

Contents

1	Dyson to GQME: 12/13	1
1.1	Explicit Construction of the Liouville Superoperator	2
2	UEG	4
2.1	MF	4
2.2	RPA	4
	Verification	5
2.3	GW	5
	2.3.1 Correlation self energy	5
	Derivation from scratch	5
	2.3.2 Spectral function	6
2.4	GW+C	6
	2.4.1 Cumulant	6
	2.4.2 Green's function	8
	2.4.3 Spectral function	10
3	TDVP	11

Derivations for Personal Learning

Patryk Kozlowski

October 18, 2025

Chapter 1

Dyson to GQME: 12/13

The Generalized Quantum Master Equation (GQME) is given by

$$\dot{\mathcal{C}}(t) = \mathcal{C}(t)\Omega_1 - \int_0^t d\tau \mathcal{C}(t-\tau)\mathcal{K}_1(\tau) + D(t) \quad (1.1)$$

where the correlation function is defined as

$$\mathcal{C}(t) = (\hat{\mu} \mid \hat{\mu}(t)), \quad (1.2)$$

the higher-order moments are

$$\Omega_n \equiv ((i\mathcal{L})^n \hat{\mu}, \hat{\mu}) / (\hat{\mu}, \hat{\mu}) \quad (1.3)$$

with the auxiliary kernels

$$K_n(t) \equiv \left((i\mathcal{L})^n \hat{f}(t), \hat{\mu} \right) / (\hat{\mu}, \hat{\mu}) \quad (1.4)$$

$\hat{f}(t)$ in the above equation is referred to as the random force operator

$$\hat{f}(t) \equiv e^{it\mathcal{L}} \mathcal{Q} i\mathcal{L} \hat{\mu} \quad (1.5)$$

with $\mathcal{Q} = \mathcal{I} - \mathcal{P}$ being the complementary projection operator. But this becomes complicated, so Wenjie found that we can express $\mathcal{K}_1(t)$ without time evolution using $\hat{f}(0) = \mathcal{Q} i\mathcal{L} \hat{\mu}$ and, we get

$$K_n(0) = \Omega_{n+1} - \Omega_n \Omega_1 \quad (1.6)$$

Therefore, we only need to consider $\dot{K}_1(t)$, which can be obtained directly:

$$\dot{K}_1(t) = \frac{(i\mathcal{L}\dot{\hat{f}}(t), \hat{\mu})}{(\hat{\mu}, \hat{\mu})} = K_2(t) - \Omega_1 K_1(t) \quad (1.7)$$

Similarly, we can show that the auxiliary kernels are coupled through

$$\dot{K}_n(t) = K_{n+1}(t) - \Omega_n K_1(t). \quad (1.8)$$

We expect that the higher order auxiliary kernels will decay quickly, so we can truncate the series at some finite n . The moments of the memory kernel are

$$\Omega_n = \frac{((i\mathcal{L})^n \hat{\mu}, \hat{\mu})}{(\hat{\mu}, \hat{\mu})}, \quad (1.9)$$

with \mathcal{L} being the Liouville superoperator with $\mathcal{L}\hat{\mu} = [\hat{H}, \hat{\mu}]$. The construction of the numerator in equation 1.9 can be thought of as the generation of a Krylov subspace up to level n , i.e. we need to build up $\mathcal{K}_n(\mathcal{L}, \hat{\mu}) = \text{span}\{\hat{\mu}, (i\mathcal{L})\hat{\mu}, (i\mathcal{L})^2\hat{\mu}, \dots, (i\mathcal{L})^{n-1}\hat{\mu}\}$, where $\hat{\mu} = \hat{c}$ or \hat{c}^\dagger . In the case if we choose $\hat{\mu} = \hat{c}$, we get the lesser Green's function

$$\mathcal{C}(t) = (\hat{c}, \hat{c}(t)) \equiv \langle \hat{c}^\dagger(0) \hat{c}(t) \rangle = \frac{G^<(t)}{i} \quad (1.10)$$

whereas if we chose $\hat{\mu} = \hat{c}^\dagger$, we get the greater Green's function

$$\mathcal{C}(t) = (\hat{c}^\dagger, \hat{c}^\dagger(t)) \equiv \langle \hat{c}(0) \hat{c}^\dagger(t) \rangle = -\frac{G^>(t)}{i} \quad (1.11)$$

Then we can construct the retarded Green's function as

$$G_R(t) = \Theta(t) (G^<(t) - G^>(t)) \quad (1.12)$$

Using Krylov subspace methods, one never has to construct the Liouvillian matrix, but instead can directly compute the extremal eigenvalues and eigenvectors of \mathcal{L} by considering the action of \mathcal{L} on the Krylov subspace.

1.1 Explicit Construction of the Liouville Superoperator

Consider that we are working with the upfolded Hamiltonian

$$\mathbf{H} = \begin{pmatrix} \mathbf{f} & \mathbf{W} \\ \mathbf{W}^\dagger & \mathbf{d} \end{pmatrix} \quad (1.13)$$

where we again have a physical space \mathbf{f} and a bath space \mathbf{d} , whose coupling is given by \mathbf{W} . Tell me what would happened if we considered the action of this on the composite operator vector defined lower? Lets consider making a Krylov subspace, corresponding to repeated applications of the Liouville superoperator to the initial operator $\hat{\mu}$. Now, The idea is to define a composite operator vector

$$\hat{\mu} \equiv \begin{pmatrix} \hat{\mu}_1 \\ \hat{\mu}_2 \end{pmatrix} = \begin{pmatrix} \hat{c} \\ \hat{c}^\dagger \end{pmatrix}, \quad (1.14)$$

where \hat{c} is the annihilation operator and \hat{c}^\dagger is the creation operator. Notice that the equation of motion for the Green's function is

$$(i\partial_t - \hat{H}_0)G(t, t') = \delta(t - t') + \int_{-\infty}^{\infty} d\tau \Sigma(t, \tau) G(\tau, t') \quad (1.15)$$

$$\rightarrow G(\dot{t}, t') = -i\hat{H}_0 G(t, t') - i\delta(t - t') + \int_{-\infty}^{\infty} d\tau' \Sigma(t, \tau') G(\tau', t') \quad (1.16)$$

So our task becomes to figure out how

$$-i\hat{H}_0 G(t, t') - i\delta(t-t') + \int_{-\infty}^{\infty} d\tau' \Sigma(t, \tau') G(\tau', t') = \mathcal{C}(t)\Omega_1 - \int_0^t d\tau \mathcal{C}(t-\tau)\mathcal{K}(\tau) + D(t) \quad (1.17)$$

I feel like it should be the case that $-i\hat{H}_0 G(t, t') = \mathcal{C}(t)\Omega_1$. Do you think that this should be the case or no? Because I think we can agree that the equation that comes first should be the same as the equation of motion for the greens function. And then try to apply a decomposed Hamiltonia like $H = H_0 + V$ to the first equation, so that we can see what happens.

To simple by things as much as possible initially consider that we only use the noninteracting Hamiltonian $\hat{H}_0 = \epsilon \hat{c}^\dagger \hat{c}$ in the action of the Liouvillian.

$$\Omega_1 = \frac{((i\mathcal{L})\hat{\mu}, \hat{\mu})}{(\hat{\mu}, \hat{\mu})} = \frac{((i[\hat{H}_0, \hat{\mu}], \hat{\mu})}{(\hat{\mu}, \hat{\mu})} \quad (1.18)$$

If we just consider the numerator, we see that

$$((i[\hat{H}_0, \hat{\mu}], \hat{\mu}) = ((i[\hat{H}_0, \hat{c}], \hat{c}) + ((i[\hat{H}_0, \hat{c}^\dagger], \hat{c}^\dagger) \quad (1.19)$$

Considering just the first term

$$((i[\hat{H}_0, \hat{c}], \hat{c}) = -i\epsilon([\hat{c}^\dagger \hat{c}, \hat{c}], \hat{c}) = -i\epsilon(\hat{c}, \hat{c}) = -i\epsilon(1 - f(\epsilon)) \quad (1.20)$$

and the second term

$$((i[\hat{H}_0, \hat{c}^\dagger], \hat{c}^\dagger) = -i\epsilon([\hat{c}^\dagger \hat{c}, \hat{c}^\dagger], \hat{c}^\dagger) = -i\epsilon(\hat{c}^\dagger, \hat{c}^\dagger) = -i\epsilon f(\epsilon) \quad (1.21)$$

which can be summarized as

$$((i[\hat{H}_0, \hat{\mu}], \hat{\mu}) = -i\epsilon \implies \Omega_1 = -i\epsilon \quad (1.22)$$

Now, the equation of motion for the interacting Green's function is given by

$$\left(i\frac{\partial}{\partial t} - h_0\right) G(t, t') = \delta(t - t') + \int dt'' \Sigma(t, t'') G(t'', t') \quad (1.23)$$

$$\frac{\partial}{\partial t} G(t, t') = \underbrace{-ih_0 G(t, t')}_{\Omega_1 \mathcal{C}(t)} - i\delta(t - t') + \int dt'' \Sigma(t, t'') G(t'', t') \quad (1.24)$$

Now come if we consider the higher-order moments

$$\Omega_n \equiv \frac{((i\mathcal{L})^n \hat{\mu}, \hat{\mu})}{(\hat{\mu}, \hat{\mu})} = \frac{(i)^n (\mathcal{L}^n \hat{\mu}, \hat{\mu})}{(\hat{\mu}, \hat{\mu})} = (i)^n \left([\hat{H}, [\hat{H}, [\hat{H}, \dots, \hat{\mu}]]] \dots \right) \quad (1.25)$$

where it is implied that we are applying the commutator n times. We want to answer the form for the $\hat{\mathbf{H}}^{G_0 W_0}$ Hamiltonian, which has the super matrix form of

$$\begin{bmatrix} \mathbf{f} + \Sigma_\infty & \mathbf{W} \\ \mathbf{W}^\dagger & \mathbf{d} \end{bmatrix} \quad (1.26)$$

and the memory kernel

$$\mathcal{K}(t) = (\mathbf{A} | \mathcal{L} \mathcal{Q} e^{i\mathcal{Q}\mathcal{L}t} \mathcal{Q} \mathcal{L} | \mathbf{A}), \quad (1.27)$$

where $\mathcal{Q} = \mathcal{I} - \mathcal{P}$ is the complementary projection operator.

Chapter 2

UEG

Throughout, I am working in the retarded time formalism. We are working with a plane wave basis, where each state has its own wavevector.

2.1 MF

Even before doing HF, I generate my basis of plane waves, and their wave vectors in 3D are just a list of integers, three entries long. From HF, I get a set of MO coefficients $C_{\mathbf{k}_\mu \mathbf{k}_p}$ and orbital energies $\epsilon_{\mathbf{k}_p}$.

2.2 RPA

For the UEG, I am first looping over all momentum transfer vectors \mathbf{k}_q . To learn which excitations are valid for the given \mathbf{k}_q , we first loop over occupied states \mathbf{k}_i . Virtual states \mathbf{k}_a are already determined by that point; we compute $\mathbf{k}_a \equiv \mathbf{k}_i + \mathbf{k}_q$, and based of whether it is a valid virtual index, we either add it to our list or continue. The criterion for validity is that the wave vector must be outside the Fermi sphere, but still within our plane wave basis, i.e. within the KE cutoff. We do the same for the second pair of indices $\mathbf{k}_j, \mathbf{k}_b$. Then, we can form the Casida eigenproblem for each \mathbf{k}_q .

$$\begin{pmatrix} \mathbf{A}(\mathbf{k}_q) & \mathbf{B}(\mathbf{k}_q) \\ -\mathbf{B}(\mathbf{k}_q) & -\mathbf{A}(\mathbf{k}_q) \end{pmatrix} \begin{pmatrix} \mathbf{X}(\mathbf{k}_q) & \mathbf{Y}(\mathbf{k}_q) \\ \mathbf{Y}(\mathbf{k}_q) & \mathbf{X}(\mathbf{k}_q) \end{pmatrix} \begin{pmatrix} \Omega(\mathbf{k}_q) & \mathbf{0} \\ \mathbf{0} & -\Omega(\mathbf{k}_q) \end{pmatrix} = \begin{pmatrix} \mathbf{X}(\mathbf{k}_q) & \mathbf{Y}(\mathbf{k}_q) \\ \mathbf{Y}(\mathbf{k}_q) & \mathbf{X}(\mathbf{k}_q) \end{pmatrix} \quad (2.1)$$

The $\mathbf{A}(\mathbf{k}_q)$ and $\mathbf{B}(\mathbf{k}_q)$ matrices are defined as

$$A_{\mathbf{k}_i \mathbf{k}_a, \mathbf{k}_b \mathbf{k}_j}(\mathbf{k}_q) = (\epsilon_{\mathbf{k}_a} - \epsilon_{\mathbf{k}_i}) \delta_{\mathbf{k}_i \mathbf{k}_j} \delta_{\mathbf{k}_a \mathbf{k}_b} + \frac{4\pi}{|\mathbf{k}_q|^2} \quad (2.2)$$

$$B_{\mathbf{k}_i \mathbf{k}_a, \mathbf{k}_j \mathbf{k}_b}(\mathbf{k}_q) = \frac{4\pi}{|\mathbf{k}_q|^2} \quad (2.3)$$

After solving the Casida eigenvalue problem, I perform the bioorthogonalization procedure, which ensures that

$$(\mathbf{X}(\mathbf{k}_q) - \mathbf{Y}(\mathbf{k}_q))^\dagger (\mathbf{X}(\mathbf{k}_q) + \mathbf{Y}(\mathbf{k}_q)) = \mathbf{I} \quad (2.4)$$

Now, I have a list of excitation energies Ω and corresponding right eigenvectors \mathbf{X}, \mathbf{Y} for each momentum transfer \mathbf{k}_q . But for the self energy, we actually need rather the transition densities $\rho(\mathbf{k}_q)$, which are lists (with length μ) of scalars, defined as

$$\rho_\nu(\mathbf{k}_q) = \sum_{\mathbf{k}_i, \mathbf{k}_a} (X_{\mathbf{k}_i \mathbf{k}_a}^\nu(\mathbf{k}_q) + Y_{\mathbf{k}_i \mathbf{k}_a}^\nu(\mathbf{k}_q)). \quad (2.5)$$

So to get them, I just need to contract over the indices $\mathbf{k}_i, \mathbf{k}_a$.

Verification

We can compute the RPA correlation energy via the plasmon formula:

$$E_c^{RPA} = \frac{1}{2} \text{Tr} \left(\sum_{\mathbf{q}} \Omega(\mathbf{q}) - \mathbf{A}(\mathbf{q}) \right) \quad (2.6)$$

$$(2.7)$$

and then we just have to divide by the number of electrons to get the correlation energy per electron.

2.3 GW

2.3.1 Correlation self energy

Derivation from scratch

We can start from the definition of the GW self energy, which is a convolution of the Green's function and the screened Coulomb interaction:

$$\Sigma(\mathbf{k}, \omega) = \frac{i}{2\pi} \int d\omega' \frac{d^3 q}{(2\pi)^3} G(\mathbf{k} - \mathbf{q}, \omega - \omega') W(\mathbf{q}, \omega') \quad (2.8)$$

The screened Coulomb interaction in the RPA is given by

$$W(\mathbf{q}, \omega) = v(\mathbf{q}) + v(\mathbf{q})\chi_0(\mathbf{q}, \omega)v(\mathbf{q}) + \dots \quad (2.9)$$

$$= \frac{v(\mathbf{q})}{1 - v(\mathbf{q})\chi_0(\mathbf{q}, \omega)} \equiv \frac{v(\mathbf{q})}{\varepsilon(\mathbf{q}, \omega)} \quad (2.10)$$

$$= v(\mathbf{q}) + v^2(\mathbf{q})\chi_{RPA}(\mathbf{q}, \omega) \quad (2.11)$$

$$\implies W_p(\mathbf{q}, \omega) \equiv W(\mathbf{q}, \omega) - v(\mathbf{q}) = v^2(\mathbf{q})\chi_{RPA}(\mathbf{q}, \omega) \quad (2.12)$$

$$= \sum_{\nu} \frac{2\omega_{\nu} v^2(\mathbf{q}) |\rho_{\nu}(\mathbf{q})|^2}{\omega^2 - \omega_{\nu}^2} \quad (2.13)$$

where it can be shown that $\varepsilon^{-1}(\mathbf{q}, \omega) = 1 + v(\mathbf{q})\chi_{RPA}(\mathbf{q}, \omega)$. At this point, we can just quote the final result of Hedin for a retarded self energy in the GW approximation:

$$\Sigma_{pol}(x, x'; \omega) = \sum_{i, s \neq 0} \frac{V^s(\mathbf{r})V^s(\mathbf{r}')\phi_i(x)\phi_i^*(x')}{\omega + \omega_s \operatorname{sgn}(\mu - \varepsilon_i) - \varepsilon_i} \quad (2.14)$$

$$\Rightarrow \Sigma(\mathbf{k}, \omega) = \sum_{q, \nu} \frac{v^2(\mathbf{q})|\rho_\nu(\mathbf{q})|^2}{\omega + \Omega_\nu \operatorname{sgn}(\mu - \epsilon_{\mathbf{k}-\mathbf{q}}) - \epsilon_{\mathbf{k}-\mathbf{q}} + i\eta} \quad (2.15)$$

since we know that we will have a diagonal self energy in momentum space for the UEG. We defined

$$V^s(\mathbf{r}) \rightarrow V^\nu(\mathbf{q}) = v(\mathbf{q})\rho_\nu(\mathbf{q}), \quad (2.16)$$

$$\omega_s \rightarrow \Omega_\nu \quad (2.17)$$

In relation to our Casida eigenproblem, we can identify that the excitation energies Ω_ν are just the eigenvalues from Eqn. 2.1, and the transition densities $\rho_\nu(\mathbf{q})$ are given by

$$\rho_\nu(\mathbf{q}) = \sum_{\mathbf{k}_i \mathbf{k}_a} (X_{\mathbf{k}_i \mathbf{k}_a}^\nu(\mathbf{q}) + Y_{\mathbf{k}_i \mathbf{k}_a}^\nu(\mathbf{q})). \quad (2.18)$$

So the expression I find has one more factor of the ERI then the one I have written below.

$$\Sigma^{\text{corr}}(\mathbf{k}_p, \omega) = \sum_{\mathbf{k}_q} \sum_{\nu}^{\text{RPA}} \frac{4\pi}{|\mathbf{k}_q|^2} |\rho_\nu(\mathbf{k}_q)|^2 \left[\frac{f_{\mathbf{k}_p - \mathbf{k}_q}}{\omega + \Omega_\nu(\mathbf{k}_q) - \epsilon_{\mathbf{k}_p - \mathbf{k}_q} + i\eta} + \frac{1 - f_{\mathbf{k}_p - \mathbf{k}_q}}{\omega - \Omega_\nu(\mathbf{k}_q) - \epsilon_{\mathbf{k}_p - \mathbf{k}_q} + i\eta} \right] \quad (2.19)$$

2.3.2 Spectral function

Finally, the spectral function is given by

$$A(\mathbf{k}_p, \omega) = \frac{1}{\pi} \frac{|\operatorname{Im} \Sigma(\mathbf{k}_p, \omega)|}{(\omega - \epsilon_{\mathbf{k}_p} - \operatorname{Re} \Sigma(\mathbf{k}_p, \omega))^2 + (\operatorname{Im} \Sigma(\mathbf{k}_p, \omega))^2} \quad (2.20)$$

2.4 GW+C

2.4.1 Cumulant

By relating the Dyson equation to the Taylor series expansion of the exponential (both to first order), we can write:

$$\mathbf{G}^0(t)\mathbf{C}(t) = \iint dt_1 dt_2 \mathbf{G}^0(t - t_1) \Sigma^c(t_1 - t_2) \mathbf{G}^0(t_2) \quad (2.21)$$

We know that all of the operators are diagonal in momentum space for the UEG, so insertion of the resolution of the identity just gives us:

$$\mathbf{G}^0(\mathbf{p}, t) \mathbf{C}(\mathbf{p}, t) = \iint dt_1 dt_2 \mathbf{G}^0(\mathbf{p}, t - t_1) \Sigma^c(\mathbf{p}, t_1 - t_2) \mathbf{G}^0(\mathbf{p}, t_2) \quad (2.22)$$

$$= \int \frac{d\omega}{2\pi} e^{-i\omega t} \mathbf{G}^0(\mathbf{p}, \omega) \Sigma^c(\mathbf{p}, \omega) \mathbf{G}^0(\mathbf{p}, \omega) \quad (2.23)$$

$$\Rightarrow \mathbf{C}(\mathbf{p}, t) = i \int \frac{d\omega}{2\pi} \frac{\Sigma^c(\mathbf{p}, \omega + \epsilon_{\mathbf{p}}^{HF})}{(\omega + i\eta)^2} e^{-i\omega t} \quad (2.24)$$

$$= i \int \frac{d\omega}{2\pi} \frac{1}{(\omega + i\eta)^2} e^{-i\omega t} \left\{ \sum_{\mathbf{q}} \sum_{\nu}^{\text{RPA}} \underbrace{\frac{4\pi}{|\mathbf{q}|^2} |\rho_{\nu}(\mathbf{q})|^2}_{M_{q\nu}^2} \left[\frac{f_{\mathbf{p}-\mathbf{q}}}{\underbrace{\omega + \Omega_{\nu}(\mathbf{q}) + (\epsilon_{\mathbf{p}} - \epsilon_{\mathbf{p}-\mathbf{q}}) + i\eta}_{-\Delta_{q\nu}^{\text{occ}}}} \right. \right. \quad (2.25)$$

$$\left. + \frac{1 - f_{\mathbf{p}-\mathbf{q}}}{\underbrace{\omega - \Omega_{\nu}(\mathbf{q}) + (\epsilon_{\mathbf{p}} - \epsilon_{\mathbf{p}-\mathbf{q}}) + i\eta}_{-\Delta_{q\nu}^{\text{virt}}}} \right\} \\ = i \sum_{q\nu} M_{q\nu}^2 \int \frac{d\omega}{2\pi} e^{-i\omega t} \left[\frac{f_{\mathbf{p}-\mathbf{q}}}{(\omega + i\eta)^2 (\omega - \Delta_{q\nu}^{\text{occ}})} + \frac{1 - f_{\mathbf{p}-\mathbf{q}}}{(\omega + i\eta)^2 (\omega - \Delta_{q\nu}^{\text{virt}})} \right] \quad (2.26)$$

$$= \sum_{q\nu} \zeta_{\mathbf{p}q\nu}^{\text{occ}} [e^{-i\Delta_{q\nu}^{\text{occ}} t} - 1 + i\Delta_{q\nu}^{\text{occ}} t] + \sum_{q\nu} \zeta_{\mathbf{p}q\nu}^{\text{virt}} [e^{-i\Delta_{q\nu}^{\text{virt}} t} - 1 + i\Delta_{q\nu}^{\text{virt}} t] \quad (2.27)$$

For the final expression, we have defined $\zeta_{\mathbf{p}q\nu}^{\text{occ}} = \left(\frac{f_{\mathbf{p}-\mathbf{q}} M_{q\nu}}{\Delta_{q\nu}^{\text{occ}}} \right)^2$ and $\zeta_{\mathbf{p}q\nu}^{\text{virt}} = \left(\frac{(1-f_{\mathbf{p}-\mathbf{q}}) M_{q\nu}}{\Delta_{q\nu}^{\text{virt}}} \right)^2$. This allows us to arrive at the something similar to the Landau form of the cumulant.

A few notes on how to evaluate the contour integral: there is a double pole at $\omega_1 = -i\eta$ and a simple pole at $\omega_2 = -\Delta - i\eta$. Closing the contour in the lower half-plane because $\text{Im}(\omega_1), \text{Im}(\omega_2) < 0$, and applying Cauchy's residue theorem, leads to

$$\int \frac{d\omega}{2\pi} e^{-i\omega t} \frac{1}{(\omega - \omega_1)^2} \frac{1}{\omega - \omega_2} = (-i) \left\{ \left[\partial_{\omega} \left(\frac{e^{-i\omega t}}{\omega - \omega_2} \right) \right]_{\omega=\omega_1} + \left[\frac{e^{-i\omega t}}{(\omega - \omega_1)^2} \right]_{\omega=\omega_2} \right\} \quad (2.28)$$

$$= \frac{(-i)}{(\omega_1 - \omega_2)^2} \{ [(-it)(\omega_1 - \omega_2) - 1] e^{-i\omega_1 t} + e^{-i\omega_2 t} \} \quad (2.29)$$

$$\Rightarrow \int \frac{d\omega}{2\pi} e^{-i\omega t} \frac{1}{[\omega - (0 - i\eta)]^2} \frac{f}{\omega - \Delta} = \frac{-if}{\Delta^2} (e^{-i\Delta t} + i\Delta t - 1) \quad (2.30)$$

2.4.2 Green's function

Now, we plug in our derived expression for $C(\mathbf{p}, t)$ into the cumulant ansatz for the retarded Green's function:

$$G^{GW+C}(\mathbf{p}, t) = G^{HF}(\mathbf{p}, t) e^{C(\mathbf{p}, t)} \quad (2.31)$$

$$= -i\Theta(t) e^{-i\epsilon_{\mathbf{p}}^{HF} t + C(\mathbf{p}, t)} \quad (2.32)$$

$$= -i\Theta(t) e^{-i\epsilon_{\mathbf{p}}^{HF} t + \sum_{\mathbf{q}\nu} \zeta_{\mathbf{p}\mathbf{q}\nu}^{\text{occ}} (e^{-i\Delta_{\mathbf{q}\nu}^{\text{occ}} t} + i\Delta_{\mathbf{q}\nu}^{\text{occ}} t - 1) + \sum_{\mathbf{q}\nu} \zeta_{\mathbf{p}\mathbf{q}\nu}^{\text{virt}} (e^{-i\Delta_{\mathbf{q}\nu}^{\text{virt}} t} + i\Delta_{\mathbf{q}\nu}^{\text{virt}} t - 1)} \quad (2.33)$$

$$= -i\Theta(t) Z_{\mathbf{p}}^{QP} e^{-i\epsilon_{\mathbf{p}}^{QP} t} e^{\sum_{\mathbf{q}\nu} \zeta_{\mathbf{p}\mathbf{q}\nu}^{\text{occ}} e^{-i\Delta_{\mathbf{q}\nu}^{\text{occ}} t} + \sum_{\mathbf{q}\nu} \zeta_{\mathbf{p}\mathbf{q}\nu}^{\text{virt}} e^{-i\Delta_{\mathbf{q}\nu}^{\text{virt}} t}} \quad (2.34)$$

$$(2.35)$$

where we have the weight of the quasiparticle peak $Z_{\mathbf{p}}^{QP} = \exp\left(-\sum_{\mathbf{q}\nu} \zeta_{\mathbf{p}\mathbf{q}\nu}^{\text{occ}} - \sum_{\mathbf{q}\nu} \zeta_{\mathbf{p}\mathbf{q}\nu}^{\text{virt}}\right)$ and the quasiparticle energy $\epsilon_{\mathbf{p}}^{QP} = \epsilon_{\mathbf{p}}^{HF} - \left(\sum_{\mathbf{q}\nu} \zeta_{\mathbf{p}\mathbf{q}\nu}^{\text{occ}} \Delta_{\mathbf{q}\nu}^{\text{occ}} + \sum_{\mathbf{q}\nu} \zeta_{\mathbf{p}\mathbf{q}\nu}^{\text{virt}} \Delta_{\mathbf{q}\nu}^{\text{virt}}\right)$.

We pause to make some important connections. Notice

$$Z_{\mathbf{p}}^{QP} = \exp\left(-\sum_{\mathbf{q}\nu} \zeta_{\mathbf{p}\mathbf{q}\nu}^{\text{occ}} - \sum_{\mathbf{q}\nu} \zeta_{\mathbf{p}\mathbf{q}\nu}^{\text{virt}}\right) \quad (2.36)$$

$$= \exp\left(-\sum_{\mathbf{q}\nu} \left(\frac{f_{\mathbf{p}-\mathbf{q}} M_{\mathbf{q}\nu}}{\Delta_{\mathbf{q}\nu}^{\text{occ}}}\right)^2 - \sum_{\mathbf{q}\nu} \left(\frac{(1-f_{\mathbf{p}-\mathbf{q}}) M_{\mathbf{q}\nu}}{\Delta_{\mathbf{q}\nu}^{\text{virt}}}\right)^2\right) \quad (2.37)$$

$$= \exp\left(\left[\frac{\partial \Sigma^c(\mathbf{p}, \omega)}{\partial \omega}\right]_{\omega=\epsilon_{\mathbf{p}}^{HF}}\right) \quad (2.38)$$

and

$$\epsilon_{\mathbf{p}}^{QP} = \epsilon_{\mathbf{p}}^{HF} - \left(\sum_{\mathbf{q}\nu} \zeta_{\mathbf{p}\mathbf{q}\nu}^{\text{occ}} \Delta_{\mathbf{q}\nu}^{\text{occ}} + \sum_{\mathbf{q}\nu} \zeta_{\mathbf{p}\mathbf{q}\nu}^{\text{virt}} \Delta_{\mathbf{q}\nu}^{\text{virt}}\right) \quad (2.39)$$

$$= \epsilon_{\mathbf{p}}^{HF} - \left(\sum_{\mathbf{q}\nu} \frac{f_{\mathbf{p}-\mathbf{q}} M_{\mathbf{q}\nu}^2}{\Delta_{\mathbf{q}\nu}^{\text{occ}}} + \sum_{\mathbf{q}\nu} \frac{(1-f_{\mathbf{p}-\mathbf{q}}) M_{\mathbf{q}\nu}^2}{\Delta_{\mathbf{q}\nu}^{\text{virt}}}\right) \quad (2.40)$$

$$= \epsilon_{\mathbf{p}}^{HF} + \Sigma^c(\mathbf{p}, \epsilon_{\mathbf{p}}^{HF}) \quad (2.41)$$

where we have used the fact that $\Sigma^c(\mathbf{p}, \omega) = \sum_{\mathbf{q}\nu} \frac{f_{\mathbf{p}-\mathbf{q}} M_{\mathbf{q}\nu}^2}{\omega + \Omega_{\nu}(\mathbf{q}) - \epsilon_{\mathbf{p}-\mathbf{q}}} + \sum_{\mathbf{q}\nu} \frac{(1-f_{\mathbf{p}-\mathbf{q}}) M_{\mathbf{q}\nu}^2}{\omega - \Omega_{\nu}(\mathbf{q}) - \epsilon_{\mathbf{p}-\mathbf{q}}} \implies \left[\frac{\partial \Sigma^c(\mathbf{p}, \omega)}{\partial \omega}\right]_{\omega=\epsilon_{\mathbf{p}}^{HF}} = -\sum_{\mathbf{q}\nu} \left(\frac{f_{\mathbf{p}-\mathbf{q}} M_{\mathbf{q}\nu}}{\Delta_{\mathbf{q}\nu}^{\text{occ}}}\right)^2 - \sum_{\mathbf{q}\nu} \left(\frac{(1-f_{\mathbf{p}-\mathbf{q}}) M_{\mathbf{q}\nu}}{\Delta_{\mathbf{q}\nu}^{\text{virt}}}\right)^2$.

Next, we want to perform a Fourier transform.

$$G^{GW+C}(\mathbf{p}, \omega) = \int_{-\infty}^{\infty} dt e^{i\omega t} G^{GW+C}(\mathbf{p}, t) \quad (2.42)$$

$$= -iZ_{\mathbf{p}}^{QP} \int_0^{\infty} dt e^{i(\omega - \epsilon_{\mathbf{p}}^{QP})t} e^{\sum_{q\nu} \zeta_{\mathbf{p}q\nu}^{\text{occ}} e^{-i\Delta_{q\nu}^{\text{occ}} t} + \sum_{q\nu} \zeta_{\mathbf{p}q\nu}^{\text{virt}} e^{-i\Delta_{q\nu}^{\text{virt}} t}} \quad (2.43)$$

$$= -iZ_{\mathbf{p}}^{QP} \int_0^{\infty} dt e^{i(\omega - \epsilon_{\mathbf{p}}^{QP})t} \left(1 + \sum_{q\nu} \zeta_{\mathbf{p}q\nu}^{\text{occ}} e^{-i\Delta_{q\nu}^{\text{occ}} t} + \sum_{q\nu} \zeta_{\mathbf{p}q\nu}^{\text{virt}} e^{-i\Delta_{q\nu}^{\text{virt}} t} + \dots \right) \quad (2.44)$$

$$= -iZ_{\mathbf{p}}^{QP} \int_0^{\infty} dt e^{[-\eta + i(\omega - \epsilon_{\mathbf{p}}^{QP})t]} \quad (2.45)$$

$$- iZ_{\mathbf{p}}^{QP} \sum_{q\nu} \zeta_{\mathbf{p}q\nu}^{\text{occ}} \int_0^{\infty} dt e^{[-\eta + i(\omega - \epsilon_{\mathbf{p}}^{QP} - \Delta_{q\nu}^{\text{occ}})t]}$$

$$- iZ_{\mathbf{p}}^{QP} \sum_{q\nu} \zeta_{\mathbf{p}q\nu}^{\text{virt}} \int_0^{\infty} dt e^{[-\eta + i(\omega - \epsilon_{\mathbf{p}}^{QP} - \Delta_{q\nu}^{\text{virt}})t]} + \dots$$

$$= \frac{Z_{\mathbf{p}}^{QP}}{\omega - \epsilon_{\mathbf{p}}^{QP} + i\eta} + \sum_{q\nu} \frac{Z_{\mathbf{p}}^{QP} \zeta_{\mathbf{p}q\nu}^{\text{occ}}}{\omega - \epsilon_{\mathbf{p}}^{QP} - \Delta_{q\nu}^{\text{occ}} + i\eta} + \sum_{q\nu} \frac{Z_{\mathbf{p}}^{QP} \zeta_{\mathbf{p}q\nu}^{\text{virt}}}{\omega - \epsilon_{\mathbf{p}}^{QP} - \Delta_{q\nu}^{\text{virt}} + i\eta} + \dots \quad (2.46)$$

$$= \frac{Z_{\mathbf{p}}^{QP}}{\omega - \epsilon_{\mathbf{p}}^{QP} + i\eta} + \sum_{q\nu} \frac{Z_{\mathbf{p}q\nu}^{\text{occ-sat}}}{\omega - \epsilon_{\mathbf{p}q\nu}^{\text{occ-sat}} + i\eta} + \sum_{q\nu} \frac{Z_{\mathbf{p}q\nu}^{\text{virt-sat}}}{\omega - \epsilon_{\mathbf{p}q\nu}^{\text{virt-sat}} + i\eta} + \dots \quad (2.47)$$

where we define the satellite energies $\epsilon_{\mathbf{p}q\nu}^{\text{occ-sat}} = \epsilon_{\mathbf{p}}^{QP} + \Delta_{q\nu}^{\text{occ}}$ and $\epsilon_{\mathbf{p}q\nu}^{\text{virt-sat}} = \epsilon_{\mathbf{p}}^{QP} + \Delta_{q\nu}^{\text{virt}}$, as well as the satellite weights $Z_{\mathbf{p}q\nu}^{\text{occ-sat}} = Z_{\mathbf{p}}^{QP} \zeta_{\mathbf{p}q\nu}^{\text{occ}}$ and $Z_{\mathbf{p}q\nu}^{\text{virt-sat}} = Z_{\mathbf{p}}^{QP} \zeta_{\mathbf{p}q\nu}^{\text{virt}}$.

2.4.3 Spectral function

The spectral function is obtained as (the virtual satellites spectral function, whose derivation will mirror that of the occupied satellites, are omitted for the sake of brevity)

$$A^{GW+C}(\mathbf{p}, \omega) = -\frac{1}{\pi} \text{Im } G^{GW+C}(\mathbf{p}, \omega) \quad (2.48)$$

$$= -\frac{1}{\pi} \text{Im} \left[\frac{Z_{\mathbf{p}}^{QP}}{\omega - \epsilon_{\mathbf{p}}^{QP} + i\eta} + \sum_{q\nu} \frac{Z_{\mathbf{pq}\nu}^{\text{occ-sat}}}{\omega - \epsilon_{\mathbf{pq}\nu}^{\text{occ-sat}} + i\eta} + \dots \right] \quad (2.49)$$

$$= -\frac{1}{\pi} \text{Im} \left[\frac{\text{Re } Z_{\mathbf{p}}^{QP} + i \text{Im } Z_{\mathbf{p}}^{QP}}{\omega - \text{Re } \epsilon_{\mathbf{p}}^{QP} + i(\eta - \text{Im } \epsilon_{\mathbf{p}}^{QP})} + \sum_{q\nu} \frac{\text{Re } Z_{\mathbf{pq}\nu}^{\text{occ-sat}} + i \text{Im } Z_{\mathbf{pq}\nu}^{\text{occ-sat}}}{\omega - \text{Re } \epsilon_{\mathbf{pq}\nu}^{\text{occ-sat}} + i(\eta - \text{Im } \epsilon_{\mathbf{pq}\nu}^{\text{occ-sat}})} + \dots \right] \quad (2.50)$$

$$= -\frac{1}{\pi} \text{Im} \left[\frac{(\text{Re } Z_{\mathbf{p}}^{QP} + i \text{Im } Z_{\mathbf{p}}^{QP}) (\omega - \text{Re } \epsilon_{\mathbf{p}}^{QP} - i(\eta - \text{Im } \epsilon_{\mathbf{p}}^{QP}))}{(\omega - \text{Re } \epsilon_{\mathbf{p}}^{QP})^2 + (\text{Im } \epsilon_{\mathbf{p}}^{QP})^2} \right] \quad (2.51)$$

$$+ \sum_{q\nu} \frac{(\text{Re } Z_{\mathbf{pq}\nu}^{\text{occ-sat}} + i \text{Im } Z_{\mathbf{pq}\nu}^{\text{occ-sat}}) (\omega - \text{Re } \epsilon_{\mathbf{pq}\nu}^{\text{occ-sat}} - i(\eta - \text{Im } \epsilon_{\mathbf{pq}\nu}^{\text{occ-sat}}))}{(\omega - \text{Re } \epsilon_{\mathbf{pq}\nu}^{\text{occ-sat}})^2 + (\text{Im } \epsilon_{\mathbf{pq}\nu}^{\text{occ-sat}})^2} + \dots \quad (2.52)$$

$$= -\frac{1}{\pi} \left[\frac{(\text{Re } Z_{\mathbf{p}}^{QP}) (\text{Im } \epsilon_{\mathbf{p}}^{QP}) + (\text{Im } Z_{\mathbf{p}}^{QP}) (\omega - \text{Re } \epsilon_{\mathbf{p}}^{QP})}{(\omega - \text{Re } \epsilon_{\mathbf{p}}^{QP})^2 + (\text{Im } \epsilon_{\mathbf{p}}^{QP})^2} \right] \quad (2.53)$$

$$+ \sum_{q\nu} \frac{(\text{Re } Z_{\mathbf{pq}\nu}^{\text{occ-sat}}) (\text{Im } \epsilon_{\mathbf{pq}\nu}^{\text{occ-sat}}) + (\text{Im } Z_{\mathbf{pq}\nu}^{\text{occ-sat}}) (\omega - \text{Re } \epsilon_{\mathbf{pq}\nu}^{\text{occ-sat}})}{(\omega - \text{Re } \epsilon_{\mathbf{pq}\nu}^{\text{occ-sat}})^2 + (\text{Im } \epsilon_{\mathbf{pq}\nu}^{\text{occ-sat}})^2} + \dots \quad (2.54)$$

Chapter 3

TDVP

We start with the definition of the action functional:

$$S = \int_{t_1}^{t_2} dt L(\psi, \bar{\psi}) \quad (3.1)$$

where Dirac took the Lagrangian as $L(\psi, \bar{\psi}) = \langle \psi(t) | i \frac{\partial}{\partial t} - H | \psi(t) \rangle$. It can be shown that taking arbitrary independent variations of S with respect to $|\psi\rangle$ and $\langle\psi|$ and demanding that the functional be stationary yields the time-dependent Schrödinger equation (and its complex conjugate). This Lagrangian is real if the wave function is normalized, but it is convenient to not have this restriction, but in that case the Lagrangian becomes complex. To avoid this complication, we define a new real Lagrangian

$$L(\psi, \bar{\psi}) = \frac{i}{2} \frac{\langle \psi | \dot{\psi} \rangle - \langle \dot{\psi} | \psi \rangle}{\langle \psi | \psi \rangle} - \frac{\langle \psi | H | \psi \rangle}{\langle \psi | \psi \rangle} \quad (3.2)$$

Note that this new Lagrangian reduces to the old one if the wave function is normalized. We can now derive the equations of motion obtained from requiring the action with the new Lagrangian L to be stationary,

$$0 = \delta S = \int \delta L dt = \int dt \left(\frac{1}{2} \frac{\{ \langle \delta \psi | \dot{\psi} \rangle + \langle \psi | \delta \dot{\psi} \rangle - \langle \delta \dot{\psi} | \psi \rangle - \langle \dot{\psi} | \delta \psi \rangle \}}{\langle \psi | \psi \rangle} \right) \quad (3.3)$$

$$- \frac{\delta \langle \psi | H | \psi \rangle}{\langle \psi | \psi \rangle} - \left(\frac{i}{2} \frac{\langle \psi | \dot{\psi} \rangle - \langle \dot{\psi} | \psi \rangle}{\langle \psi | \psi \rangle} - \frac{\langle \psi | H | \psi \rangle}{\langle \psi | \psi \rangle} \right) \frac{\delta \langle \psi | \psi \rangle}{\langle \psi | \psi \rangle} \right) \\ = \int dt \left(\frac{i \langle \delta \psi | \dot{\psi} \rangle - \langle \delta \psi | H | \psi \rangle}{\langle \psi | \psi \rangle} - \frac{\langle \psi | i \partial / \partial t - H | \psi \rangle}{\langle \psi | \psi \rangle^2} \langle \delta \psi | \psi \rangle \right) + \text{c.c.} \quad (3.4)$$

$$\implies \left(i \frac{\partial}{\partial t} - H \right) |\psi\rangle = \frac{\langle \psi | i \partial / \partial t - H | \psi \rangle}{\langle \psi | \psi \rangle} |\psi\rangle \quad (3.5)$$

Briefly, doing some integration by parts allowed us to go from the first to the second step, and then by assuming that the variations of the bra and ket can be arbitrary and independent we get the third equation. Now, if we tack on a time-dependent phase factor to the wave

function to get

$$|\phi(t)\rangle = |\psi(t)\rangle \exp \left[i \int^t d\tau \frac{\langle \psi | i\partial_\tau - H | \psi \rangle}{\langle \psi | \psi \rangle} \right] \quad (3.6)$$

it is normalized and satisfies the TDSE.¹ So we have shown that this new Lagrangian formulation allows us to work with wave functions that are not normalized and can differ by a phase.

¹We can start by computing the time derivative as

$$i \frac{\partial}{\partial t} |\phi\rangle = i \frac{\partial}{\partial t} \left(|\psi\rangle e^{i \int^t \frac{\langle \psi | i\partial_\tau - H | \psi \rangle}{\langle \psi | \psi \rangle} d\tau} \right) \quad (3.7)$$

$$= i(\partial_t |\psi\rangle) e^{i \int^t \dots} + |\psi\rangle \underbrace{i \partial_t e^{i \int^t \dots}}_{-\frac{\langle \psi | i\partial_t - H | \psi \rangle}{\langle \psi | \psi \rangle} e^{i \int^t \dots}} \quad (3.8)$$

$$= e^{i \int^t \dots} \left[i \partial_t |\psi\rangle - \frac{\langle \psi | i\partial_t - H | \psi \rangle}{\langle \psi | \psi \rangle} |\psi\rangle \right] \quad (3.9)$$

$$= e^{i \int^t \dots} [H |\psi\rangle] = H |\phi\rangle \quad (3.10)$$

Bibliography

- [1] Ferdi Aryasetiawan and Fredrik Nilsson. *Downfolding Methods in Many-Electron Theory*. AIP Publishing LLC. ISBN 978-0-7354-2246-9. doi: 10.1063/9780735422490. URL <https://doi.org/10.1063/9780735422490>. eprint: <https://pubs.aip.org/book-pdf/12252618/9780735422490.pdf>.
- [2] Oliver J Backhouse, Marcus K Allen, Charles JC Scott, and George H Booth. Self-consistent gw via conservation of spectral moments. *Journal of Chemical Theory and Computation*, 2025.
- [3] Sylvia J Bintrim and Timothy C Berkelbach. Full-frequency gw without frequency. *The Journal of Chemical Physics*, 154(4), 2021.
- [4] Giampaolo Co'. Introducing the random phase approximation theory. *Universe*, 9(3): 141, 2023.
- [5] Filipp Furche. On the density matrix based approach to time-dependent density functional response theory. *The Journal of Chemical Physics*, 114(14):5982–5992, 2001.
- [6] Weiwei Gao, Zhao Tang, Jijun Zhao, and James R Chelikowsky. Efficient full-frequency gw calculations using a lanczos method. *Physical Review Letters*, 132(12):126402, 2024.
- [7] Dorothea Golze, Marc Dvorak, and Patrick Rinke. The GW Compendium: A Practical Guide to Theoretical Photoemission Spectroscopy. *Frontiers in Chemistry*, 7, 2019. ISSN 2296-2646. URL <https://www.frontiersin.org/articles/10.3389/fchem.2019.00377>.
- [8] Giovanni Onida, Lucia Reining, and Angel Rubio. Electronic excitations: density-functional versus many-body green’s-function approaches. *Rev. Mod. Phys.*, 74(2):601–659, June 2002.
- [9] DJ Rowe. Equations-of-motion method and the extended shell model. *Reviews of Modern Physics*, 40(1):153, 1968.
- [10] Tobias Sander, Emanuele Maggio, and Georg Kresse. Beyond the tamm-dancoff approximation for extended systems using exact diagonalization. *Phys. Rev. B*, 92(4):045209, July 2015.
- [11] Charles JC Scott, Oliver J Backhouse, and George H Booth. A “moment-conserving” reformulation of gw theory. *The Journal of chemical physics*, 158(12), 2023.

- [12] Johannes Tölle and Garnet Kin-Lic Chan. Exact relationships between the gw approximation and equation-of-motion coupled-cluster theories through the quasi-boson formalism. *The Journal of Chemical Physics*, 158(12), 2023.
- [13] Johannes Tölle and Garnet Kin-Lic Chan. Ab-g0w0: A practical g0w0 method without frequency integration based on an auxiliary boson expansion. *The Journal of Chemical Physics*, 160(16), 2024.
- [14] Erik GCP Van Loon, Malte Rösner, Mikhail I Katsnelson, and Tim O Wehling. Random phase approximation for gapped systems: Role of vertex corrections and applicability of the constrained random phase approximation. *Physical Review B*, 104(4):045134, 2021.
- [15] Tianyu Zhu and Garnet Kin-Lic Chan. All-electron gaussian-based g_0w_0 for valence and core excitation energies of periodic systems. *arXiv [cond-mat.mtrl-sci]*, July 2020.