GW/BSE methods in chemistry: Computational aspects

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)

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 $N = O + V$

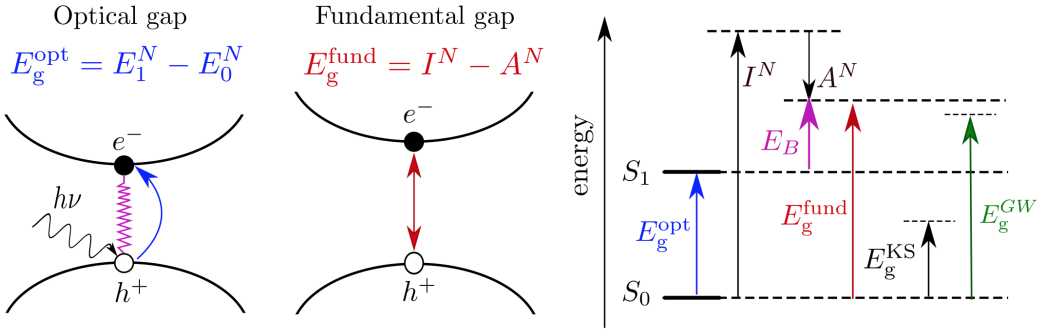
- $\phi_p(\mathbf{r})$ is a (real) spatial orbital
- i, j, k, l are occupied orbitals
- a, b, c, d are vacant orbitals
- p, q, r, s are arbitrary (occupied or vacant) orbitals
- $\mu, \nu, \lambda, \sigma$ are basis function indexes

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

Useful papers/programs

- molGW: 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)
- GW100: IPs for a set of 100 molecules. van Setten et al. JCTC 11 (2015) 5665 (http://gw100.wordpress.com)

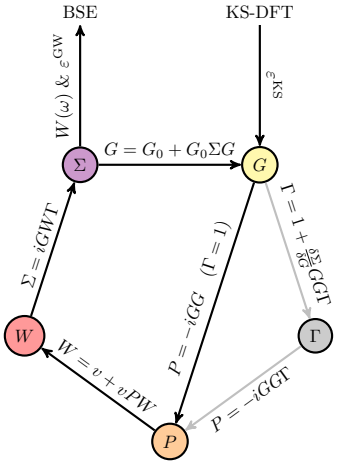
Fundamental and optical gaps (© Bruno Senjean)



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

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

Hedin's pentagon



Hedin, Phys Rev 139 (1965) A796

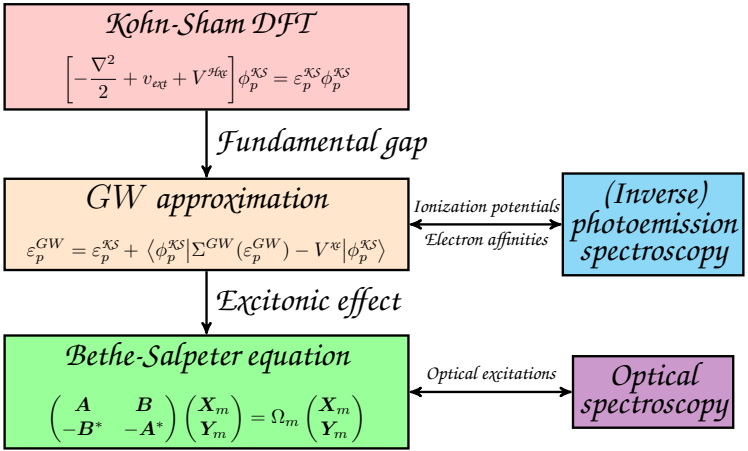
What can you calculate with *GW*?

- 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?

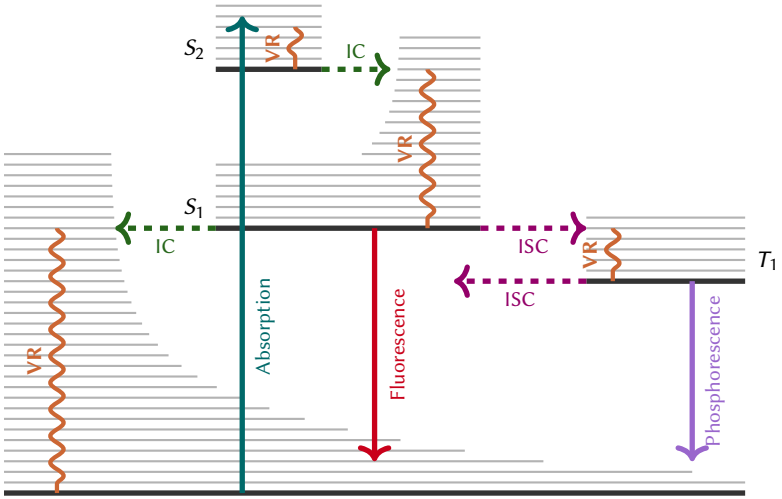
- Singlet and triplet optical excitations (vertical absorption energies)
- Oscillator strengths (absorption intensities)
- Correlation and total energies

The MBPT chain of actions

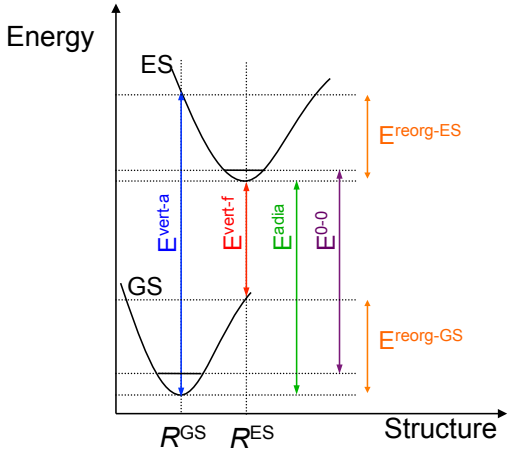


Blase et al. JPCL 11 (2020) 7371

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

$$G(\boldsymbol{r}_1, \boldsymbol{r}_2; \omega) = \underbrace{\sum_i \frac{\phi_i(\boldsymbol{r}_1)\phi_i(\boldsymbol{r}_2)}{\omega - \epsilon_i - i\eta}}_{\text{removal part = IPs}} + \underbrace{\sum_a \frac{\phi_a(\boldsymbol{r}_1)\phi_a(\boldsymbol{r}_2)}{\omega - \epsilon_a + i\eta}}_{\text{addition part = EAs}} \tag{3}$$

Polarizability

$$P(\boldsymbol{r}_1, \boldsymbol{r}_2; \omega) = -\frac{i}{\pi} \int G(\boldsymbol{r}_1, \boldsymbol{r}_2; \omega + \omega') G(\boldsymbol{r}_1, \boldsymbol{r}_2; \omega') d\omega' \tag{4}$$

Dielectric function and dynamically-screened Coulomb potential

$$\epsilon(\boldsymbol{r}_1, \boldsymbol{r}_2; \omega) = \delta(\boldsymbol{r}_1 - \boldsymbol{r}_2) - \int \frac{P(\boldsymbol{r}_1, \boldsymbol{r}_3; \omega)}{|\boldsymbol{r}_2 - \boldsymbol{r}_3|} d\boldsymbol{r}_3 \tag{5}$$

$$W(\boldsymbol{r}_1, \boldsymbol{r}_2; \omega) = \int \frac{\epsilon^{-1}(\boldsymbol{r}_1, \boldsymbol{r}_3; \omega)}{|\boldsymbol{r}_2 - \boldsymbol{r}_3|} d\boldsymbol{r}_3 \tag{6}$$

Dynamical screening in the orbital basis

Spectral representation of W

$$W_{pq,rs}(\omega) = \iint \phi_p(\boldsymbol{r}_1)\phi_q(\boldsymbol{r}_1) W(\boldsymbol{r}_1, \boldsymbol{r}_2; \omega)\phi_r(\boldsymbol{r}_2)\phi_s(\boldsymbol{r}_2) d\boldsymbol{r}_1 d\boldsymbol{r}_2$$

$$= \underbrace{(pq|rs)}_{\text{(static) exchange part}} + \underbrace{2\sum_m (pq|m)(rs|m)\left[\frac{1}{\omega - \Omega_m^{\text{RPA}} + i\eta} - \frac{1}{\omega + \Omega_m^{\text{RPA}} - i\eta}\right]}_{\text{(dynamical) correlation part } W^{\text{c}}_{pq,rs}(\omega)} \tag{7}$$

Electron repulsion integrals (ERIs)

$$(pq|rs) = \iint \frac{\phi_p(\boldsymbol{r}_1)\phi_q(\boldsymbol{r}_1)\phi_r(\boldsymbol{r}_2)\phi_s(\boldsymbol{r}_2)}{|\boldsymbol{r}_1 - \boldsymbol{r}_2|} d\boldsymbol{r}_1 d\boldsymbol{r}_2 \tag{8}$$

Screened ERIs (or spectral weights)

$$(pq|m) = \sum_{ia} (pq|ia)(\boldsymbol{X}_m^{\text{RPA}} + \boldsymbol{Y}_m^{\text{RPA}})_{ia} \tag{9}$$

Computation of the dynamical screening

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

$$\begin{pmatrix} \boldsymbol{A}^{\mathrm{RPA}} & \boldsymbol{B}^{\mathrm{RPA}} \\ -\boldsymbol{B}^{\mathrm{RPA}} & -\boldsymbol{A}^{\mathrm{RPA}} \end{pmatrix} \cdot \begin{pmatrix} \boldsymbol{X}_m^{\mathrm{RPA}} \\ \boldsymbol{Y}_m^{\mathrm{RPA}} \end{pmatrix} = \Omega_m^{\mathrm{RPA}} \begin{pmatrix} \boldsymbol{X}_m^{\mathrm{RPA}} \\ \boldsymbol{Y}_m^{\mathrm{RPA}} \end{pmatrix} \tag{10}$$

For singlet states: $A^{\mathrm{RPA}}_{ia,jb} = \delta_{ij}\delta_{ab}(\epsilon_a - \epsilon_i) + 2(ia|bj) \qquad B^{\mathrm{RPA}}_{ia,jb} = 2(ia|jb)$ (11)

Non-hermitian to hermitian

$$(\boldsymbol{A}-\boldsymbol{B})^{1/2} \cdot (\boldsymbol{A}+\boldsymbol{B}) \cdot (\boldsymbol{A}-\boldsymbol{B})^{1/2} \cdot \boldsymbol{Z}_m = \Omega_m^2 \boldsymbol{Z}_m \tag{12}$$

$$(\boldsymbol{X}_m + \boldsymbol{Y}_m) = \Omega_m^{-1/2} (\boldsymbol{A}-\boldsymbol{B})^{+1/2} \cdot \boldsymbol{Z}_m \tag{13}$$

$$(\boldsymbol{X}_m - \boldsymbol{Y}_m) = \Omega_m^{+1/2} (\boldsymbol{A}-\boldsymbol{B})^{-1/2} \cdot \boldsymbol{Z}_m \tag{14}$$

Tamm-Dancoff approximation (TDA)

$$\boldsymbol{B} = \boldsymbol{0} \quad \Rightarrow \quad \boldsymbol{A} \cdot \boldsymbol{X}_m = \Omega_m^{\mathrm{TDA}} \boldsymbol{X}_m \tag{15}$$

The self-energy

GW Self-energy

$$\underbrace{\Sigma^{\mathrm{xc}}(\boldsymbol{r}_1, \boldsymbol{r}_2; \omega)}_{GW \text{ self-energy}} = \underbrace{\Sigma^{\mathrm{x}}(\boldsymbol{r}_1, \boldsymbol{r}_2)}_{\text{exchange}} + \underbrace{\Sigma^{\mathrm{c}}(\boldsymbol{r}_1, \boldsymbol{r}_2; \omega)}_{\text{correlation}} = \frac{i}{2\pi} \int G(\boldsymbol{r}_1, \boldsymbol{r}_2; \omega + \omega') W(\boldsymbol{r}_1, \boldsymbol{r}_2; \omega') e^{i\eta\omega'} d\omega' \tag{16}$$

Exchange part of the (static) self-energy

$$\Sigma^{\mathrm{x}}_{pq} = -\sum_i (pi|iq) \tag{17}$$

Correlation part of the (dynamical) self-energy

$$\Sigma^{\mathrm{c}}_{pq}(\omega) = 2 \sum_{im} \frac{(pi|m)(qi|m)}{\omega - \epsilon_i + \Omega^{\mathrm{RPA}}_m - i\eta} + 2 \sum_{am} \frac{(pa|m)(qa|m)}{\omega - \epsilon_a - \Omega^{\mathrm{RPA}}_m + i\eta} \tag{18}$$

Quasiparticle equation

Dyson equation

$$[G(\boldsymbol{r}_1,\boldsymbol{r}_2;\omega)]^{-1} = \underbrace{[G_{\rm KS}(\boldsymbol{r}_1,\boldsymbol{r}_2;\omega)]^{-1}}_{\text{KS Green's function}} + \Sigma^{\rm xc}(\boldsymbol{r}_1,\boldsymbol{r}_2;\omega) - \underbrace{v^{\rm xc}(\boldsymbol{r}_1)}_{\text{KS potential}}\ \delta(\boldsymbol{r}_1-\boldsymbol{r}_2) \tag{19}$$

Non-linear quasiparticle (QP) equation

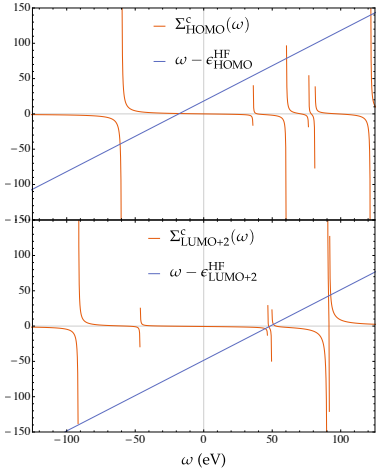
$$\omega = \epsilon_p^{\rm KS} + \Sigma_{pp}^{\rm xc}(\omega) - V_p^{\rm xc} \quad \text{with} \quad V_p^{\rm xc} = \int \phi_p(\boldsymbol{r}) v^{\rm xc}(\boldsymbol{r}) \phi_p(\boldsymbol{r}) d\boldsymbol{r} \tag{20}$$

Linearized QP equation

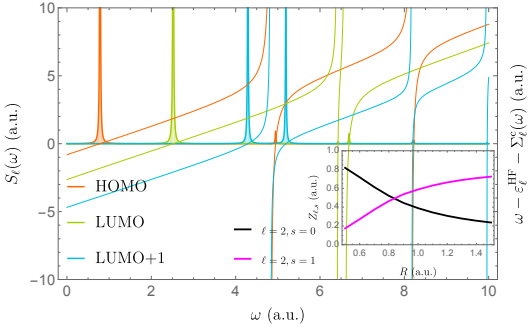
$$\Sigma_{pp}^{\rm xc}(\omega) \approx \Sigma_{pp}^{\rm xc}(\epsilon_p^{\rm KS}) + (\omega-\epsilon_p^{\rm KS}) \left.\frac{\partial \Sigma_{pp}^{\rm xc}(\omega)}{\partial\omega}\right|_{\omega=\epsilon_p^{\rm KS}} \quad \Rightarrow \quad \epsilon_p^{GW} = \epsilon_p^{\rm KS} + Z_p[\Sigma_{pp}^{\rm xc}(\epsilon_p^{\rm KS}) - V_p^{\rm xc}] \tag{21}$$

$$\underbrace{Z_p}_{\text{renormalization factor}} = \left[1 - \left.\frac{\partial \Sigma_{pp}^{\rm xc}(\omega)}{\partial\omega}\right|_{\omega=\epsilon_p^{\rm KS}}\right]^{-1} \quad \text{with} \quad 0 \leq Z_p \leq 1 \tag{22}$$

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 $G_0 W_0$ LIN@KS
  Perform KS calculation to get ϵ^{KS}, $\boldsymbol{c}^{\mathrm{KS}}$, and $\boldsymbol{V}^{\mathrm{xc}}$
  AO to MO transformation for ERIs: $(\mu\nu|\lambda\sigma) \xrightarrow{\boldsymbol{c}^{\mathrm{KS}}} (pq|rs)$
  Construct RPA matrices $\boldsymbol{A}^{\mathrm{RPA}}$ and $\boldsymbol{B}^{\mathrm{RPA}}$ from ϵ^{KS} and $(pq|rs)$
  Compute RPA eigenvalues $\boldsymbol{\Omega}^{\mathrm{RPA}}$ and eigenvectors $\boldsymbol{X}^{\mathrm{RPA}} + \boldsymbol{Y}^{\mathrm{RPA}}$ ▷ 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 $\Sigma^{\mathrm{c}}_{pp}(\omega)$ at $\omega = \epsilon^{\mathrm{KS}}_p$
    Compute renormalization factors Z_p
    Evaluate $\epsilon^{G_0 W_0}_p = \epsilon^{\mathrm{KS}}_p + Z_p \left\{ \mathrm{Re}[\Sigma^{\mathrm{c}}_{pp}(\epsilon^{\mathrm{KS}}_p)] - V^{\mathrm{xc}}_p \right\}$
  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 ϵ^{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 ϵ^{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 $\omega = \epsilon^{\text{KS}}_p + \text{Re}[\Sigma^{\text{c}}_{pp}(\omega)] - V^{\text{xc}}_p$ to get $\epsilon^{G_0W_0}_p$ 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: $(\mu\nu|\lambda\sigma) \overset{\boldsymbol{c}^{\text{KS}}}{\hookrightarrow} (pq|rs)$

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

end for

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

$n \leftarrow n + 1$

end while

end procedure

Example from QuAcK (Ne/cc-pVDZ)

```
 Self-consistent evGBW8 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 $\boldsymbol{\epsilon}^{\mathrm{HF}}$ and $\boldsymbol{c}^{\mathrm{HF}}$ (optional)

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

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

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

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

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

Form screened ERIs $(pq|m)$

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

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

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 qsG1G1W16 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]

$$\Sigma^{\mathrm{GF2}}_{pq}(\omega) = \frac{1}{2}\sum_{iab}\frac{\langle iq||ab\rangle\,\langle ab||ip\rangle}{\omega+\epsilon_i-\epsilon_a-\epsilon_b} + \frac{1}{2}\sum_{ija}\frac{\langle aq||ij\rangle\,\langle ij||ap\rangle}{\omega+\epsilon_a-\epsilon_i-\epsilon_j} \tag{23}$$

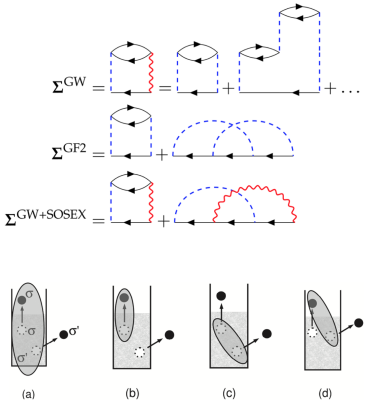
T-matrix [Romaniello et al. PRB 85 (2012) 155131; Zhang et al. JPCL 8 (2017) 3223]

$$\Sigma^{GT}_{pq}(\omega) = \sum_{im}\frac{\langle pi|\chi^{N+2}_m\rangle\,\langle qi|\chi^{N+2}_m\rangle}{\omega+\epsilon_i-\Omega^{N+2}_m} + \sum_{am}\frac{\langle pa|\chi^{N-2}_m\rangle\,\langle qa|\chi^{N-2}_m\rangle}{\omega+\epsilon_i-\Omega^{N-2}_m} \tag{24}$$

$$\langle pi|\chi^{N+2}_m\rangle = \sum_{c<d}\langle pi||cd\rangle\,X^{N+2,m}_{cd} + \sum_{k<l}\langle pi||kl\rangle\,Y^{N+2,m}_{kl} \tag{25}$$

$$\langle pa|\chi^{N-2}_m\rangle = \sum_{c<d}\langle pa||cd\rangle\,X^{N-2,m}_{cd} + \sum_{k<l}\langle pa||kl\rangle\,Y^{N-2,m}_{kl} \tag{26}$$

pp-RPA problem:
$$\begin{pmatrix} \boldsymbol{A} & \boldsymbol{B} \\ -\boldsymbol{B}^{\intercal} & -\boldsymbol{C} \end{pmatrix}\cdot\begin{pmatrix} \boldsymbol{X}^{N\pm2}_m \\ \boldsymbol{Y}^{N\pm2}_m \end{pmatrix} = \Omega^{N\pm2}_m \begin{pmatrix} \boldsymbol{X}^{N\pm2}_m \\ \boldsymbol{Y}^{N\pm2}_m \end{pmatrix} \tag{27}$$



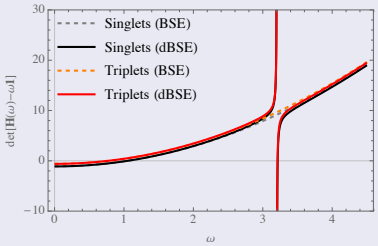
Martin, Reining & Ceperley, Interacting Electrons (Cambridge University Press)

Dynamical vs static kernels

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

$$\begin{pmatrix} \boldsymbol{A}(\omega) & \boldsymbol{B}(\omega) \\ -\boldsymbol{B}(-\omega) & -\boldsymbol{A}(-\omega) \end{pmatrix} \cdot \begin{pmatrix} \boldsymbol{X} \\ \boldsymbol{Y} \end{pmatrix} = \omega \begin{pmatrix} \boldsymbol{X} \\ \boldsymbol{Y} \end{pmatrix} \quad \textbf{Hard to solve!} \tag{28}$$

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]

Löwdin partitioning technique

Folding or dressing process

$$\underbrace{\boldsymbol{H}\cdot\boldsymbol{c}=\omega\,\boldsymbol{c}}_{\text{A large linear system with } N \text{ solutions...}} \quad\Rightarrow\quad \begin{pmatrix} \overbrace{\boldsymbol{H}_1}^{N_1\times N_1} & \boldsymbol{h}^{\mathsf{T}} \\ \boldsymbol{h} & \underbrace{\boldsymbol{H}_2}_{N_2\times N_2} \end{pmatrix} \cdot \begin{pmatrix} \boldsymbol{c}_1 \\ \boldsymbol{c}_2 \end{pmatrix} = \omega \begin{pmatrix} \boldsymbol{c}_1 \\ \boldsymbol{c}_2 \end{pmatrix} \qquad N = N_1 + N_2 \tag{29}$$

$$\textbf{Row \#2:}\quad \boldsymbol{h}\cdot\boldsymbol{c}_1 + \boldsymbol{H}_2\cdot\boldsymbol{c}_2 = \omega\,\boldsymbol{c}_2 \quad\Rightarrow\quad \boldsymbol{c}_2 = (\omega\,\mathbf{1}-\boldsymbol{H}_2)^{-1}\cdot\boldsymbol{h}\cdot\boldsymbol{c}_1 \tag{30}$$

$$\textbf{Row \#1:}\quad \boldsymbol{H}_1\cdot\boldsymbol{c}_1 + \boldsymbol{h}^{\mathsf{T}}\cdot\boldsymbol{c}_2 = \omega\,\boldsymbol{c}_1 \quad\Rightarrow\quad \underbrace{\tilde{\boldsymbol{H}}_1(\omega)\cdot\boldsymbol{c}_1 = \omega\,\boldsymbol{c}_1}_{\text{A smaller non-linear system with } N \text{ solutions...}} \tag{31}$$

$$\boxed{\underbrace{\tilde{\boldsymbol{H}}_1(\omega)}_{\text{Effective Hamitonian}} = \boldsymbol{H}_1 + \boldsymbol{h}^{\mathsf{T}}\cdot(\omega\,\mathbf{1}-\boldsymbol{H}_2)^{-1}\cdot\boldsymbol{h}} \tag{32}$$

Static approx. (e.g. $\omega = 0$):

$$\underbrace{\tilde{\boldsymbol{H}}_1(\omega=0)}_{\text{A smaller linear system with } N_1 \text{ solutions...}} = \boldsymbol{H}_1 - \underbrace{\boldsymbol{h}^{\mathsf{T}}\cdot\boldsymbol{H}_2^{-1}\cdot\boldsymbol{h}}_{\text{approximations possible...}} \tag{33}$$

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

$$A_{ia,jb} = \left(\epsilon_a^{\mathrm{KS}} - \epsilon_i^{\mathrm{KS}}\right)\delta_{ij}\delta_{ab} + 2(ia|bj) + f^{xc}_{ia,bj} \qquad B_{ia,jb} = 2(ia|jb) + f^{xc}_{ia,jb} \tag{34}$$

$$f^{xc}_{ia,bj} = \iint \phi_i(\boldsymbol{r})\phi_a(\boldsymbol{r}) \frac{\delta^2 E^{xc}}{\delta\rho(\boldsymbol{r})\delta\rho(\boldsymbol{r}')} \phi_b(\boldsymbol{r})\phi_j(\boldsymbol{r}) d\boldsymbol{r} d\boldsymbol{r}' \tag{35}$$

Red pill: BSE within the static approximation

$$A_{ia,jb} = \left(\epsilon_a^{GW} - \epsilon_i^{GW}\right)\delta_{ij}\delta_{ab} + 2(ia|bj) - W^{\mathrm{stat}}_{ij,ba} \qquad B_{ia,jb} = 2(ia|jb) - W^{\mathrm{stat}}_{ib,ja} \tag{36}$$

$$W^{\mathrm{stat}}_{ij,ab} \equiv W_{ij,ab}(\omega = 0) = (ij|ab) - W^{c}_{ij,ab}(\omega = 0) \tag{37}$$

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 $W_{pq,rs}^{\mathrm{stat}}$

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

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

end procedure

Removing the correlation part: TDHF and CIS

Linear response problem

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

TDHF = RPA with exchange (RPAx)

$$A_{ia,jb} = \left(\epsilon_a^{\text{HF}} - \epsilon_i^{\text{HF}}\right)\delta_{ij}\delta_{ab} + 2(ia|bj) - (ij|ba) \qquad B_{ia,jb} = 2(ia|jb) - (ib|ja) \tag{38}$$

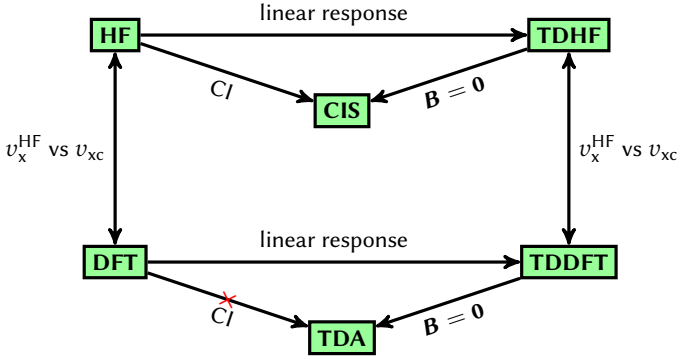
Linear response problem within the Tamm-Dancoff approximation

$$\boxed{\boldsymbol{A} \cdot \boldsymbol{X}_m = \Omega_m \boldsymbol{X}_m} \tag{39}$$

TDHF within TDA = CIS

$$A_{ia,jb} = \left(\epsilon_a^{\text{HF}} - \epsilon_i^{\text{HF}}\right)\delta_{ij}\delta_{ab} + 2(ia|bj) - (ij|ba) \tag{40}$$

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 $\boldsymbol{X}_m^{\mathrm{TDA}}$

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**
          $jb \leftarrow jb + 1$
          $A_{ia,jb} = \delta_{ij}\delta_{ab}(\epsilon_a^{GW} - \epsilon_i^{GW}) + 2(ia|bj) - (ij|ba) + W^{c}_{ij,ba}(\omega = 0)$
        end for
      end for
    end for
  end for
end procedure

Properties

Oscillator strength (length gauge)

$$f_m = \frac{2}{3}\Omega_m\left[(\mu_m^x)^2 + (\mu_m^y)^2 + (\mu_m^z)^2\right] \tag{41}$$

Transition dipole

$$\mu_m^x = \sum_{ia}(i|x|a)(\mathbf{X}_m + \mathbf{Y}_m)_{ia} \qquad (p|x|q) = \int \phi_p(\boldsymbol{r})\, x\, \phi_q(\boldsymbol{r})\, d\boldsymbol{r} \tag{42}$$

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

$$\left\langle \hat{S}^2 \right\rangle_m = \left\langle \hat{S}^2 \right\rangle_0 + \underbrace{\Delta\left\langle \hat{S}^2 \right\rangle_m}_{\text{JCP 134101 (2011) 134}} \qquad \left\langle \hat{S}^2 \right\rangle_0 = \frac{n_\alpha - n_\beta}{2}\left(\frac{n_\alpha - n_\beta}{2} + 1\right) + n_\beta + \sum_p (p_\alpha|p_\beta) \tag{43}$$

Example from QuAcK (H_2O/cc-pVDZ)

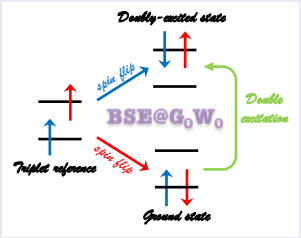
```
---------------------------------------------------------------
Excitation n.   1:   8.411378 eV  f = 0.0255  <S**2> = 0.0000
---------------------------------------------------------------
 5 ->   6 =    0.704168

---------------------------------------------------------------
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
```

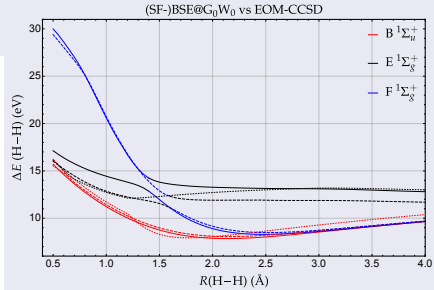
```
---------------------------------------------------------------
Excitation n.   1:   7.632804 eV  f = 0.0000  <S**2> = 2.0000
---------------------------------------------------------------
 5 ->   6 =    0.700599
 5 ->   9 =   -0.089914

---------------------------------------------------------------
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)






```
Excitation n.   1:  -4.891498 eV  f = 0.0000  <S**2> = 0.0217
1A ->  2B =   0.111265
1A ->  4B =  -0.121073
2A ->  1B =   0.961211
2A ->  3B =  -0.212041

Excitation n.   2:   0.691826 eV  f = 0.0000  <S**2> = 1.9964
1A ->  1B =  -0.680242
1A ->  3B =   0.202252
2A ->  2B =  -0.590377
2A ->  4B =   0.373424

Excitation n.   3:   5.625694 eV  f = 0.0000  <S**2> = 0.1795
1A ->  1B =  -0.617840
1A ->  3B =   0.196687
2A ->  2B =   0.753811

Excitation n.   4:   7.474558 eV  f = 0.0000  <S**2> = 0.9821
1A ->  4B =  -0.111548
2A ->  1B =  -0.231266
2A ->  3B =  -0.960135
```

Monino & Loos, JCTC 17 (2021) 2852

Correlation energy at the GW or BSE level

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

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

Galitskii-Migdal functional

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

ACFDT@BSE@GW correlation energy from the adiabatic connection

$$E_c^{\mathrm{ACFDT}} = \frac{1}{2}\int_0^1 \mathrm{Tr}\left(\boldsymbol{K}\boldsymbol{P}^{\lambda}\right)d\lambda \tag{44}$$

Adiabatic connection fluctuation dissipation theorem (ACFDT)

Adiabatic connection

$$\boxed{E_c^{\text{ACFDT}} = \frac{1}{2}\int_0^1 \text{Tr}\left(\boldsymbol{K}\boldsymbol{P}^{\lambda}\right) d\lambda \overset{\text{quad}}{\approx} \frac{1}{2}\sum_{k=1}^{K} w_k \, \text{Tr}\left(\boldsymbol{K}\boldsymbol{P}^{\lambda_k}\right)} \tag{45}$$

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

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

Interaction kernel

$$\boldsymbol{K} = \begin{pmatrix} \tilde{\boldsymbol{A}} & \tilde{\boldsymbol{B}} \\ \tilde{\boldsymbol{B}} & \tilde{\boldsymbol{A}} \end{pmatrix} \qquad \tilde{A}_{ia,jb} = 2(ia|bj) \qquad \tilde{B}_{ia,jb} = 2(ia|jb) \tag{46}$$

Correlation part of the two-particle density matrix

$$\boldsymbol{P}^{\lambda} = \begin{pmatrix} \boldsymbol{Y}^{\lambda} \cdot (\boldsymbol{Y}^{\lambda})^{\intercal} & \boldsymbol{Y}^{\lambda} \cdot (\boldsymbol{X}^{\lambda})^{\intercal} \\ \boldsymbol{X}^{\lambda} \cdot (\boldsymbol{Y}^{\lambda})^{\intercal} & \boldsymbol{X}^{\lambda} \cdot (\boldsymbol{X}^{\lambda})^{\intercal} \end{pmatrix} - \begin{pmatrix} \boldsymbol{0} & \boldsymbol{0} \\ \boldsymbol{0} & \boldsymbol{1} \end{pmatrix} \tag{47}$$

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 $k = 1, \ldots, K$."

$$\int_a^b f(x)\,w(x)\,dx \approx \sum_k^K \underbrace{w_k}_{\text{weights}} f\Big(\underbrace{x_k}_{\text{roots}}\Big) \tag{48}$$

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

$$A^{\lambda,\mathrm{RPA}}_{ia,jb} = \delta_{ij}\delta_{ab}(\epsilon^{\mathrm{HF}}_a - \epsilon^{\mathrm{HF}}_i) + 2\lambda(ia|bj) \qquad B^{\lambda,\mathrm{RPA}}_{ia,jb} = 2\lambda(ia|jb) \tag{49}$$

$$\boxed{E^{\mathrm{RPA}}_{\mathrm{c}} = \frac{1}{2}\int_0^1 \mathrm{Tr}\left(\boldsymbol{K}\boldsymbol{P}^{\lambda}\right) d\lambda = \frac{1}{2}\left[\sum_m \Omega^{\mathrm{RPA}}_m - \mathrm{Tr}\left(\boldsymbol{A}^{\mathrm{RPA}}\right)\right]} \tag{50}$$

RPAx matrix elements

$$A^{\lambda,\mathrm{RPAx}}_{ia,jb} = \delta_{ij}\delta_{ab}(\epsilon^{\mathrm{HF}}_a - \epsilon^{\mathrm{HF}}_i) + \lambda[2(ia|bj) - (ij|ab)] \qquad B^{\lambda,\mathrm{RPAx}}_{ia,jb} = \lambda[2(ia|jb) - (ib|aj)] \tag{51}$$

$$\boxed{E^{\mathrm{RPAx}}_{\mathrm{c}} = \frac{1}{2}\int_0^1 \mathrm{Tr}\left(\boldsymbol{K}\boldsymbol{P}^{\lambda}\right) d\lambda \neq \frac{1}{2}\left[\sum_m \Omega^{\mathrm{RPAx}}_m - \mathrm{Tr}\left(\boldsymbol{A}^{\mathrm{RPAx}}\right)\right]} \tag{52}$$

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

$$E^{\mathrm{RPAx}}_{\mathrm{c}} = \frac{1}{4}\int_0^1 \mathrm{Tr}\left(\boldsymbol{K}^{\mathrm{x}}\boldsymbol{P}^{\lambda}\right) d\lambda = \frac{1}{4}\left[\sum_m \Omega^{\mathrm{RPAx}}_m - \mathrm{Tr}(\boldsymbol{A}^{\mathrm{RPAx}})\right] \tag{53}$$

ACFDT at the BSE level

BSE matrix elements

$$A^{\lambda,\mathrm{BSE}}_{ia,jb} = \delta_{ij}\delta_{ab}(\epsilon^{GW}_a - \epsilon^{GW}_i) + \lambda\Big[2(ia|bj) - W^{\lambda}_{ij,ab}(\omega=0)\Big] \qquad B^{\lambda,\mathrm{BSE}}_{ia,jb} = \lambda\Big[2(ia|jb) - W^{\lambda}_{ib,ja}(\omega=0)\Big] \tag{54}$$

$$\boxed{E_c^{\mathrm{BSE}} = \frac{1}{2}\int_0^1 \mathrm{Tr}\Big(\boldsymbol{K}\boldsymbol{P}^{\lambda}\Big)\,d\lambda \neq \frac{1}{2}\left[\sum_m \Omega_m^{\mathrm{BSE}} - \mathrm{Tr}\Big(\boldsymbol{A}^{\mathrm{BSE}}\Big)\right]} \tag{55}$$

λ-dependent screening

$$W^{\lambda}_{pq,rs}(\omega) = (pq|rs) + 2\sum_m (pq|m)^{\lambda}(rs|m)^{\lambda}\left[\frac{1}{\omega - \Omega_m^{\lambda,\mathrm{RPA}} + i\eta} - \frac{1}{\omega + \Omega_m^{\lambda,\mathrm{RPA}} - i\eta}\right] \tag{56}$$

$$(pq|m)^{\lambda} = \sum_{ia}(pq|ia)(\boldsymbol{X}^{\lambda,\mathrm{RPA}}_m + \boldsymbol{Y}^{\lambda,\mathrm{RPA}}_m)_{ia} \tag{57}$$

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 $\{w_k, \lambda_k\}_{1 \leq k \leq K}$

$E_c \leftarrow 0$

for $k = 1, \ldots, K$ **do**

Compute static screening elements $W^{\lambda_k}_{pq,rs}(\omega = 0)$

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!

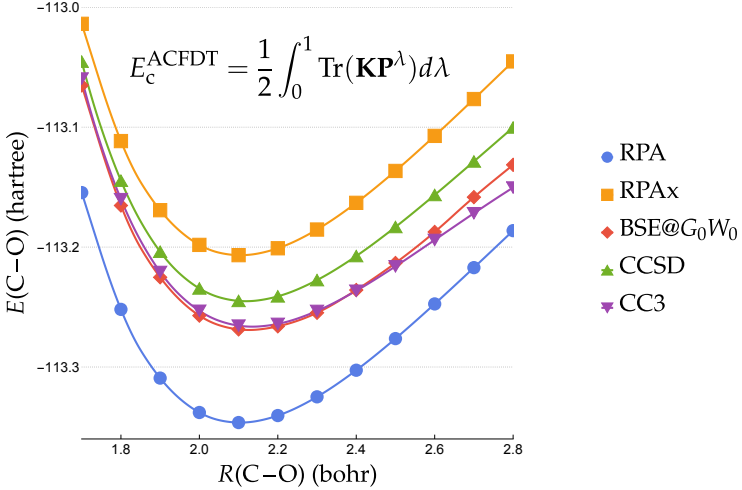
Form two-particle density matrix $\boldsymbol{P}^{\lambda_k}$

$E_c \leftarrow E_c + w_k \, \mathrm{Tr}\left(\boldsymbol{K}\boldsymbol{P}^{\lambda_k}\right)$

end for

end procedure

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



Loos et al. JPCL 11 (2020) 3536

Useful papers/programs

- molGW: 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
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