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Laboratoire de Chimie et Physique Quantiques

The elephant in the room of Green's function methods

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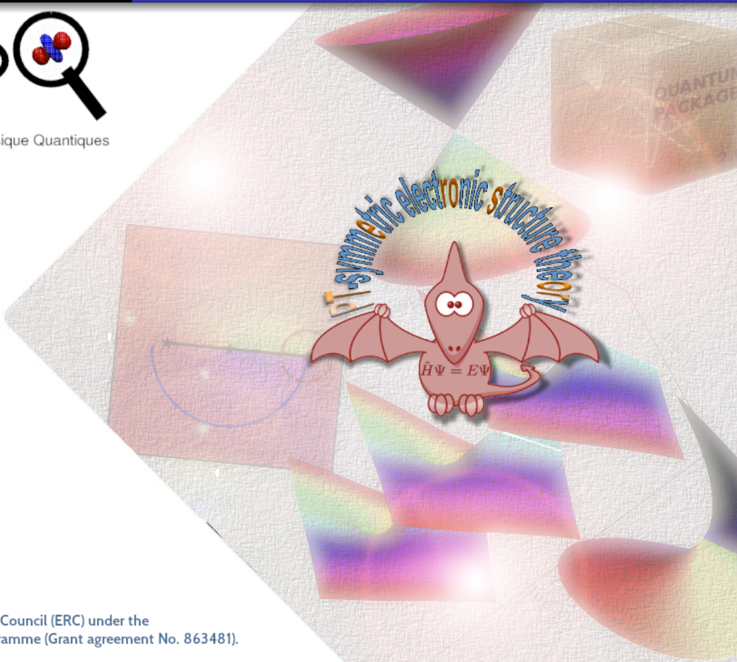
https://lcpq.github.io/pterosor



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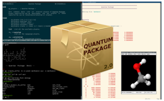
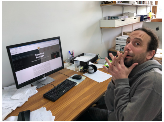
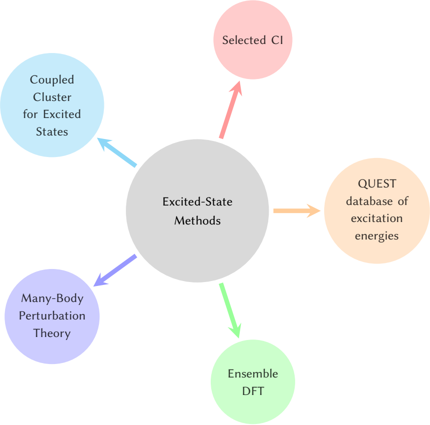
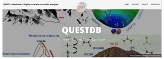
General overview of our research group

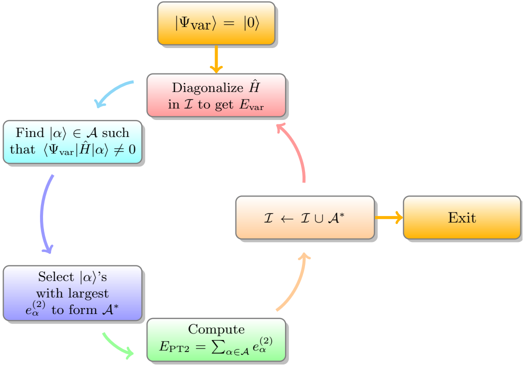






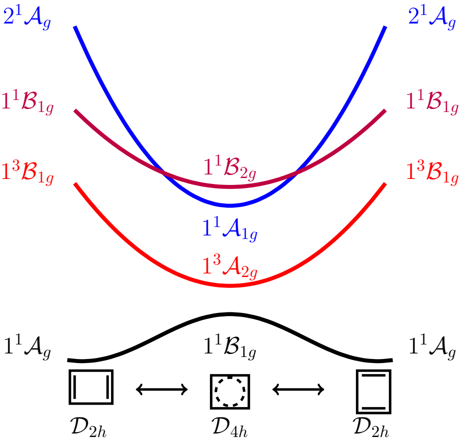


PA-5: Selected CI for dipole moments and oscillator strengths



Yann Damour

"Quantum Package 2.0: An Open-Source Determinant-Driven Suite of Programs",
Garniron et al., JCTC 15 (2019) 3591



Enzo Monino

Monino et al. JPCA (submitted) arXiv:2204.05098.

		$+\bar{e}$	$+2\bar{e}$	$\dots$	$+m\bar{e}$
	(0,0)	(1,0)	(2,0)	$\dots$	(m,0)
$-\bar{e}$	(0,1)	(1,1)	(2,1)	$\dots$	(m,1)
$-2\bar{e}$	(0,2)	(1,2)	(2,2)	$\dots$	(m,2)
$\vdots$	$\vdots$	$\vdots$	$\vdots$	$\ddots$	$\vdots$
$-n\bar{e}$	(0,n)	(1,n)	(2,n)	$\dots$	(m,n)


Raul Quintero

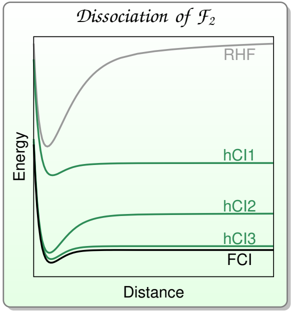
Hierarchy configuration interaction (hCI)

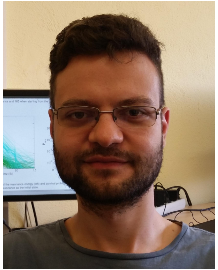
Excitation degree e

Seniority number s

Hierarchy parameter $h = \frac{e+s/2}{2}$

e/s	0	2	4	6
0	HF			
1		hCI1		
2		hCI1.5	hCI2	
3			hCI2.5	hCI3
4				
5				
6				





Fábris Kossoski

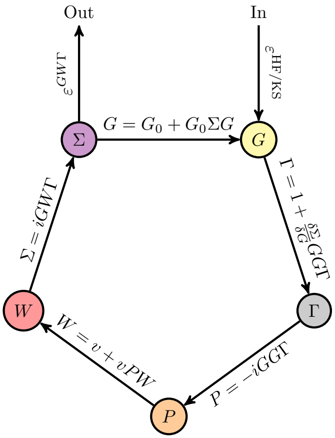
Kossoski, Damour & Loos, JPCL 13 (2022) 4342.

One-body Green's function in the quasiparticle approximation

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

What can we calculate with Green's function methods?

- Ionization potentials (IPs) given by occupied MO energies $\quad \text{IP} = -\epsilon_{\text{HOMO}}$
- Electron affinities (EAs) given by virtual MO energies $\quad \text{EA} = -\epsilon_{\text{LUMO}}$
- Fundamental (HOMO-LUMO) gap (or band gap in solids) $\quad E_{\text{g}}^{\text{fund}} = \text{IP} - \text{EA}$
- Correlation and total energies



Hedin, Phys Rev 139 (1965) A796

Hedin's equations

$$\underbrace{G(12)}_{\text{Green's function}} = G_0(12) + \int G_0(13)\Sigma(34)G(42)d(34)$$

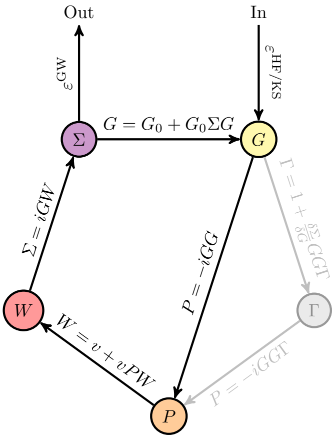
$$\underbrace{\Gamma(123)}_{\text{vertex}} = \delta(12)\delta(13) + \int \frac{\delta\Sigma(12)}{\delta G(45)} G(46)G(75)\Gamma(673)d(4567)$$

$$\underbrace{P(12)}_{\text{polarizability}} = -i\int G(13)\Gamma(324)G(41)d(34)$$

$$\underbrace{W(12)}_{\text{screening}} = v(12) + \int v(13)P(34)W(42)d(34)$$

$$\underbrace{\Sigma(12)}_{\text{self-energy}} = i\int G(13)W(14)\Gamma(324)d(34)$$

Hedin's ~~pentagon~~ square



Hedin, Phys Rev 139 (1965) A796

The GW approximation

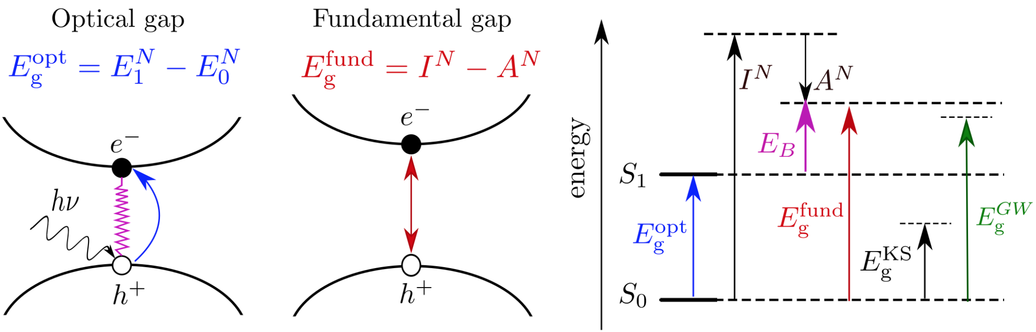
$$\underbrace{G(12)}_{\text{Green's function}} = G_0(12) + \int G_0(13)\Sigma(34)G(42)d(34)$$

$$\underbrace{\Gamma(123)}_{\text{vertex}} = \delta(12)\delta(13) + \cancel{\int \frac{\delta\Sigma(12)}{\delta G(45)} G(46)G(75)\Gamma(673)d(4567)}$$

$$\underbrace{P(12)}_{\text{polarizability}} = -i\cancel{\int} G(12)\cancel{\Gamma(324)}G(21)\cancel{d(34)} = -iG(12)G(21)$$

$$\underbrace{W(12)}_{\text{screening}} = v(12) + \int v(13)P(34)W(42)d(34)$$

$$\underbrace{\Sigma(12)}_{\text{self-energy}} = i\cancel{\int} G(12)W(12)\cancel{\Gamma(324)d(34)} = iG(12)W(12)$$



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

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

Blase et al. JPCL 11 (2020) 7371; Loos & Blase, JCP 153 (2020) 114120.

- Dyson equation

$$[G(\boldsymbol{r}_1, \boldsymbol{r}_2; \omega)]^{-1} = \underbrace{[G_{\text{HF}}(\boldsymbol{r}_1, \boldsymbol{r}_2; \omega)]^{-1}}_{\text{HF Green's function}} + \underbrace{\Sigma^{\text{c}}(\boldsymbol{r}_1, \boldsymbol{r}_2; \omega)}_{\text{correlation part}}$$

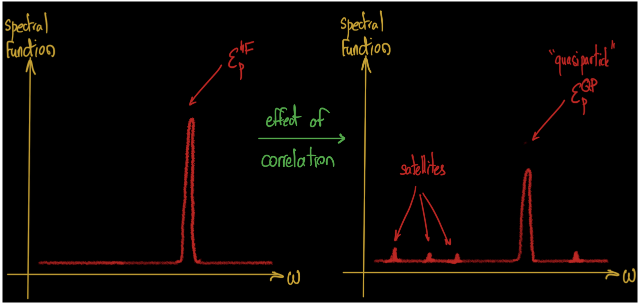
- Non-linear quasiparticle (QP) equation

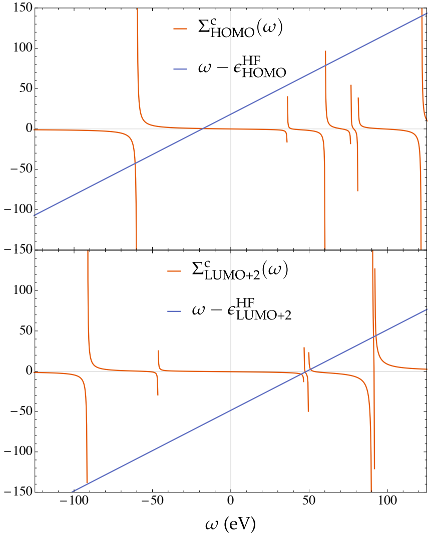
$$\boxed{\epsilon_p^{\text{HF}} + \Sigma_p^{\text{c}}(\omega) - \omega = 0} \quad \Rightarrow \quad \epsilon_{p,s}^{GW} \quad (s \text{ numbers the solutions})$$

- Spectral weight or renormalization factor

$$0 \le Z_{p,s} = \frac{1}{1 - \left. \frac{\partial \Sigma_p^{\text{c}}(\omega)}{\partial \omega} \right|_{\omega = \epsilon_{p,s}^{GW}}} \le 1$$

Solutions of the non-linear QP equation: G_0W_0@HF/6-31G for H_2 at $R = 1$ bohr





- mol*GW*: Bruneval et al. Comp. Phys. Comm. 208 (2016) 149
- Fiesta: Blase et al. Chem. Soc. Rev. 47 (2018) 1022
- PySCF: Zhu & Chan, JCTC 17 (2021) 727
- Turbomole: van Setten et al. JCTC 9 (2013) 232; Kaplan et al. JCTC 12 (2016) 2528
- *GW*100: IPs for a set of 100 molecules. van Setten et al. JCTC 11 (2015) 5665 (http://gw100.wordpress.com)

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Check for updates

The GW Miracle in Many-Body Perturbation Theory for the Ionization Potential of Molecules

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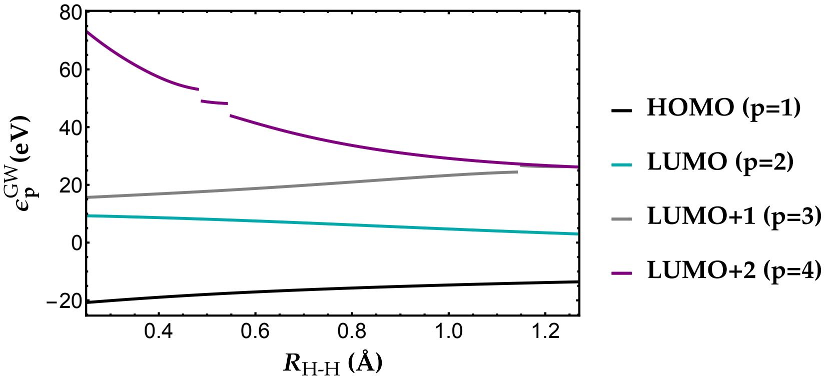
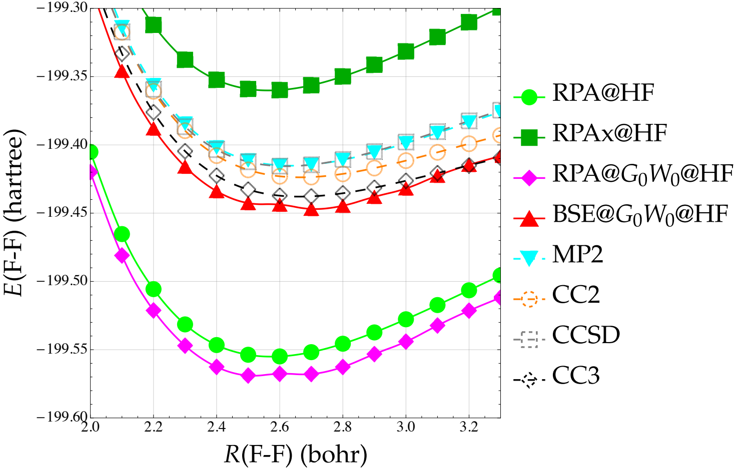
QP energies of H_2 at the G_0W_0@HF/6-31G level with $\eta = 0$



Enzo Monino

Loos et al. JCTC 14 (2018) 3071
Véril et al. JCTC 14 (2018) 5220
Monino & Loos, JCP 156 (2022) 231101

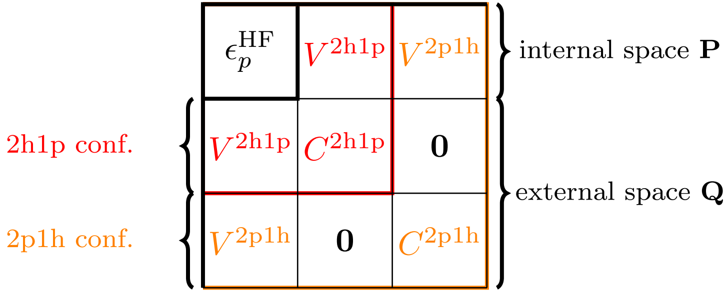
Total energies: F_2 at the G_0W_0@HF/cc-pVQZ level



Loos et al. JPCL 11 (2020) 3536; Berger et al. JCTC 17 (2021) 191

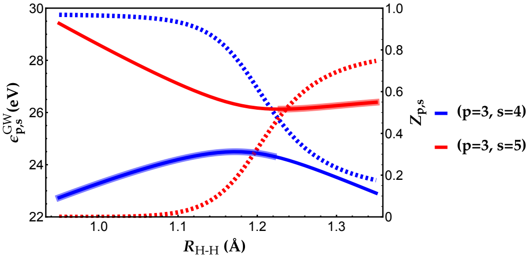
A linear version of GW

$$
\boldsymbol{H}^{(p)} \cdot \boldsymbol{c}^{(p,s)} = \epsilon_{p,s}^{GW} \boldsymbol{c}^{(p,s)} \quad \text{with} \quad \boldsymbol{H}^{(p)} = \begin{pmatrix} \epsilon_p^{\text{HF}} & \boldsymbol{V}_p^{\text{2h1p}} & \boldsymbol{V}_p^{\text{2p1h}} \\ (\boldsymbol{V}_p^{\text{2h1p}})^{\mathsf{T}} & \boldsymbol{C}^{\text{2h1p}} & \boldsymbol{0} \\ (\boldsymbol{V}_p^{\text{2p1h}})^{\mathsf{T}} & \boldsymbol{0} & \boldsymbol{C}^{\text{2p1h}} \end{pmatrix} \quad \text{and} \quad Z_{p,s} = \left[c_1^{(p,s)} \right]^2
$$



Bintrim & Berkelbach, JCP 154 (2021) 041101; Monino & Loos, JCP 156 (2022) 231101.

QP and satellite energies of H_2 at the G_0W_0@HF/6-31G level



The reference 1p determinant $|1\bar{1}3\rangle$ and the external 2p1h determinant $|12\bar{2}\rangle$ are involved!

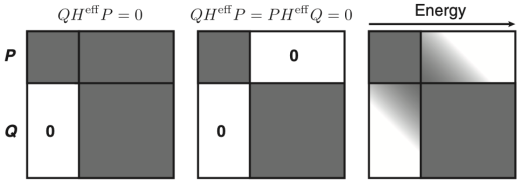
Intruder-state problem $\Leftrightarrow$ a determinant in **Q** becomes near-degenerate with a determinant in **P**

$\Rightarrow$ appearance of small denominators

$\Rightarrow$ numerical issues!

How to avoid intruder states? $\Rightarrow$ do not enforce $QH^{\text{eff}}P = 0$

$\Leftrightarrow$ near-degenerate determinants are not decoupled



$\Leftarrow$ Continuous similarity renormalization group (SRG) transformation

Glazek & Wilson, PRD 48 (1993) 5863; *ibid* 49, 4214 (1994); Wegner, Ann. Phys. 506 (1994) 77

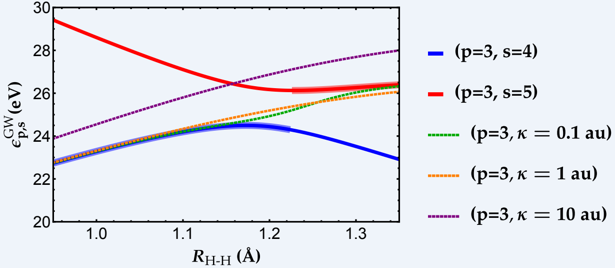
Regularized GW self-energy & quasiparticle equation

$$\epsilon_p^{\text{HF}} + \tilde{\Sigma}_p^{\text{c}}(\omega;\kappa) - \omega = 0$$

with

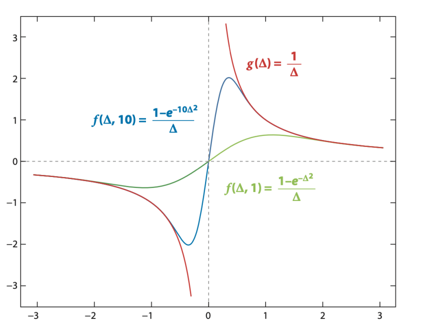
$$\lim_{\kappa\to 0} \tilde{\Sigma}_p^{\text{c}}(\omega;\kappa) = \Sigma_p^{\text{c}}(\omega)$$

$$f_\kappa(\Delta) = (1 - e^{-2\Delta^2/\kappa^2})/\Delta$$



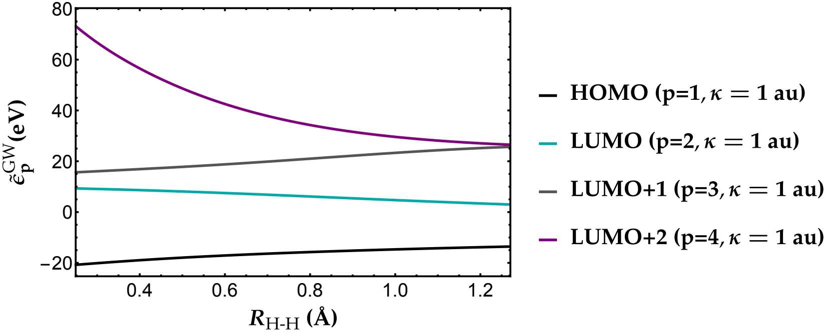
SRG-based energy-dependent regularizer

$$f_\kappa(\Delta) = \frac{1 - e^{-2\Delta^2/\kappa^2}}{\Delta}$$

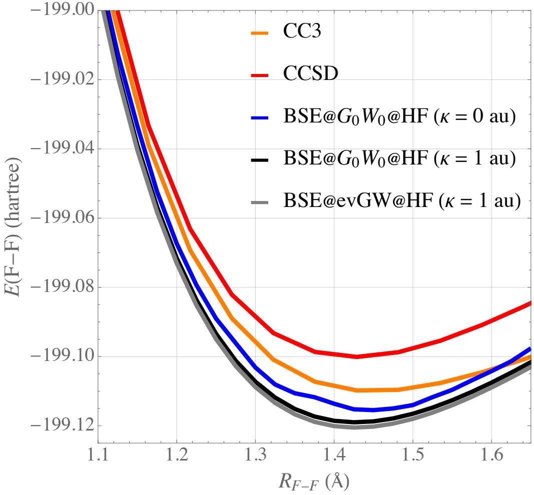


Evangelista, JCP 140 (2014) 124114

QP and satellite energies of H_2 at the G_0W_0@HF/6-31G level



Total energy of F_2 at the G_0W_0@HF/cc-pVDZ level



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- Yann Damour
- Raul Quintero
- Enzo Monino

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