Finite-size error in quantum chemistry methods for periodic systems

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Joint work with

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- Martin Head-Gordon (Berkeley)

Outline

Electronic structure theory and earlier works on DFT

Finite-size error and quantum chemistry methods

Main theoretical results and proof ideas

Conclusion

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Electronic structure theory

- Born-Oppenheimer approximation: atoms are fixed at $\{\boldsymbol{R}_I\}_{I=1}^{M}$.
- Quantum many body Hamiltonian for electrons

$$H = -\frac{1}{2}\sum_{i=1}^{N_e}\Delta_{\boldsymbol{r}_i} - \sum_{I=1}^{M}\sum_{i=1}^{N_e}\frac{Z_I}{|\boldsymbol{r}_i - \boldsymbol{R}_I|} + \frac{1}{2}\sum_{i,j=1,i\neq j}^{N_e}\frac{1}{|\boldsymbol{r}_i - \boldsymbol{r}_j|}$$

- Ground state energy: an eigenvalue problem (EVP)

$$H\,|\Psi_0\rangle = E_0\left(\{\boldsymbol{R}_I\}_{I=1}^{M}\right)|\Psi_0\rangle$$

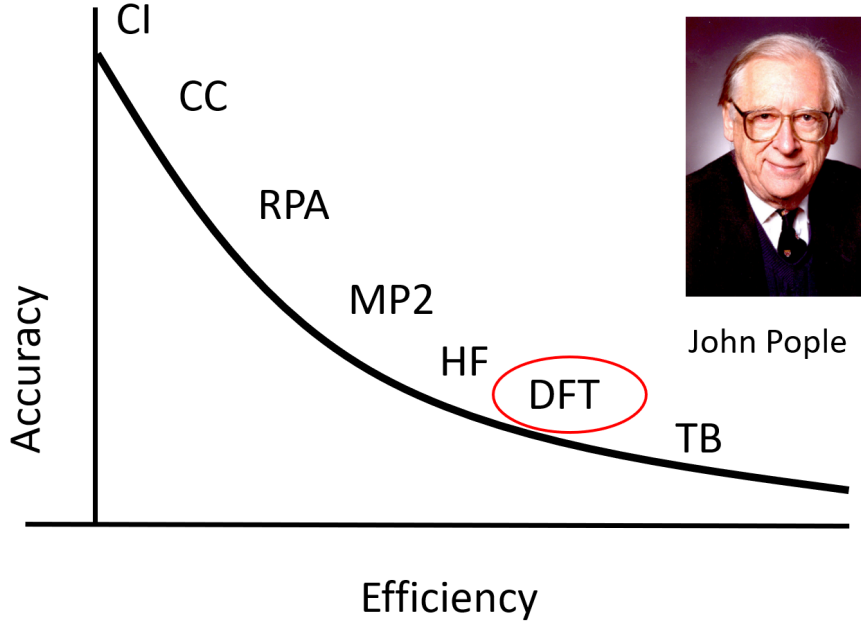
Linear PDE EVP in $\mathbb{R}^{3N_e}$.

Curse of dimensionality

The fundamental laws necessary to the mathematical treatment of large parts of physics and the whole of chemistry are thus fully known, and the difficulty lies only in the fact that application of these laws leads to equations that are too complex to be solved.

–P. Dirac, 1929

Pople diagram



John Pople

Walter Kohn

- Kohn-Sham density functional theory (KSDFT): best compromise between efficiency and accuracy. Most widely used electronic structure theory.

(Kohn, Sham, 1965); Nobel Prize in Chemistry 1998

Kohn-Sham density functional theory

$$\left(-\frac{1}{2}\Delta + V_{en}(\mathbf{r}) + V_{\text{hxc}}^{\text{DFT}}[\rho](\mathbf{r})\right)\psi_i(\mathbf{r}) = \varepsilon_i\psi_i(\mathbf{r}), \quad i = 1, \ldots, N_e$$

$$P(\mathbf{r}, \mathbf{r}') = \sum_{i=1}^{N_e} \psi_i(\mathbf{r})\psi_i^*(\mathbf{r}'), \quad \rho(\mathbf{r}) = P(\mathbf{r}, \mathbf{r})$$

- $V_{\text{hxc}}^{\text{DFT}}[\rho](\mathbf{r})$ depends only on density ρ
- Dimension reduction:
  1 Linear EVP in $\mathbb{R}^{3N_e}$ $\Rightarrow$ N_e coupled nonlinear EVP in $\mathbb{R}^3$

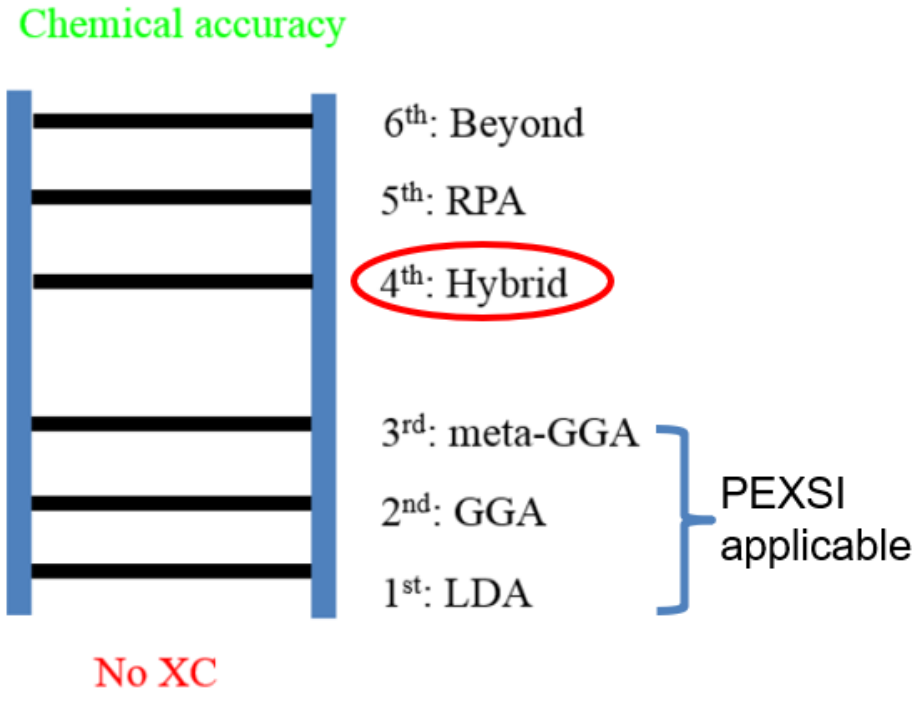
[**L.**, Lu, *A Mathematical Introduction to Electronic Structure Theory*, SIAM, 2019]

[**L.**, Lu, Ying, *Numerical methods for Kohn-Sham density functional theory*, Acta Numerica 2019]

KSDFT with hybrid exchange correlation functional

John Perdew

Axel Becke



Density-functional thermochemistry. I. **The effect** of **the exchange**-only gradient correction

AD **Becke** - **The** Journal of chemical physics, 1992 - pubs.aip.org

… **the** kinetic energy of **the** noninteracting reference system, **the** second and third terms are **the** nuclear interaction energy and **the** … , and **the** last term Exc is **the** density-functional **exchange**-…

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KSDFT with hybrid exchange correlation functional (Hartree-Fock-like)

$$\left(-\frac{1}{2}\Delta + V_{en}(\mathbf{r}) + V_{\text{hxc}}^{\text{DFT}}[\rho](\mathbf{r})\right)\psi_i(\mathbf{r}) + \alpha\big(V_X[P]\psi_i\big)(\mathbf{r}) = \varepsilon_i\psi_i(\mathbf{r}),$$

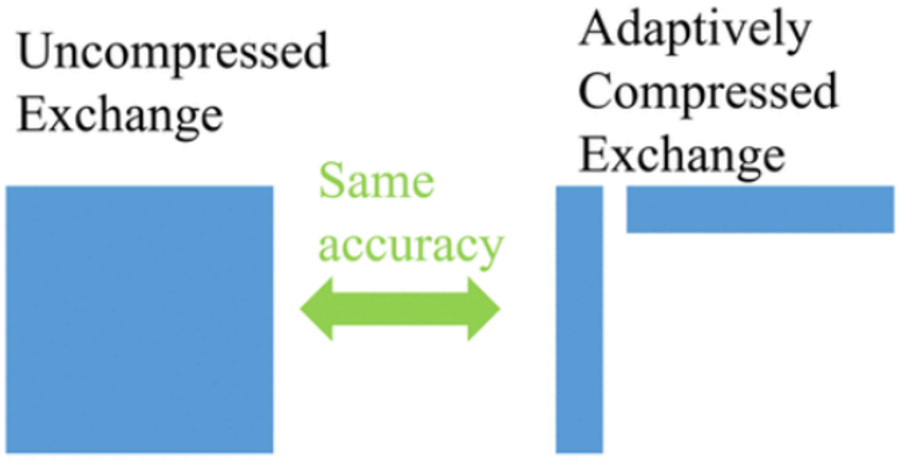
$$P(\mathbf{r},\mathbf{r}') = \sum_{i=1}^{N_e}\psi_i(\mathbf{r})\psi_i^*(\mathbf{r}'), \quad \rho(\mathbf{r}) = P(\mathbf{r},\mathbf{r})$$

- Fock exchange operator depending on density matrix P

$$\big(V_X[P]\psi_i\big)(\mathbf{r}) = -\int \frac{P(\mathbf{r},\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}\psi_i(\mathbf{r}')\,\mathrm{d}\mathbf{r}'.$$

- N_e coupled nonlinear integro-differential EVP in $\mathbb{R}^3$.
- Repeated application of the full rank Fock exchange operator costs >95% of the runtime in standard hybrid DFT calculations

Adaptively compressed exchange operator (ACE)



[**L.**, J. Chem. Theory Comput. 12, 2242, 2016]
[**L.**, Lindsey, Commun. Pure Appl. Math. 2019]

ACE is default in VASP (and many other packages)

LFOCKACE

Page Discussion Read View source View history

LFOCKACE = .TRUE. | .FALSE.
Default: **LFOCKACE** = .TRUE.

Default: **LFOCKACE** = .TRUE. for VASP.6
= N/A for VASP.5.X and older

Description: **LFOCKACE** determines whether the Adaptively Compressed Exchange Operator is used.[1]

- N.B.:Available for CPU and OpenACC version of VASP.6 when compiled with -Dfock_dblbuf.

For **LFOCKACE**=.TRUE. the Cholesky decomposition $X = LL^{\dagger}$ of the Fock exchange matrix $X_{ij} = \langle \tilde{\psi}_i \mid \tilde{V}_X \mid \tilde{\psi}_j \rangle$ is calculated and the adaptively compressed exchange operator $\tilde{V}_{ACE} = -\sum_i \mid \tilde{X}_i \rangle \langle \tilde{X}_i \mid$ is used for the action of the Fock exchange on the pseudo orbitals. This method can be used for hybrid functionals in combination with the Davidson algorithm (ALGO=Normal) to save a factor of ≈ 3 in computation time.

For **LFOCKACE**=.FALSE. the conventional orbital representation is used.

Note: it is good scientific practice to cite the original publication (Ref. [1]) if you use this feature. The feature is used by default, if the Davidson algorithm (ALGO = Normal) is used; ACE is not used for ALGO = Damped or ALGO = All.

Related tags and articles

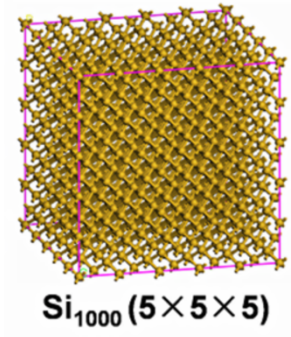
AEXX, AEXX, AGGAX, AGGAC, LHFCALC, List of hybrid functionals, Hybrid functionals: formalism

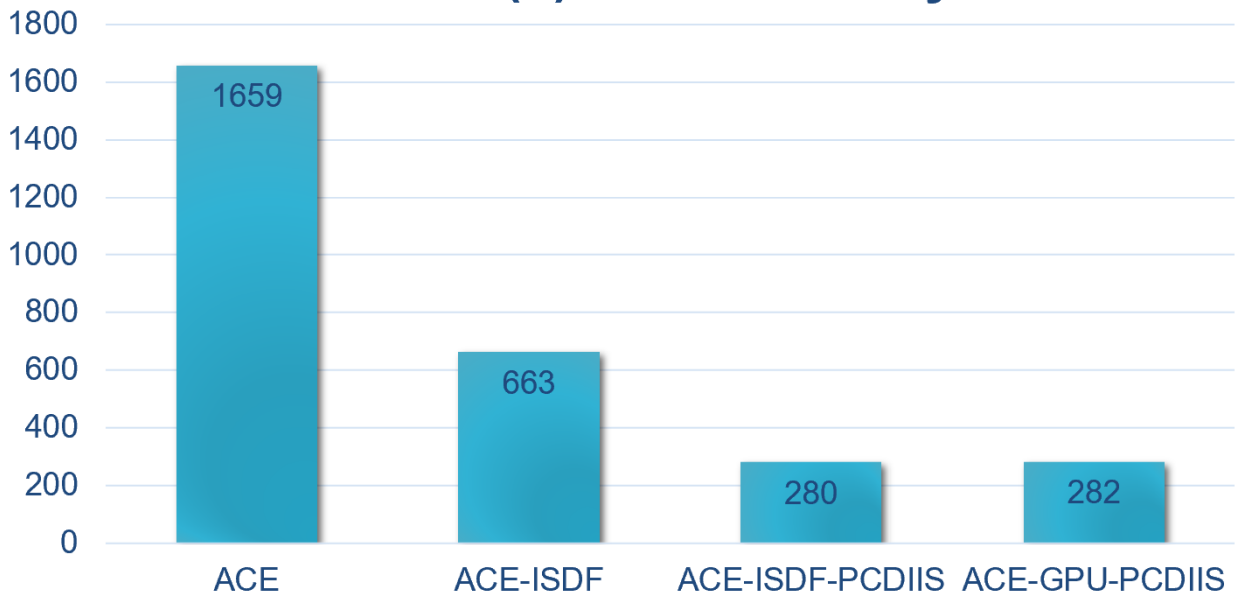
Examples that use this tag

References

1. ↑ [a] [b] L. Lin, J. Chem. Theory Comput. **12**, 2242-2249 (2016).

Reduction of computational time





Hybrid(conventional): 12425 s

44 x speed up

~ GGA time (more iterations)

Adaptively compressed exchange (ACE) integrated into ABINIT, PWMat, Quantum ATK, Quantum ESPRESSO, VASP

Algorithms beyond mean-field-like electronic structure theories? (2018–present)

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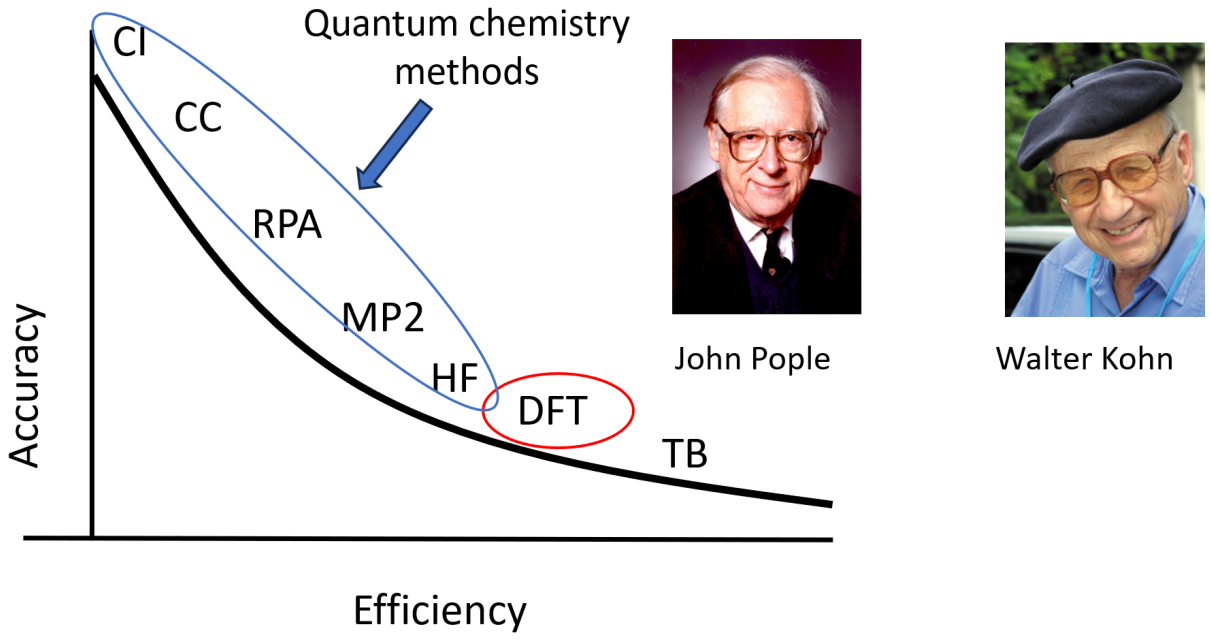
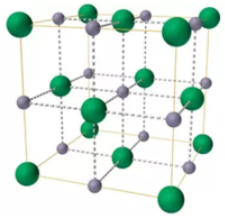


- Quantum chemistry methods: systematically improvable.
- CCSD(T): Coupled cluster (CC) singles, doubles and (perturbative) triples: gold standard of molecular chemistry.
- In the ML era: more accurate training data.

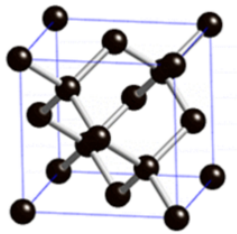
Periodic systems

Crystal System Table

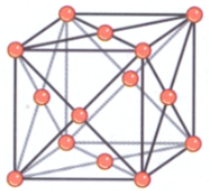
System	Axial length	Axial Angle	Unit Cell Geometry
Cubic	a = b = c	α = β = γ = 90°	
Tetragonal	a = b ≠ c	α = β = γ = 90°	
Orthorhombic	a ≠ b ≠ c	α = β = γ = 90°	
Rhombohedral	a = b = c	α = β = γ ≠ 90°	
Hexagonal	a = b ≠ c	α = β = 90°, γ=120°	
Monoclinic	a ≠ b ≠ c	α = γ = 90°, β≠90°	
Triclinic	a ≠ b ≠ c	α ≠ β ≠ γ	



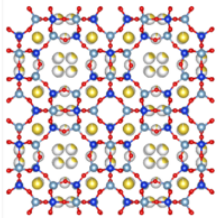
NaCl



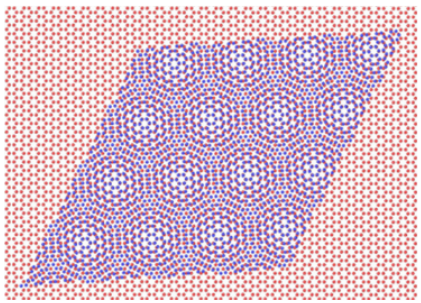
Diamond



Al/Cu

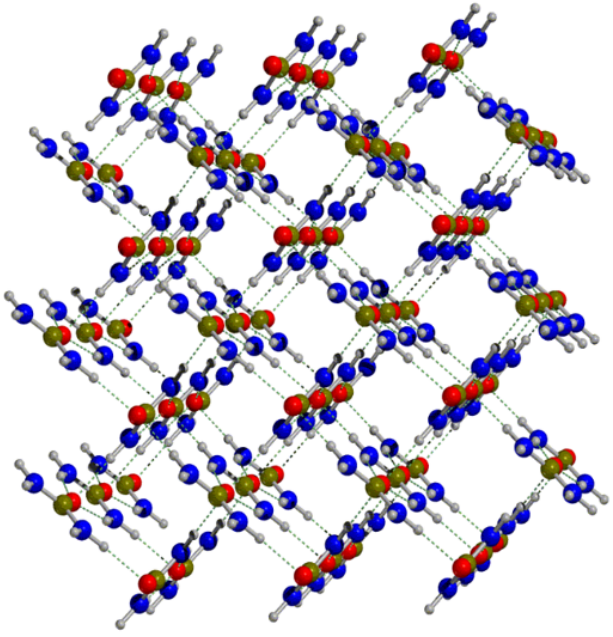


Zeolite Na-A



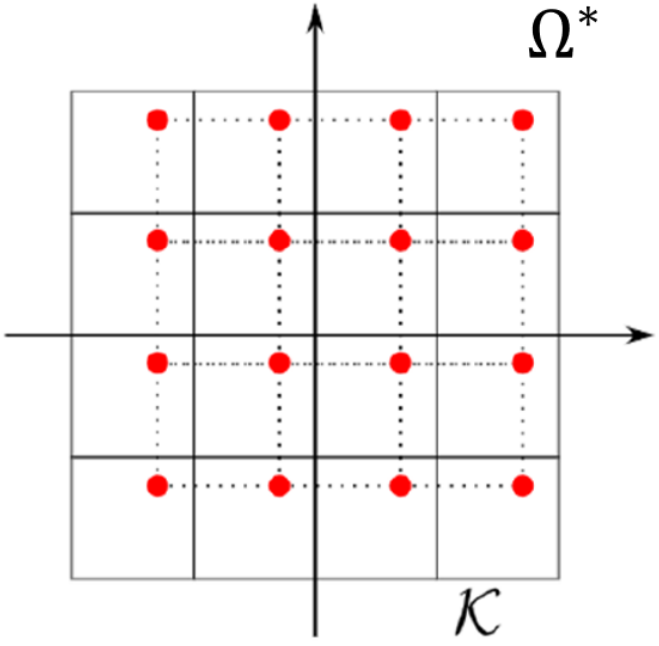
"Magic angle" twisted bilayer graphene

Two (equivalent) perspectives of periodic systems



Real space (supercell)

Translation invariance



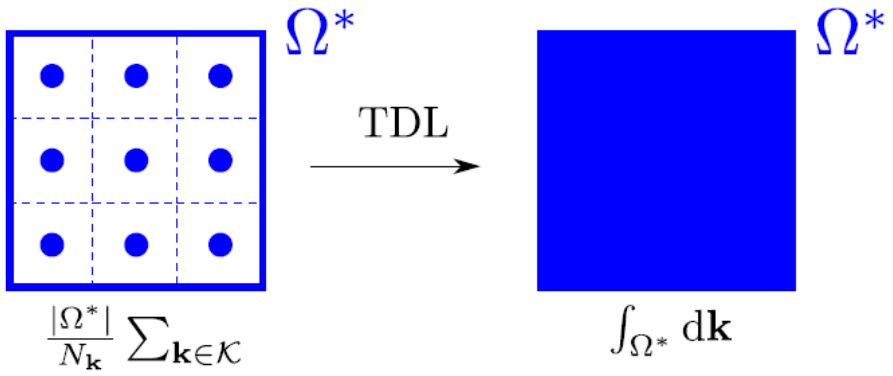
Reciprocal space (unit cell)

Crystal Momentum conservation

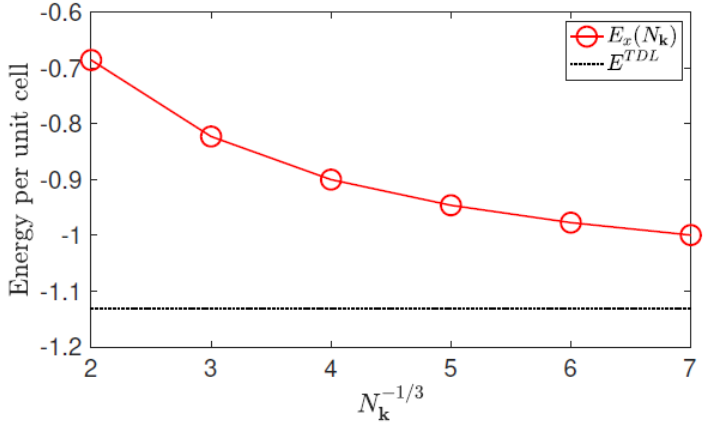
$$\mathbf{k} + \mathbf{k}' = \mathbf{k}'' + \mathbf{k}''' + \mathbf{G}$$

Finite-size effect (FSE)

- Thermodynamic limit (TDL): $N_{\mathbf{k}} = |\mathcal{K}| \to \infty$. For every level of theory.



- Convergence to TDL: $E(N_{\mathbf{k}}) \xrightarrow{N_{\mathbf{k}}\to\infty} E^{\mathrm{TDL}}$. Can be slow!



Quantum chemistry methods for periodic systems

- Hartree-Fock (and variants) widely used for periodic systems
- More recent: Post-HF methods for periodic systems: MP2, MP3, ADC, RPA, CCSD, CCSD(T), EOM-CCSD...[1]
- Approach TDL via power-law extrapolation

$$E(N_{\mathbf{k}}) \approx E^{\mathrm{TDL}} + CN_{\mathbf{k}}^{-\alpha}$$

- $N_{\mathbf{k}} \propto$ volume of supercell; $N_{\mathbf{k}}^{\frac{1}{3}} \propto$ length of supercell $\alpha = 1$: Inverse volume scaling; $\alpha = \frac{1}{3}$: Inverse length scaling;
- Resolve by brute force is often prohibitively expensive: cost of CCSD(T) scales as $\mathcal{O}(N_{\mathbf{k}}^5)$ (with crystal momentum conservation). Inverse linear scaling: increase cost $(2^3)^5 = 32768$ times, reduce error by just $\frac{1}{2}$!

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

Status of FSE analysis and its correction

- Analysis often for special systems (e.g. uniform electron gas)[1] especially from Quantum Monte Carlo community.
- To our knowledge, no rigorous analysis for general systems[2].
- For quantum chemistry methods[3], empirical correction methods: ng constant; Power-law extrapolation; Twist averaging; Structure factor extrapolation

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

[2] For HF, analysis can be performed in real space but difficult to generalize. This also leads to special correction schemes: Gygi, Baldereschi 1986; Carrier et al 2007; Sundararaman, Arias 2013; Shepherd, Henderson, Scuseria, 2014...

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

An example of new results: Fock exchange energy

$$E_{\mathbf{X}}^{\mathrm{TDL}} - E_{\mathbf{X}}\left(N_{\mathbf{k}}\right) = \frac{a_0}{N_{\mathbf{k}}^{\frac{1}{3}}} + \frac{a_1}{N_{\mathbf{k}}} + \frac{a_2}{N_{\mathbf{k}}^{\frac{5}{3}}} + \cdots$$

Theorem (Xing–Li–L., 2024, Fock exchange energy)

In the absence of finite-size corrections,

$$\left|E_{\mathbf{X}}^{\mathrm{TDL}} - E_{\mathbf{X}}\left(N_{\mathbf{k}}\right)\right| = \widetilde{\mathcal{O}}\left(N_{\mathbf{k}}^{-\frac{1}{3}}\right).$$

Madelung constant correction evaluates a_0 up to h.o.t. then

$$\left|E_{\mathbf{X}}^{\mathrm{TDL}} - E_{\mathbf{X}}^{\mathrm{corr}}\left(N_{\mathbf{k}}\right)\right| = \widetilde{\mathcal{O}}\left(N_{\mathbf{k}}^{-1}\right).$$

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Reciprocal space treatment of periodic systems

- Periodic system with unit cell Ω and Bravais lattice $\mathbb{L}$. Reciprocal lattice $\mathbb{L}^*$ and reciprocal unit cell (Brillouin zone) Ω^*.
- Monkhorst-Pack mesh $\mathcal{K}$ of size $N_{\mathbf{k}}^{\frac{1}{3}} \times N_{\mathbf{k}}^{\frac{1}{3}} \times N_{\mathbf{k}}^{\frac{1}{3}}$ in Ω^*
- Eigenvectors (orbitals) and eigenvalues (orbital energies) of Hartree-Fock Hamiltonian on $\mathcal{K}$

$$\left\{ \psi_{n\mathbf{k}}(\mathbf{r}) = \frac{1}{\sqrt{N_{\mathbf{k}}}} e^{i\mathbf{k}\cdot\mathbf{r}} u_{n\mathbf{k}}(\mathbf{r}), \varepsilon_{n\mathbf{k}} \right\} \quad \text{for } \mathbf{k} \in \mathcal{K}$$

$u_{n\mathbf{k}}(\mathbf{r})$ is periodic: $u_{n\mathbf{k}}(\mathbf{r}+\mathbf{R}) = u_{n\mathbf{k}}(\mathbf{r}), \quad \mathbf{R} \in \mathbb{L}$.

- Occupied orbitals, i,j,k,l; Unoccupied orbitals, a,b,c,d; General orbitals, m,n,p,q,r,s
- Electron density: $\rho_{N_{\mathbf{k}}}(\mathbf{r}) = \frac{1}{N_{\mathbf{k}}} \sum_{\mathbf{k}\in\mathcal{K}} \sum_i |u_{i\mathbf{k}}(\mathbf{r})|^2$

Energies

- Pair product of orbitals

$$\varrho_{n'\mathbf{k}',n\mathbf{k}}(\mathbf{r}) = \overline{u}_{n'\mathbf{k}'}(\mathbf{r})u_{n\mathbf{k}}(\mathbf{r}) = \frac{1}{|\Omega|}\sum_{\mathbf{G}\in\mathbb{L}^*}\hat{\varrho}_{n'\mathbf{k}',n\mathbf{k}}(\mathbf{G})e^{i\mathbf{G}\cdot\mathbf{r}}.$$

- Two-electron repulsion integral (ERI) $\langle n_1\mathbf{k}_1, n_2\mathbf{k}_2 | n_3\mathbf{k}_3, n_4\mathbf{k}_4\rangle$:

$$\frac{1}{|\Omega|\,N_{\mathbf{k}}}\sum_{\mathbf{G}\in\mathbb{L}^*}{}'\frac{4\pi}{|\mathbf{q}+\mathbf{G}|^2}\hat{\varrho}_{n_1\mathbf{k}_1,n_3\mathbf{k}_3}(\mathbf{G})\hat{\varrho}_{n_2\mathbf{k}_2,n_4\mathbf{k}_4}(\mathbf{G}^{\mathbf{k}_3,\mathbf{k}_4}_{\mathbf{k}_1,\mathbf{k}_2}-\mathbf{G})$$

- Fock Exchange energy

$$E_{\mathrm{X}}(N_{\mathbf{k}}) = -\frac{1}{N_{\mathbf{k}}}\sum_{ij}\sum_{\mathbf{k}_i\mathbf{k}_j\in\mathcal{K}}\langle i\mathbf{k}_i, j\mathbf{k}_j | j\mathbf{k}_j, i\mathbf{k}_i\rangle$$

Beyond Hartree-Fock

- Total energy = Hartree Fock energy + Correlation energy
- Nesbet's theorem for correlation energy

$$E_{\#}^{N_{\mathbf{k}}} = \frac{1}{N_{\mathbf{k}}^3} \sum_{\mathbf{k}_i \mathbf{k}_j \mathbf{k}_a \in \mathcal{K}} \sum_{ijab} \left(2 \langle i\mathbf{k}_i, j\mathbf{k}_j | a\mathbf{k}_a, b\mathbf{k}_b \rangle - \langle i\mathbf{k}_i, j\mathbf{k}_j | b\mathbf{k}_b, a\mathbf{k}_a \rangle \right) T_{ijab}^{\#, N_{\mathbf{k}}}(\mathbf{k}_i, \mathbf{k}_j, \mathbf{k}_a)$$

where T_{ijab} is called the T_2 amplitude, # indicates level of theory.

- e.g., Møller-Plesset perturbation theory

$$T_{ijab}^{\mathrm{MP2}, N_{\mathbf{k}}}(\mathbf{k}_i, \mathbf{k}_j, \mathbf{k}_a) = \frac{1}{\varepsilon_{i\mathbf{k}_i, j\mathbf{k}_j}^{a\mathbf{k}_a, b\mathbf{k}_b}} \langle a\mathbf{k}_a, b\mathbf{k}_b | i\mathbf{k}_i, j\mathbf{k}_j \rangle$$

$$T_{ijab}^{\text{MP3-4h2p}, N_{\mathbf{k}}}(\mathbf{k}_i, \mathbf{k}_j, \mathbf{k}_a) = \frac{1}{N_{\mathbf{k}}} \sum_{\mathbf{k}_k \in \mathcal{K}} \sum_{kl} \frac{1}{\varepsilon_{i\mathbf{k}_i, j\mathbf{k}_j}^{a\mathbf{k}_a, b\mathbf{k}_b}} \langle k\mathbf{k}_k, l\mathbf{k}_l | i\mathbf{k}_i, j\mathbf{k}_j \rangle \times \frac{\langle a\mathbf{k}_a, b\mathbf{k}_b | k\mathbf{k}_k, l\mathbf{k}_l \rangle}{\varepsilon_{k\mathbf{k}_k, l\mathbf{k}_l}^{a\mathbf{k}_a, b\mathbf{k}_b}}$$

Madelung constant correction

- Physical origin: electrostatic energy of an infinite periodic array of point charges diverges in 3D. Madelung constant (ξ) provides a fictitious uniform compensation charge.

- Madelung constant correction
  1. Replace ERI by

$$\langle n_1\mathbf{k}_1, n_2\mathbf{k}_2 | n_3\mathbf{k}_3, n_4\mathbf{k}_4\rangle - \delta_{n_1 n_3}\delta_{n_2 n_4}\delta_{\mathbf{k}_1\mathbf{k}_3}\delta_{\mathbf{k}_2\mathbf{k}_4}\xi.$$

  2. (For correlation energy) Replace occupied orbital energy $\varepsilon_{i\mathbf{k}}$ by

$$\varepsilon_{i\mathbf{k}} - \xi$$

- Physically intuitive, but no rigorous proof of its effectivess!

Main results

Theory	Correction to orbital energies ε	Correction to amplitudes $\mathcal{A}$	Finite-size scaling	Reference
HF	N/A	✗	$N_{\mathbf{k}}^{-\frac{1}{3}}$	[1,Thm 3.1]
HF	N/A	✓	$N_{\mathbf{k}}^{-1}$	[1,Thm 5.1]
MP2	✓	N/A	$N_{\mathbf{k}}^{-1}$	[1,Thm 4.1]
MP3	✓	✗	$N_{\mathbf{k}}^{-\frac{1}{3}}$	[2, Cor 2]
MP3	✓	✓	$N_{\mathbf{k}}^{-1}$	[3, Thm 1]
CCD(n)/CCD	✓	✗	$N_{\mathbf{k}}^{-\frac{1}{3}}$ / $N_{\mathbf{k}}^{-\frac{1}{3}}$	[2, Thm 1 / Cor 3]
CCD(n)/CCD	✓	✓	$N_{\mathbf{k}}^{-1}$ / $N_{\mathbf{k}}^{-1}$	[3, Thm 1 / Thm 2]
CCD(n)/CCD	✗	✓	$N_{\mathbf{k}}^{-\frac{1}{3}}$ / $N_{\mathbf{k}}^{-\frac{1}{3}}$	[3, Thm 1 / Thm 2]
CCD(n)/CCD	✗	✗	$N_{\mathbf{k}}^{-\frac{1}{3}}$ / $N_{\mathbf{k}}^{-1}$	[3, Thm 1 / Cor 3]

✓With Madelung constant correction; ✗Without correction

[1] (Xing, Li, **L.**, Math. Comp. 93, 679, 2024)

[2] (Xing, **L.**, J. Comput. Phys. 500, 112755, 2024)

[3] (Xing, **L.**, Phys. Rev. X 14, 011059, 2024)

From reviewers

“The results settle once and for all, that fully converged CCD calculations have a finite-size error that scales inversely with the volume considered. The results settle once and for all the conditions that must be met for this to be achieved.. the results are highly original and technically impressive.. the overall presentation is bordering on superb..”

Proof ideas for analyzing finite-size errors in Hartree-Fock theory

Main results

Theory	Correction to orbital energies ε	Correction to amplitudes $\mathcal{A}$	Finite-size scaling	Reference
HF	N/A	✗	$N_{\mathbf{k}}^{-\frac{1}{3}}$	[1,Thm 3.1]
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MP3	✓	✓	$N_{\mathbf{k}}^{-1}$	[3, Thm 1]
CCD(n)/CCD	✓	✗	$N_{\mathbf{k}}^{-\frac{1}{3}}$ / $N_{\mathbf{k}}^{-\frac{1}{3}}$	[2, Thm 1 / Cor 3]
CCD(n)/CCD	✓	✓	$N_{\mathbf{k}}^{-1}$ / $N_{\mathbf{k}}^{-1}$	[3, Thm 1 / Thm 2]
CCD(n)/CCD	✗	✓	$N_{\mathbf{k}}^{-\frac{1}{3}}$ / $N_{\mathbf{k}}^{-\frac{1}{3}}$	[3, Thm 1 / Thm 2]
CCD(n)/CCD	✗	✗	$N_{\mathbf{k}}^{-\frac{1}{3}}$ / $N_{\mathbf{k}}^{-1}$	[3, Thm 1 / Cor 3]

✓With Madelung constant correction; ✗Without correction

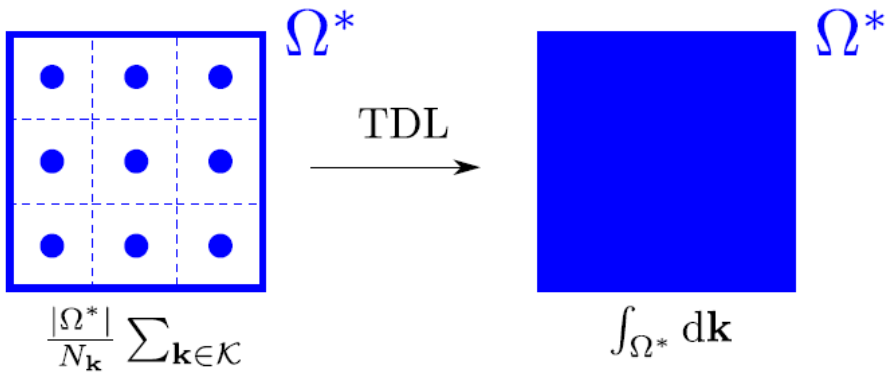
[1](Xing, Li, **L.**, Math. Comp. 93, 679, 2024)
[2](Xing, **L.**, J. Comput. Phys. 500, 112755, 2024)
[3](Xing, **L.**, Phys. Rev. X 14, 011059, 2024)

Electron density

$$\rho_{N_{\mathbf{k}}}(\mathbf{r}) = \frac{|\Omega^*|}{N_{\mathbf{k}}} \sum_{\mathbf{k}\in\mathcal{K}} \left(\frac{1}{|\Omega^*|} \sum_i |u_{i\mathbf{k}}(\mathbf{r})|^2 \right)$$

$$= \frac{|\Omega^*|}{N_{\mathbf{k}}} \sum_{\mathbf{k}\in\mathcal{K}} F_e(\mathbf{k},\mathbf{r}) \xrightarrow{\text{TDL}} \rho_{\text{TDL}}(\mathbf{r}) = \int_{\Omega^*} \mathrm{d}\mathbf{k} F_e(\mathbf{k},\mathbf{r})$$

Thermodynamic limit (TDL): $N_{\mathrm{k}} \to \infty$ and $\mathcal{K} \to \Omega^*$



Finite-size error: quadrature error of trapezoidal rule.

Trapezoidal rule in $\mathbb{R}^d$

- Hypercube $V = [0, L]^d + \mathbf{b}$ for some $\mathbf{b} \in \mathbb{R}^d$.
- $\mathcal{X}$: an $m \times \cdots \times m$ uniform mesh inside V

$$\mathcal{X} = \left\{ \mathbf{b} + \frac{L}{m} \left((j_1, j_2, \cdots, j_d) + \mathbf{x}_* \right),\ j_1, j_2, \ldots, j_d = 0, 1, \ldots, m-1 \right\},$$

$\mathbf{x}_* \in [0, 1]^d$: *relative offset* of $\mathcal{X}$ with respect to V.

- Trapezoidal rule: $\mathcal{Q}_V(g, \mathcal{X}) = \frac{|V|}{|\mathcal{X}|} \sum_{\mathbf{x}_i \in \mathcal{X}} g(\mathbf{x}_i)$
- Quadrature error

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

Euler-Maclaurin formula[1]

Theorem (Euler-Maclaurin formula)

For $g \in C^l(V)$, quadrature error:

$$\mathcal{E}_V(g, \mathcal{X}) = \sum_{s=1}^{l-1} \frac{L^s}{m^s} \sum_{|\beta|=s} c_\beta(\mathbf{x}_*) \int_V g^{(\beta)}(\mathbf{x})\, \mathrm{d}\mathbf{x} + \frac{L^l}{m^l} \times \text{bounded}.$$

with $B_k(x)$ the periodic Bernoulli polynomial of order k and

$$c_\beta(\mathbf{x}) = -\frac{B_{\beta_1}(x_1)}{\beta_1!} \frac{B_{\beta_2}(x_2)}{\beta_2!} \cdots \frac{B_{\beta_d}(x_d)}{\beta_d!}.$$

Corollary

$g(\mathbf{x})$ periodic and smooth w.r.t. V, quadrature error:

$$\left| \int_V \mathrm{d}\mathbf{x} g(\mathbf{x}) - \frac{|V|}{m^d} \sum_{\mathbf{x}_i \in \mathcal{X}} g(\mathbf{x}_i) \right| = \mathcal{O}\left(m^{-l}\right), \quad \forall l > 0.$$

[1] Results can be improved for complex analytic functions in 1D, see e.g., (Trefethen, Weideman, SIAM Review 2014)

Quadrature error in electron density

- Electron density: $\rho_{N_{\mathbf{k}}}(\mathbf{r}) = \frac{|\Omega^*|}{N_{\mathbf{k}}} \sum_{\mathbf{k}\in\mathcal{K}} \left(\frac{1}{|\Omega^*|} \sum_i |u_{i\mathbf{k}}(\mathbf{r})|^2 \right)$
- Quadrature error:

$$\rho_{\mathrm{TDL}}(\mathbf{r}) - \rho_{N_{\mathbf{k}}}(\mathbf{r}) = \int_{\Omega^*} \mathrm{d}\mathbf{k} F_e(\mathbf{k},\mathbf{r}) - \frac{|\Omega^*|}{N_{\mathbf{k}}} \sum_{\mathbf{k}\in\mathcal{K}} F_e(\mathbf{k},\mathbf{r})$$

- Properties of integrand: $F_e(\mathbf{k},\mathbf{r}) = \frac{1}{|\Omega^*|} \sum_i |u_{i\mathbf{k}}(\mathbf{r})|^2$ periodic and smooth w.r.t. $\mathbf{k} \in \Omega^*$

Lemma

$$\left|\rho_{\mathrm{TDL}}(\mathbf{r}) - \rho_{N_{\mathbf{k}}}(\mathbf{r})\right| = \mathcal{O}\left(N_{\mathbf{k}}^{-I}\right), \quad \forall I > 0.$$

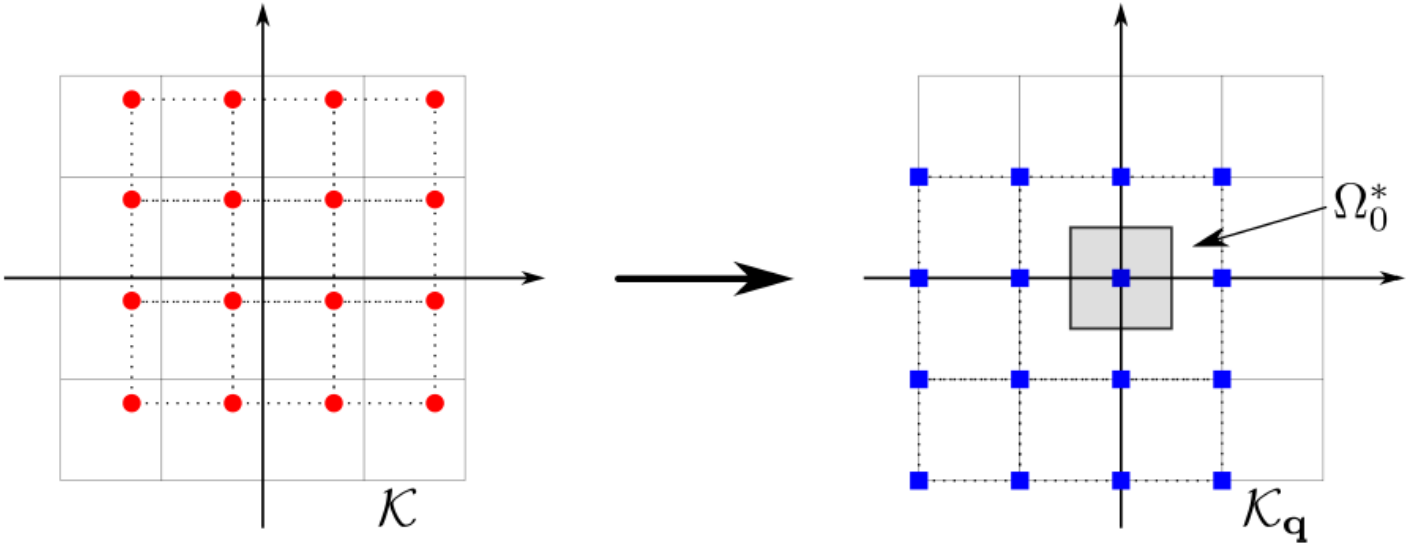
Quadrature error in Fock exchange

- Quadrature error:

$$E_{\mathbf{X}}^{\mathrm{TDL}} - E_{\mathbf{X}}\left(N_{\mathbf{k}}\right) = \left(\int_{\Omega^* \times \Omega^*} \mathrm{d}\mathbf{k}_i \, \mathrm{d}\mathbf{q} - \frac{\left|\Omega^*\right|^2}{N_{\mathbf{k}}^2} \sum_{\mathbf{k}_i \in \mathcal{K}, \mathbf{q} \in \mathcal{K}_{\mathbf{q}}} \right) F_{\mathbf{x}}\left(\mathbf{k}_i, \mathbf{q}\right)$$

- Momentum transfer $\mathbf{q} = \mathbf{k}_j - \mathbf{k}_i$.

- $\mathcal{K}_{\mathbf{q}} = \mathcal{K} - \mathcal{K}$ always contains $\mathbf{q} = \mathbf{0}$



Singular integrand

$$F_{\mathbf{x}}(\mathbf{k}_i, \mathbf{q}) \sim \sum_{ij} \frac{1}{|\Omega|} \sum_{\mathbf{G}\in\mathbb{L}^*}{}' \frac{4\pi}{|\mathbf{q}+\mathbf{G}|^2} \left|\hat{\varrho}_{i\mathbf{k}_i, j(\mathbf{k}_i+\mathbf{q})}(\mathbf{G})\right|^2$$

- smooth and periodic with respect to $\mathbf{k}_i$
- periodic with respect to $\mathbf{q}$ but discontinuous at $\mathbf{q} = \mathbf{0}$. Euler-Maclaurin formula is not applicable.
- Punctured summation $\sum'_{\mathbf{G}\in\mathbb{L}^*}$ excludes the singular term with $\mathbf{q}+\mathbf{G} = \mathbf{0}$.

$$\frac{|\Omega^*|}{N_{\mathbf{k}}} \frac{4\pi}{|\mathbf{q}|^2} \sum_{ij} \left|\hat{\varrho}_{i\mathbf{k}_i, j(\mathbf{k}_i+\mathbf{q})}(\mathbf{0})\right|^2 \longrightarrow \int_{\Omega_0^*} \mathrm{d}\mathbf{q} \frac{\mathcal{O}(1)}{|\mathbf{q}|^2} = \mathcal{O}\left(N_{\mathbf{k}}^{-\frac{1}{3}}\right)$$

- Finite-size error is at least $\mathcal{O}\left(N_{\mathbf{k}}^{-\frac{1}{3}}\right)$.

Algebraic singularity

Definition

$g(\mathbf{x})$ has algebraic singularity of order $\gamma \in \mathbb{R}$ at $\mathbf{x}_0 \in \mathbb{R}^d$ if $\exists \delta > 0$,

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

Example	Singular point and order γ
$\frac{1}{\lvert\mathbf{q}\rvert^2}$	$\mathbf{q} = \mathbf{0}$ 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

Analysis of “punctured” trapezoidal rule with singular integrands in *d*-dimension

- (Lyness, Math. Comp. 1976), generalized Euler-Maclaurin, homogeneous function
- (Xing, Li, **L.**, Math. Comp. 93, 679, 2024) generalized Euler-Maclaurin, functions with algebraic singularity
- Improvement
  (Xing, **L.**, J. Comput. Phys. 500, 112755, 2024)
  (Xing, **L.**, Phys. Rev. X 14, 011059, 2024) Poisson summation inspired by (Izzo, Runborg, Tsai, Adv. Comp. Math., 2023)

Generalized Euler-Maclaurin formula

Theorem (Xing–Li–L., 2024, simplified)

$V = [-\frac{1}{2}, \frac{1}{2}]^d$. $g(\mathbf{x}) = \frac{f(\mathbf{x})}{(\mathbf{x}^T M \mathbf{x})^p}$ for some $M \succ 0$. $f(\mathbf{x})$ smooth in $\mathbb{R}^d$, $f(\mathbf{x}) = \mathcal{O}(|\mathbf{x}|^a)$ near $\mathbf{x} = \mathbf{0}$, and $\gamma = a - 2p > -d$. Then

$$\mathcal{E}_V(g, \mathcal{X}) = \sum_{s=1}^{d+\gamma-1} \frac{1}{m^s} \left(\sum_{|\beta|=s} c_\beta(\mathbf{x}) \int_V g^{(\beta)} \, \mathrm{d}\mathbf{x} \right) + \mathcal{O}\left(\frac{\ln m}{m^{d+\gamma}} \right).$$

- If g is periodic in V, then $\mathcal{E}_V(g, \mathcal{X}) = \widetilde{\mathcal{O}}(m^{-(d+\gamma)})$.
- Proof sketch: Separate into bad domain $V_{\mathcal{T}} = [-\frac{1}{m}, \frac{1}{m}]^d$ and good domain $V \setminus V_{\mathcal{T}}$.
  Apply Euler-Maclaurin in each volume element of size $|V_{\mathcal{T}}|$.

Quadrature error in Fock exchange

- $F_{\mathbf{x}}(\mathbf{k}_i, \mathbf{q})$ with non-smooth terms $\frac{\mathcal{O}(1)}{|\mathbf{q}|^2}, \frac{\mathcal{O}(\mathbf{q}^2)}{|\mathbf{q}|^2}, \frac{\mathcal{O}(\mathbf{q}^4)}{|\mathbf{q}|^2}, \dots$

$$\Longrightarrow E_{\mathbf{X}}^{\mathrm{TDL}} - E_{\mathbf{X}}(N_{\mathbf{k}}) = \frac{a_0}{N_{\mathbf{k}}^{\frac{1}{3}}} + \frac{a_1}{N_{\mathbf{k}}} + \frac{a_2}{N_{\mathbf{k}}^{\frac{5}{3}}} + \cdots$$

Theorem (Xing–Li–L., 2024, Fock exchange energy)

In the absence of finite-size corrections,

$$\left| E_{\mathbf{X}}^{\mathrm{TDL}} - E_{\mathbf{X}}(N_{\mathbf{k}}) \right| = \widetilde{\mathcal{O}}\left(N_{\mathbf{k}}^{-\frac{1}{3}} \right).$$

Madelung constant correction evaluates a_0 up to h.o.t. then

$$\left| E_{\mathbf{X}}^{\mathrm{TDL}} - E_{\mathbf{X}}^{\mathrm{corr}}(N_{\mathbf{k}}) \right| = \widetilde{\mathcal{O}}\left(N_{\mathbf{k}}^{-1} \right).$$

Outline

Electronic structure theory and earlier works on DFT

Finite-size error and quantum chemistry methods

Main theoretical results and proof ideas

Conclusion

Conclusion and future works

- First rigorous analysis of FSE in HF (in reciprocal space) and correlation energy for a range of quantum chemistry methods
- Gapless systems and finite temperature analysis requires new tools. Green's function based ideas.
- Other physical properties. Charge gap and optical gaps.
- Analysis inspired algorithms: (1) staggered mesh method (2) singularity subtraction method (superalgebraic convergence)
- Staggered mesh method implemented in PySCF and QChem.

Acknowledgment

Thank you for your attention!

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

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NSF
AFOSR AIR FORCE OFFICE OF SCIENTIFIC RESEARCH
Google AI Quantum
SIMONS FOUNDATION

Pole expansion and selected inversion (PEXSI)

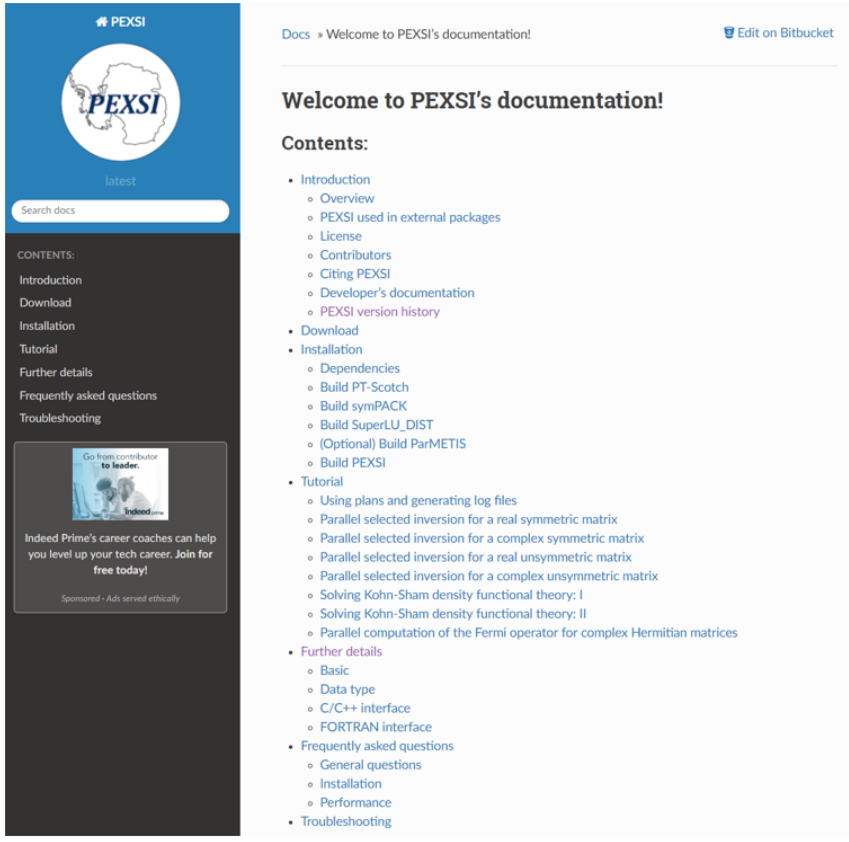
- At most $O(N_e^2)$ scaling (insulators, semiconductor and metals). Standard method scales as $O(N_e^3)$
- Solve systems > 10,000 atoms (Cubic scaling methods previously solve up to a few thousand atoms)
- Massively parallelizable to >100,000 cores.

- Integrated with a number of community electronic structure software packages
- BigDFT
- CP2K
- DFTB+
- DGDFT
- FHI-aims
- QuantumWise AtK
- SIESTA

- "Electronic structure infrastructure" (ELSI)

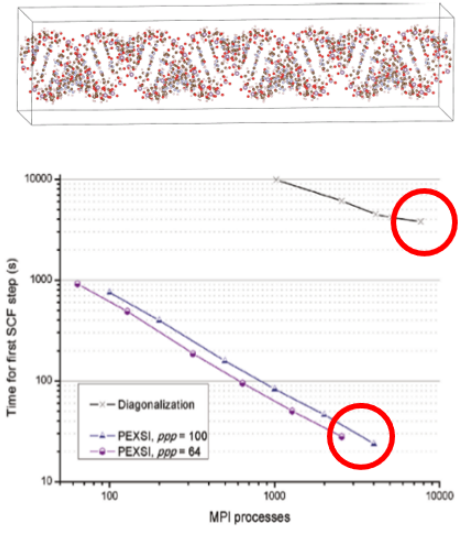
https://wordpress.elsi-interchange.org/

http://www.pexsi.org/



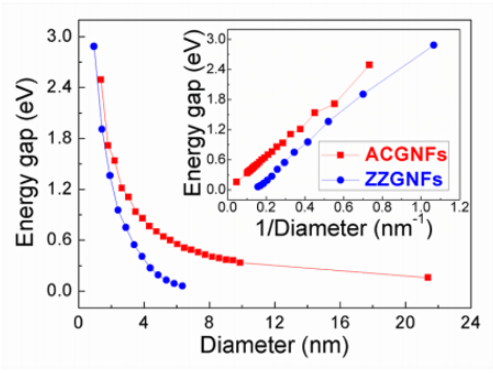
[**L.**, Lu, Ying, Car and E, Commun. Math. Sci. 2009]
[**L.** Yang, Meza, Lu, Ying, E, ACM TOMS, 2011]
[**L.**, Garcia, Huhs, Yang, JPCM 2014]

Pole expansion and selected inversion (PEXSI)

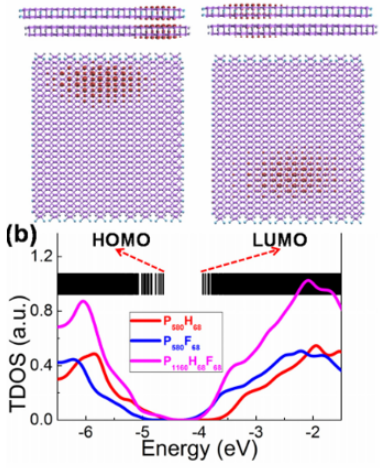


(a) DNA-25

Large scale DNA calculation (20000 atoms)



Electronic structure of large scale graphene nanoflake (10000 atoms)

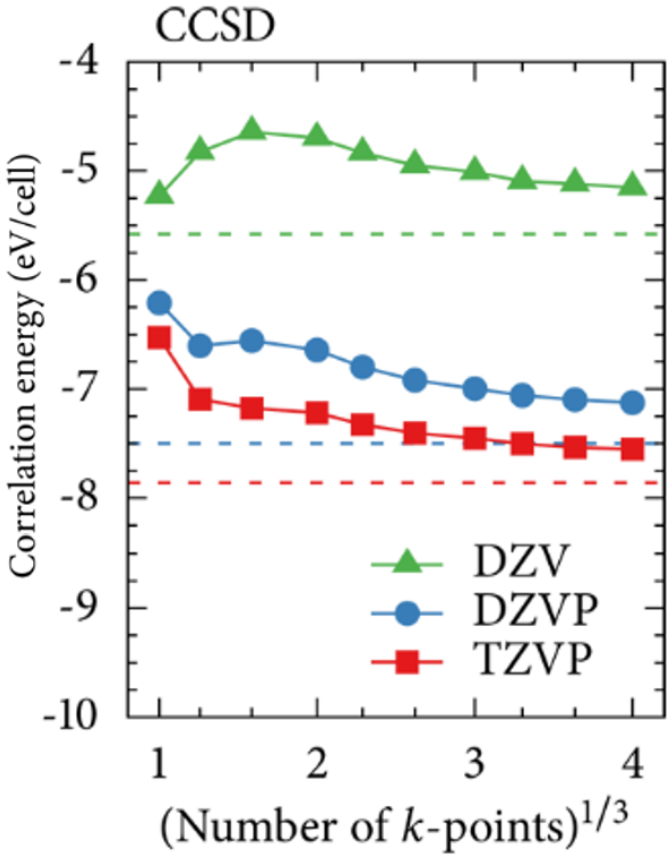


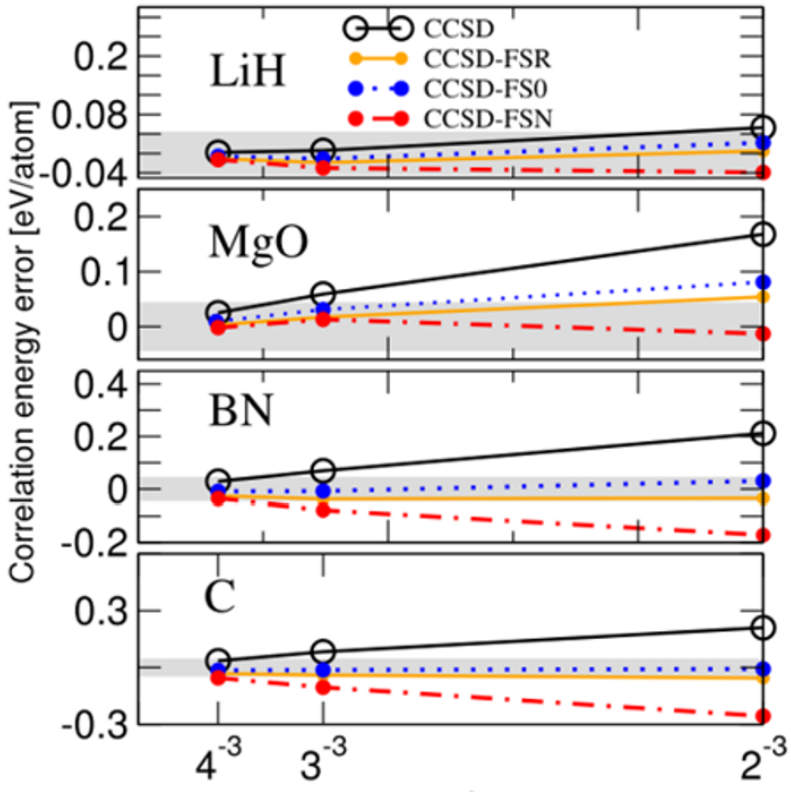
Predict large scale phospherene nanoflake (PNF) heterojunction as new candidates of solar cells (9000 atoms)

[**L.**, Lu, Ying, Car and E, Commun. Math. Sci. 2009]
[**L.**-Yang-Meza-Lu-Ying-E, ACM TOMS, 2011]
[**L.**, Garcia, Huhs, Yang, JPCM 2014]

[Hu, **L.**, Yang, Yang, J. Chem. Phys. 2014]
[Hu, **L.** and Yang, Phys. Chem. Chem. Phys. 2015]
[Hu, **L.**, Yang, Dai and Yang, Nano Lett., 2016]

FSE can be both significant and hard to pin down





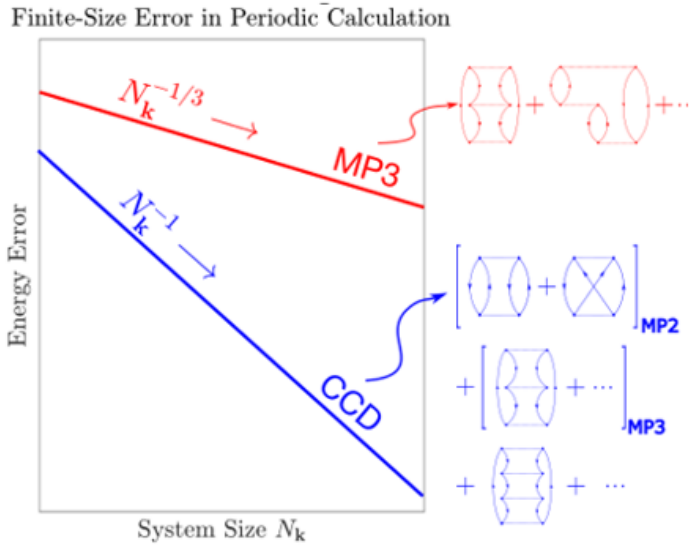
$N_k^{-1/3}$ scaling ?

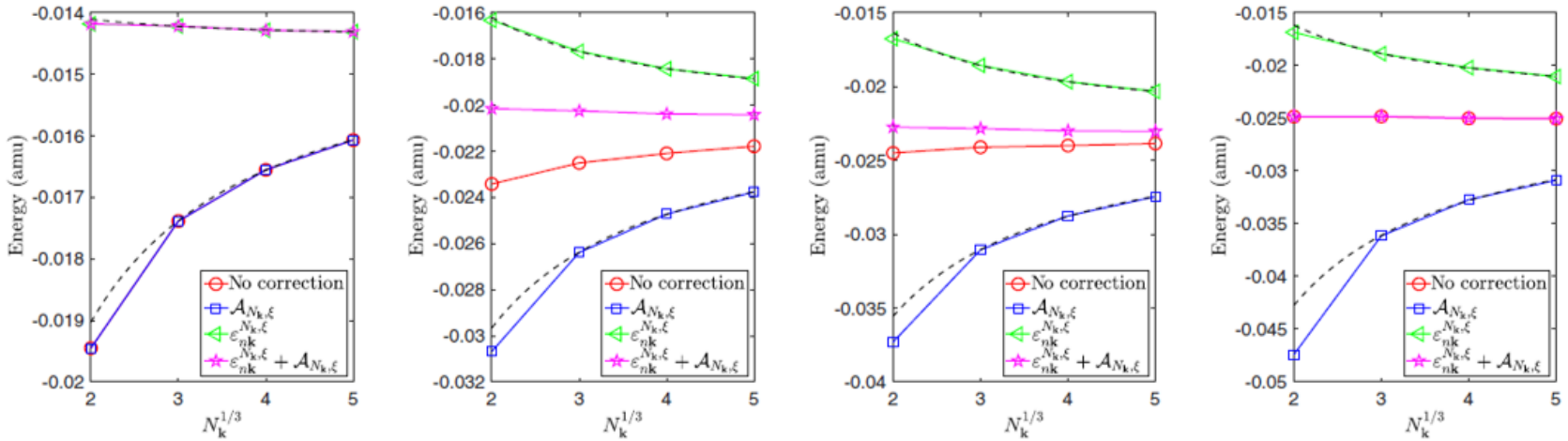
(McClain, Sun, Chan, Berkelbach, JCTC 2017)

N_k^{-1} scaling ?

(Liao, Gruneis, JCP 2016)

Inverse volume scaling in coupled cluster calculations





(a) CCD(1) (b) CCD(2) (c) CCD(3) (d) CCD

(Xing, **L.**, Phys. Rev. X 14, 011059, 2024)

Two common misinterpretations

CC exhibits superior FSE scaling because

- *CC is size extensive.*
  A: No. (1) size extensivity is only a necessary condition for periodic calculations. (2) HF, MP2, MP3 etc are all size extensive.

- *CC can be reformulated without referring to orbital energies.*
  A: Yes. This is along the right track, but many steps in between are still missing.

Proof sketch of inverse volume scaling result

- Key step: Madelung constant correction[1] improves $N_{\mathbf{k}}^{-\frac{1}{3}}$ to $N_{\mathbf{k}}^{-1}$ for CCD(n).
- Upon convergence of the CCD amplitude equations, Madelung constant corrections cancels out.

Conclusion: Without finite size corrections, FSE of any CCD(n) is $N_{\mathbf{k}}^{-\frac{1}{3}}$, and only at convergence, it improves to $N_{\mathbf{k}}^{-1}$.

[1] Must be properly applied to both orbital energies and ERI contractions.

Singular integrand

- Asymptotic non-smooth form near $\mathbf{q} = \mathbf{0}$

$$F_{\mathrm{x}}(\mathbf{k}_i, \mathbf{q}) \sim \frac{\sum_{ij} \hat{\varrho}_{i\mathbf{k}_i, j(\mathbf{k}_i+\mathbf{q})}(\mathbf{0})}{|\mathbf{q}|^2} + \sum_{\mathbf{G}\neq\mathbf{0}} \frac{\cdots}{|\mathbf{G}+\mathbf{q}|^2}$$

$$\sim \frac{N_{\mathrm{occ}} + \sum_{|\boldsymbol{\alpha}|=2} c_{\boldsymbol{\alpha}} \mathbf{q}^{\boldsymbol{\alpha}} + \mathcal{O}\left(|\mathbf{q}|^4\right)}{|\mathbf{q}|^2} + \sum_{\mathbf{G}\neq\mathbf{0}} \frac{\cdots}{|\mathbf{G}+\mathbf{q}|^2}$$

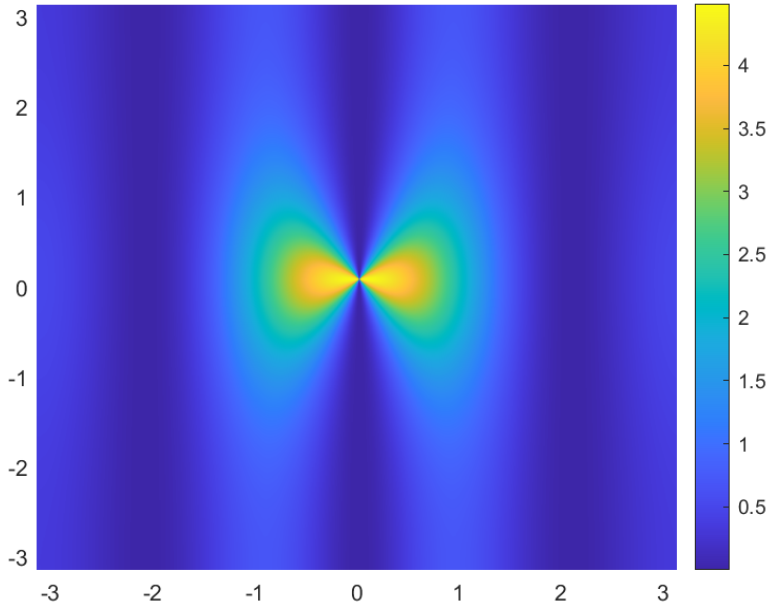
- Non-smooth integrands:

$$\frac{1}{|\mathbf{q}|^2}, \quad \frac{\mathbf{q}^{\alpha}}{|\mathbf{q}|^2} = \frac{q_1^{\alpha_1} q_2^{\alpha_2} q_3^{\alpha_3}}{|\mathbf{q}|^2}, \quad |\alpha| = 2, 4, \ldots$$

Anisotropic singularity

$$\int_{\Omega^*} \frac{f(\mathbf{q})}{|\mathbf{q}|^2}\, \mathrm{d}\mathbf{q}.$$

- f compactly supported in Ω^* with isolated singularity at $\mathbf{q} = \mathbf{0}$.
- $f(\mathbf{q}) = \mathcal{O}(|\mathbf{q}|^2) \quad \not\Rightarrow \quad f(\mathbf{q}) = C\,|\mathbf{q}|^2 + o(|\mathbf{q}|^2)$

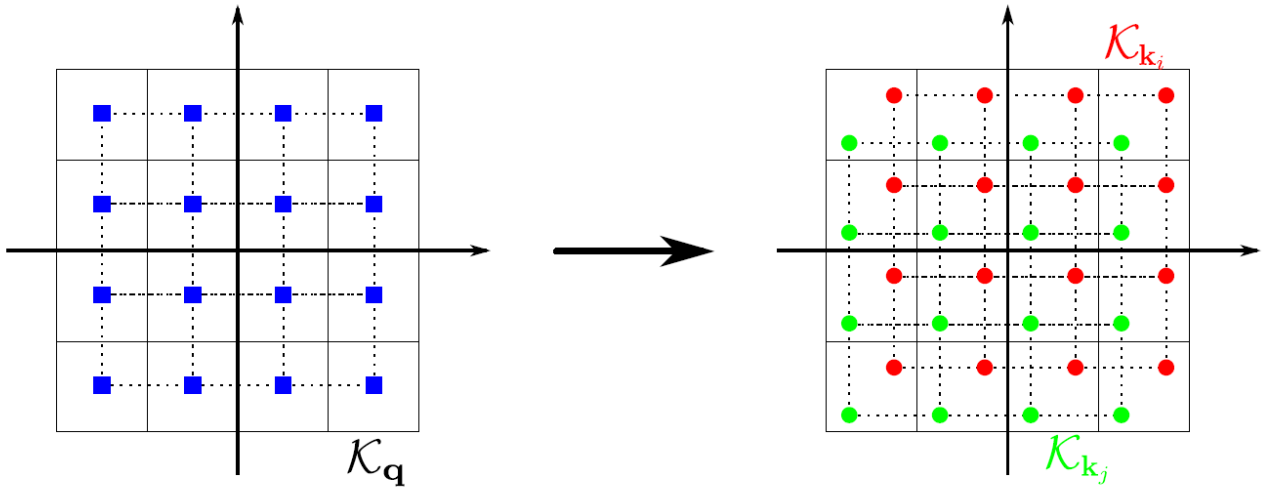


Staggered mesh method for Fock exchange

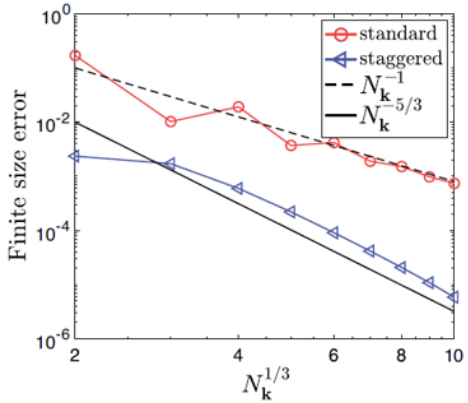
- Two staggered meshes $\mathcal{K}_i$ and $\mathcal{K}_j$ for $i\mathbf{k}_i$ and $j\mathbf{k}_j$:
  New $\mathcal{K}_{\mathbf{q}}$ with half-mesh-size shift

- Staggered mesh method:

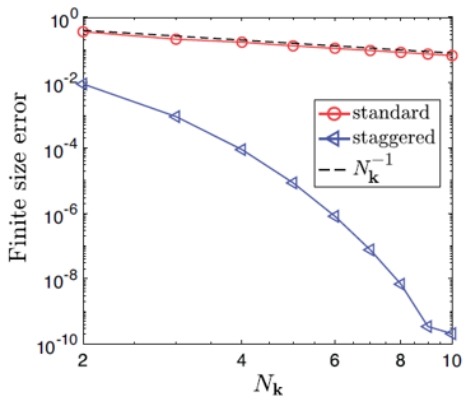
$$E_{\mathrm{x}}^{\mathrm{stagger}}(N_{\mathbf{k}}) = \frac{1}{N_{\mathbf{k}}} \sum_{ij} \sum_{\mathbf{k}_i \in \mathcal{K}_i, \mathbf{k}_j \in \mathcal{K}_j} -\frac{1}{2} \left\langle i\mathbf{k}_i, j\mathbf{k}_j \mid j\mathbf{k}_j, i\mathbf{k}_i \right\rangle$$



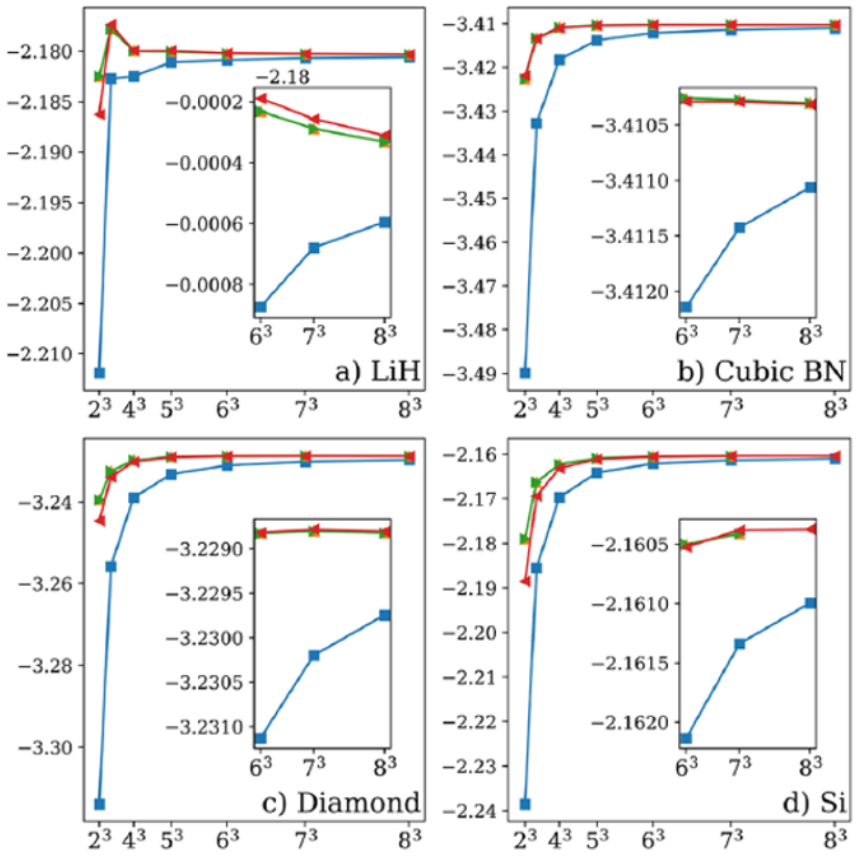
Staggered mesh method for Fock exchange



(a) 3D system



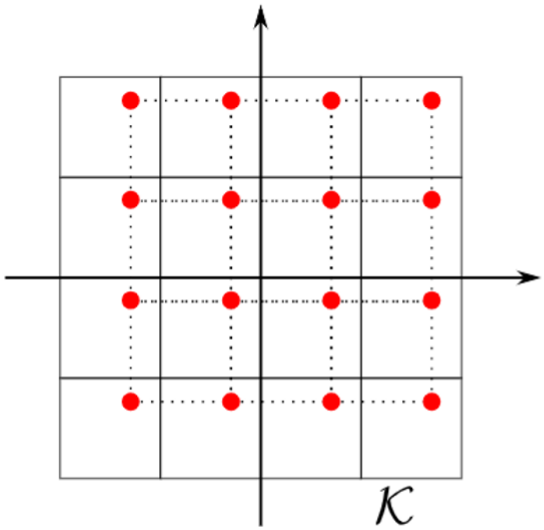
(b) Quasi-1D system



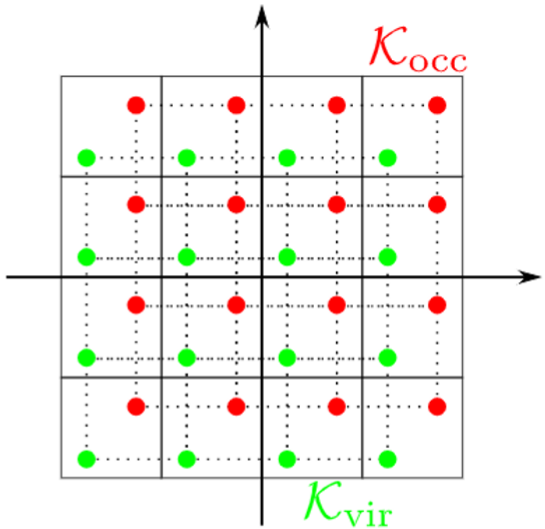
(Xing, Li, **L.**, Math. Comp. 93, 679, 2024)

(Quiton, Wu, Xing, **L.**, Head-Gordon, J. Chem. Theory Comput. 2024)

Staggered mesh method for MP2



Standard mesh

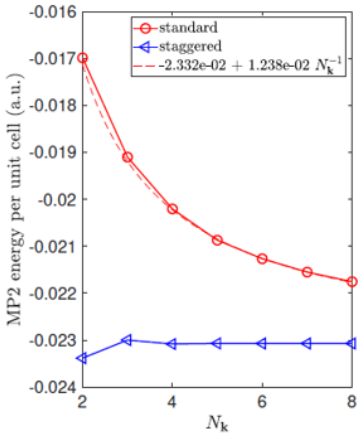


Staggered mesh

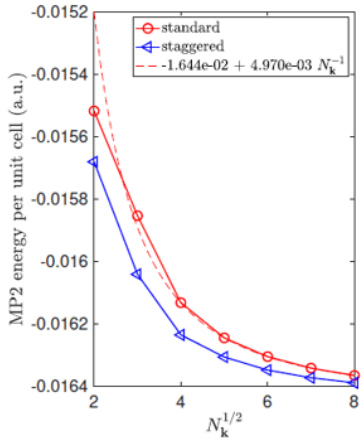
- Two staggered Monkhorst-Pack meshes for occupied orbitals and virtual orbitals[1] .
- Avoid the zero momentum transfer $\mathbf{q} = \mathbf{k}_a - \mathbf{k}_i = \mathbf{0}$.

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

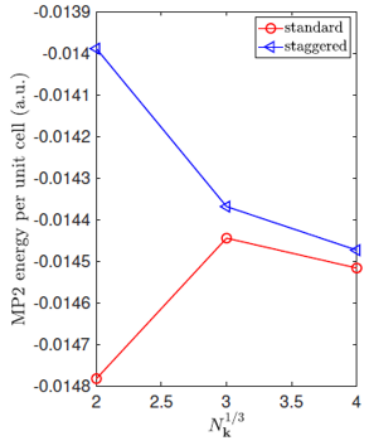
MP2 correlation energy



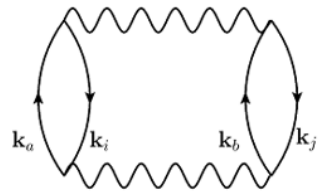
Quasi-1D H2

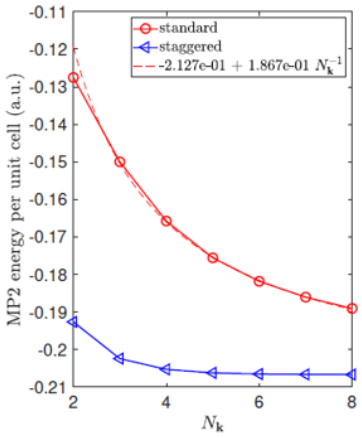


Quasi-2D H2

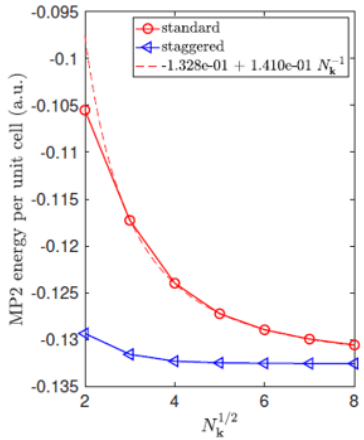


3D H2

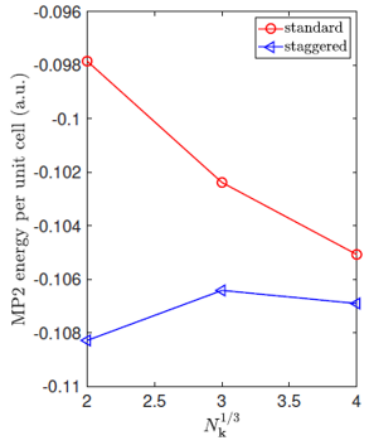




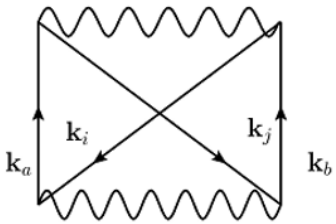
Quasi-1D diamond



Quasi-2D diamond

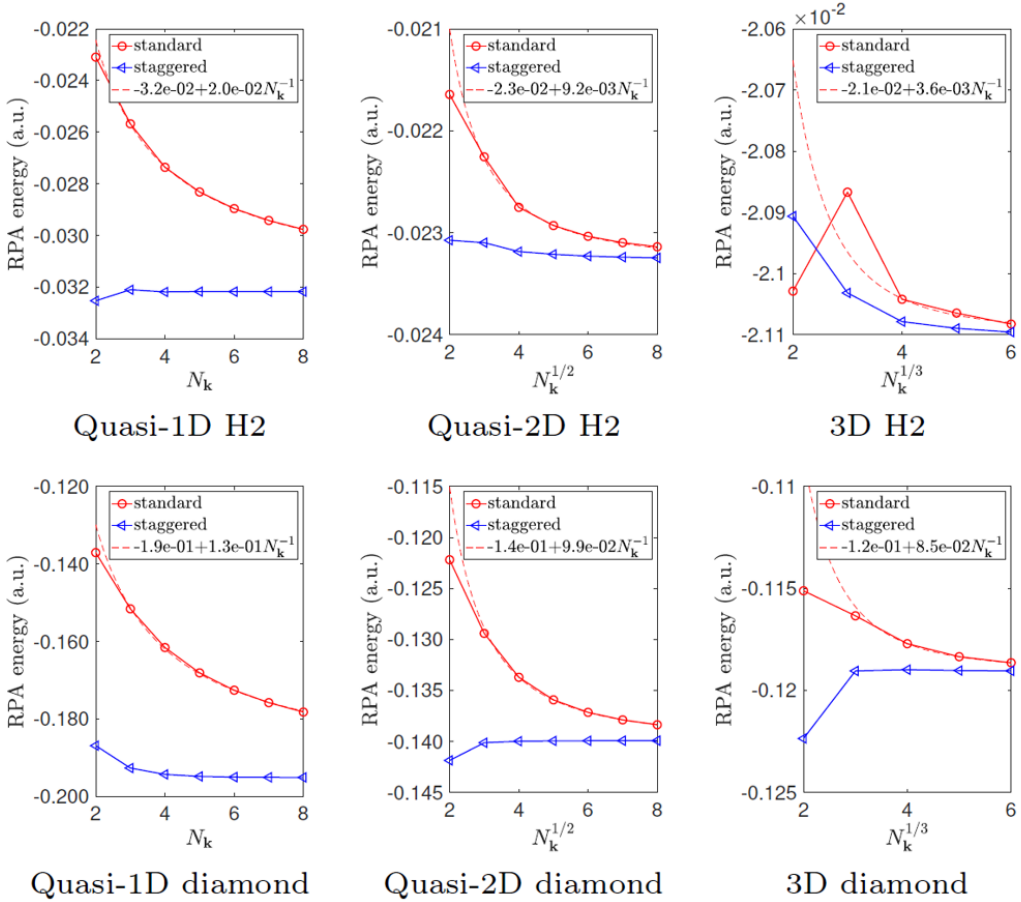


3D diamond



(Xing, Li, **L.**, J. Chem. Theory Comput. 17, 4733, 2021)

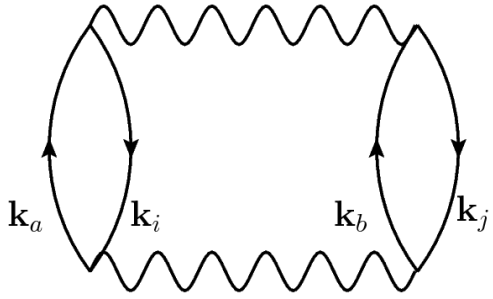
RPA correlation energy



- Direct ring coupled cluster doubles (drCCD) and adiabatic connection (AC) formalism
- Works for second order screened exchange (SOSEX)
- Staggered mesh outperforms head-wing correction for RPA correlation energies.

(Xing, **L.**, J. Chem. Theory Comput. 18, 763, 2022)

MP2, direct term

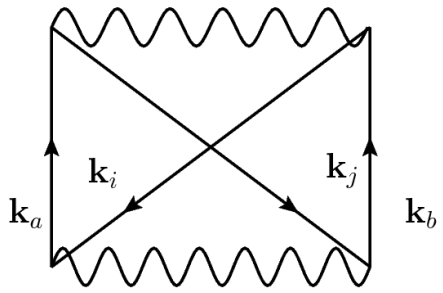


- Momentum transfer $\mathbf{q} = \mathbf{k}_a - \mathbf{k}_i = \mathbf{k}_j - \mathbf{k}_b$
- Change of variable $\mathbf{k}_a \to \mathbf{q}$
- Reduction of error (singularity only along $\mathbf{q}$ direction)

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

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

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

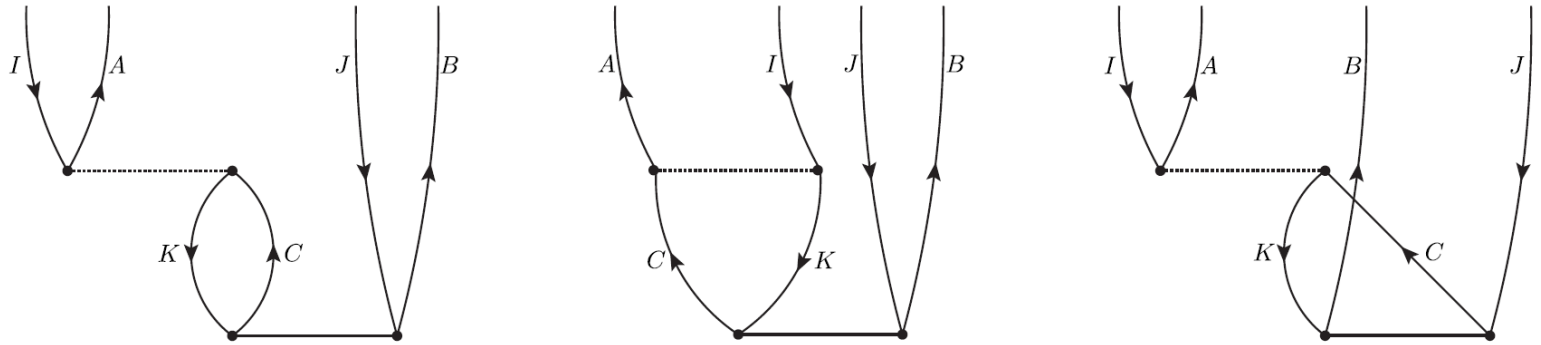
- MP2 exchange:

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

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

Diagrams in CCD (linear in t)

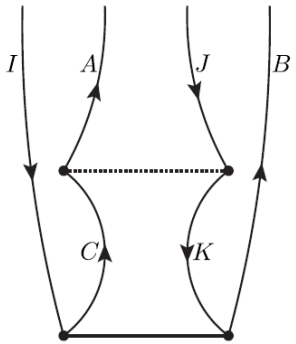
Fix I, J, A, B, focus on $K = (k\mathbf{k}_k)$ [1]
Dotted line: ERI. Solid line: t amplitude



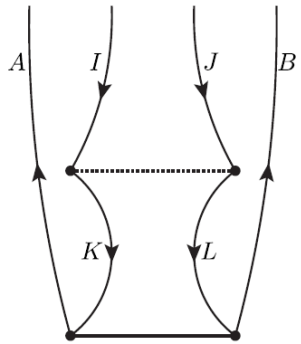
(a) $\langle AK|IC\rangle\, t^{CB}_{KJ}$

(b) $\langle AK|CI\rangle\, t^{CB}_{KJ}$

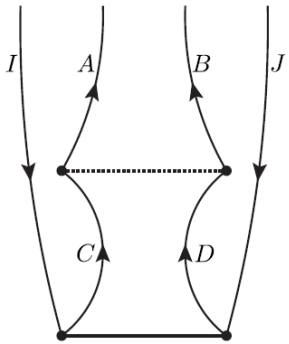
(c) $\langle AK|IC\rangle\, t^{BC}_{KJ}$



(d) $\langle AK|CJ\rangle\, t^{CB}_{IK}$



(e) $\langle KL|IJ\rangle\, t^{AB}_{KL}$



(f) $\langle AB|CD\rangle\, t^{CD}_{IJ}$

[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 γ	$m^{-(d+\gamma)}$
$\int_V \mathrm{d}\mathbf{x} f_1(\mathbf{x}) f_2(\mathbf{x})$	$f_1(\mathbf{x})$: $\mathbf{x} = \mathbf{0}$ of order γ; $f_2(\mathbf{x})$: $\mathbf{x} = \mathbf{z}$ 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 γ_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 γ_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	$N_{\mathbf{k}}^{-1}$