Green functions and self-consistency: an unhappy marriage?

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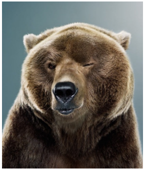
Collaborators

- Selected CI and QMC "team"

Anthony Scemama



Yann Garniron

Michel Caffarel

- Green function methods "team"

Mika Véril

Pina Romaniello

Arjan Berger

Selected CI methods (CIPSI)

Ground state

- sCI+QMC: Water molecule
  Caffarel, Applencourt, Giner, & Scemama, JCP 144 (2016) 151103
- sCI+QMC: "Challenging" case of FeS
  Scemama, Garniron, Caffarel & Loos, JCTC 14 (2018) 1395

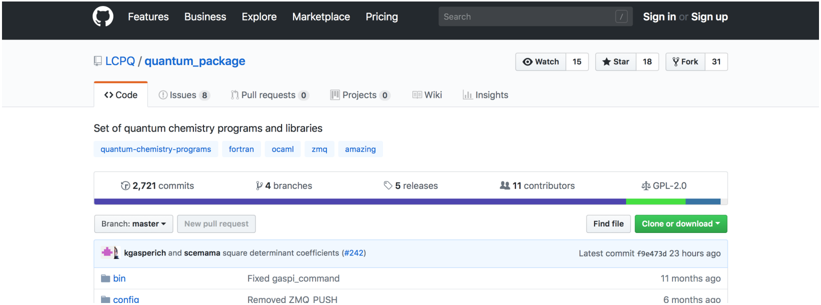
Excited states

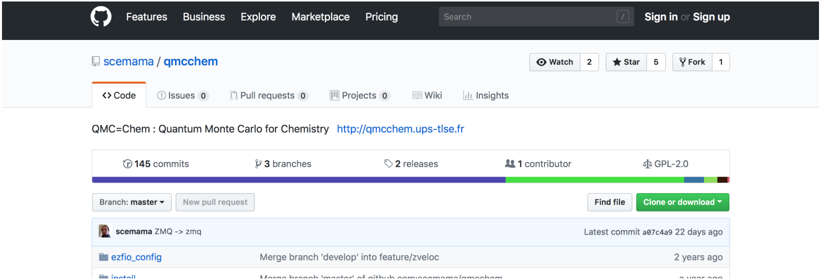
- sCI+PT2: Benchmarking excited-state methods
  Loos, Scemama, Blondel, Garniron, Caffarel & Jacquemin, JCTC (revised)
- sCI+QMC: excitation energies with "deterministic" nodes
  Scemama, Benali, Jacquemin, Caffarel & Loos, JCP (revised) arxiv:1805.09553

Developments

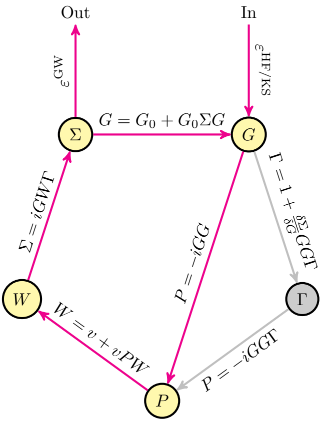
- Semi-stochastic PT2
  Garniron, Scemama, Loos & Caffarel, JCP 147 (2017) 034101
- Internally-decontrated version (shifted-Bk)
  Garniron, Scemama, Giner, Caffarel & Loos, JCP (submitted) arxiv:1806.04970

A tale of two softwares (http://scemama.github.io)





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

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

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

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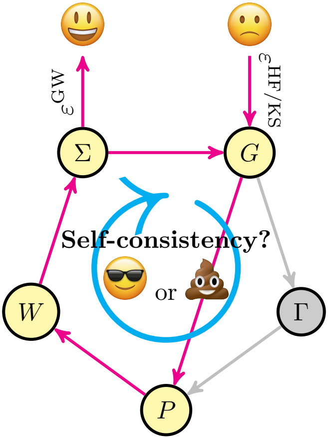

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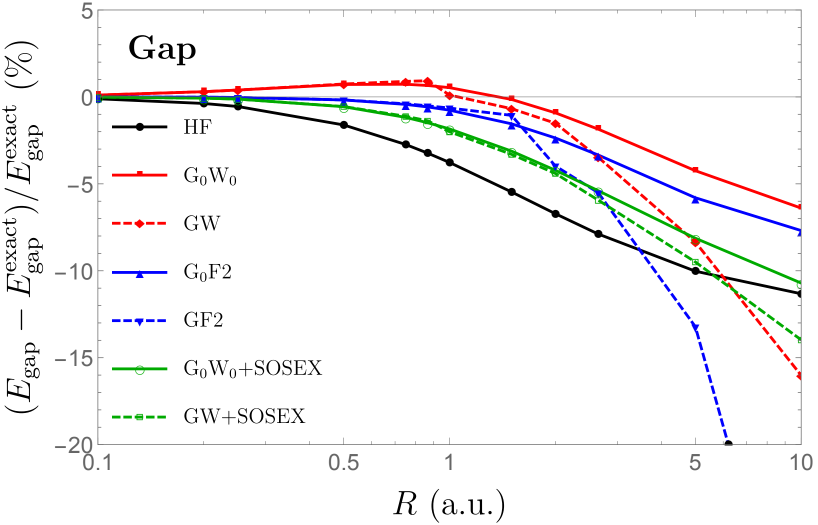
The appearance of the glitch



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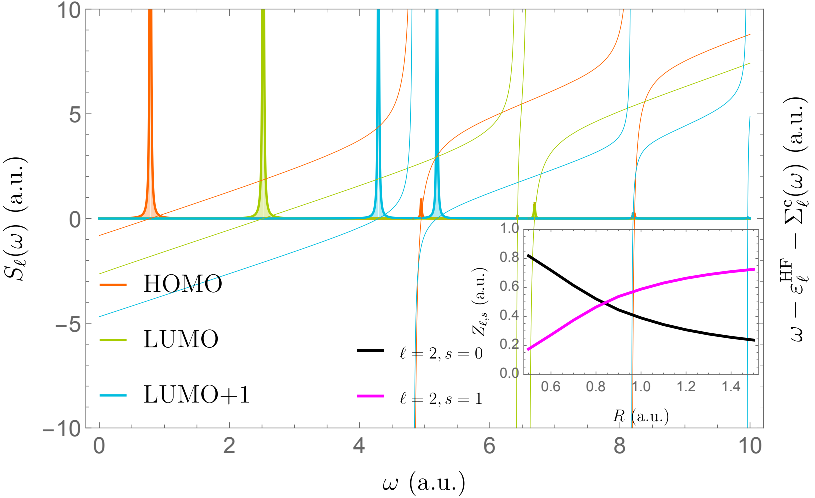
The explanation of the glitch



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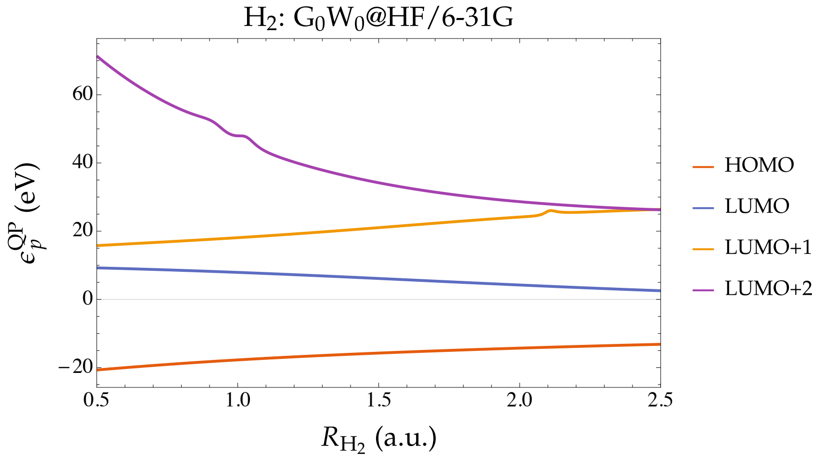
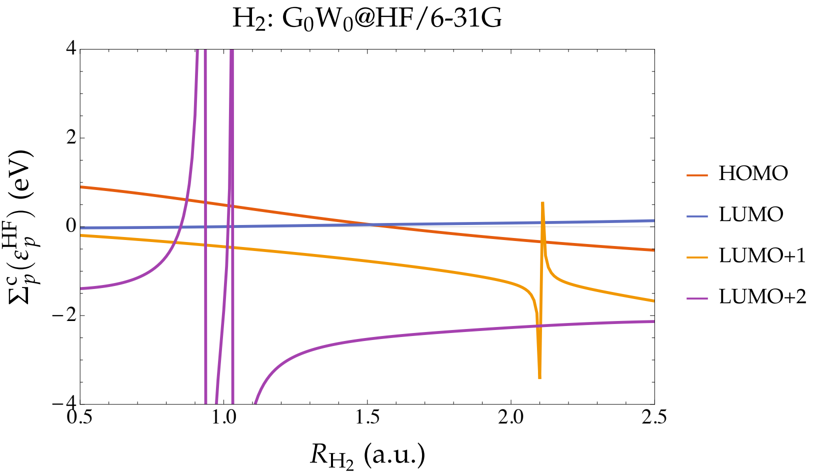
Glitch in molecular systems: G_0W_0@H_2



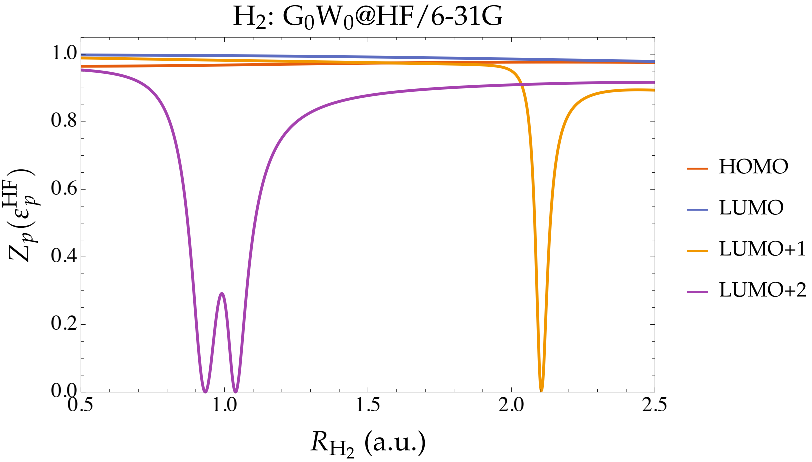
$$\boxed{\epsilon_p^{G_0W_0} = \epsilon_p^{HF} + Z_p(\epsilon_p^{HF})\,\mathrm{Re}[\Sigma_p^c(\epsilon_p^{HF})]}$$

Glitch in molecular systems: G_0W_0@H_2



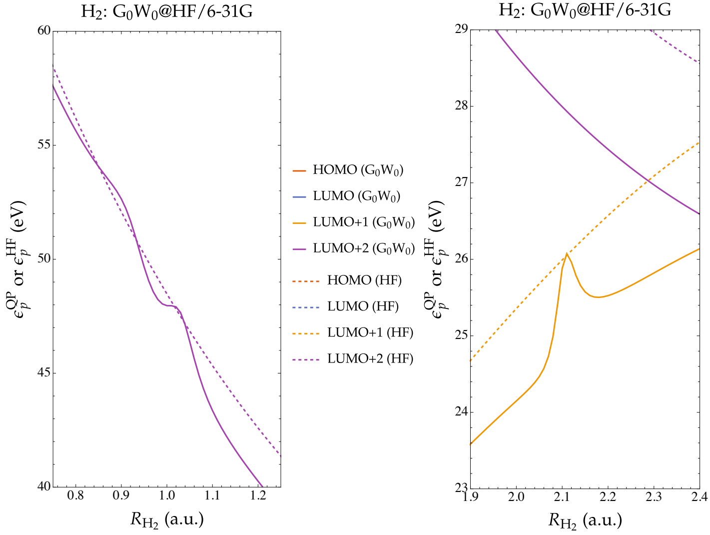
$$\boxed{\Sigma_p^c(\omega) = 2\sum_{ix} \frac{[pi|x]^2}{\omega - \epsilon_i^{HF} + \Omega_x - i\eta} + 2\sum_{ax} \frac{[pa|x]^2}{\omega - \epsilon_a^{HF} - \Omega_x + i\eta}}$$

Glitch in molecular systems: G_0W_0@H_2

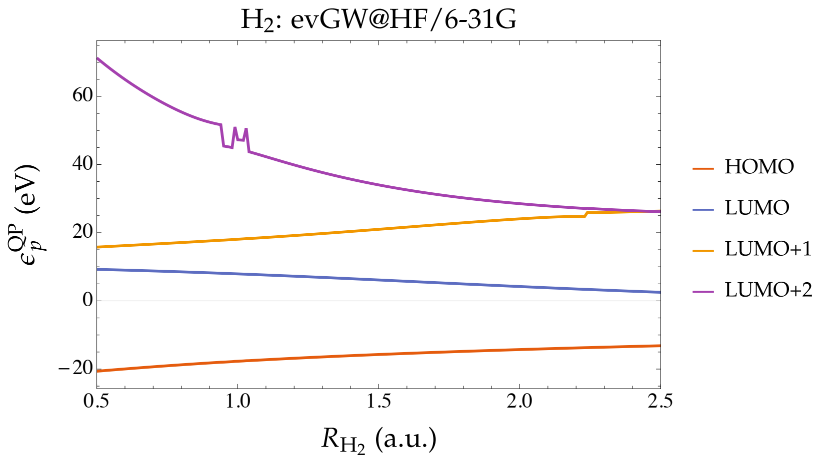


$$\boxed{Z_p(\omega) = \left[1 - \frac{\partial \,\text{Re}[\Sigma_p^{\text{c}}(\omega)]}{\partial \omega}\right]^{-1}}$$

Glitch in molecular systems: G_0W_0@H_2

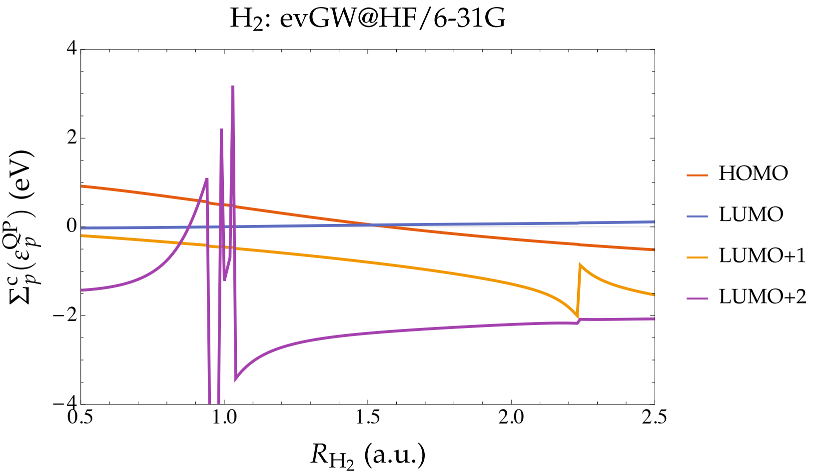


Glitch in molecular systems: evGW@H_2



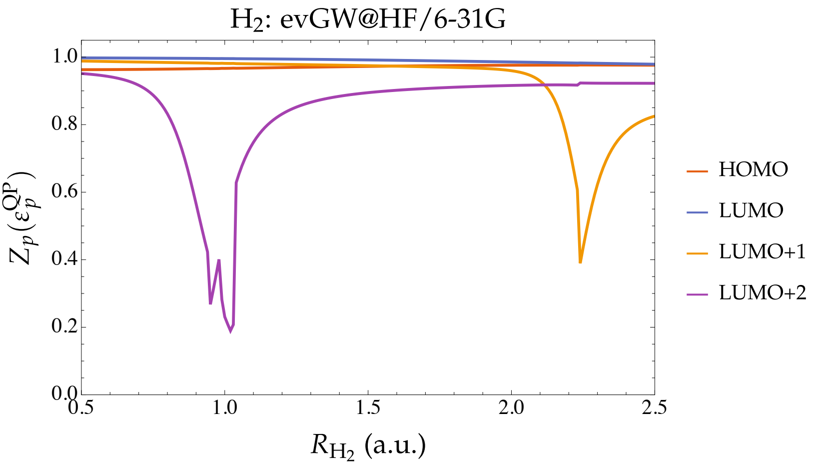
$$\boxed{\epsilon_p^{G_n W_n} = \epsilon_p^{\text{HF}} + \text{Re}[\Sigma_p^{\text{c}}(\epsilon_p^{G_{n-1} W_{n-1}})]}$$

Glitch in molecular systems: evGW@H_2



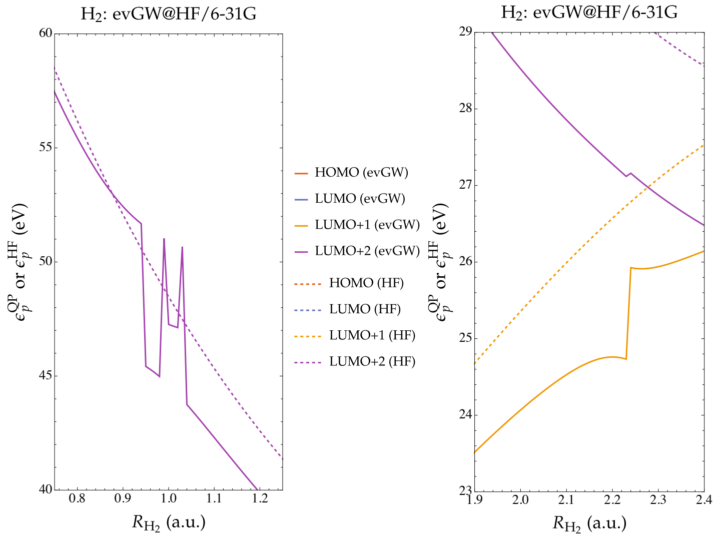
$$\boxed{\Sigma_p^{\text{c}}(\omega) = 2 \sum_{ix} \frac{[pi|x]^2}{\omega - \epsilon_i + \Omega_x - i\eta} + 2 \sum_{ax} \frac{[pa|x]^2}{\omega - \epsilon_a - \Omega_x + i\eta}}$$

Glitch in molecular systems: evGW@H_2

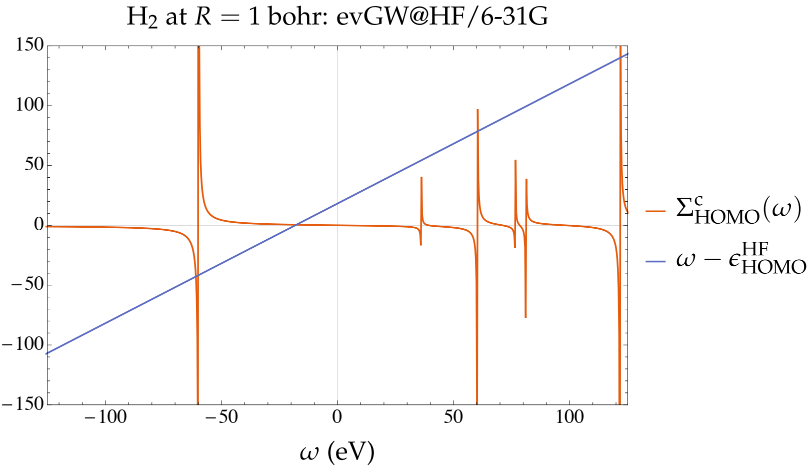


$$\boxed{Z_p(\omega) = \left[1 - \frac{\partial \operatorname{Re}[\Sigma_p^{\mathrm{c}}(\omega)]}{\partial \omega}\right]^{-1}}$$

Glitch in molecular systems: evGW@H_2

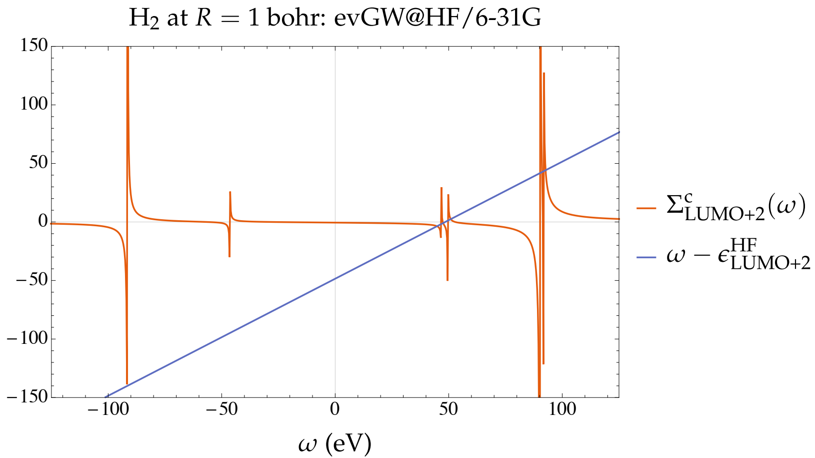


Multiple solutions of the quasiparticle equation



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

Multiple solutions of the quasiparticle equation



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

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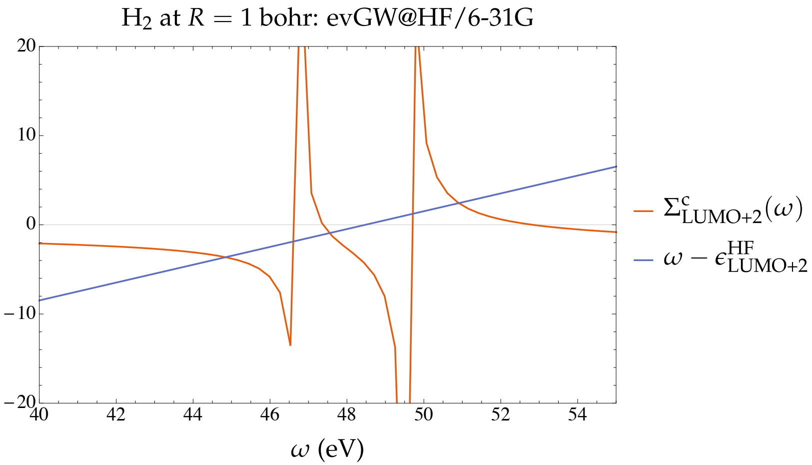
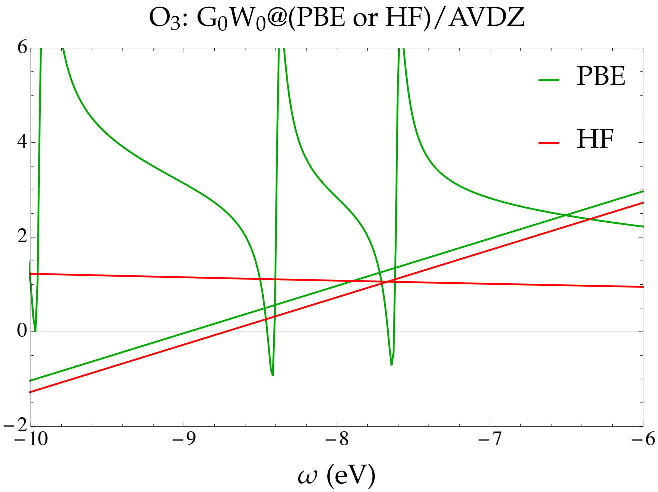


$$\boxed{\Sigma_p^{c}(\omega) = 2 \sum_{ix} \frac{[pi|x]^2}{\omega - \epsilon_i + \Omega_x - i\eta} + 2 \sum_{ax} \frac{[pa|x]^2}{\omega - \epsilon_a - \Omega_x + i\eta}}$$

Problem with HOMO



MolGW: F. Bruneval (http://www.molgw.org)
van Setten et al. JCTC 11 (2015) 5665

Concluding remarks

Take-home messages

- happens in many other cases (HeH^+, LiF, etc)
- 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 total energies, as well as 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...

useful papers for chemists

- 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. 86 (2012) 081102
- Review: Reining, WIREs Comput Mol Sci 2017, e1344. doi: 10.1002/wcms.1344; Onida et al. Rev. Mod. Phys. 74 (2002) 601.
- GW100: Data set of 100 molecules. van Setten et al. JCTC 11 (2015) 5665

qsGW

qsGW subroutine

procedure PARTIALLY SELF-CONSISTENT QSGW
Perform HF calculation to get $\boldsymbol{\epsilon}^{\text{HF}}$ and $\boldsymbol{c}^{\text{HF}}$
Set $\boldsymbol{\epsilon}^{\text{G}_{-1}\text{W}_{-1}} = \boldsymbol{\epsilon}^{\text{HF}}$, $\boldsymbol{c}^{\text{G}_{-1}\text{W}_{-1}} = \boldsymbol{c}^{\text{HF}}$ and $n = 0$
while $\max|\boldsymbol{\Delta}| < \tau$ **do**
Form $\boldsymbol{\Sigma}^{\text{c}}(\omega)$ and symmetrize it: $\boldsymbol{\Sigma}^{\text{c}}(\omega) \leftarrow (\boldsymbol{\Sigma}^{\text{c}}(\omega)^\dagger + \boldsymbol{\Sigma}^{\text{c}}(\omega))/2$
Form $\boldsymbol{F}(\omega) = \boldsymbol{F}^{\text{HF}} + \boldsymbol{\Sigma}^{\text{c}}(\omega)$
Diagonalize $\boldsymbol{F}(\boldsymbol{\epsilon}^{\text{G}_{n-1}\text{W}_{n-1}})$ to get $\boldsymbol{\epsilon}^{\text{G}_n\text{W}_n}$ and $\boldsymbol{c}^{\text{G}_n\text{W}_n}$
$\boldsymbol{\Delta} = \boldsymbol{\epsilon}^{\text{G}_n\text{W}_n} - \boldsymbol{\epsilon}^{\text{G}_{n-1}\text{W}_{n-1}}$
$n \leftarrow n + 1$
end while
if BSE **then**
Compute BSE excitations energies
end if
end procedure

BSE

Bethe-Salpeter equation

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

$$(\boldsymbol{A} - \boldsymbol{B})^{1/2} (\boldsymbol{A} + \boldsymbol{B}) (\boldsymbol{A} - \boldsymbol{B})^{1/2} \boldsymbol{Z} = \boldsymbol{\Omega}^2 \boldsymbol{Z},$$

$$\boldsymbol{X} + \boldsymbol{Y} = \boldsymbol{\Omega}^{-1/2} (\boldsymbol{A} - \boldsymbol{B})^{1/2} \boldsymbol{Z}.$$

$$A_{ia,jb}^{\text{BSE}} = A_{ia,jb}^{\text{RPA}} - (ij|ab) + 4 \sum_x \frac{[ij|x][ab|x]}{\Omega_x}$$

$$B_{ia,jb}^{\text{BSE}} = B_{ia,jb}^{\text{RPA}} - (ib|aj) + 4 \sum_x \frac{[ib|x][aj|x]}{\Omega_x}$$

Correlation energy

RPA correlation energy or Klein functional

$$E_{\text{c}}^{\text{RPA}} = -\sum_{p} \left(A_{pp}^{\text{RPA}} - \Omega_p \right)$$

Galitskii-Migdal functional

$$E_{\text{c}}^{\text{GM}} = \frac{-i}{2} \sum_{pq}^{\infty} \int \frac{d\omega}{2\pi} \Sigma_{pq}^{\text{c}}(\omega) G_{pq}(\omega) e^{i\omega\eta}$$