Unphysical Discontinuities in GW Methods

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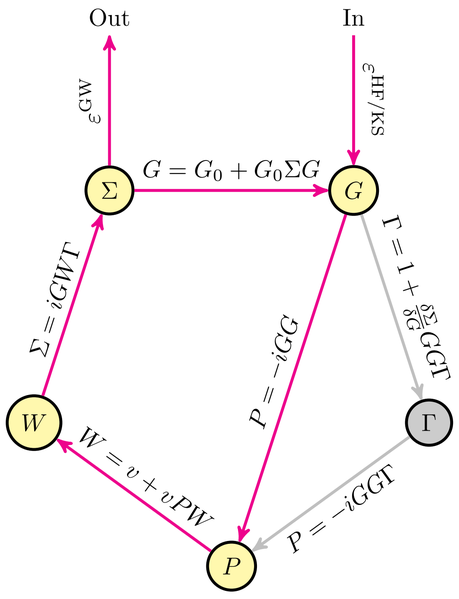
Motivations [2]

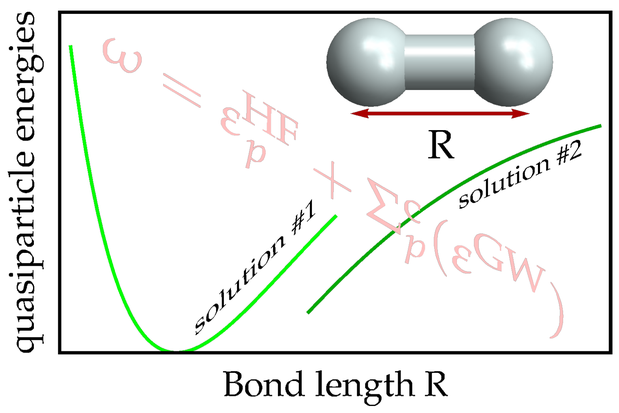
The purpose of this poster is to study **unphysical irregularities and discontinuities in some key experimentally measurable quantities** (IP, EA, HOMO-LUMO gap, excitation energies, etc) computed within the **GW approximation of many-body perturbation theory** applied to molecular systems.



Hedin's pentagon [1]

Methods [3, 4, 5]

- **G_0W_0**
  Perturbative GW or one-shot GW
- **evGW**
  Eigenvalues only GW
  Self-consistent on orbitals energies only
- **qsGW**
  Quasiparticule self-consistent GW
  Self consistent on both molecular orbitals and their energies



Quasiparticle equation

$$\boxed{\omega = \epsilon_p^{\mathrm{HF}} + \Sigma_p^{\mathrm{c}}(\omega)}$$

In practice,

- **G_0W_0: linearized quasiparticle equation**

$$\epsilon_p^{\mathrm{QP}} = \epsilon_p^{\mathrm{HF}} + Z_p(\epsilon_p^{\mathrm{HF}})\Sigma_p^{\mathrm{c}}(\epsilon_p^{\mathrm{HF}})$$

- **evGW: self-consistent process**

$$\epsilon_p^{\mathrm{QP}} \leftarrow \epsilon_p^{\mathrm{HF}} + \Sigma_p^{\mathrm{c}}(\epsilon_p^{\mathrm{QP}})$$

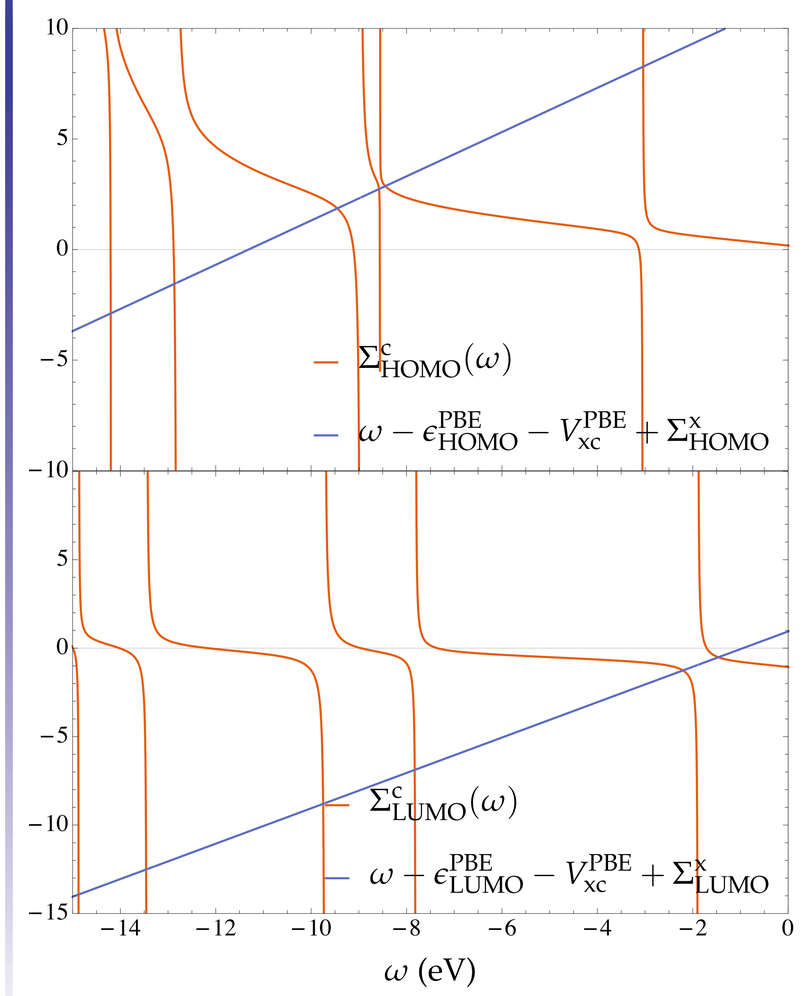
Self-energy and renormalization factor

Correlation part of the self-energy: $\Sigma_p^{\mathrm{c}}(\omega) = \Sigma_p^{\mathrm{h}}(\omega) + \Sigma_p^{\mathrm{p}}(\omega)$

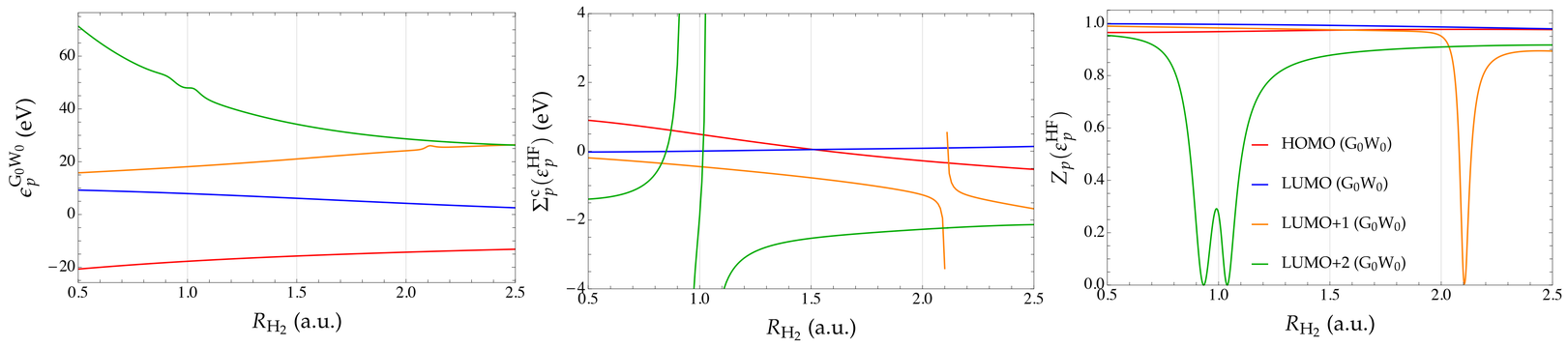
$$\Sigma_p^{\mathrm{h}}(\omega) = 2\sum_i^{\mathrm{occ}}\sum_x \frac{[pi|x]^2}{\omega - \epsilon_i + \Omega_x - i\eta} \qquad \Sigma_p^{\mathrm{p}}(\omega) = 2\sum_a^{\mathrm{virt}}\sum_x \frac{[pa|x]^2}{\omega - \epsilon_a - \Omega_x + i\eta}$$

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

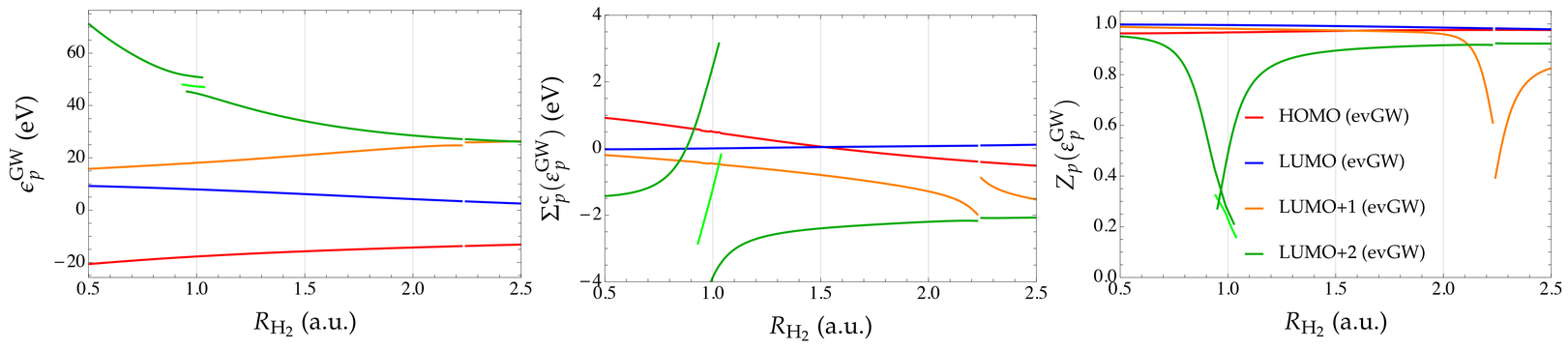
BeO at G_0W_0@PBE/cc-pVDZ



H_2 scan at G_0W_0@HF/6-31G level



H_2 scan at evGW@HF/6-31G level



HOMO-LUMO GAP

$$\epsilon_{\mathrm{HOMO}} - \Omega_0 < \omega < \epsilon_{\mathrm{LUMO}} + \Omega_0$$

$$\Omega_0 \simeq E_{\mathrm{gap}} \quad \text{and} \quad E_{\mathrm{F}} = \epsilon_{\mathrm{LUMO}} - \epsilon_{\mathrm{HOMO}}$$

$$\boxed{E_{\mathrm{F}} - \frac{3}{2}E_{\mathrm{gap}} < \omega < E_{\mathrm{F}} + \frac{3}{2}E_{\mathrm{gap}}}$$

Conclusion

We have evidenced that one can hit **multiple solution issues** within G_0W_0 and evGW due to the **location of the quasiparticle solution near poles of the self-energy**. Within linearized G_0W_0, this implies **irregularities in key experimentally-measurable quantities** of simple diatomics, while, at the partially self-consistent evGW level, **discontinues arise**.

Future Research

- Exploring different routes in order to remove these unphysical features (Padé resummation, regularization techniques, etc)
- We believe that such discontinuities would not exist within a fully self-consistent scheme

References

[1] L. Hedin, *Phys. Rev.*, **139** (1965) A796.

[2] M. Veril, P. Romaniello, J. A. Berger, and P. F. Loos, *J. Chem. Theory Comput.*, **14** (2018) doi:10.1021/acs.jctc.8b00745.

[3] M. J. van Setten, et al. *J. Chem. Theory Comput.*, **11** (2015) 5665–5687.

[4] Fabien Bruneval, et al. *Comput. Phys. Commun.*, **208** (2016) 149–161,

[5] P. F. Loos, P. Romaniello, and J. A. Berger. *J. Chem. Theory Comput.*, **14** (2018) 3071–3082.

Acknowlegments

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