Staggered mesh method for periodic second order Møller-Plesset perturbation theory

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New Frontiers in Electron Correlation,
Telluride, June 2021

arXiv:2102.09652 (JCTC in press)

Outline

Staggered mesh method for MP2

Finite-size error analysis for MP2

Second order Møller-Plesset theory (MP2)

- Simplest wavefunction based theory for correlation energies

$$E_{\text{mp2}} = \sum_{ijab} \frac{\langle ij|ab\rangle \left(2\langle ab|ij\rangle - \langle ba|ij\rangle\right)}{\varepsilon_i + \varepsilon_j - \varepsilon_a - \varepsilon_b}$$

  i, j: occupied molecular orbitals (MO); a, b: virtual MOs.

- Routine for molecular systems
- Diverge for some solids: 3D uniform electron gas[1]

[1] Gell-Mann, Brueckner, 1957

MP2 for solids

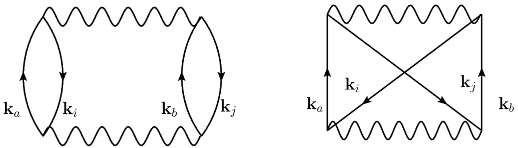
- Need $\mathbf{k}$-dependence ($i, \mathbf{k}_i$ are independent variables)

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

- Costly to evaluate but increasingly gains attention.

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

- 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 error for solids

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

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

Applicable to MP2:

- Power-law extrapolation (curve-fitting)
- Twist averaging
- Structure factor extrapolation

[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

Finite-size error: Main result

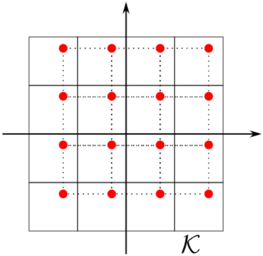
- Unified analysis based on quadrature error (applicable to Fock exchange and MP2).
- Finite-size error:

$$|E_{\text{mp2}}(N_k) - E_{\text{mp2}}^{\text{TDL}}| = \mathcal{O}(N_k^{-\alpha})$$

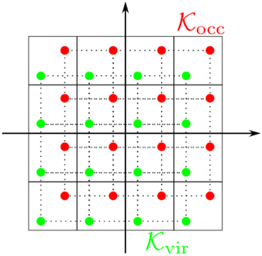
- Main result[1]:
  - $\alpha = 1$ for using the standard Monkhorst-Pack mesh.
  - $\alpha \geq 1$ for a new staggered mesh (with almost no additional cost)

[1] Xing, Li, L., *Unified analysis of finite-size error for periodic Hartree-Fock and second order Møller-Plesset perturbation theory*, in preparation (theory); 2102.09652 (staggered mesh)

Staggered mesh method



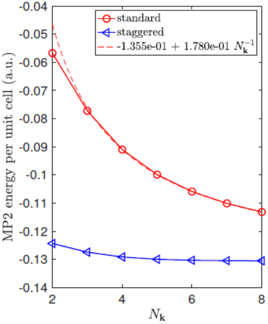
Standard mesh



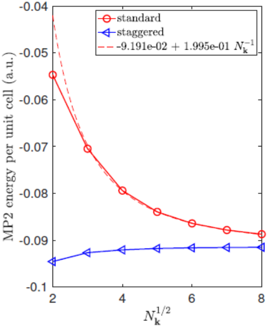
Staggered mesh

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

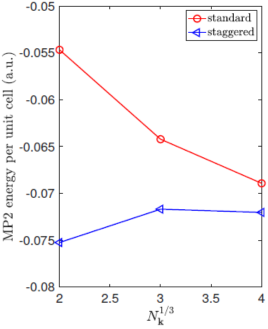
Silicon (gth-szv basis)



(a) Quasi-1D

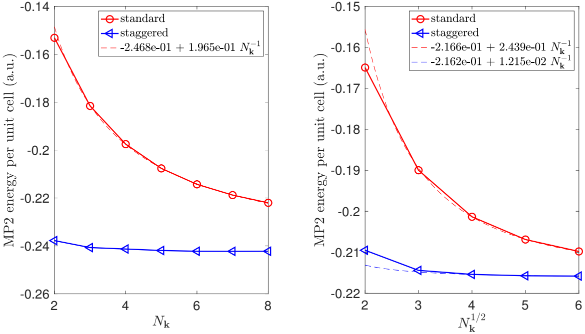


(b) Quasi-2D



(c) 3D

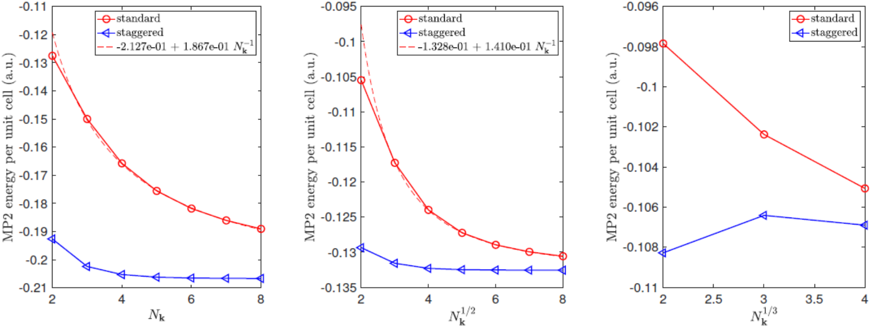
Silicon (gth-dzvp basis)



(a) Quasi-1D silicon

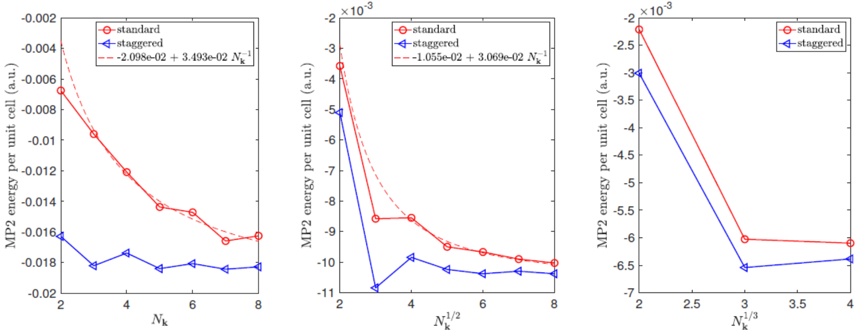
(b) Quasi-2D silicon

Diamond (gth-szv basis)



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

Periodic H_2-dimer (gth-szv basis)



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

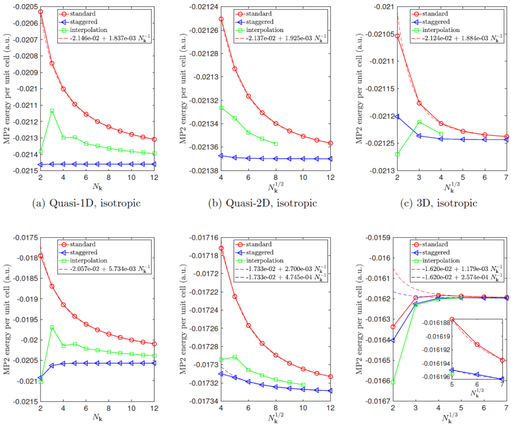
Significant improvement for quasi-1D systems.

Small/no improvement for some (anisotropic) quasi-2D / 3D systems

Model system

Effective potential $V(\mathbf{r}) = \sum_{\mathbf{R}\in\mathbb{L}} C \exp\left(-\frac{1}{2}(\mathbf{r}+\mathbf{R}-\mathbf{r}_0)^\top \Sigma^{-1}(\mathbf{r}+\mathbf{R}-\mathbf{r}_0)\right)$

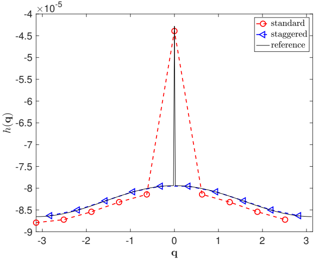
- Isotropic: $\Sigma = \mathrm{diag}(0.2^2, 0.2^2, 0.2^2)$, $C = -200$, $n_{\mathrm{occ}} = 1$, $n_{\mathrm{vir}} = 3$.
- Anisotropic: $\Sigma = \mathrm{diag}(0.1^2, 0.2^2, 0.3^2)$, $C = -200$, $n_{\mathrm{occ}} = 1$, $n_{\mathrm{vir}} = 1$.
- Also compare with structure factor interpolation (Liao, Grueneis 2016; Gruber et al, 2018)



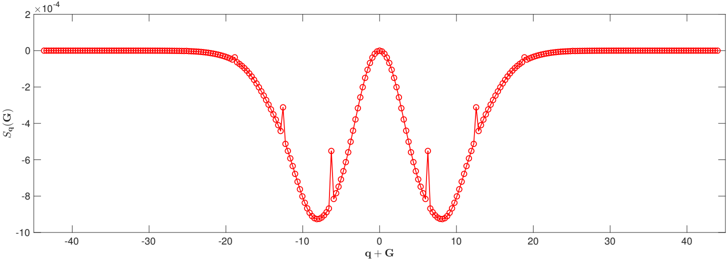
(a) Quasi-1D, isotropic (b) Quasi-2D, isotropic (c) 3D, isotropic

(d) Quasi-1D, anisotropic (e) Quasi-2D, anisotropic (f) 3D, anisotropic

Reason: smoothness of the integrand



$$E_c^{\mathrm{TDL}} = \int_{\Omega^*} \mathrm{d}\mathbf{q} \sum_{\mathbf{G}\in\mathbb{L}^*}{}' \frac{4\pi}{|\mathbf{q}+\mathbf{G}|^2} S_{\mathbf{q}}(\mathbf{G})$$
$$=: \int_{\Omega^*} \mathrm{d}\mathbf{q}\, h(\mathbf{q})$$



Outline

Staggered mesh method for MP2

Finite-size error analysis for MP2

Assumptions

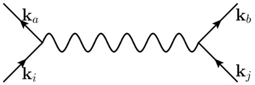
Focus on error due to $|\mathcal{K}| \to \infty$ (i.e. quadrature error)

- Direct band gap (insulator)

$$\varepsilon_{i\mathbf{k}_i} + \varepsilon_{j\mathbf{k}_j} - \varepsilon_{a\mathbf{k}_a} - \varepsilon_{b\mathbf{k}_b} \leq -\varepsilon_g < 0$$

- Finite sum over i, j, a, b (truncation of virtual bands)
- Finite sum over $\mathbf{G}$ (truncation of Fourier modes)
- Exact Hartree-Fock energies and orbitals

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 Ω^*. Then $\mathbf{q}+\mathbf{G}=\mathbf{0} \Leftrightarrow \mathbf{q}=\mathbf{G}=\mathbf{0}$.

Quadrature representation

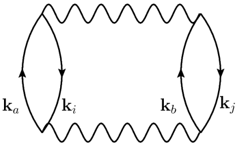
- Quadrature error of trapezoidal rule on a domain V with a uniform grid $\mathcal{X}$

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

- 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



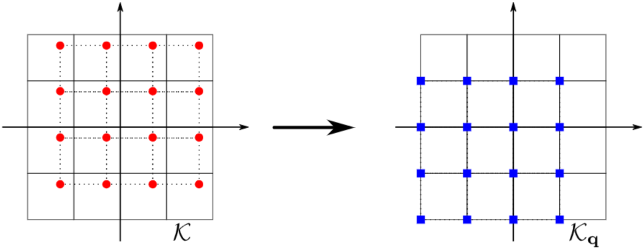
- Momentum transfer $\mathbf{q} = \mathbf{k}_a - \mathbf{k}_i = \mathbf{k}_j - \mathbf{k}_b$
- Change of variable $\mathbf{k}_a \to \mathbf{q}$
- Reduction of error (singularity only along $\mathbf{q}$ direction)

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

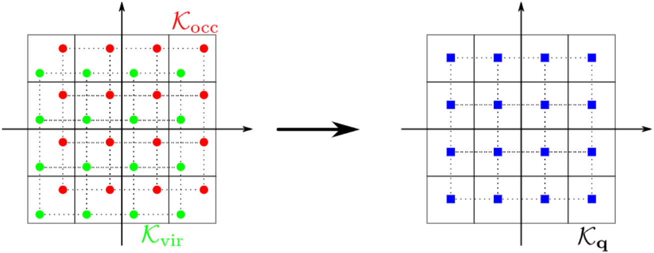
$$\lesssim \max_{\mathbf{k}_i,\mathbf{k}_j} \mathcal{E}_{\Omega^*}\left(\widetilde{F}_{\text{mp2,d}}(\mathbf{k}_i,\mathbf{k}_j,\mathbf{q}),\mathcal{K}_{\mathbf{q}}\right)$$

$\mathcal{K}_{\mathbf{q}}$-mesh

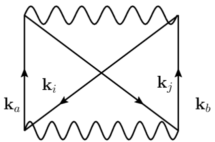
Standard mesh:



Staggered mesh:



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:

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

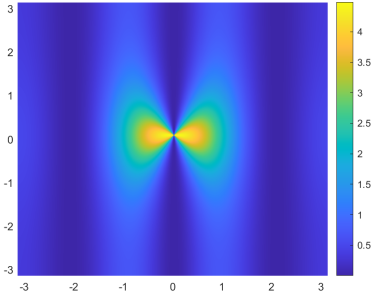
f_1, f_2 compactly supported in Ω^*. Isolated singularity at $\mathbf{q} = \mathbf{0}$.
$f_1(\mathbf{q}) = \mathcal{O}(|\mathbf{q}|^2), f_2(\mathbf{q}) = \mathcal{O}(|\mathbf{q}|^4)$

- 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 $\mathbf{q}_1 = \mathbf{q}_2 = \mathbf{0}$.
$f_3(\mathbf{q}_1, \mathbf{q}_2) = \mathcal{O}(|\mathbf{q}_1|^2 \, |\mathbf{q}_2|^2)$.

Singularity due to anisotropicity



- $f(\mathbf{q}) = \mathcal{O}(|\mathbf{q}|^2) \quad \not\Rightarrow \quad f(\mathbf{q}) = C\,|\mathbf{q}|^2 + o(|\mathbf{q}|^2)$
- Hence $f(\mathbf{q})/\,|\mathbf{q}|^2$ may not be continuous.
- Happens in anisotropic materials

Standard analysis

- $f(\mathbf{q})$ smooth, periodic, $f(\mathbf{q}) = \mathcal{O}(|q|^\alpha)$. $|\mathcal{K}_\mathbf{q}| = N_\mathbf{k} = m^d$.
- Standard Euler-Maclaurin analysis:

$$\mathcal{E}_{\Omega^*}\left(f(\mathbf{q})/\left|\mathbf{q}\right|^{2p}, \mathcal{K}_\mathbf{q}\right) = \mathcal{O}(m^{-(\gamma-1)}), \quad \gamma = \alpha - 2p.$$

- In MP2, $\gamma = 0 \quad \Rightarrow$ no convergence rate

Main technical result

Theorem (Xing, Li, L., in preparation)

$$\mathcal{E}_{\Omega^*}\left(f(\mathbf{q})/\left|\mathbf{q}\right|^{2p}, \mathcal{K}_{\mathbf{q}}\right) = \mathcal{O}(m^{-(\gamma+d)}), \quad \gamma = \alpha - 2p.$$

- with $\gamma = 0$, MP2 error (direct term) is $\mathcal{O}(m^{-d}) = \mathcal{O}(N_{\mathbf{k}}^{-1})$.
- Similar result for the exchange term.
- Simplified and generalized results of Lyness[1]

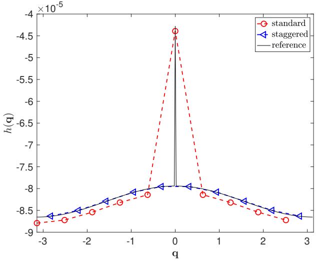
[1] Lyness, Math. Comp. 1976

Symmetry and removable discontinuity

- For systems with high symmetries (e.g. cubic symmetry), we do have

$$f(\mathbf{q}) = C\,|\mathbf{q}|^2 + o(|\mathbf{q}|^2)$$

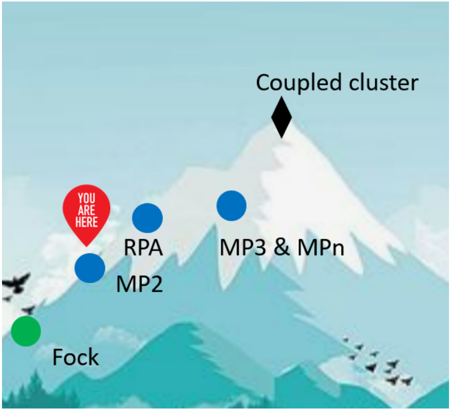
- Standard mesh: set $f(\mathbf{q})/\,|\mathbf{q}|^2$ to 0 at $\mathbf{q} = \mathbf{0}$
- Always error of $\mathcal{O}(N_{\mathbf{k}}^{-1})$.
- Similar for the $f_2(\mathbf{q})/\,|\mathbf{q}|^4$ term.
- Staggered mesh: avoid all these errors. Convergence rate $\mathcal{O}\left(N_{\mathbf{k}}^{-\frac{d+2}{d}}\right)$ or better.



Conclusion

- Quadrature based analysis for finite-size errors of Fock exchange energy: a new derivation for Shifted Coulomb operator $\sim$ Madelung constant correction
- For MP3: $\langle ij|kl\rangle$ or $\langle ab|cd\rangle$ (work in progress)
- For RPA: analysis of an infinite number of diagrams.
- Coupled cluster theory.

Thank you for your attention!



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