Green's function and self-consistency: an unhappy marriage?

Pierre-François (Titou) Loos

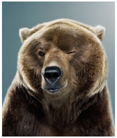
Laboratoire de Chimie et Physique Quantiques,
Université Paul Sabatier, Toulouse, France
loos@irsamc.ups-tlse.fr

15th May 2019

Collaborators

- Selected CI and QMC "team"

Anthony Scemama



Yann Garniron

Michel Caffarel

- Green's function methods "team"

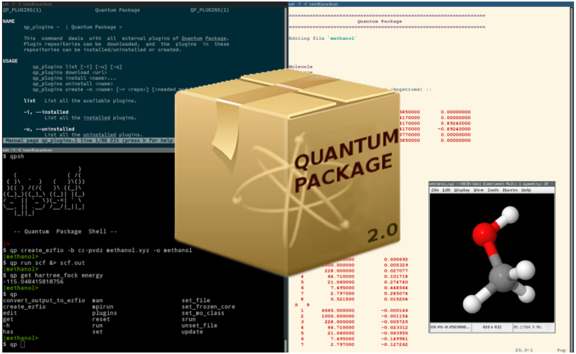
Mika Véril

Pina Romaniello

Arjan Berger

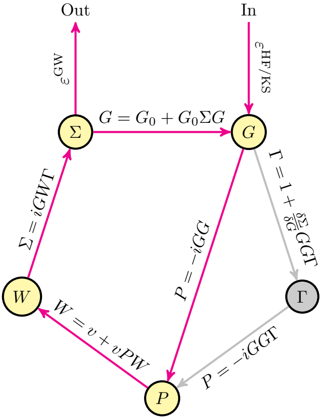
- Fabien Bruneval, Valerio Olevano & Xavier Blase

Quantum Package 2.0 (https://quantumpackage.github.io/qp2)



"Quantum Package 2.0: An Open-Source Determinant-Driven Suite of Programs"
Garniron et al. JCTC (in press), arXiv:1902.08154

Hedin's pentagon



Hedin, Phys Rev 139 (1965) A796

What can we calculate with GW?

- Ionization potentials (IP) given by occupied MO energies
- Electron affinities (EA) given by virtual MO energies
- HOMO-LUMO gap (or band gap in solids)
- Singlet and triplet neutral excitations (vertical absorption energies) via BSE
- Correlation and total energies via RPA or Galitskii-Migdal functional

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
- BSE or Bethe-Salpeter equation for neutral excitations

G_0W_0

G_0W_0 subroutine

procedure PERTURBATIVE GW
  Perform HF calculation to get $\boldsymbol{\epsilon}^{\text{HF}}$ and $\boldsymbol{c}^{\text{HF}}$
  for $p = 1, \ldots, N$ **do**
    Compute $\Sigma_p^{\text{c}}(\omega)$ and $Z_p(\omega)$
    $\epsilon_p^{G_0W_0} = \epsilon_p^{\text{HF}} + Z_p(\epsilon_p^{\text{HF}}) \, \text{Re}[\Sigma_p^{\text{c}}(\epsilon_p^{\text{HF}})]$
    ▷ This is the linearized version of the
    ▷ quasiparticle (QP) equation $\omega = \epsilon_p^{\text{HF}} + \text{Re}[\Sigma_p^{\text{c}}(\omega)]$
  end for
  if BSE **then**
    Compute BSE excitations energies if you wish
  end if
end procedure

G_0W_0

Correlation part of the self-energy:

$$\Sigma_p^{c}(\omega) = 2 \sum_{ix} \frac{[pi|x]^2}{\omega - \epsilon_i + \Omega_x - i\eta} + 2 \sum_{ax} \frac{[pa|x]^2}{\omega - \epsilon_a - \Omega_x + i\eta}$$

Renormalization factor

$$Z_p(\omega) = \left[1 - \frac{\partial \,\mathrm{Re}[\Sigma_p^{c}(\omega)]}{\partial \omega} \right]^{-1}$$

Screened two-electron MO integrals

$$[pq|x] = \sum_{ia} (pq|ia)(\boldsymbol{X} + \boldsymbol{Y})_{ia}^{x}$$

RPA excitation energies

$$\begin{pmatrix} \boldsymbol{A} & \boldsymbol{B} \\ \boldsymbol{B} & \boldsymbol{A} \end{pmatrix} \begin{pmatrix} \boldsymbol{X} \\ \boldsymbol{Y} \end{pmatrix} = \boldsymbol{\Omega} \begin{pmatrix} \boldsymbol{1} & \boldsymbol{0} \\ \boldsymbol{0} & -\boldsymbol{1} \end{pmatrix} \begin{pmatrix} \boldsymbol{X} \\ \boldsymbol{Y} \end{pmatrix}$$

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

evGW

evGW subroutine

procedure PARTIALLY SELF-CONSISTENT EVGW

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

Set $\boldsymbol{\epsilon}^{\text{G}_{-1}\text{W}_{-1}} = \boldsymbol{\epsilon}^{\text{HF}}$ and $n = 0$

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

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

Compute $\Sigma_p^{\text{c}}(\omega)$

Solve $\omega = \epsilon_p^{\text{HF}} + \text{Re}[\Sigma_p^{\text{c}}(\omega)]$ to obtain $\epsilon_p^{\text{G}_n\text{W}_n}$

end for

$\boldsymbol{\Delta} = \boldsymbol{\epsilon}^{\text{G}_n\text{W}_n} - \boldsymbol{\epsilon}^{\text{G}_{n-1}\text{W}_{n-1}}$

$n \leftarrow n + 1$

end while

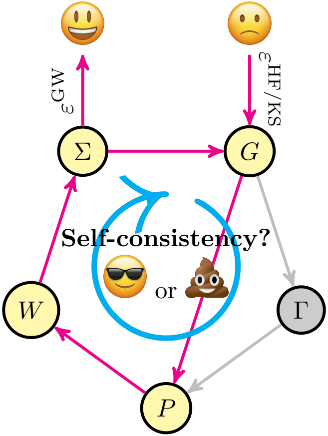
if BSE **then**

Compute BSE excitations energies if you wish

end if

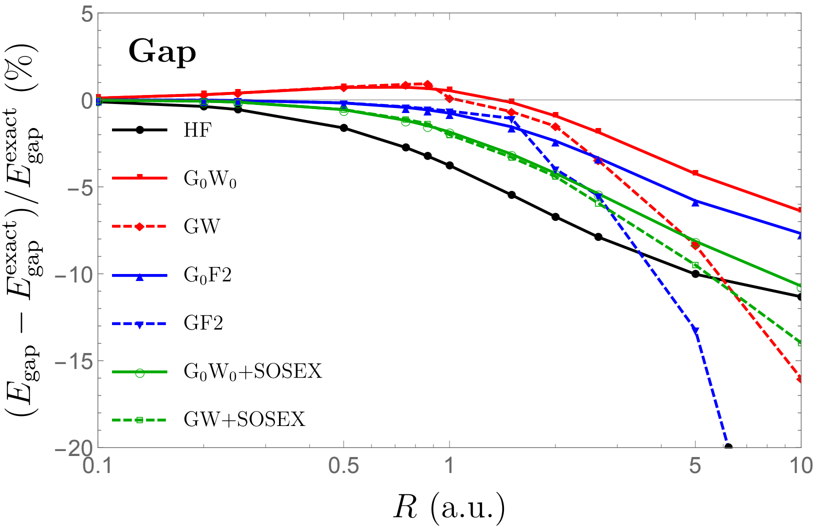
end procedure

Green's function and self-consistency: an unhappy marriage?



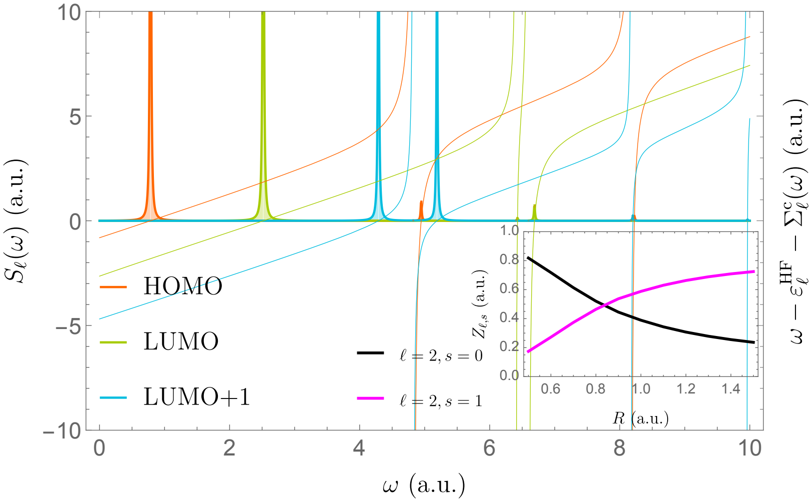
Loos, Romaniello & Berger, JCTC 14 (2018) 3071

The appearance of the glitch



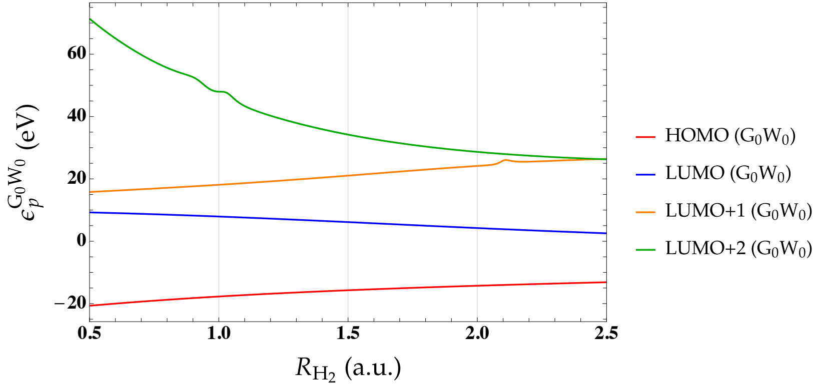
Loos, Romaniello & Berger, JCTC 14 (2018) 3071

The explanation of the glitch



Loos, Romaniello & Berger, JCTC 14 (2018) 3071

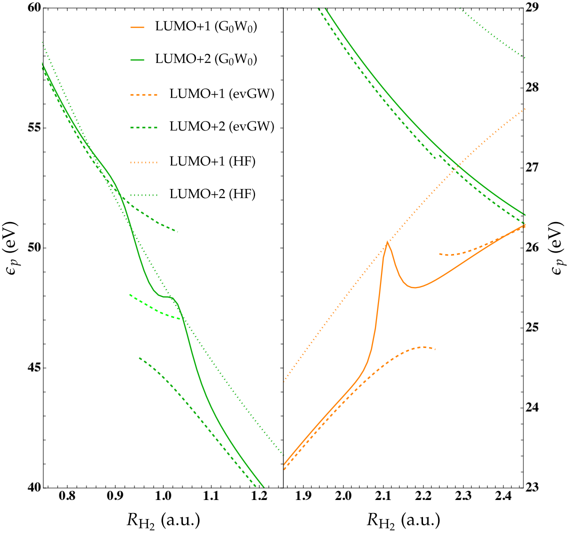
Glitch in molecular systems: G_0W_0@HF/6-31G for H_2



$$\epsilon_p^{G_0W_0} = \epsilon_p^{HF} + Z_p(\epsilon_p^{HF}) \, \text{Re}[\Sigma_p^c(\epsilon_p^{HF})]$$

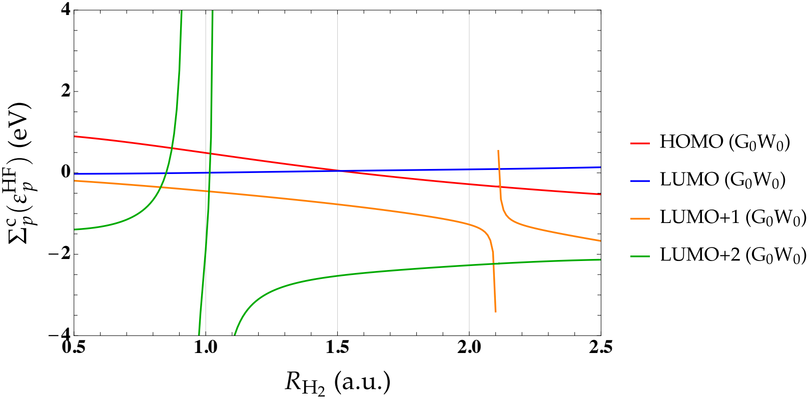
Véril, Romaniello, Berger & Loos, JCTC 14 (2018) 5220

Glitch in molecular systems: G_0W_0@HF/6-31G for H_2



Véril, Romaniello, Berger & Loos, JCTC 14 (2018) 5220

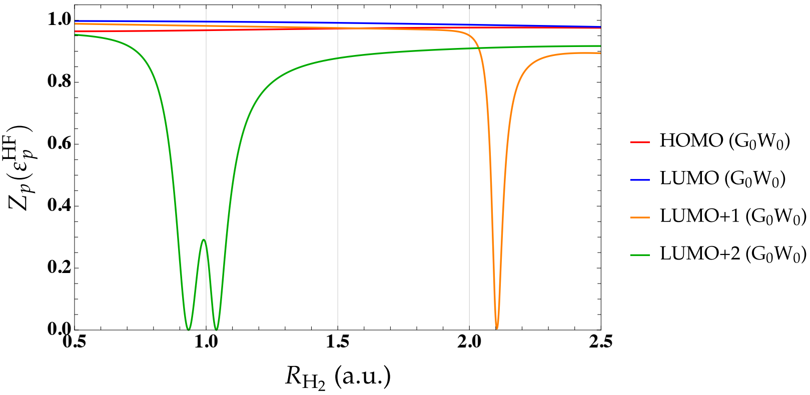
Glitch in molecular systems: G_0W_0@HF/6-31G for H_2



$$\Sigma_p^{c}(\omega) = 2 \sum_{ix} \frac{[pi|x]^2}{\omega - \epsilon_i^{HF} + \Omega_x - i\eta} + 2 \sum_{ax} \frac{[pa|x]^2}{\omega - \epsilon_a^{HF} - \Omega_x + i\eta}$$

Véril, Romaniello, Berger & Loos, JCTC 14 (2018) 5220

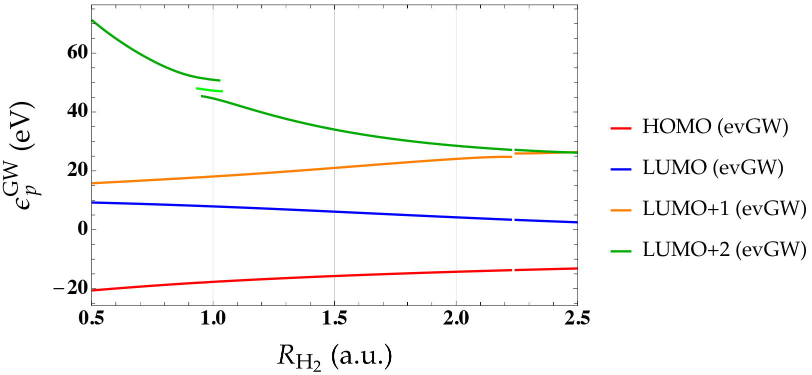
Glitch in molecular systems: G_0W_0@HF/6-31G for H_2



$$Z_p(\omega) = \left[1 - \frac{\partial \,\mathrm{Re}[\Sigma_p^{\mathrm{c}}(\omega)]}{\partial \omega}\right]^{-1}$$

Véril, Romaniello, Berger & Loos, JCTC 14 (2018) 5220

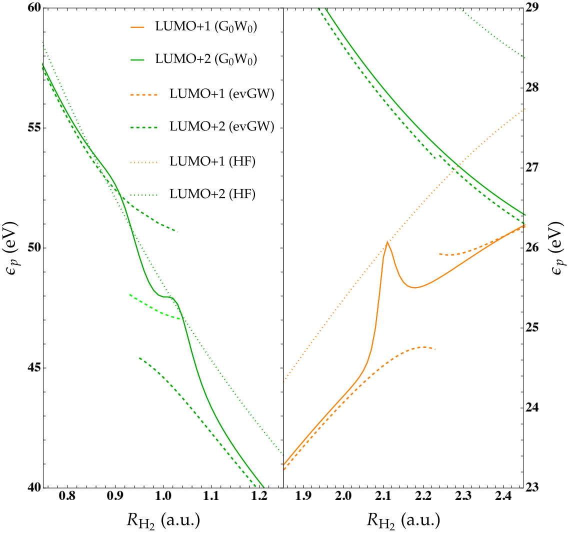
Glitch in molecular systems: evGW@HF/6-31G for H_2



$$\epsilon_p^{G_n W_n} = \epsilon_p^{\mathrm{HF}} + \mathrm{Re}[\Sigma_p^{\mathrm{c}}(\epsilon_p^{G_{n-1} W_{n-1}})]$$

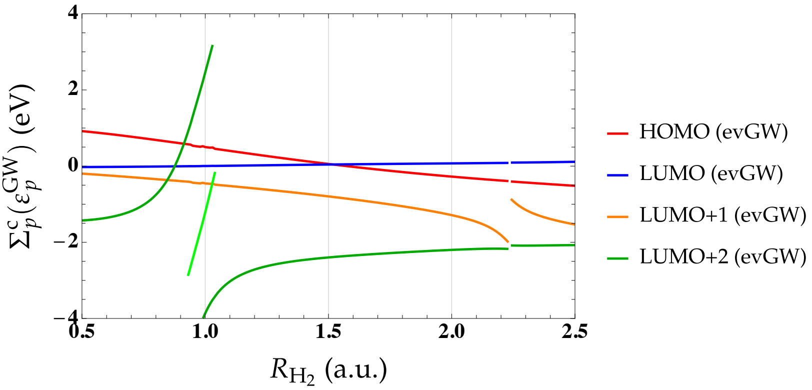
Véril, Romaniello, Berger & Loos, JCTC 14 (2018) 5220

Glitch in molecular systems: evGW@HF/6-31G for H_2



Véril, Romaniello, Berger & Loos, JCTC 14 (2018) 5220

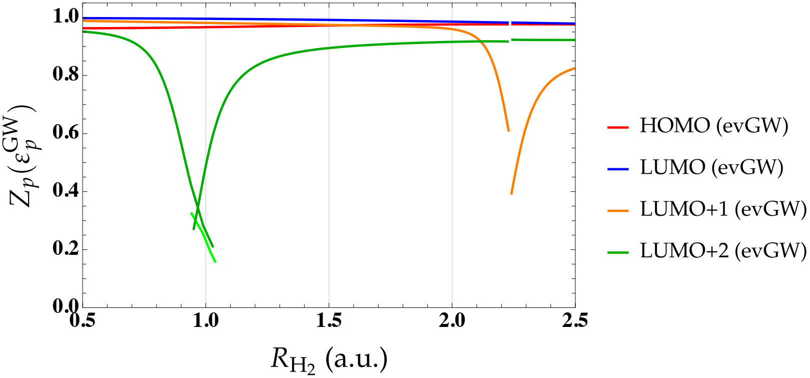
Glitch in molecular systems: evGW@HF/6-31G for H_2



$$\Sigma_p^c(\omega) = 2\sum_{ix} \frac{[pi|x]^2}{\omega - \epsilon_i + \Omega_x - i\eta} + 2\sum_{ax} \frac{[pa|x]^2}{\omega - \epsilon_a - \Omega_x + i\eta}$$

Véril, Romaniello, Berger & Loos, JCTC 14 (2018) 5220

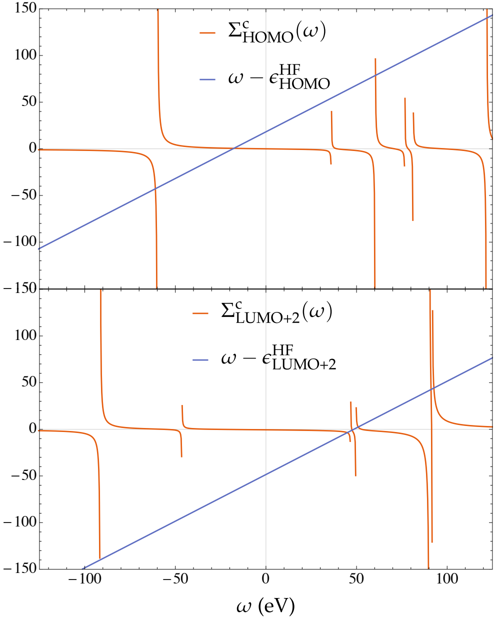
Glitch in molecular systems: evGW@HF/6-31G for H_2



$$Z_p(\omega) = \left[1 - \frac{\partial \, \text{Re}[\Sigma_p^c(\omega)]}{\partial \omega}\right]^{-1}$$

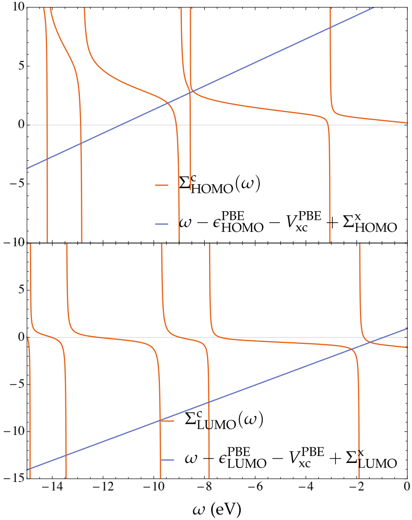
Véril, Romaniello, Berger & Loos, JCTC 14 (2018) 5220

Quasiparticle equation: evGW@HF/6-31G for H_2 at $R_{H_2} = 1$ bohr



$$\Sigma^c_p(\omega) = 2\sum_{ix} \frac{[pi|x]^2}{\omega - \epsilon_i + \Omega_x - i\eta} + 2\sum_{ax} \frac{[pa|x]^2}{\omega - \epsilon_a - \Omega_x + i\eta}$$

G_0W_0@PBE/cc-pVDZ for BeO at $R_{\text{BeO}} = 2.515$ bohr



MolGW: F. Bruneval
(`http://www.molgw.org`)

HOMO-LUMO gap

- PBE/cc-pVDZ = 1.35 eV
- HF/cc-pVDZ = 8.96 eV
- G_0W_0@PBE/cc-pVDZ = 5.60 eV
- G_0W_0@HF/cc-pVDZ = 7.54 eV

van Setten et al. JCTC 11 (2015) 5665

Concluding remarks

Take-home messages

- happens in many other cases (HeH^+, LiF, F_2, etc)
- happens also for occupied orbitals
- Similar behavior is found in qsGW
- Discontinuities induces convergence problems in self-consistent GW (we use DIIS, not linear mixing)
- Discontinuities also present in correlation and (BSE) excitation energies
- Problems with HOMO frequent due to small KS gap (LiH, O_3, BN, BeO, etc.) van Setten et al. JCTC 11 (2015) 5665
- If you do not throw away the satellites, you won't see these...