An algebraic-diagrammatic construction scheme for vertex corrections to the GW self-energy

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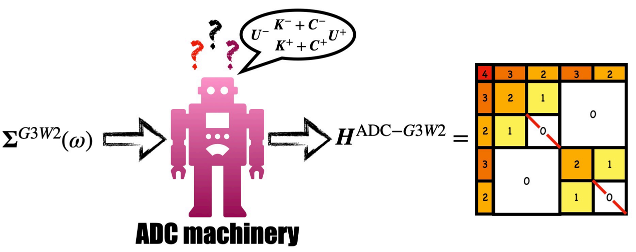
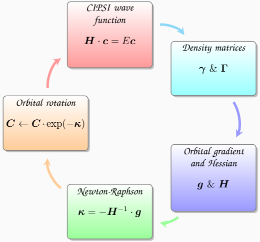
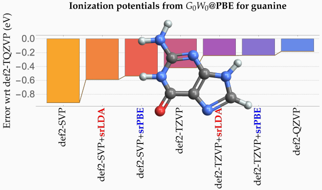
https://pfloos.github.io/WEB_LOOS

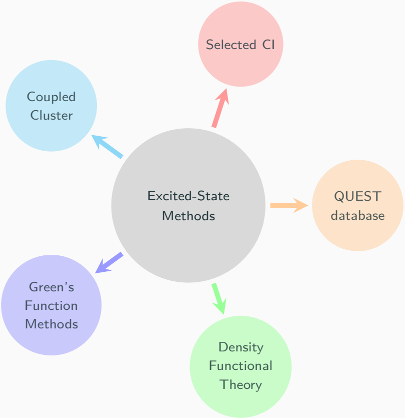
June 2nd 2026

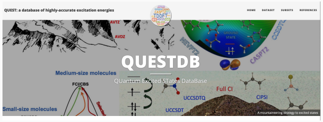


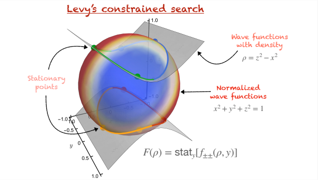
General Overview of our Research Group











https://pfloos.github.io/WEB_LOOS

Green's Function Methods

Antoine Marie (PhD)

Marios-Petros Kitsaras (Postdoc)

Johannes Tölle (Hamburg)

One-Body Green's Function

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"*

Links With Other Reduced Quantities

Link to RDMFT & DFT

$$n_1(\boldsymbol{r},\boldsymbol{r}') = -\mathrm{i} \lim_{t'\to t} G(\boldsymbol{r},\boldsymbol{r}';t-t') \qquad n(\boldsymbol{r}) = -\mathrm{i} \lim_{t'\to t} \lim_{\boldsymbol{r}'\to \boldsymbol{r}} G(\boldsymbol{r},\boldsymbol{r}';t-t')$$

Galitskii-Migdal Energy Functional

$$\begin{aligned} E &= \frac{\mathrm{i}}{2}\int \mathrm{d}\boldsymbol{r} \lim_{t'\to t} \lim_{\boldsymbol{r}'\to \boldsymbol{r}} \nabla^2_{\boldsymbol{r}} G(\boldsymbol{r},\boldsymbol{r}';t-t') + \frac{1}{2}\int \mathrm{d}\boldsymbol{r} \lim_{t'\to t} \lim_{\boldsymbol{r}'\to \boldsymbol{r}} \left[\frac{\partial}{\partial t} + \mathrm{i}\hat{h}(\boldsymbol{r})\right] G(\boldsymbol{r},\boldsymbol{r}',t-t') + E_V \\ &= \frac{1}{2}\int \mathrm{d}\boldsymbol{r} \lim_{t'\to t} \lim_{\boldsymbol{r}'\to \boldsymbol{r}} \left[\frac{\partial}{\partial t} - \mathrm{i}\hat{h}(\boldsymbol{r})\right] G(\boldsymbol{r},\boldsymbol{r}';t-t') \end{aligned}$$

Galitskii & Migdal, JETP 7 (1958) 96

Lehmann Representation

One-Body Propagator in the Frequency Domain

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

νth ionization potential (IP)

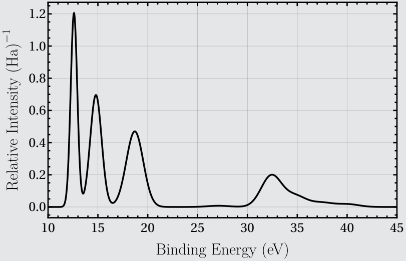
νth electron affinity (EA)

Spectral function

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

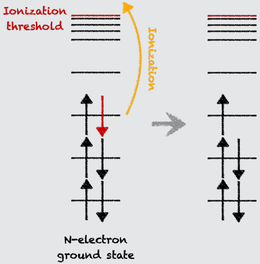
Marie & Loos, JCTC 20 (2024) 4751

Photoemission spectrum of water

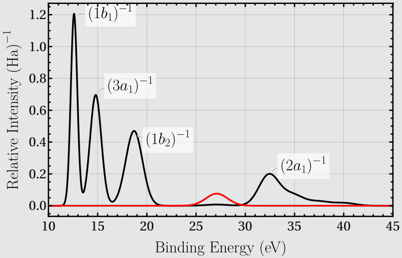


Photoemission Spectroscopy

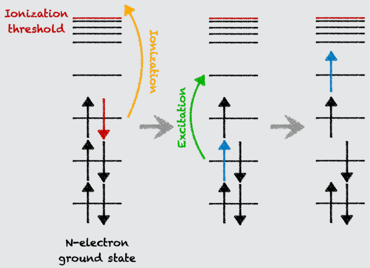
Single ionization (quasiparticle)



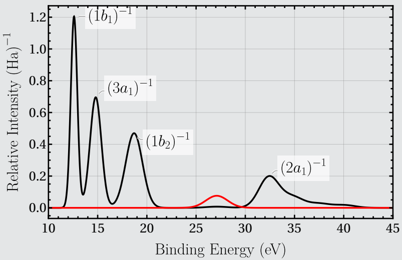
Experimental spectrum of water



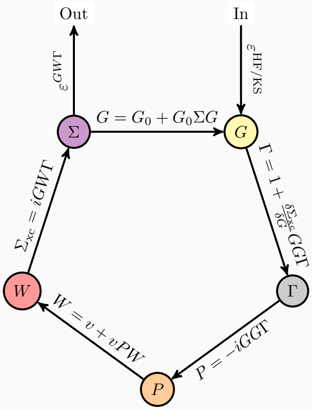
Shake-up transition (satellite)



Experimental spectrum of water



Hedin's Pentagon



Hedin, Phys. Rev. 139 (1965) A796

Hedin's Equations

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

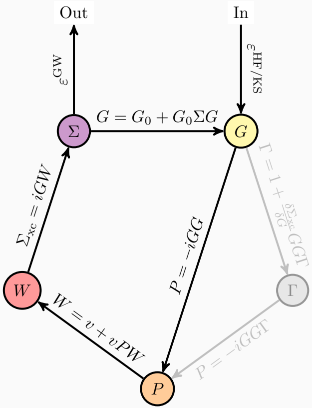
$$\underbrace{\Gamma(123)}_{\text{vertex}} = \delta(12)\delta(13) + \int \frac{\delta\Sigma_{\mathrm{xc}}(12)}{\delta G(45)} G(46)G(75)\Gamma(673)\,\mathrm{d}(4567)$$

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

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

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

Hedin's Square



Hedin, Phys. Rev. 139 (1965) A796

The *GW* Approximation

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

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

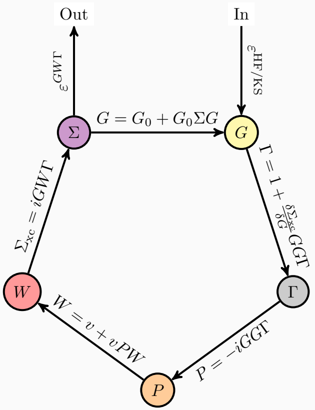
$$\underbrace{P(12)}_{\text{polarizability}} = -\mathrm{i}G(12)G(21)$$

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

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

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

Vertex Corrections



Hedin, Phys. Rev. 139 (1965) A796

Beyond *GW*

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

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

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

↑ inner-vertex correction

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

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

↑ outer-vertex correction

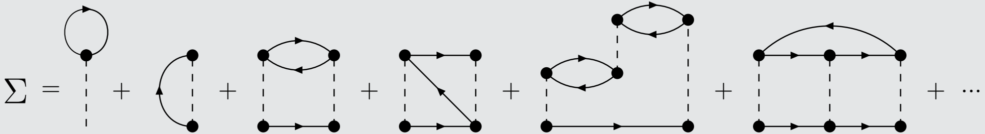
Mejuto-Zaera & Vlcek, PRB 106 (2022) 165129

Self-Energy

Self-Energy as a Function of the Bare Coulomb Operator

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

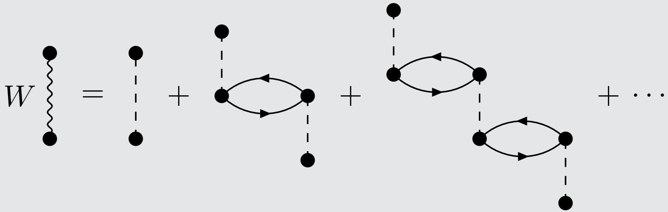
Diagrammatic Representation



Hirata et al. JCTC 11 (2015) 1595; JCP 147 (2017) 044108

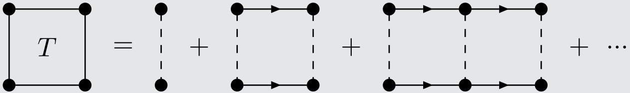
Hedin's Equations

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

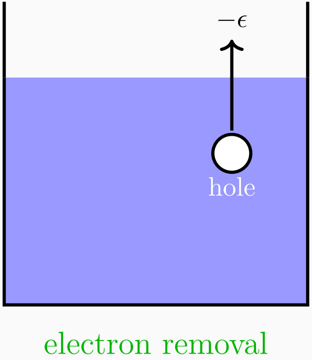
self-energy

Dyson orbitals

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

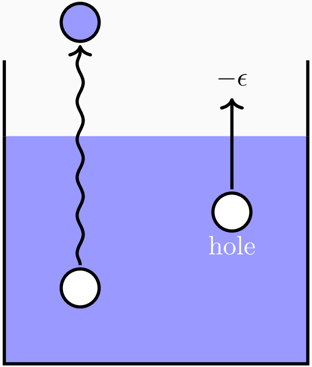
mean-field Hamiltonian

poles of the Green's function



- 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
  Tölle & Chan, JCP 158 (2023) 124123
  Tölle et al. arXiv:2602.10887 (poster #38)
- Analytic nuclear gradients:
  Tölle, JPCL 16 (2025) 3672
  Tölle, Kitsaras & Loos, JPCL 16 (2025) 11134
  Kitsaras, Tölle & Loos, JCP 164 (2026) 044122

Quasiparticle Concept



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
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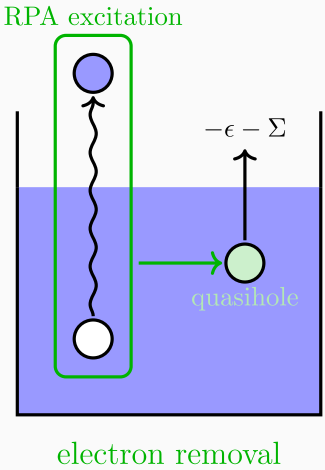
Quasiparticle Concept



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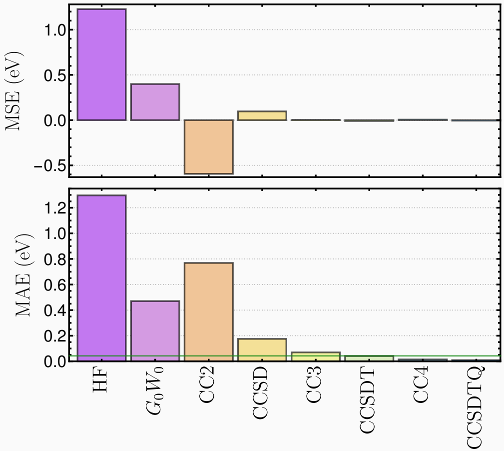
  Kitsaras, Tölle & Loos, JCP 164 (2026) 044122

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



Marie & Loos, JCTC 20 (2024) 4751

Computational cost

- HF $\mathcal{O}(K^4)$
- G_0W_0 $\mathcal{O}(K^6) \to \mathcal{O}(K^4)$
- 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!
- Error compensation?
- Systematic improvable?

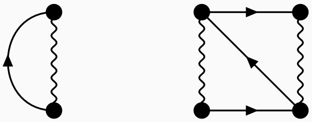
Going Beyond GW: Outer-Vertex Corrections

The $G3W2$ self-energy

$$\Sigma^{G3W2}(\omega) = \mathrm{i}G \cdot W + \mathrm{i}^2 G \cdot W \cdot G \cdot W \cdot G$$
$$= \Sigma^{-}(\omega) + \Sigma^{+}(\omega)$$

hole part　　electron part

Bruneval & Forster, JCTC 20 (2024) 3218



Going Beyond GW: Outer-Vertex Corrections

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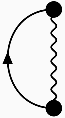
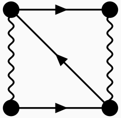
hole part — electron part

Bruneval & Forster, JCTC 20 (2024) 3218





$$\Sigma^{-}(\omega) = \left[\boldsymbol{U}^{\text{2h1p},(1)}\right]^{\dagger} \cdot \left(\omega - \boldsymbol{K}^{\text{2h1p}}\right)^{-1} \cdot \boldsymbol{U}^{\text{2h1p},(1)}$$

$$+ \left[\boldsymbol{U}^{\text{2h1p},(2)}\right]^{\dagger} \cdot \left(\omega - \boldsymbol{K}^{\text{2h1p}}\right)^{-1} \cdot \boldsymbol{U}^{\text{2h1p},(1)} + \left[\boldsymbol{U}^{\text{2h1p},(1)}\right]^{\dagger} \cdot \left(\omega - \boldsymbol{K}^{\text{2h1p}}\right)^{-1} \cdot \boldsymbol{U}^{\text{2h1p},(2)}$$

$$+ \left[\boldsymbol{U}^{\text{2h1p},(1)}\right]^{\dagger} \cdot \left(\omega - \boldsymbol{K}^{\text{2h1p}}\right)^{-1} \cdot \boldsymbol{C}^{\text{2h1p},(1)} \cdot \left(\omega - \boldsymbol{K}^{\text{2h1p}}\right)^{-1} \cdot \boldsymbol{U}^{\text{2h1p},(1)}$$

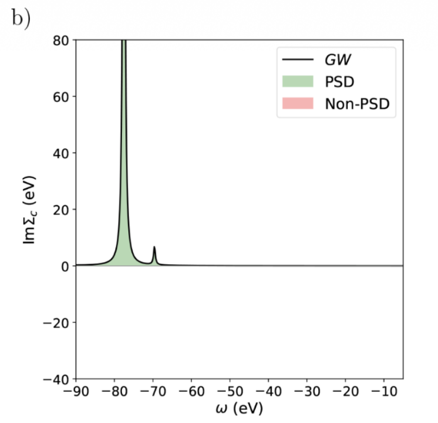
$$+ \left[\boldsymbol{U}^{\text{2h1p},(3)}\right]^{\dagger} \cdot \left(\omega - \boldsymbol{K}^{\text{2h1p}}\right)^{-1} \cdot \boldsymbol{U}^{\text{2h1p},(1)} + \left[\boldsymbol{U}^{\text{2h1p},(1)}\right]^{\dagger} \cdot \left(\omega - \boldsymbol{K}^{\text{2h1p}}\right)^{-1} \cdot \boldsymbol{U}^{\text{2h1p},(3)}$$

$$+ \left[\boldsymbol{U}^{\text{3h2p},(1)} + \boldsymbol{C}^{\text{2h1p/3h2p},(1)} \cdot \left(\omega - \boldsymbol{K}^{\text{2h1p}}\right)^{-1} \cdot \boldsymbol{U}^{\text{2h1p},(1)}\right]^{\dagger} \cdot \left(\omega - \boldsymbol{K}^{\text{3h2p}}\right)^{-1}$$

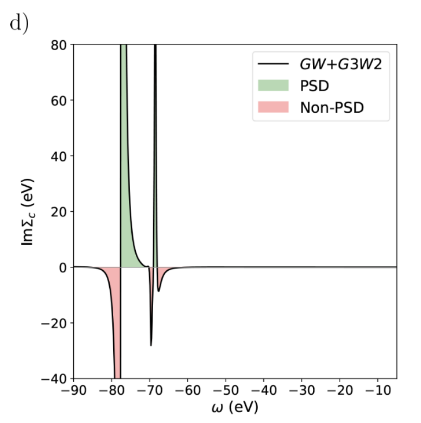
$$\cdot \left[\boldsymbol{U}^{\text{3h2p},(1)} + \boldsymbol{C}^{\text{2h1p/3h2p},(1)} \cdot \left(\omega - \boldsymbol{K}^{\text{2h1p}}\right)^{-1} \cdot \boldsymbol{U}^{\text{2h1p},(1)}\right]$$

Is the $G3W2$ Self-Energy Positive Semi-Definite (PSD)?

GW Self-Energy of Ne



$G3W2$ Self-Energy of Ne



Bruneval, Forster & Pavlyukh, JCTC 21 (2025) 10223

"The procedure is best explained by actually performing it."

Jochen Schirmer, *Many-Body Methods for Atoms, Molecules and Clusters*, Lecture Notes in Chemistry, Vol. 94, Springer.

Self-Energy

Static self-energy

$$\boldsymbol{\Sigma}(\omega) = \boldsymbol{\Sigma}(\infty) + \boldsymbol{\Sigma}^{-}(\omega) + \boldsymbol{\Sigma}^{+}(\omega)$$

hole part

electron part

Diagonal Spectral Representation

$$\boldsymbol{\Sigma}^{\pm}(\omega) = (\boldsymbol{V}^{\pm})^{\dagger} \cdot (\omega - \boldsymbol{\mathcal{E}}^{\pm})^{-1} \cdot \boldsymbol{V}^{\pm} \quad \Leftrightarrow \quad \Sigma^{\pm}_{pq}(\omega) = \sum_{\nu} \frac{(V^{\pm}_{\nu p})^{\dagger} V^{\pm}_{\nu q}}{\omega - \mathcal{E}^{\pm}_{\nu}}$$

The ADC Form

Non-Diagonal ADC Form

$$\boxed{\Sigma^{\pm}(\omega) = (\boldsymbol{U}^{\pm})^{\dagger} \cdot (\omega - \boldsymbol{K}^{\pm} - \boldsymbol{C}^{\pm})^{-1} \cdot \boldsymbol{U}^{\pm}}$$

$$\boldsymbol{U}^{\pm} = \boldsymbol{Q}^{\pm} \cdot \boldsymbol{V}^{\pm} \qquad \boldsymbol{K}^{\pm} + \boldsymbol{C}^{\pm} = \boldsymbol{Q}^{\pm} \cdot \boldsymbol{\mathcal{E}}^{\pm} \cdot (\boldsymbol{Q}^{\pm})^{\dagger}$$

Unitary transformation ($\boldsymbol{Q}^{\pm}$)

zeroth order ($\boldsymbol{K}^{\pm}$)

Hermitian ADC Matrix

$$\boldsymbol{H} = \begin{pmatrix} \boldsymbol{f} + \Sigma(\infty) & (\boldsymbol{U}^{-})^{\dagger} & (\boldsymbol{U}^{+})^{\dagger} \\ \boldsymbol{U}^{-} & \boldsymbol{K}^{-} + \boldsymbol{C}^{-} & \boldsymbol{0} \\ \boldsymbol{U}^{+} & \boldsymbol{0} & \boldsymbol{K}^{+} + \boldsymbol{C}^{+} \end{pmatrix}$$

$\boldsymbol{H}\Psi_{\nu} = \epsilon_{\nu}\Psi_{\nu} \quad \Rightarrow$ quasiparticle and satellite energies

Taylor-Expanded ADC Form

Perturbative Expansions of ADC Blocks

$$\boldsymbol{U}^{\pm} = \boldsymbol{U}^{\pm,(1)} + \boldsymbol{U}^{\pm,(2)} + \cdots \qquad \boldsymbol{C}^{\pm} = \boldsymbol{C}^{\pm,(1)} + \boldsymbol{C}^{\pm,(2)} + \cdots$$

$$\begin{aligned}
\boldsymbol{\Sigma}^{\pm}(\omega) &= \left(\boldsymbol{U}^{\pm}\right)^{\dagger} \cdot \left(\omega - \boldsymbol{K}^{\pm}\right)^{-1} \cdot \sum_{k=0}^{\infty} \left[\boldsymbol{C}^{\pm} \cdot \left(\omega - \boldsymbol{K}^{\pm}\right)^{-1}\right]^{k} \cdot \boldsymbol{U}^{\pm} \\
&= \left[\boldsymbol{U}^{\pm,(1)}\right]^{\dagger} \cdot \left(\omega - \boldsymbol{K}^{\pm}\right)^{-1} \cdot \boldsymbol{U}^{\pm,(1)} \\
&+ \left[\boldsymbol{U}^{\pm,(2)}\right]^{\dagger} \cdot \left(\omega - \boldsymbol{K}^{\pm}\right)^{-1} \cdot \boldsymbol{U}^{\pm,(1)} \\
&+ \left[\boldsymbol{U}^{\pm,(1)}\right]^{\dagger} \cdot \left(\omega - \boldsymbol{K}^{\pm}\right)^{-1} \cdot \boldsymbol{U}^{\pm,(2)} \\
&+ \left[\boldsymbol{U}^{\pm,(1)}\right]^{\dagger} \cdot \left(\omega - \boldsymbol{K}^{\pm}\right)^{-1} \cdot \boldsymbol{C}^{\pm,(1)} \cdot \left(\omega - \boldsymbol{K}^{\pm}\right)^{-1} \cdot \boldsymbol{U}^{\pm,(1)} \\
&+ \cdots
\end{aligned}$$

ADC blocks found by identification — order by order — with the “massaged” $G3W2$ self-energy.

Application to the GW Self-Energy

$$\left[\boldsymbol{f} + \boldsymbol{\Sigma}^{GW}\left(\omega = \epsilon_\nu^{GW}\right)\right]\psi_\nu^{GW} = \epsilon_\nu^{GW}\psi_\nu^{GW}$$

$$\boldsymbol{\Sigma}^{GW}(\omega) = \left(\boldsymbol{U}^{\text{2h1p},(1)}\right)^\dagger \cdot \left(\omega - \boldsymbol{K}^{\text{2h1p}}\right)^{-1} \cdot \boldsymbol{U}^{\text{2h1p},(1)} + \left(\boldsymbol{U}^{\text{2p1h},(1)}\right)^\dagger \cdot \left(\omega - \boldsymbol{K}^{\text{2p1h}}\right)^{-1} \cdot \boldsymbol{U}^{\text{2p1h},(1)}$$

$$\underset{\text{upfold}}{\overset{\text{downfold}}{\rightleftharpoons}}$$

$$\boldsymbol{H}\Psi_\nu^{GW} = \epsilon_\nu^{GW}\Psi_\nu^{GW}$$

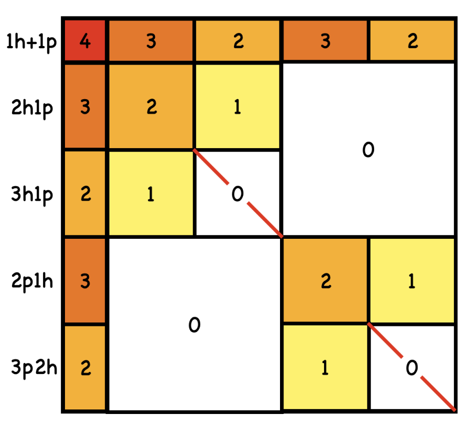
$$\boldsymbol{H} = \begin{pmatrix} \boldsymbol{f} & \left(\boldsymbol{U}^{\text{2h1p},(1)}\right)^\dagger & \left(\boldsymbol{U}^{\text{2p1h},(1)}\right)^\dagger \\ \boldsymbol{U}^{\text{2h1p},(1)} & \boldsymbol{K}^{\text{2h1p}} & \mathbf{0} \\ \boldsymbol{U}^{\text{2p1h},(1)} & \mathbf{0} & \boldsymbol{K}^{\text{2p1h}} \end{pmatrix}$$

Bintrim & Berkelbach, JCP 154 (2021) 041101; Monino & Loos, JCP 156 (2022) 231101

	1h+1p	2h1p	2p1h
1h+1p	2	1	1
2h1p	1	0	0
2p1h	1	0	0

Dreuw et al. JPCA 127 (2023) 6635

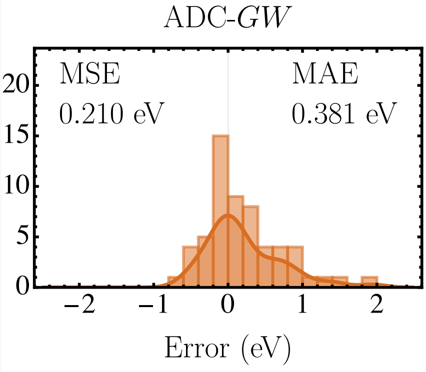
Hermitian Hamitonian for ADC-$G3W2$

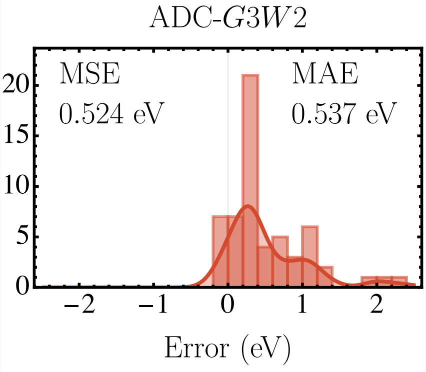


This is the most complete ADC matrix one can construct from $G3W2$

Schirmer et al. PRA 28 (1983) 1237; Leitner et al. JPCA 128 (2024) 7680

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





Error compensation saves the day for *GW*! [see Forster & Bruneval, JPCL 15 (2024) 12526]

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