Green's function methods in quantum chemistry

Pierre-François LOOS

Laboratoire de Chimie et Physique Quantiques (UMR 5626),
Université de Toulouse, CNRS, UPS, Toulouse, France.

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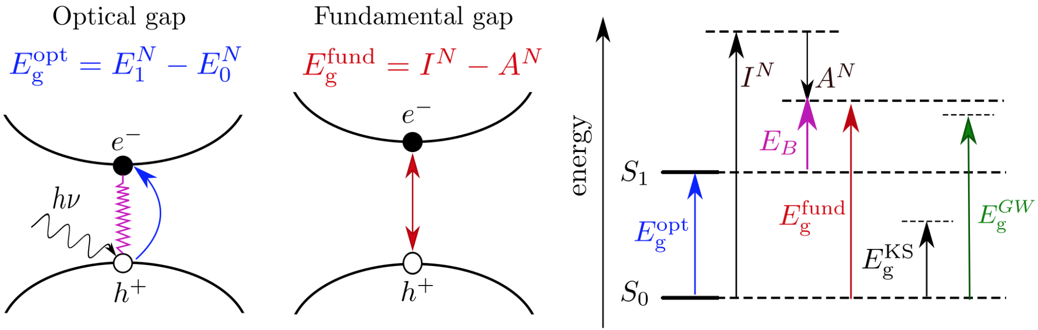
Today's program

- **Charged excitations**
  - One-shot GW (G_0W_0)
  - Partially self-consistent eigenvalue GW (evGW)
  - Quasiparticle self-consistent GW (qsGW)
  - Other self-energies (GF2, SOSEX, T-matrix, etc)
- **Neutral excitations**
  - Random-phase approximation (RPA)
  - Configuration interaction with singles (CIS)
  - Time-dependent Hartree-Fock (TDHF) or RPA with exchange (RPAx)
  - Time-dependent density-functional theory (TDDFT)
  - Bethe-Salpeter equation (BSE) formalism
- **Correlation energy**
  - Plasmon (or trace) formula
  - Galitski-Migdal formulation
  - Adiabatic connection fluctuation-dissipation theorem (ACFDT)

Fundamental and optical gaps



$$\underbrace{E_g^{KS}}_{\text{KS gap}} = \epsilon_{LUMO}^{KS} - \epsilon_{HOMO}^{KS} \ll \underbrace{E_g^{GW}}_{GW\text{ gap}} = \epsilon_{LUMO}^{GW} - \epsilon_{HOMO}^{GW} \quad (1)$$

$$\underbrace{E_g^{opt}}_{\text{optical gap}} = E_1^N - E_0^N = \underbrace{E_g^{fund}}_{\text{fundamental gap}} + \underbrace{E_B}_{\text{excitonic effect}} \quad (2)$$

1. Motivations
2. Context
3. Charged excitations
4. Neutral excitations
5. Correlation energy

Löwdin partitioning technique

Folding or dressing process

$$\underbrace{\boldsymbol{H} \cdot \boldsymbol{c} = \omega\, \boldsymbol{c}}_{\text{A large linear system with } N \text{ solutions...}} \quad \Rightarrow \quad \begin{pmatrix} \overbrace{\boldsymbol{H}_0}^{N_0 \times N_0} & \boldsymbol{h}^\mathsf{T} \\ \boldsymbol{h} & \underbrace{\boldsymbol{H}_1}_{N_1 \times N_1} \end{pmatrix} \cdot \begin{pmatrix} \boldsymbol{c}_0 \\ \boldsymbol{c}_1 \end{pmatrix} = \omega \begin{pmatrix} \boldsymbol{c}_0 \\ \boldsymbol{c}_1 \end{pmatrix} \qquad N = N_0 + N_1 \tag{3}$$

$$\textbf{Row \#2:} \quad \boldsymbol{h} \cdot \boldsymbol{c}_0 + \boldsymbol{H}_1 \cdot \boldsymbol{c}_1 = \omega\, \boldsymbol{c}_1 \quad \Rightarrow \quad \boldsymbol{c}_1 = (\omega\, \boldsymbol{1} - \boldsymbol{H}_1)^{-1} \cdot \boldsymbol{h} \cdot \boldsymbol{c}_0 \tag{4}$$

$$\textbf{Row \#1:} \quad \boldsymbol{H}_0 \cdot \boldsymbol{c}_0 + \boldsymbol{h}^\mathsf{T} \cdot \boldsymbol{c}_1 = \omega\, \boldsymbol{c}_0 \quad \Rightarrow \quad \underbrace{\tilde{\boldsymbol{H}}_0(\omega) \cdot \boldsymbol{c}_0 = \omega\, \boldsymbol{c}_0}_{\text{A smaller non-linear system with } N \text{ solutions...}} \tag{5}$$

$$\boxed{\underbrace{\tilde{\boldsymbol{H}}_0(\omega)}_{\text{Effective Hamitonian}} = \boldsymbol{H}_0 + \underbrace{\boldsymbol{h}^\mathsf{T} \cdot (\omega\, \boldsymbol{1} - \boldsymbol{H}_1)^{-1} \cdot \boldsymbol{h}}_{\text{Self-Energy } \boldsymbol{\Sigma}(\omega)}} \tag{6}$$

$$\text{Static approx. (e.g. } \omega = 0\text{):} \quad \underbrace{\tilde{\boldsymbol{H}}_0(\omega = 0)}_{\text{A smaller linear system with } N_0 \text{ solutions...}} = \boldsymbol{H}_0 - \underbrace{\boldsymbol{h}^\mathsf{T} \cdot \boldsymbol{H}_1^{-1} \cdot \boldsymbol{h}}_{\text{approximations possible...}} \tag{7}$$

Green's Function

Many-Body Green's Function

$$\boxed{(\omega \mathbf{1} - \boldsymbol{H}) \cdot \boldsymbol{G} = \mathbf{1}} \tag{8}$$

Dyson equation

$$\tilde{\boldsymbol{H}}_0(\omega) \cdot \boldsymbol{c}_0 = \omega \boldsymbol{c}_0 \quad \Rightarrow \quad [\boldsymbol{H}_0 + \boldsymbol{\Sigma}(\omega)] \cdot \boldsymbol{c}_0 = \omega \boldsymbol{c}_0 \quad \Rightarrow \quad \underbrace{[\omega \mathbf{1} - \boldsymbol{H}_0 - \boldsymbol{\Sigma}(\omega)]}_{\boldsymbol{G}^{-1}(\omega)} \cdot \boldsymbol{c}_0 = \mathbf{0} \tag{9}$$

$$\boldsymbol{G}^{-1}(\omega) = \underbrace{\omega \mathbf{1} - \boldsymbol{H}_0}_{\boldsymbol{G}_0^{-1}(\omega)} - \boldsymbol{\Sigma}(\omega) \quad \Rightarrow \quad \boldsymbol{G}^{-1}(\omega) = \boldsymbol{G}_0^{-1}(\omega) - \boldsymbol{\Sigma}(\omega) \tag{10}$$

$$\Rightarrow \quad \boxed{\boldsymbol{G}(\omega) = \boldsymbol{G}_0(\omega) + \boldsymbol{G}_0(\omega) \cdot \boldsymbol{\Sigma}(\omega) \cdot \boldsymbol{G}(\omega)} \tag{11}$$

$$\Rightarrow \quad \boldsymbol{G}(\omega) = [\mathbf{1} - \boldsymbol{G}_0(\omega) \cdot \boldsymbol{\Sigma}(\omega)]^{-1} \boldsymbol{G}_0(\omega) \tag{12}$$

Non-Interacting Green's Function

Matrix representation

$$\boldsymbol{H}_0 \cdot \boldsymbol{c} = \boldsymbol{c} \cdot \boldsymbol{E} \quad \Rightarrow \quad \boldsymbol{H}_0 \cdot \underbrace{\boldsymbol{c} \cdot \boldsymbol{c}^\dagger}_{\boldsymbol{1}} = \boldsymbol{c}_0 \cdot \boldsymbol{E} \cdot \boldsymbol{c}^\dagger \quad \Rightarrow \quad \boldsymbol{H}_0 = \boldsymbol{c} \cdot \boldsymbol{E} \cdot \boldsymbol{c}^\dagger \tag{13}$$

$$\omega \boldsymbol{1} - \boldsymbol{H}_0 = \boldsymbol{c} \cdot (\omega \boldsymbol{1} - \boldsymbol{E}) \cdot \boldsymbol{c}^\dagger \quad \Rightarrow \quad \underbrace{(\omega \boldsymbol{1} - \boldsymbol{H}_0)^{-1}}_{\boldsymbol{G}_0} = \boldsymbol{c} \cdot (\omega \boldsymbol{1} - \boldsymbol{E})^{-1} \cdot \boldsymbol{c}^\dagger \tag{14}$$

$$\boldsymbol{G}_0 = \boldsymbol{c} \cdot (\omega \boldsymbol{1} - \boldsymbol{E})^{-1} \cdot \boldsymbol{c}^\dagger \quad \Rightarrow \quad (\boldsymbol{G}_0)_{pq} = \sum_r \frac{c_{pr} c_{qr}^*}{\omega - E_r} \tag{15}$$

Hartree-Fock Green's function

$$(\boldsymbol{G}_{\text{HF}})_{pq} = \sum_r \frac{c_{pr} c_{qr}^*}{\omega - \epsilon_r^{\text{HF}}} = \underbrace{\sum_i \frac{c_{pi} c_{qi}^*}{\omega - \epsilon_i^{\text{HF}}}}_{\text{removal}} + \underbrace{\sum_a \frac{c_{pa} c_{qa}^*}{\omega - \epsilon_a^{\text{HF}}}}_{\text{addition}} \tag{16}$$

Solving Dyson's Equation

We're looking for the poles of $\boldsymbol{G}(\omega)$:

$$\boxed{\boldsymbol{G}^{-1}(\omega) = \boldsymbol{G}_0^{-1}(\omega) - \boldsymbol{\Sigma}(\omega)} \quad \Rightarrow \quad \boldsymbol{G}_0^{-1}(\omega) - \boldsymbol{\Sigma}(\omega) = \boldsymbol{0} \quad \Rightarrow \quad \det[\omega \boldsymbol{1} - \boldsymbol{\epsilon} - \boldsymbol{\Sigma}(\omega)] = 0 \tag{17}$$

Diagonal approximation

$$\det[\omega \boldsymbol{1} - \boldsymbol{\epsilon} - \boldsymbol{\Sigma}(\omega)] = 0 \quad \Rightarrow \quad \omega - \epsilon_p^{\text{HF}} - \Sigma_{pp}(\omega) = 0 \tag{18}$$

Linearization

$$\Sigma_{pp}(\omega) \approx \Sigma_{pp}(\omega = \epsilon_p^{\text{HF}}) + \left(\omega - \epsilon_p^{\text{HF}}\right) \left. \frac{\partial \Sigma_{pp}(\omega)}{\partial \omega} \right|_{\omega = \epsilon_p^{\text{HF}}} \quad \Rightarrow \quad \epsilon_p = \epsilon_p^{\text{HF}} + Z_p \Sigma_{pp}(\omega) \tag{19}$$

$$\text{Renormalization Factor:} \quad Z_p = \frac{1}{1 - \left. \frac{\partial \Sigma_{pp}(\omega)}{\partial \omega} \right|_{\omega = \epsilon_p^{\text{HF}}}} \tag{20}$$

Spectral Function

The following decomposition of the self-energy

$$\boldsymbol{\Sigma}(\omega) = \text{Re}\,\boldsymbol{\Sigma}(\omega) + i\,\text{Im}\,\boldsymbol{\Sigma}(\omega) \tag{21}$$

leads to the following expression for the spectral function (related to photoemission spectra)

$$\begin{aligned} \boldsymbol{A}(\omega) &= -\frac{1}{\pi}\,\text{Im}\left|\boldsymbol{G}(\omega)\right| \\ &= -\frac{1}{\pi}\frac{\left|\text{Im}\,\boldsymbol{\Sigma}(\omega)\right|}{\left[\omega\mathbf{1} - \boldsymbol{\epsilon} - \text{Re}\,\boldsymbol{\Sigma}(\omega)\right]^2 + \left[\text{Im}\,\boldsymbol{\Sigma}(\omega)\right]^2} \end{aligned} \tag{22}$$

Assumptions & Notations

Let's talk about notations

- We consider closed-shell systems (2 opposite-spin electrons per orbital)
- We only deal with singlet excited states but triplets can also be obtained

- Number of occupied orbitals O
- Number of vacant orbitals V
- Total number of orbitals $N = O + V$

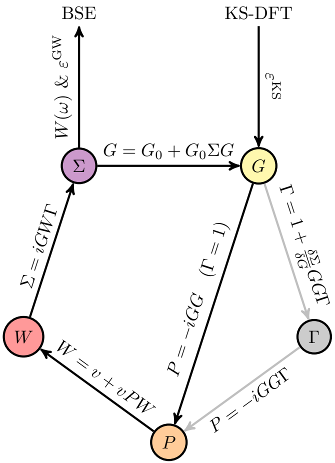
- $\phi_p(\boldsymbol{r})$ is a (real) spatial orbital
- i, j, k, l are occupied orbitals
- a, b, c, d are vacant orbitals
- p, q, r, s are arbitrary (occupied or vacant) orbitals
- $\mu, \nu, \lambda, \sigma$ are basis function indexes

- m indexes the OV single excitations ($i \to a$)

Useful papers/programs

- mol*GW*: Bruneval et al. Comp. Phys. Comm. 208 (2016) 149
- Turbomole: van Setten et al. JCTC 9 (2013) 232; Kaplan et al. JCTC 12 (2016) 2528
- Fiesta: Blase et al. Chem. Soc. Rev. 47 (2018) 1022
- FHI-AIMS: Caruso et al. PRB 86 (2012) 081102
- Reviews & Books:
  - Reining, WIREs Comput Mol Sci 2017, e1344. doi: 10.1002/wcms.1344
  - Onida et al. Rev. Mod. Phys. 74 (2002) 601
  - Blase et al. Chem. Soc. Rev. , 47 (2018) 1022
  - Golze et al. Front. Chem. 7 (2019) 377
  - Blase et al. JPCL 11 (2020) 7371
  - Martin, Reining & Ceperley *Interacting Electrons* (Cambridge University Press)
- *GW*100: IPs for a set of 100 molecules. van Setten et al. JCTC 11 (2015) 5665 (http://gw100.wordpress.com)

Hedin's pentagon



Hedin, Phys Rev 139 (1965) A796

What can you calculate with *GW*?

- Ionization potentials (IPs) given by occupied MO energies
- Electron affinities (EAs) given by virtual MO energies
- Fundamental (HOMO-LUMO) gap (or band gap in solids)
- Correlation and total energies

What can you calculate with BSE?

- Singlet and triplet optical excitations (vertical absorption energies)
- Oscillator strengths (absorption intensities)
- Correlation and total energies

The MBPT chain of actions

Kohn-Sham DFT

$$\left[-\frac{\nabla^2}{2} + v_{ext} + V^{\mathcal{H}xc}\right]\phi_p^{\mathcal{KS}} = \varepsilon_p^{\mathcal{KS}}\phi_p^{\mathcal{KS}}$$

↓ *Fundamental gap*

GW approximation

$$\varepsilon_p^{GW} = \varepsilon_p^{\mathcal{KS}} + \langle\phi_p^{\mathcal{KS}}|\Sigma^{GW}(\varepsilon_p^{GW}) - V^{xc}|\phi_p^{\mathcal{KS}}\rangle$$

↔ *Ionization potentials* / *Electron affinities* ↔ **(Inverse) photoemission spectroscopy**

↓ *Excitonic effect*

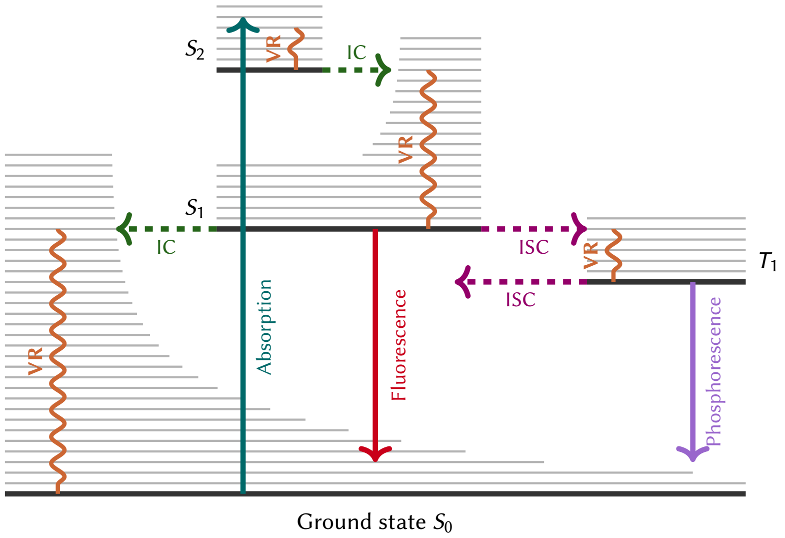
Bethe-Salpeter equation

$$\begin{pmatrix} \boldsymbol{A} & \boldsymbol{B} \\ -\boldsymbol{B}^* & -\boldsymbol{A}^* \end{pmatrix}\begin{pmatrix} \boldsymbol{X}_m \\ \boldsymbol{Y}_m \end{pmatrix} = \Omega_m \begin{pmatrix} \boldsymbol{X}_m \\ \boldsymbol{Y}_m \end{pmatrix}$$

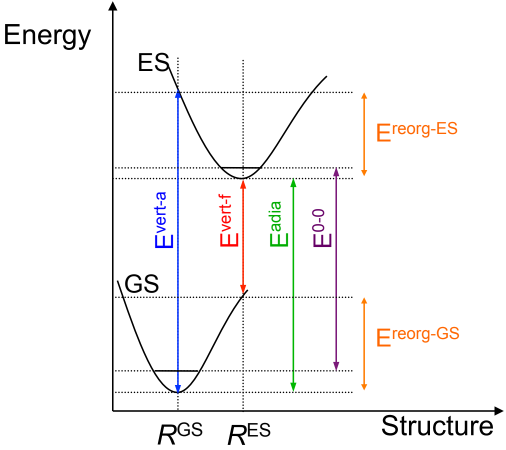
↔ *Optical excitations* ↔ **Optical spectroscopy**

Blase et al. JPCL 11 (2020) 7371

Photochemistry: Jablonski diagram



Photochemistry: absorption, emission, and 0-0



Vertical excitation energies cannot be computed experimentally!!!

Green's function and dynamical screening

One-body Green's function

$$G(\mathbf{r}_1, \mathbf{r}_2; \omega) = \underbrace{\sum_i \frac{\phi_i(\mathbf{r}_1)\phi_i(\mathbf{r}_2)}{\omega - \epsilon_i - i\eta}}_{\text{removal part = IPs}} + \underbrace{\sum_a \frac{\phi_a(\mathbf{r}_1)\phi_a(\mathbf{r}_2)}{\omega - \epsilon_a + i\eta}}_{\text{addition part = EAs}} \tag{23}$$

Polarizability

$$P(\mathbf{r}_1, \mathbf{r}_2; \omega) = -\frac{i}{\pi} \int G(\mathbf{r}_1, \mathbf{r}_2; \omega + \omega') G(\mathbf{r}_1, \mathbf{r}_2; \omega') d\omega' \tag{24}$$

Dielectric function and dynamically-screened Coulomb potential

$$\epsilon(\mathbf{r}_1, \mathbf{r}_2; \omega) = \delta(\mathbf{r}_1 - \mathbf{r}_2) - \int \frac{P(\mathbf{r}_1, \mathbf{r}_3; \omega)}{|\mathbf{r}_2 - \mathbf{r}_3|} d\mathbf{r}_3 \tag{25}$$

$$W(\mathbf{r}_1, \mathbf{r}_2; \omega) = \int \frac{\epsilon^{-1}(\mathbf{r}_1, \mathbf{r}_3; \omega)}{|\mathbf{r}_2 - \mathbf{r}_3|} d\mathbf{r}_3 \tag{26}$$

Dynamical screening in the orbital basis

Spectral representation of W

$$W_{pq,rs}(\omega) = \iint \phi_p(\mathbf{r}_1)\phi_q(\mathbf{r}_1) W(\mathbf{r}_1, \mathbf{r}_2; \omega)\phi_r(\mathbf{r}_2)\phi_s(\mathbf{r}_2) d\mathbf{r}_1 d\mathbf{r}_2$$
$$= \underbrace{(pq|rs)}_{\text{(static) exchange part}} + \underbrace{2\sum_m (pq|m)(rs|m)\left[\frac{1}{\omega - \Omega_m^{\text{RPA}} + i\eta} - \frac{1}{\omega + \Omega_m^{\text{RPA}} - i\eta}\right]}_{\text{(dynamical) correlation part } W^{\text{c}}_{pq,rs}(\omega)} \tag{27}$$

Electron repulsion integrals (ERIs)

$$(pq|rs) = \iint \frac{\phi_p(\mathbf{r}_1)\phi_q(\mathbf{r}_1)\phi_r(\mathbf{r}_2)\phi_s(\mathbf{r}_2)}{|\mathbf{r}_1 - \mathbf{r}_2|} d\mathbf{r}_1 d\mathbf{r}_2 \tag{28}$$

Screened ERIs (or spectral weights)

$$(pq|m) = \sum_{ia} (pq|ia)(\mathbf{X}_m^{\text{RPA}} + \mathbf{Y}_m^{\text{RPA}})_{ia} \tag{29}$$

Computation of the dynamical screening

Direct (ph-)RPA calculation (pseudo-hermitian linear problem)

$$\begin{pmatrix} \boldsymbol{A}^{\text{RPA}} & \boldsymbol{B}^{\text{RPA}} \\ -\boldsymbol{B}^{\text{RPA}} & -\boldsymbol{A}^{\text{RPA}} \end{pmatrix} \cdot \begin{pmatrix} \boldsymbol{X}_m^{\text{RPA}} \\ \boldsymbol{Y}_m^{\text{RPA}} \end{pmatrix} = \Omega_m^{\text{RPA}} \begin{pmatrix} \boldsymbol{X}_m^{\text{RPA}} \\ \boldsymbol{Y}_m^{\text{RPA}} \end{pmatrix} \tag{30}$$

$$\text{For singlet states:} \quad A_{ia,jb}^{\text{RPA}} = \delta_{ij}\delta_{ab}(\epsilon_a - \epsilon_i) + 2(ia|bj) \qquad B_{ia,jb}^{\text{RPA}} = 2(ia|jb) \tag{31}$$

Non-hermitian to hermitian

$$(\boldsymbol{A} - \boldsymbol{B})^{1/2} \cdot (\boldsymbol{A} + \boldsymbol{B}) \cdot (\boldsymbol{A} - \boldsymbol{B})^{1/2} \cdot \boldsymbol{Z}_m = \Omega_m^2 \boldsymbol{Z}_m \tag{32}$$

$$(\boldsymbol{X}_m + \boldsymbol{Y}_m) = \Omega_m^{-1/2} (\boldsymbol{A} - \boldsymbol{B})^{+1/2} \cdot \boldsymbol{Z}_m \tag{33}$$

$$(\boldsymbol{X}_m - \boldsymbol{Y}_m) = \Omega_m^{+1/2} (\boldsymbol{A} - \boldsymbol{B})^{-1/2} \cdot \boldsymbol{Z}_m \tag{34}$$

Tamm-Dancoff approximation (TDA)

$$\boldsymbol{B} = \boldsymbol{0} \quad \Rightarrow \quad \boldsymbol{A} \cdot \boldsymbol{X}_m = \Omega_m^{\text{TDA}} \boldsymbol{X}_m \tag{35}$$

The self-energy

GW Self-energy

$$\underbrace{\Sigma^{\text{xc}}(\mathbf{r}_1,\mathbf{r}_2;\omega)}_{GW\text{ self-energy}} = \underbrace{\Sigma^{\text{x}}(\mathbf{r}_1,\mathbf{r}_2)}_{\text{exchange}} + \underbrace{\Sigma^{\text{c}}(\mathbf{r}_1,\mathbf{r}_2;\omega)}_{\text{correlation}} = \frac{i}{2\pi}\int G(\mathbf{r}_1,\mathbf{r}_2;\omega+\omega')W(\mathbf{r}_1,\mathbf{r}_2;\omega')e^{i\eta\omega'}d\omega' \tag{36}$$

Exchange part of the (static) self-energy

$$\Sigma^{\text{x}}_{pq} = -\sum_i (pi|iq) \tag{37}$$

Correlation part of the (dynamical) self-energy

$$\Sigma^{\text{c}}_{pq}(\omega) = 2\sum_{im}\frac{(pi|m)(qi|m)}{\omega-\epsilon_i+\Omega^{\text{RPA}}_m-i\eta} + 2\sum_{am}\frac{(pa|m)(qa|m)}{\omega-\epsilon_a-\Omega^{\text{RPA}}_m+i\eta} \tag{38}$$

Quasiparticle equation

Dyson equation

$$[G(\mathbf{r}_1, \mathbf{r}_2; \omega)]^{-1} = \underbrace{[G_{\text{KS}}(\mathbf{r}_1, \mathbf{r}_2; \omega)]^{-1}}_{\text{KS Green's function}} + \Sigma^{\text{xc}}(\mathbf{r}_1, \mathbf{r}_2; \omega) - \underbrace{v^{\text{xc}}(\mathbf{r}_1)}_{\text{KS potential}} \delta(\mathbf{r}_1 - \mathbf{r}_2) \tag{39}$$

Non-linear quasiparticle (QP) equation

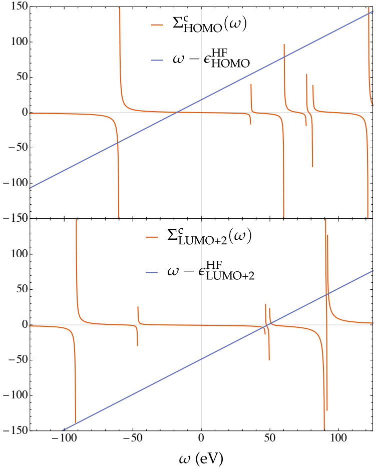
$$\omega = \epsilon_p^{\text{KS}} + \Sigma_{pp}^{\text{xc}}(\omega) - V_p^{\text{xc}} \quad \text{with} \quad V_p^{\text{xc}} = \int \phi_p(\mathbf{r}) v^{\text{xc}}(\mathbf{r}) \phi_p(\mathbf{r}) d\mathbf{r} \tag{40}$$

Linearized QP equation

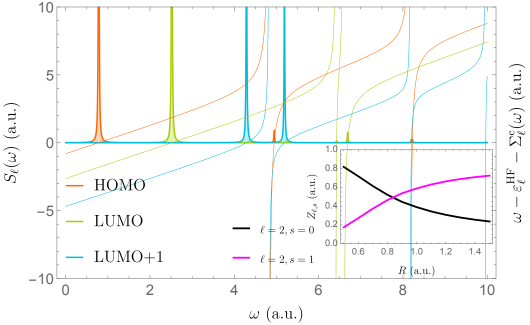
$$\Sigma_{pp}^{\text{xc}}(\omega) \approx \Sigma_{pp}^{\text{xc}}(\epsilon_p^{\text{KS}}) + (\omega - \epsilon_p^{\text{KS}}) \left. \frac{\partial \Sigma_{pp}^{\text{xc}}(\omega)}{\partial \omega} \right|_{\omega = \epsilon_p^{\text{KS}}} \quad \Rightarrow \quad \epsilon_p^{GW} = \epsilon_p^{\text{KS}} + Z_p [\Sigma_{pp}^{\text{xc}}(\epsilon_p^{\text{KS}}) - V_p^{\text{xc}}] \tag{41}$$

$$\underbrace{Z_p}_{\text{renormalization factor}} = \left[1 - \left. \frac{\partial \Sigma_{pp}^{\text{xc}}(\omega)}{\partial \omega} \right|_{\omega = \epsilon_p^{\text{KS}}} \right]^{-1} \quad \text{with} \quad 0 \leq Z_p \leq 1 \tag{42}$$

Solutions of the non-linear QP equation: evGW@HF/6-31G for H_2 at $R = 1$ bohr



Véril et al, JCTC 14 (2018) 5220



Loos et al, JCTC 14 (2018) 3071

GW flavours

Acronyms

- perturbative GW, one-shot GW, or G_0W_0
- evGW or eigenvalue-only (partially) self-consistent GW
- qsGW or quasiparticle (partially) self-consistent GW
- scGW or (fully) self-consistent GW

Perturbative GW with linearized solution

procedure G_0W_0LIN@KS

Perform KS calculation to get $\boldsymbol{\epsilon}^{\text{KS}}$, $\boldsymbol{c}^{\text{KS}}$, and $\boldsymbol{V}^{\text{xc}}$

AO to MO transformation for ERIs: $(\mu\nu|\lambda\sigma) \xrightarrow{\boldsymbol{c}^{\text{KS}}} (pq|rs)$

Construct RPA matrices $\boldsymbol{A}^{\text{RPA}}$ and $\boldsymbol{B}^{\text{RPA}}$ from $\boldsymbol{\epsilon}^{\text{KS}}$ and $(pq|rs)$

Compute RPA eigenvalues $\boldsymbol{\Omega}^{\text{RPA}}$ and eigenvectors $\boldsymbol{X}^{\text{RPA}} + \boldsymbol{Y}^{\text{RPA}}$ ▷ This is a $\mathcal{O}(N^6)$ step!

Form screened ERIs $(pq|m)$

for $p = 1, \ldots, N$ **do**

Compute diagonal of the self-energy $\Sigma^{\text{c}}_{pp}(\omega)$ at $\omega = \epsilon^{\text{KS}}_p$

Compute renornalization factors Z_p

Evaluate $\epsilon_p^{G_0W_0} = \epsilon_p^{\text{KS}} + Z_p \left\{ \text{Re}[\Sigma^{\text{c}}_{pp}(\epsilon_p^{\text{KS}})] - V_p^{\text{xc}} \right\}$

end for

end procedure

For contour deformation technique, see, for example, Duchemin & Blase, JCTC 16 (2020) 1742

Example from QuAcK (Ne/cc-pVDZ)

```
-------------------------------------------------------------------------------
 One-shot G0W0 calculation
-------------------------------------------------------------------------------
|  #  |     e_HF (eV)    |     Sig_c (eV)   |        Z         |    e_QP (eV)    |
-------------------------------------------------------------------------------
|   1 |     -891.591504  |      18.364427   |      0.859504    |   -875.807142   |
|   2 |      -52.218791  |       4.035435   |      0.956042    |    -48.360659   |
|   3 |      -22.647397  |       1.832273   |      0.965238    |    -20.878718   |
|   4 |      -22.647397  |       1.832273   |      0.965238    |    -20.878718   |
|   5 |      -22.647397  |       1.832273   |      0.965238    |    -20.878718   |
|   6 |       46.107752  |      -0.820124   |      0.982086    |     45.302383   |
|   7 |       46.107752  |      -0.820124   |      0.982086    |     45.302383   |
|   8 |       46.107752  |      -0.820124   |      0.982086    |     45.302383   |
|   9 |       54.167043  |      -1.061182   |      0.985754    |     53.121001   |
|  10 |      141.402085  |      -2.617768   |      0.898641    |    139.049684   |
|  11 |      141.402085  |      -2.617768   |      0.898641    |    139.049684   |
|  12 |      141.402085  |      -2.617768   |      0.898641    |    139.049684   |
|  13 |      141.402085  |      -2.617768   |      0.898641    |    139.049684   |
|  14 |      141.402085  |      -2.617768   |      0.898641    |    139.049684   |
|  15 |      282.545807  |      -3.872629   |      0.944019    |    278.890026   |
-------------------------------------------------------------------------------
         G0W0 HOMO      energy:    -20.878718 eV
         G0W0 LUMO      energy:     45.302383 eV
         G0W0 HOMO-LUMO gap    :     66.181102 eV
-------------------------------------------------------------------------------
  RPA@G0W0 total energy       :   -128.714946 au
  RPA@G0W0 correlation energy:     -0.226138 au
  GM@G0W0  total energy       :   -128.887856 au
  GM@G0W0  correlation energy:     -0.399048 au
-------------------------------------------------------------------------------
```

https://github.com/pfloos/QuAcK

Perturbative GW with graphical solution

procedure G_0W_0GRAPH@KS
  Perform KS calculation to get $\boldsymbol{\epsilon}^{\text{KS}}$, $\boldsymbol{c}^{\text{KS}}$, and $\boldsymbol{V}^{\text{xc}}$
  AO to MO transformation for ERIs: $(\mu\nu|\lambda\sigma) \xrightarrow{\boldsymbol{c}^{\text{KS}}} (pq|rs)$
  Construct RPA matrices $\boldsymbol{A}^{\text{RPA}}$ and $\boldsymbol{B}^{\text{RPA}}$ from $\boldsymbol{\epsilon}^{\text{KS}}$ and $(pq|rs)$
  Compute RPA eigenvalues Ω^{RPA} and eigenvectors $\boldsymbol{X}^{\text{RPA}} + \boldsymbol{Y}^{\text{RPA}}$ ▷ This is a $\mathcal{O}(N^6)$ step!
  Form screened ERIs $(pq|m)$
  for $p = 1, \ldots, N$ **do**
    Compute diagonal of the self-energy $\Sigma^{\text{c}}_{pp}(\omega)$
    Solve $\omega = \epsilon_p^{\text{KS}} + \text{Re}[\Sigma^{\text{c}}_{pp}(\omega)] - V_p^{\text{xc}}$ to get $\epsilon_p^{G_0W_0}$ via Newton's method
  end for
end procedure

Newton's method

https://en.wikipedia.org/wiki/Newton%27s_method

Partially self-consistent eigenvalue GW

procedure evGW@KS

Perform KS calculation to get $\boldsymbol{\epsilon}^{\text{KS}}$, $\boldsymbol{c}^{\text{KS}}$, and $\boldsymbol{V}^{\text{xc}}$

AO to MO transformation for ERIs: $(\mu\nu|\lambda\sigma) \xrightarrow{\boldsymbol{c}^{\text{KS}}} (pq|rs)$

Set $\boldsymbol{\epsilon}^{G_{-1}W_{-1}} = \boldsymbol{\epsilon}^{\text{KS}}$ and $n = 0$

while $\max|\boldsymbol{\Delta}| > \tau$ **do**

Construct RPA matrices $\boldsymbol{A}^{\text{RPA}}$ and $\boldsymbol{B}^{\text{RPA}}$ from $\boldsymbol{\epsilon}^{G_{n-1}W_{n-1}}$ and $(pq|rs)$

Compute RPA eigenvalues $\boldsymbol{\Omega}^{\text{RPA}}$ and eigenvectors $\boldsymbol{X}^{\text{RPA}} + \boldsymbol{Y}^{\text{RPA}}$ ▷ This is a $\mathcal{O}(N^6)$ step!

Form screened ERIs $(pq|m)$

for $p = 1, \ldots, N$ **do**

Compute diagonal of the self-energy $\Sigma^{\text{c}}_{pp}(\omega)$

Solve $\omega = \epsilon^{\text{KS}}_p + \text{Re}[\Sigma^{\text{c}}_{pp}(\omega)] - V^{\text{xc}}_p$ to get $\epsilon^{G_n W_n}_p$

end for

$\boldsymbol{\Delta} = \boldsymbol{\epsilon}^{G_n W_n} - \boldsymbol{\epsilon}^{G_{n-1}W_{n-1}}$

$n \leftarrow n + 1$

end while

end procedure

Example from QuAcK (Ne/cc-pVDZ)

```
-------------------------------------------------------------------------
 Self-consistent evG8W8 calculation
-------------------------------------------------------------------------
|  # |       e_HF (eV) |   Sigma_c (eV) |          Z |     e_QP (eV) |
-------------------------------------------------------------------------
|  1 |     -891.591504 |      18.746313 |   0.853211 |   -872.845115 |
|  2 |      -52.218791 |       4.097592 |   0.954012 |    -48.121107 |
|  3 |      -22.647397 |       1.872062 |   0.963351 |    -20.775232 |
|  4 |      -22.647397 |       1.872062 |   0.963351 |    -20.775232 |
|  5 |      -22.647397 |       1.872062 |   0.963351 |    -20.775232 |
|  6 |       46.107752 |      -0.834752 |   0.981106 |     45.273065 |
|  7 |       46.107752 |      -0.834752 |   0.981106 |     45.273065 |
|  8 |       46.107752 |      -0.834752 |   0.981106 |     45.273065 |
|  9 |       54.167043 |      -1.078523 |   0.984963 |     53.088542 |
| 10 |      141.402085 |      -3.068193 |   0.763837 |    138.333929 |
| 11 |      141.402085 |      -3.068193 |   0.763837 |    138.333929 |
| 12 |      141.402085 |      -3.068193 |   0.763837 |    138.333929 |
| 13 |      141.402085 |      -3.068193 |   0.763837 |    138.333929 |
| 14 |      141.402085 |      -3.068193 |   0.763837 |    138.333929 |
| 15 |      282.545807 |      -4.009519 |   0.941599 |    278.536345 |
-------------------------------------------------------------------------
 Iteration    8
 Convergence =          0.00000
-------------------------------------------------------------------------
         evGW HOMO      energy:      -20.775232 eV
         evGW LUMO      energy:       45.273065 eV
         evGW HOMO-LUMO gap   :       66.048297 eV
-------------------------------------------------------------------------
   RPA@evGW total energy       :    -128.715585 au
   RPA@evGW correlation energy:       -0.226777 au
   GM@evGW  total energy       :    -128.898601 au
   GM@evGW  correlation energy:       -0.409794 au
-------------------------------------------------------------------------
```

https://github.com/pfloos/QuAcK

Quasiparticle self-consistent GW (qsGW)

procedure qsGW

Perform HF calculation to get $\boldsymbol{\epsilon}^{\text{HF}}$ and $\boldsymbol{c}^{\text{HF}}$ (optional)

Set $\boldsymbol{\epsilon}^{G_{-1}W_{-1}} = \boldsymbol{\epsilon}^{\text{HF}}$, $\boldsymbol{c}^{G_{-1}W_{-1}} = \boldsymbol{c}^{\text{HF}}$ and $n = 0$

while $\max|\boldsymbol{\Delta}| > \tau$ **do**

AO to MO transformation for ERIs: $(\mu\nu|\lambda\sigma) \xrightarrow{\boldsymbol{c}^{G_{n-1}W_{n-1}}} (pq|rs)$ ▷ This is a $\mathcal{O}(N^5)$ step!

Construct RPA matrices $\boldsymbol{A}^{\text{RPA}}$ and $\boldsymbol{B}^{\text{RPA}}$ from $\boldsymbol{\epsilon}^{G_{n-1}W_{n-1}}$ and $(pq|rs)$

Compute RPA eigenvalues $\boldsymbol{\Omega}^{\text{RPA}}$ and eigenvectors $\boldsymbol{X}^{\text{RPA}} + \boldsymbol{Y}^{\text{RPA}}$ ▷ This is a $\mathcal{O}(N^6)$ step!

Form screened ERIs $(pq|m)$

Evaluate $\boldsymbol{\Sigma}^{\text{c}}(\boldsymbol{\epsilon}^{G_{n-1}W_{n-1}})$ and form $\tilde{\boldsymbol{\Sigma}}^{\text{c}} \leftarrow \left[\boldsymbol{\Sigma}^{\text{c}}(\boldsymbol{\epsilon}^{G_{n-1}W_{n-1}})^{\dagger} + \boldsymbol{\Sigma}^{\text{c}}(\boldsymbol{\epsilon}^{G_{n-1}W_{n-1}})\right]/2$

Form $\boldsymbol{F}^{\text{HF}}$ from $\boldsymbol{c}^{G_{n-1}W_{n-1}}$ and then $\tilde{\boldsymbol{F}} = \boldsymbol{F}^{\text{HF}} + \tilde{\boldsymbol{\Sigma}}^{\text{c}}$

Diagonalize $\tilde{\boldsymbol{F}}$ to get $\boldsymbol{\epsilon}^{G_nW_n}$ and $\boldsymbol{c}^{G_nW_n}$

$\boldsymbol{\Delta} = \boldsymbol{\epsilon}^{G_nW_n} - \boldsymbol{\epsilon}^{G_{n-1}W_{n-1}}$

$n \leftarrow n + 1$

end while

end procedure

Example from QuAcK (Ne/cc-pVDZ)

```
 -------------------------------------------------------------------------------------------
  Self-consistent qsG16W16 calculation
 -------------------------------------------------------------------------------------------
 |  # |       e_HF (eV) |       Sig_c (eV) |          Z |      e_QP (eV) |
 -------------------------------------------------------------------------------------------
 |  1 |   -891.591504 |     18.755754 |   0.853363 |   -873.652325 |
 |  2 |    -52.218791 |      4.058060 |   0.954380 |    -48.405559 |
 |  3 |    -22.647397 |      1.855512 |   0.963520 |    -21.066156 |
 |  4 |    -22.647397 |      1.855512 |   0.963520 |    -21.066156 |
 |  5 |    -22.647397 |      1.855512 |   0.963520 |    -21.066156 |
 |  6 |     46.107752 |     -0.848683 |   0.980977 |     45.067534 |
 |  7 |     46.107752 |     -0.848683 |   0.980977 |     45.067534 |
 |  8 |     46.107752 |     -0.848683 |   0.980977 |     45.067534 |
 |  9 |     54.167043 |     -1.102700 |   0.984676 |     52.926661 |
 | 10 |    141.402085 |     -3.043127 |   0.776916 |    138.069002 |
 | 11 |    141.402085 |     -3.043127 |   0.776916 |    138.069002 |
 | 12 |    141.402085 |     -3.043127 |   0.776916 |    138.069002 |
 | 13 |    141.402085 |     -3.043127 |   0.776916 |    138.069002 |
 | 14 |    141.402085 |     -3.043127 |   0.776916 |    138.069002 |
 | 15 |    282.545807 |     -3.998794 |   0.941677 |    278.156200 |
 -------------------------------------------------------------------------------------------
  Iteration   16
  Convergence =        0.00001
 -------------------------------------------------
         qsGW HOMO      energy:     -21.066156 eV
         qsGW LUMO      energy:      45.067534 eV
         qsGW HOMO-LUMO gap    :      66.133690 eV
 -------------------------------------------------
       qsGW total       energy:    -128.488468 au
       qsGW exchange    energy:     -12.101095 au
    GM@qsGW correlation energy:      -0.410249 au
   RPA@qsGW correlation energy:      -0.227077 au
 -------------------------------------------------
```

```
 ----------------------------------------------------
  Summary
 ----------------------------------------------------
  One-electron energy:    -182.4760110151 au
  Kinetic      energy:     128.2215634186 au
  Potential    energy:    -310.6975744337 au
 ----------------------------------------------------
  Two-electron energy:      53.9875434022 au
  Hartree      energy:      66.0886388591 au
  Exchange     energy:     -12.1010954570 au
  Correlation  energy:      -0.4102491313 au
 ----------------------------------------------------
  Electronic   energy:    -128.4884676130 au
  Nuclear   repulsion:       0.0000000000 au
  qsGW         energy:    -128.4884676130 au
 ----------------------------------------------------
 Dipole moment (Debye)
        X          Y          Z        Tot.
   0.000000   0.000000   0.000000   0.000000
 ----------------------------------------------------
```

https://github.com/pfloos/QuAcK

Other self-energies

Second-order Green's function (GF2) [Hirata et al. JCP 147 (2017) 044108]

$$\Sigma_{pq}^{\text{GF2}}(\omega) = \frac{1}{2} \sum_{iab} \frac{\langle iq||ab\rangle \langle ab||ip\rangle}{\omega + \epsilon_i - \epsilon_a - \epsilon_b} + \frac{1}{2} \sum_{ija} \frac{\langle aq||ij\rangle \langle ij||ap\rangle}{\omega + \epsilon_a - \epsilon_i - \epsilon_j} \quad (43)$$

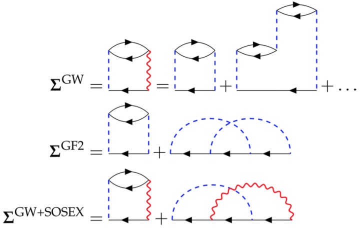
T-matrix [Romaniello et al. PRB 85 (2012) 155131; Zhang et al. JPCL 8 (2017) 3223]

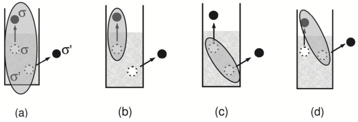
$$\Sigma_{pq}^{GT}(\omega) = \sum_{im} \frac{\langle pi|\chi_m^{N+2}\rangle \langle qi|\chi_m^{N+2}\rangle}{\omega + \epsilon_i - \Omega_m^{N+2}} + \sum_{am} \frac{\langle pa|\chi_m^{N-2}\rangle \langle qa|\chi_m^{N-2}\rangle}{\omega + \epsilon_i - \Omega_m^{N-2}} \quad (44)$$

$$\langle pi|\chi_m^{N+2}\rangle = \sum_{c<d} \langle pi||cd\rangle X_{cd}^{N+2,m} + \sum_{k<l} \langle pi||kl\rangle Y_{kl}^{N+2,m} \quad (45)$$

$$\langle pa|\chi_m^{N-2}\rangle = \sum_{c<d} \langle pa||cd\rangle X_{cd}^{N-2,m} + \sum_{k<l} \langle pa||kl\rangle Y_{kl}^{N-2,m} \quad (46)$$

pp-RPA problem: $$\begin{pmatrix} \boldsymbol{A} & \boldsymbol{B} \\ -\boldsymbol{B}^{\intercal} & -\boldsymbol{C} \end{pmatrix} \cdot \begin{pmatrix} \boldsymbol{X}_m^{N\pm2} \\ \boldsymbol{Y}_m^{N\pm2} \end{pmatrix} = \Omega_m^{N\pm2} \begin{pmatrix} \boldsymbol{X}_m^{N\pm2} \\ \boldsymbol{Y}_m^{N\pm2} \end{pmatrix} \quad (47)$$





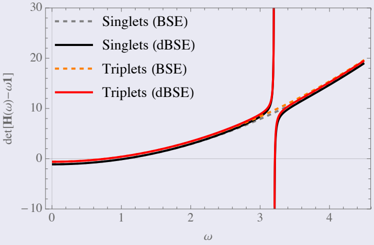
Martin, Reining & Ceperley, Interacting Electrons (Cambridge University Press)

Dynamical vs static kernels

A non-linear BSE problem [Strinati, Riv. Nuovo Cimento 11 (1988) 1]

$$\begin{pmatrix} \boldsymbol{A}(\omega) & \boldsymbol{B}(\omega) \\ -\boldsymbol{B}(-\omega) & -\boldsymbol{A}(-\omega) \end{pmatrix} \cdot \begin{pmatrix} \boldsymbol{X} \\ \boldsymbol{Y} \end{pmatrix} = \omega \begin{pmatrix} \boldsymbol{X} \\ \boldsymbol{Y} \end{pmatrix} \quad \textbf{Hard to solve!} \tag{48}$$

Static BSE vs dynamic BSE for HeH^+/STO-3G



Dynamical kernels can give you more than static kernels... Sometimes, too much...

Authier & Loos, JCP 153 (2020) 184105 [see also Romaniello et al, JCP 130 (2009) 044108]

TD-DFT and BSE in practice: Casida-like equations

Linear response problem

$$\begin{pmatrix} \boldsymbol{A} & \boldsymbol{B} \\ -\boldsymbol{B} & -\boldsymbol{A} \end{pmatrix} \cdot \begin{pmatrix} \boldsymbol{X}_m \\ \boldsymbol{Y}_m \end{pmatrix} = \Omega_m \begin{pmatrix} \boldsymbol{X}_m \\ \boldsymbol{Y}_m \end{pmatrix}$$

Blue pill: TD-DFT within the adiabatic approximation

$$A_{ia,jb} = \left(\epsilon_a^{\text{KS}} - \epsilon_i^{\text{KS}}\right)\delta_{ij}\delta_{ab} + 2(ia|bj) + f_{ia,bj}^{xc} \qquad B_{ia,jb} = 2(ia|jb) + f_{ia,jb}^{xc} \tag{49}$$

$$f_{ia,bj}^{xc} = \iint \phi_i(\mathbf{r})\phi_a(\mathbf{r}) \frac{\delta^2 E^{xc}}{\delta\rho(\mathbf{r})\delta\rho(\mathbf{r}')} \phi_b(\mathbf{r})\phi_j(\mathbf{r}) d\mathbf{r} d\mathbf{r}' \tag{50}$$

Red pill: BSE within the static approximation

$$A_{ia,jb} = \left(\epsilon_a^{GW} - \epsilon_i^{GW}\right)\delta_{ij}\delta_{ab} + 2(ia|bj) - W_{ij,ba}^{\text{stat}} \qquad B_{ia,jb} = 2(ia|jb) - W_{ib,ja}^{\text{stat}} \tag{51}$$

$$W_{ij,ab}^{\text{stat}} \equiv W_{ij,ab}(\omega = 0) = (ij|ab) - W_{ij,ab}^{c}(\omega = 0) \tag{52}$$

The bridge between TD-DFT and BSE

TD-DFT	Connection	BSE
One-point density $\rho(1)$	$\rho(1) = -iG(11^+)$	Two-point Green's function $G(12)$
Two-point susceptibility $\chi(12) = \frac{\partial \rho(1)}{\partial U(2)}$	$\chi(12) = -iL(12;1^+2^+)$	Four-point susceptibility $L(12;34) = \frac{\partial G(13)}{\partial U(42)}$
Two-point kernel $K(12) = v(12) + \frac{\partial V^{xc}(1)}{\partial \rho(2)}$		Four-point kernel $i\Xi(1234) = v(13)\delta(12)\delta(34) - \frac{\partial \Sigma^{xc}(12)}{\partial G(34)}$

For dynamical correction within BSE, see, for example, Loos & Blase, JCP 153 (2020) 114120

BSE in a computer

Vertical excitation energies from BSE

procedure BSE@GW

Compute GW quasiparticle energies ϵ_p^{GW} at the G_0W_0, evGW, or qsGW level

Compute static screening $W_{pq,rs}^{\text{stat}}$

Construct BSE matrices $\boldsymbol{A}^{\text{BSE}}$ and $\boldsymbol{B}^{\text{BSE}}$ from ϵ_p^{GW}, $(pq|rs)$, and $W_{pq,rs}^{\text{stat}}$

Compute lowest eigenvalues Ω_m^{BSE} and eigenvectors $\boldsymbol{X}_m^{\text{BSE}} + \boldsymbol{Y}_m^{\text{BSE}}$ (optional) ▷ This is a $\mathcal{O}(N^4)$ step!

end procedure

Removing the correlation part: TDHF and CIS

Linear response problem

$$\begin{pmatrix} \boldsymbol{A} & \boldsymbol{B} \\ -\boldsymbol{B} & -\boldsymbol{A} \end{pmatrix} \cdot \begin{pmatrix} \boldsymbol{X}_m \\ \boldsymbol{Y}_m \end{pmatrix} = \Omega_m \begin{pmatrix} \boldsymbol{X}_m \\ \boldsymbol{Y}_m \end{pmatrix}$$

TDHF = RPA with exchange (RPAx)

$$A_{ia,jb} = \left(\epsilon_a^{\text{HF}} - \epsilon_i^{\text{HF}}\right)\delta_{ij}\delta_{ab} + 2(ia|bj) - (ij|ba) \qquad B_{ia,jb} = 2(ia|jb) - (ib|ja) \tag{53}$$

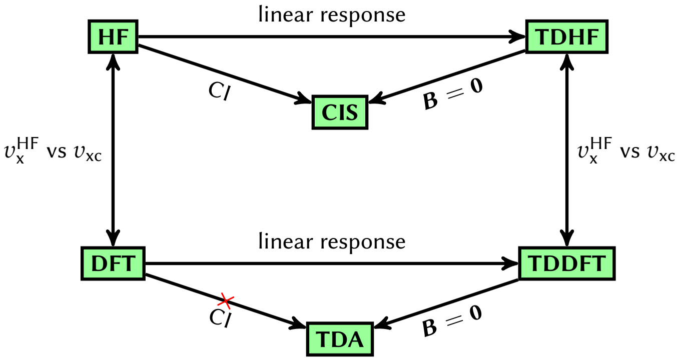
Linear response problem within the Tamm-Dancoff approximation

$$\boldsymbol{A} \cdot \boldsymbol{X}_m = \Omega_m \boldsymbol{X}_m \tag{54}$$

TDHF within TDA = CIS

$$A_{ia,jb} = \left(\epsilon_a^{\text{HF}} - \epsilon_i^{\text{HF}}\right)\delta_{ij}\delta_{ab} + 2(ia|bj) - (ij|ba) \tag{55}$$

Relationship between CIS, TDHF, DFT and TDDFT



Linear response

General linear response problem

procedure LINEAR RESPONSE
- Compute $\boldsymbol{A}$ matrix at a given level of theory (RPA, RPAx, TD-DFT, BSE, etc)
- **if** TDA **then**
  - Diagonalize $\boldsymbol{A}$ to get Ω_m^{TDA} and $\boldsymbol{X}_m^{\text{TDA}}$
- **else**
  - Compute $\boldsymbol{B}$ matrix at a given level of theory
  - Diagonalize $\boldsymbol{A} - \boldsymbol{B}$ to form $(\boldsymbol{A} - \boldsymbol{B})^{1/2}$
  - Form and diagonalize $(\boldsymbol{A} - \boldsymbol{B})^{1/2} \cdot (\boldsymbol{A} + \boldsymbol{B}) \cdot (\boldsymbol{A} - \boldsymbol{B})^{1/2}$ to get Ω_m^2 and $\boldsymbol{Z}_m$
  - Compute $\sqrt{\Omega_m^2}$ and $(\boldsymbol{X}_m + \boldsymbol{Y}_m) = \Omega_m^{-1/2} (\boldsymbol{A} - \boldsymbol{B})^{1/2} \cdot \boldsymbol{Z}_m$
- **end if**

end procedure

Form linear response matrices

Linear-response matrices for BSE

procedure FORM $\boldsymbol{A}$ FOR SINGLET STATES
    Set $\boldsymbol{A} = \mathbf{0}$
    $ia \leftarrow 0$
    for $i = 1, \ldots, O$ **do**
        for $a = 1, \ldots, V$ **do**
            $ia \leftarrow ia + 1$
            $jb \leftarrow 0$
            for $j = 1, \ldots, O$ **do**
                for $b = 1, \ldots, V$ **do**
                    $jb \leftarrow jb + 1$
                    $A_{ia,jb} = \delta_{ij}\delta_{ab}(\epsilon_a^{GW} - \epsilon_i^{GW}) + 2(ia|bj) - (ij|ba) + W_{ij,ba}^{c}(\omega = 0)$
                end for
            end for
        end for
    end for
end procedure

Properties

Oscillator strength (length gauge)

$$f_m = \frac{2}{3}\Omega_m \left[(\mu_m^x)^2 + (\mu_m^y)^2 + (\mu_m^z)^2 \right] \tag{56}$$

Transition dipole

$$\mu_m^x = \sum_{ia} (i|x|a)(\mathbf{X}_m + \mathbf{Y}_m)_{ia} \qquad (p|x|q) = \int \phi_p(\mathbf{r})\, x\, \phi_q(\mathbf{r}) d\mathbf{r} \tag{57}$$

Monitoring possible spin contamination [Monino & Loos, JCTC 17 (2021) 2852]

$$\langle \hat{S}^2 \rangle_m = \langle \hat{S}^2 \rangle_0 + \underbrace{\Delta \langle \hat{S}^2 \rangle_m}_{\text{JCP 134101 (2011) 134}} \qquad \langle \hat{S}^2 \rangle_0 = \frac{n_\alpha - n_\beta}{2}\left(\frac{n_\alpha - n_\beta}{2} + 1 \right) + n_\beta + \sum_p (p_\alpha | p_\beta) \tag{58}$$

Example from QuAcK (H_2O/cc-pVDZ)

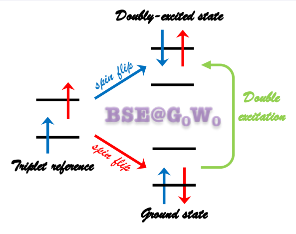
```
---------------------------------------------------------------
Excitation n.   1:   8.411378 eV   f = 0.0255   <S**2> = 0.0000
---------------------------------------------------------------
 5 ->    6 =    0.704168

---------------------------------------------------------------
Excitation n.   2:  10.496539 eV   f = 0.0000   <S**2> = 0.0000
---------------------------------------------------------------
 5 ->    7 =    0.699391
 5 ->    8 =   -0.095559

---------------------------------------------------------------
Excitation n.   3:  11.080888 eV   f = 0.0924   <S**2> = 0.0000
---------------------------------------------------------------
 4 ->    6 =   -0.703496

---------------------------------------------------------------
Excitation n.   4:  13.165908 eV   f = 0.0706   <S**2> = 0.0000
---------------------------------------------------------------
 4 ->    7 =    0.701946

---------------------------------------------------------------
Excitation n.   5:  14.913736 eV   f = 0.2678   <S**2> = 0.0000
---------------------------------------------------------------
 3 ->    6 =    0.704100
```

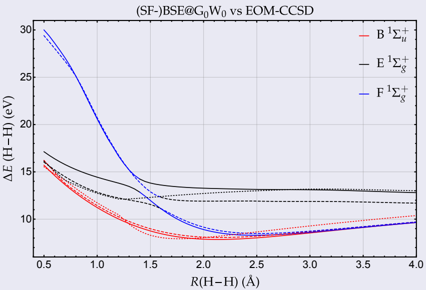
```
---------------------------------------------------------------
Excitation n.   1:   7.632804 eV   f = 0.0000   <S**2> = 2.0000
---------------------------------------------------------------
 5 ->    6 =    0.700599
 5 ->    9 =   -0.089914

---------------------------------------------------------------
Excitation n.   2:   9.897068 eV   f = 0.0000   <S**2> = 2.0000
---------------------------------------------------------------
 4 ->    6 =   -0.695522
 4 ->    9 =    0.093664

---------------------------------------------------------------
Excitation n.   3:  10.002114 eV   f = 0.0000   <S**2> = 2.0000
---------------------------------------------------------------
 5 ->    7 =    0.695328
 5 ->    8 =   -0.117774

---------------------------------------------------------------
Excitation n.   4:  11.995497 eV   f = 0.0000   <S**2> = 2.0000
---------------------------------------------------------------
 3 ->    6 =    0.228354
 4 ->    7 =    0.651412
 4 ->    8 =   -0.135998

---------------------------------------------------------------
Excitation n.   5:  13.698483 eV   f = 0.0000   <S**2> = 2.0000
---------------------------------------------------------------
 3 ->    6 =   -0.656938
 3 ->    9 =    0.101160
 4 ->    7 =    0.234306
```

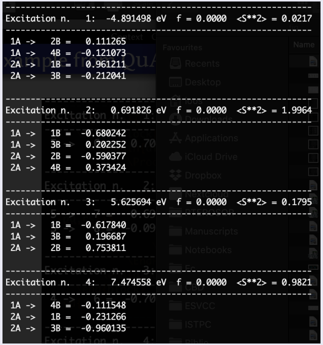
https://github.com/pfloos/QuAcK

Open-shell systems and double excitations

Spin-flip formalism (H2/cc-pVQZ)







Monino & Loos, JCTC 17 (2021) 2852

Correlation energy at the GW or BSE level

RPA@GW correlation energy: plasmon (or trace) formula

$$E_\text{c}^\text{RPA} = \frac{1}{2} \left[\sum_p \Omega_m^\text{RPA} - \text{Tr}\left(\boldsymbol{A}^\text{RPA} \right) \right] = \frac{1}{2} \sum_m \left(\Omega_m^\text{RPA} - \Omega_m^\text{TDA} \right)$$

Galitskii-Migdal functional

$$E_\text{c}^\text{GM} = \frac{-i}{2} \sum_{pq}^{\infty} \int \frac{d\omega}{2\pi} \Sigma_{pq}^\text{c}(\omega) G_{pq}(\omega) e^{i\omega\eta} = 4 \sum_{ia} \sum_m \frac{(ai|m)^2}{\epsilon_a^{GW} - \epsilon_i^{GW} + \Omega_m^\text{RPA}}$$

ACFDT@BSE@GW correlation energy from the adiabatic connection

$$E_\text{c}^\text{ACFDT} = \frac{1}{2} \int_0^1 \text{Tr}\left(\boldsymbol{K} \boldsymbol{P}^\lambda \right) d\lambda \tag{59}$$

Adiabatic connection fluctuation dissipation theorem (ACFDT)

Adiabatic connection

$$\boxed{E_c^{\text{ACFDT}} = \frac{1}{2} \int_0^1 \text{Tr}\left(\boldsymbol{K} \boldsymbol{P}^{\lambda}\right) d\lambda \overset{\text{quad}}{\approx} \frac{1}{2} \sum_{k=1}^{K} w_k \, \text{Tr}\left(\boldsymbol{K} \boldsymbol{P}^{\lambda_k}\right)} \tag{60}$$

λ is the **strength** of the electron-electron interaction:

- $\lambda = 0$ for the non-interacting system
- $\lambda = 1$ for the physical system

Interaction kernel

$$\boldsymbol{K} = \begin{pmatrix} \tilde{\boldsymbol{A}} & \tilde{\boldsymbol{B}} \\ \tilde{\boldsymbol{B}} & \tilde{\boldsymbol{A}} \end{pmatrix} \qquad \tilde{A}_{ia,jb} = 2(ia|bj) \qquad \tilde{B}_{ia,jb} = 2(ia|jb) \tag{61}$$

Correlation part of the two-particle density matrix

$$\boldsymbol{P}^{\lambda} = \begin{pmatrix} \boldsymbol{Y}^{\lambda} \cdot (\boldsymbol{Y}^{\lambda})^{\mathsf{T}} & \boldsymbol{Y}^{\lambda} \cdot (\boldsymbol{X}^{\lambda})^{\mathsf{T}} \\ \boldsymbol{X}^{\lambda} \cdot (\boldsymbol{Y}^{\lambda})^{\mathsf{T}} & \boldsymbol{X}^{\lambda} \cdot (\boldsymbol{X}^{\lambda})^{\mathsf{T}} \end{pmatrix} - \begin{pmatrix} \boldsymbol{0} & \boldsymbol{0} \\ \boldsymbol{0} & \boldsymbol{1} \end{pmatrix} \tag{62}$$

Gaussian quadrature

Numerical integration by quadrature

"A K-point Gaussian quadrature rule is a quadrature rule constructed to yield an exact result for polynomials up to degree $2K-1$ by a suitable choice of the roots x_k and weights w_k for $k = 1, \ldots, K$."

$$\int_a^b f(x) w(x) dx \approx \sum_k^K \underbrace{w_k}_{\text{weights}} f(\underbrace{x_k}_{\text{roots}}) \tag{63}$$

Quadrature rules

Interval $[a,b]$	Weight function $w(x)$	Orthogonal polynomials	Name
$[-1,1]$	1	Legendre $P_n(x)$	Gauss-Legendre
$(-1,1)$	$(1-x)^\alpha (1+x)^\beta, \quad \alpha,\beta > -1$	Jacobi $P_n^{\alpha,\beta}(x)$	Gauss-Jacobi
$(-1,1)$	$1/\sqrt{1-x^2}$	Chebyshev (1st kind) $T_n(x)$	Gauss-Chebyshev
$[-1,1]$	$\sqrt{1-x^2}$	Chebyshev (2nd kind) $U_n(x)$	Gauss-Chebyshev
$[0,\infty)$	$\exp(-x)$	Laguerre $L_n(x)$	Gauss-Laguerre
$[0,\infty)$	$x^\alpha \exp(-x), \quad \alpha > -1$	Generalized Laguerre $L_n^\alpha(x)$	Gauss-Laguerre
$(-\infty,\infty)$	$\exp(-x^2)$	Hermite $H_n(x)$	Gauss-Hermite

https://en.wikipedia.org/wiki/Gaussian_quadrature

ACFDT at the RPA/RPAx level

RPA matrix elements

$$A_{ia,jb}^{\lambda,\text{RPA}} = \delta_{ij}\delta_{ab}(\epsilon_a^{\text{HF}} - \epsilon_i^{\text{HF}}) + 2\lambda(ia|bj) \qquad B_{ia,jb}^{\lambda,\text{RPA}} = 2\lambda(ia|jb) \tag{64}$$

$$\boxed{E_\text{c}^{\text{RPA}} = \frac{1}{2}\int_0^1 \text{Tr}\left(\boldsymbol{K}\boldsymbol{P}^\lambda\right) d\lambda = \frac{1}{2}\left[\sum_m \Omega_m^{\text{RPA}} - \text{Tr}\left(\boldsymbol{A}^{\text{RPA}}\right)\right]} \tag{65}$$

RPAx matrix elements

$$A_{ia,jb}^{\lambda,\text{RPAx}} = \delta_{ij}\delta_{ab}(\epsilon_a^{\text{HF}} - \epsilon_i^{\text{HF}}) + \lambda[2(ia|bj) - (ij|ab)] \qquad B_{ia,jb}^{\lambda,\text{RPAx}} = \lambda[2(ia|jb) - (ib|aj)] \tag{66}$$

$$\boxed{E_\text{c}^{\text{RPAx}} = \frac{1}{2}\int_0^1 \text{Tr}\left(\boldsymbol{K}\boldsymbol{P}^\lambda\right) d\lambda \neq \frac{1}{2}\left[\sum_m \Omega_m^{\text{RPAx}} - \text{Tr}\left(\boldsymbol{A}^{\text{RPAx}}\right)\right]} \tag{67}$$

If exchange added to kernel, i.e., $\boldsymbol{K} = \boldsymbol{K}^\text{x}$, then [Angyan et al. JCTC 7 (2011) 3116]

$$E_\text{c}^{\text{RPAx}} = \frac{1}{4}\int_0^1 \text{Tr}\left(\boldsymbol{K}^\text{x}\boldsymbol{P}^\lambda\right) d\lambda = \frac{1}{4}\left[\sum_m \Omega_m^{\text{RPAx}} - \text{Tr}\left(\boldsymbol{A}^{\text{RPAx}}\right)\right] \tag{68}$$

ACFDT at the BSE level

BSE matrix elements

$$A_{ia,jb}^{\lambda,\text{BSE}} = \delta_{ij}\delta_{ab}(\epsilon_a^{GW} - \epsilon_i^{GW}) + \lambda\left[2(ia|bj) - W_{ij,ab}^{\lambda}(\omega = 0)\right] \qquad B_{ia,jb}^{\lambda,\text{BSE}} = \lambda\left[2(ia|jb) - W_{ib,ja}^{\lambda}(\omega = 0)\right] \tag{69}$$

$$\boxed{E_c^{\text{BSE}} = \frac{1}{2}\int_0^1 \text{Tr}\left(\boldsymbol{K}\boldsymbol{P}^{\lambda}\right) d\lambda \neq \frac{1}{2}\left[\sum_m \Omega_m^{\text{BSE}} - \text{Tr}\left(\boldsymbol{A}^{\text{BSE}}\right)\right]} \tag{70}$$

λ-dependent screening

$$W_{pq,rs}^{\lambda}(\omega) = (pq|rs) + 2\sum_m (pq|m)^{\lambda}(rs|m)^{\lambda}\left[\frac{1}{\omega - \Omega_m^{\lambda,\text{RPA}} + i\eta} - \frac{1}{\omega + \Omega_m^{\lambda,\text{RPA}} - i\eta}\right] \tag{71}$$

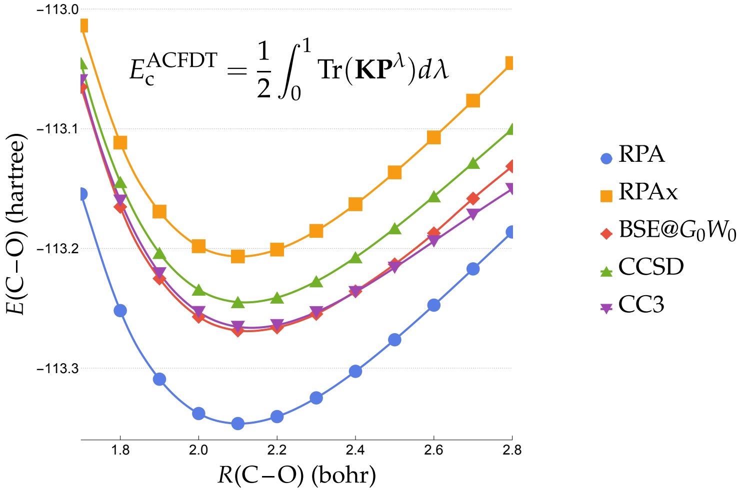
$$(pq|m)^{\lambda} = \sum_{ia}(pq|ia)(\boldsymbol{X}_m^{\lambda,\text{RPA}} + \boldsymbol{Y}_m^{\lambda,\text{RPA}})_{ia} \tag{72}$$

ACFDT in a computer

ACFDT correlation energy from BSE

procedure ACFDT for BSE
    Compute GW quasiparticle energies ϵ^{GW} and interaction kernel $\boldsymbol{K}$
    Get Gauss-Legendre weights and roots $\{w_k, \lambda_k\}_{1 \le k \le K}$
    $E_c \leftarrow 0$
    for $k = 1, \ldots, K$ **do**
        Compute static screening elements $W_{pq,rs}^{\lambda_k}(\omega = 0)$
        Perform BSE calculation at $\lambda = \lambda_k$ to get $\boldsymbol{X}^{\lambda_k}$ and $\boldsymbol{Y}^{\lambda_k}$ ▷ This is a $\mathcal{O}(N^6)$ step done many times!
        Form two-particle density matrix $\boldsymbol{P}^{\lambda_k}$
        $E_c \leftarrow E_c + w_k \operatorname{Tr}\left(\boldsymbol{K}\boldsymbol{P}^{\lambda_k}\right)$
    end for
end procedure

Ground-state potential energy surface of CO/cc-pVQZ



Loos et al. JPCL 11 (2020) 3536

Useful papers/programs

- mol*GW*: Bruneval et al. Comp. Phys. Comm. 208 (2016) 149
- Turbomole: van Setten et al. JCTC 9 (2013) 232; Kaplan et al. JCTC 12 (2016) 2528
- Fiesta: Blase et al. Chem. Soc. Rev. 47 (2018) 1022
- FHI-AIMS: Caruso et al. PRB 86 (2012) 081102
- Reviews & Books:
  - Reining, WIREs Comput Mol Sci 2017, e1344. doi: 10.1002/wcms.1344
  - Onida et al. Rev. Mod. Phys. 74 (2002) 601
  - Blase et al. Chem. Soc. Rev. , 47 (2018) 1022
  - Golze et al. Front. Chem. 7 (2019) 377
  - Blase et al. JPCL 11 (2020) 7371
  - Martin, Reining & Ceperley *Interacting Electrons* (Cambridge University Press)
- *GW*100: IPs for a set of 100 molecules. van Setten et al. JCTC 11 (2015) 5665 (http://gw100.wordpress.com)