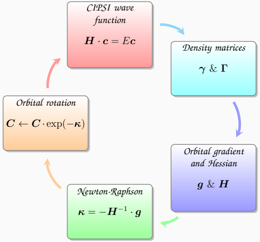
Green's function methods for quantum chemistry

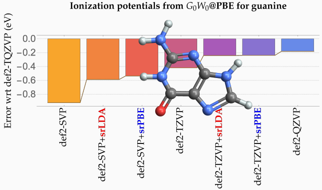
Pierre-François (Titou) Loos

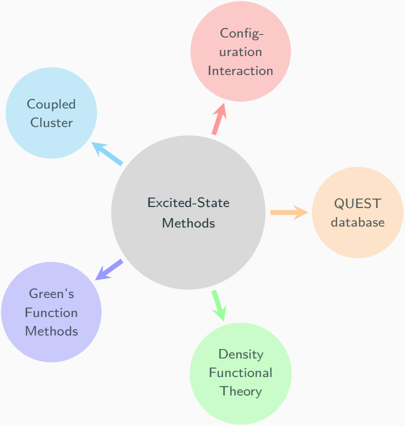
Laboratoire de Chimie et Physique Quantiques, IRSAMC, UPS/CNRS, Toulouse
https://lcpq.github.io/PTEROSOR

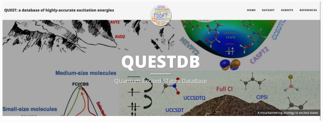
Dec 9th 2024

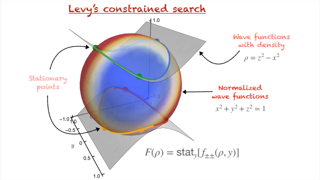
General Overview of our Research Group











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

Green's Function Methods

Antoine Marie (PhD)

Xavier Blase (Grenoble)

Pina Romaniello (Toulouse)

Electronic Schrödinger Equation

Wave Function Theory

Hamiltonian, Energy, Wave function:

$$\hat{H}\,\Psi(\boldsymbol{r}_1,\dots,\boldsymbol{r}_N) = E\,\Psi(\boldsymbol{r}_1,\dots,\boldsymbol{r}_N)$$

kinetic, electron repulsion, external potential:

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

Reduced Quantities

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)

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

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)

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

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

(Even Less) Reduced Quantities

Density Matrix Functional Theory (2nd order)

2nd-order reduced density matrix

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

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

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

One-Body Green's Function

One-Body Propagator in the Time Domain

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

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

Field operators

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

- $\left\langle \Psi_0^N \middle| \hat{\psi}(\boldsymbol{r}t)\hat{\psi}^\dagger(\boldsymbol{r}'t') \middle| \Psi_0^N \right\rangle$ 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

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

νth ionization potential (IP)

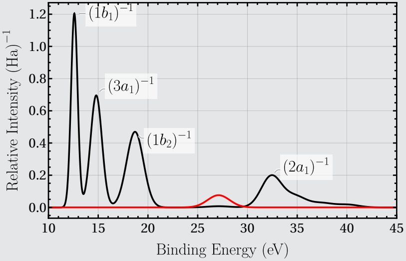
νth electron affinity (EA)

Spectral function

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

Marie & Loos, JCTC 20 (2024) 4751

Photoemission spectrum of water



Links With Other Reduced Quantities

Link to RDMFT & DFT

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

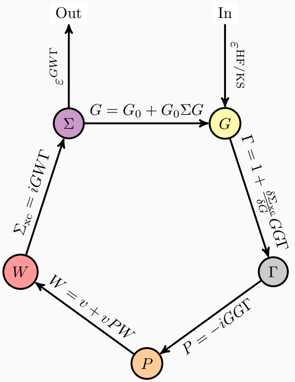
Galitskii-Migdal Energy Functional

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

Wave Function Theory (WFT) $\rightsquigarrow$ Green's Function Functional Theory (GFFT) ?!

Galitskii & Migdal, JETP 7 (1958) 96

Hedin's Pentagon



Hedin, Phys. Rev. 139 (1965) A796

Hedin's Equations

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

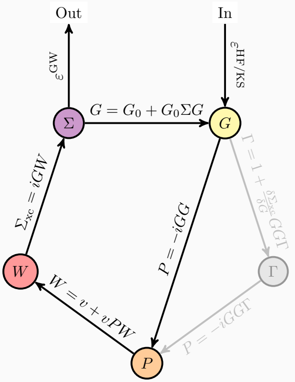
$$\underbrace{\Gamma(123)}_{\text{vertex}} = \delta(12)\delta(13) + \int \frac{\delta \Sigma_{xc}(12)}{\delta G(45)} G(46)G(75)\Gamma(673)d(4567)$$

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

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

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

Hedin's Square



Hedin, Phys. Rev. 139 (1965) A796

The *GW* Approximation

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

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

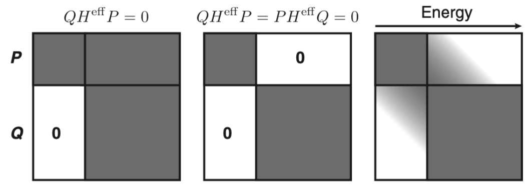
$$\underbrace{P(12)}_{\text{polarizability}} = -\mathrm{i}G(12)G(21)$$

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

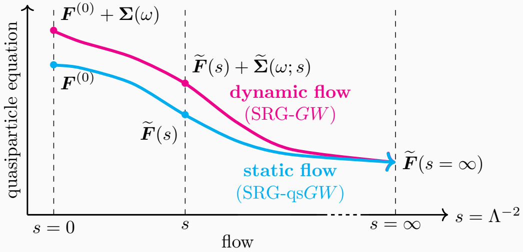
$$\underbrace{\Sigma_{\text{xc}}(12)}_{\text{self-energy}} = \mathrm{i}G(12)W(12)$$

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

Regularization via the Similarity Renormalization Group (SRG)



$\Leftarrow$ Continuous (unitary) SRG transformation

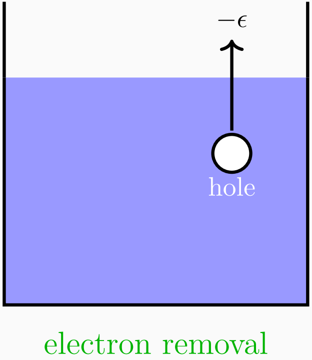


Idea based on Evangelista's DSRG method

Chenyang Li & Evangelista, Annu. Rev. Phys. Chem. 70 (2019) 275

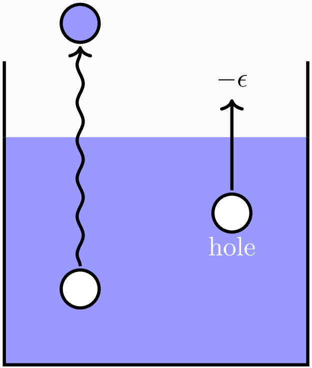
Monino & Loos, JCP 156 (2022) 231101; Marie & Loos, JCTC 19 (2023) 3943

Quasiparticle Concept



- 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

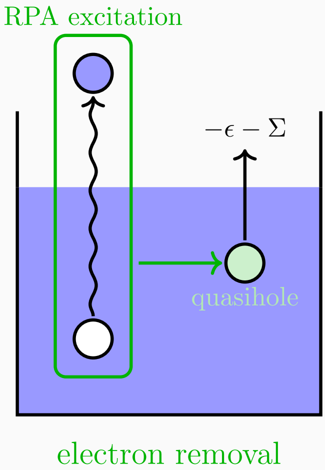


electron removal

- 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

Quasiparticle Concept



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

Quasihorse Concept

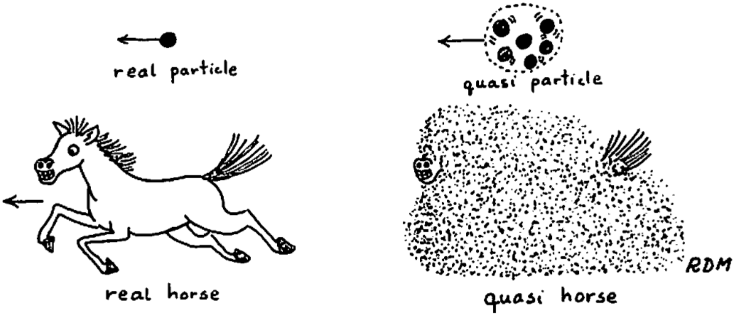
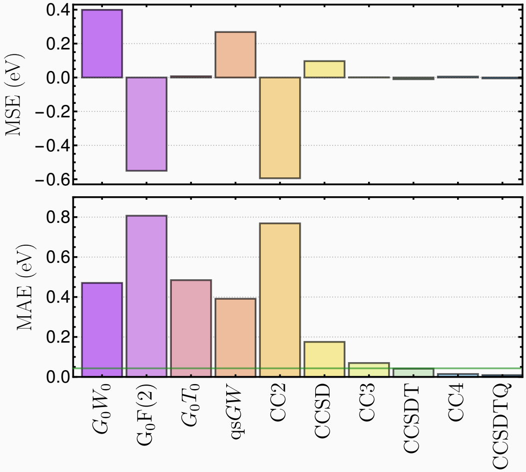


Fig. 0.4 ***Quasi Particle Concept***

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

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



Marie & Loos, JCTC 20 (2024) 4751

Propagation Can be Longer Than Expected

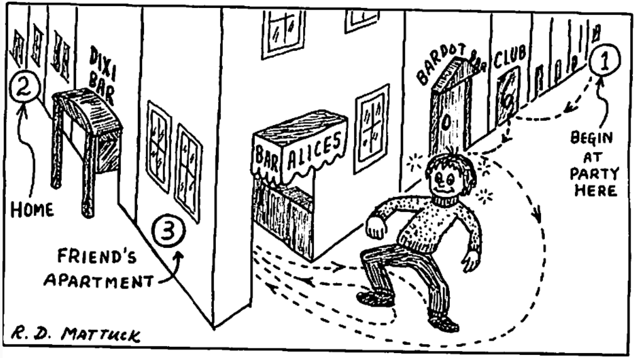


Fig. 1.1 *Propagation of Drunken Man*

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

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

Two-Body Green's Function

Two-Body Propagator in the Time Domain

two-body Green's function

$1 = (\boldsymbol{r}_1, t_1)$

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

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

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

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

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

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

νth excitation energy

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

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

eh kernel

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

Electron-Hole Effective Interaction Kernel

Effective Interaction Kernel

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

Casida Equations for eh-BSE

$$\begin{pmatrix} \boldsymbol{A} & \boldsymbol{B} \\ -\boldsymbol{B} & -\boldsymbol{A} \end{pmatrix} \begin{pmatrix} \boldsymbol{X}_\nu \\ \boldsymbol{Y}_\nu \end{pmatrix} = \Omega_\nu^N \begin{pmatrix} \boldsymbol{X}_\nu \\ \boldsymbol{Y}_\nu \end{pmatrix}$$

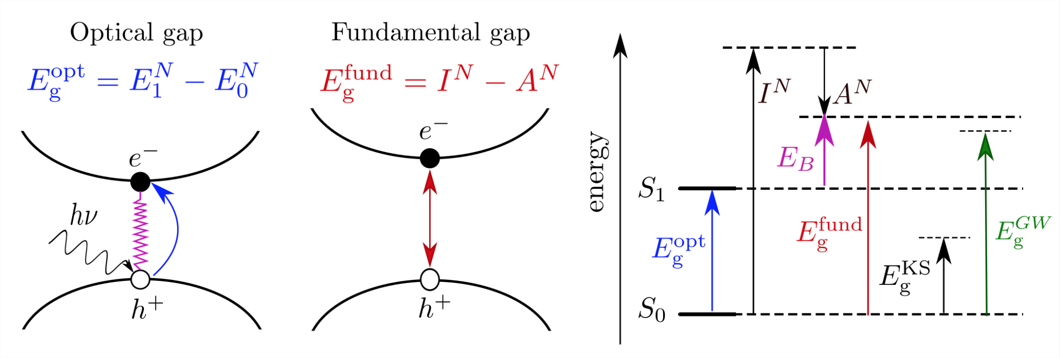
If no correlation, $W_{ij,ab} = \langle ib|ja \rangle$, then
eh-BSE becomes RPAx (or TDHF)!

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



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

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

The Particle-Particle Channel

Particle-Particle Correlation Function

pp correlation function

anomalous propagators

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

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

νth double EA (DEA)

νth double IP (DIP)

Particle-Particle Bethe-Salpeter Equation (pp-BSE)

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

pp kernel

Marie, Romaniello, Loos, PRB 110 (2024) 115155; Marie et al. arXiv:2411.13167

Particle-Particle Effective Interaction Kernel

Effective Interaction Kernel

Bogoliubov-correlation

$$\Xi^{\mathrm{pp}}(11';22') = \left.\frac{\delta\Sigma^{\mathrm{ee}}(22')}{\delta G^{\mathrm{ee}}(11')}\right|_{U=0} \qquad \Sigma_{\mathrm{Bc}}^{GW} = -\mathrm{i}G^{\mathrm{ee}}W \quad \Rightarrow \quad \mathrm{i}\frac{\delta\Sigma_{\mathrm{Bc}}^{GW}(11')}{\delta G^{\mathrm{ee}}(22')} = \frac{1}{2}[W(11';22') - W(11';2'2)]$$

Essenberger, PhD thesis (2014)

Casida Equations for pp-BSE

$$\begin{pmatrix} \boldsymbol{C} & \boldsymbol{B} \\ -\boldsymbol{B}^{\dagger} & -\boldsymbol{D} \end{pmatrix} \begin{pmatrix} \boldsymbol{X}_{\nu} \\ \boldsymbol{Y}_{\nu} \end{pmatrix} = \Omega_{\nu}^{N\pm 2} \begin{pmatrix} \boldsymbol{X}_{\nu} \\ \boldsymbol{Y}_{\nu} \end{pmatrix}$$

If no correlation, $W_{pq,rs} = \langle ps|qr\rangle$, then pp-BSE becomes pp-RPA!

Matrix Elements With Static Screening

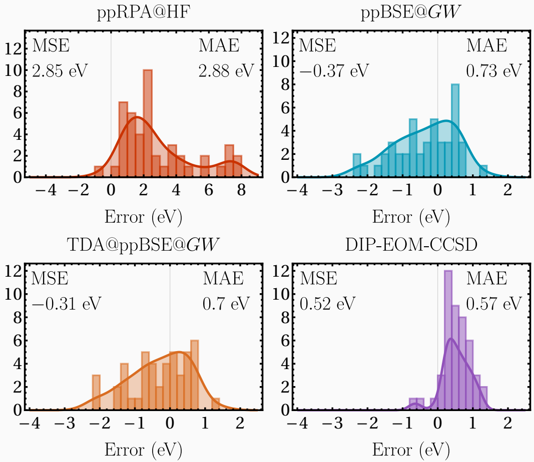
$$C_{ab,cd} = \overbrace{(\epsilon_a + \epsilon_b)}^{\text{quasiparticle energies}} \delta_{ac}\delta_{bd} + \underbrace{W_{ac,bd} - W_{ad,bc}}_{\text{Bogoliubov-correlation}}$$

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

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

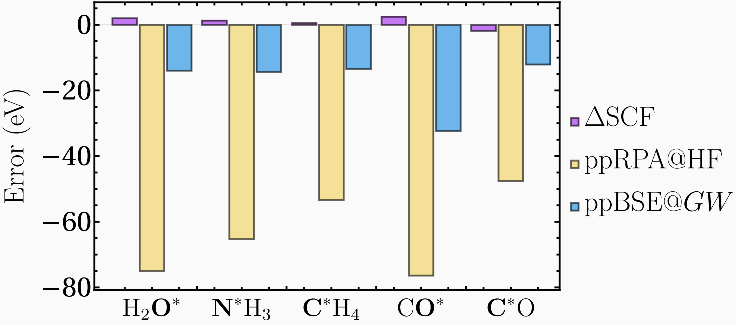
Deilmann, Drüppel & Rohlfing, PRL 116 (2016) 196804

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



Marie & Loos, JCTC 20 (2024) 4751; Marie et al. arXiv:2411.13167

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



Cederbaum et al. JCP 85 (1986) 6513; Marie et al. arXiv:2411.13167

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- Roberto Orlando
- Raúl Quintero-Monsebaiz

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