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Derivations for Personal Learning

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October 6, 2025

Chapter 1

Dyson to GQME: 12/13

The Generalized Quantum Master Equation (GQME) is given by

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

where the correlation function is defined as

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

the higher-order moments are

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

with the auxiliary kernels

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

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

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

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

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

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

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

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

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

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

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

with $\mathcal{L}$ being the Liouville superoperator with $\mathcal{L}\hat{\mu} = \left[\hat{H}, \hat{\mu}\right]$. 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 $\mathcal{K}_n(\mathcal{L}, \hat{\mu}) = \text{span}\{\hat{\mu}, (i\mathcal{L})\hat{\mu}, (i\mathcal{L})^2\hat{\mu}, \ldots, (i\mathcal{L})^{n-1}\hat{\mu}\}$, 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

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

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

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

Then we can construct the retarded Green's function as

$$G_R(t) = \Theta(t)\left(G^<(t) - G^>(t)\right) \tag{1.12}$$

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

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

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 $\hat{\boldsymbol{\mu}}$. Now, The idea is to define a composite operator vector

$$\hat{\boldsymbol{\mu}} \equiv \begin{pmatrix} \hat{\mu}_1 \\ \hat{\mu}_2 \end{pmatrix} = \begin{pmatrix} \hat{c} \\ \hat{c}^\dagger \end{pmatrix}, \tag{1.14}$$

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

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

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

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.

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

If we just consider the numerator, we see that

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

Considering just the first term

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

and the second term

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

which can be summarized as

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

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

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

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

Now come if we consider the higher-order moments

$$\Omega_n \equiv \frac{((i\mathcal{L})^n \hat{\boldsymbol{\mu}}, \hat{\boldsymbol{\mu}})}{(\hat{\boldsymbol{\mu}}, \hat{\boldsymbol{\mu}})} = \frac{(i)^n \, (\mathcal{L}^n \hat{\boldsymbol{\mu}}, \hat{\boldsymbol{\mu}})}{(\hat{\boldsymbol{\mu}}, \hat{\boldsymbol{\mu}})} = (i)^n \Big([\hat{H}, [\hat{H}, [\hat{H}, \cdots, \hat{\boldsymbol{\mu}}]]] \cdots\Big) \quad (1.25)$$

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

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

and the memory kernel

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

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

Chapter 2

UEG

2.1 MF

Even before doing HF, I generate my basis of plain waves, and they're we vectors in 3d are just a list of anteaters, three entries long. From HF, I get a set of MO coefficients $C_{\mu p}$ and orbital energies ϵ_p.

2.2 RPA

I am most familiar with doing this by just diagonalizing the Casida equation, which in the UEG looks like

$$\begin{pmatrix} \boldsymbol{A} & \boldsymbol{B} \\ -\boldsymbol{B} & -\boldsymbol{A} \end{pmatrix} \begin{pmatrix} \boldsymbol{X} & \boldsymbol{Y} \\ \boldsymbol{Y} & \boldsymbol{X} \end{pmatrix} \begin{pmatrix} \boldsymbol{\Omega} & \boldsymbol{0} \\ \boldsymbol{0} & -\boldsymbol{\Omega} \end{pmatrix} = \begin{pmatrix} \boldsymbol{X} & \boldsymbol{Y} \\ \boldsymbol{Y} & \boldsymbol{X} \end{pmatrix} \tag{2.1}$$

The $\boldsymbol{A}$ and $\boldsymbol{B}$ matrices are defined as

$$A_{ia,jb} = (\epsilon_a - \epsilon_i)\,\delta_{ij}\delta_{ab} + \mathcal{K}_{ia,bj} \tag{2.2}$$

$$B_{ia,jb} = \mathcal{K}_{ia,jb} \tag{2.3}$$

Is it not going to be enough to loop overall the occupied states i, j and then for each occupied state, loop over all the virtual states a, b? This would determine the momentum index $\boldsymbol{q}$, which is the difference between the virtual and occupied states, $\boldsymbol{q} = \boldsymbol{k}_a - \boldsymbol{k}_i = \boldsymbol{k}_b - \boldsymbol{k}_j$. So after this procedure, I would in effect be sampling all $\boldsymbol{q}$. If I do it this way do I have to build a Casida matrix for each $\boldsymbol{q}$ separately, or can I just build one big Casida matrix. If so, then why? If I don't do this, I would just get a set of excitation energies and transition densities over all of the $\boldsymbol{q}$ values, but I wouldn't know which excitation energy corresponds to which $\boldsymbol{q}$. And then it is process sly these excitation enteritis and transition densities that go into building the GW correlation self-energy as:

$$\Sigma^{\text{corr}}_{pp}(\omega) = \sum_{\mu}^{\text{RPA}} \left(\sum_{i}^{\text{occupied}} \frac{w^{\mu}_{pi} w^{\mu}_{ip}}{\omega - (\epsilon_i - \Omega_\mu)} + \sum_{a}^{\text{virtual}} \frac{w^{\mu}_{pa} w^{\mu}_{ap}}{\omega - (\epsilon_a + \Omega_\mu)} \right) \tag{2.4}$$

I know that for the UEG, I really would be interested in $\Sigma^{\text{corr}}_{pp}(\boldsymbol{k}, \omega)$, but if I am interested in getting the spectral function $A(\boldsymbol{k}, \omega)$ for a certain $\boldsymbol{k}$ point, then I think I only need to compute $\Sigma^{\text{corr}}_{pp}(\boldsymbol{k}, \omega) \to G_{pp}(\boldsymbol{k}, \omega) \to A(\boldsymbol{k}, \omega)$ for that certain $\boldsymbol{k}$ point.

How do I determine $\mathcal{K}$ for UEG? In the ab-initio case, I just computed the ERIs in MO basis, and then selected the appropriate OV elements.

UEG

I am not sure for the UEG how to compute the occupied i, j and virtual indices a, b. I am interested in computing the spectral function for a certain state p with wavevector $\boldsymbol{q}$, so I think I only have to solve the above Casida eigenproblem at $\boldsymbol{q}$. And then while I construct the $A(\boldsymbol{q})$ and $B(\boldsymbol{q})$ matrices, I choose an occupied index i by simply looping over the occupied plane wave states in my basis, but I am not sure how to select the appropriate virtual state a. Do my choices of i and p uniquely determine what value the virtual index a is going to be, or do I have to manually loop over the virtual index a? If it is uniquely determined, how? Let's say that I have access to the k-space wave vectors of the HOMO index and the occupied orbital of interest. And then I am also unsure about how to compute the Coulomb Interaction Kernel that appears in the $A(\boldsymbol{q})$ and $B(\boldsymbol{q})$ matrices alike, but with the J and B parts of the ERIs in the Ab-Initio case flipped. What is the value of the Interaction Kernel in the UEG case for the RPA? And then, I want to do this first the brute force way, by actually denoting and adding or subtracting the plane wave indices instead of doing the fancy lookup table and things like that. I guess we can move to that once I have my base implementation solidified. Does it make any sense to make this direct approximation in the case of the UEG? As where $\chi_{\mathrm{RPA}}(\omega) = (\chi_0(\omega)^{-1} - \mathcal{K})^{-1}$, where $\chi_0(\omega)$ is the irreducible polarizability of the reference state.

Chapter 3

TDVP

We start with the definition of the action functional:

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

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 habe this restriction, but in that case the Lagrangian becomes complex. To avoid this complication, we define a new real Lagrangian

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

Note that this knew Lagrangian reduces to the old one one 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,

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

$$\left. - \frac{\delta\langle \psi | H | \psi \rangle}{\langle \psi \mid \psi \rangle} - \left(\frac{i}{2} \frac{\langle \psi \mid \dot{\psi} \rangle - \langle \dot{\psi} \mid \psi \rangle}{\langle \psi \mid \psi \rangle} - \frac{\langle \psi | H | \psi \rangle}{\langle \psi \mid \psi \rangle} \right) \frac{\delta\langle \psi \mid \psi \rangle}{\langle \psi \mid \psi \rangle} \right)$$

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

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

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 cat 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

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

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.

[1] We can start by computing the time derivative as

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

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

$$= e^{i\int^t\cdots}\left[i\partial_t|\psi\rangle - \frac{\langle\psi|i\partial_t - H|\psi\rangle}{\langle\psi|\psi\rangle}|\psi\rangle\right] \tag{3.9}$$

$$= e^{i\int^t\cdots}[H|\psi\rangle] = H|\phi\rangle \tag{3.10}$$

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