

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

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# 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

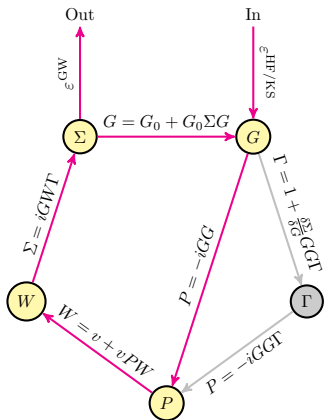
# Quantum Package 2.0 (<https://quantumpackage.github.io/qp2>)

The screenshot displays the Quantum Package 2.0 terminal interface. The terminal shows the 'qpsh' shell prompt and various commands being executed, such as 'qp create\_effio', 'qp run', and 'qp get\_hermitian\_fock\_energy'. A 3D model of a cardboard box labeled 'QUANTUM PACKAGE 2.0' is overlaid on the terminal. To the right, a window displays a ball-and-stick molecular model of methanol (CH3OH) and a table of numerical data.

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*"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<sub>0</sub>W<sub>0</sub> subroutine

**procedure** PERTURBATIVE GW

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

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

Compute  $\Sigma_p^c(\omega)$  and  $Z_p(\omega)$

$$\epsilon_p^{\text{G}_0\text{W}_0} = \epsilon_p^{\text{HF}} + Z_p(\epsilon_p^{\text{HF}}) \text{Re}[\Sigma_p^c(\epsilon_p^{\text{HF}})]$$

▷ This is the linearized version of the

▷ quasiparticle (QP) equation  $\omega = \epsilon_p^{\text{HF}} + \text{Re}[\Sigma_p^c(\omega)]$

**end for**

**if** BSE **then**

Compute BSE excitations energies if you wish

**end if**

**end procedure**

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

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

Screened two-electron MO integrals

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

RPA excitation energies

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

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

$$B_{ia,jb}^{\text{RPA}} = 2(ia|bj)$$

## evGW subroutine

**procedure** PARTIALLY SELF-CONSISTENT EVGW

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

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

**while**  $\max |\Delta| < \tau$  **do**

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

    Compute  $\Sigma_p^c(\omega)$

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

**end for**

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

$n \leftarrow n + 1$

**end while**

**if** BSE **then**

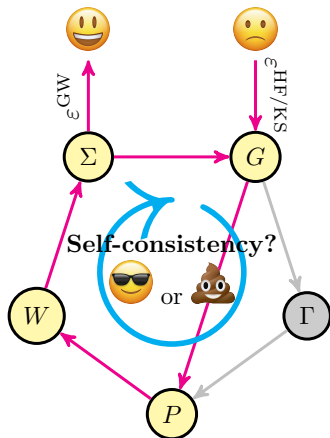
  Compute BSE excitations energies if you wish

**end if**

**end procedure**

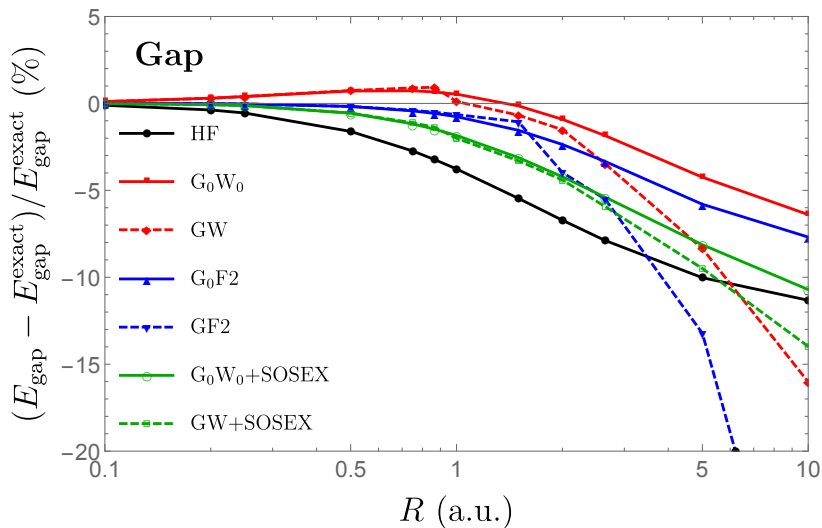


## Green's function and self-consistency: an unhappy marriage?



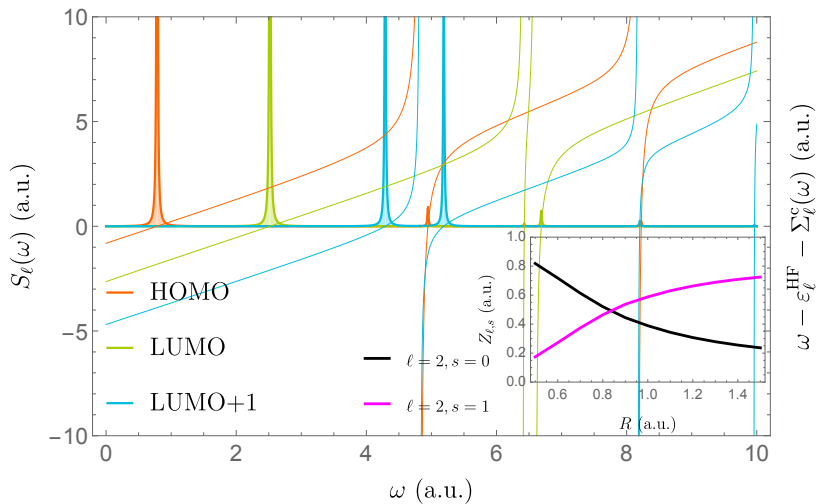
Loos, Romaniello & Berger, JCTC 14 (2018) 3071

## The appearance of the glitch

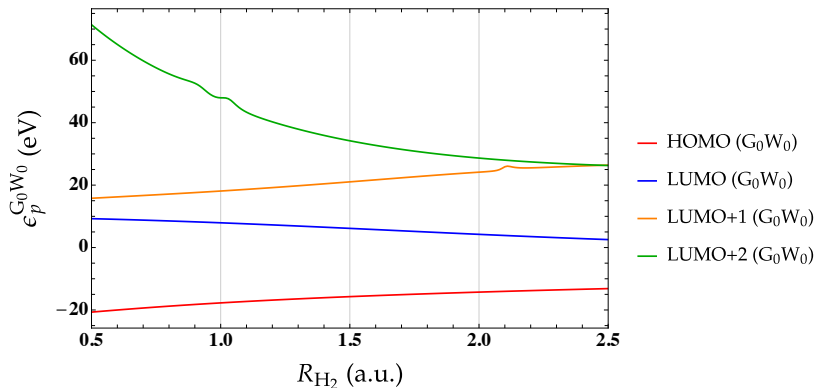


Loos, Romaniello & Berger, JCTC 14 (2018) 3071

## The explanation of the glitch

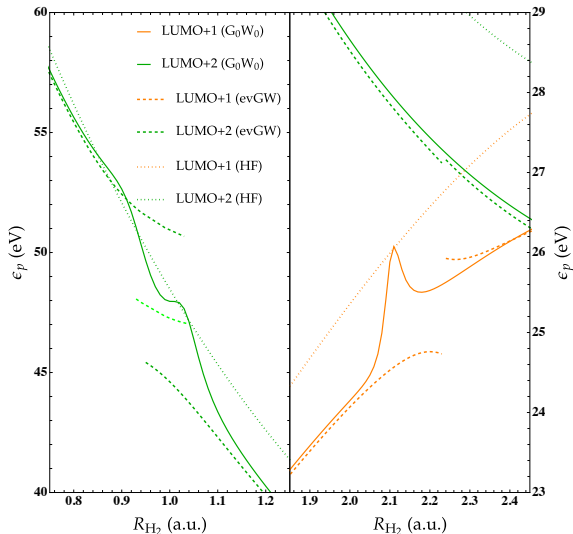


Loos, Romaniello &amp; Berger, JCTC 14 (2018) 3071

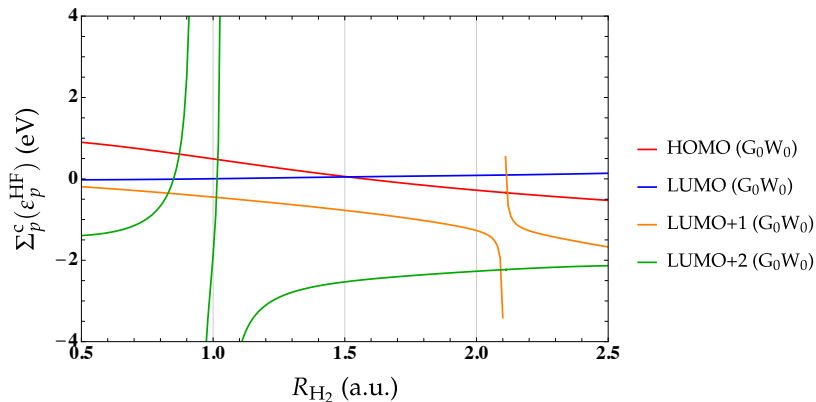
Glitch in molecular systems: G<sub>0</sub>W<sub>0</sub>@HF/6-31G for H<sub>2</sub>

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

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

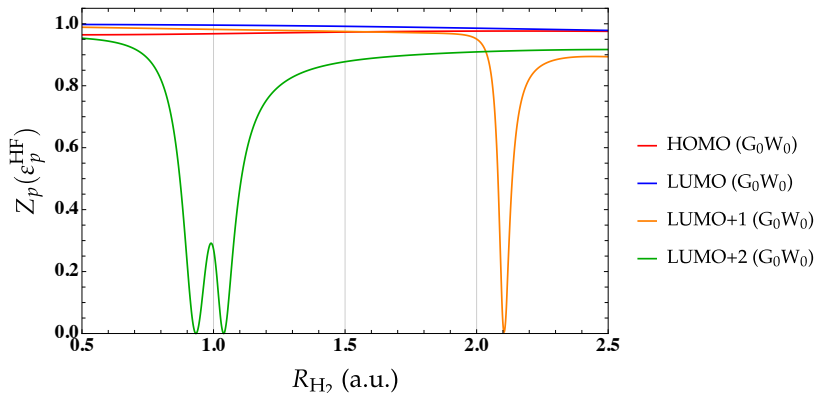
Glitch in molecular systems:  $G_0W_0@HF/6-31G$  for  $H_2$ 

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

Glitch in molecular systems: G<sub>0</sub>W<sub>0</sub>@HF/6-31G for H<sub>2</sub>

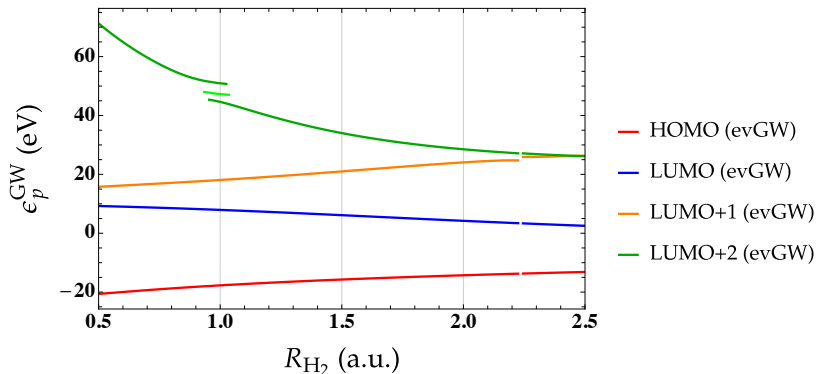
$$\Sigma_p^c(\omega) = 2 \sum_{ix} \frac{[pi|x]^2}{\omega - \epsilon_i^{\text{HF}} + \Omega_x - i\eta} + 2 \sum_{ax} \frac{[pa|x]^2}{\omega - \epsilon_a^{\text{HF}} - \Omega_x + i\eta}$$

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

Glitch in molecular systems: G<sub>0</sub>W<sub>0</sub>@HF/6-31G for H<sub>2</sub>

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

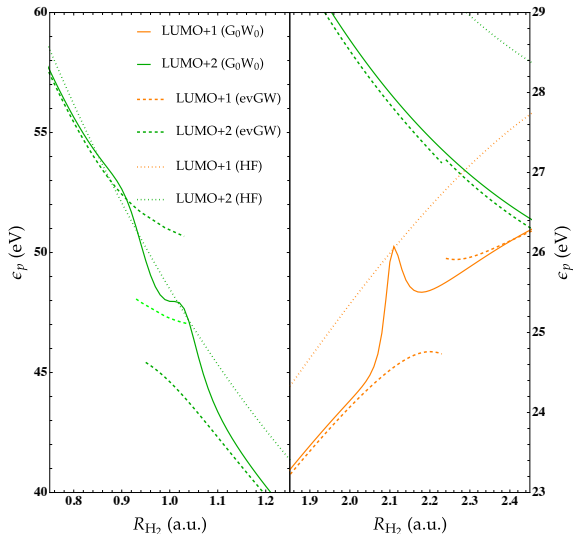
Véril, Romaniello, Berger & Loos, JCTC 14 (2018) 5220

Glitch in molecular systems: evGW@HF/6-31G for H<sub>2</sub>

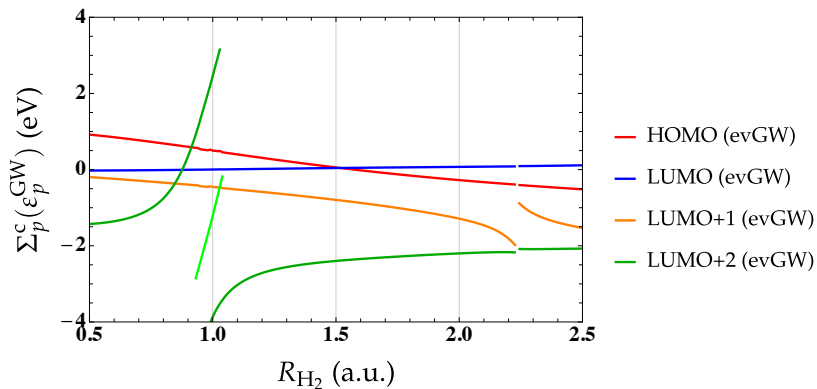
$$\epsilon_p^{G_n W_n} = \epsilon_p^{HF} + \text{Re}[\sum_p^c (\epsilon_p^{G_{n-1} W_{n-1}})]$$

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



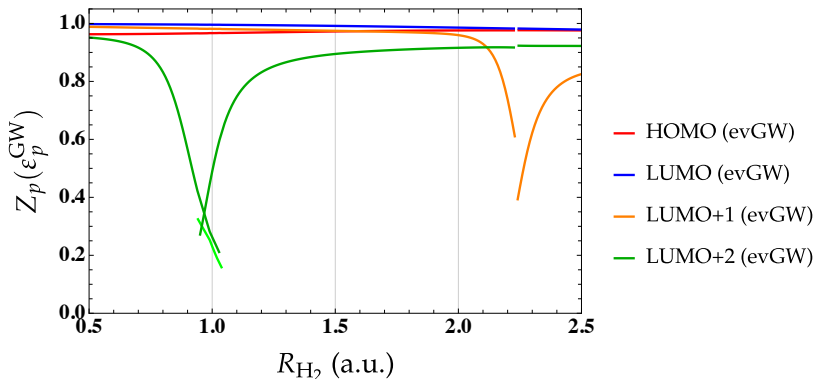
Glitch in molecular systems: evGW@HF/6-31G for  $H_2$ 

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

Glitch in molecular systems: evGW@HF/6-31G for H<sub>2</sub>

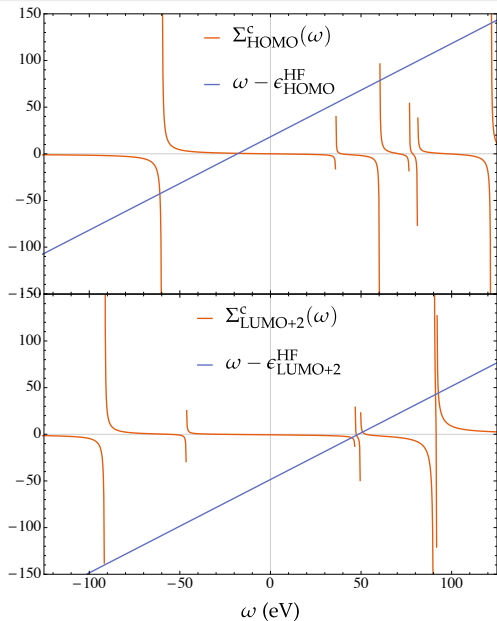
$$\Sigma_p^c(\omega) = 2 \sum_{ix} \frac{[pi|x]^2}{\omega - \epsilon_i + \Omega_x - i\eta} + 2 \sum_{ax} \frac{[pa|x]^2}{\omega - \epsilon_a - \Omega_x + i\eta}$$

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

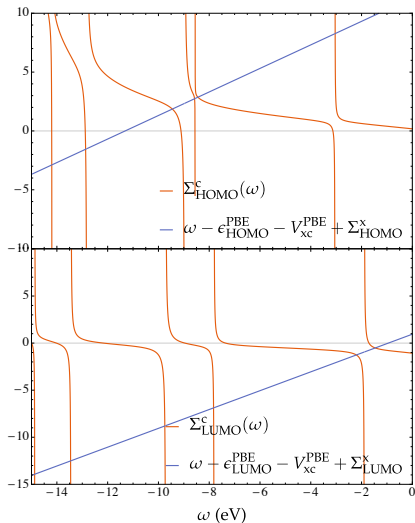
Glitch in molecular systems: evGW@HF/6-31G for  $H_2$ 

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

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

Quasiparticle equation: evGW@HF/6-31G for H<sub>2</sub> at R<sub>H<sub>2</sub></sub> = 1 bohr

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

$G_0W_0@PBE/cc-pVDZ$  for BeO at  $R_{BeO} = 2.515$  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 ( $\text{HeH}^+$ ,  $\text{LiF}$ ,  $\text{F}_2$ , 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 ( $\text{LiH}$ ,  $\text{O}_3$ ,  $\text{BN}$ ,  $\text{BeO}$ , etc.) [van Setten et al. JCTC 11 \(2015\) 5665](#)
- If you do not throw away the satellites, you won't see these...