# Single-particle excitation energies from second-order MBPT

## The Effect of Coulomb singularity

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# Today’s talk:

- Charged or single-particle excitations from MBPT
- Bartlett’s diagrammatic theory and beyond
- K-grid convergence
- Coulomb matrix singularity analysis
- How to integrate a singular function

# Single-particle or charged excitation

## addition or removal of an electron

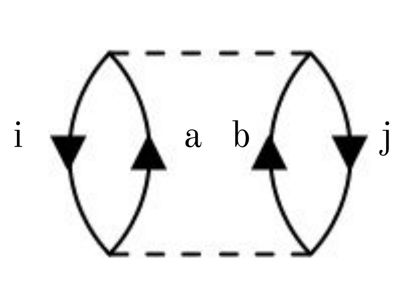
$$\epsilon_p^- = E(N) - E_p(N-1) \qquad \epsilon_p^+ = E_p(N+1) - E(N)$$

$$\widehat{H}^N|\Psi^N>= E^N|\Psi^N> \quad \widehat{H}^{N\pm1}|\Psi_p^{N\pm1}>= E_p^{N\pm1}|\Psi_p^{N\pm1}>$$

Applying MBPT:

$$\pm\epsilon_p^{\mp} = E(N) - E_p(N\mp1) =$$
$$[E^{(0)}(N) - E_p^{(0)}(N\mp1)] + [E^{(1)}(N) - E_p^{(1)}(N\mp1)]$$
$$+ [E^{(2)}(N) - E_p^{(2)}(N\mp1)]+\ldots =$$
$$\pm\epsilon_p^{\mp(0)} + \pm\epsilon_p^{\mp(1)} + \pm\epsilon_p^{\mp(2)} + \ldots$$

# 2nd order Møller-Plesset PT




$$E^{MP2} = E^{HF} + \frac{1}{4}\sum_{\sigma,\sigma'}\sum_{i,j,a,b}\frac{1}{N_{\mathbf{k}}N_{\mathbf{k}'}N_{\mathbf{q}'}N_{\mathbf{q}}}\sum_{\mathbf{k},\mathbf{k}'\mathbf{q}\mathbf{q}'}\frac{\left|V^{a\mathbf{q}\sigma,b\mathbf{q}'\sigma'}_{i\mathbf{k}\sigma,j\mathbf{k}'\sigma'}\right|^2}{\epsilon^{HF}_{i\mathbf{k}\sigma}+\epsilon^{HF}_{j\mathbf{k}'\sigma'}-\epsilon^{HF}_{a\mathbf{q}\sigma}-\epsilon^{HF}_{b\mathbf{q}'\sigma'}}$$

Coulomb matrix elements: $$V^{q\mathbf{k}'\sigma',r\mathbf{q}'\sigma'}_{p\mathbf{k}\sigma,s\mathbf{q}\sigma} = \int d\mathbf{r}\int d\mathbf{r}'\,\psi^*_{p\mathbf{k}\sigma}(\mathbf{r})\psi^*_{q\mathbf{k}'\sigma'}(\mathbf{r}')\frac{1}{|\mathbf{r}-\mathbf{r}'|}\psi_{r\mathbf{q}'\sigma'}(\mathbf{r}')\psi_{s\mathbf{q}\sigma}(\mathbf{r})$$

# MBPT for single-particle (charged) excitations

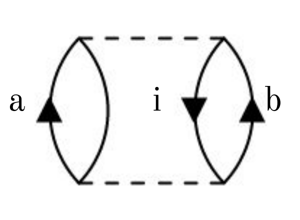
## J.-Q. Sun and R. J. Bartlett

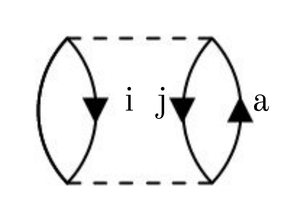
J. Chem. Phys., Vol. 107, No. 13, 1997

> "extend the theory to give any order corrections to IPs and EAs"

➔ Corrections to any order for sp-excitations

2nd order diagrams (with HF):




sp-MP2:

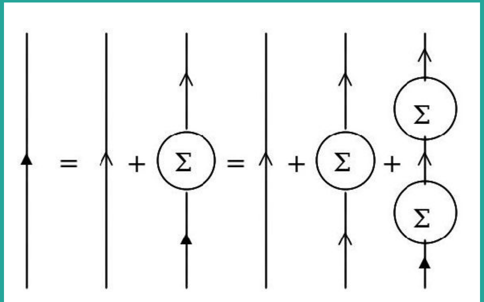
$$\epsilon^{MP2}_{p\mathbf{k}\sigma} = \epsilon^{HF}_{p\mathbf{k}\sigma} + \frac{1}{2}\sum_{\sigma'}\sum_{i,a,b}\frac{1}{N_{\mathbf{k}'}N_{\mathbf{q}'}N_{\mathbf{q}}}\sum_{\mathbf{k}'\mathbf{q}\mathbf{q}'}\frac{\left|V^{a\mathbf{q}\sigma,b\mathbf{q}'\sigma'}_{p\mathbf{k}\sigma,i\mathbf{k}'\sigma'}\right|^2}{\epsilon^{HF}_{p\mathbf{k}\sigma}+\epsilon^{HF}_{i\mathbf{k}'\sigma'}-\epsilon^{HF}_{a\mathbf{q}\sigma}-\epsilon^{HF}_{b\mathbf{q}'\sigma'}} +$$

$$\frac{1}{2}\sum_{\sigma'}\sum_{i,j,a}\frac{1}{N_{\mathbf{k}'}N_{\mathbf{q}'}N_{\mathbf{q}}}\sum_{\mathbf{k}'\mathbf{q}\mathbf{q}'}\frac{\left|V^{i\mathbf{q}\sigma,j\mathbf{q}'\sigma'}_{p\mathbf{k}\sigma,a\mathbf{k}'\sigma'}\right|^2}{\epsilon^{HF}_{p\mathbf{k}\sigma}+\epsilon^{HF}_{a\mathbf{k}'\sigma'}-\epsilon^{HF}_{i\mathbf{q}\sigma}-\epsilon^{HF}_{i\mathbf{q}'\sigma'}}$$

# Dyson's equation
## for single-particle (charged) excitations

Dyson's equation:

$$G(p,q;\epsilon) = G^0(p,q;\epsilon) + \sum_{rs} G^0(p,r;\epsilon)\Sigma(r,s;\epsilon)G(s,q;\epsilon)$$




Green's function:

$$G(p,q;\epsilon) = \lim_{\eta\to 0}\left[\sum_n \frac{\langle\Psi^N|\hat{\alpha}_p^\dagger|\Psi_n^{N-1}\rangle\langle\Psi_n^{N-1}|\hat{\alpha}_q|\Psi^N\rangle}{\epsilon-[E(N)-E_n(N-1)]-i\eta} + \sum_m \frac{\langle\Psi^N|\hat{\alpha}_p|\Psi_m^{N+1}\rangle\langle\Psi_m^{N+1}|\hat{\alpha}_q^\dagger|\Psi^N\rangle}{\epsilon-[E_m(N+1)-E(N)]+i\eta}\right]$$

# Dyson(D2)

Self energy in diagonal approximation:

$$\Sigma^{D2}(p;\epsilon) = \frac{1}{2}\sum_{iab}\frac{|<\phi_p\phi_i|\phi_a\phi_b>|^2}{\epsilon+\epsilon_i-\epsilon_a-\epsilon_b+i\eta} + \frac{1}{2}\sum_{ija}\frac{|<\phi_i\phi_j|\phi_p\phi_a>|^2}{\epsilon+\epsilon_a-\epsilon_i-\epsilon_j-i\eta}$$

Poles of the Green's function:

$$\epsilon^{D(2)}_{p\mathbf{k}\sigma} = \epsilon^{HF}_{p\mathbf{k}\sigma} + \frac{1}{2}\sum_{\sigma'}\sum_{i,a,b}\frac{1}{N_{\mathbf{k}'}N_{\mathbf{q}'}N_{\mathbf{q}}}\sum_{\mathbf{k}'\mathbf{q}\mathbf{q}'}\frac{\left|V^{a\mathbf{q}\sigma,b\mathbf{q}'\sigma'}_{p\mathbf{k}\sigma,i\mathbf{k}'\sigma'}\right|^2}{\epsilon^{D(2)}_{p\mathbf{k}\sigma}+\epsilon^{HF}_{i\mathbf{k}'\sigma'}-\epsilon^{HF}_{a\mathbf{q}\sigma}-\epsilon^{HF}_{b\mathbf{q}'\sigma'}} +$$

$$\frac{1}{2}\sum_{\sigma'}\sum_{i,j,a}\frac{1}{N_{\mathbf{k}'}N_{\mathbf{q}'}N_{\mathbf{q}}}\sum_{\mathbf{k}'\mathbf{q}\mathbf{q}'}\frac{\left|V^{i\mathbf{q}\sigma,j\mathbf{q}'\sigma'}_{p\mathbf{k}\sigma,a\mathbf{k}'\sigma'}\right|^2}{\epsilon^{D(2)}_{p\mathbf{k}\sigma}+\epsilon^{HF}_{a\mathbf{k}'\sigma'}-\epsilon^{HF}_{i\mathbf{q}\sigma}-\epsilon^{HF}_{i\mathbf{q}'\sigma'}}$$

# What is implemented in FHI-aims:

Corrections for:

- sp-MP2
  - Band structure
  - Band gap
- Dyson(D2)
  - Band gap
  - Other specified HF-energy

$$\epsilon^{MP2}_{p\mathbf{k}\sigma} = \epsilon^{HF}_{p\mathbf{k}\sigma} + \frac{1}{2}\sum_{\sigma'}\sum_{i,a,b}\frac{1}{N_{\mathbf{k}'}N_{\mathbf{q}'}N_{\mathbf{q}}}\sum_{\mathbf{k}'\mathbf{q}\mathbf{q}'}\frac{\left|V^{a\mathbf{q}\sigma,b\mathbf{q}'\sigma'}_{p\mathbf{k}\sigma,i\mathbf{k}'\sigma'}\right|^2}{\epsilon^{HF}_{p\mathbf{k}\sigma}+\epsilon^{HF}_{i\mathbf{k}'\sigma'}-\epsilon^{HF}_{a\mathbf{q}\sigma}-\epsilon^{HF}_{b\mathbf{q}'\sigma'}} +$$

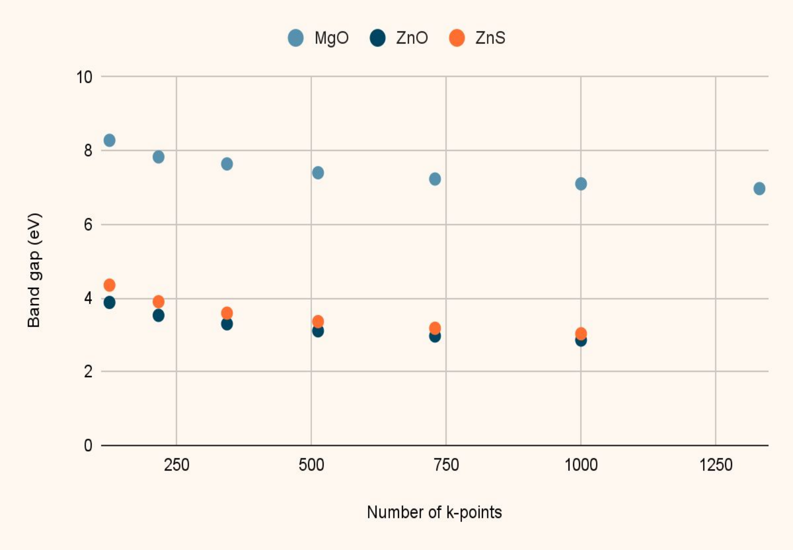
$$\frac{1}{2}\sum_{\sigma'}\sum_{i,j,a}\frac{1}{N_{\mathbf{k}'}N_{\mathbf{q}'}N_{\mathbf{q}}}\sum_{\mathbf{k}'\mathbf{q}\mathbf{q}'}\frac{\left|V^{i\mathbf{q}\sigma,j\mathbf{q}'\sigma'}_{p\mathbf{k}\sigma,a\mathbf{k}'\sigma'}\right|^2}{\epsilon^{HF}_{p\mathbf{k}\sigma}+\epsilon^{HF}_{a\mathbf{k}'\sigma'}-\epsilon^{HF}_{i\mathbf{q}\sigma}-\epsilon^{HF}_{i\mathbf{q}'\sigma'}}$$

$$\epsilon^{D(2)}_{p\mathbf{k}\sigma} = \epsilon^{HF}_{p\mathbf{k}\sigma} + \frac{1}{2}\sum_{\sigma'}\sum_{i,a,b}\frac{1}{N_{\mathbf{k}'}N_{\mathbf{q}'}N_{\mathbf{q}}}\sum_{\mathbf{k}'\mathbf{q}\mathbf{q}'}\frac{\left|V^{a\mathbf{q}\sigma,b\mathbf{q}'\sigma'}_{p\mathbf{k}\sigma,i\mathbf{k}'\sigma'}\right|^2}{\epsilon^{D(2)}_{p\mathbf{k}\sigma}+\epsilon^{HF}_{i\mathbf{k}'\sigma'}-\epsilon^{HF}_{a\mathbf{q}\sigma}-\epsilon^{HF}_{b\mathbf{q}'\sigma'}} +$$

$$\frac{1}{2}\sum_{\sigma'}\sum_{i,j,a}\frac{1}{N_{\mathbf{k}'}N_{\mathbf{q}'}N_{\mathbf{q}}}\sum_{\mathbf{k}'\mathbf{q}\mathbf{q}'}\frac{\left|V^{i\mathbf{q}\sigma,j\mathbf{q}'\sigma'}_{p\mathbf{k}\sigma,a\mathbf{k}'\sigma'}\right|^2}{\epsilon^{D(2)}_{p\mathbf{k}\sigma}+\epsilon^{HF}_{a\mathbf{k}'\sigma'}-\epsilon^{HF}_{i\mathbf{q}\sigma}-\epsilon^{HF}_{i\mathbf{q}'\sigma'}}$$

LIMITATION: $\epsilon_{VBm} - G < \epsilon < \epsilon_{CBm} + G$

# Convergence with k-points of Dyson(D2)




Why is the convergence so slow?

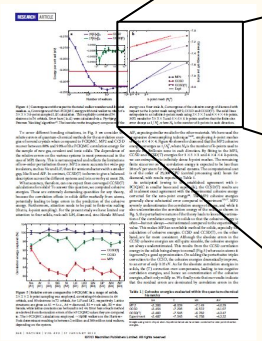
➢ Coulomb matrix singularity

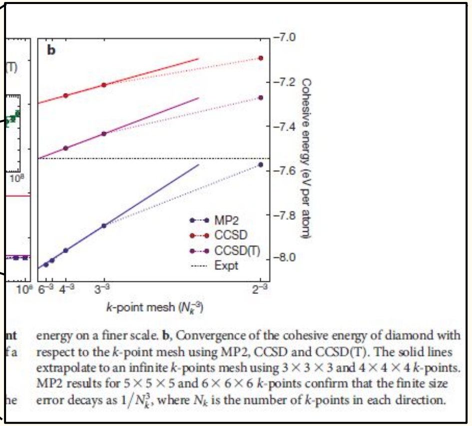
What is done so far?

- For HF:
  - Integrant ∝ V
  - CutCoulomb
  - Gygi-Baldereschi
- For MP2
  - Integrant ∝ $V^2$
  - Extrapolation
- For sp-MP2 and Dyson(D2)?
  - Integrant also ∝ $V^2$
  - Extrapolation?

# What is done until now for MP2

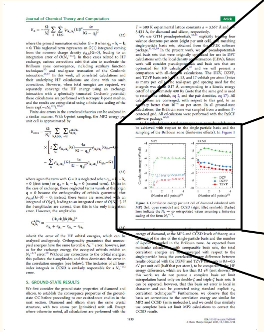
⇨ Extrapolation

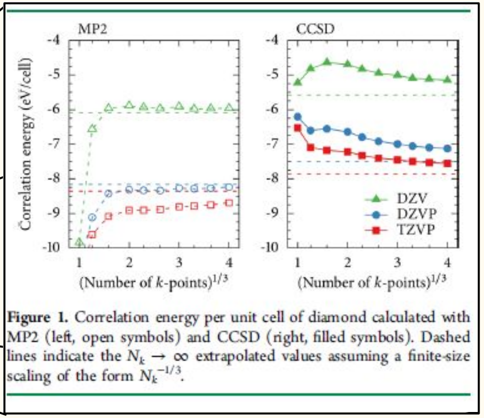





Booth GH, Grüneis A, Kresse G, Alavi A. Towards an exact description of electronic wavefunctions in real solids. Nature. 2013 Jan 17;493(7432):365-70.

Extrapolation with 1/N^3






Gaussian-Based Coupled-Cluster Theory for the Ground-State and Band Structure of Solids, James McClain, Qiming Sun, Garnet Kin-Lic Chan, and Timothy C. Berkelbach, *J. Chem. Theory Comput.* 2017, 13, 3, 1209–1218

Extrapolation with 1/N

How does the finite-size error scales for sp-MP2 and Dyson(D2)?

# Coulomb matrix elements

$$V_{p\mathbf{k}\sigma,s\mathbf{q}\sigma}^{q\mathbf{k}'\sigma',r\mathbf{q}'\sigma'} = \int d\mathbf{r} \int d\mathbf{r}' \psi^*_{p\mathbf{k}\sigma}(\mathbf{r})\psi^*_{q\mathbf{k}'\sigma'}(\mathbf{r}')\frac{1}{|\mathbf{r}-\mathbf{r}'|}\psi_{r\mathbf{q}'\sigma'}(\mathbf{r}')\psi_{s\mathbf{q}\sigma}(\mathbf{r})$$

## Auxiliary basis set

$$\psi^*_{p\mathbf{k}\sigma}(\mathbf{r})\psi_{q\mathbf{q}\sigma'}(\mathbf{r}) = \sum_{\mu} M^{\mu}_{p\mathbf{k}\sigma,q\mathbf{q}\sigma'} P^{\mathbf{q}-\mathbf{k}}_{\mu}(\mathbf{r})$$

$$P^{\mathbf{k}}_{\mu}(\mathbf{r}) = \sum_{\mathbf{R}} e^{i\mathbf{k}\mathbf{R}} P_{\mu}(\mathbf{r}-\mathbf{R}-\mathbf{R}_{at'})$$

$$V_{p\mathbf{k}\sigma,s\mathbf{q}\sigma}^{q\mathbf{k}'\sigma',r\mathbf{q}'\sigma'} = \delta_{\mathbf{q}-\mathbf{k},\mathbf{q}'-\mathbf{k}'} \sum_{\mu\mu'} M^{\mu}_{p\mathbf{k}\sigma,s\mathbf{q}\sigma} M^{\mu'}_{q\mathbf{k}'\sigma',r\mathbf{q}'\sigma'} V^{\mathbf{q}-\mathbf{k}}_{\mu,\mu'}$$

Where: $V^{\mathbf{p}}_{\mu,\mu'} = \sum_{\mathbf{R}} e^{i\mathbf{p}\mathbf{R}} \int d\mathbf{r} \int d\mathbf{r}' \frac{P_{\mu'}(\mathbf{r}-\mathbf{R})P_{\mu}(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}$

Real space summation

# Reciprocal space:

$$V^{\mathbf{p}}_{\mu,\mu'} = V_{\mathbf{G}} \sum_{\mathbf{G}} \tilde{P}^*_{\mu'}(\mathbf{G}-\mathbf{p})\tilde{P}_{\mu}(\mathbf{G}-\mathbf{p})\frac{4\pi}{|\mathbf{G}-\mathbf{p}|^2}$$

- Ewald summation applied
- Divergent for: $\mathbf{G}-\mathbf{p}=0$
- Integrable when integrand $\propto V^{\mathbf{p}}_{\mu,\mu'}$
- What happens with second order?

Integrand $\propto V^{\mathbf{p}}_{\mu,\mu'} V^{\mathbf{p}}_{\mu'',\mu'''}$

Cancelation of terms due to orthogonality

# Coulomb matrix elements

$$V^{q\mathbf{q}\sigma',r\mathbf{q}'\sigma'}_{p\mathbf{k}\sigma,s\mathbf{k}'\sigma} = \delta_{\mathbf{k}-\mathbf{k}',\mathbf{q}'-\mathbf{q}} \sum_{\mu\mu'} M^{\mu}_{p\mathbf{k}\sigma,s\mathbf{k}'\sigma} M^{\mu'}_{q\mathbf{q}\sigma',r\mathbf{q}'\sigma'} V^{\mathbf{k}-\mathbf{k}'}_{\mu,\mu'}$$

For: $\mathbf{G}_0 - \mathbf{p} = \mathbf{p}_0 \to 0$

$$V^{\mathbf{p}_0}_{\mu,\mu'} = V_N \Big[ \underbrace{\tilde{P}_\mu(\mathbf{p}_0)\tilde{P}_{\mu'}(\mathbf{p}_0)\tilde{V}(\mathbf{p}_0)}_{\text{Singular}} + \underbrace{\sum_{\mathbf{G}}{}' \tilde{P}^*_{\mu'}(\mathbf{G}-\mathbf{G}_0+\mathbf{p}_0)\tilde{P}_\mu(\mathbf{G}-\mathbf{G}_0+\mathbf{p}_0)\tilde{V}(\mathbf{G}-\mathbf{G}_0+\mathbf{p}_0)}_{\text{Well-defined}} \Big]$$

$$\tilde{P}_\mu(\mathbf{p}_0) = \int d\mathbf{r} e^{\mathbf{p}_0\mathbf{r}} P_\mu(\mathbf{r}) = \int d\mathbf{r} P_\mu(\mathbf{r}) + \mathbf{p}_0 \int d\mathbf{r}\mathbf{r} P_\mu(\mathbf{r}) + \dots$$

$$V^{sing} = \sum_{\mu\mu'} M^{\mu}_{p\mathbf{k}\sigma,s\mathbf{k}'\sigma} M^{\mu'}_{q\mathbf{q}\sigma',r\mathbf{q}'\sigma'} \tilde{P}_\mu(\mathbf{p}_0)\tilde{P}_{\mu'}(\mathbf{q}_0)\tilde{V}(\mathbf{p}_0) =$$

$$\frac{4\pi}{|\mathbf{p}_0|^2}\left(\delta_{ps} + \mathbf{p}_0 M^{\mu}_{q\mathbf{k}\sigma,s\mathbf{k}'\sigma} \int d\mathbf{r}\mathbf{r} P_\mu(\mathbf{r}) + \dots\right)\left(\delta_{qr} + \mathbf{p}_0 M^{\mu'}_{q\mathbf{q}\sigma',r\mathbf{q}'\sigma'} \int d\mathbf{r}\mathbf{r} P_{\mu'}(\mathbf{r}) + \dots\right)$$

# Rewriting orthogonality relation

$$\int d\mathbf{r} \psi_{a\sigma\mathbf{k}}(\mathbf{r})\psi_{i\sigma'\mathbf{k}'}(\mathbf{r}) = N_{\mathbf{G}} \delta_{\mathbf{k}-\mathbf{k}',\mathbf{G}} \delta_{a,i}\delta_{\sigma\sigma'}$$

↓ Auxiliary basis

$$\int d\mathbf{r} \sum_\mu M^{\mu}_{a\mathbf{k}\sigma,i\mathbf{k}'\sigma'} P^{\mathbf{k}-\mathbf{k}'}_\mu(\mathbf{r}) = N_{\mathbf{G}} \delta_{\mathbf{k}-\mathbf{k}',\mathbf{G}} \delta_{a,i}\delta_{\sigma\sigma'}$$

↓ For: $\mathbf{k}-\mathbf{k}' = \mathbf{G}_0$

$$\sum_\mu M^{\mu}_{a\mathbf{k}\sigma,i\mathbf{k}'\sigma'} \int d\mathbf{r} P_\mu(\mathbf{r}) = \delta_{a,i}\delta_{\sigma\sigma'}$$

↓ $\int d\mathbf{r} P_\mu(\mathbf{r}) = V_N \tilde{P}_\mu(0)$

$$\sum_\mu M^{\mu}_{a\mathbf{k}\sigma,i\mathbf{k}'\sigma'} V_N \tilde{P}_\mu(0) = \delta_{a,i}\delta_{\sigma\sigma'}$$

- For sp-MP2, p,s or q,r will be zero
- Still terms $\propto \frac{1}{|\mathbf{p}_0|}$
- We need to integrate:

$$\propto \left(V^{q\mathbf{q}\sigma',r\mathbf{q}'\sigma'}_{p\mathbf{k}\sigma,s\mathbf{k}'\sigma}\right)^2$$

# How can we integrate a function with an integrable singularity?

Skip singular point!

$$\int_V d(\mathbf{p}) f(\mathbf{p}) \to \frac{V}{N^3} \sum_{\mathbf{p} \neq 0} f(\mathbf{p})$$

How wrong are we?

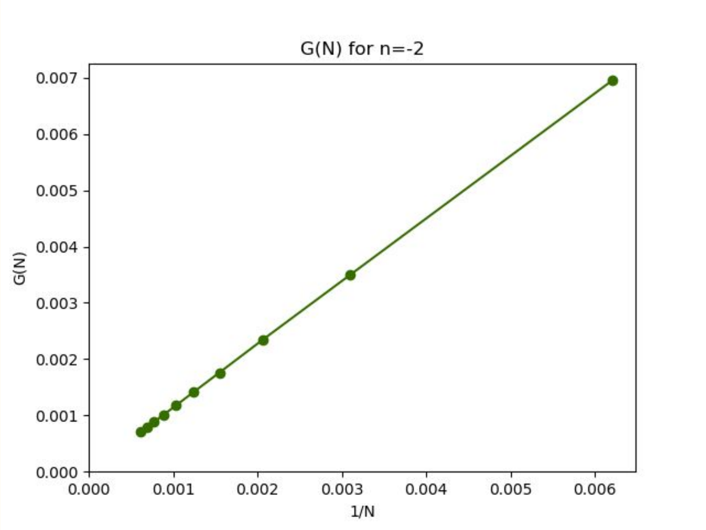
$$G(N) = \int_V dp f(\mathbf{p}) - \frac{V}{N^3} \sum_{\mathbf{p} \neq 0} f(\mathbf{p})$$

# Function with an Integrable Singularity

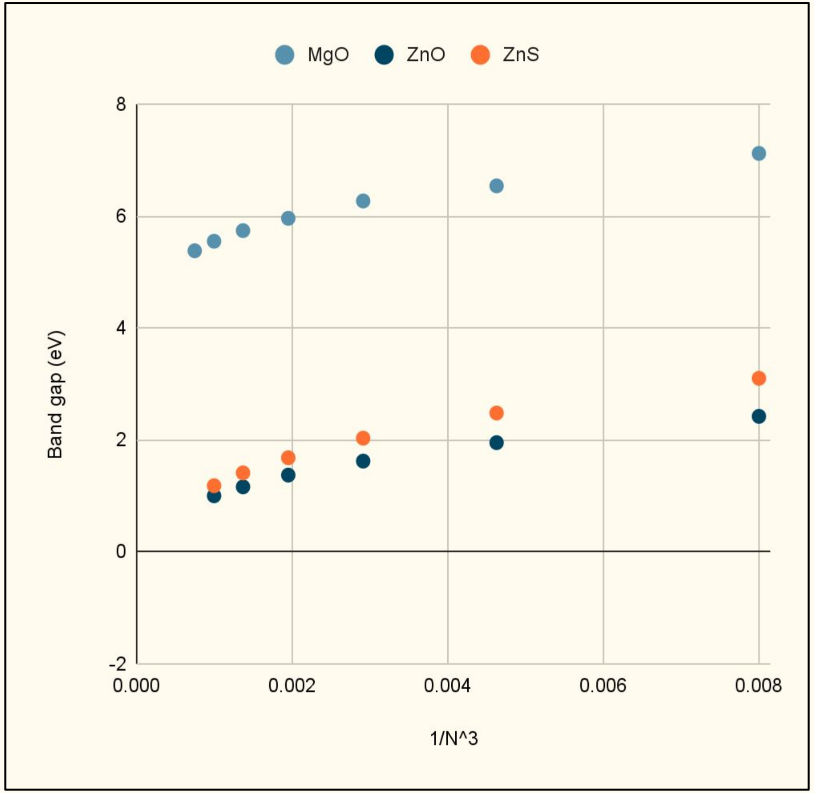
For $f_n(\theta,\phi)$ constant:

Laurent series: $f(\mathbf{p}) = \frac{f_{-2}((\theta,\phi))}{p^2} + \frac{f_{-1}(\theta,\phi)}{p^1} + \frac{f_0(\theta,\phi)}{p^0} + f_1(\theta,\phi)p + \dots$

Error: $G_n(N) = \int d\mathbf{p} f_n((\theta,\phi))p^n - \frac{V}{N^3}\sum_{\mathbf{p}}{}' f_n((\theta,\phi))p^n$

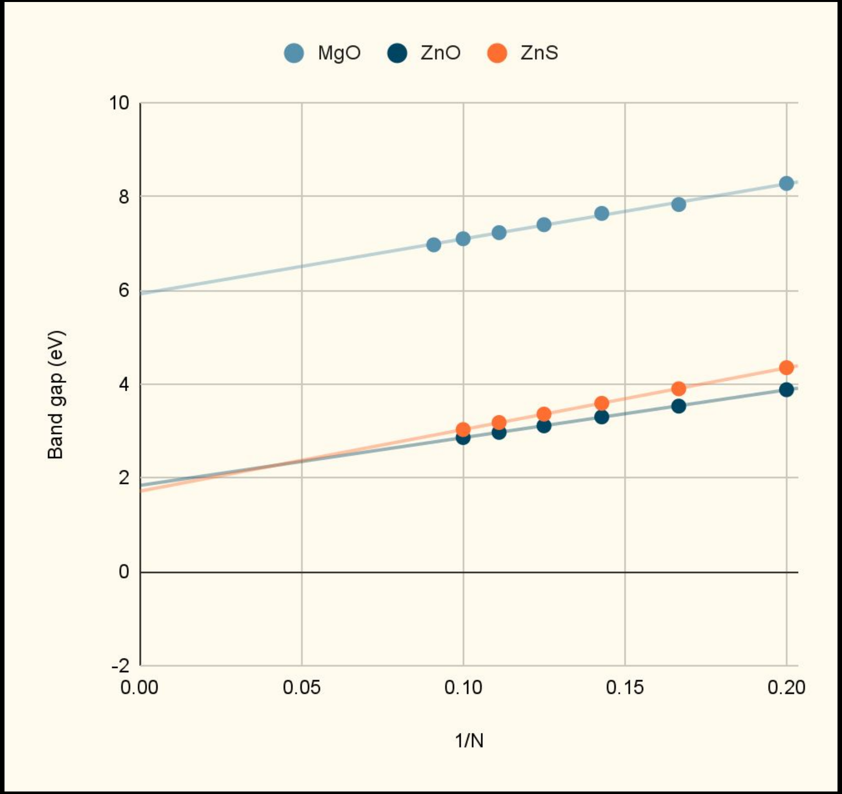


## Convergence with k-points as a function of $N^3$




sp-MP2 finite-size error does <u>NOT</u> scale as $1/N^3$

## Convergence with k-points as a function of N




sp-MP2 finite-size error scales as $1/N$

# How can we integrate a function with a singularity?

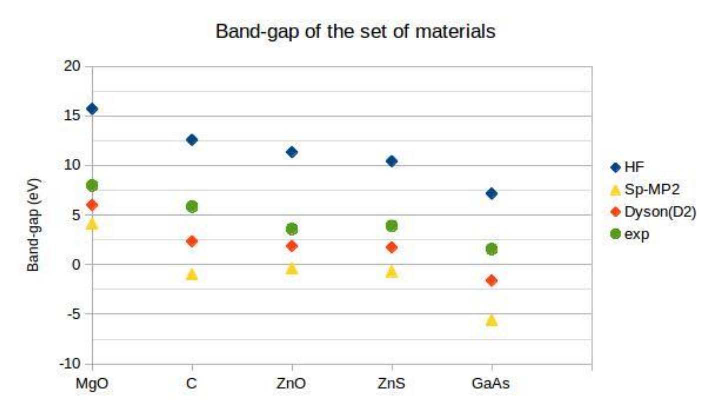
- Examine analytical behavior of integrand (is singularity power $\leq 2$?)
- Write the integrand in the form:

$$f(\mathbf{p}) = \frac{f_{-2}((\theta,\phi))}{p^2} + \frac{f_{-1}(\theta,\phi)}{p^1} + \frac{f_0(\theta,\phi)}{p^0} + f_1(\theta,\phi)p + \dots$$

- Apply the appropriate law for extrapolation

For sp-MP2 and Dyson(D2) finite size error: $\propto 1/N$

# Band gaps with sp-MP2 and Dyson(D2) after extrapolation



# Conclusions

- MBPT can approach s-p excitation energies with:
    1) Total energy differences
    2) Diagrammatic approach by Bartlett → 2nd order: sp-MP2
    3) Dyson equation→ 2nd order: Dyson(D2).
- No previous analysis of the convergence of sp-MP2 or Dyson(D2).
- Knowing the behavior of the integrand around the singularity, we can extrapolate properly to the dense grid limit.
- Our analytical and computational work shows that the finite size error of sp-MP2 and Dyson(D2) scales as 1/N.
- We report band gaps with sp-MP2 and Dyson(D2) extrapolated to dense k-grid limit
    - sp-MP2 underestimtes band gaps
    - Dyson(D2) improves significantly sp-MP2