European Research Council

Established by the European Commission

Laboratoire de Chimie et Physique Quantiques

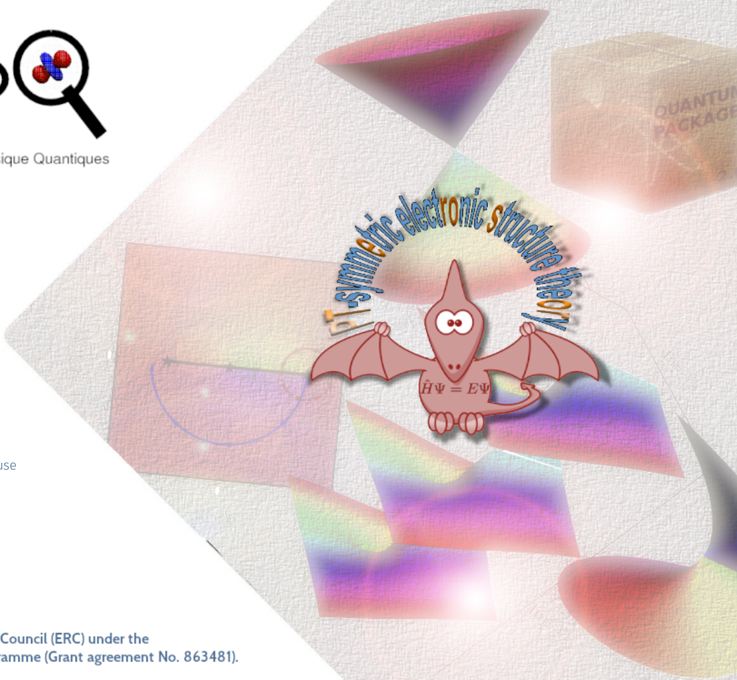
# Green’s function methods for quantum chemistry

Pierre-François (Titou) Loos

Oct 10th 2024

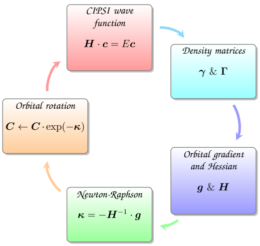
Laboratoire de Chimie et Physique Quantiques, IRSAMC, UPS/CNRS, Toulouse

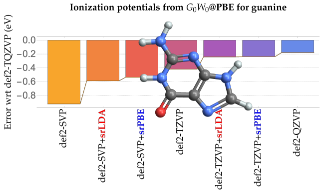
https://lcpq.github.io/PTEROSOR

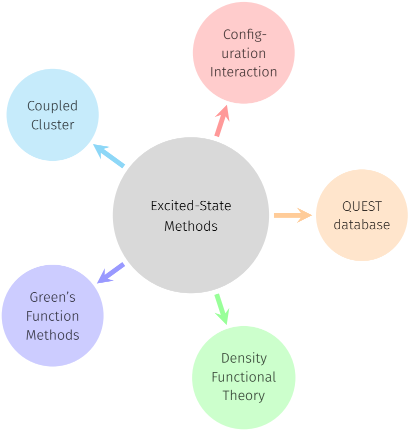


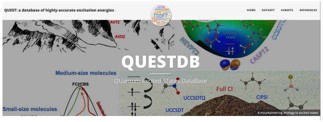

PTEROSOR has received funding from the European Research Council (ERC) under the European Union’s Horizon 2020 research and innovation programme (Grant agreement No. 863481).

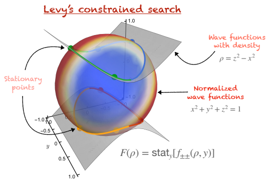
# General Overview of our Research Group




https://lcpq.github.io/PTEROSOR/

Antoine Marie (PhD)

Xavier Blase (Grenoble)

Pina Romaniello (Toulouse)

## Wave Function Theory

Hamiltonian → $\hat{H}$; Energy → $E$; Wave function → $\Psi(\mathbf{r}_1, \ldots, \mathbf{r}_N)$

$$\hat{H}\,\Psi(\mathbf{r}_1, \ldots, \mathbf{r}_N) = E\,\Psi(\mathbf{r}_1, \ldots, \mathbf{r}_N)$$

kinetic → $\hat{T}$; electron repulsion → $\hat{W}_{\text{ee}}$; external potential → $\hat{V}_{\text{ext}}$

$$\hat{H} = \hat{T} + \hat{W}_{\text{ee}} + \hat{V}_{\text{ext}} \quad \Rightarrow \quad \boxed{E = E_T + E_W + E_V}$$

## Density Functional Theory

electron density

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

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

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

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

## Density Matrix Functional Theory

1st-order reduced density matrix

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

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

## Density Matrix Functional Theory (2nd order)

2nd-order reduced density matrix

$$\frac{N(N-1)}{2}\int\cdots\int \Psi^*(\mathbf{r}_1,\mathbf{r}_2,\ldots,\mathbf{r}_N)\Psi(\mathbf{r}_1,\mathbf{r}_2,\ldots,\mathbf{r}_N)\mathrm{d}\mathbf{r}_3\cdots\mathrm{d}\mathbf{r}_N = n_2(\mathbf{r}_1,\mathbf{r}_2)$$

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

$$E = -\frac{1}{2}\int \nabla^2_{\mathbf{r}} n_1(\mathbf{r},\mathbf{r}')\Big|_{\mathbf{r}'=\mathbf{r}}\mathrm{d}\mathbf{r} + \int\int \frac{n_2(\mathbf{r}_1,\mathbf{r}_2)}{r_{12}}\mathrm{d}\mathbf{r}_1\mathrm{d}\mathbf{r}_2 + \int v(\mathbf{r})n(\mathbf{r})\mathrm{d}\mathbf{r}$$

## One-Body Propagator in the Time Domain

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

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

Field operators

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

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

## One-Body Propagator in the Frequency Domain

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

$\nu$th ionization potential (IP)

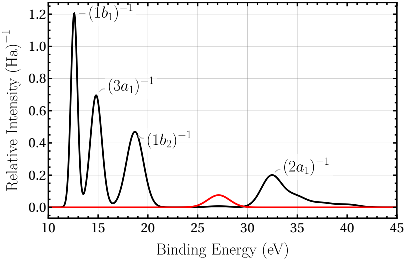
$\nu$th electron affinity (EA)

## Spectral function

$$A(\omega) = \frac{1}{\pi}|\mathrm{Im}\, G(\omega)|$$

Marie & Loos, JCTC 20 (2024) 4751

## Photoemission spectrum of water



## Link to RDMFT

$$n_1(\mathbf{r},\mathbf{r}') = -\mathrm{i}\lim_{t'\to t} G(\mathbf{r}t,\mathbf{r}'t')$$

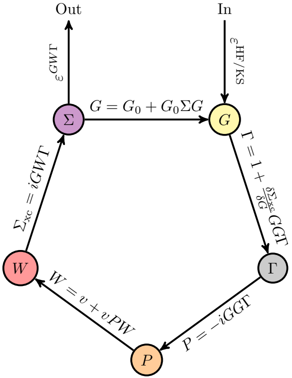
## Link to DFT

$$n(\mathbf{r}) = -\mathrm{i}\lim_{t'\to t}\lim_{\mathbf{r}'\to\mathbf{r}} G(\mathbf{r}t,\mathbf{r}'t')$$

## Galitskii-Migdal Energy Functional

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

Galitskii & Migdal, JETP 7 (1958) 96




Hedin, Phys. Rev. 139 (1965) A796

## Hedin's Equations

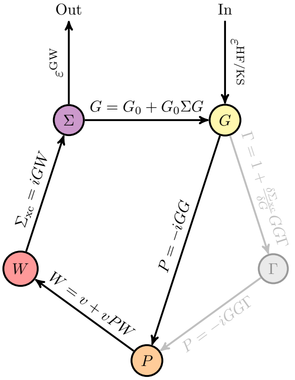
$$\underbrace{G(12)}_{\text{Green's function}} = G_0(12) + \int G_0(13)\Sigma(34)G(42)d(34)$$

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

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

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

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




Hedin, Phys. Rev. 139 (1965) A796

## The *GW* Approximation

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

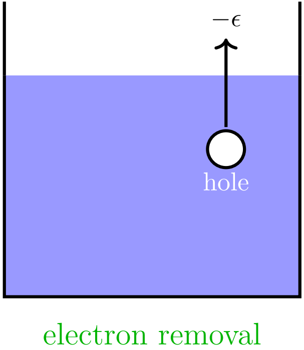
$$\underbrace{\Gamma(123)}_{\text{vertex}} = \delta(12)\delta(13)$$

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

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

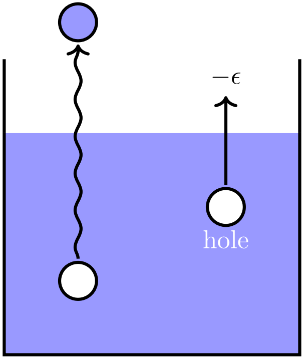
$$\underbrace{\Sigma_{\text{xc}}(12)}_{\text{self-energy}} = \mathrm{i}G(12)W(12)$$

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




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

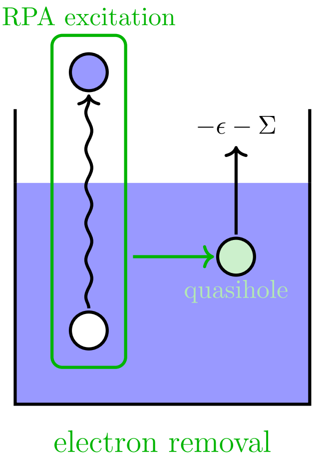
- Link to coupled-cluster theory:
  Lange & Berkelbach, JCTC 14 (2018) 4224
  Quintero-Monsebaiz et al. JCP 157 (2022) 231102
  Tolle & Chan, JCP 158 (2023) 124123




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




- 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

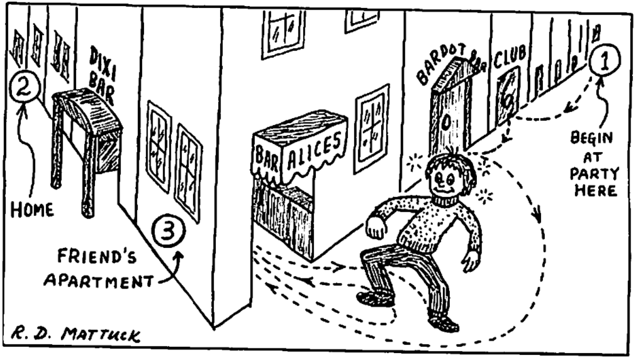



Fig. 1.1 *Propagation of Drunken Man*

(Reproduced with the kind permission of *The Encyclopedia of Physics*)

Mattuck, *"A Guide to Feynman Diagrams in the Many-Body Problem"*

## Two-Body Propagator in the Time Domain

two-body Green's function

$1 = (r_1, t_1)$

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

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

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

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

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

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

## Electron-Hole Correlation Function

eh correlation function

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

$$L(\mathbf{r}_1\mathbf{r}_2;\mathbf{r}_{1'}\mathbf{r}_{2'};\omega) = \sum_{\nu>0} \frac{L_\nu^N(\mathbf{r}_2\mathbf{r}_{2'})R_\nu^N(\mathbf{r}_1\mathbf{r}_{1'})}{\omega - (E_\nu^N - E_0^N - i\eta)} - \sum_{\nu>0} \frac{L_\nu^N(\mathbf{r}_2\mathbf{r}_{2'})R_\nu^N(\mathbf{r}_1\mathbf{r}_{1'})}{\omega - (E_0^N - E_\nu^N + i\eta)}$$

$\nu$th excitation energy

## Electron-Hole Bethe-Salpeter Equation (ehBSE)

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

eh kernel

Strinati, Riv. Nuovo Cimento 11 (1988) 1; Blase et al. JPCL 11 (2020) 7371

## Effective Interaction Kernel

$$\Xi^{\text{eh}}(12;1'2') = \frac{\delta\Sigma(11')}{\delta G(2'2)} \qquad \underbrace{\Sigma_{\text{xc}}}_{\text{exchange-correlation}} = iGW \quad \Rightarrow \quad \frac{\delta\Sigma_{\text{xc}}}{\delta G} = i\frac{\delta G}{\delta G}W + iG\underbrace{\frac{\delta W}{\delta G}}_{=0} = iW$$

## Casida Equations for ehBSE

$$\begin{pmatrix} A & B \\ -B & -A \end{pmatrix}\begin{pmatrix} X_\nu \\ Y_\nu \end{pmatrix} = \Omega_\nu^N \begin{pmatrix} X_\nu \\ Y_\nu \end{pmatrix}$$

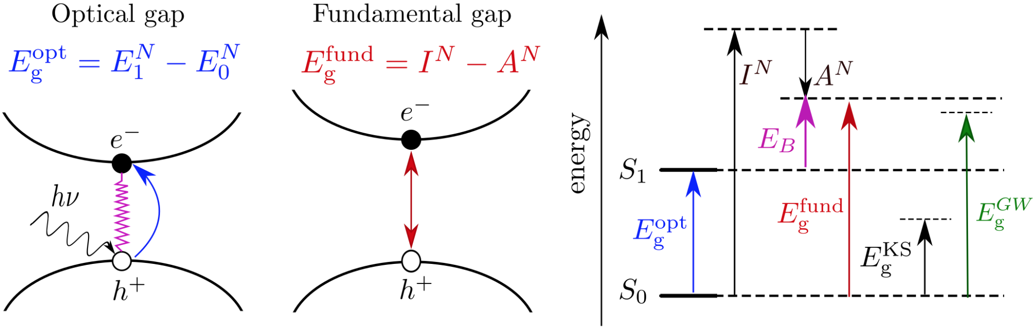
If no correlation, $W_{ij,ab} = \langle ib|ja\rangle$, then ehBSE becomes RPAx (or TDHF)!

## Matrix Elements With Static Screening

$$A_{ia,jb} = \overbrace{(\epsilon_a^{GW} - \epsilon_i^{GW})}^{\text{quasiparticle energies}} \delta_{ij}\delta_{ab} + \underbrace{\langle ib|aj\rangle}_{\text{Hartree}} - \underbrace{W_{ij,ab}}_{\text{exchange-correlation}}$$

$$B_{ia,jb} = \langle ij|ab\rangle - W_{ib,aj}$$

# Fundamental and Optical Gaps




$$\underbrace{E_g^{KS}}_{\text{KS gap}} = \epsilon_{LUMO}^{KS} - \epsilon_{HOMO}^{KS} \ll \underbrace{E_g^{GW}}_{\text{GW gap}} = \epsilon_{LUMO}^{GW} - \epsilon_{HOMO}^{GW}$$

$$\underbrace{E_g^{opt}}_{\text{optical gap}} = E_1^N - E_0^N = \underbrace{E_g^{fund}}_{\text{fundamental gap}} + \underbrace{E_B}_{\text{excitonic effect}}$$

## Particle-Particle Correlation Function

pp correlation function

anomalous propagators

$$K(12;1'2') = -G_2(12;1'2') + G^{\text{hh}}(12)G^{\text{ee}}(2'1')$$

$$K(\mathbf{r}_1\mathbf{r}_2;\mathbf{r}_{1'}\mathbf{r}_{2'};\omega) = \sum_\nu \frac{L_\nu^{N+2}(\mathbf{r}_1\mathbf{r}_2)R_\nu^{N+2}(\mathbf{r}'_1\mathbf{r}'_2)}{\omega - (E_\nu^{N+2} - E_0^N - i\eta)} - \sum_\nu \frac{L_\nu^{N-2}(\mathbf{r}'_1\mathbf{r}'_2)R_\nu^{N-2}(\mathbf{r}_1\mathbf{r}_2)}{\omega - (E_0^N - E_\nu^{N-2} + i\eta)}$$

$\nu$th double EA (DEA)

$\nu$th double IP (DIP)

## Particle-Particle Bethe-Salpeter Equation (ppBSE)

$$K(12;1'2') = \underbrace{K_0(12;1'2')}_{\frac{1}{2}[G(21')G(12')-G(11')G(22')]} - \int d(33'44')K(12;44')\,\Xi^{\text{pp}}(44';33')\,K_0(33';1'2')$$

pp kernel

Marie, Romaniello, Loos, PRB 110 (2024) 115155; Marie et al. (in preparation)

## Effective Interaction Kernel

Bogoliubov-correlation

$$\Xi^{\mathrm{pp}}(11';22') = \frac{\delta\Sigma^{\mathrm{ee}}(22')}{\delta G^{\mathrm{ee}}(11')}\bigg|_{U=0} \quad \Sigma^{GW}_{\mathrm{Bc}} = -\mathrm{i}G^{\mathrm{ee}}W \quad \Rightarrow \quad \frac{\delta\Sigma^{GW}_{\mathrm{Bc}}(11')}{\delta G^{\mathrm{ee}}(22')} = -\frac{\mathrm{i}}{2}\left[W(22';11') - W(2'2;11')\right]$$

## Casida Equations for ppBSE

$$\begin{pmatrix} C & B \\ -B^{\dagger} & -D \end{pmatrix}\begin{pmatrix} X_\nu \\ Y_\nu \end{pmatrix} = \Omega_\nu^{N\pm2}\begin{pmatrix} X_\nu \\ Y_\nu \end{pmatrix}$$

If no correlation, $W_{pq,rs} = \langle ps|qr\rangle$, then ppBSE becomes ppRPA!

## Matrix Elements With Static Screening

$$C_{ab,cd} = \overbrace{(\epsilon_a + \epsilon_b)}^{\text{quasiparticle energies}}\delta_{ac}\delta_{bd} + \underbrace{W_{ac,bd} - W_{ad,bc}}_{\text{Bogoliubov-correlation}}$$

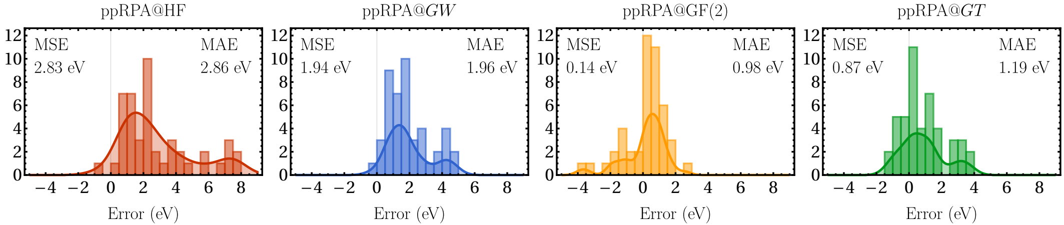
$$B_{ab,ij} = W_{ai,bj} - W_{aj,bi}$$

$$D_{ij,kl} = -(\epsilon_i + \epsilon_j)\delta_{ik}\delta_{jl} + W_{ik,jl} - W_{il,jk}$$

Deilmann, Drüppel & Rohlfing, PRL 116 (2016) 196804

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

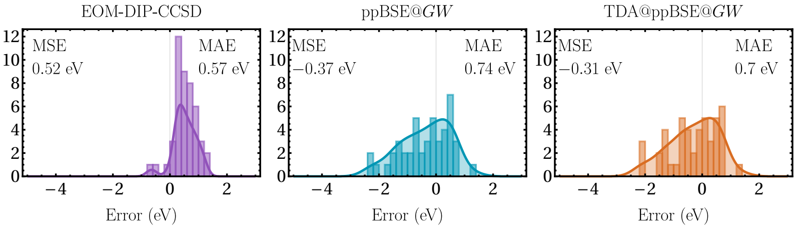
## Effect of the Quasiparticle Energies




Marie & Loos, JCTC 20 (2024) 4751; Marie et al. (in preparation)

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

## Effect of the Tamm-Dancoff Approximation (TDA)




Marie & Loos, JCTC 20 (2024) 4751; Marie et al. (in preparation)

- **Antoine Marie**
- **Pina Romaniello**
- **Xavier Blase**
- Enzo Monino
- Roberto Orlando
- Raúl Quintero-Monsebaiz

European Research Council
Established by the European Commission


https://pfloos.github.io/WEB_LOOS

https://lcpq.github.io/PTEROSOR