Slides for Patryk's Notes

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Outline

1. Diagonal GW+C
2. Off-diagonal GW+C
3. Cumulant with second order self-energy
4. Real-time EOM-CC Cumulant GF

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Cumulant

This is the simplest approach to deriving the cumulant expansion for the retarded Green function. Equating the Dyson equation and the Taylor expansion of the exponential to first order gives

$$\boldsymbol{G}^0_{pp}(t)\boldsymbol{C}_{pq}(t) = \iint \mathrm{d}t_1\mathrm{d}t_2\,\boldsymbol{G}^0_{pp}(t-t_1)\boldsymbol{\Sigma}^c_{pq}(t_1-t_2)\boldsymbol{G}^0_{qq}(t_2) \tag{1}$$

$$\implies C_{pp}(t) = i\int \frac{d\omega}{2\pi}\frac{\Sigma^c_{pp}\left(\omega+\epsilon^{HF}_p\right)}{(\omega+i\eta)^2}e^{-i\omega t} \tag{2}$$

Loos plugs in the GW self-energy here to get

$$C_{pp}(t) = \sum_{i\nu}\zeta_{pi\nu}\left[e^{-i\Delta_{pi\nu}t}-1+i\Delta_{pi\nu}t\right]+\sum_{a\nu}\zeta_{pa\nu}\left[e^{-i\Delta_{pa\nu}t}-1+i\Delta_{pa\nu}t\right] \tag{3}$$

This first order expansion is exact up to the first order in the screened Coulomb interaction W. An open research question would be to insert the BWs2 self-energy here instead.

Green's function

Plugging back this form gives

$$G_{pp}(t) = -i\Theta(t)Z_p^{QP} e^{-i\epsilon_p^{QP} t} e^{\sum_{i\nu} \zeta_{pi\nu} e^{-i\Delta_{pi\nu} t} + \sum_{a\nu} \zeta_{pa\nu} e^{-i\Delta_{pa\nu} t}} \tag{4}$$

The weight of the quasiparticle peak is

$$Z_p^{QP} = e^{-\sum_{i\nu} \zeta_{pi\nu} - \sum_{a\nu} \zeta_{pa\nu}} = \exp\left(\left[\frac{\partial \Sigma_{pp}^c(\omega)}{\partial \omega}\right]_{\omega=\epsilon_p^{HF}}\right) \tag{5}$$

with the quasiparticle energy

$$\epsilon_p^{QP} = \epsilon_p^{HF} - \left(\sum_{i\nu} \zeta_{pi\nu}\Delta_{pi\nu} + \sum_{a\nu} \zeta_{pa\nu}\Delta_{pa\nu}\right) = \epsilon_p^{HF} + \Sigma_{pp}^c\left(\epsilon_p^{HF}\right) \tag{6}$$

With the Fourier transform and a first order expansion of the exponential:

$$G_{pp}(\omega) = \frac{Z_p^{QP}}{\omega - \epsilon_p^{QP} + i\eta} + \sum_{i\nu} \frac{Z_p^{QP}\zeta_{pi\nu}}{\omega - \epsilon_p^{QP} - \Delta_{pi\nu} + i\eta} + \sum_{a\nu} \cdots \tag{7}$$

Spectral function

$$A_p(\omega) = -\frac{1}{\pi}\,\mathrm{Im}\,G_{pp}(\omega) \tag{8}$$

$$= -\frac{1}{\pi}\left[\frac{\left(\mathrm{Re}\,Z_p^{QP}\right)\left(\mathrm{Im}\,\epsilon_p^{QP}\right) + \left(\mathrm{Im}\,Z_p^{QP}\right)\left(\omega - \mathrm{Re}\,\epsilon_p^{QP}\right)}{\left(\omega - \mathrm{Re}\,\epsilon_p^{QP}\right)^2 + \left(\mathrm{Im}\,\epsilon_p^{QP}\right)^2}\right. \tag{9}$$

$$\left. + \sum_{i\nu} \frac{\left(\mathrm{Re}\,Z_{pi\nu}^{sat}\right)\left(\mathrm{Im}\,\epsilon_{pi\nu}^{sat}\right) + \left(\mathrm{Im}\,Z_{pi\nu}^{sat}\right)\left(\omega - \mathrm{Re}\,\epsilon_{pi\nu}^{sat}\right)}{\left(\omega - \mathrm{Re}\,\epsilon_{pi\nu}^{sat}\right)^2 + \left(\mathrm{Im}\,\epsilon_{pi\nu}^{sat}\right)^2} + \sum_{a\nu}\cdots\right] \tag{10}$$

It would not be useful to include higher order terms because this would be including higher powers of W, but we already made the truncation with the hope of being exact up to first order in W.

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C to G

We can instead consider (with $\Xi_{i\nu} \equiv \epsilon_i - \Omega_\nu$, $\Xi_{a\nu} \equiv \epsilon_a + \Omega_\nu$, and $\Delta \equiv \epsilon_q - \epsilon_p$)

$$C_{pq}(t) = i \int \frac{d\omega}{2\pi} e^{-i(\omega - \epsilon_p^{HF})t} \frac{\Sigma^c_{pq}(\omega)}{(\omega - \epsilon_p^{HF} + i\eta)(\omega - \epsilon_q^{HF} + i\eta)} \tag{11}$$

$$= i^2 \left[\sum_{i\nu} W_{pi\nu} W_{qi\nu} \frac{1}{\Delta} \left[\frac{e^{-i(\Xi_{i\nu} - \epsilon_p)t} - 1}{\Xi_{i\nu} - \epsilon_p} + \frac{e^{i\Delta t} - e^{-i(\Xi_{i\nu} - \epsilon_p)t}}{\Xi_{i\nu} - \epsilon_q} \right] \right. \tag{12}$$

$$\left. + \sum_{a\nu} W_{pa\nu} W_{qa\nu} \frac{1}{\Delta} \left[\frac{e^{-i(\Xi_{a\nu} - \epsilon_p)t} - 1}{\Xi_{a\nu} - \epsilon_p} + \frac{e^{i\Delta t} - e^{-i(\Xi_{a\nu} - \epsilon_p)t}}{\Xi_{a\nu} - \epsilon_q} \right] \right]$$

$$\implies G_{pq}(t) = -i \int_0^\infty dt e^{i(\omega - \epsilon_p)t} \left[1 - \sum_{i\nu} W_{pi\nu} W_{qi\nu} T_{i\nu}(t) - \sum_{a\nu} W_{pa\nu} W_{qa\nu} \right. \tag{13}$$

G to A

$$A_{pq}(\omega) = \tag{14}$$

$$\delta(\omega - \epsilon_p) - \sum_{i\nu} W_{pi\nu} W_{qi\nu} \left[-\frac{\delta(\omega - \epsilon_p)}{(\epsilon_p - \epsilon_q)(\Xi_{i\nu} - \epsilon_p)} + \frac{\delta(\omega - \epsilon_q)}{(\epsilon_p - \epsilon_q)(\Xi_{i\nu} - \epsilon_q)} + \right. \tag{15}$$

$$\left. + \frac{\delta(\omega - \Xi_{i\nu})}{(\Xi_{i\nu} - \epsilon_p)(\Xi_{i\nu} - \epsilon_q)} - \frac{2\Xi_{i\nu}\delta(\omega - \Xi_{i\nu})}{(\epsilon_p - \epsilon_q)(\Xi_{i\nu} - \epsilon_p)(\Xi_{i\nu} - \epsilon_q)} \right] - \sum_{a\nu} \dots$$

We can replace all of the delta functions with Lorentzians in practice.

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Expression for the cumulant

With a frequency shift, the diagonal part of the second order self-energy is

$$\Sigma_{pp}^{(2)}(\omega + \epsilon_p) = \frac{1}{2}\sum_{iab} \frac{\langle pi \,||\, ab\rangle^2}{\omega - \epsilon_{pi}^{ab}} + \frac{1}{2}\sum_{ija} \frac{\langle pa \,||\, ij\rangle^2}{\omega - \epsilon_{pa}^{ij}} \tag{16}$$

Then the cumulant can be brought to the Landau form

$$C_{pp}^{(2)}(t) = \int d\omega\, \beta(\omega) f(\omega) \tag{17}$$

with $f(\omega) \equiv \frac{e^{-i\omega t} + i\omega t - 1}{\omega^2}$ and

$$\beta(\omega) = -\frac{1}{\pi}\,\mathrm{Im}\,\Sigma_{pp}^{(2)}(\omega + \epsilon_p) \tag{18}$$

$$= \frac{1}{2}\sum_{iab}\langle pi \| ab\rangle^2 \delta\left(\omega - \epsilon_{pi}^{ab}\right) + \frac{1}{2}\sum_{ija}\langle pa \| ij\rangle^2 \delta\left(\omega - \epsilon_{pa}^{ij}\right) \tag{19}$$

This is similar to $\beta(\omega) = \sum_q g_q^2 \delta(\omega - \omega_q)$ kernel for electrons coupled to bosons at the frequencies $\omega_q \equiv \epsilon_{pq}^{rs}$ with coupling coefficients $g_q \equiv \langle pq \| rs\rangle$.

Connecting back to the Dyson equation

The CC GF can be written in frequency space as

$$G_{pq}^{R}(\omega) = \left\langle \Phi \middle| (1+\Lambda)\bar{a_q^\dagger}(\omega + \bar{H}_N + i\delta)^{-1}\bar{a_p} \middle| \Phi \right\rangle + EA \tag{20}$$

Truncating the CC expansion to doubles and introducing

$$X_p(\omega) \equiv (\omega + \bar{H}_N + i\delta)^{-1}\bar{a_p} \tag{21}$$

$$= \sum_i x^i(\omega)_p a_i + \frac{1}{2!}\sum_{ij,a} x_a^{ij}(\omega)_p a_a^\dagger a_j a_i \tag{22}$$

and something analogous for the EA sector. By considering a perturbation series in the cluster amplitudes up to second order, we can get

$$G_{pq}^{(2)R}(\omega) = G_{pq}^{R(0)}(\omega) + G_{pq}^{R(0)}(\omega)\Sigma_{pq}^{(2)}(\omega)G_{pq}^{R(0)}(\omega) \tag{23}$$

with the second order self-energy $\Sigma_{pq}^{(2)}(\omega)$ and $G_{pq}^{(0)R}(\omega) = \frac{1}{(\omega-\epsilon_q)}$.

Connecting back to the Dyson equation

We can start with the CC GF in frequency space as

$$G^R_{pq}(\omega) = \left\langle \Phi \left| (1+\Lambda)\bar{a}^\dagger_q(\omega + \bar{H}_N + i\delta)^{-1}\bar{a}_p \right| \Phi \right\rangle + EA \tag{24}$$

Because in CC, the exact grand state can be written as $|\Psi_0\rangle = e^T|\Phi\rangle$ and $\langle\Psi_0| = \langle\Phi|(1+\Lambda)e^{-T}$ and also by decomposing the similarity-transformed operators, we can arrive at

$$G^R_{pq}(t-t') = -i\,\Theta(t-t')\langle 0|\{a_p(t), a^\dagger_q(t')\}|0\rangle. \tag{25}$$

The retarded Green's function for one core orbital c is diagonal as

$$G^R_c(t) = -i\Theta(t)e^{iE_0 t}\left\langle 0 \left| a_c e^{-iHt} a^\dagger_c \right| 0 \right\rangle - i\Theta(t)e^{-iE_0 t}\left\langle 0 \left| a^\dagger_c e^{iHt} a_c \right| 0 \right\rangle \tag{26}$$

$$\tag{27}$$

We could only do this because via the separable approximation to the ground state $|0\rangle \simeq a^\dagger_c\,|N-1\rangle$, which is justified for core states, but not for valence states.

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Simplification from just considering the core hole GGF

For a given deep core level $p = c$:

$$G_c^R(t) = -i\Theta(t-t')\left\langle 0 \middle| \left\{ a_c(t), a_c^\dagger(t') \right\} \middle| 0 \right\rangle \tag{28}$$

$$= -i\Theta(t) e^{-iE_0 t} \langle N-1 | N-1, t \rangle \tag{29}$$

where $|0\rangle \simeq a_c^\dagger |N-1\rangle$ and $|N-1, t\rangle = e^{iHt}|N-1\rangle \approx N(t)e^{T(t)}|\phi\rangle$. Inserting the latter states and left multiplying by $e^{-T(t)}$ gives

$$-i\frac{d\,|N-1,t\rangle}{dt} = H\,|N-1,t\rangle \tag{30}$$

$$\implies -i\left(\frac{d\ln N(t)}{dt} + \frac{dT(t)}{dt}\right)|\phi\rangle = \left(\bar{H}_N(t) + E^{N-1}\right)|\phi\rangle \tag{31}$$

Projection yields coupled DEs for $N(t)$ and $T(t)$, but we will just display here the former because it seems most relevant to the cumulant

$$-\,i\frac{d\ln N(t)}{dt} = \left\langle \phi \middle| \bar{H}_N(t) \middle| \phi \right\rangle + E^{N-1} \tag{32}$$

Continued

Assuming $|N-1\rangle \simeq a_c|\Phi\rangle = |\phi\rangle \implies \langle N-1|\, N-1,t\rangle = N(t)$, plugging back in gives

$$G_c^R(t) = -i\Theta(t)e^{-i\epsilon_c t}e^{C_c^R(t)} \tag{33}$$

with $\epsilon_c = E^{N-1} - E_0$ and the Landau form of the cumulant is

$$\begin{aligned} C_c^R(t) &= i\int_0^t \left\langle \phi \left| \bar{H}_N(t) \right| \phi \right\rangle dt' &(34)\\ &= \int \mathrm{d}\omega \beta_c(\omega)\frac{e^{-i\omega t} + i\omega t - 1}{\omega^2} &(35)\end{aligned}$$

with $\beta_c(\omega) = \frac{1}{\pi}\mathrm{Re}\int_0^\infty dte^{-i\omega t}\left[-i\frac{d}{dt}\left\langle \phi \left| \bar{H}_N(t) \right| \phi \right\rangle\right]$. So we see that the cumulant obeys the differential equation

$$\begin{aligned} -i\frac{dC_c^R(t)}{dt} &= \left\langle \phi \left| \bar{H}_N(t) \right| \phi \right\rangle \\ &= \sum_{ia} f_{ia}t_i^a + \frac{1}{2}\sum_{ijab} v_{ij}^{ab}t_j^b t_i^a, \end{aligned} \tag{36}$$