

## Cumulant Green's function methods for molecules

Pierre-François Loos,<sup>a)</sup> Antoine Marie,<sup>b)</sup> and Abdallah Ammar<sup>c)</sup>

Laboratoire de Chimie et Physique Quantiques (UMR 5626), Université de Toulouse, CNRS, UPS, France

This document contains a detailed derivation of the cumulant expansion. Notations are defined in the main manuscript.

### I. RETARDED ONE-BODY GREEN'S FUNCTION

The matrix elements of the Hartree-Fock (HF) retarded Green's function in the time domain are

$$G_{pq}^{\text{HF}}(t) = -i \Theta(t) e^{-i\epsilon_p^{\text{HF}} t} \delta_{pq} \quad (1)$$

Thanks to the following definition of the Heaviside step function

$$\Theta(t) = -\frac{1}{2\pi i} \int_{-\infty}^{\infty} d\omega \frac{e^{-i\omega t}}{\omega + i\eta} \quad (2)$$

one can compute the Fourier transform of Eq. (1) and obtain the expression of the matrix elements in the frequency domain

$$\begin{aligned} G_{pq}^{\text{HF}}(\omega) &= \int dt e^{i\omega t} G_{pq}^{\text{HF}}(t) \\ &= -i \delta_{pq} \int_{-\infty}^{\infty} dt e^{i(\omega - \epsilon_p^{\text{HF}})t} \Theta(t) \\ &= -i \delta_{pq} \int_{-\infty}^{\infty} dt e^{i(\omega - \epsilon_p^{\text{HF}})t} \left[ -\frac{1}{2\pi i} \int_{-\infty}^{\infty} d\omega' \frac{e^{-i\omega' t}}{\omega' + i\eta} \right] \\ &= \frac{1}{2\pi} \delta_{pq} \int_{-\infty}^{\infty} d\omega' \frac{1}{\omega' + i\eta} \int_{-\infty}^{\infty} dt e^{i(\omega - \omega' - \epsilon_p^{\text{HF}})t} \\ &= \frac{1}{2\pi} \delta_{pq} \int_{-\infty}^{\infty} d\omega' \frac{1}{\omega' + i\eta} (2\pi) \delta(\omega - \omega' - \epsilon_p^{\text{HF}}) \\ &= \frac{\delta_{pq}}{\omega - (\epsilon_p^{\text{HF}} - i\eta)}. \end{aligned} \quad (3)$$

### II. CUMULANT

The general definition of the cumulant, obtained by equating the first-order term in  $W$  (refer to the manuscript), is expressed as

$$G^{\text{HF}}(t)C(t) = \iint dt_1 dt_2 G^{\text{HF}}(t - t_1) \Sigma^c(t_1 - t_2) G^{\text{HF}}(t_2) \quad (4)$$

Projecting this equation in the spinorbital basis yields

$$\begin{aligned} \sum_r G_{pr}^{\text{HF}}(t) C_{rq}(t) &= \sum_{rs} \iint dt_1 dt_2 G_{pr}^{\text{HF}}(t - t_1) \Sigma_{rs}^c(t_1 - t_2) G_{sq}^{\text{HF}}(t_2) \\ \Rightarrow -i \sum_r \Theta(t) e^{-i\epsilon_p^{\text{HF}} t} \delta_{pr} C_{rq}(t) &= \sum_{rs} \iint dt_1 dt_2 G_{pr}^{\text{HF}}(t - t_1) \Sigma_{rs}^c(t_1 - t_2) G_{sq}^{\text{HF}}(t_2) \\ \Rightarrow -i \Theta(t) e^{-i\epsilon_p^{\text{HF}} t} C_{pq}(t) &= \sum_{rs} \iint dt_1 dt_2 G_{pr}^{\text{HF}}(t - t_1) \Sigma_{rs}^c(t_1 - t_2) G_{sq}^{\text{HF}}(t_2) \\ \Rightarrow \Theta(t) C_{pq}(t) &= i e^{i\epsilon_p^{\text{HF}} t} \sum_{rs} \iint dt_1 dt_2 G_{pr}^{\text{HF}}(t - t_1) \Sigma_{rs}^c(t_1 - t_2) G_{sq}^{\text{HF}}(t_2) \end{aligned} \quad (5)$$

<sup>a)</sup>Electronic mail: [loos@irsamc.ups-tlse.fr](mailto:loos@irsamc.ups-tlse.fr)

<sup>b)</sup>Electronic mail: [amarie@irsamc.ups-tlse.fr](mailto:amarie@irsamc.ups-tlse.fr)

<sup>c)</sup>Electronic mail: [aammar@irsamc.ups-tlse.fr](mailto:aammar@irsamc.ups-tlse.fr)

Assuming  $t$  to be positive, we obtain

$$C_{pq}(t) = i \int \frac{d\omega}{2\pi} e^{-i(\omega - \epsilon_p^{\text{HF}})t} G_{pp}^{\text{HF}}(\omega) \Sigma_{pq}^c(\omega) G_{qq}^{\text{HF}}(\omega) \quad (6)$$

Using the diagonal approximation  $\Sigma_{pq}(\omega) \approx \delta_{pq} \Sigma_{pp}(\omega)$  leads to

$$\begin{aligned} C_{pq}(t) &= i \delta_{pq} \int \frac{d\omega}{2\pi} e^{-i(\omega - \epsilon_p^{\text{HF}})t} \left[ G_{pp}^{\text{HF}}(\omega) \right]^2 \Sigma_{pp}^c(\omega) \\ &= i \delta_{pq} \int \frac{d\omega}{2\pi} e^{-i(\omega - \epsilon_p^{\text{HF}})t} \Sigma_{pp}^c(\omega) \left[ \frac{1}{\omega - (\epsilon_p^{\text{HF}} - i\eta)} \right]^2 \\ &= i \delta_{pq} \int \frac{d\omega}{2\pi} e^{-i\omega t} \frac{\Sigma_{pp}^c(\omega + \epsilon_p^{\text{HF}})}{[\omega - (0 - i\eta)]^2} \end{aligned} \quad (7)$$

Inserting the frequency expression of the self-energy

$$\Sigma_{pp}^c(\omega + \epsilon_p^{\text{HF}}) = \sum_{iv} \frac{M_{piv}^2}{\omega - \Delta_{piv}} + \sum_{av} \frac{M_{pav}^2}{\omega - \Delta_{pav}} \quad (8)$$

with

$$\Delta_{piv} = \epsilon_i - \epsilon_p^{\text{HF}} - \Omega_v - i\eta \quad \Delta_{pav} = \epsilon_a - \epsilon_p^{\text{HF}} + \Omega_v - i\eta \quad (9)$$

we obtain

$$\begin{aligned} C_{pp}(t) &= i \sum_{iv} M_{piv}^2 \int \frac{d\omega}{2\pi} e^{-i\omega t} \frac{1}{[\omega - (0 - i\eta)]^2} \frac{1}{\omega - \Delta_{piv}} \\ &+ i \sum_{av} M_{pav}^2 \int \frac{d\omega}{2\pi} e^{-i\omega t} \frac{1}{[\omega - (0 - i\eta)]^2} \frac{1}{\omega - \Delta_{pav}}. \end{aligned} \quad (10)$$

Applying the residue theorem on the following integral [where  $\text{Im}(\omega_1), \text{Im}(\omega_2) < 0$ ] leads to

$$\begin{aligned} \int \frac{d\omega}{2\pi} e^{-i\omega t} \frac{1}{(\omega - \omega_1)^2} \frac{1}{\omega - \omega_2} &= (-i) \left\{ \left[ \partial_\omega \left( \frac{e^{-i\omega t}}{\omega - \omega_2} \right) \right]_{\omega=\omega_1} + \left[ \frac{e^{-i\omega t}}{(\omega - \omega_1)^2} \right]_{\omega=\omega_2} \right\} \\ &= \frac{(-i)}{(\omega_1 - \omega_2)^2} \left\{ [(-it)(\omega_1 - \omega_2) - 1] e^{-i\omega_1 t} + e^{-i\omega_2 t} \right\}, \end{aligned} \quad (11)$$

we find

$$\int \frac{d\omega}{2\pi} e^{-i\omega t} \frac{1}{[\omega - (0 - i\eta)]^2} \frac{1}{\omega - \Delta_{piv}} = \frac{-i}{\Delta_{piv}^2} (e^{-i\Delta_{piv}t} + i\Delta_{piv}t - 1) \quad (12)$$

and

$$\int \frac{d\omega}{2\pi} e^{-i\omega t} \frac{1}{[\omega - (0 - i\eta)]^2} \frac{1}{\omega - \Delta_{pav}} = \frac{-i}{\Delta_{pav}^2} (e^{-i\Delta_{pav}t} + i\Delta_{pav}t - 1). \quad (13)$$

Therefore, the diagonal elements of the cumulant are given by the following expression

$$\begin{aligned} C_{pp}(t) &= \sum_{iv} \frac{M_{piv}^2}{\Delta_{piv}^2} (e^{-i\Delta_{piv}t} + i\Delta_{piv}t - 1) + \sum_{av} \frac{M_{pav}^2}{\Delta_{pav}^2} (e^{-i\Delta_{pav}t} + i\Delta_{pav}t - 1) \\ &= \sum_{iv} \zeta_{piv} (e^{-i\Delta_{piv}t} + i\Delta_{piv}t - 1) + \sum_{av} \zeta_{pav} (e^{-i\Delta_{pav}t} + i\Delta_{pav}t - 1), \end{aligned} \quad (14)$$

where we have introduced the following intermediate quantities:

$$\zeta_{piv} = \left( \frac{M_{piv}}{\Delta_{piv}} \right)^2, \quad \zeta_{pav} = \left( \frac{M_{pav}}{\Delta_{pav}} \right)^2. \quad (15)$$

### III. LANDAU FORM

In this section, we derive the Landau form of the cumulant. The first step is to derive the spectral representation of the self-energy

$$\begin{aligned}
\Sigma_{pp}^c(\omega) &= \text{Re}[\Sigma_{pp}^c(\omega)] + i \text{Im}[\Sigma_{pp}^c(\omega)] \\
&= \frac{1}{\pi} \mathcal{P} \int d\omega' \frac{\text{Im}[\Sigma_{pp}^c(\omega')]}{\omega' - \omega} + i \int d\omega' \text{Im}[\Sigma_{pp}^c(\omega')] \delta(\omega' - \omega) \\
&= \frac{1}{\pi} \int d\omega' \frac{\text{Im}[\Sigma_{pp}^c(\omega')]}{\omega' - \omega - i\eta} = \int d\omega' \frac{\beta_p(\omega')}{\omega - \omega' + i\eta}.
\end{aligned} \tag{16}$$

To obtain this expression, we first used the Kramers-Kronig relation, then the identity

$$\frac{1}{x \pm i\eta} = \mathcal{P}\left(\frac{1}{x}\right) \mp i\pi \delta(x), \tag{17}$$

and finally we introduced

$$\beta_p(\omega) = -\frac{1}{\pi} \text{Im} \Sigma_{pp}^c(\omega) \tag{18}$$

This expression of the self-energy is now inserted into the cumulant

$$\begin{aligned}
C_{pq}(t) &= i \delta_{pq} \int \frac{d\omega}{2\pi} e^{-i\omega t} \frac{\Sigma_{pp}^c(\omega + \epsilon_p^{\text{HF}})}{[\omega - (0 - i\eta)]^2} \\
&= i \delta_{pq} \int \frac{d\omega}{2\pi} \frac{e^{-i\omega t}}{[\omega - (0 - i\eta)]^2} \int d\omega' \frac{\beta_p(\omega')}{\omega + \epsilon_p^{\text{HF}} - \omega' + i\eta} \\
&= \frac{i \delta_{pq}}{2\pi} \int d\omega' \beta_p(\omega') \int d\omega \frac{e^{-i\omega t}}{[\omega - (0 - i\eta)]^2 [\omega - (\omega' - \epsilon_p^{\text{HF}} - i\eta)]} \\
&= \frac{i \delta_{pq} (-2\pi i)}{2\pi} \int d\omega' \beta_p(\omega') \left[ \partial_\omega \left\{ \frac{e^{-i\omega t}}{[\omega - (\omega' - \epsilon_p^{\text{HF}} - i\eta)]} \right\} \right]_{\omega=-i\eta} + \left( \frac{e^{-i\omega t}}{(\omega + i\eta)^2} \right)_{\omega=\omega' - \epsilon_p^{\text{HF}} - i\eta} \\
&= \delta_{pq} \int d\omega' \beta_p(\omega') \left[ \frac{it(\omega' - \epsilon_p^{\text{HF}}) - 1}{(\omega' - \epsilon_p^{\text{HF}})^2} + \frac{e^{-i(\omega' - \epsilon_p^{\text{HF}} - i\eta)t}}{(\omega' - \epsilon_p^{\text{HF}})^2} \right] \\
&= \delta_{pq} \int d\omega \frac{\beta_p(\omega + \epsilon_p^{\text{HF}})}{\omega^2} (e^{-i\omega t} + i\omega t - 1).
\end{aligned} \tag{19}$$

which yields the so-called Landau form of the cumulant.

### IV. GW+C PROPAGATOR

The GW+C ansatz in the time domain reads

$$\begin{aligned}
G_{pp}(t) &= G_{pp}^{\text{HF}}(t) \exp[C_{pp}(t)] \\
&= -i \Theta(t) \exp[-i\epsilon_p^{\text{HF}} t + C_{pp}(t)] \\
&= -i \Theta(t) \exp \left[ -i\epsilon_p^{\text{HF}} t + \sum_{iv} \zeta_{piv} (e^{-i\Delta_{piv} t} + i\Delta_{piv} t - 1) + \sum_{av} \zeta_{pav} (e^{-i\Delta_{pav} t} + i\Delta_{pav} t - 1) \right] \\
&= -i \Theta(t) Z_p^{\text{QP}} \exp(-i\epsilon_p^{\text{QP}} t) \exp \left( \sum_{iv} \zeta_{piv} e^{-i\Delta_{piv} t} + \sum_{av} \zeta_{pav} e^{-i\Delta_{pav} t} \right)
\end{aligned} \tag{20}$$

where the weight of the quasiparticle peak is

$$Z_p^{\text{QP}} = \exp \left( - \sum_{iv} \zeta_{piv} - \sum_{av} \zeta_{pav} \right) \tag{21}$$

and the quasiparticle energy is given by

$$\epsilon_p^{\text{QP}} = \epsilon_p^{\text{HF}} - \left( \sum_{iv} \zeta_{piv} \Delta_{piv} + \sum_{av} \zeta_{pav} \Delta_{pav} \right) \quad (22)$$

Expanding up to first order and applying the Fourier transform leads to

$$\begin{aligned} G_{pp}(\omega) &= \int_{-\infty}^{+\infty} dt e^{i\omega t} G_{pp}(t) \\ &= -i Z_p^{\text{QP}} \int_0^{+\infty} dt e^{i(\omega - \epsilon_p^{\text{QP}})t} \exp \left( \sum_{iv} \zeta_{piv} e^{-i\Delta_{piv}t} + \sum_{av} \zeta_{pav} e^{-i\Delta_{pav}t} \right) \\ &\approx -i Z_p^{\text{QP}} \int_0^{+\infty} dt e^{i(\omega - \epsilon_p^{\text{QP}})t} \left( 1 + \sum_{iv} \zeta_{piv} e^{-i\Delta_{piv}t} + \sum_{av} \zeta_{pav} e^{-i\Delta_{pav}t} \right) \\ &= -i Z_p^{\text{QP}} \int_0^{+\infty} dt e^{[-\eta + i(\omega - \epsilon_p^{\text{QP}})]t} \\ &\quad - i Z_p^{\text{QP}} \sum_{iv} \zeta_{piv} \int_0^{+\infty} dt e^{\{-\eta + i[\omega - (\epsilon_p^{\text{QP}} + \Delta_{piv})]\}t} - i Z_p^{\text{QP}} \sum_{av} \zeta_{pav} \int_0^{+\infty} dt e^{\{-\eta + i[\omega - (\epsilon_p^{\text{QP}} + \Delta_{pav})]\}t} \\ &= \frac{Z_p^{\text{QP}}}{\omega - \epsilon_p^{\text{QP}} + i\eta} + \sum_{iv} \frac{Z_{piv}^{\text{sat}}}{\omega - \epsilon_{piv}^{\text{sat}} + i\eta} + \sum_{av} \frac{Z_{pav}^{\text{sat}}}{\omega - \epsilon_{pav}^{\text{sat}} + i\eta} \end{aligned} \quad (23)$$

where we have introduced two sets of satellites at energies

$$\epsilon_{piv}^{\text{sat}} = \epsilon_p^{\text{QP}} + \Delta_{piv}, \quad \epsilon_{pav}^{\text{sat}} = \epsilon_p^{\text{QP}} + \Delta_{pav}, \quad (24)$$

with the respective weights

$$Z_{piv}^{\text{sat}} = Z_p^{\text{QP}} \zeta_{piv}, \quad Z_{pav}^{\text{sat}} = Z_p^{\text{QP}} \zeta_{pav}. \quad (25)$$

## V. SPECTRAL FUNCTION

The diagonal elements of the spectral function are obtained as

$$\begin{aligned} A_{pp}^{\text{GW+C}}(\omega) &= -\frac{1}{\pi} \text{Im} G_{pp}(\omega) \\ &= -\frac{1}{\pi} \text{Im} \left[ \frac{Z_p^{\text{QP}}}{\omega - \epsilon_p^{\text{QP}} + i\eta} + \sum_{qv} \frac{Z_{pqv}^{\text{sat}}}{\omega - \epsilon_{pqv}^{\text{sat}} + i\eta} \right] \\ &= -\frac{1}{\pi} \text{Im} \left[ \frac{\text{Re} Z_p^{\text{QP}} + i \text{Im} Z_p^{\text{QP}}}{\omega - \text{Re} \epsilon_p^{\text{QP}} + i(\eta - \text{Im} \epsilon_p^{\text{QP}})} + \sum_{qv} \frac{\text{Re} Z_{pqv}^{\text{sat}} + i \text{Im} Z_{pqv}^{\text{sat}}}{\omega - \text{Re} \epsilon_{pqv}^{\text{sat}} + i(\eta - \text{Im} \epsilon_{pqv}^{\text{sat}})} \right] \\ &= -\frac{1}{\pi} \text{Im} \left[ \frac{(\text{Re} Z_p^{\text{QP}} + i \text{Im} Z_p^{\text{QP}})(\omega - \text{Re} \epsilon_p^{\text{QP}} - i(\eta - \text{Im} \epsilon_p^{\text{QP}}))}{(\omega - \text{Re} \epsilon_p^{\text{QP}})^2 + (\text{Im} \epsilon_p^{\text{QP}})^2} + \sum_{qv} \frac{(\text{Re} Z_{pqv}^{\text{sat}} + i \text{Im} Z_{pqv}^{\text{sat}})(\omega - \text{Re} \epsilon_{pqv}^{\text{sat}} - i(\eta - \text{Im} \epsilon_{pqv}^{\text{sat}}))}{(\omega - \text{Re} \epsilon_{pqv}^{\text{sat}})^2 + (\text{Im} \epsilon_{pqv}^{\text{sat}})^2} \right] \\ &= -\frac{1}{\pi} \left[ \frac{(\text{Re} Z_p^{\text{QP}})(\text{Im} \epsilon_p^{\text{QP}}) + (\text{Im} Z_p^{\text{QP}})(\omega - \text{Re} \epsilon_p^{\text{QP}})}{(\omega - \text{Re} \epsilon_p^{\text{QP}})^2 + (\text{Im} \epsilon_p^{\text{QP}})^2} + \sum_{qv} \frac{(\text{Re} Z_{pqv}^{\text{sat}})(\text{Im} \epsilon_{pqv}^{\text{sat}}) + (\text{Im} Z_{pqv}^{\text{sat}})(\omega - \text{Re} \epsilon_{pqv}^{\text{sat}})}{(\omega - \text{Re} \epsilon_{pqv}^{\text{sat}})^2 + (\text{Im} \epsilon_{pqv}^{\text{sat}})^2} \right]. \end{aligned} \quad (26)$$