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Cumulant Green's function methods for molecules

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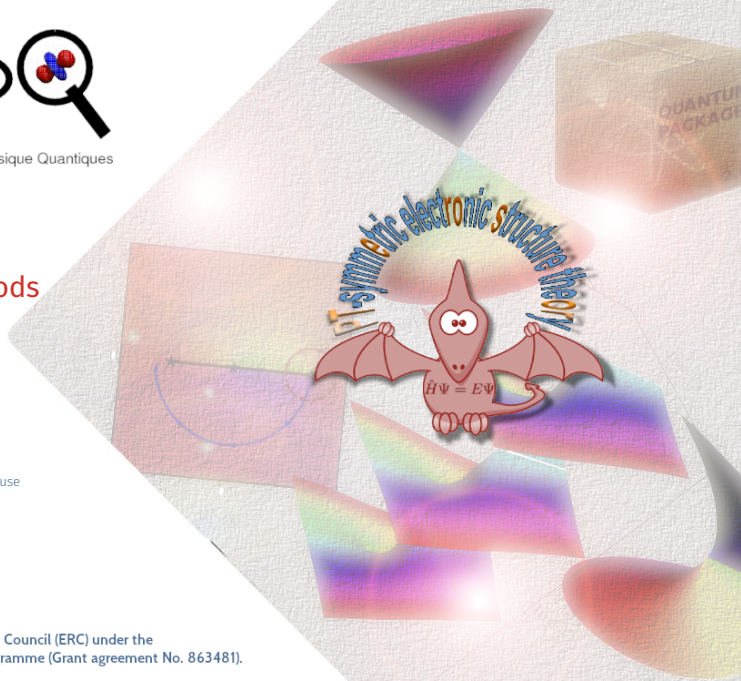
https://lcpq.github.io/PTEROSOR



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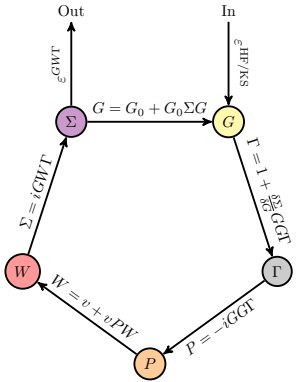


Hedin, Phys Rev 139 (1965) A796

Hedin's equations

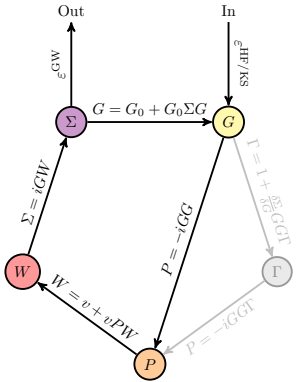
$$\underbrace{G(12)}_{\text{Green's function}} = G_0(12) + \int G_0(13)\Sigma(34)G(42)d(34)$$

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

$$\underbrace{P(12)}_{\text{polarizability}} = -i \int G(13)\Gamma(342)G(41)d(34)$$

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

$$\underbrace{\Sigma(12)}_{\text{self-energy}} = i \int G(14)W(13)\Gamma(423)d(34)$$



Hedin, Phys Rev 139 (1965) A796

The *GW* approximation

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

$$\underbrace{\Gamma(123)}_{\text{vertex}} = \delta(12)\delta(13)$$

$$\underbrace{P(12)}_{\text{polarizability}} = -iG(12)G(21)$$

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

$$\underbrace{\Sigma(12)}_{\text{self-energy}} = iG(12)W(12)$$

Shortcomings of *GW*

- It's cheap and fairly accurate for IPs but it relies on error cancelation
- *GW* is not suitable for strongly correlated systems
  Ammar et al. JCP 160 (2024) 114101
- It's complicated to go beyond *GW*
  Lewis & Berkelbach JCTC 15 (2019) 2925; Mejuto-Zaera & Vlcek 106 (2022) 165129
- It's (extremely) bad for satellite transitions
  Marie & Loos JCTC 20 (2024) 4751

Cumulant ansatz in the time domain

One-body Green's function

Cumulant

$$G(t) = G_0(t)\, e^{C(t)}$$

Reference Green's function

- Cumulant is a cheap beyond-*GW* scheme rooted to electron-boson models
  Langreth PRB 1 (1970) 471; Hedin JPCM 11 (1999) 489
- It's been very successful for materials to describe satellite features
  Aryasetiawan et al. PRL 77 (1996) 2268; Guzzo et al. PRL 107 (2011) 166401
- How does it perform for molecules?
  Vlcek et al. PRM 2 (2018) 030801; McClain et al. PRB 93 (2016) 235139

Landau form of the cumulant

Poisson series of satellites

Quasiparticle shift

$$C_{pp}(t) = \int \mathrm{d}\omega \frac{\beta_p(\omega + \epsilon_p^{\mathrm{HF}})}{\omega^2} \left(e^{-\mathrm{i}\omega t} + \mathrm{i}\omega t - 1 \right)$$

Renormalization

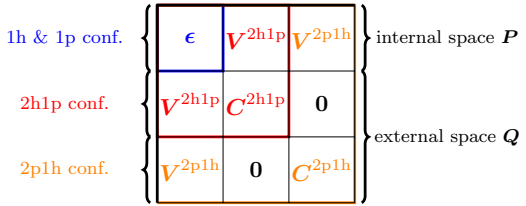
$$\beta_p(\omega) = -\frac{1}{\pi} \mathrm{Im}\, \Sigma^{\mathrm{c}}_{pp}(\omega)$$

Correlation part of the self-energy

Main outcomes

- *GW*+C sometimes improves upon *GW* but far from being systematic
- Cumulant estimates satellite energies without solving dynamical equations
- Beyond-*GW* schemes describing satellites accurately would be useful!

$$\left.\begin{aligned} \left[\boldsymbol{\epsilon} + \boldsymbol{\Sigma}^{GW}\left(\omega = \epsilon_p^{GW}\right)\right]\psi_p^{GW} &= \epsilon_p^{GW}\psi_p^{GW} \\ \boldsymbol{\Sigma}^{GW}(\omega) &= \boldsymbol{V}^{2h1p} \cdot \left(\omega\mathbf{1} - \boldsymbol{C}^{2h1p}\right)^{-1} \cdot (\boldsymbol{V}^{2h1p})^{\dagger} \\ &+ \boldsymbol{V}^{2p1h} \cdot \left(\omega\mathbf{1} - \boldsymbol{C}^{2p1h}\right)^{-1} \cdot (\boldsymbol{V}^{2p1h})^{\dagger} \end{aligned}\right\} \xrightleftharpoons[\text{upfolding}]{\text{downfolding}} \left\{\begin{aligned} &H\Psi_{p,s} = \epsilon_{p,s}^{GW}\Psi_{p,s} \\ &H = \begin{pmatrix} \boldsymbol{\epsilon} & \boldsymbol{V}^{2h1p} & \boldsymbol{V}^{2p1h} \\ (\boldsymbol{V}^{2h1p})^{\dagger} & \boldsymbol{C}^{2h1p} & \mathbf{0} \\ (\boldsymbol{V}^{2p1h})^{\dagger} & \mathbf{0} & \boldsymbol{C}^{2p1h} \end{pmatrix} \end{aligned}\right.$$



Backhouse et al. JCTC 16 (2020) 1090; Bintrim & Berkelbach, JCP 154 (2021) 041101; Monino & Loos JCP 156 (2022) 231101