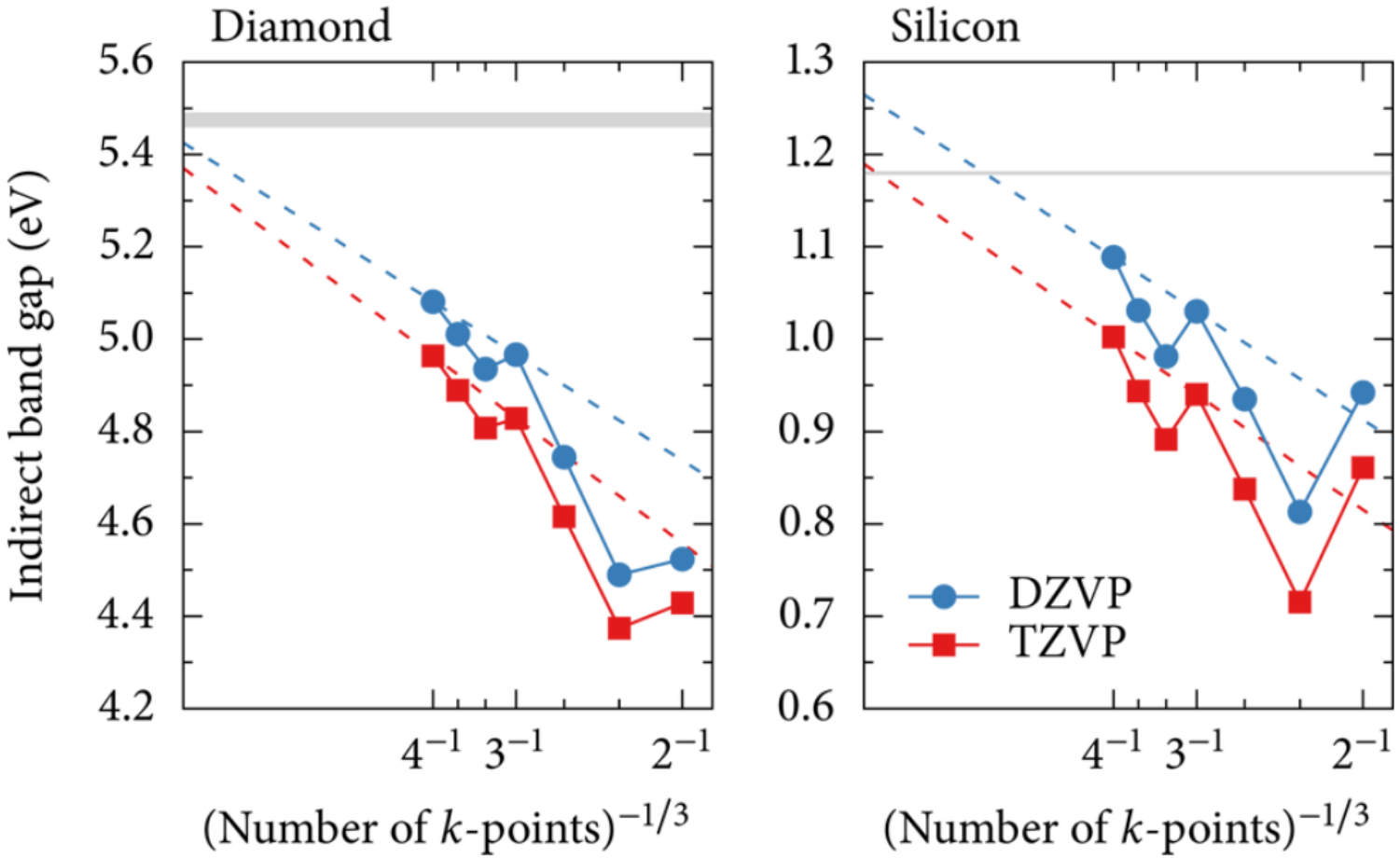


McClain et al. JCTC 13,3 (2017): 1209-1218

Problem of the finite-size error of charged excitations

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.

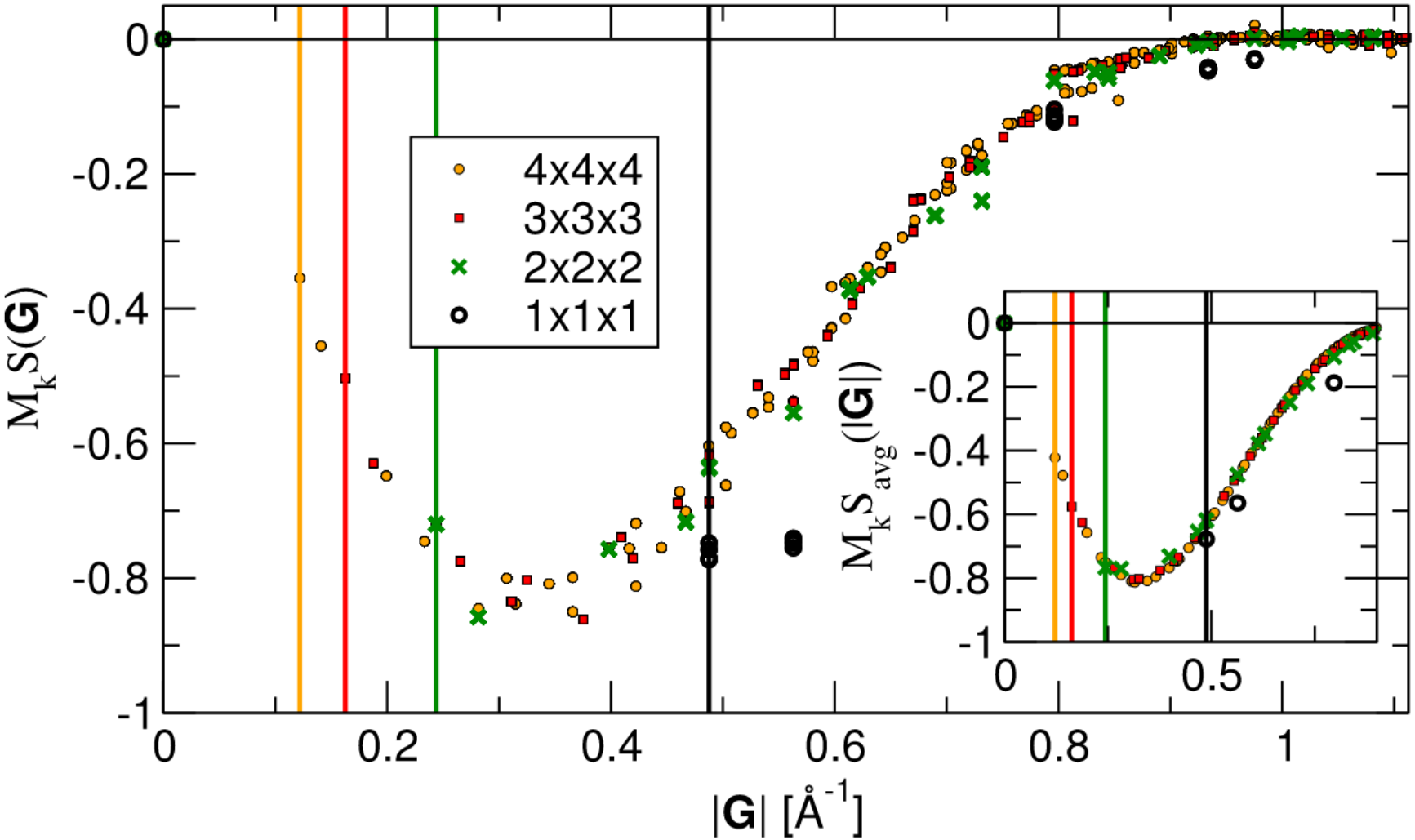
Structure factor-based finite-size correction

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

Can we do the same for excited states?

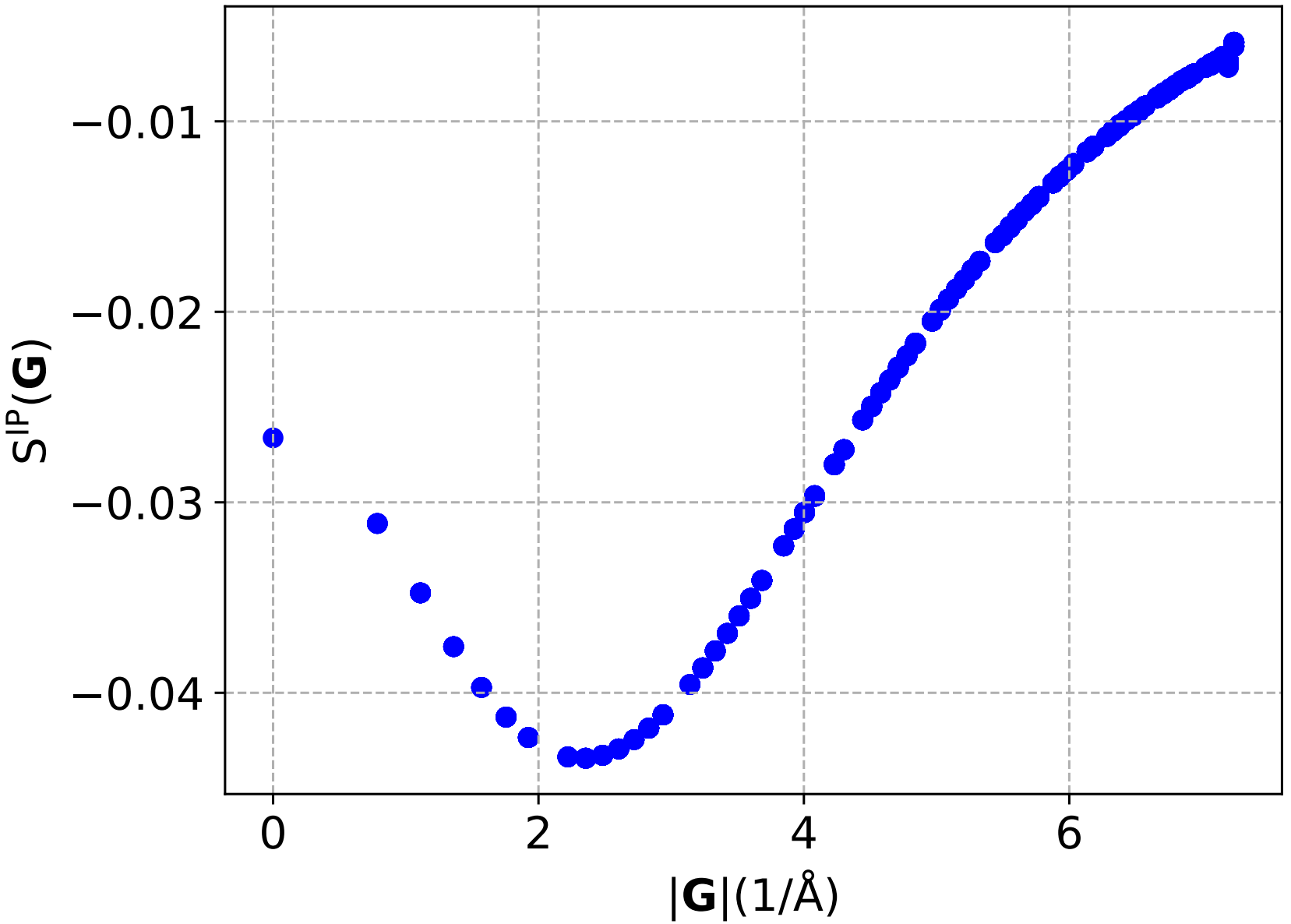
Similarly, let's define the EOM structure factor $S_n^{IP/EA}(\boldsymbol{G})$:

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

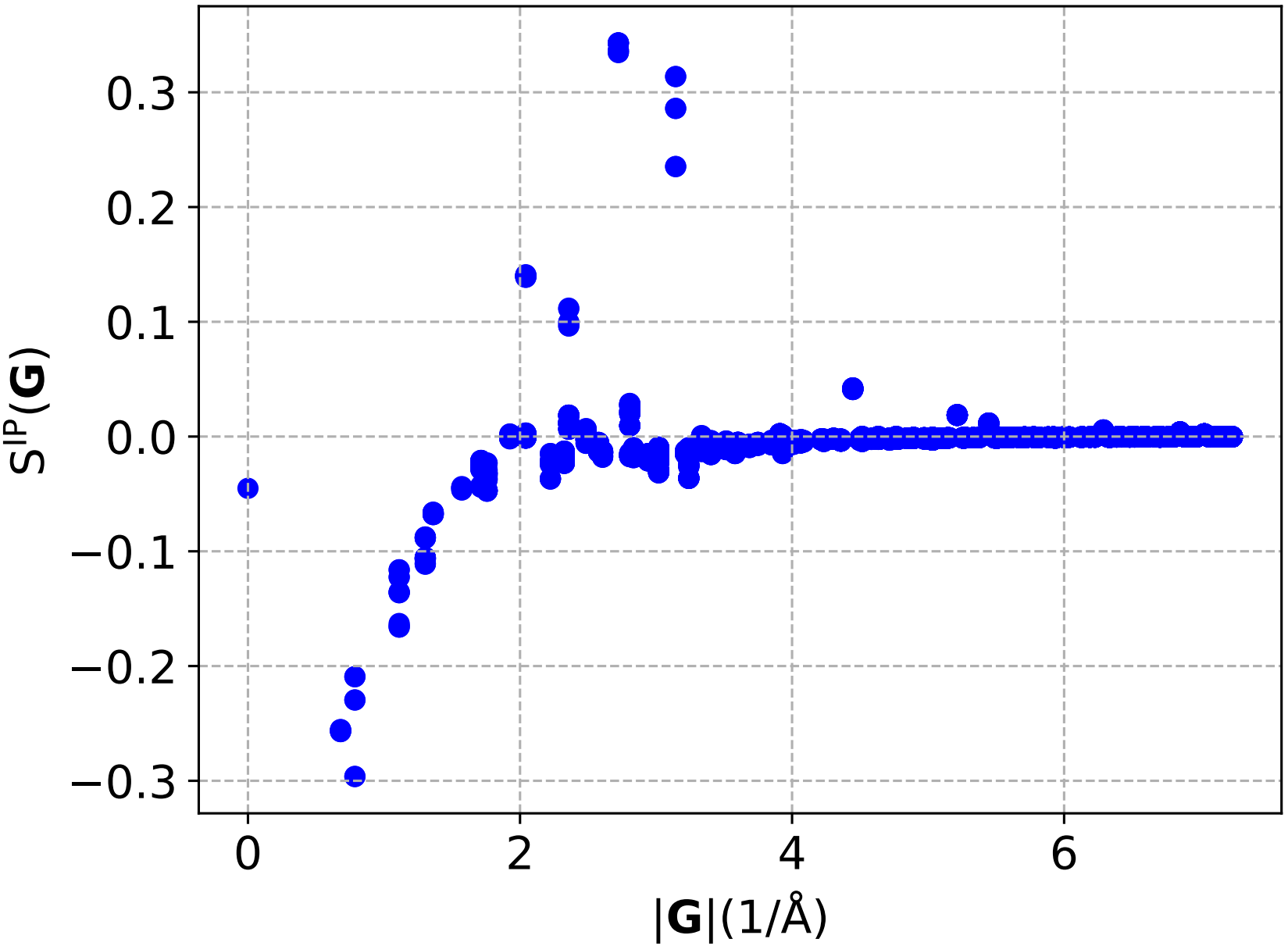
for the n-th ionization or electron capture.

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

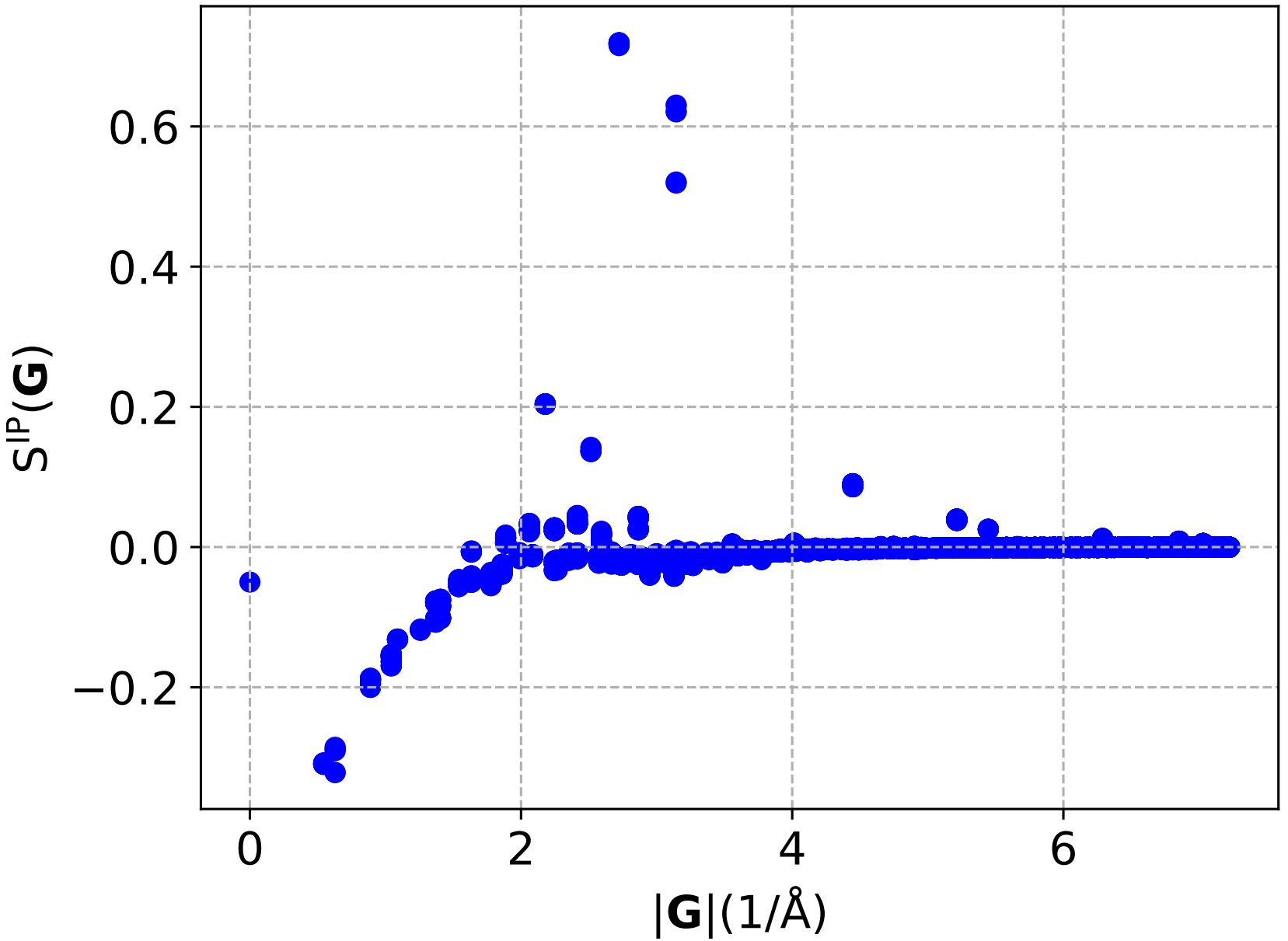
$S_1^{IP}(\boldsymbol{G})$ of a He-atom in a 8Åx8Åx8Å box



$S_1^{IP}(\boldsymbol{G})$ 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 $S(\boldsymbol{G})$.

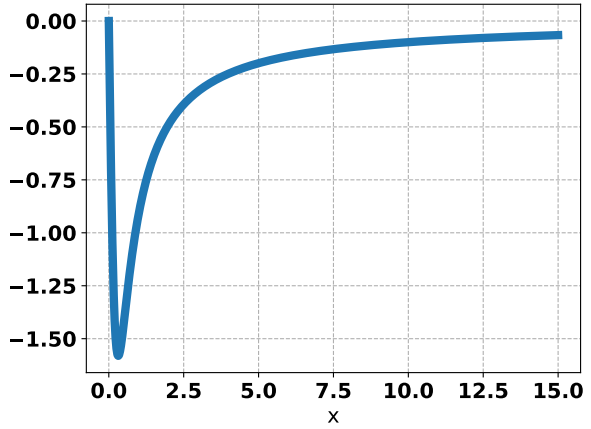
$\left(\frac{\partial S}{\partial \boldsymbol{G}}\right)_{\boldsymbol{G}=\boldsymbol{0}}$ can be approximated using the dipole matrix

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

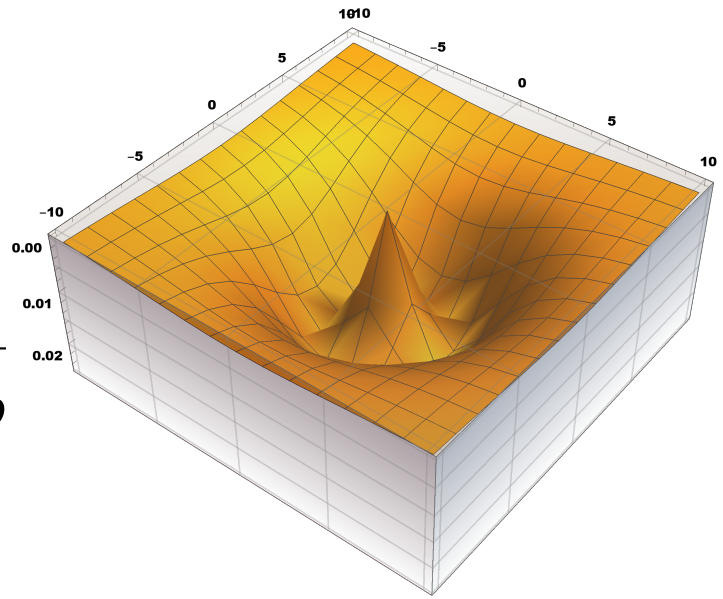
(comparable to "head" and "wing" of the macroscopic dielectric tensor routinely used in GW).

The modified Drude-Lorentz model

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

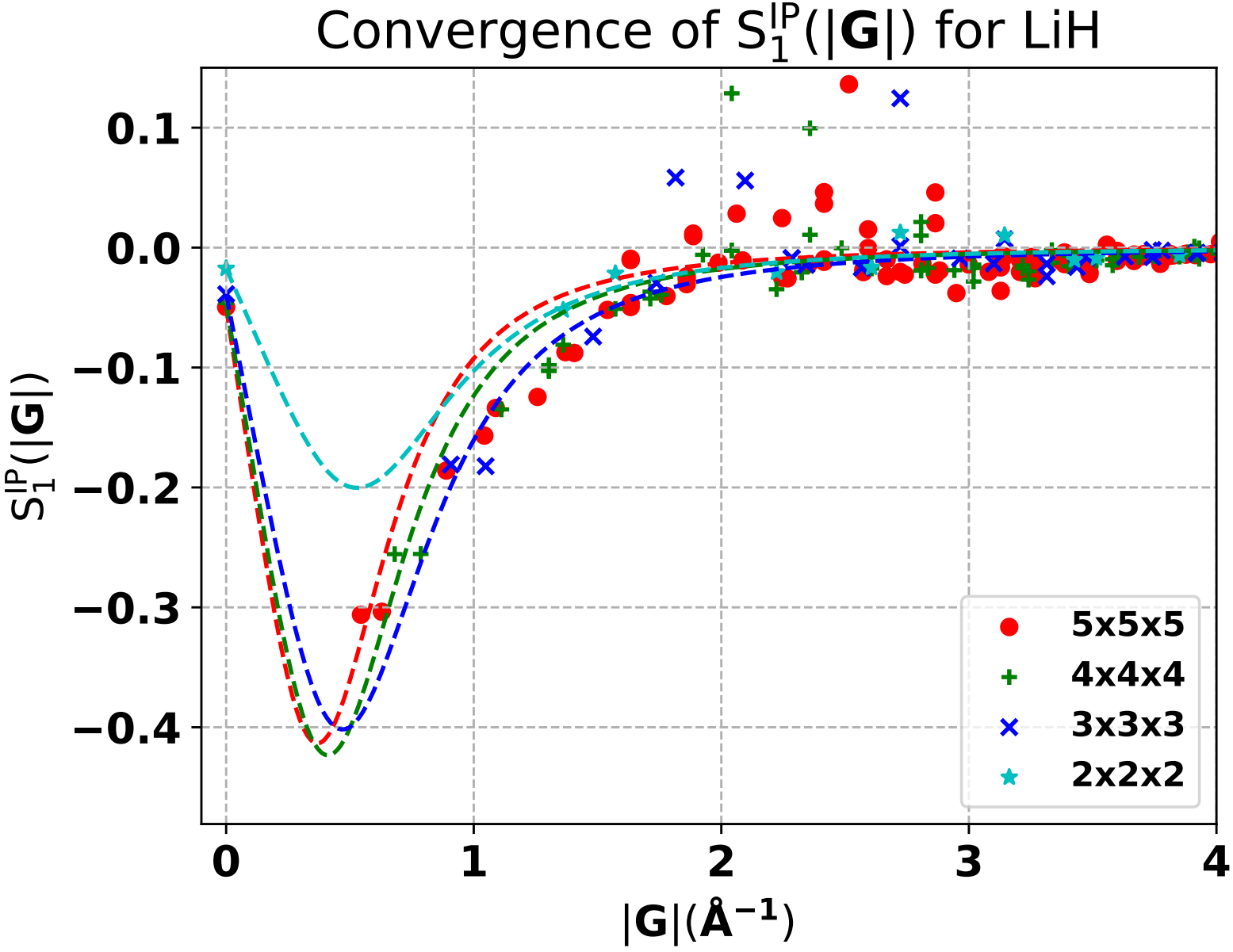


$$m(x_1, x_2, x_3) := -d\frac{\sqrt{c_1x_1^2 + c_2x_2^2 + c_3x_3^2} - a}{(\sqrt{c_1x_1^2 + c_2x_2^2 + c_3x_3^2} - a)^4 + b}$$

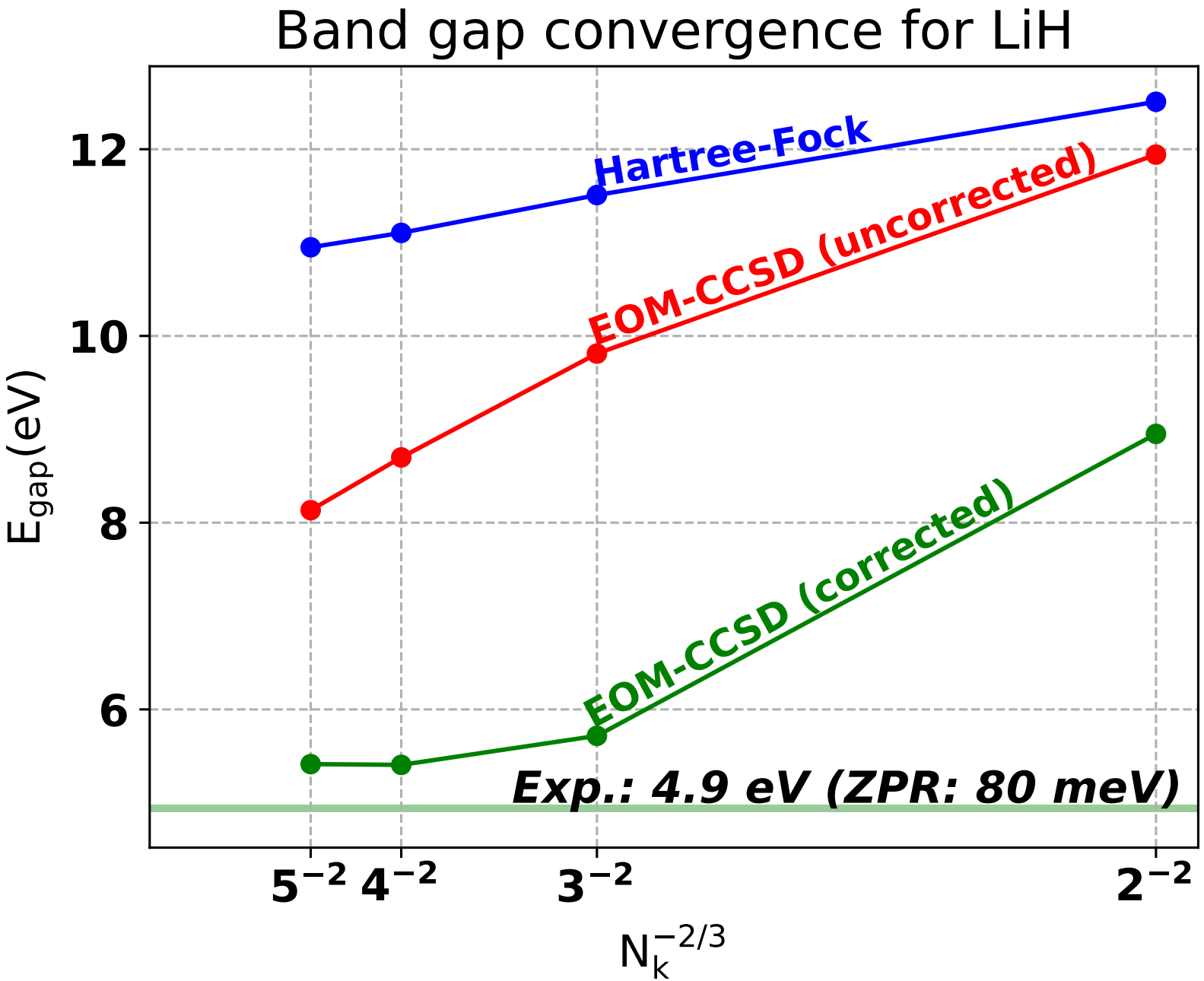


The modified Drude-Lorentz model

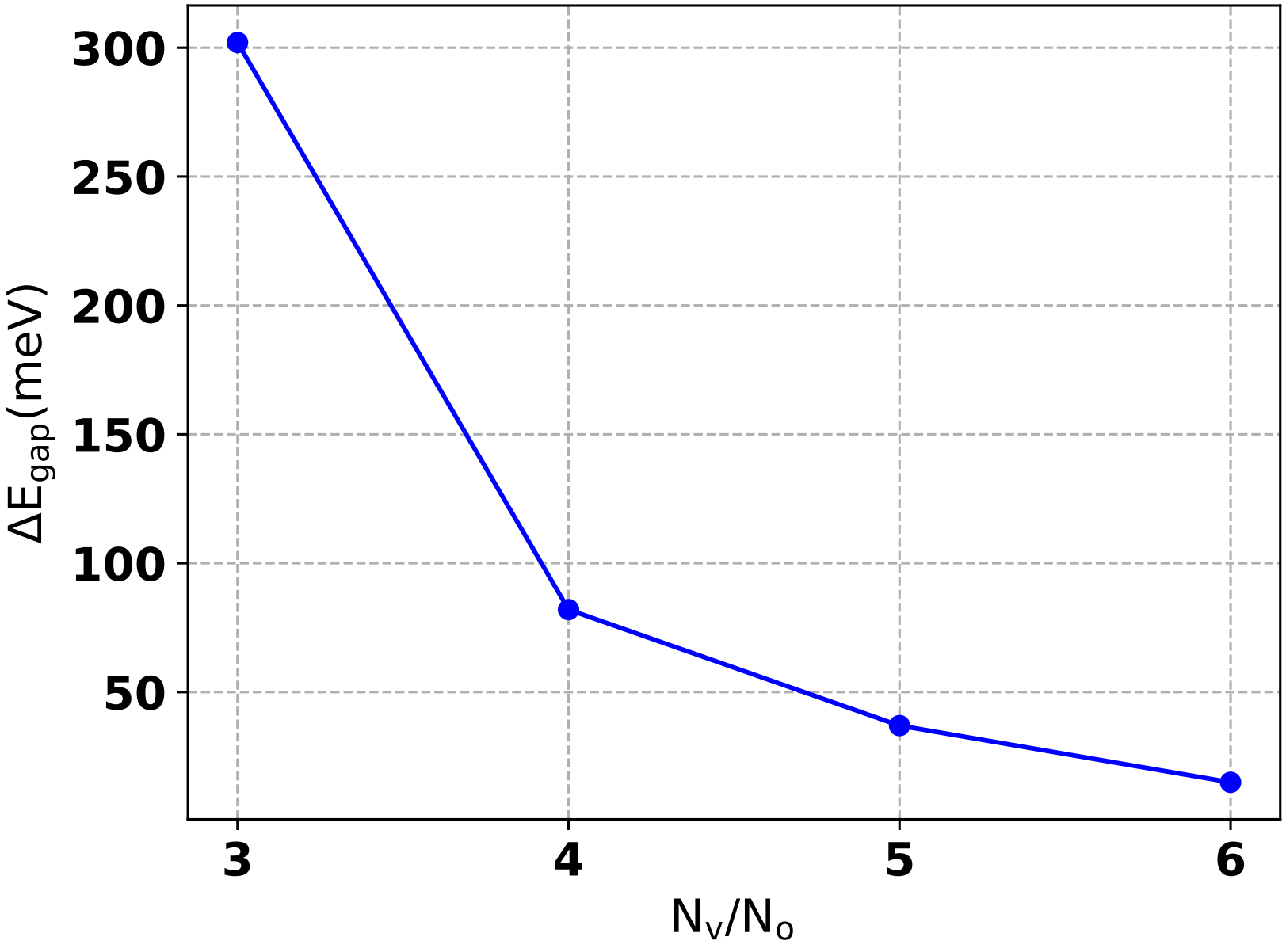
Simply perform constrained least-square fit of $S(\boldsymbol{G})$ using $m(\boldsymbol{G})$



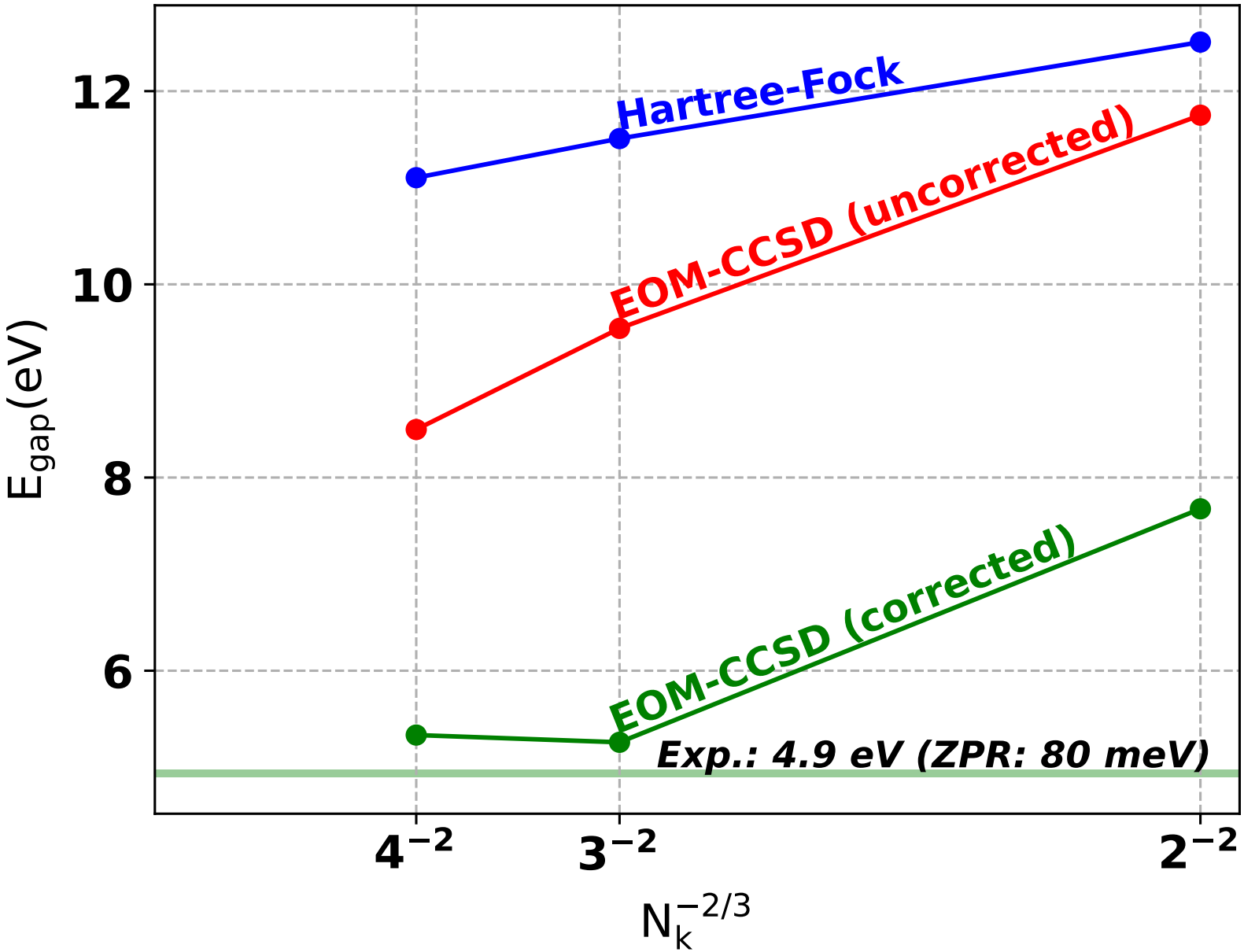
Initial results with a small basis ($N_v/N_o = 3$)



Basis set convergence



Final result with converged basis



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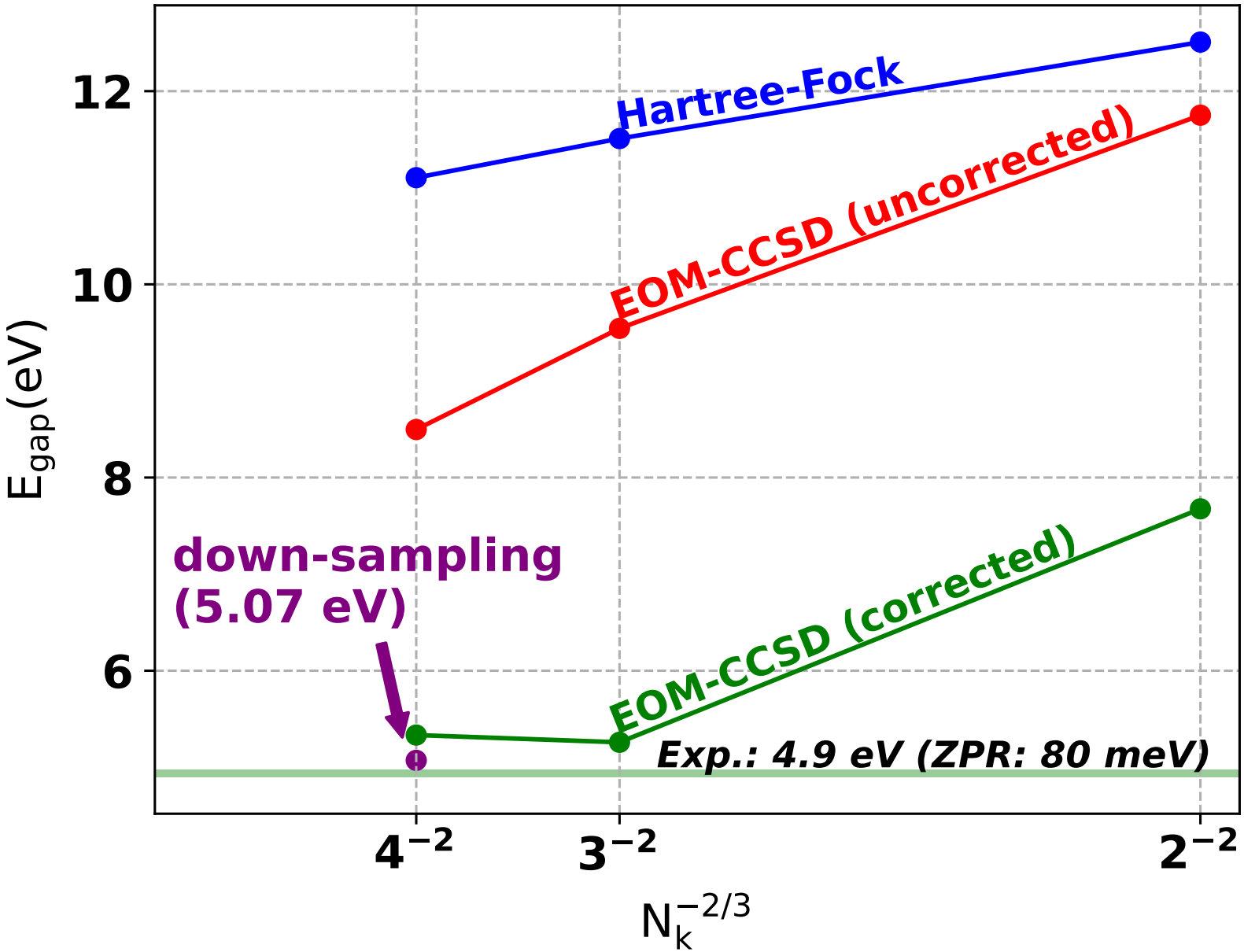


The final chapter: Coupled-cluster finite-size correction in FHI-aims

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

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

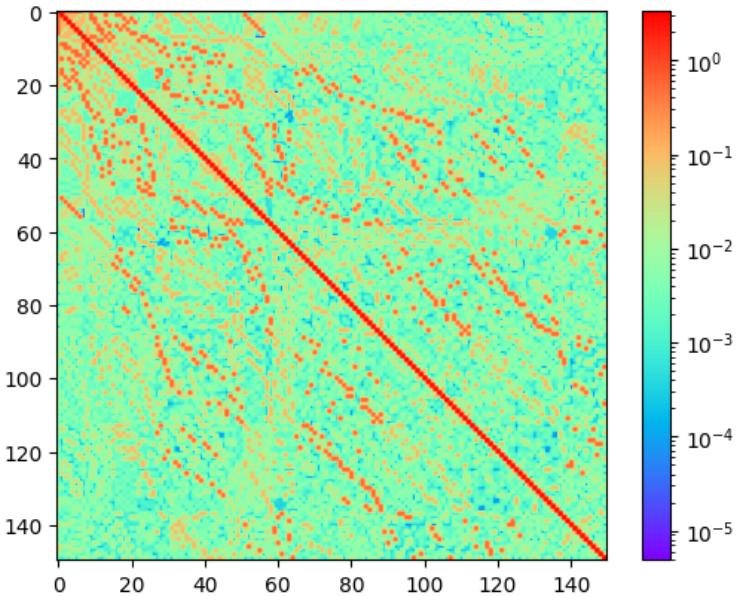
,where

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

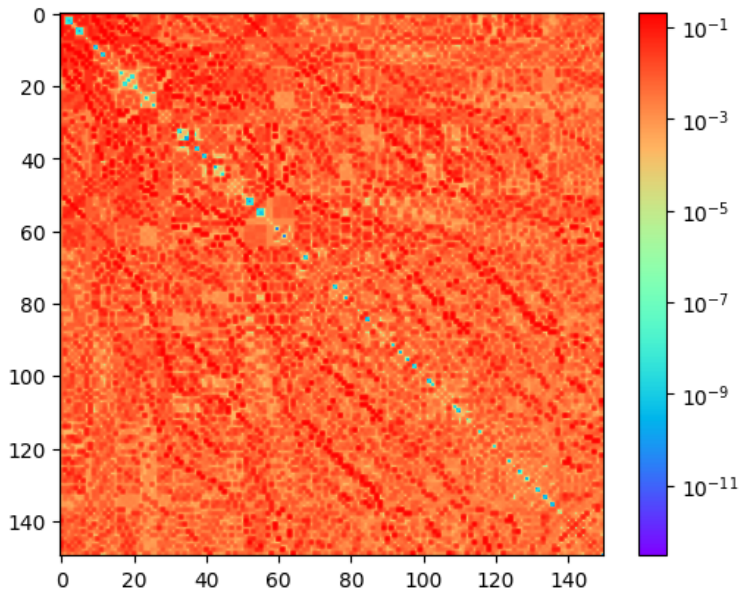
So...how well does it work?

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

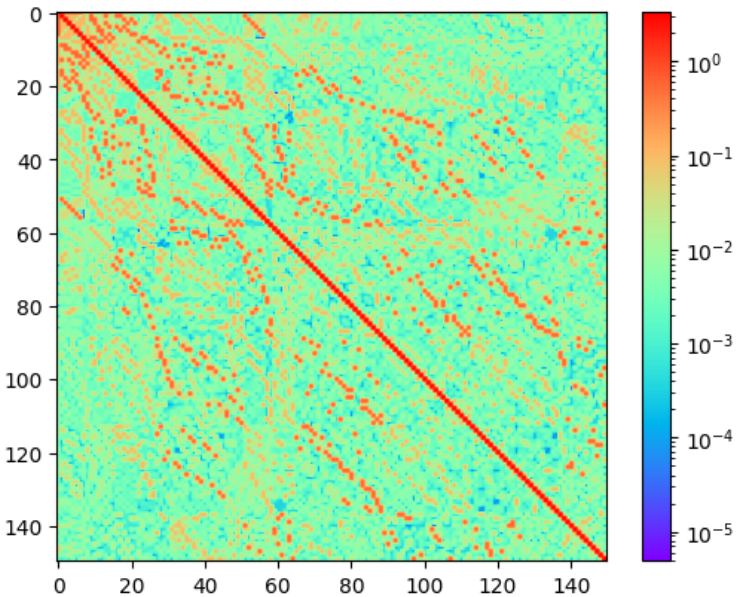


(b) $\Im(S^{PW}_{\boldsymbol{G},\boldsymbol{G'}})$

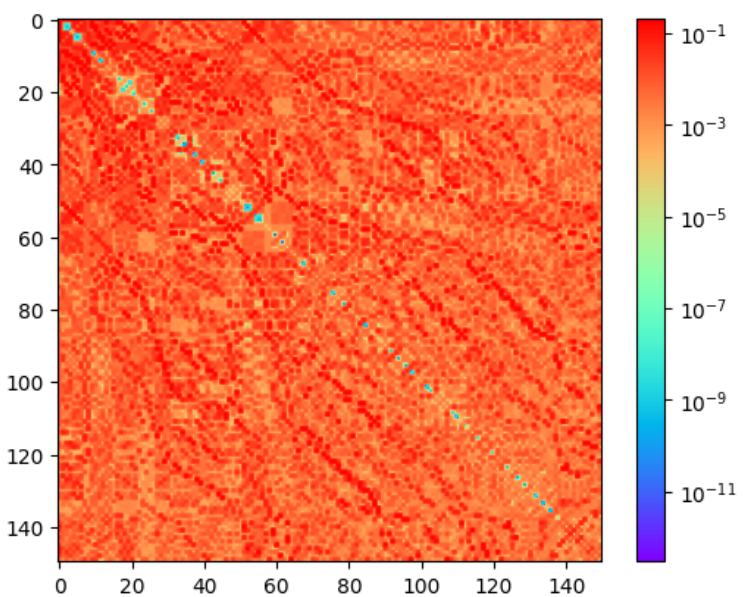
So...how well does it work?

It's not quite working yet:

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

What could it be?

- There is a bug in the code
- Artifact of small auxiliary basis
- There's nothing wrong, AOs are just very unfit for representing PWs

Summary and outlook

What has been done:

- The EOM-CCSD algorithm has been implemented in `Cc4s`
- The structure factor $S(\boldsymbol{G})$ and its derivative $\left(\frac{\partial S(\boldsymbol{G})}{\partial G}\right)_{\boldsymbol{G}=\boldsymbol{0}}$ has been implemented in `Cc4s`
- A new, affordable and accurate finite-size correction scheme for EOM-CC has been developed

What remains to be done:

- Benchmark the correction scheme for a variety of materials
- Apply correction scheme to band structures
- Resolve the issues with FHI-aims (Is it a bug or a feature?)

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 $S(\boldsymbol{G})$.

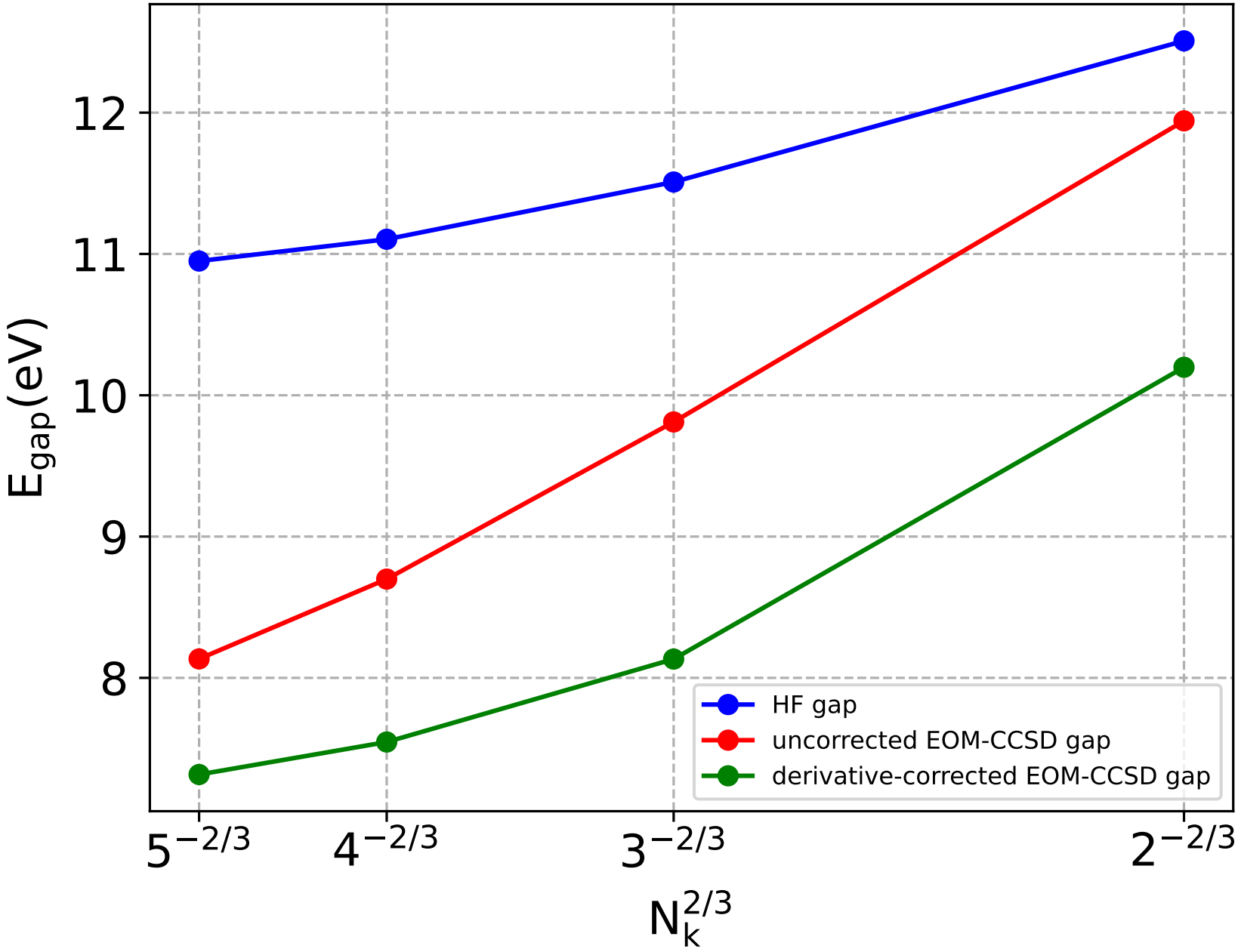
$\Rightarrow$ Smaller calculations can be sufficient to get a good estimate of the finite-size error.

$\left(\frac{\partial S}{\partial \boldsymbol{G}}\right)_{\boldsymbol{G}=\boldsymbol{0}}$ 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