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A similarity renormalization group (SRG) approach to *GW*

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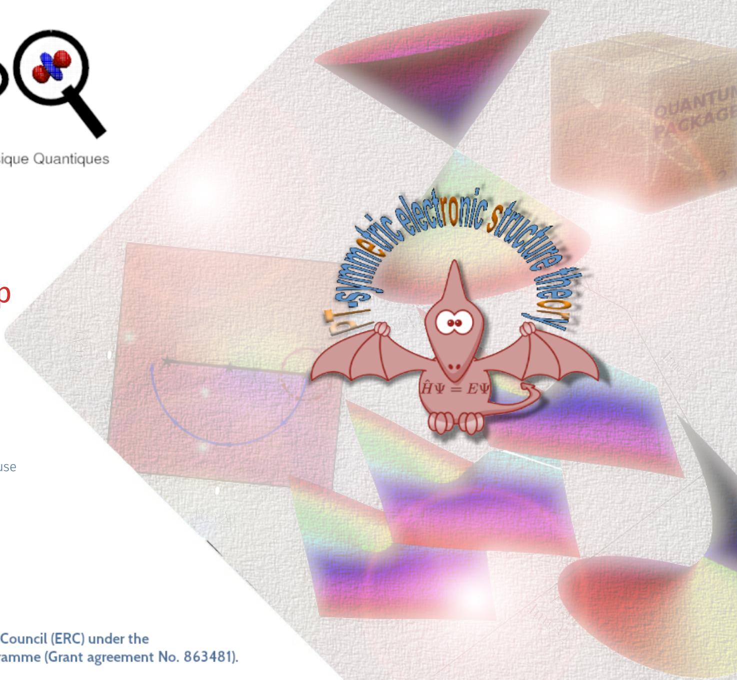
https://lcpq.github.io/PTEROSOR



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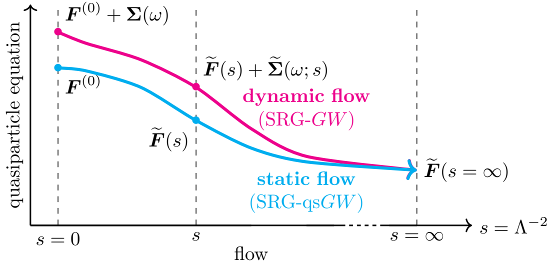


Antoine Marie (PhD)

Marie & Loos, JCTC DOI:10.1021/acs.jctc.3c00281

See also our work on the connections between CC and Green's function methods
Quintero-Monsebaiz, Monino, Marie & Loos, JCP 157 (2022) 231102

$\hookrightarrow$ Scuseria et al. JCP 129 (2008) 231101
$\hookrightarrow$ Berkelbach, JCP 149 (2018) 041103; Lange & Berkelbach, JCTC 14 (2018) 4224
$\hookrightarrow$ Tölle & Chan, JCP 158 (2023) 124123

The *GW* Approximation

- The *GW* approximation allows us to access charged excitations (IPs & EAs)
  Hedin, Phys. Rev. 139 (1965) A796

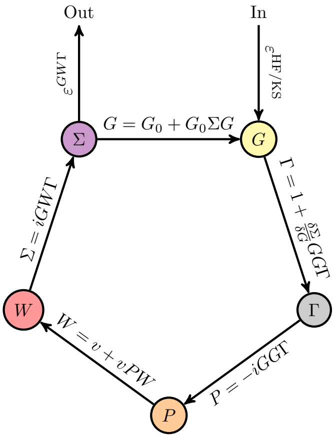
- It yields accurate fundamental gaps at an affordable price for solids and molecules
  Bruneval et al. Front. Chem. 9 (2021) 749779

- *GW* corresponds to an elegant resummation of the direct ring diagrams

- Hence, it is adequate for weak correlation or in the high-density regime
  Gell-Mann & Brueckner, Phys. Rev. 106 (1957) 364

- Self-consistent *GW* calculations can be tricky to converge due to intruder states
  Monino & Loos JCP 156 (2022) 231101

- Going beyond *GW* is, let's say, difficult...
  Romaniello, Reining, Godby, Yang, Bruneval, Kresse, etc.



Hedin, Phys Rev 139 (1965) A796

The wonderful equations of Hedin

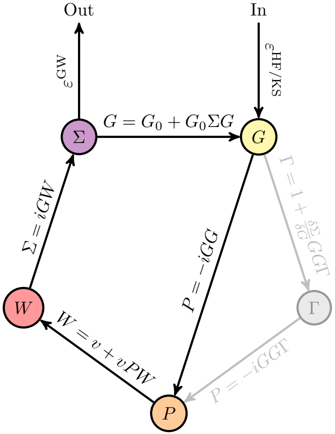
$$\underbrace{G(12)}_{\text{Green's function}} = G_0(12) + \int G_0(13)\Sigma(34)G(42)d(34)$$

$$\underbrace{\Gamma(123)}_{\text{vertex}} = \delta(12)\delta(13) + \int \frac{\delta\Sigma(12)}{\delta G(45)} G(46)G(75)\Gamma(673)d(4567)$$

$$\underbrace{P(12)}_{\text{polarizability}} = -i \int G(13)\Gamma(342)G(41)d(34)$$

$$\underbrace{W(12)}_{\text{screening}} = v(12) + \int v(13)P(34)W(42)d(34)$$

$$\underbrace{\Sigma(12)}_{\text{self-energy}} = i \int G(14)W(13)\Gamma(423)d(34)$$



Hedin, Phys Rev 139 (1965) A796

The *GW* approximation

$$\underbrace{G(12)}_{\text{Green's function}} = G_0(12) + \int G_0(13)\Sigma(34)G(42)d(34)$$

$$\underbrace{\Gamma(123)}_{\text{vertex}} = \delta(12)\delta(13) + \cancel{\int \frac{\delta\Sigma(12)}{\delta G(45)} G(46)G(75)\Gamma(673)d(4567)}$$

$$\underbrace{P(12)}_{\text{polarizability}} = -i\cancel{\int} G(12)\cancel{\Gamma(342)}G(21)\cancel{d(34)} = -iG(12)G(21)$$

$$\underbrace{W(12)}_{\text{screening}} = v(12) + \int v(13)P(34)W(42)d(34)$$

$$\underbrace{\Sigma(12)}_{\text{self-energy}} = i\cancel{\int} G(12)W(12)\cancel{\Gamma(423)d(34)} = iG(12)W(12)$$

Quasiparticle equation (in a general setting)

$$\Big[\underbrace{F}_{\text{Fock matrix}} + \underbrace{\Sigma^{GW}\left(\omega = \epsilon_p^{GW}\right)}_{\text{dynamic self-energy}}\Big]\psi_p^{GW} = \underbrace{\epsilon_p^{GW}}_{\text{quasiparticle energies}} \psi_p^{GW}$$

Practical issues

- dynamic
- highly non-linear
- non-Hermitian

GW self-energy

$$\Sigma_{pq}^{GW}(\omega) = \sum_{i\nu} \frac{W_{pi}^{\nu} W_{qi}^{\nu}}{\omega - \epsilon_i^{GW} + \Omega_\nu - \underbrace{i\eta}_{\text{regularizer}}} + \sum_{a\nu} \frac{W_{pa}^{\nu} W_{qa}^{\nu}}{\omega - \epsilon_a^{GW} - \underbrace{\Omega_\nu}_{\text{RPA excitation}} + i\eta}$$

Screened two-electron integrals

$$W_{pq}^{\nu} = \sum_{ia} \langle pi|qa\rangle \underbrace{(X+Y)_{ia}^{\nu}}_{\text{RPA eigenvectors}}$$

G_0W_0 features

- Diagonal approximation
- A single loop of Hedin's equations

Quasiparticle equation (assuming a HF starting point)

Dynamic version: $$\omega = \epsilon_p^{\text{HF}} + \underbrace{\Sigma_{pp}^{GW}(\omega)}_{\text{built with HF quantities}}$$

Linearized (static) version: $$\epsilon_p^{GW} = \epsilon_p^{\text{HF}} + Z_p \Sigma_{pp}^{GW}(\omega = \epsilon_p^{\text{HF}}) \quad \text{with} \quad Z_p = \underbrace{\left[1 - \left. \frac{\partial \Sigma_{pp}^{GW}(\omega)}{\partial \omega} \right|_{\omega = \epsilon_p^{\text{HF}}} \right]^{-1}}_{\text{renormalization factor}}$$

G_0W_0 issues

- Highly starting point dependent

ev*GW* features

- Diagonal approximation
- Self-consistency on the quasiparticle energies only

Quasiparticle equation (assuming a HF starting point)

$$\omega = \epsilon_p^{\text{HF}} + \underbrace{\Sigma_{pp}^{GW}(\omega)}_{\text{built with } GW \text{ quantities}}$$

ev*GW* issues

- Lack of self-consistency on the orbitals
- Challenging to converge (even with DIIS)

qs*GW* features

- Static approximation of the self-energy
- Brute-force symmetrization

Quasiparticle equation

$$\left[F + \underbrace{\boldsymbol{\Sigma}^{\text{qs}GW}}_{\text{static self-energy}} \right] \psi_p^{GW} = \epsilon_p^{GW} \psi_p^{GW} \quad \text{with} \quad \Sigma_{pq}^{\text{qs}GW} = \underbrace{\frac{\Sigma_{pq}^{GW}(\epsilon_p^{GW}) + \Sigma_{pq}^{GW}(\epsilon_q^{GW})}{2}}_{\text{symmetrization}}$$

Faleev et al. PRL 93 (2004) 126406

qs*GW* issues

- “Empirical” symmetrization [Ismail-Beigi, JPCM 29 (2017) 385501]
- Very challenging to converge (even with DIIS)

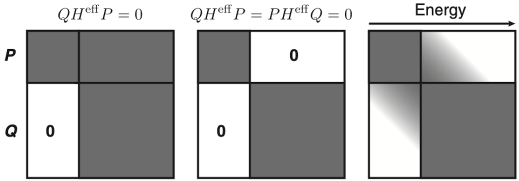
Intruder-state problem $\Leftrightarrow$ a determinant in Q becomes near-degenerate with a determinant in P

$\Rightarrow$ appearance of small denominators

$\Rightarrow$ convergence issues!

How to avoid intruder states? $\Rightarrow$ do not enforce $QH^{\text{eff}}P = \mathbf{0}$

$\Leftrightarrow$ near-degenerate determinants are not decoupled



$\Leftarrow$ Continuous (unitary) SRG transformation

SRG decouples the Hamiltonian starting from states that have the largest energy separation and progressing to states with smaller energy separation

Historical Overview of SRG

- Introduced independently by
  - Glazek and Wilson in quantum field theory [PRD 48 (1993) 5863, ibid 49 (1994) 4214]
  - Wegner in condensed matter systems [Ann. Phys. 506 (1994) 77]
- (In-Medium) SRG is used a lot in nuclear physics
  [Hergert et al. Phys. Rep. 621 (2016) 165]
- First introduced in chemistry by Steven White
  [JCP 117 (2002) 7472]
- More recently developed by the group of Francesco Evangelista (SR/MR-DSRG)
  [JCP 141 (2014) 054109; Annu. Rev. Phys. Chem. 70 (2019) 275]

Unitary transformation of the Hamiltonian

$$\boxed{H \to H(s) = U(s)\, H\, U^{\dagger}(s), \quad s \in [0, \infty)}$$

- For $s > 0$, $H(s)$ has a more (block) diagonal form than H
- The flow variable s is a time-like parameter that controls the extent of the transformation
  - If $s = 0$, then $U(s) = \mathbf{1}$, i.e., $H(s = 0) = H$
  - In the limit $s \to \infty$, $H(s)$ becomes (block) diagonal

$$H(s) = \underbrace{H_{\mathrm{d}}(s)}_{\text{diagonal}} + \underbrace{H_{\mathrm{od}}(s)}_{\text{off-diagonal}} \quad \Rightarrow \quad \lim_{s \to \infty} H_{\mathrm{od}}(s) = 0$$

The SRG flow equation

$$\boxed{\frac{\mathrm{d}H(s)}{\mathrm{d}s} = [\boldsymbol{\eta}(s), H(s)], \quad H(0) = H}$$

where the flow generator $\boldsymbol{\eta}(s) = \frac{\mathrm{d}U(s)}{\mathrm{d}s} U^{\dagger}(s) = -\boldsymbol{\eta}^{\dagger}(s)$ is an anti-Hermitian operator

Suitable parametrization of $\hat{\eta}(s)$ allows to integrate the flow equation and find a numerical solution of $\hat{H}(s)$ that satisfies the boundary conditions without having to explicitly construct $\hat{U}(s)$

Wegner's canonical generator

$$\boxed{\boldsymbol{\eta}^{\mathrm{W}}(s) = [H_{\mathrm{d}}(s), H_{\mathrm{od}}(s)]}$$

As long as $\boldsymbol{\eta}^{\mathrm{W}}(s) \neq 0$, $\frac{\mathrm{d}}{\mathrm{d}s} \mathrm{Tr}\left[H_{\mathrm{od}}(s)^2\right] \leq 0$ $\Rightarrow$ off-diagonal decreases in a monotonic way

Partitionning of the initial problem

$$H(s=0) = \underbrace{H_\text{d}(s=0)}_{\text{zeroth order}} + \lambda \underbrace{H_\text{od}(s=0)}_{\text{first order}}$$

Perturbative analysis of the SRG equations

$$H(s) = H^{(0)}(s) + \lambda H^{(1)}(s) + \lambda^2 H^{(2)}(s) + \cdots$$
$$\boldsymbol{\eta}(s) = \boldsymbol{\eta}^{(0)}(s) + \lambda \boldsymbol{\eta}^{(1)}(s) + \lambda^2 \boldsymbol{\eta}^{(2)}(s) + \cdots$$

How to identify the diagonal and off-diagonal terms in *GW*?

Static Version of GW

$$
\left.
\begin{aligned}
&\left[F + \Sigma^{GW}\left(\omega = \epsilon_p^{GW}\right)\right]\psi_p^{GW} = \epsilon_p^{GW}\psi_p^{GW} \\
&\Sigma^{GW}(\omega) = W^{\text{2h1p}}\left(\omega\mathbf{1} - C^{\text{2h1p}}\right)^{-1}\left(W^{\text{2h1p}}\right)^{\dagger} \\
&\qquad + W^{\text{2p1h}}\left(\omega\mathbf{1} - C^{\text{2p1h}}\right)^{-1}\left(W^{\text{2p1h}}\right)^{\dagger}
\end{aligned}
\right\}
\underset{\text{upfolding}}{\overset{\text{downfolding}}{\rightleftharpoons}}
\left\{
\begin{aligned}
&H\Psi_p^{GW} = \epsilon_p^{GW}\Psi_p^{GW} \\
&H = \begin{pmatrix} F & W^{\text{2h1p}} & W^{\text{2p1h}} \\ \left(W^{\text{2h1p}}\right)^{\dagger} & C^{\text{2h1p}} & \mathbf{0} \\ \left(W^{\text{2p1h}}\right)^{\dagger} & \mathbf{0} & C^{\text{2p1h}} \end{pmatrix}
\end{aligned}
\right.
$$

$$
\begin{array}{r|c|c|c|l}
\hline
\text{1h \& 1p conf.} & \boldsymbol{F} & \boldsymbol{W}^{\text{2h1p}} & \boldsymbol{W}^{\text{2p1h}} & \text{internal space } \boldsymbol{P} \\
\hline
\text{2h1p conf.} & \boldsymbol{W}^{\text{2h1p}} & \boldsymbol{C}^{\text{2h1p}} & \mathbf{0} & \\
\hline
\text{2p1h conf.} & \boldsymbol{W}^{\text{2p1h}} & \mathbf{0} & \boldsymbol{C}^{\text{2p1h}} & \text{external space } \boldsymbol{Q} \\
\hline
\end{array}
$$

Bintrim & Berkelbach, JCP 154 (2021) 041101; Monino & Loos JCP 156 (2022) 231101; Tölle & Chan, JCP 158 (2023) 124123

Regularized GW equations up to second order

$$\left[\widetilde{F}(s) + \widetilde{\Sigma}^{\text{SRG-GW}}(\omega = \epsilon_p^{GW}; s)\right]\psi_p^{GW} = \epsilon_p^{GW}\psi_p^{GW}$$

Energy-dependent regularization

$$\widetilde{F}_{pq}(s) = \delta_{pq}\epsilon_p^{\text{HF}} + \sum_{r\nu} \frac{\Delta_{pr}^{\nu} + \Delta_{qr}^{\nu}}{(\Delta_{pr}^{\nu})^2 + (\Delta_{qr}^{\nu})^2}\left[W_{pr}^{\nu}W_{qr}^{\nu} - W_{pr}^{\nu}(s)W_{qr}^{\nu}(s)\right] \quad \text{with} \quad \Delta_{pr}^{\nu} = \epsilon_p^{GW} - \epsilon_r^{GW} \pm \Omega_{\nu}$$

$$\widetilde{\Sigma}_{pq}^{\text{SRG-GW}}(\omega; s) = \sum_{i\nu} \frac{W_{pi}^{\nu}(s)W_{qi}^{\nu}(s)}{\omega - \epsilon_i^{GW} + \Omega_{\nu}} + \sum_{a\nu} \frac{W_{pa}^{\nu}(s)W_{qa}^{\nu}(s)}{\omega - \epsilon_a^{GW} - \Omega_{\nu}} \quad \text{with} \quad \boxed{W_{pr}^{\nu}(s) = W_{pr}^{\nu} e^{-(\Delta_{pr}^{\nu})^2 s}}$$

For a fixed value of the energy cut-off $\Lambda = s^{-1/2}$,

if	$\lvert\Delta_{pr}^{\nu}\rvert \gg \Lambda$	then	$W_{pr}^{\nu}(s) = W_{pr}^{\nu} e^{-(\Delta_{pr}^{\nu})^2 s} \approx 0$	(decoupled)
if	$\lvert\Delta_{pr}^{\nu}\rvert \ll \Lambda$	then	$W_{pr}^{\nu}(s) \approx W_{pr}^{\nu}$	(remains coupled)

Limit as $s \to 0$

$$\widetilde{F}(s=0) = F \quad \text{and} \quad \widetilde{\Sigma}^{\text{SRG-GW}}(\omega; s=0) = \Sigma^{GW}(\omega)$$

Limit as $s \to \infty$

$$\widetilde{\Sigma}^{\text{SRG-GW}}(\omega; s \to \infty) = \mathbf{0} \quad \text{and} \quad \widetilde{F}_{pq}(s \to \infty) = \delta_{pq}\epsilon_p^{\text{HF}} + \underbrace{\sum_{r\nu} \frac{\Delta_{pr}^{\nu} + \Delta_{qr}^{\nu}}{(\Delta_{pr}^{\nu})^2 + (\Delta_{qr}^{\nu})^2} W_{pr}^{\nu} W_{qr}^{\nu}}_{\text{static correction}}$$

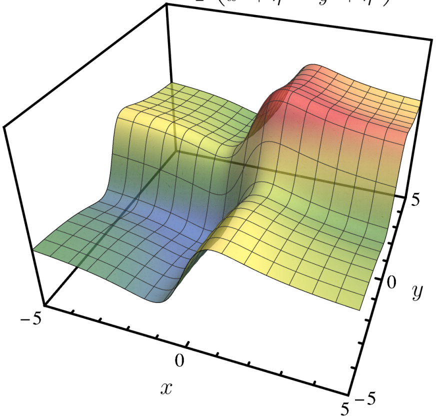
By removing the coupling terms, SRG transforms continuously the dynamic problem into a static one

SRG-qs*GW* self-energy from first principles

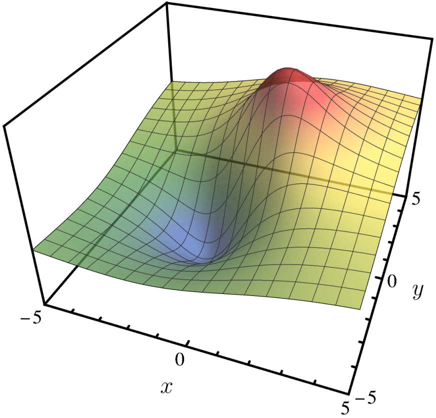
$$\widetilde{\Sigma}^{\text{SRG-qs}GW}(\omega; s) = \sum_{r\nu} \frac{\Delta_{pr}^{\nu} + \Delta_{qr}^{\nu}}{(\Delta_{pr}^{\nu})^2 + (\Delta_{qr}^{\nu})^2} \left[W_{pr}^{\nu} W_{qr}^{\nu} - W_{pr}^{\nu}(s) W_{qr}^{\nu}(s) \right]$$

qsGW vs SRG-qsGW functional forms for $s = 1/(2\eta^2)$

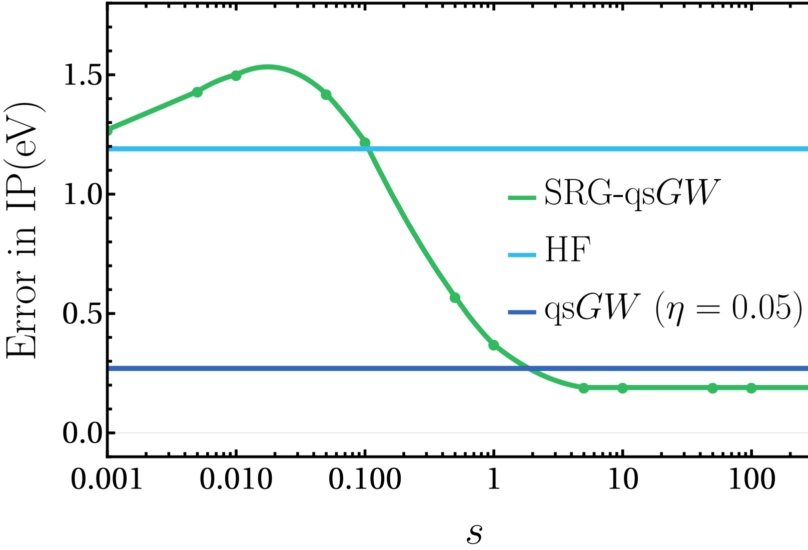
$$f^{\text{qs}GW}(x,y;\eta) = \frac{1}{2}\left(\frac{x}{x^2+\eta^2} + \frac{y}{y^2+\eta^2}\right)$$



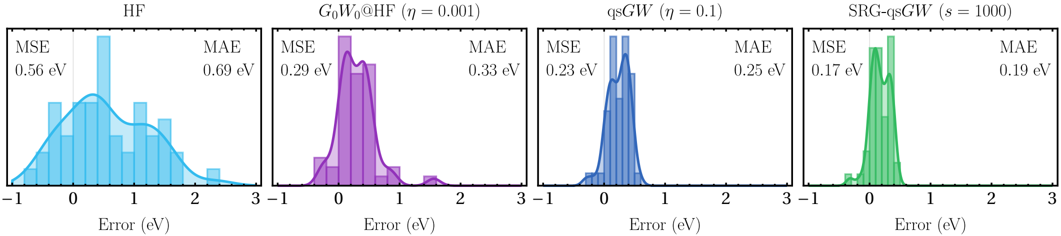
$$f^{\text{SRG-qs}GW}(x,y;\eta) = \frac{x+y}{x^2+y^2}\left[1 - e^{-(x^2+y^2)/(2\eta^2)}\right]$$



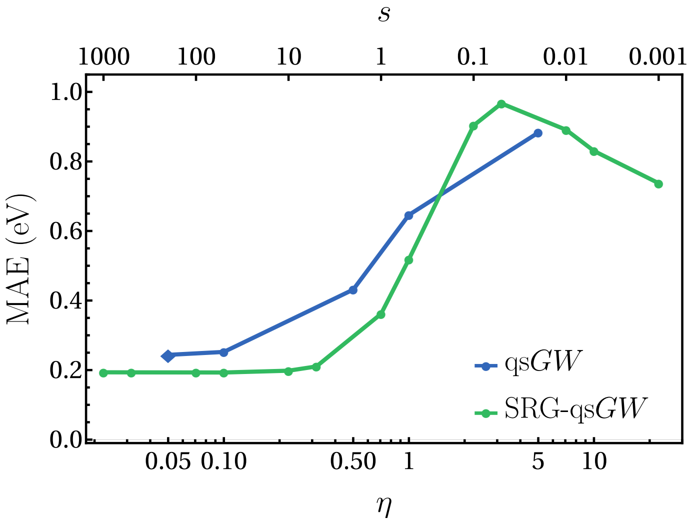
Example: Principal IP of water (aug-cc-pVTZ) wrt ΔCCSD(T)



Principal IPs for $GW50$ set (aug-cc-pVTZ) wrt ΔCCSD(T)



MAE Convergence wrt s or η



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