European Research Council
Established by the European Commission

Laboratoire de Chimie et Physique Quantiques

Unphysical Discontinuities, Intruder States and Regularization in *GW* Methods

Enzo Monino & Pierre-François (Titou) Loos

Discussion meeting on correlation — April 28th, 2022

Laboratoire de Chimie et Physique Quantiques, IRSAMC, UPS/CNRS, Toulouse
https://lcpq.github.io/pterosor

PT-symmetric electronic structure theory

PTEROSOR has received funding from the European Research Council (ERC) under the European Union's Horizon 2020 research and innovation programme (Grant agreement No. 863481).

Preprint arXiv:2202.11589

Physics > Chemical Physics

[Submitted on 23 Feb 2022 (v1), last revised 23 Mar 2022 (this version, v3)]

Unphysical Discontinuities, Intruder States and Regularization in GW Methods

Enzo Monino, Pierre-François Loos

By recasting the non-linear frequency-dependent GW quasiparticle equation into a linear eigenvalue problem, we explain the appearance of multiple solutions and unphysical discontinuities in various physical quantities computed within the GW approximation. Considering the GW self-energy as an effective Hamiltonian, it is shown that these issues are key signatures of strong correlation in the $(N \pm 1)$-electron states and can be directly related to the intruder state problem. A simple and efficient regularization procedure inspired by the similarity renormalization group is proposed to avoid such issues and speed up convergence of partially self-consistent GW calculations.

Comments: 7 pages, 5 figures

Subjects: **Chemical Physics (physics.chem-ph)**; Materials Science (cond-mat.mtrl-sci); Strongly Correlated Electrons (cond-mat.str-el); Nuclear Theory (nucl-th)

Cite as: arXiv:2202.11589 **[physics.chem-ph]**

(or arXiv:2202.11589v3 **[physics.chem-ph]** for this version)

https://doi.org/10.48550/arXiv.2202.11589

Submission history

From: Pierre-François Loos Dr [view email]

[v1] Wed, 23 Feb 2022 16:01:48 UTC (344 KB)

[v2] Thu, 24 Feb 2022 14:54:24 UTC (456 KB)

[v3] Wed, 23 Mar 2022 11:02:46 UTC (457 KB)

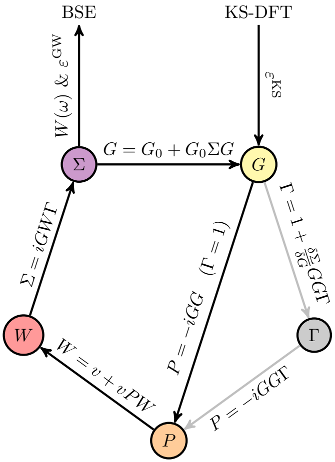
Notations

- We consider closed-shell molecules (2 opposite-spin electrons per orbital)
- ... with finite (atom-centered) gaussian basis sets

- Number of occupied orbitals O
- Number of vacant orbitals V
- Total number of orbitals $N = O + V$

- $\phi_p(\boldsymbol{r})$ is a (real) spatial orbital
- i, j, k, l are occupied orbitals
- a, b, c, d are vacant orbitals
- p, q, r are arbitrary (occupied or vacant) orbitals

- m indexes the OV single excitations ($i \to a$)



Hedin, Phys Rev 139 (1965) A796

What can you calculate with *GW*?

- Ionization potentials (IPs) given by occupied MO energies
- Electron affinities (EAs) given by virtual MO energies
- Fundamental (HOMO-LUMO) gap (or band gap in solids)
- Correlation and total energies

One-body Green's function in the quasiparticle approximation

$$G(\mathbf{r}_1, \mathbf{r}_2; \omega) = \underbrace{\sum_i \frac{\phi_i(\mathbf{r}_1)\phi_i(\mathbf{r}_2)}{\omega - \epsilon_i - i\eta}}_{\text{removal part = IPs}} + \underbrace{\sum_a \frac{\phi_a(\mathbf{r}_1)\phi_a(\mathbf{r}_2)}{\omega - \epsilon_a + i\eta}}_{\text{addition part = EAs}} \tag{1}$$

Polarizability

$$P(\mathbf{r}_1, \mathbf{r}_2; \omega) = -\frac{i}{\pi} \int G(\mathbf{r}_1, \mathbf{r}_2; \omega + \omega') G(\mathbf{r}_1, \mathbf{r}_2; \omega') d\omega' \tag{2}$$

Dielectric function and dynamically-screened Coulomb potential

$$\epsilon(\mathbf{r}_1, \mathbf{r}_2; \omega) = \delta(\mathbf{r}_1 - \mathbf{r}_2) - \int \frac{P(\mathbf{r}_1, \mathbf{r}_3; \omega)}{|\mathbf{r}_2 - \mathbf{r}_3|} d\mathbf{r}_3 \tag{3}$$

$$W(\mathbf{r}_1, \mathbf{r}_2; \omega) = \int \frac{\epsilon^{-1}(\mathbf{r}_1, \mathbf{r}_3; \omega)}{|\mathbf{r}_2 - \mathbf{r}_3|} d\mathbf{r}_3 \tag{4}$$

Spectral representation of W

$$
\begin{aligned}
W_{ij,ab}(\omega) &= \iint \phi_i(\mathbf{r}_1)\phi_j(\mathbf{r}_1) W(\mathbf{r}_1,\mathbf{r}_2;\omega)\phi_a(\mathbf{r}_2)\phi_b(\mathbf{r}_2) d\mathbf{r}_1 d\mathbf{r}_2 \\
&= \underbrace{(ij|ab)}_{\text{(static) exchange part}} \quad \underbrace{+ 2\sum_m (ij|m)(ab|m)\left[\frac{1}{\omega - \Omega_m^{\text{RPA}} + i\eta} - \frac{1}{\omega + \Omega_m^{\text{RPA}} - i\eta}\right]}_{\text{(dynamical) correlation part } W^{\text{c}}_{pq,rs}(\omega)}
\end{aligned}
\tag{5}
$$

Electron repulsion integrals (ERIs)

$$
(ij|ab) = \iint \frac{\phi_i(\mathbf{r}_1)\phi_j(\mathbf{r}_1)\phi_a(\mathbf{r}_2)\phi_b(\mathbf{r}_2)}{|\mathbf{r}_1 - \mathbf{r}_2|} d\mathbf{r}_1 d\mathbf{r}_2 \tag{6}
$$

Screened ERIs

$$
(pq|m) = \sum_{ia} (pq|ia)(\boldsymbol{X}_m^{\text{RPA}} + \boldsymbol{Y}_m^{\text{RPA}})_{ia} \tag{7}
$$

Direct (ph-)RPA calculation (pseudo-hermitian linear problem)

$$\begin{pmatrix} \boldsymbol{A}^{\text{RPA}} & \boldsymbol{B}^{\text{RPA}} \\ -\boldsymbol{B}^{\text{RPA}} & -\boldsymbol{A}^{\text{RPA}} \end{pmatrix} \cdot \begin{pmatrix} \boldsymbol{X}_m^{\text{RPA}} \\ \boldsymbol{Y}_m^{\text{RPA}} \end{pmatrix} = \Omega_m^{\text{RPA}} \begin{pmatrix} \boldsymbol{X}_m^{\text{RPA}} \\ \boldsymbol{Y}_m^{\text{RPA}} \end{pmatrix} \tag{8}$$

$$\text{For singlet states:} \quad A_{ia,jb}^{\text{RPA}} = \delta_{ij}\delta_{ab}(\epsilon_a^{\text{HF}} - \epsilon_i^{\text{HF}}) + 2(ia|bj) \qquad B_{ia,jb}^{\text{RPA}} = 2(ia|jb) \tag{9}$$

Non-hermitian to hermitian

$$(\boldsymbol{A} - \boldsymbol{B})^{1/2} \cdot (\boldsymbol{A} + \boldsymbol{B}) \cdot (\boldsymbol{A} - \boldsymbol{B})^{1/2} \cdot \boldsymbol{Z}_m = \Omega_m^2 \boldsymbol{Z}_m \tag{10}$$

$$(\boldsymbol{X}_m + \boldsymbol{Y}_m) = \Omega_m^{-1/2} (\boldsymbol{A} - \boldsymbol{B})^{+1/2} \cdot \boldsymbol{Z}_m \tag{11}$$

$$(\boldsymbol{X}_m - \boldsymbol{Y}_m) = \Omega_m^{+1/2} (\boldsymbol{A} - \boldsymbol{B})^{-1/2} \cdot \boldsymbol{Z}_m \tag{12}$$

Tamm-Dancoff approximation (TDA)

$$\boldsymbol{B} = \boldsymbol{0} \quad \Rightarrow \quad \boldsymbol{A} \cdot \boldsymbol{X}_m = \Omega_m^{\text{TDA}} \boldsymbol{X}_m \tag{13}$$

GW self-energy

$$\Sigma(\mathbf{r}_1, \mathbf{r}_2; \omega) = \frac{i}{2\pi} \int G(\mathbf{r}_1, \mathbf{r}_2; \omega + \omega') W(\mathbf{r}_1, \mathbf{r}_2; \omega') e^{i\eta\omega'} d\omega' \tag{14}$$

Correlation part of the (dynamical) self-energy

$$\Sigma^{\text{c}}_{pq}(\omega) = 2 \sum_{im} \frac{(pi|m)(qi|m)}{\omega - \epsilon_i^{\text{HF}} + \Omega_m^{\text{RPA}} - i\eta} + 2 \sum_{am} \frac{(pa|m)(qa|m)}{\omega - \epsilon_a^{\text{HF}} - \Omega_m^{\text{RPA}} + i\eta} \tag{15}$$

Diagonal part of the *GW* self-energy

$$\Sigma^{\text{c}}_{p}(\omega) \equiv \Sigma^{\text{c}}_{pp}(\omega) = 2 \sum_{im} \frac{(pi|m)^2}{\omega - \epsilon_i^{\text{HF}} + \Omega_m^{\text{RPA}} - i\eta} + 2 \sum_{am} \frac{(pa|m)^2}{\omega - \epsilon_a^{\text{HF}} - \Omega_m^{\text{RPA}} + i\eta} \tag{16}$$

Dyson equation

$$[G(\mathbf{r}_1, \mathbf{r}_2; \omega)]^{-1} = \underbrace{[G_{\text{HF}}(\mathbf{r}_1, \mathbf{r}_2; \omega)]^{-1}}_{\text{HF Green's function}} + \Sigma^{\text{c}}(\mathbf{r}_1, \mathbf{r}_2; \omega) \tag{17}$$

Non-linear quasiparticle (QP) equation for $G_0 W_0$

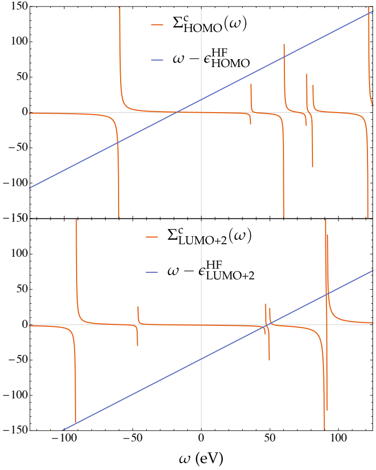
$$\boxed{\epsilon_p^{\text{HF}} + \Sigma_p^{\text{c}}(\omega) - \omega = 0} \quad \Rightarrow \quad \epsilon_{p,s}^{GW} \quad (s \text{ numbers the solutions}) \tag{18}$$

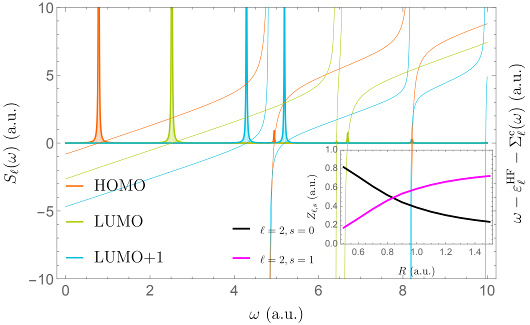
Spectral weight or renormalization factor

$$0 \leq Z_{p,s} = \left[1 - \left. \frac{\partial \Sigma_p^{\text{c}}(\omega)}{\partial \omega} \right|_{\omega = \epsilon_{p,s}^{GW}} \right]^{-1} \leq 1 \tag{19}$$

$$\text{Conservation rules:} \quad \sum_s Z_{p,s} = 1 \quad \text{and} \quad \sum_s Z_{p,s} \epsilon_{p,s}^{GW} = \epsilon_p^{\text{HF}} \tag{20}$$

Solutions of the non-linear QP equation: $G_0 W_0$@HF/6-31G for H_2 at $R = 1$ bohr

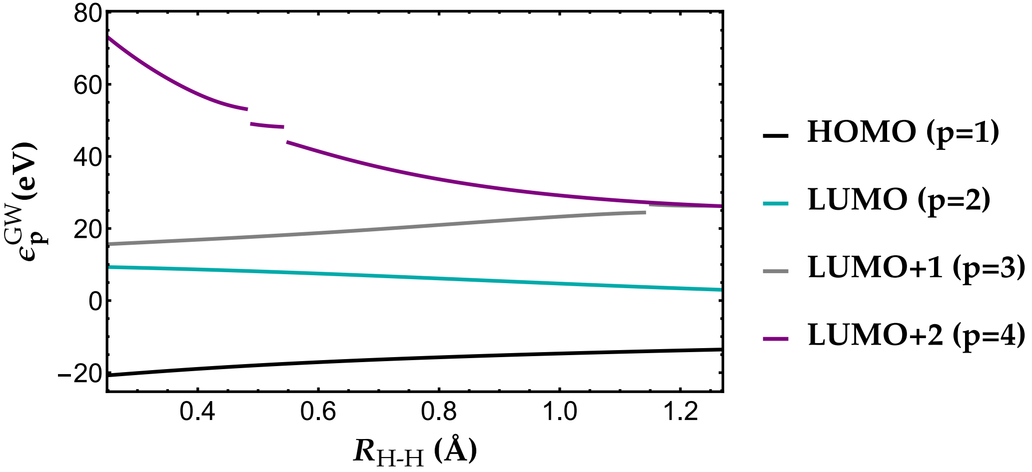




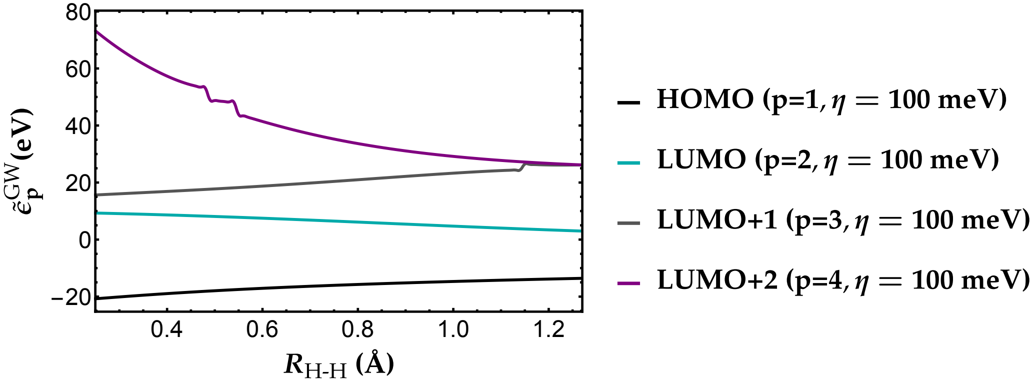
Loos et al, JCTC 14 (2018) 3071

Véril et al, JCTC 14 (2018) 5220

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



QP energies of H_2 at the G_0W_0@HF/6-31G level with $\eta = 100$ meV



A linear version of GW [Bintrim & Berkelbach, JCP 154 (2021) 041101]

$$\boldsymbol{H}^{(p)} \cdot \boldsymbol{c}^{(p,s)} = \epsilon_{p,s}^{GW} \boldsymbol{c}^{(p,s)} \quad \text{with} \quad \boldsymbol{H}^{(p)} = \begin{pmatrix} \epsilon_p^{\text{HF}} & \boldsymbol{V}_p^{\text{2h1p}} & \boldsymbol{V}_p^{\text{2p1h}} \\ (\boldsymbol{V}_p^{\text{2h1p}})^{\mathsf{T}} & \boldsymbol{C}^{\text{2h1p}} & \boldsymbol{0} \\ (\boldsymbol{V}_p^{\text{2p1h}})^{\mathsf{T}} & \boldsymbol{0} & \boldsymbol{C}^{\text{2p1h}} \end{pmatrix} \quad \text{and} \quad Z_{p,s} = \left[c_1^{(p,s)} \right]^2 \tag{21}$$

2h1p and 2p1h blocks

$$C_{ija,kcl}^{\text{2h1p}} = \left[\left(\epsilon_i^{\text{HF}} + \epsilon_j^{\text{HF}} - \epsilon_a^{\text{HF}} \right) \delta_{jl} \delta_{ac} - 2(ja|cl) \right] \delta_{ik} \qquad V_{p,klc}^{\text{2h1p}} = \sqrt{2}(pk|cl) \tag{22}$$

$$C_{iab,kcd}^{\text{2p1h}} = \left[\left(\epsilon_a^{\text{HF}} + \epsilon_b^{\text{HF}} - \epsilon_i^{\text{HF}} \right) \delta_{ik} \delta_{ac} + 2(ai|kc) \right] \delta_{bd} \qquad V_{p,kcd}^{\text{2p1h}} = \sqrt{2}(pd|kc) \tag{23}$$

Recovering the self-energy via downfolding

$$\Sigma_p^{\text{c}}(\omega) = \boldsymbol{V}_p^{\text{2h1p}} \cdot \left(\omega \mathbf{1} - \boldsymbol{C}^{\text{2h1p}} \right)^{-1} \cdot \left(\boldsymbol{V}_p^{\text{2h1p}} \right)^{\mathsf{T}} + \boldsymbol{V}_p^{\text{2p1h}} \cdot \left(\omega \mathbf{1} - \boldsymbol{C}^{\text{2p1h}} \right)^{-1} \cdot \left(\boldsymbol{V}_p^{\text{2p1h}} \right)^{\mathsf{T}} \tag{24}$$

Downfolding or dressing process [Romaniello et al, JCP 130 (2009) 044108]

$$\underbrace{\boldsymbol{H} \cdot \boldsymbol{c} = \omega\, \boldsymbol{c}}_{\text{A large linear system with } N \text{ solutions...}} \quad \Rightarrow \quad \begin{pmatrix} \overbrace{\boldsymbol{H}_1}^{N_1 \times N_1} & \boldsymbol{h}^\mathsf{T} \\ \boldsymbol{h} & \underbrace{\boldsymbol{H}_2}_{N_2 \times N_2} \end{pmatrix} \cdot \begin{pmatrix} \boldsymbol{c}_1 \\ \boldsymbol{c}_2 \end{pmatrix} = \omega \begin{pmatrix} \boldsymbol{c}_1 \\ \boldsymbol{c}_2 \end{pmatrix} \qquad N = N_1 + N_2 \tag{25}$$

$$\textbf{Row \#2:} \quad \boldsymbol{h} \cdot \boldsymbol{c}_1 + \boldsymbol{H}_2 \cdot \boldsymbol{c}_2 = \omega\, \boldsymbol{c}_2 \quad \Rightarrow \quad \boldsymbol{c}_2 = (\omega\, \boldsymbol{1} - \boldsymbol{H}_2)^{-1} \cdot \boldsymbol{h} \cdot \boldsymbol{c}_1 \tag{26}$$

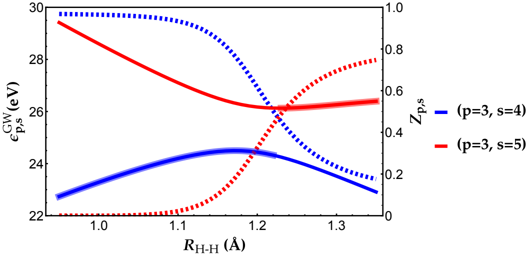
$$\textbf{Row \#1:} \quad \boldsymbol{H}_1 \cdot \boldsymbol{c}_1 + \boldsymbol{h}^\mathsf{T} \cdot \boldsymbol{c}_2 = \omega\, \boldsymbol{c}_1 \quad \Rightarrow \quad \underbrace{\tilde{\boldsymbol{H}}_1(\omega) \cdot \boldsymbol{c}_1 = \omega\, \boldsymbol{c}_1}_{\text{A smaller non-linear system with } N \text{ solutions...}} \tag{27}$$

$$\boxed{\underbrace{\tilde{\boldsymbol{H}}_1(\omega)}_{\text{Effective Hamitonian}} = \boldsymbol{H}_1 + \boldsymbol{h}^\mathsf{T} \cdot (\omega\, \boldsymbol{1} - \boldsymbol{H}_2)^{-1} \cdot \boldsymbol{h}} \tag{28}$$

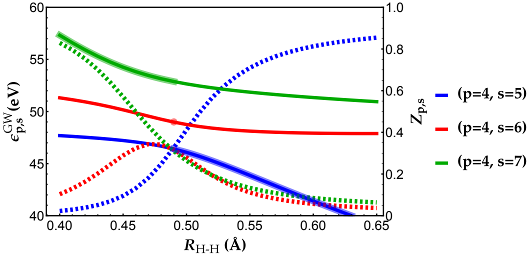
Static approx. (e.g. $\omega = 0$):

$$\underbrace{\tilde{\boldsymbol{H}}_1(\omega = 0)}_{\text{A smaller linear system with } N_1 \text{ solutions...}} = \boldsymbol{H}_1 - \underbrace{\boldsymbol{h}^\mathsf{T} \cdot \boldsymbol{H}_2^{-1} \cdot \boldsymbol{h}}_{\text{approximations possible...}} \tag{29}$$

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!



The reference 1p determinant $|1\bar{1}4\rangle$ and the external 2p1h determinants $|1\bar{2}3\rangle$ and $|12\bar{3}\rangle$ are involved!

Regularized *GW* self-energy

$$\tilde{\Sigma}_p^{\text{c}}(\omega;\eta) = \sum_{im} 2(pi|m)^2 f_\eta(\omega - \epsilon_i^{\text{HF}} + \Omega_m^{\text{RPA}}) + \sum_{am} 2(pa|m)^2 f_\eta(\omega - \epsilon_a^{\text{HF}} - \Omega_m^{\text{RPA}}) \quad (30)$$

Regularized quasiparticle equation

$$\epsilon_p^{\text{HF}} + \tilde{\Sigma}_p^{\text{c}}(\omega;\eta) - \omega = 0 \quad \text{with} \quad \lim_{\eta \to 0} \tilde{\Sigma}_p^{\text{c}}(\omega;\eta) = \Sigma_p^{\text{c}}(\omega) \quad (31)$$

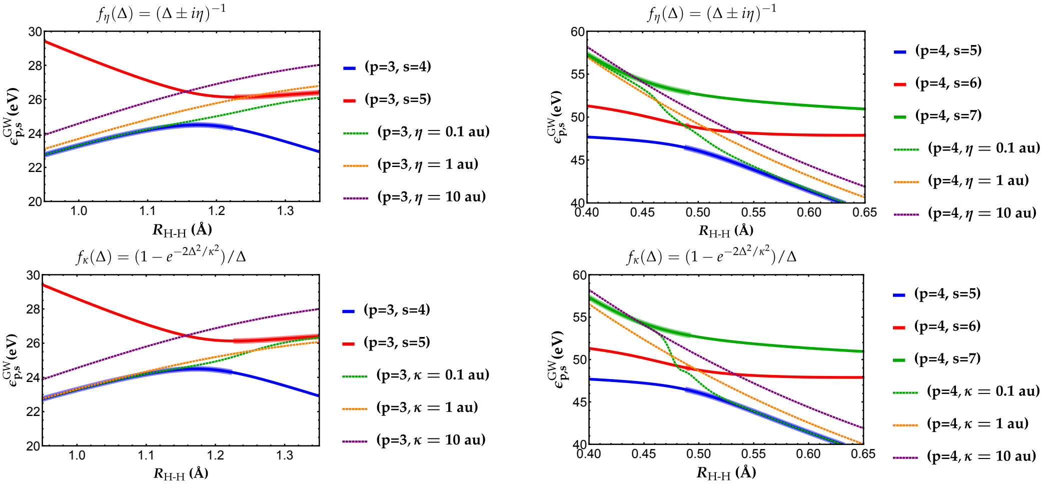
Conventional energy-independent regularizer

$$f_\eta(\Delta) = (\Delta \pm i\eta)^{-1} \quad (32)$$

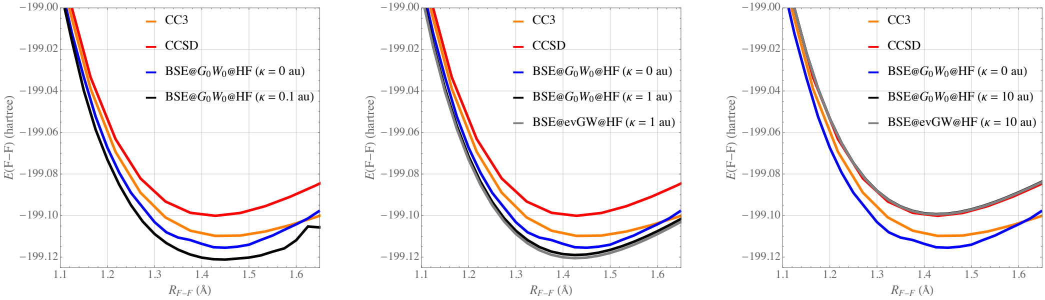
SRG-based energy-dependent regularizer [Evangelista, JCP 140 (2014) 124114]

$$f_\kappa(\Delta) = \frac{1 - e^{-2\Delta^2/\kappa^2}}{\Delta} \quad (33)$$

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



This is the end...

Thanks!

Linear *GW* with a two-determinant reference

$$\boldsymbol{H}^{(P,QIA)} = \begin{pmatrix} \epsilon_P^{\text{HF}} & V_{P,QIA} & \boldsymbol{V}_P^{\text{2h1p}} & \boldsymbol{V}_P^{\text{2p1h}} \\ V_{QIA,P} & C_{QIA,QIA} & \boldsymbol{C}_{QIA}^{\text{2h1p}} & \boldsymbol{C}_{QIA}^{\text{2p1h}} \\ (\boldsymbol{V}_P^{\text{2h1p}})^{\mathsf{T}} & (\boldsymbol{C}_{QIA}^{\text{2h1p}})^{\mathsf{T}} & \boldsymbol{C}^{\text{2h1p}} & \boldsymbol{0} \\ (\boldsymbol{V}_P^{\text{2p1h}})^{\mathsf{T}} & (\boldsymbol{C}_{QIA}^{\text{2p1h}})^{\mathsf{T}} & \boldsymbol{0} & \boldsymbol{C}^{\text{2p1h}} \end{pmatrix} \tag{34}$$

$$V_{P,QIA} = \sqrt{2}(PQ|IA) \tag{35}$$

$$C_{QIA,QIA} = \text{sgn}(\epsilon_Q^{\text{HF}} - \mu)\left[\left(\epsilon_Q^{\text{HF}} + \epsilon_A^{\text{HF}} - \epsilon_I^{\text{HF}}\right) + 2(IA|IA)\right] \tag{36}$$

$$C_{QIA,klc}^{\text{2h1p}} = -2(IA|cl)\delta_{Qk} \tag{37}$$

$$C_{QIA,klc}^{\text{2p1h}} = +2(IA|kc)\delta_{Qd} \tag{38}$$

Dynamical *GW* with a two-determinant reference

$$\boldsymbol{\Sigma}^{(P,QIA)}(\omega) = \begin{pmatrix} \epsilon_P^{\text{HF}} + \Sigma_P^{\text{c}}(\omega) & V_{P,QIA} + \Sigma_{P,QIA}^{\text{c}}(\omega) \\ V_{QIA,P} + \Sigma_{QIA,P}^{\text{c}}(\omega) & C_{QIA,QIA} + \Sigma_{QIA}^{\text{c}}(\omega) \end{pmatrix} \tag{39}$$

$$\Sigma_P^{\text{c}}(\omega) = \boldsymbol{V}_P^{\text{2h1p}} \cdot \left(\omega \mathbf{1} - \boldsymbol{C}^{\text{2h1p}}\right)^{-1} \cdot \left(\boldsymbol{V}_P^{\text{2h1p}}\right)^{\mathsf{T}} + \boldsymbol{V}_P^{\text{2p1h}} \cdot \left(\omega \mathbf{1} - \boldsymbol{C}^{\text{2p1h}}\right)^{-1} \cdot \left(\boldsymbol{V}_P^{\text{2p1h}}\right)^{\mathsf{T}} \tag{40}$$

$$\Sigma_{QIA}^{\text{c}}(\omega) = \boldsymbol{C}_{QIA}^{\text{2h1p}} \cdot \left(\omega \mathbf{1} - \boldsymbol{C}^{\text{2h1p}}\right)^{-1} \cdot \left(\boldsymbol{V}_{QIA}^{\text{2h1p}}\right)^{\mathsf{T}} + \boldsymbol{C}_{QIA}^{\text{2p1h}} \cdot \left(\omega \mathbf{1} - \boldsymbol{C}^{\text{2p1h}}\right)^{-1} \cdot \left(\boldsymbol{V}_{QIA}^{\text{2p1h}}\right)^{\mathsf{T}} \tag{41}$$

$$\Sigma_{P,QIA}^{\text{c}}(\omega) = \boldsymbol{V}_P^{\text{2h1p}} \cdot \left(\omega \mathbf{1} - \boldsymbol{C}^{\text{2h1p}}\right)^{-1} \cdot \left(\boldsymbol{V}_{QIA}^{\text{2h1p}}\right)^{\mathsf{T}} + \boldsymbol{V}_P^{\text{2p1h}} \cdot \left(\omega \mathbf{1} - \boldsymbol{C}^{\text{2p1h}}\right)^{-1} \cdot \left(\boldsymbol{V}_{QIA}^{\text{2p1h}}\right)^{\mathsf{T}} \tag{42}$$

$$\Sigma_{QIA,P}^{\text{c}}(\omega) = \boldsymbol{C}_{QIA}^{\text{2h1p}} \cdot \left(\omega \mathbf{1} - \boldsymbol{C}^{\text{2h1p}}\right)^{-1} \cdot \left(\boldsymbol{V}_P^{\text{2h1p}}\right)^{\mathsf{T}} + \boldsymbol{C}_{QIA}^{\text{2p1h}} \cdot \left(\omega \mathbf{1} - \boldsymbol{C}^{\text{2p1h}}\right)^{-1} \cdot \left(\boldsymbol{V}_P^{\text{2p1h}}\right)^{\mathsf{T}} \tag{43}$$

Static and dynamic Bethe–Salpeter equations in the *T*-matrix approximation

Cite as: J. Chem. Phys. 156, 164101 (2022); doi: 10.1063/5.0088364
Submitted: 16 February 2022 • Accepted: 3 April 2022 •
Published Online: 26 April 2022

View Online
Export Citation
CrossMark

Pierre-François Loos[1,a] and Pina Romaniello[2,3,b)]