Parquet Theory for Molecular Systems

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https://pfloos.github.io/WEB_LOOS

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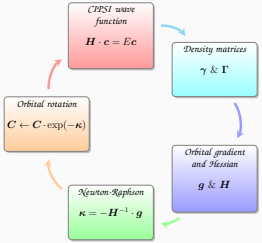
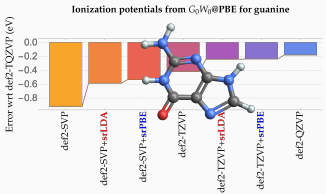
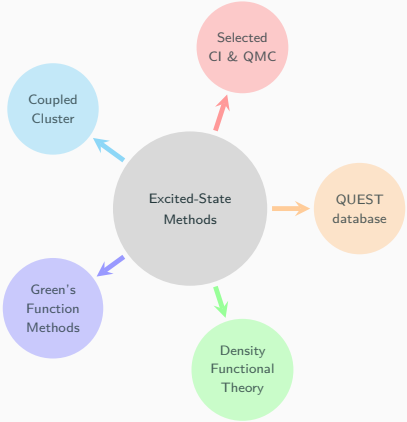
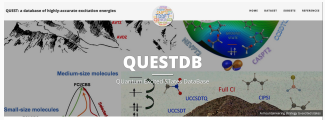
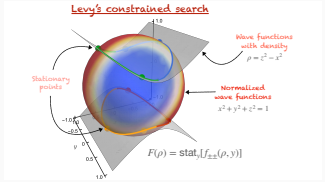
General Overview of our Research Group









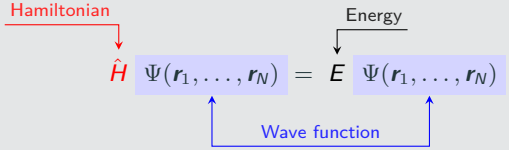


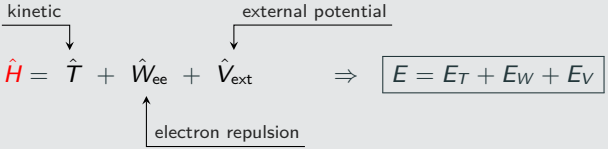
https://lcpq.github.io/PTEROSOR

Antoine Marie (PhD)

The Man, The Myth, The Legend...

Wave Function Theory





Density Functional Theory

$$N \int \cdots \int \Psi^*(\boldsymbol{r}, \ldots, \boldsymbol{r}_N)\Psi(\boldsymbol{r}, \ldots, \boldsymbol{r}_N)\mathrm{d}\boldsymbol{r}_2 \cdots \mathrm{d}\boldsymbol{r}_N = n(\boldsymbol{r})$$

electron density

Wave Function Theory (WFT) $\rightsquigarrow$ Density Functional Theory (DFT)

$$E = \underset{\times}{E_T} + \underset{\times}{E_W} + \underset{\checkmark}{E_V}$$

Hohenberg & Kohn, Phys. Rev. 1964 (B864) 136

(Less) Reduced Quantities

Density Matrix Functional Theory

1st-order reduced density matrix

$$N \int \cdots \int \Psi^*(\boldsymbol{r}, \ldots, \boldsymbol{r}_N) \Psi(\boldsymbol{r}', \ldots, \boldsymbol{r}_N) \mathrm{d}\boldsymbol{r}_2 \cdots \mathrm{d}\boldsymbol{r}_N = n_1(\boldsymbol{r}, \boldsymbol{r}')$$

Wave Function Theory (WFT) $\rightsquigarrow$ Reduced Density Matrix Functional Theory (RDMF)

$$E = \underset{\checkmark}{E_T} + \underset{\times}{E_W} + \underset{\checkmark}{E_V}$$

Gilbert, Phys. Rev. B 12 (1975) 2111

One-Body Green's Function: The Sweet Spot?

One-Body Propagator in the Time Domain

one-body Green's function — time-ordering — N-electron ground state

$$G(\boldsymbol{r},\boldsymbol{r}';t-t') = -\mathrm{i}\left\langle \Psi_0^N \right| \hat{T}\left[\hat{\psi}(\boldsymbol{r}t)\;\hat{\psi}^\dagger(\boldsymbol{r}'t')\right]\left|\Psi_0^N\right\rangle$$

Field operators

$$G(\boldsymbol{r},\boldsymbol{r}';t-t') = \begin{cases} -\mathrm{i}\left\langle \Psi_0^N \middle| \hat{\psi}(\boldsymbol{r}t)\hat{\psi}^\dagger(\boldsymbol{r}'t') \middle| \Psi_0^N \right\rangle & \text{for} \quad t > t' \\ +\mathrm{i}\left\langle \Psi_0^N \middle| \hat{\psi}^\dagger(\boldsymbol{r}'t')\hat{\psi}(\boldsymbol{r}t) \middle| \Psi_0^N \right\rangle & \text{for} \quad t' < t \end{cases}$$

- $\left\langle \Psi_0^N \middle| \hat{\psi}(\boldsymbol{r}t)\hat{\psi}^\dagger(\boldsymbol{r}'t') \middle| \Psi_0^N \right\rangle$ measures the propagation of an electron (electron branch)
- $\left\langle \Psi_0^N \middle| \hat{\psi}^\dagger(\boldsymbol{r}'t')\hat{\psi}(\boldsymbol{r}t) \middle| \Psi_0^N \right\rangle$ measures the propagation of a hole (hole branch)

Martin, Reining & Ceperley, *"Interacting Electrons"*

Lehmann Representation

One-Body Propagator in the Frequency Domain

$$G(\boldsymbol{r},\boldsymbol{r}';\omega) = \sum_{\nu} \frac{\mathcal{I}_\nu(\boldsymbol{r})\mathcal{I}_\nu^*(\boldsymbol{r}')}{\omega - (E_0^N - E_\nu^{N-1}) - \mathrm{i}\eta} + \sum_{\nu} \frac{\mathcal{A}_\nu(\boldsymbol{r})\mathcal{A}_\nu^*(\boldsymbol{r}')}{\omega - (E_\nu^{N+1} - E_0^N) + \mathrm{i}\eta}$$

νth ionization potential (IP)

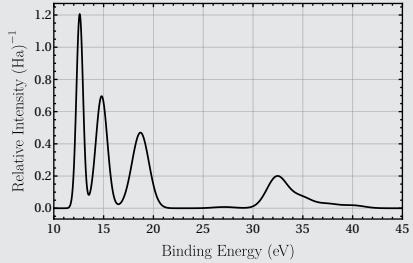
νth electron affinity (EA)

Spectral function

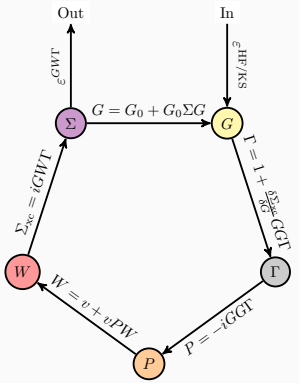
$$A(\omega) = \frac{1}{\pi}\int \mathrm{d}\boldsymbol{r}\mathrm{d}\boldsymbol{r}' \left|\mathrm{Im}\, G(\boldsymbol{r},\boldsymbol{r}';\omega)\right|$$

Marie & Loos, JCTC 20 (2024) 4751

Photoemission spectrum of water



Hedin's Pentagon



Hedin, Phys. Rev. 139 (1965) A796

Hedin's Equations

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

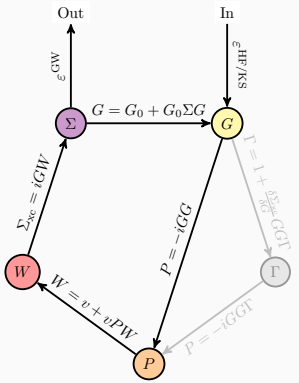
$$\underbrace{\Gamma(123)}_{\text{vertex}} = \delta(12)\delta(13) + \int \frac{\delta\Sigma_{\text{xc}}(12)}{\delta G(45)} G(46)G(75)\Gamma(673)d(4567)$$

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

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

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

Hedin's Square



Hedin, Phys. Rev. 139 (1965) A796

The *GW* Approximation

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

$$\underbrace{\Gamma(123)}_{\text{vertex}} = \delta(12)\delta(13)$$

$$\underbrace{P(12)}_{\text{polarizability}} = -\mathrm{i}G(12)G(21)$$

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

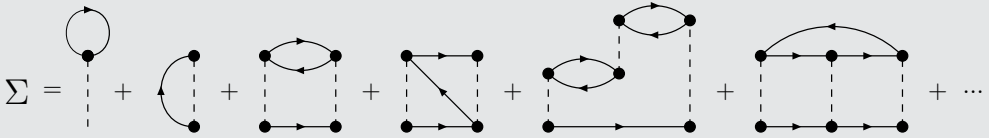
$$\underbrace{\Sigma_{\text{xc}}(12)}_{\text{self-energy}} = \mathrm{i}G(12)W(12)$$

Golze et al. Front. Chem. 7 (2019) 377; Marie et al. Adv. Quantum Chem. 90 (2024) 157

Self-Energy as a Function of the Bare Coulomb Operator

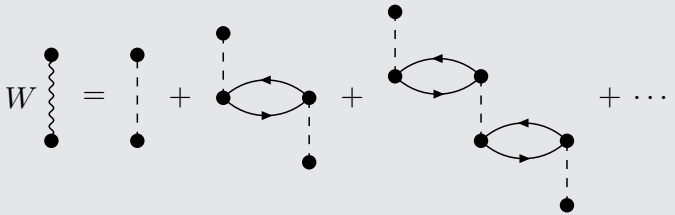
$$\Sigma(11') = \underbrace{-\mathrm{i}\bar{v}(12;1'2')G(2'2)}_{\text{first-order terms}} + \underbrace{\frac{1}{2}\bar{v}(12;3'2')G(3'3)G(4'2)G(2'4)\bar{v}(34;1'4')}_{\text{second-order terms}} + \dots$$

Diagrammatic Representation



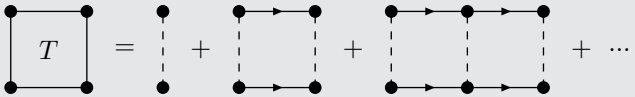
Hedin's Equations

GW Approximation



Hedin, Phys. Rev. 139 (1965) A796

pp T-matrix Approximation



Marie, Romaniello & Loos, PRB 110 (2024) 115155

How to Compute G?

The Dyson Equation

mean-field propagator

$$G(11') = G_0(11') + \int \mathrm{d}(22')\, G_0(12)\, \Sigma(22')\, G(2'1')$$

one-body Green's function — self-energy

$$G^{-1}(11') = G_0^{-1}(11') - \Sigma(11')$$

Quasi-Particle Equation

self-energy — Dyson orbitals

$$\left[\boldsymbol{H}_0 + \boldsymbol{\Sigma}\left(\omega = \epsilon_p\right) \right] \psi_p(\boldsymbol{x}) = \epsilon_p \, \psi_p(\boldsymbol{x}) \,,$$

mean-field Hamiltonian — poles of the Green's function

Two-Body Green's Function

Two-Body Propagator in the Time Domain

two-body Green's function

$$G_2(12;1'2') = (-\mathrm{i})^2 \left\langle \Psi_0^N \middle| \hat{T}\left[\hat{\psi}(2)\hat{\psi}^\dagger(2')\hat{\psi}(1)\hat{\psi}^\dagger(1')\right] \middle| \Psi_0^N \right\rangle$$

Propagation of electron-hole pairs ($t_{1'} > t_1$ and $t_{2'} > t_2$)

$$G_2^{\mathrm{eh}}(12;1'2') = (-\mathrm{i})^2 \left\langle \Psi_0^N \middle| \hat{\psi}^\dagger(1')\hat{\psi}(1)\hat{\psi}^\dagger(2')\hat{\psi}(2) + \hat{\psi}^\dagger(2')\hat{\psi}(2)\hat{\psi}^\dagger(1')\hat{\psi}(1) \middle| \Psi_0^N \right\rangle$$

Propagation of electron-electron and hole-hole pairs ($t_{1'} > t_{2'}$ and $t_1 > t_2$)

$$G_2^{\mathrm{ee}}(12;1'2') = (-\mathrm{i})^2 \left\langle \Psi_0^N \middle| \hat{\psi}(1)\hat{\psi}(2)\hat{\psi}^\dagger(1')\hat{\psi}^\dagger(2') \middle| \Psi_0^N \right\rangle$$

$$G_2^{\mathrm{hh}}(12;1'2') = (-\mathrm{i})^2 \left\langle \Psi_0^N \middle| \hat{\psi}^\dagger(1')\hat{\psi}^\dagger(2')\hat{\psi}(1)\hat{\psi}(2) \middle| \Psi_0^N \right\rangle$$

The Electron-Hole Channel

Electron-Hole Correlation Function

eh correlation function

$$L(12;1'2') = -G_2(12;1'2') + G(11')G(22')$$

$$L(\boldsymbol{r}_1\boldsymbol{r}_2;\boldsymbol{r}_{1'}\boldsymbol{r}_{2'};\omega) = \sum_{\nu>0} \frac{L^N_\nu(\boldsymbol{r}_2\boldsymbol{r}_{2'})R^N_\nu(\boldsymbol{r}_1\boldsymbol{r}_{1'})}{\omega - (E^N_\nu - E^N_0 - \mathrm{i}\eta)} - \sum_{\nu>0} \frac{L^N_\nu(\boldsymbol{r}_2\boldsymbol{r}_{2'})R^N_\nu(\boldsymbol{r}_1\boldsymbol{r}_{1'})}{\omega - (E^N_0 - E^N_\nu + \mathrm{i}\eta)}$$

νth (de)excitation energy

Electron-Hole Bethe-Salpeter Equation (eh-BSE)

$$L(12;1'2') = \underbrace{L_0(12;1'2')}_{G(12')G(21')} + \int \mathrm{d}(33'44')\, L_0(13';1'3)\, \Xi^{\mathrm{eh}}(34';3'4)\, L(42;4'2')$$

eh kernel

Strinati, Riv. Nuovo Cimento 11 (1988) 1; Blase et al. JPCL 11 (2020) 7371; Marie et al. JCP 162 (2025) 134105

Schwinger-Dyson Relationship

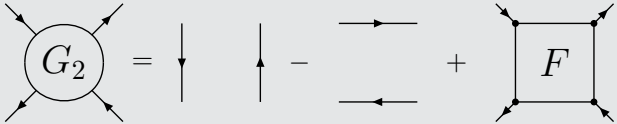
$$G^{-1}(11') = G_0^{-1}(11') - \Sigma(11')$$

$$\Sigma(11') = -\mathrm{i}v(12;3'2')\,G_2(3'2';32)\,G^{-1}(31')$$

Two-body Vertex

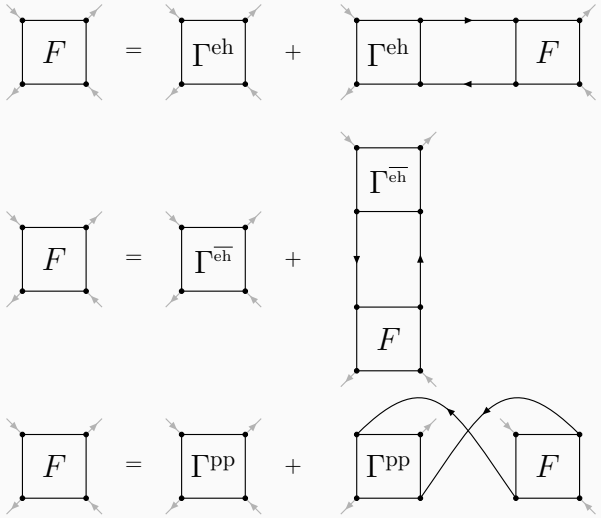
Full two-body vertex

$$G_2(12;34) = G(13)G(24) - G(14)G(23) - G(11')G(3'3)\,F\,(1'2';3'4')G(4'4)G(22')$$



Parquet theory aims at computing F, hence G_2, through Dyson equations

Bethe-Salpeter Equations



Two-body Vertex

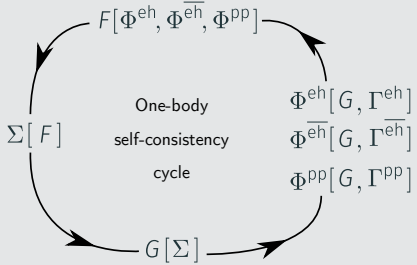
Parquet Decomposition

$$F(12;34) = \underbrace{\Lambda(12;34)}_{\text{Irreducible vertex}} + \underbrace{\Phi^{\text{eh}}(12;34) + \Phi^{\overline{\text{eh}}}(12;34) + \Phi^{\text{pp}}(12;34)}_{\text{can be computed with Bethe-Salpeter equations}}$$

Proper way to account for different correlation channels in the self-energy without double counting!

De Dominicis & Martin, J. Math. Phys. 5 (1964) 14; ibid 5 (1964) 31
Bickers, *"Self-consistent many-body theory for condensed matter systems"* in Theoretical Methods for Strongly Correlated Electrons (2004) 237

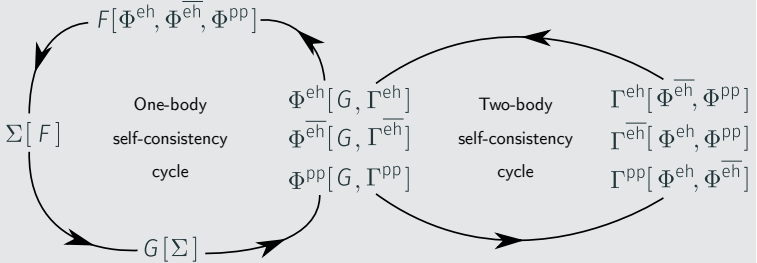
Self-Consistent Algorithm



Approximations

- Parquet approximation $\Lambda = -\mathrm{i}\bar{v}$
- One-shot approximation
- Static kernel approximation for Γ

Self-Consistent Algorithm



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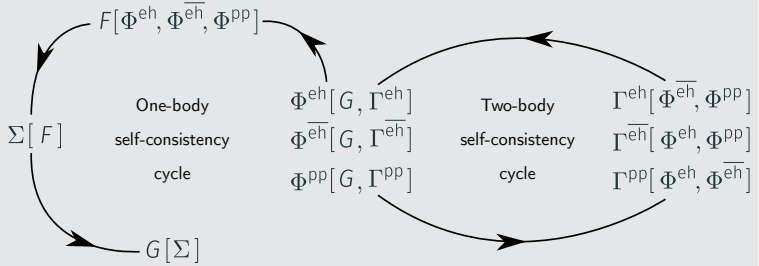
Self-Consistent Algorithm



Approximations

- Parquet approximation $\Lambda = -\mathrm{i}\bar{\nu}$
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- Static kernel approximation for Γ

One-shot parquet approximation (osPA)

Full two-body self-consistency, single one-body iteration in the diagonal approximation

Preliminary Results on Principal IPs

Preliminary statistics on 20 IPs in the aug-cc-pVTZ basis set

Method	osPA	G_0W_0	G_0T_0
MAE	0.29	0.37	0.34

Marie & Loos, JCP 163 (2025) 194115

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- Enzo Monino
- Roberto Orlando
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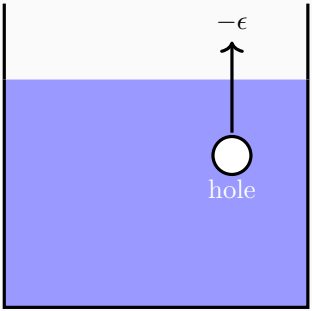
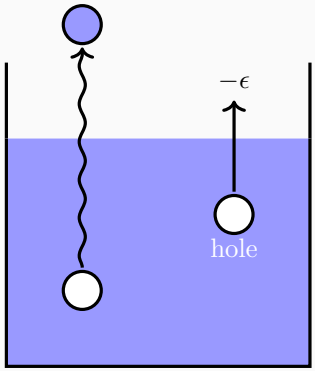


electron removal

- Link to electron-boson Hamiltonian:
  Langreth, PRB 1 (1970) 471
  Hedin, JPCM 11 (1999) R489

- Link to coupled-cluster theory:
  Lange & Berkelbach, JCTC 14 (2018) 4224
  Quintero-Monsebaiz et al. JCP 157 (2022) 231102
  Tolle & Chan, JCP 158 (2023) 124123



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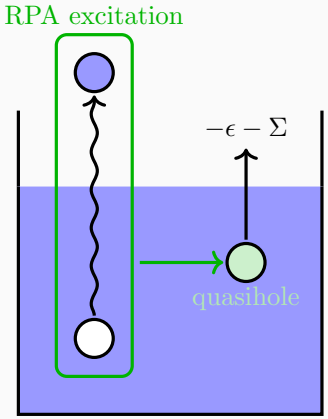

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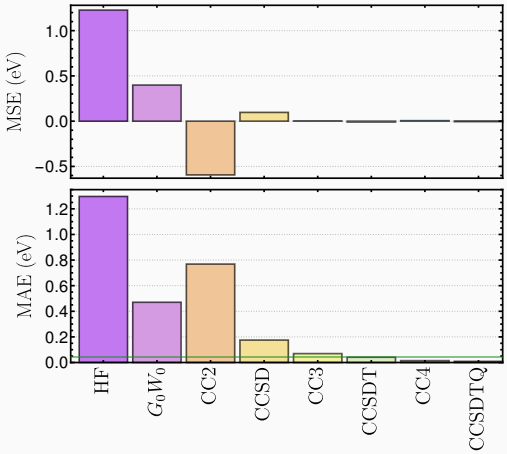
Inner- and Outer-valence IPs (aug-cc-pVTZ) for 23 small molecules (FCI reference)



Computational cost

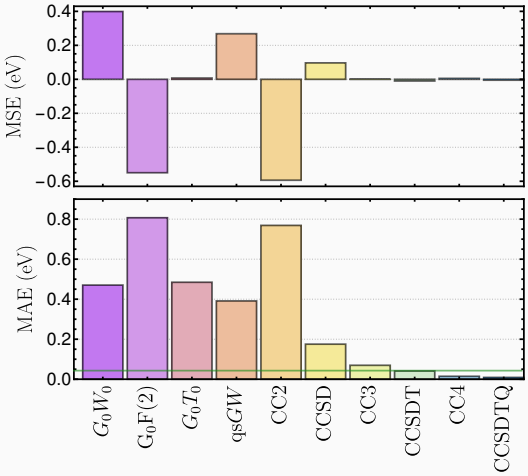
- HF $\mathcal{O}(K^4)$
- G_0W_0 $\mathcal{O}(K^6)$ $\rightarrow\mathcal{O}(K^4)$
- IP-EOM-CC2 $\mathcal{O}(K^5)$
- IP-EOM-CCSD $\mathcal{O}(K^6)$
- IP-EOM-CCSDT $\mathcal{O}(K^8)$

Some issues:

- Highly starting point dependent!
- Systematic improvable?

Marie & Loos, JCTC 20 (2024) 4751

Inner- and Outer-valence IPs (aug-cc-pVTZ) for 23 small molecules (FCI reference)



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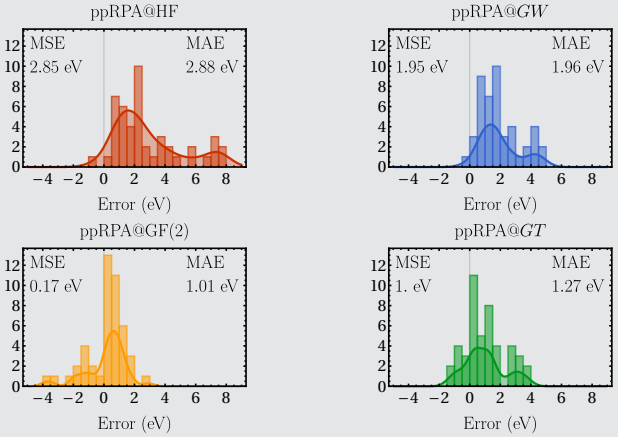
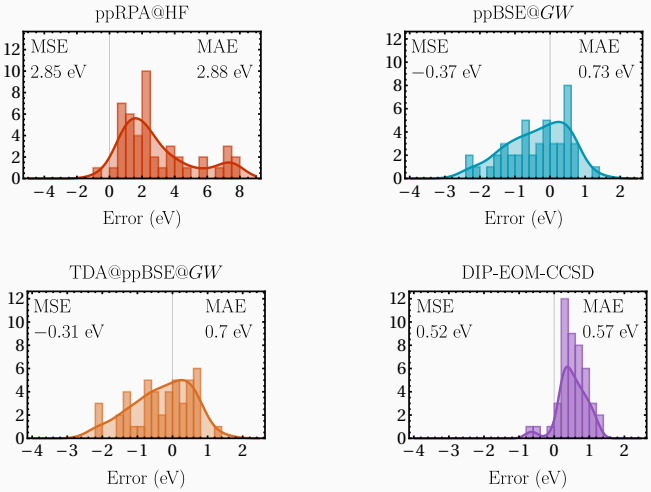
Singlet and Triplet DIPs (aug-cc-pVTZ) for 23 small molecules (FCI reference)

Effect of the Quasiparticle Energies



Marie & Loos, JCTC 20 (2024) 4751; Marie et al. JCP 162 (2025) 134105

Singlet and Triplet DIPs (aug-cc-pVTZ) for 23 small molecules (FCI reference)



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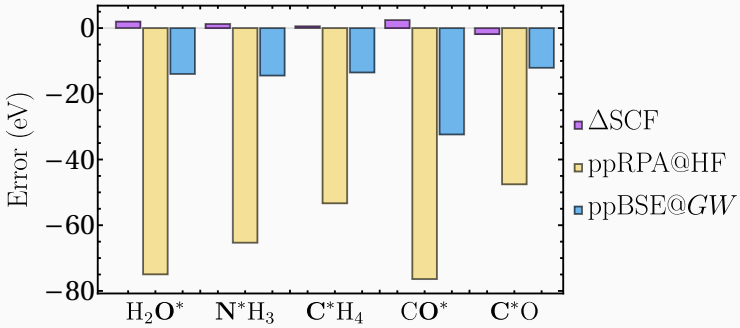
(Single-Site) Double Core Holes (aug-cc-pCVTZ & CVS-FCI reference)



Cederbaum et al. JCP 85 (1986) 6513; Marie et al. JCP 162 (2025) 134105

Parquet Algorithm