# Finite-size error in periodic many-body perturbation and coupled cluster calculations

Lin Lin

Department of Mathematics, UC Berkeley
Lawrence Berkeley National Laboratory

62nd Sanibel Symposium,
February, 2023

Joint work with Xin Xing (Berkeley), Xiaoxu Li (Berkeley and BNU)

arXiv:2302.06043

# Outline

# Outline

# Quantum chemistry methods for periodic systems

- Treat $\psi_{n\mathbf{k}}(\mathbf{r})$ as a standard orbital: Supercell approach.
- Crystal momentum conservation:

$$\mathbf{k} + \mathbf{k}' = \mathbf{k}'' + \mathbf{k}''' + \mathbf{G}$$

- Hartree-Fock
- More recent post-HF quantum chemistry endeavors: MP2, MP3, ADC, RPA, CCSD, EOM-CCSD...[1]
- Discretizing Brillouin zone $N_{\mathbf{k}} \to \infty$: Thermodynamic limit (TDL). Finite $N_{\mathbf{k}} \to$ finite size effect.

[1] Bartlett, Chan, Berkelbach, Grüneis, Hirata, Pedersen, Scuseria, Shepherd, Sokolov, Zgid..

# MP2 for solids

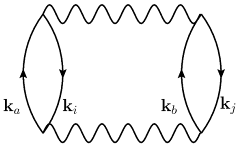
- Need **k**-dependence ($i, \mathbf{k}_i$ are independent variables)

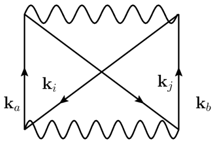
$$E_{\text{mp2}}(N_{\mathbf{k}}) = \frac{1}{N_{\mathbf{k}}} \sum_{\mathbf{k}_i \mathbf{k}_j \mathbf{k}_a \in \mathcal{K}} \sum_{ijab} \frac{\langle i\mathbf{k}_i, j\mathbf{k}_j | a\mathbf{k}_a, b\mathbf{k}_b \rangle \left(2 \langle a\mathbf{k}_a, b\mathbf{k}_b | i\mathbf{k}_i, j\mathbf{k}_j \rangle - \langle b\mathbf{k}_b, a\mathbf{k}_a | i\mathbf{k}_i, j\mathbf{k}_j \rangle\right)}{\varepsilon_{i\mathbf{k}_i} + \varepsilon_{j\mathbf{k}_j} - \varepsilon_{a\mathbf{k}_a} - \varepsilon_{b\mathbf{k}_b}}$$

- Costly to evaluate but increasingly gains attention.

- $\Omega$: unit cell with lattice $\mathbb{L}$;
  $\Omega^*$: reciprocal unit cell with lattice $\mathbb{L}^*$;
  $\mathcal{K}$: Monkhorst-Pack grid for discretizing $\Omega^*$.

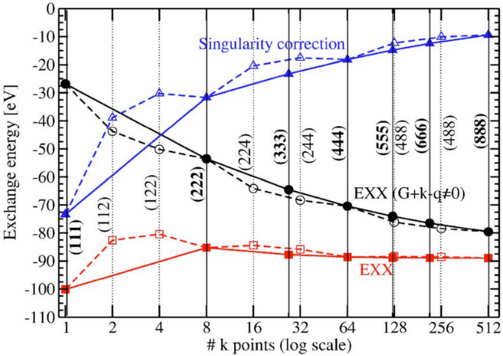
- Thermodynamic limit (TDL)
  $\mathcal{K} \to \Omega^* \quad \Rightarrow \quad \frac{1}{N_{\mathbf{k}}} \sum_{\mathbf{k} \in \mathcal{K}} \to \frac{1}{|\Omega^*|} \int_{\Omega^*} \mathrm{d}\mathbf{k}.$






Marsman et al JCP 2009; Gruneis, Marsman, Kresse JCP 2010; Müller, Paulus, PCCP 2012; McClain et al, JCTC 2017; Schäfer et al, JCP 2017; Banerjee, Sokolov, JCP 2020...

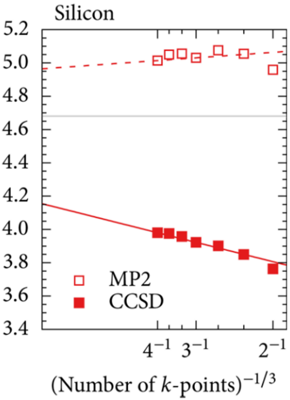
# Finite-size effects can be significant




Fock exchange energy in diamond.

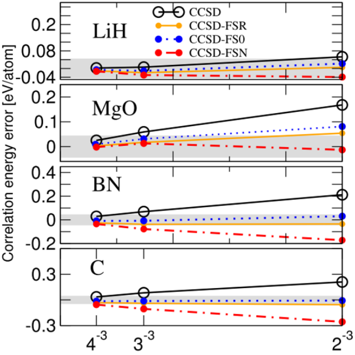
(Carrier, Rohra, Gorling PRB 2007)

# Finite-size scaling may not be obvious




$N_k^{-1/3}$ scaling

(McClain, Sun, Chan, Berkelbach, JCTC 2017)




$N_k^{-1}$ scaling

(Liao, Gruneis, JCP 2016)

# Finite-size error analysis and its correction

Analysis often for special systems (e.g. UEG). No general analysis.
A number of correction schemes to finite-size errors.

- Fock exchange[1] (special correction schemes available)
- Quantum Monte Carlo[2]
- MP2, coupled cluster theories[3]

Applicable to MP2/CC:

- Power-law extrapolation (curve-fitting)
- Twist averaging, special twist angle
- Structure factor extrapolation
- Staggered mesh method

[1] Gygi, Baldereschi 1986; Carrier et al 2007; Sundararaman, Arias 2013; Shepherd, Henderson, Scuseria, 2014...

[2] Fraser, Foulkes et al, 1996; Chiesa et al 2006; Drummond et al, 2008; Holzmann et al, 2016...

[3] Liao, Grueneis2016; Gruber et al, 2018; Mihm, McIsaac, Shepherd, 2019; Mihm et al, 2021

# Outline

# Main assumptions

Hartree-Fock band $\psi_{n\mathbf{k}}(\mathbf{r})$ and band energy $\varepsilon_{n\mathbf{k}}$.
$n$: general band. $i, j, k, l$ occupied band. $a, b, c, d$: virtual band

- 3D insulator with a indirect gap: $\varepsilon_{a\mathbf{k}_a} - \varepsilon_{i\mathbf{k}_i} > 0$.
- $\varepsilon_{n\mathbf{k}}, \psi_{n\mathbf{k}}(\mathbf{r})$ can be obtained exactly at any $\mathbf{k}$.
- Technical assumption (to simplify presentation):
  $\varepsilon_{n\mathbf{k}}, \psi_{n\mathbf{k}}(\mathbf{r})$ are smooth in $\mathbf{k}$. No topological obstruction.

# Main results

| Diagram | Method | Scaling |
| --- | --- | --- |
| Particle-hole | MP2[1] | $\mathcal{O}(N_{\mathbf{k}}^{-1})$ |
| | RPA[3] | $\mathcal{O}(N_{\mathbf{k}}^{-1})$ |
| | Staggered mesh MP2[1,2] | $\mathcal{O}(N_{\mathbf{k}}^{-5/3})$ |
| | Staggered mesh RPA[3] | $\mathcal{O}(N_{\mathbf{k}}^{-5/3})$ |
| Particle-hole<br>Particle-particle<br>Hole-hole | MP3[4] | $\mathcal{O}(N_{\mathbf{k}}^{-1/3})$ |
| | CCD[4] | $\mathcal{O}(N_{\mathbf{k}}^{-1/3})$ |

All assume exact HF orbitals and orbital energies.

Random phase approximation (RPA)=direct ring CCD (drCCD). Same result applies to second order screened exchange (SOSEX)

Improvement of staggered mesh is mainly for systems with high symmetries

[1] (Xing, Li, **Lin**, arXiv:2108.00206)

[2] (Xing, Li, **Lin**, JCTC 17, 4733, 2021)

[3] (Xing, **Lin**, JCTC 18, 763, 2022).

[4] (Xing, **Lin**, arXiv:2302.06043)

# Coupled cluster doubles (CCD)

- Simplest and yet representative CC theory.
- CCD amplitude equation as a fixed point iteration $I = (i\mathbf{k}_i)$ etc

$$t_{IJ}^{AB} = \frac{1}{\varepsilon_{IJ}^{AB}} \langle AB|IJ\rangle + \frac{1}{\varepsilon_{IJ}^{AB}} \mathcal{P}\left(\sum_{C} \kappa_C^A t_{IJ}^{CB} - \sum_{K} \kappa_I^K t_{KJ}^{AB}\right) + \frac{1}{\varepsilon_{IJ}^{AB}}\left[\frac{1}{N_{\mathbf{k}}}\sum_{KL} \chi_{IJ}^{KL} t_{KL}^{AB}\right.$$
$$\left. + \frac{1}{N_{\mathbf{k}}}\sum_{CD} \chi_{CD}^{AB} t_{IJ}^{CD} + \mathcal{P}\left(\frac{1}{N_{\mathbf{k}}}\sum_{KC} (2\chi_{IC}^{AK} - \chi_{CI}^{AK}) t_{KJ}^{CB} - \chi_{IC}^{AK} t_{KJ}^{BC} - \chi_{CJ}^{AK} t_{KI}^{BC}\right)\right].$$

- Starting from $t = 0$, fixed point iteration is a quasi-Newton iteration.
- Diagrammatically, CCD(1)=MP2, CCD(2) $\supset$ MP3, ... CCD($n$)

(Xing, **Lin**, arXiv:2302.06043)

# Convergence of CCD($n$)

**Theorem (Xing-Lin, 2302.06043)**

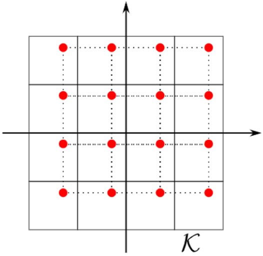
*For CCD($n$), using exact HF orbitals and orbital energies, the finite-size error scaling is:*

- *CC amplitude:* $\mathcal{O}(N_{\mathbf{k}}^{-1/3})$;
- *CC energy:* $\mathcal{O}(N_{\mathbf{k}}^{-1/3})$;
- *CC energy with exact amplitude:* $\mathcal{O}(N_{\mathbf{k}}^{-1})$.

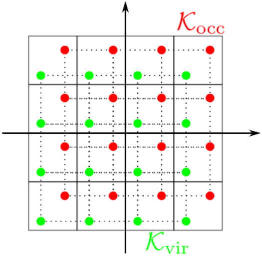
Path towards $\mathcal{O}(N_{\mathbf{k}}^{-1})$ convergence?
Correct the amplitude, or
(counter-intuitively) do not use exact orbital energy

Results for CCD($n$) can be boosted to converged CCD under additional assumptions

# Staggered mesh method




Standard mesh

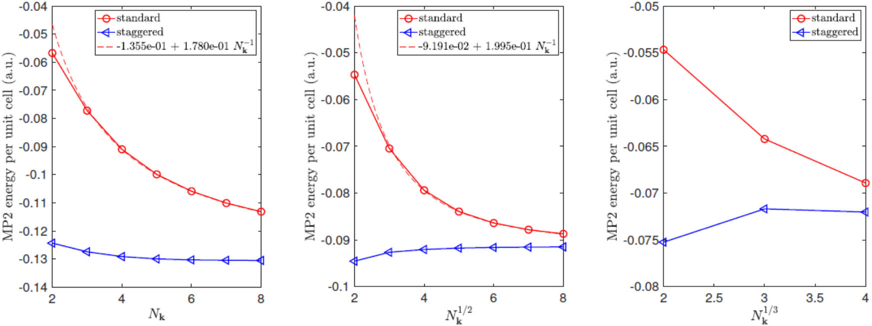



Staggered mesh

- Idea: two staggered Monkhorst-Pack meshes for occupied orbitals and virtual orbitals[1] .
- Avoid the zero momentum transfer $\mathbf{q} = \mathbf{k}_a - \mathbf{k}_i = \mathbf{0}$.

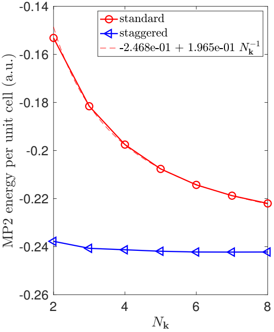
[1] (Xing, Li, **Lin**, JCTC 17, 4733, 2021)

# Silicon (gth-szv basis), MP2

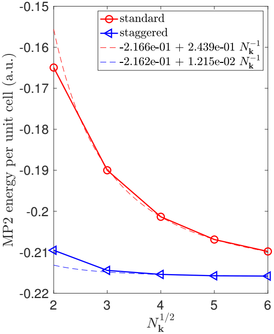



(a) Quasi-1D (b) Quasi-2D (c) 3D

# Silicon (gth-dzvp basis), MP2

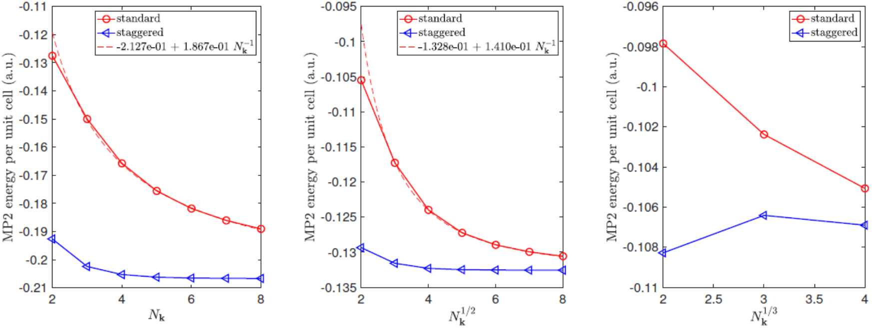



(a) Quasi-1D silicon



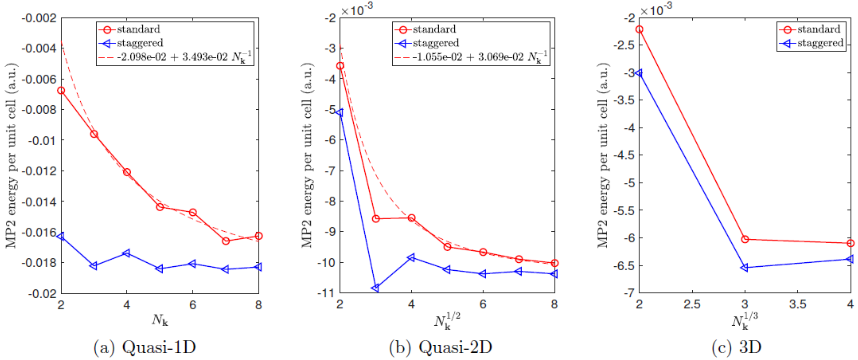

(b) Quasi-2D silicon

# Diamond (gth-szv basis), MP2




(a) Quasi-1D (b) Quasi-2D (c) 3D

# Periodic $H_2$-dimer (gth-szv basis), MP2

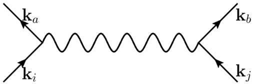



Significant improvement for quasi-1D systems.
Small/no improvement for some (anisotropic) quasi-2D / 3D systems
Similar results for RPA, drCCD, RPA+SOSEX[1]

[1] (Xin, **Lin**, JCTC 18, 763, 2022).

# Outline

# Origin of low-order power law scaling




- Crystal momentum conservation: $\mathbf{k}_i + \mathbf{k}_j - \mathbf{k}_a - \mathbf{k}_b = \mathbf{G}_{\mathbf{k}_i,\mathbf{k}_j}^{\mathbf{k}_a,\mathbf{k}_b} \in \mathbb{L}^*$
- Integrand is periodic w.r.t. all $\mathbf{k}$'s $\Rightarrow$ Fix $\mathbf{k}_i, \mathbf{k}_j, \mathbf{k}_a$, conceptually shift $\mathbf{k}_b$ s.t. $\mathbf{k}_b = \mathbf{k}_i + \mathbf{k}_j - \mathbf{k}_a$ $\Rightarrow$ Integrate w.r.t. $\mathbf{k}_i, \mathbf{k}_j, \mathbf{k}_a$.
- $\mathbf{q} = \mathbf{k}_a - \mathbf{k}_i = \mathbf{k}_j - \mathbf{k}_b$.
- Coulomb singularity $1/\left|\mathbf{q}+\mathbf{G}\right|^2$ $\Rightarrow$ Problematic when $\mathbf{q}+\mathbf{G}=\mathbf{0}$.
- Shift $\mathbf{q}$ to Brillouin zone $\Omega^*$. Then $\mathbf{q}+\mathbf{G}=\mathbf{0} \Leftrightarrow \mathbf{q}=\mathbf{G}=\mathbf{0}$.

# Interpreting finite-size error as quadrature error

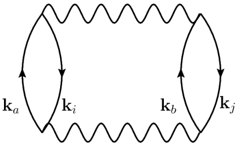
- Quadrature error of trapezoidal rule on a domain $V$ with a uniform grid $\mathcal{X}$ (Monkhorst-Pack grid)

$$\mathcal{E}_V(f,\mathcal{X}) = \int_V \mathrm{d}\mathbf{x} f(\mathbf{x}) - \frac{|V|}{|\mathcal{X}|}\sum_{\mathbf{x}_i\in\mathcal{X}} f(\mathbf{x}_i),$$

- For instance, finite-size error for MP2:

$$E_{\text{mp2}}^{\text{TDL}} - E_{\text{mp2}}(N_{\mathbf{k}}) = \frac{1}{|\Omega^*|^3}\mathcal{E}_{(\Omega^*)^{\times 3}}\left(\sum_{ijab} F_{\text{mp2,d}}^{ijab}(\mathbf{k}_i,\mathbf{k}_j,\mathbf{k}_a) + F_{\text{mp2,x}}^{ijab}(\mathbf{k}_i,\mathbf{k}_j,\mathbf{k}_a), (\mathcal{K})^{\times 3}\right).$$

# MP2, direct term

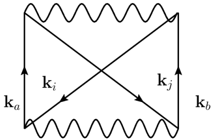



- Momentum transfer $\mathbf{q} = \mathbf{k}_a - \mathbf{k}_i = \mathbf{k}_j - \mathbf{k}_b$
- Change of variable $\mathbf{k}_a \to \mathbf{q}$
- Reduction of error (singularity only along $\mathbf{q}$ direction)

$$\mathcal{E}_{(\Omega^*)^{\times 3}}\left(\sum_{ijab} F^{ijab}_{\text{mp2,d}}(\mathbf{k}_i, \mathbf{k}_j, \mathbf{k}_a), (\mathcal{K})^{\times 3}\right) \lesssim \mathcal{E}_{(\Omega^*)^{\times 3}}\left(\widetilde{F}_{\text{mp2,d}}(\mathbf{k}_i, \mathbf{k}_j, \mathbf{q}), \mathcal{K} \times \mathcal{K} \times \mathcal{K}_{\mathbf{q}}\right)$$

$$\lesssim \max_{\mathbf{k}_i, \mathbf{k}_j} \mathcal{E}_{\Omega^*}\left(\widetilde{F}_{\text{mp2,d}}(\mathbf{k}_i, \mathbf{k}_j, \mathbf{q}), \mathcal{K}_{\mathbf{q}}\right)$$

# MP2, exchange term




Error sources: integrand and quadrature error

- Momentum transfer $\mathbf{q}_1 = \mathbf{k}_b - \mathbf{k}_i$ and $\mathbf{q}_2 = \mathbf{k}_i - \mathbf{k}_a$
- Change of variable $\mathbf{k}_a \to \mathbf{k}_i - \mathbf{q}_2$ and $\mathbf{k}_j \to \mathbf{k}_i + \mathbf{q}_1 - \mathbf{q}_2$.
- Reduction of error (singularity only along $\mathbf{q}_1, \mathbf{q}_2$ direction)

$$\mathcal{E}_{(\Omega^*)^{\times 3}}\left(\sum_{ijab} F^{ijab}_{\text{mp2,x}}(\mathbf{k}_i, \mathbf{k}_j, \mathbf{k}_a), (\mathcal{K})^{\times 3}\right) \lesssim \mathcal{E}_{(\Omega^*)^{\times 3}}\left(\widetilde{F}_{\text{mp2,x}}(\mathbf{k}_i, \mathbf{q}_1, \mathbf{q}_2), \mathcal{K} \times \mathcal{K}_{\mathbf{q}} \times \mathcal{K}_{\mathbf{q}}\right)$$

$$\lesssim \max_{\mathbf{k}_i} \mathcal{E}_{\Omega^* \times \Omega^*}\left(\widetilde{F}_{\text{mp2,x}}(\mathbf{k}_i, \mathbf{q}_1, \mathbf{q}_2), \mathcal{K}_{\mathbf{q}} \times \mathcal{K}_{\mathbf{q}}\right)$$

# Boils down to quadrature error of singular integrals

- MP2 direct:

$$\int_{\Omega^*} \frac{f_1(\mathbf{q})}{|\mathbf{q}|^2} \,\mathrm{d}\mathbf{q}, \quad \int_{\Omega^*} \frac{f_2(\mathbf{q})}{|\mathbf{q}|^4} \,\mathrm{d}\mathbf{q}.$$

  $f_1, f_2$ compactly supported in $\Omega^*$. Isolated singularity at $\mathbf{q} = \mathbf{0}$.
  $f_1(\mathbf{q}) = \mathcal{O}(|\mathbf{q}|^2), f_2(\mathbf{q}) = \mathcal{O}(|\mathbf{q}|^4)$

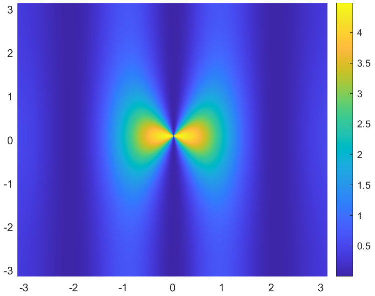
- MP2 exchange:

$$\int_{\Omega^* \times \Omega^*} \frac{f_3(\mathbf{q}_1, \mathbf{q}_2)}{|\mathbf{q}_1|^2 \, |\mathbf{q}_2|^2} \,\mathrm{d}\mathbf{q}_1 \,\mathrm{d}\mathbf{q}_2.$$

  $f_3$ compactly supported in $\Omega^*$. Isolated singularity at $\mathbf{q}_1 = \mathbf{q}_2 = \mathbf{0}$.
  $f_3(\mathbf{q}_1, \mathbf{q}_2) = \mathcal{O}(|\mathbf{q}_1|^2 \, |\mathbf{q}_2|^2)$.

# Singularity due to anisotropicity

$$f(\mathbf{q}) = \mathcal{O}(|\mathbf{q}|^2) \quad \not\Rightarrow \quad f(\mathbf{q}) = C\,|\mathbf{q}|\,{-}^2 + o(|\mathbf{q}|^2)$$



# Algebraic singularity

## Definition

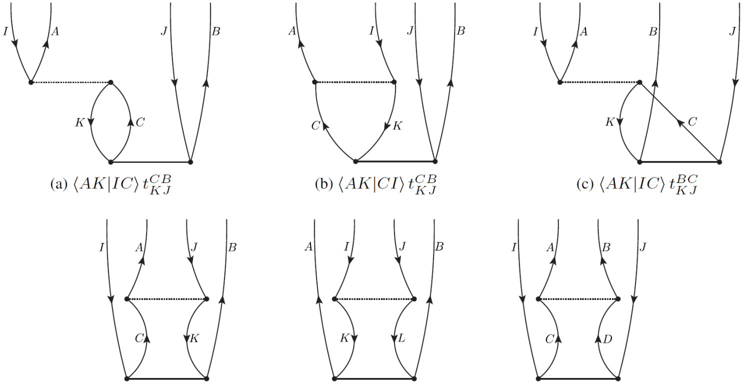
*A function $f(\mathbf{x})$ has algebraic singularity of order $\gamma$ at $\mathbf{x}_0 \in \mathbb{R}^d$ if*

$$\left|\frac{\partial^{\boldsymbol{\alpha}}}{\partial \mathbf{x}^{\boldsymbol{\alpha}}} f(\mathbf{x})\right| \leqslant C_{\boldsymbol{\alpha}} |\mathbf{x} - \mathbf{x}_0|^{\gamma - |\boldsymbol{\alpha}|}, \qquad \forall 0 < |\mathbf{x} - \mathbf{x}_0| < \delta,\ \forall \boldsymbol{\alpha} \geqslant 0.$$

| Example | Singular point and order $\gamma$ |
|---|---|
| $\frac{1}{\lvert\mathbf{q}\rvert^2}$ | $\mathbf{q} = \mathbf{0}$ order $-2$ |
| $\frac{\mathbf{q}^T M \mathbf{q}}{\lvert\mathbf{q}\rvert^2}$ | $\mathbf{q} = \mathbf{0}$ order 0 |
| $\frac{\mathbf{q}^T M_1 \mathbf{q}}{\lvert\mathbf{q}\rvert^2} \frac{(\mathbf{q}-\mathbf{z})^T M_2 (\mathbf{q}-\mathbf{z})}{\lvert\mathbf{q}-\mathbf{z}\rvert^2}$ | $\mathbf{q} = \mathbf{0}, \mathbf{z}$ order 0 |

# Diagrams in CCD (linear in $t$)

Fix $I, J, A, B$, focus on $K = (k\mathbf{k}_k)$ [1]
Dotted line: ERI. Solid line: $t$ amplitude




(a) $\langle AK|IC\rangle\, t_{KJ}^{CB}$ (b) $\langle AK|CI\rangle\, t_{KJ}^{CB}$ (c) $\langle AK|IC\rangle\, t_{KJ}^{BC}$

(d) $\langle AK|CJ\rangle\, t_{IK}^{CB}$ (e) $\langle KL|IJ\rangle\, t_{KL}^{AB}$ (f) $\langle AB|CD\rangle\, t_{IJ}^{CD}$

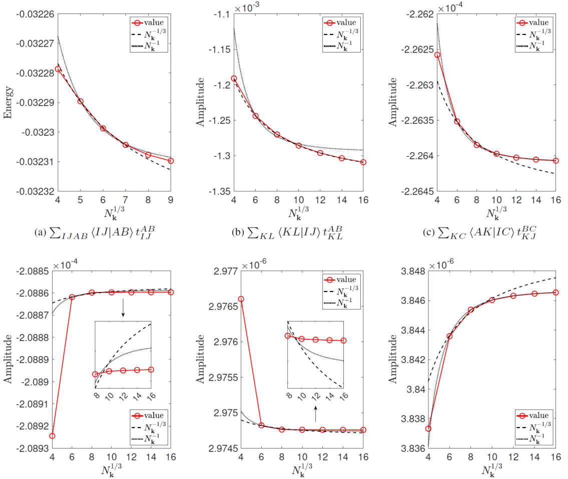
[1] $C = (c\mathbf{k}_c)$ is determined by crystal momentum conservation.

# Bounding quadrature error in CCD

| Description | Singular points and order | Estimate |
| --- | --- | --- |
| $\int_V \mathrm{d}\mathbf{x} f(\mathbf{x})$ | None | Super-Algebraic |
| $\int_V \mathrm{d}\mathbf{x} f(\mathbf{x})$ | $\mathbf{x} = \mathbf{0}$ of order $\gamma$ | $m^{-(d+\gamma)}$ |
| $\int_V \mathrm{d}\mathbf{x} f_1(\mathbf{x}) f_2(\mathbf{x})$ | $f_1(\mathbf{x})$: $\mathbf{x} = \mathbf{0}$ of order $\gamma$; $f_2(\mathbf{x})$: $\mathbf{x} = \mathbf{z}$ of order 0 | $m^{-(d+\gamma)}$ |
| $\int_{V\times V} \mathrm{d}\mathbf{x}_1 \, \mathrm{d}\mathbf{x}_2 f_1(\mathbf{x}_1, \mathbf{x}_2) f_2(\mathbf{x}_1, \mathbf{x}_2)$ | $f_i(\mathbf{x}_1, \mathbf{x}_2)$: $\mathbf{x}_i = \mathbf{0}$ of order $\gamma_i$, $i = 1, 2$ | $m^{-(d+\min_i \gamma_i)}$ |
| $\int_{V\times V} \mathrm{d}\mathbf{x}_1 \, \mathrm{d}\mathbf{x}_2 f_1(\mathbf{x}_1, \mathbf{x}_2) f_2(\mathbf{x}_1, \mathbf{x}_2) f_3(\mathbf{x}_1, \mathbf{x}_2 \pm \mathbf{x}_1)$ | $f_i(\mathbf{x}_1, \mathbf{x}_2)$: $\mathbf{x}_i = \mathbf{0}$ of order $\gamma_i$, $i = 1, 2$; $f_3(\mathbf{x}_1, \mathbf{z})$: $\mathbf{z} = \mathbf{0}$ of order 0 | $m^{-(d+\min_i \gamma_i)}$ |

| | Type | Terms | Error Estimate |
| --- | --- | --- | --- |
| Energy | | $\sum_{IJAB} \langle IJ\|AB\rangle \, t_{IJ}^{AB}$, $\sum_{IJAB} \langle IJ\|BA\rangle \, t_{IJ}^{AB}$ | $N_{\mathbf{k}}^{-1}$ |
| Amplitude | constant | $\langle AB\|IJ\rangle$ | 0 |
| | linear | $\langle KL\|IJ\rangle \, t_{KL}^{AB}$, $\langle AB\|CD\rangle \, t_{IJ}^{CD}$, $\langle AK\|CI\rangle \, t_{KJ}^{CB}$, $\langle AK\|CJ\rangle \, t_{KI}^{BC}$ | $N_{\mathbf{k}}^{-\frac{1}{3}}$ |
| | | $\langle AK\|IC\rangle \, t_{KJ}^{BC}$ | $N_{\mathbf{k}}^{-1}$ |
| | | $\langle AK\|IC\rangle \, t_{KJ}^{CB}$ | Super-Algebraic |
| | quadratic | $\langle LK\|DC\rangle \, t_{IL}^{AD} t_{KJ}^{CB}$ | Super-Algebraic |
| | | all other terms | $N_{\mathbf{k}}^{-1}$ |

# Quadrature error




(a) $\sum_{IJAB} \langle IJ|AB\rangle t_{IJ}^{AB}$ (b) $\sum_{KL} \langle KL|IJ\rangle t_{KL}^{AB}$ (c) $\sum_{KC} \langle AK|IC\rangle t_{KJ}^{BC}$

(d) $\sum_{KC} \langle AK|IC\rangle t_{KJ}^{CB}$ (e) $\sum_{KLCD} \langle LK|DC\rangle t_{IL}^{AD} t_{KJ}^{CB}$ (f) $\sum_{KLCD} \langle KL|CD\rangle t_{IJ}^{CD} t_{KL}^{AB}$

Use model potential with exact amplitude from MP2/CCD(1).

# Future works

- CCD with $N_{\mathbf{k}}^{-1}$ convergence: Madelung constant correction and singularity subtraction. Implication in MP3.
- Staggered mesh for MP3, CCD.
- EOM-CCD, GW, ADC as quadrature analysis

# Acknowledgment

## Thank you for your attention!

Lin Lin
https://math.berkeley.edu/~linlin/