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Derivations for Personal Learning

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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

RPA

2.1 RPA Derivations

Here I will enumerate the different routes that can be taken to derive the RPA. See the review [4] for an excellent introduction.

2.1.1 Green's function approach

In this section we combined spacetime coordinates into a single index, i.e. $1 \equiv (t_1, \mathbf{x}_1)$. In the RPA, we approximate the four point kernel $\hat{\mathcal{K}}$ by just the two-point $\hat{\mathcal{U}}$ as

$$\hat{\mathcal{K}}^{\mathrm{RPA}}(1,2,3,4) = \hat{\mathcal{U}}(1,4)\left[\delta(1-2)\,\delta(3-4) - \delta(1-3)\,\delta(2-4)\right] \tag{2.1}$$

So the Dyson equation for the two-body Green's function becomes

$$\mathrm{G}(1,2,3,4) = \mathrm{G}^0(1,2,3,4) + \int d5d6d7d8\mathrm{G}^0(1,2,5,6)\,\hat{\mathcal{K}}(5,6,7,8)\,\mathrm{G}(7,8,3,4) \tag{2.2}$$

$$\tilde{\mathrm{G}}(1,2,3,4) = \mathrm{G}^0(1,2,3,4) \tag{2.3}$$

$$+ \int d5d6\mathrm{G}^0(1,2,5,6)\,\hat{\mathcal{U}}(5,6)\,\tilde{\mathrm{G}}(6,5,3,4) \tag{2.4}$$

$$- \int d5d6\mathrm{G}^0(1,2,5,6)\,\hat{\mathcal{U}}(5,6)\,\tilde{\mathrm{G}}(5,6,3,4) \tag{2.5}$$

where $\tilde{\mathrm{G}}$ is the RPA approximation of the Green's function and we identify that the first term is direct and the second term is exchange. After making the Fourier transform into the energy space and introducing the single particle basis ν, we get

$$\tilde{G}(\nu_1,\nu_2,\nu_3,\nu_4,E) = G^0(\nu_1,\nu_2,\nu_3,\nu_4,E) + \frac{1}{\hbar}\sum_{\bar{1},\bar{2},\bar{3},\bar{4}} G^0(\nu_1,\nu_2,\bar{1},\bar{2},E)\left[\hat{V}_{1234} - \hat{V}_{1423}\right]\tilde{G}(\bar{3},\bar{4},\nu_3,\nu_4,E) \tag{2.6}$$

where $\hat{V}_{1234} = \langle\bar{1}\bar{3}|\hat{V}|\bar{2}\bar{4}\rangle$ and $\hat{V}_{1423} = \langle\bar{1}\bar{2}|\hat{V}|\bar{4}\bar{3}\rangle$ and we have introduced $\hat{\mathcal{U}} = \frac{\hat{V}}{\hbar}$. Now, we note that the two body Green's function can be expressed as:

$$\frac{i}{\hbar}G\left(\nu_1,\nu_2,\nu_3,\nu_4,E\right) = \frac{1}{\langle\Psi_0 \mid \Psi_0\rangle}\sum_n\left[\frac{\langle\Psi_0|\,\hat{a}_{\nu_1}\hat{a}^+_{\nu_3}\,|\Psi_n\rangle\,\langle\Psi_n|\,\hat{a}_{\nu_2}\hat{a}^+_{\nu_4}\,|\Psi_0\rangle}{E-(E_n-E_0)-i\eta} - \frac{\langle\Psi_0|\,\hat{a}_{\nu_2}\hat{a}^+_{\nu_4}\,|\Psi_n\rangle\,\langle\Psi_n|\,\hat{a}_{\nu_1}\hat{a}^+_{\nu_3}\,|\Psi_0\rangle}{E+(E_n-E_0)+i\eta}\right] \tag{2.7}$$

so in particular, the form of the unperturbed Green's function, with $m,n\ldots$ and $i,j\ldots$ representing particle and hole indices respectively, is

$$G^0(m,i,j,n,E) = \hbar\frac{\delta_{ij}\delta_{mn}}{\epsilon_m-\epsilon_i-E-i\eta}, \tag{2.8}$$

$$G^0(i,m,n,j,E) = \hbar\frac{\delta_{ij}\delta_{mn}}{\epsilon_m-\epsilon_i+E-i\eta}, \tag{2.9}$$

$$G^0(m,i,n,j,E) = G^0(i,m,j,n,E) = 0. \tag{2.10}$$

Insertion of these identities into **??** gives rise to the equations

$$\sum_{q,l}\left\{\left[A_{miql}-E\delta_{m,q}\delta_{i,l}\right]\tilde{G}(q,l,j,n,E)+B_{miql}\tilde{G}(l,q,j,n,E)\right\} = \delta_{m,n}\delta_{i,j}, \tag{2.11}$$

$$\sum_{q,l}\left\{\left[A^*_{miql}+E\delta_{m,q}\delta_{i,l}\right]\tilde{G}(l,q,j,n,E)+B^*_{miql}\tilde{G}(q,l,j,n,E)\right\} = 0, \tag{2.12}$$

$$\sum_{q,l}\left\{\left[A_{miql}-E\right)\delta_{m,q}\delta_{i,l}\right]\tilde{G}(q,l,n,j,E)+B_{miql}\tilde{G}(l,q,n,j,E)\right\} = 0, \tag{2.13}$$

$$\sum_{q,l}\left\{\left[A^*_{miql}+E\delta_{m,q}\delta_{i,l}\right]\tilde{G}(l,q,n,j,E)+B^*_{miql}\tilde{G}(q,l,n,j)\right\} = \delta_{m,n}\delta_{i,j}, \tag{2.14}$$

with $A_{miql} = (\epsilon_m-\epsilon_i)\,\delta_{m,q}\delta_{i,l}+\bar{V}_{iqml}$ and $B_{miql} = -\bar{V}_{ilmq}$. Defining the matrices

$$G_1(E) \equiv \tilde{G}(m,i,j,n,E), \tag{2.15}$$

$$G_2(E) \equiv \tilde{G}(m,i,n,j,E), \tag{2.16}$$

$$G_3(E) \equiv \tilde{G}(i,m,j,n,E), \tag{2.17}$$

$$G_4(E) \equiv \tilde{G}(i,m,n,j,E) \tag{2.18}$$

and rewriting the equations in matrix form gives

$$\begin{pmatrix} A-E\mathbb{I} & B \\ B^* & A^*+E\mathbb{I}\end{pmatrix}\begin{pmatrix} G_1(E) & G_2(E) \\ G_3(E) & G_4(E)\end{pmatrix} = \begin{pmatrix}\mathbb{I} & 0 \\ 0 & \mathbb{I}\end{pmatrix} \tag{2.19}$$

The poles E of these RPA Green's functions are the RPA excitation energies. Because the value of the RPA Green's function goes to infinity at each of these poles, correspondingly, we must have that the matrix of coefficients goes to zero in these cases, implying that we can get the RPA excitation energies ω_n through a solution of the equation

$$\begin{pmatrix} A-\omega_n\mathbb{I} & B \\ B^* & A^*+\omega_n\mathbb{I}\end{pmatrix}\begin{pmatrix} X_n \\ \\ Y_n\end{pmatrix} = 0. \tag{2.20}$$

2.1.2 TDHF approach

See the review [4] for the derivation.

2.1.3 Equation of motion approach

The ideas here are based of [9]. The idea is to define an oscillator that satisfies

$$[H, O^\dagger] = \omega O^\dagger, \qquad [H, O] = -\omega O, \qquad [O, O^\dagger] = 1 \tag{2.21}$$

and it has the usual ladder properties. But we cannot have an ideal harmonic oscillator because there will not be an infinite number of excitations, so we define the operators as

$$O^\dagger = \sum_{n=0}^{m} (n+1)^{1/2} |n+1\rangle\langle n| + \sum_{p,q>m} C_{pq} |p\rangle\langle q| \tag{2.22}$$

where m is the maximum number of excitations, which gives

$$\left[H, O^\dagger\right] = \omega O^\dagger + P, \qquad [H, O] = -\omega O - P^\dagger, \qquad [O, O^\dagger] = 1 + Q \tag{2.23}$$

where

$$P|n\rangle = P^\dagger|n\rangle = Q|n\rangle = Q^\dagger|n\rangle = 0, \quad \text{all } n \leq m.$$

Now define an arbitrary operator R, so

$$\begin{aligned}
\langle\phi|[R,[H,O^\dagger]]|\phi\rangle &= \langle\phi|R[H,O^\dagger] + R^\dagger[H,O]|\phi\rangle && (2.24)\\
&= \langle\phi|R(\omega O^\dagger + P) + R^\dagger(-\omega O - P^\dagger)|\phi\rangle && (2.25)\\
&= \omega\langle\phi|RO^\dagger|\phi\rangle - \omega\langle\phi|R^\dagger O|\phi\rangle && (2.26)\\
&= \omega\left(\langle\phi|RO^\dagger|\phi\rangle - \langle\phi|R^\dagger O|\phi\rangle\right) && (2.27)\\
&= \omega\left(\langle\phi|RO^\dagger|\phi\rangle - \langle\phi|O^\dagger R|\phi\rangle^*\right) && (2.28)\\
&= \omega\left(\langle\phi|RO^\dagger|\phi\rangle - \langle\phi|O^\dagger R|\phi\rangle\right) && (2.29)\\
&= \omega\langle\phi|[R,O^\dagger]|\phi\rangle && (2.30)
\end{aligned}$$

and similarly,

$$\langle\phi|[R,[H,O]]|\phi\rangle = -\omega\langle\phi|[R,O]|\phi\rangle \tag{2.31}$$

These manipulations can introduce some significant computational savings. Notice how the first equation is the Hermitian conjugate of the second, so we make a savings by just considering the first. But Hermicity is not guaranteed for our approximate ground state $|\phi\rangle$, so we can define the double commutator

$$2\left[R, H, O^\dagger\right] = \left[R, \left[H, O^\dagger\right]\right] + \left[[R, H], O^\dagger\right] \tag{2.32}$$

and now

$$\langle\phi|\left[R, H, O^\dagger\right]|\phi\rangle = \omega\langle\phi|\left[R, O^\dagger\right]|\phi\rangle \tag{2.33}$$

Also, the commutator of two operators is of lower particle rank than the product, and hence its matrix elements require less knowledge of the wave functions, so we can get more bang for our buck by starting from an imperfect ϕ. Next we make that expansion in terms of a basis $\{\eta_\alpha\}$ with $\eta_{\bar{\alpha}^\dagger} \equiv \eta_\alpha$ into

$$O_k^\dagger = \sum_\alpha X_\alpha(\kappa)\eta_\alpha^\dagger \tag{2.34}$$

Equivalence to what Garnet did

Note that this is equivalent to what they did in Garnet's paper when they chose to describe via an auxiliary bosonic basis

$$\hat{b}_\nu^\dagger \approx \sum_Q^{N_{\mathrm{AB}}} C_\nu^Q \hat{b}_Q^\dagger \tag{2.35}$$

Then, they used the RI technique to get the C_ν^Q coefficients by defining

$$(ia \mid jb) \approx \sum_L R_{ia}^L R_{jb}^L \tag{2.36}$$

$$\implies C_\nu^Q = \sum_{LM} R_\nu^L \left[\mathbf{S}^{-1/2}\right]_{LM} P_M^Q \quad \text{with } S_{LM} = \sum_\nu R_\nu^L R_\nu^M = \sum_Q P_L^Q E_Q P_M^Q \tag{2.37}$$

Plugging **??** into **??** gives

$$\sum_\beta \underbrace{\langle\phi|\left[\eta_\alpha, H, \eta_\beta^\dagger\right]|\phi\rangle}_{M_{\alpha\beta}} X_\beta(\kappa) = \omega_\kappa \sum_\beta \underbrace{\langle\phi|\left[\eta_\alpha, \eta_\beta^\dagger\right]|\phi\rangle}_{N_{\alpha\beta}} X_\beta(\kappa) \tag{2.38}$$

The stability condition for real eigenvalues is that M is positive definite. Note that if we assume that $|\phi\rangle$ is the exact ground state, so $H|\phi\rangle = E_0|\phi\rangle$, and set up the excited state configurations $|\alpha\rangle = \eta_\alpha^\dagger|\phi\rangle, \quad \eta_\alpha|\phi\rangle = 0$ then a Tamm-Dancoff approximation gives

$$\sum_{\beta>0}\langle\alpha|H|\beta\rangle X_\beta(\kappa) = (E_0 + \omega_k)\sum_{\beta>0}\langle\alpha \mid \beta\rangle X_\beta(\kappa) \tag{2.39}$$

Particle-hole RPA

Now approximate $O^\dagger$ by restricting to particle–hole operators $\hat{O}^\dagger = \sum_{ai}\left(Y_{ai}\, a_a^\dagger a_i - Z_{ia}\, a_i^\dagger a_a\right)$. and identify two sets of basis operators $\eta_{ai}^\dagger = a_a^\dagger a_i, \eta_{ia}^\dagger = a_i^\dagger a_a$. In this basis the nonzero matrix elements are

$$A_{ai,bj} = \langle\phi|\left[a_i^\dagger a_a,\, H,\, a_b^\dagger a_j\right]|\phi\rangle \tag{2.40}$$

$$B_{ai,bj} = -\langle\phi|\left[a_i^\dagger a_a,\, H,\, a_j^\dagger a_b\right]|\phi\rangle \tag{2.41}$$

$$U_{ai,bj} = \langle\phi|\left[a_i^\dagger a_a,\, a_b^\dagger a_j\right]|\phi\rangle \tag{2.42}$$

Finally, collecting the amplitudes Y and Z into one vector, the coupled equations take on the block-matrix form

$$\begin{pmatrix} A & B \\ B^\dagger & A^* \end{pmatrix} \begin{pmatrix} Y \\ Z \end{pmatrix} = \omega \begin{pmatrix} U & 0 \\ 0 & -U^* \end{pmatrix} \begin{pmatrix} Y \\ Z \end{pmatrix}. \tag{2.43}$$

and by considering a Hamiltonian of the form

$$H = \sum_{\nu\nu'} T_{\nu\nu'} a_\nu^\dagger a_{\nu'} + \frac{1}{4} \sum_{\mu\nu\mu'\nu'} V_{\mu\nu\mu'\nu'} a_\mu^\dagger a_\nu^\dagger a_{\nu'} a_{\mu'} \tag{2.44}$$

where we choose the single-particle basis as the one which diagonalizes the single-particle Hamiltonian, so

$$\langle | a_a \left[H, a_b^\dagger \right] | \rangle = \delta_{ab} \varepsilon_a \tag{2.45}$$

$$\langle | a_i^\dagger \left[H, a_j \right] | \rangle = -\delta_{ij} \varepsilon_i. \tag{2.46}$$

we get the RPA form of

$$A_{aibj} = \delta_{ab}\delta_{ij} \left(\varepsilon_i - \varepsilon_a \right) + V_{ajib} \tag{2.47}$$

$$B_{aibj} = V_{abij} \tag{2.48}$$

$$U_{aibj} = \delta_{ab}\delta_{ij}. \tag{2.49}$$

Quasiparticle RPA

Here, we are starting from a correlated ground state. This is relevant for the BSE, where a GW calculation is performed first to get the quasiparticle energies, which form the correlated ground state. So it is more appropriate to define the excitation operator as

$$O^\dagger = \sum_{\mu\nu} \left(Y_{\mu\nu} \alpha_\mu^\dagger \alpha_\nu^\dagger + Z_{\mu\nu} \alpha_\mu \alpha_\nu \right) \tag{2.50}$$

Then, we define the quasi-particles by the Bogolyubov transformation

$$\alpha_\nu^\dagger = U_\nu a_\nu^\dagger - V_\nu a_\nu \tag{2.51}$$

$$\alpha_{\bar{\nu}}^\dagger = U_\nu a_{\bar{\nu}}^\dagger + V_\nu a_\nu \tag{2.52}$$

where U_ν and V_ν are positive real numbers subject to the normalization $U_\nu^2 + V_\nu^2 = 1$. Plugging in this ansatz for the excitation operator into the equations of motion **??** gives

$$A_{\mu\nu\mu'\nu'} = \langle \phi | \left[\alpha_\nu \alpha_\mu, H, \alpha_{\mu'}^\dagger \alpha_{\nu'}^\dagger \right] | \phi \rangle, \tag{2.53}$$

$$B_{\mu\nu\mu'\nu'} = \langle \phi | \left[\alpha_\nu \alpha_\mu, H, \alpha_{\mu'} \alpha_{\nu'} \right] | \phi \rangle, \tag{2.54}$$

$$U_{\mu\nu\mu'\nu'} = \langle \phi | \left[\alpha_\nu \alpha_\mu, \alpha_{\mu'}^\dagger \alpha_{\nu'}^\dagger \right] | \phi \rangle. \tag{2.55}$$

Idea

Take H^{eB} and plug it in here and see what happens.

This expands into

$$\begin{aligned}
A_{\mu\nu\mu'\nu'} =& (1-\hat{p}_{\mu\nu})\left[(1+\hat{p}_{\mu\nu}\hat{p}_{\mu'\nu'})\left(\langle\phi|\alpha_\nu\left[H,\alpha^\dagger_{\nu'}\right]|\phi\rangle\delta_{\mu\mu'}\right.\right.\\
&\left.-\langle\phi|\left\{\alpha_\nu,\left[H,\alpha^\dagger_{\nu'}\right]\right\}|\phi\rangle\langle\phi|\alpha^\dagger_{\mu'}\alpha_\mu|\phi\rangle\right)+\mathcal{V}^{(\mathrm{F})}_{\mu\nu\mu'\nu'}\\
&-\frac{1}{2}(1-\hat{p}_{\mu\nu})\langle\phi|\left[\alpha_\mu,\left\{\left[H,\alpha^\dagger_{\mu'}\right],\alpha^\dagger_{\nu'}\right\}\right]\alpha_\nu|\phi\rangle\\
&-\frac{1}{2}(1-\hat{p}_{\mu'\nu'})\langle\phi|\alpha^\dagger_{\nu'}\left[\alpha_\nu,\left\{\alpha_\mu,\left[H,\alpha^\dagger_{\mu'}\right]\right\}\right]|\phi\rangle\\
&-(1+\hat{p}_{\mu\nu}\hat{p}_{\mu'\nu'})\langle\phi|:\alpha^\dagger_{\mu'}\left\{\alpha_\nu,\left[H,\alpha^\dagger_{\nu'}\right]\right\}\alpha_\mu:|\phi\rangle\Big]\\
B_{\mu\nu\mu'\nu'} =& (1-\hat{p}_{\mu\nu})(1+\hat{p}_{\mu\nu}\hat{p}_{\mu'\nu'})\langle\phi|\{\alpha_\mu,[H,\alpha_{\mu'}]\}\rangle\langle\phi|\alpha_\nu\alpha_{\nu'}|\phi\rangle\\
&+\mathcal{V}^{(\mathrm{B})}_{\mu\nu\mu'\nu'}\\
&+\frac{1}{2}(1-\hat{p}_{\mu\nu})\langle\phi|\left[\alpha_\mu,\{[H,\alpha_{\mu'}],\alpha_{\nu'}\}\right]\alpha_\nu|\phi\rangle\\
&+\frac{1}{2}(1-\hat{p}_{\mu'\nu'})\langle\phi|\left[\alpha_\nu,\{\alpha_\mu,[H,\alpha_{\mu'}]\}\right]\alpha_{\nu'}|\phi\rangle\\
&+(1+\hat{p}_{\mu\nu}\hat{p}_{\mu'\nu'})\langle\phi|:\{\alpha_\mu,[H,\alpha_{\mu'}]\}\alpha_\nu\alpha_{\nu'}:|\phi\rangle\Big],\\
U_{\mu\nu\mu'\nu'} =& (1-\hat{p}_{\mu\nu})\left[\delta_{\mu\mu'}\delta_{\nu\nu'}-\delta_{\mu\mu'}\langle\phi|\alpha_{\nu'}\alpha_\nu|\phi\rangle-\delta_{\nu\nu'}\langle\phi|\alpha^\dagger_{\mu'}\alpha_\mu|\phi\rangle\right],
\end{aligned}\tag{2.56}$$

where $\hat{p}_{\mu\nu}$ is an operator which permutes the indices μ,ν. $\mathcal{V}^{(\mathrm{F})}_{\mu\nu\mu'\nu'}$ is the quasi-particle generalization of a forwardgoing particle-hole graph defined by

$$\mathcal{V}^{(\mathrm{F})}_{\mu\nu\mu'\nu'}=\frac{1}{2}\left\{\alpha_\nu,\left[\alpha_\mu,\left\{\left[H,\alpha^\dagger_{\mu'}\right],\alpha^\dagger_{\nu'}\right\}\right]\right\}\tag{2.57}$$

$\mathcal{V}^{(\mathrm{B})}_{\mu\nu\mu'\nu'}$ is the quasi-particle generalization of a backwardgoing particle-hole graph defined by

$$\mathcal{V}^{(\mathrm{B})}_{\mu\nu\mu'\nu'}=-\frac{1}{2}\{\alpha_\nu,[\alpha_\mu,\{[H,\alpha_{\mu'}],\alpha_{\nu'}\}]\}\tag{2.58}$$

If we demand that the correlated ground state takes a quasi-particle vacuum form, as

$$|\tilde{\phi}\rangle=\prod_{\nu>0}\left(U_\nu+V_\nu a^\dagger_\nu a^\dagger_{\overline{\nu}}\right)|-\rangle\tag{2.59}$$

where $|-\rangle$ is the bare vacuum, we find that

$$A_{\mu\nu\mu'\nu'}=(1-\hat{p}_{\mu\nu})\left[(1+\hat{p}_{\mu\nu}\hat{p}_{\mu'\nu'})\langle\tilde{\phi}|\alpha_\nu\left[H,\alpha^\dagger_{\nu'}\right]|\tilde{\phi}\rangle\delta_{\mu\mu'}+\mathcal{V}^{(\mathrm{F})}_{\mu\nu\mu'\nu'}\right].\tag{2.60}$$

Now a single-particle basis is chosen as the one which diagonalizes

$$\langle\tilde{\phi}|\left\{a_\nu,\left[H,{a_{\nu'}}^\dagger\right]\right\}|\tilde{\phi}\rangle=\delta_{\nu\nu'}(\varepsilon_\nu-\lambda).\tag{2.61}$$

where λ is the chemical potential. The coefficients U_ν and V_ν are defined by the requirement that

$$\langle\tilde{\phi}|\left\{\alpha_{\bar{\nu}}^\dagger,\left[H,\alpha_{\nu'}^\dagger\right]\right\}|\tilde{\phi}\rangle=\delta_{\nu'\nu}\left[\left({U_\nu}^2-{V_\nu}^2\right)\Delta_\nu-2U_\nu V_\nu\left(\varepsilon_\nu-\lambda\right)\right]=0 \tag{2.62}$$

where Δ_ν is the gap parameter defined by

$$\langle\tilde{\phi}|\left\{a_{\bar{\nu}},[H,a_{\nu'}]\right\}|\tilde{\phi}\rangle=\langle\tilde{\phi}|\left\{{a_\nu}^\dagger,\left[H,{a_{\bar{\nu}'}}^\dagger\right]\right\}|\tilde{\phi}\rangle=\delta_{\nu'}\Delta_\nu. \tag{2.63}$$

Explicitly,

$$\Delta_\nu=\frac{1}{2}\sum_\mu V_{\bar{\mu}\mu\bar{\nu}\bar{\nu}}\langle|a_{\bar{\mu}}^\dagger a_\mu^\dagger|\rangle=-\frac{1}{2}\sum_\mu V_{\bar{\mu}\mu\bar{\nu}}U_\mu V_\mu. \tag{2.64}$$

These equations, together with the normalization $U_\nu^2+V_\nu^2=1$ and the number equation $\langle\tilde{\phi}|n|\tilde{\phi}\rangle=A$, define the quasi-particles completely. The quasi-particle energy E_ν, defined by

$$\langle\tilde{\phi}|\left\{\alpha_\nu,\left[H,{\alpha_{\nu'}}^\dagger\right]\right\}|\tilde{\phi}\rangle=\delta_{\nu\nu'}\langle\tilde{\phi}|\left\{\alpha_\nu,\left[H,{\alpha_\nu}^\dagger\right]\right\}|\tilde{\phi}\rangle=\delta_{\nu\nu'}E_\nu, \tag{2.65}$$

is given by

$$E_\nu=\left(U_\nu^2-V_\nu^2\right)\left(\varepsilon_\nu-\lambda\right)+2U_\nu V_\nu\Delta_\nu \tag{2.66}$$

$$\tag{2.67}$$

With this choice of quasi-particle basis, the submatrices of the QRPA become

$$A_{\mu\nu\mu'\nu'}=\left(1-\hat{p}_{\mu\nu}\right)\left[\delta_{\mu\mu'}\delta_{\nu\nu'}\left(E_\mu+E_\nu\right)+{\mathcal{V}^{(\mathrm{F})}}_{\mu\nu\mu'\nu'}\right], \tag{2.68}$$

$$B_{\mu\nu\mu'\nu'}=\left(1-\hat{p}_{\mu\nu}\right){\mathcal{V}^{(\mathrm{B})}}_{\mu\nu\mu'\nu'}, \tag{2.69}$$

$$U_{\mu\nu\mu'\nu'}=\left(1-\hat{p}_{\mu\nu}\right)\delta_{\mu\mu'}\delta_{\nu\nu'}. \tag{2.70}$$

2.2 Extra

2.2.1 Comments about the correlation energy

The well known form is $E_c^{RPA}=\frac{1}{2}\mathrm{Tr}\left[\boldsymbol{\Omega}-\boldsymbol{A}\right]$. Now we will provide an interpretation for what this means. First, consider the fact that in the TDA, we are solving the eigenproblem $\boldsymbol{AX}=\boldsymbol{\Omega X}$, so E_c^{RPA} is actually zero. To understand why this is the case, consider that the TDA is defining the excited state as:

$$|\nu\rangle=\hat{O}_\nu^\dagger|\nu_0\rangle \tag{2.71}$$

, where ν_0 is the TDA ground state, where we used the definition

$$\hat{O}_\nu^\dagger=\sum_{ia}\left(X_{ai}^\nu a_a^\dagger a_i\right). \tag{2.72}$$

so actually the TDA ground state is equivalent to the "best" single Slater determinant predicted by our SCF procedure Φ_0 (HF) and thus it does not contain any correlation

by definition. Meanwhile, in the full RPA the excitation operator is defined as $\hat{O}_\nu^\dagger = \sum_{ia}\left(X_{ai}^\nu a_a^\dagger a_i + Y_{ai}^\nu a_i^\dagger a_a\right)$. The RPA ground state $|\nu_0\rangle$ is defined by $\hat{O}\,|\nu_0\rangle = 0$. So we see that it cannot be just a single Slater determinant, because

$$\hat{O}_\nu\,|\Phi_0\rangle = \sum_{ia}\left(X_{ai}^\nu a_a a_i^\dagger + Y_{ai}^\nu a_i a_a^\dagger\right)|\Phi_0\rangle \neq 0 \tag{2.73}$$

in which the second term cannot be zero.

2.2.2 Proving $\chi_{RPA} = \frac{\chi_0}{1-v\chi_0}$: 11/29

Trying direct evaluation

We know

$$\chi_{RPA}^{-1}(\omega) = \frac{1-v\chi_0}{\chi_0} = \chi_0^{-1} - \mathbf{v} \tag{2.74}$$

The Lehmann representation for χ_0 is

$$\chi_0\left(\mathbf{r},\mathbf{r}',\omega\right) = \sum_{ia}\frac{\psi_i(\mathbf{r})\psi_a^*(\mathbf{r}')\psi_i(\mathbf{r}')\psi_a^*(\mathbf{r})}{\omega\,\mathrm{sgn}\left(\epsilon_a-\epsilon_i-\mu\right) + \underbrace{\left(\epsilon_a-\epsilon_i\right)}_{\text{KS bare }\Omega_0} + i\eta\,\mathrm{sgn}\left(\epsilon_a-\epsilon_i-\mu\right)} \tag{2.75}$$

Let's start by considering the right-hand side of equation **??**. We know that in the particle-hole basis $\chi_0(\omega) = \chi_0^+(\omega) + \chi_0^-(\omega) = \begin{pmatrix}\chi_0^+(\omega) & 0\\ 0 & \chi_0^-(\omega)\end{pmatrix}$ is diagonal, where we define $\chi_0^\pm(\omega) = \frac{1}{\pm\omega+[\epsilon_a-\epsilon_i]}$ as the KS excitation/de-excitations polarizabilities.

$$\chi_0^{-1}(\omega) = \begin{pmatrix}\frac{1}{\chi_0^+(\omega)} & 0\\ 0 & \frac{1}{\chi_0^-(\omega)}\end{pmatrix} = \begin{pmatrix}\omega+[\epsilon_a-\epsilon_i] & 0\\ 0 & -\omega+[\epsilon_a-\epsilon_i]\end{pmatrix} \tag{2.76}$$

The Coulomb interaction in the particle-hole basis is

$$\mathbf{v} = \begin{pmatrix}\mathbf{v}^{++} & \mathbf{v}^{+-}\\ \mathbf{v}^{-+} & \mathbf{v}^{--}\end{pmatrix} \tag{2.77}$$

Note the permutational symmetries, so $v_{pq,rs}^{++} \equiv (ia|jb) = (ai|bj) \equiv v_{pq,rs}^{--}$ and $v_{pq,rs}^{+-} \equiv (ia|bj) = (ai|jb) \equiv v_{pq,rs}^{-+}$. So the RHS of equation **??** is

$$\chi_{RPA}^{-1}(\omega) = \chi_0^{-1}(\omega) - \mathbf{v} = \begin{pmatrix}(\omega+[\epsilon_a-\epsilon_i]) - \mathbf{v}^{++} & -\mathbf{v}^{+-}\\ -\mathbf{v}^{-+} & (-\omega+[\epsilon_a-\epsilon_i]) - \mathbf{v}^{--}\end{pmatrix} = \omega\boldsymbol{\Sigma}_\mathbf{z} + \mathbf{M} \tag{2.78}$$

where

$$\boldsymbol{\Sigma}_\mathbf{z} = \begin{pmatrix}\mathbf{I} & 0\\ 0 & -\mathbf{I}\end{pmatrix} \quad \text{and} \quad \mathbf{M} = \begin{pmatrix}\mathbf{A} & \mathbf{B}\\ \mathbf{B} & \mathbf{A}\end{pmatrix} \tag{2.79}$$

where $A_{ij,ab} = \delta_{ij}\delta_{ab}(\epsilon_a - \epsilon_i) - (ia|jb)$ and $B_{ij,ab} = -(ia|bj)$. So we have found that $\chi_{RPA}(\omega) = [\omega\mathbf{\Sigma_z} + \mathbf{M}]^{-1}$. And so we recover

$$\chi_{RPA}(\omega) = \left[\begin{pmatrix} \mathbf{A} & \mathbf{B} \\ \mathbf{B} & \mathbf{A} \end{pmatrix} + \omega \begin{pmatrix} \mathbf{I} & 0 \\ 0 & -\mathbf{I} \end{pmatrix}\right]^{-1} \tag{2.80}$$

To forced further, recognize that the matrix $\omega\mathbf{\Sigma_z} + \mathbf{M}$ is diagonal in the RPA eigenbasis, so we can write

$$\omega\mathbf{\Sigma_z} + \mathbf{M} = \begin{pmatrix} \mathbf{X} \\ \mathbf{Y} \end{pmatrix} \begin{pmatrix} \mathbf{\Omega} - \omega & 0 \\ 0 & \mathbf{\Omega} + \omega \end{pmatrix} \begin{pmatrix} \mathbf{X} \\ \mathbf{Y} \end{pmatrix}^{\dagger} \tag{2.81}$$

$$\chi_{RPA}(\omega) = (\omega\mathbf{\Sigma_z} + \mathbf{M})^{-1} = \begin{pmatrix} \mathbf{X} \\ \mathbf{Y} \end{pmatrix} \begin{pmatrix} \frac{1}{\mathbf{\Omega}-\omega} & 0 \\ 0 & \frac{1}{\mathbf{\Omega}+\omega} \end{pmatrix} \begin{pmatrix} \mathbf{X} \\ \mathbf{Y} \end{pmatrix}^{\dagger} \tag{2.82}$$

$$\chi_{RPA}(\omega) = \sum_{\mathrm{I}} \left[\frac{1}{\Omega_{\mathrm{I}} + \omega} \begin{pmatrix} X^{\mathrm{I}} \\ Y^{\mathrm{I}} \end{pmatrix} \begin{pmatrix} X^{\mathrm{I}} & Y^{\mathrm{I}} \end{pmatrix} + \frac{1}{\Omega_{\mathrm{I}} - \omega} \begin{pmatrix} Y^{\mathrm{I}} \\ X^{\mathrm{I}} \end{pmatrix} \begin{pmatrix} Y^{\mathrm{I}} & X^{\mathrm{I}} \end{pmatrix} \right] \tag{2.83}$$

How to determine the excitations?

To just determine the locations of the poles, we take a different route here. We have the form:

$$\chi_{RPA} = \chi_0 + \chi_0 v \chi_{RPA} = \frac{\chi_0}{1 - v\chi_0} \tag{2.84}$$

This implies that we are faced with a matrix inversion problem. The condition for the matrix $[\mathbf{I} - \mathbf{v}\chi_{\mathbf{0}}(\omega)]$ to be invertible is one this matrix is non-singular; therefore, the poles of the RPA occur where $[\mathbf{I} - \mathbf{v}\chi_{\mathbf{0}}(\omega)]$ is singular, i.e. where $\det[\mathbf{I} - \mathbf{v}\chi_{\mathbf{0}}(\omega)] = 0$. This condition implies that we must have a nonzero eigenvector $\mathbf{F}$ such that

$$[\mathbf{I} - \mathbf{v}\chi_{\mathbf{0}}(\omega)]\,\mathbf{F} = 0 \implies \mathbf{v}\chi_{\mathbf{0}}(\omega)\mathbf{F} = \mathbf{F} \tag{2.85}$$

We need to determine what the matrix element of the operator $\mathbf{v}\chi_0(\omega)$ is in a basis that we will specify later. With the resolution of the identity, we have

$$\langle pq|\,\mathbf{v}\chi_0(\omega)\,|rs\rangle = \sum_{tu} \langle pq|\,\mathbf{v}\,|tu\rangle\,\langle tu|\,\chi_0(\omega)\,|rs\rangle \tag{2.86}$$

But we know that the χ_0 is diagonal in a particle-hole basis, so we will have

$$\langle \tilde{pq}|\,\mathbf{v}\chi_0(\omega)\,|\tilde{rs}\rangle = v_{\tilde{pq}\tilde{rs}}\chi_{0,\tilde{rs}}(\omega) \tag{2.87}$$

where it is understood that $\tilde{pq}, \tilde{rs}$ form an occupied-virtual pair. Now consider partitioning χ_0 into two pieces, χ_0^+ for OV excitations and χ_0^- for VO de-excitations:

$$\chi_0(\omega) = \chi_0^+(\omega) + \chi_0^-(\omega) \tag{2.88}$$

We know that since $\chi_0^{\pm}(\omega) = \frac{1}{\pm(\omega - [\epsilon_a - \epsilon_i])} \implies \chi_0^+(\omega) = \tilde{\chi}_0(\omega)$ and $\chi_0^-(\omega) = -\tilde{\chi}_0(\omega)$, where $\tilde{\chi}_0(\omega) = \frac{1}{\omega - [\epsilon_a - \epsilon_i]}$. Notice from equation **??** that the occupied virtual combination of χ_0

constrains the second index of $\mathbf{v}$, so we can formulate a matrix for equation **??** in this pair basis:

$$\begin{pmatrix} \mathbf{v}^{++}\tilde{\chi}_0(\omega) & -\mathbf{v}^{+-}\tilde{\chi}_0(\omega) \\ \mathbf{v}^{-+}\tilde{\chi}_0(\omega) & -\mathbf{v}^{--}\tilde{\chi}_0(\omega) \end{pmatrix} \begin{pmatrix} \mathbf{F}^{+} \\ \mathbf{F}^{-} \end{pmatrix} = \begin{pmatrix} \mathbf{F}^{+} \\ \mathbf{F}^{-} \end{pmatrix} \tag{2.89}$$

This implies the system of equations

$$\left(\mathbf{v}^{++}\tilde{\chi}_0(\omega) - \mathbf{I}\right)\mathbf{F}^{+} - \mathbf{v}^{+-}\tilde{\chi}_0(\omega)\mathbf{F}^{-} = 0 \tag{2.90}$$

$$\mathbf{v}^{-+}\tilde{\chi}_0(\omega)\mathbf{F}^{+} - \left(\mathbf{v}^{--}\tilde{\chi}_0(\omega) + \mathbf{I}\right)\mathbf{F}^{-} = 0 \tag{2.91}$$

but we can multiply through by $\tilde{\chi}_0(\omega)^{-1} = \omega - [\epsilon_a - \epsilon_i]$ to yield

$$\mathbf{v}^{++}\mathbf{F}^{+} - \mathbf{v}^{+-}\mathbf{F}^{-} = (\omega - [\epsilon_a - \epsilon_i])\mathbf{F}^{+} \tag{2.92}$$

$$\mathbf{v}^{-+}\mathbf{F}^{+} - \mathbf{v}^{--}\mathbf{F}^{-} = -(\omega - [\epsilon_a - \epsilon_i])\mathbf{F}^{-} \tag{2.93}$$

$$\begin{pmatrix} \mathbf{v}^{++} & \mathbf{v}^{+-} \\ \mathbf{v}^{-+} & \mathbf{v}^{--} \end{pmatrix} \begin{pmatrix} \mathbf{F}^{+} \\ -\mathbf{F}^{-} \end{pmatrix} = (\omega - [\epsilon_a - \epsilon_i]) \begin{pmatrix} \mathbf{F}^{+} \\ -\mathbf{F}^{-} \end{pmatrix} \tag{2.94}$$

$$\begin{pmatrix} \mathbf{v}^{++} & \mathbf{v}^{+-} \\ \mathbf{v}^{-+} & \mathbf{v}^{--} \end{pmatrix} \begin{pmatrix} \mathbf{F}^{+} \\ -\mathbf{F}^{-} \end{pmatrix} = \omega \begin{pmatrix} \mathbf{F}^{+} \\ -\mathbf{F}^{-} \end{pmatrix} - [\epsilon_a - \epsilon_i] \begin{pmatrix} \mathbf{F}^{+} \\ -\mathbf{F}^{-} \end{pmatrix} \tag{2.95}$$

$$\begin{pmatrix} [\epsilon_a - \epsilon_i] + \mathbf{v}^{++} & \mathbf{v}^{+-} \\ \mathbf{v}^{-+} & [\epsilon_a - \epsilon_i] + \mathbf{v}^{--} \end{pmatrix} \begin{pmatrix} \mathbf{F}^{+} \\ -\mathbf{F}^{-} \end{pmatrix} = \omega \begin{pmatrix} \mathbf{F}^{+} \\ -\mathbf{F}^{-} \end{pmatrix} \tag{2.96}$$

where now we recognize $\mathbf{A}$ and $\mathbf{B}$ with elements in the particle-hole basis as

$$A_{iajb} = \delta_{ij}\delta_{ab}(\epsilon_a - \epsilon_i) - (ia|jb) \tag{2.97}$$

$$B_{iajb} = (ia|bj) \tag{2.98}$$

and note that we can make this work because $(ia|jb) = (ai|bj)$ and $(ia|bj) = (ai|jb)$ by permutation symmetry, so we can rewrite the matrix problem as

$$\begin{pmatrix} \mathbf{A} & \mathbf{B} \\ -\mathbf{B} & -\mathbf{A} \end{pmatrix} \begin{pmatrix} \mathbf{F}^{+} \\ \mathbf{F}^{-} \end{pmatrix} = \omega\sigma_{\mathbf{z}} \begin{pmatrix} \mathbf{F}^{+} \\ \mathbf{F}^{-} \end{pmatrix} \tag{2.99}$$

with Pauli matrix $\sigma_{\mathbf{z}} = \begin{pmatrix} \mathbf{I} & 0 \\ 0 & -\mathbf{I} \end{pmatrix}$. So, by solving this eigenvalue problem, we determine the poles of the RPA $\omega \equiv \mathbf{\Omega}^{I}$ with excitation vectors $\begin{pmatrix} \mathbf{F}^{+} \\ \mathbf{F}^{-} \end{pmatrix} \equiv \begin{pmatrix} \mathbf{X}^{\mathrm{I}} \\ \mathbf{Y}^{\mathrm{I}} \end{pmatrix}$.

Chapter 3

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.

3.1 MF

3.1.1 Basic relationships

The Wigner-Seitz radius r_s is defined as the radius of a sphere that contains one electron on average. In a finite simulation cell of length L containing N electrons, we can relate r_s to L and N via the following steps.

$$\frac{4\pi}{3} r_s^3 = \frac{1}{n} = \frac{L^3}{N} \tag{3.1}$$

$$\implies n = \frac{3}{4\pi r_s^3} \tag{3.2}$$

$$\tag{3.3}$$

We know that the Fermi wavevector of a uniform 3D gas has the definition:

$$k_F = \left(3\pi^2 n\right)^{1/3} \tag{3.4}$$

$$= \frac{(9\pi/4)^{1/3}}{r_s} \tag{3.5}$$

For periodic boundary conditions, the allowed single-particle wavevectors are:

$$\mathbf{k} = \frac{2\pi}{L}\mathbf{n}, \quad \mathbf{n} = (n_x, n_y, n_z), \quad n_i \in \mathbb{Z} \tag{3.6}$$

So the spacing of the k-grid is $\Delta k = 2\pi/L$. Using the definition that at $T = 0$, all states with $|\mathbf{k}| \leq k_F$ are occupied, with two electrons (spin up/down) per k-point, the number of

electrons is

$$N = 2 \times \frac{L^3}{(2\pi)^3} \times \frac{4\pi}{3} k_F^3 \tag{3.7}$$

$$= \frac{L^3}{3\pi^2} k_F^3 \tag{3.8}$$

$$\implies \frac{L^3}{3\pi^2} k_F^3 = \frac{3L^3}{4\pi r_s^3} \tag{3.9}$$

$$\implies k_F = \left(\frac{9\pi}{4r_s^3} \right)^{1/3} \tag{3.10}$$

This implies that the following definition should hold in my code:

$$\frac{2\pi}{L} |\mathbf{n}_{\max}| = \frac{(9\pi/4)^{1/3}}{r_s}, \quad \mathbf{n}_{\max} = (n_{x,\max}, n_{y,\max}, n_{z,\max}) \quad n_{i,\max} \in \mathbb{Z} \tag{3.11}$$

where $\mathbf{n}_{\max}$ is the highest occupied wavevector in my plane wave basis.

This is the algebraic identity your assert is verifying. 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 $C_{\boldsymbol{k}_\mu \boldsymbol{k}_p}$ and orbital energies $\epsilon_{\boldsymbol{k}_p}$.

3.2 RPA

For the UEG, I am first looping over all momentum transfer vectors $\boldsymbol{k}_q$. To learn which excitations are valid for the given $\boldsymbol{k}_q$, we first loop over occupied states $\boldsymbol{k}_i$. Virtual states $\boldsymbol{k}_a$ are already determined by that point; we compute $\boldsymbol{k}_a \equiv \boldsymbol{k}_i + \boldsymbol{k}_q$, and based of 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 $\boldsymbol{k}_j, \boldsymbol{k}_b$. Then, we can form the Casida eigenproblem for each $\boldsymbol{k}_q$.

$$\begin{pmatrix} \boldsymbol{A}(\boldsymbol{k}_q) & \boldsymbol{B}(\boldsymbol{k}_q) \\ -\boldsymbol{B}(\boldsymbol{k}_q) & -\boldsymbol{A}(\boldsymbol{k}_q) \end{pmatrix} \begin{pmatrix} \boldsymbol{X}(\boldsymbol{k}_q) & \boldsymbol{Y}(\boldsymbol{k}_q) \\ \boldsymbol{Y}(\boldsymbol{k}_q) & \boldsymbol{X}(\boldsymbol{k}_q) \end{pmatrix} \begin{pmatrix} \boldsymbol{\Omega}(\boldsymbol{k}_q) & \boldsymbol{0} \\ \boldsymbol{0} & -\boldsymbol{\Omega}(\boldsymbol{k}_q) \end{pmatrix} = \begin{pmatrix} \boldsymbol{X}(\boldsymbol{k}_q) & \boldsymbol{Y}(\boldsymbol{k}_q) \\ \boldsymbol{Y}(\boldsymbol{k}_q) & \boldsymbol{X}(\boldsymbol{k}_q) \end{pmatrix} \tag{3.12}$$

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

$$A_{\boldsymbol{k}_i \boldsymbol{k}_a, \boldsymbol{k}_b \boldsymbol{k}_j}(\boldsymbol{k}_q) = (\epsilon_{\boldsymbol{k}_a} - \epsilon_{\boldsymbol{k}_i}) \, \delta_{\boldsymbol{k}_i \boldsymbol{k}_j} \delta_{\boldsymbol{k}_a \boldsymbol{k}_b} + \frac{4\pi}{|\boldsymbol{k}_q|^2} \tag{3.13}$$

$$B_{\boldsymbol{k}_i \boldsymbol{k}_a, \boldsymbol{k}_j \boldsymbol{k}_b}(\boldsymbol{k}_q) = \frac{4\pi}{|\boldsymbol{k}_q|^2} \tag{3.14}$$

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

$$(\boldsymbol{X}(\boldsymbol{k}_q) - \boldsymbol{Y}(\boldsymbol{k}_q))^\dagger \, (\boldsymbol{X}(\boldsymbol{k}_q) + \boldsymbol{Y}(\boldsymbol{k}_q)) = \boldsymbol{I} \tag{3.15}$$

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

$$\rho_\nu(\boldsymbol{k}_q) = \sum_{\boldsymbol{k}_i \boldsymbol{k}_a} \left(X^\nu_{\boldsymbol{k}_i \boldsymbol{k}_a}(\boldsymbol{k}_q) + Y^\nu_{\boldsymbol{k}_i \boldsymbol{k}_a}(\boldsymbol{k}_q) \right). \tag{3.16}$$

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

Analytic dielectric function

The expression is:

$$\epsilon(\mathbf{q}, \omega) = 1 - v(\mathbf{q})\chi_0(\mathbf{q}, \omega) \tag{3.17}$$

$$= 1 + \frac{\alpha r_s}{8\pi q^3}[H(q + u/q) - H(q - u/q)] \tag{3.18}$$

where $H(q) = 2q + (1 - q^2)\ln[(q + 1)/(q - 1)], \alpha = (4/9\pi)^{1/3}$. Here we followed the notation of Ref. 9 where q denotes momenta in units of $2k_\mathrm{F}$ and u are energies in units of 4μ; thus, $q = |\mathbf{q}|/(2k_\mathrm{F})$ and $u = \omega/(4\mu)$. The Wigner-Seitz radius r_s is defined by $4\pi r_s^3/3 = 1/n$, where n is the electron density.

Verification

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

$$E_c^{RPA} = \frac{1}{2}\,\mathrm{Tr}(\sum_{\boldsymbol{q}} \boldsymbol{\Omega}(\boldsymbol{q}) - \boldsymbol{A}(\boldsymbol{q})) \tag{3.19}$$

$$\tag{3.20}$$

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

3.3 GW

3.3.1 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:

$$\Sigma(\mathbf{k}, \omega) = \frac{i}{2\pi} \int d\omega' \frac{d^3q}{(2\pi)^3} G\left(\mathbf{k} - \mathbf{q}, \omega - \omega'\right) W\left(\mathbf{q}, \omega'\right) \tag{3.21}$$

The screened Coulomb interaction in the RPA is given by

$$W(\mathbf{q},\omega) = v(\mathbf{q}) + v(\mathbf{q})\chi_0(\mathbf{q},\omega)v(\mathbf{q}) + \dots \tag{3.22}$$

$$= \frac{v(\mathbf{q})}{1 - v(\mathbf{q})\chi_0(\mathbf{q},\omega)} \equiv \frac{v(\mathbf{q})}{\varepsilon(\mathbf{q},\omega)} \tag{3.23}$$

$$= v(\mathbf{q}) + v^2(\mathbf{q})\chi_{RPA}(\mathbf{q},\omega) \tag{3.24}$$

$$\implies W_p(\mathbf{q},\omega) \equiv W(\mathbf{q},\omega) - v(\mathbf{q}) = v^2(\mathbf{q})\chi_{RPA}(\mathbf{q},\omega) \tag{3.25}$$

$$= \sum_\nu \frac{2\omega_\nu v^2(\mathbf{q})|\rho_\nu(\mathbf{q})|^2}{\omega^2 - \omega_\nu^2} \tag{3.26}$$

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:

$$\Sigma_{pol}(x,x';\omega) = \sum_{i,s\neq 0} \frac{V^s(\boldsymbol{r})V^s(\boldsymbol{r}')\,\phi_i(x)\phi_i^*(x')}{\omega + \omega_s\,\mathrm{sgn}(\mu - \varepsilon_i) - \varepsilon_i} \tag{3.27}$$

$$\implies \Sigma(\boldsymbol{k},\omega) = \sum_{q,\nu} \frac{v^2(\mathbf{q})|\rho_\nu(\mathbf{q})|^2}{\omega + \Omega_\nu\,\mathrm{sgn}(\mu - \epsilon_{\boldsymbol{k}-\boldsymbol{q}}) - \epsilon_{\boldsymbol{k}-\boldsymbol{q}} + i\eta} \tag{3.28}$$

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

$$V^s(\mathbf{r}) \to V^\nu(\mathbf{q}) = v(\mathbf{q})\rho_\nu(\mathbf{q}), \tag{3.29}$$

$$\omega_s \to \Omega_\nu \tag{3.30}$$

In relation to our Casida eigenproblem, we can identify that the excitation energies Ω_ν are just the eigenvalues from Eqn. 2.12, and the transition densities $\rho_\nu(\boldsymbol{q})$ are given by

$$\rho_\nu(\boldsymbol{q}) = \sum_{\boldsymbol{k}_i\boldsymbol{k}_a} (X^\nu_{\boldsymbol{k}_i\boldsymbol{k}_a}(\boldsymbol{q}) + Y^\nu_{\boldsymbol{k}_i\boldsymbol{k}_a}(\boldsymbol{q})). \tag{3.31}$$

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

$$\Sigma^{\mathrm{corr}}(\boldsymbol{k}_p,\omega) = \sum_{\boldsymbol{k}_q}\sum_\nu^{\mathrm{RPA}} \frac{4\pi}{|\boldsymbol{k}_q|^2}|\rho_\nu(\boldsymbol{k}_q)|^2 \left[\frac{f_{\boldsymbol{k}_p-\boldsymbol{k}_q}}{\omega + \Omega_\nu(\boldsymbol{k}_q) - \epsilon_{\boldsymbol{k}_p-\boldsymbol{k}_q} + i\eta} + \frac{1 - f_{\boldsymbol{k}_p-\boldsymbol{k}_q}}{\omega - \Omega_\nu(\boldsymbol{k}_q) - \epsilon_{\boldsymbol{k}_p-\boldsymbol{k}_q} + i\eta}\right] \tag{3.32}$$

3.3.2 Spectral function

Finally, the spectral function is given by

$$A(\boldsymbol{k}_p,\omega) = \frac{1}{\pi}\frac{|\mathrm{Im}\,\Sigma(\boldsymbol{k}_p,\omega)|}{\left(\omega - \epsilon_{\boldsymbol{k}_p} - \mathrm{Re}\,\Sigma(\boldsymbol{k}_p,\omega)\right)^2 + \left(\mathrm{Im}\,\Sigma(\boldsymbol{k}_p,\omega)\right)^2} \tag{3.33}$$

3.4 GW+C

3.4.1 Cumulant

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

$$\boldsymbol{G}^0(t)\boldsymbol{C}(t) = \iint \mathrm{d}t_1 \mathrm{d}t_2 \boldsymbol{G}^0(t-t_1)\boldsymbol{\Sigma}^c(t_1-t_2)\boldsymbol{G}^0(t_2) \tag{3.34}$$

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:

$$\boldsymbol{G}^0(\boldsymbol{p},t)\boldsymbol{C}(\boldsymbol{p},t) = \iint \mathrm{d}t_1 \mathrm{d}t_2 \boldsymbol{G}^0(\boldsymbol{p},t-t_1)\boldsymbol{\Sigma}^c(\boldsymbol{p},t_1-t_2)\boldsymbol{G}^0(\boldsymbol{p},t_2) \tag{3.35}$$

$$= \int \frac{\mathrm{d}\omega}{2\pi} e^{-i\omega t}\boldsymbol{G}^0(\boldsymbol{p},\omega)\boldsymbol{\Sigma}^c(\boldsymbol{p},\omega)\boldsymbol{G}^0(\boldsymbol{p},\omega) \tag{3.36}$$

$$\implies \boldsymbol{C}(\boldsymbol{p},t) = i\int \frac{\mathrm{d}\omega}{2\pi} \frac{\boldsymbol{\Sigma}^c(\boldsymbol{p},\omega+\epsilon^{HF}_{\boldsymbol{p}})}{(\omega+i\eta)^2} e^{-i\omega t} \tag{3.37}$$

$$= i\int \frac{d\omega}{2\pi} \frac{1}{(\omega+i\eta)^2} e^{-i\omega t} \left\{ \sum_{\boldsymbol{q}} \sum_{\nu}^{\mathrm{RPA}} \underbrace{\frac{4\pi}{|\boldsymbol{q}|^2}|\rho_\nu(\boldsymbol{q})|^2}_{M^2_{\boldsymbol{q}\nu}} \left[\frac{f_{\boldsymbol{p}-\boldsymbol{q}}}{\omega \underbrace{+\Omega_\nu(\boldsymbol{q}) + (\epsilon_{\boldsymbol{p}} - \epsilon_{\boldsymbol{p}-\boldsymbol{q}}) + i\eta}_{-\Delta^{\mathrm{occ}}_{\boldsymbol{q}\nu}}} \right. \right. \tag{3.38}$$

$$\left. \left. + \frac{1-f_{\boldsymbol{p}-\boldsymbol{q}}}{\omega \underbrace{-\Omega_\nu(\boldsymbol{q}) + (\epsilon_{\boldsymbol{p}} - \epsilon_{\boldsymbol{p}-\boldsymbol{q}}) + i\eta}_{-\Delta^{\mathrm{virt}}_{\boldsymbol{q}\nu}}} \right] \right\}$$

$$= i\sum_{\boldsymbol{q}\nu} M^2_{\boldsymbol{q}\nu} \int \frac{d\omega}{2\pi} e^{-i\omega t} \left[\frac{f_{\boldsymbol{p}-\boldsymbol{q}}}{(\omega+i\eta)^2(\omega-\Delta^{\mathrm{occ}}_{\boldsymbol{q}\nu})} + \frac{1-f_{\boldsymbol{p}-\boldsymbol{q}}}{(\omega+i\eta)^2(\omega-\Delta^{\mathrm{virt}}_{\boldsymbol{q}\nu})} \right] \tag{3.39}$$

$$= \sum_{\boldsymbol{q}\nu} \zeta^{\mathrm{occ}}_{\boldsymbol{p}\boldsymbol{q}\nu} \left[e^{-i\Delta^{\mathrm{occ}}_{\boldsymbol{q}\nu}t} - 1 + i\Delta^{\mathrm{occ}}_{\boldsymbol{q}\nu}t \right] + \sum_{\boldsymbol{q}\nu} \zeta^{\mathrm{virt}}_{\boldsymbol{p}\boldsymbol{q}\nu} \left[e^{-i\Delta^{\mathrm{virt}}_{\boldsymbol{q}\nu}t} - 1 + i\Delta^{\mathrm{virt}}_{\boldsymbol{q}\nu}t \right] \tag{3.40}$$

For the final expression, we have defined $\zeta^{\mathrm{occ}}_{\boldsymbol{p}\boldsymbol{q}\nu} = \left(\frac{f_{\boldsymbol{p}-\boldsymbol{q}}M_{\boldsymbol{q}\nu}}{\Delta^{\mathrm{occ}}_{\boldsymbol{q}\nu}}\right)^2$ and $\zeta^{\mathrm{virt}}_{\boldsymbol{p}\boldsymbol{q}\nu} = \left(\frac{(1-f_{\boldsymbol{p}-\boldsymbol{q}})M_{\boldsymbol{q}\nu}}{\Delta^{\mathrm{virt}}_{\boldsymbol{q}\nu}}\right)^2$. 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 $\mathrm{Im}\left(\omega_1\right), \mathrm{Im}\left(\omega_2\right) < 0$, and applying Cauchy's residue theorem, leads to

$$\int \frac{\mathrm{d}\omega}{2\pi} e^{-\mathrm{i}\omega t} \frac{1}{\left(\omega-\omega_1\right)^2} \frac{1}{\omega-\omega_2} = (-\mathrm{i}) \left\{ \left[\partial_\omega \left(\frac{e^{-\mathrm{i}\omega t}}{\omega-\omega_2} \right) \right]_{\omega=\omega_1} + \left[\frac{e^{-\mathrm{i}\omega t}}{\left(\omega-\omega_1\right)^2} \right]_{\omega=\omega_2} \right\} \tag{3.41}$$

$$= \frac{(-\mathrm{i})}{\left(\omega_1-\omega_2\right)^2} \left\{ \left[(-\mathrm{i}t)\left(\omega_1-\omega_2\right) - 1 \right] e^{-\mathrm{i}\omega_1 t} + e^{-\mathrm{i}\omega_2 t} \right\} \tag{3.42}$$

$$\implies \int \frac{\mathrm{d}\omega}{2\pi} e^{-i\omega t} \frac{1}{[\omega-(0-\mathrm{i}\eta)]^2} \frac{f}{\omega-\Delta} = \frac{-\mathrm{i}f}{\Delta^2} \left(e^{-\mathrm{i}\Delta t} + \mathrm{i}\Delta t - 1 \right) \tag{3.43}$$

3.4.2 Green's function

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

$$G^{GW+C}(\boldsymbol{p}, t) = G^{HF}(\boldsymbol{p}, t) e^{C(\boldsymbol{p},t)} \tag{3.44}$$

$$= -i\Theta(t) e^{-i\epsilon^{HF}_{\boldsymbol{p}} t + C(\boldsymbol{p},t)} \tag{3.45}$$

$$= -i\Theta(t) e^{-i\epsilon^{HF}_{\boldsymbol{p}} t + \sum_{\boldsymbol{q}\nu} \zeta^{\mathrm{occ}}_{\boldsymbol{p}\boldsymbol{q}\nu} \left(e^{-i\Delta^{\mathrm{occ}}_{\boldsymbol{q}\nu} t} + i\Delta^{\mathrm{occ}}_{\boldsymbol{q}\nu} t - 1 \right) + \sum_{\boldsymbol{q}\nu} \zeta^{\mathrm{virt}}_{\boldsymbol{p}\boldsymbol{q}\nu} \left(e^{-i\Delta^{\mathrm{virt}}_{\boldsymbol{q}\nu} t} + i\Delta^{\mathrm{virt}}_{\boldsymbol{q}\nu} t - 1 \right)} \tag{3.46}$$

$$= -i\Theta(t) Z^{QP}_{\boldsymbol{p}} e^{-i\epsilon^{QP}_{\boldsymbol{p}} t} e^{\sum_{\boldsymbol{q}\nu} \zeta^{\mathrm{occ}}_{\boldsymbol{p}\boldsymbol{q}\nu} e^{-i\Delta^{\mathrm{occ}}_{\boldsymbol{q}\nu} t} + \sum_{\boldsymbol{q}\nu} \zeta^{\mathrm{virt}}_{\boldsymbol{p}\boldsymbol{q}\nu} e^{-i\Delta^{\mathrm{virt}}_{\boldsymbol{q}\nu} t}} \tag{3.47}$$

$$\tag{3.48}$$

where we have the weight of the quasiparticle peak $Z^{QP}_{\boldsymbol{p}} = \exp\left(-\sum_{\boldsymbol{q}\nu} \zeta^{\mathrm{occ}}_{\boldsymbol{p}\boldsymbol{q}\nu} - \sum_{\boldsymbol{q}\nu} \zeta^{\mathrm{virt}}_{\boldsymbol{p}\boldsymbol{q}\nu} \right)$ and the quasiparticle energy $\epsilon^{QP}_{\boldsymbol{p}} = \epsilon^{HF}_{\boldsymbol{p}} - \left(\sum_{\boldsymbol{q}\nu} \zeta^{\mathrm{occ}}_{\boldsymbol{p}\boldsymbol{q}\nu} \Delta^{\mathrm{occ}}_{\boldsymbol{q}\nu} + \sum_{\boldsymbol{q}\nu} \zeta^{\mathrm{virt}}_{\boldsymbol{p}\boldsymbol{q}\nu} \Delta^{\mathrm{virt}}_{\boldsymbol{q}\nu} \right)$.

We pause to make some important connections. Notice

$$Z_{\boldsymbol{p}}^{QP} = \exp\left(-\sum_{\boldsymbol{q}\nu}\zeta_{\boldsymbol{p}\boldsymbol{q}\nu}^{\text{occ}} - \sum_{\boldsymbol{q}\nu}\zeta_{\boldsymbol{p}\boldsymbol{q}\nu}^{\text{virt}}\right) \tag{3.49}$$

$$= \exp\left(-\sum_{\boldsymbol{q}\nu}\left(\frac{f_{\boldsymbol{p}-\boldsymbol{q}}M_{\boldsymbol{q}\nu}}{\Delta_{\boldsymbol{q}\nu}^{\text{occ}}}\right)^2 - \sum_{\boldsymbol{q}\nu}\left(\frac{(1-f_{\boldsymbol{p}-\boldsymbol{q}})M_{\boldsymbol{q}\nu}}{\Delta_{\boldsymbol{q}\nu}^{\text{virt}}}\right)^2\right) \tag{3.50}$$

$$= \exp\left(\left[\frac{\partial\Sigma^c(\boldsymbol{p},\omega)}{\partial\omega}\right]_{\omega=\epsilon_{\boldsymbol{p}}^{HF}}\right) \tag{3.51}$$

and

$$\epsilon_{\boldsymbol{p}}^{QP} = \epsilon_{\boldsymbol{p}}^{HF} - \left(\sum_{\boldsymbol{q}\nu}\zeta_{\boldsymbol{p}\boldsymbol{q}\nu}^{\text{occ}}\Delta_{\boldsymbol{q}\nu}^{\text{occ}} + \sum_{\boldsymbol{q}\nu}\zeta_{\boldsymbol{p}\boldsymbol{q}\nu}^{\text{virt}}\Delta_{\boldsymbol{q}\nu}^{\text{virt}}\right) \tag{3.52}$$

$$= \epsilon_{\boldsymbol{p}}^{HF} - \left(\sum_{\boldsymbol{q}\nu}\frac{f_{\boldsymbol{p}-\boldsymbol{q}}M_{\boldsymbol{q}\nu}^2}{\Delta_{\boldsymbol{q}\nu}^{\text{occ}}} + \sum_{\boldsymbol{q}\nu}\frac{(1-f_{\boldsymbol{p}-\boldsymbol{q}})M_{\boldsymbol{q}\nu}^2}{\Delta_{\boldsymbol{q}\nu}^{\text{virt}}}\right) \tag{3.53}$$

$$= \epsilon_{\boldsymbol{p}}^{HF} + \Sigma^c(\boldsymbol{p},\epsilon_{\boldsymbol{p}}^{HF}) \tag{3.54}$$

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

Next, we want to perform a Fourier transform.

$$G^{GW+C}(\boldsymbol{p},\omega) = \int_{-\infty}^{\infty} dt\, e^{i\omega t} G^{GW+C}(\boldsymbol{p},t) \tag{3.55}$$

$$= -iZ_{\boldsymbol{p}}^{QP} \int_0^{\infty} dt\, e^{i(\omega-\epsilon_{\boldsymbol{p}}^{QP})t} e^{\sum_{\boldsymbol{q}\nu}\zeta_{\boldsymbol{pq}\nu}^{\text{occ}} e^{-i\Delta_{\boldsymbol{q}\nu}^{\text{occ}}t} + \sum_{\boldsymbol{q}\nu}\zeta_{\boldsymbol{pq}\nu}^{\text{virt}} e^{-i\Delta_{\boldsymbol{q}\nu}^{\text{virt}}t}} \tag{3.56}$$

$$= -iZ_{\boldsymbol{p}}^{QP} \int_0^{\infty} dt\, e^{i(\omega-\epsilon_{\boldsymbol{p}}^{QP})t} \left(1 + \sum_{\boldsymbol{q}\nu}\zeta_{\boldsymbol{pq}\nu}^{\text{occ}} e^{-i\Delta_{\boldsymbol{q}\nu}^{\text{occ}}t} + \sum_{\boldsymbol{q}\nu}\zeta_{\boldsymbol{pq}\nu}^{\text{virt}} e^{-i\Delta_{\boldsymbol{q}\nu}^{\text{virt}}t} + \dots\right) \tag{3.57}$$

$$= -iZ_{\boldsymbol{p}}^{QP} \int_0^{\infty} dt\, e^{[-\eta+i(\omega-\epsilon_{\boldsymbol{p}}^{QP})t]} \tag{3.58}$$

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

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

$$= \frac{Z_{\boldsymbol{p}}^{QP}}{\omega-\epsilon_{\boldsymbol{p}}^{QP}+i\eta} + \sum_{\boldsymbol{q}\nu}\frac{Z_{\boldsymbol{p}}^{QP}\zeta_{\boldsymbol{pq}\nu}^{\text{occ}}}{\omega-\epsilon_{\boldsymbol{p}}^{QP}-\Delta_{\boldsymbol{q}\nu}^{\text{occ}}+i\eta} + \sum_{\boldsymbol{q}\nu}\frac{Z_{\boldsymbol{p}}^{QP}\zeta_{\boldsymbol{pq}\nu}^{\text{virt}}}{\omega-\epsilon_{\boldsymbol{p}}^{QP}-\Delta_{\boldsymbol{q}\nu}^{\text{virt}}+i\eta} + \dots \tag{3.59}$$

$$= \frac{Z_{\boldsymbol{p}}^{QP}}{\omega-\epsilon_{\boldsymbol{p}}^{QP}+i\eta} + \sum_{\boldsymbol{q}\nu}\frac{Z_{\boldsymbol{pq}\nu}^{\text{occ-sat}}}{\omega-\epsilon_{\boldsymbol{pq}\nu}^{\text{occ-sat}}+i\eta} + \sum_{\boldsymbol{q}\nu}\frac{Z_{\boldsymbol{pq}\nu}^{\text{virt-sat}}}{\omega-\epsilon_{\boldsymbol{pq}\nu}^{\text{virt-sat}}+i\eta} + \dots \tag{3.60}$$

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

3.4.3 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)

$$A^{GW+C}(\boldsymbol{p},\omega) = -\frac{1}{\pi}\operatorname{Im} G^{GW+C}(\boldsymbol{p},\omega) \tag{3.61}$$

$$= -\frac{1}{\pi}\operatorname{Im}\left[\frac{Z^{QP}_{\boldsymbol{p}}}{\omega-\epsilon^{QP}_{\boldsymbol{p}}+i\eta}+\sum_{\boldsymbol{q}\nu}\frac{Z^{\text{occ-sat}}_{\boldsymbol{pq}\nu}}{\omega-\epsilon^{\text{occ-sat}}_{\boldsymbol{pq}\nu}+i\eta}+\dots\right] \tag{3.62}$$

$$= -\frac{1}{\pi}\operatorname{Im}\left[\frac{\operatorname{Re} Z^{QP}_{\boldsymbol{p}}+i\operatorname{Im} Z^{QP}_{\boldsymbol{p}}}{\omega-\operatorname{Re}\epsilon^{QP}_{\boldsymbol{p}}+i\left(\eta-\operatorname{Im}\epsilon^{QP}_{\boldsymbol{p}}\right)}+\sum_{\boldsymbol{q}\nu}\frac{\operatorname{Re} Z^{\text{occ-sat}}_{\boldsymbol{pq}\nu}+i\operatorname{Im} Z^{\text{occ-sat}}_{\boldsymbol{pq}\nu}}{\omega-\operatorname{Re}\epsilon^{\text{occ-sat}}_{\boldsymbol{pq}\nu}+i\left(\eta-\operatorname{Im}\epsilon^{\text{occ-sat}}_{\boldsymbol{pq}\nu}\right)}+\dots\right] \tag{3.63}$$

$$= -\frac{1}{\pi}\operatorname{Im}\left[\frac{\left(\operatorname{Re} Z^{QP}_{\boldsymbol{p}}+i\operatorname{Im} Z^{QP}_{\boldsymbol{p}}\right)\left(\omega-\operatorname{Re}\epsilon^{QP}_{\boldsymbol{p}}-i\left(\eta-\operatorname{Im}\epsilon^{QP}_{\boldsymbol{p}}\right)\right)}{\left(\omega-\operatorname{Re}\epsilon^{QP}_{\boldsymbol{p}}\right)^2+\left(\operatorname{Im}\epsilon^{QP}_{\boldsymbol{p}}\right)^2}\right. \tag{3.64}$$

$$\left.+\sum_{\boldsymbol{q}\nu}\frac{\left(\operatorname{Re} Z^{\text{occ-sat}}_{\boldsymbol{pq}\nu}+i\operatorname{Im} Z^{\text{occ-sat}}_{\boldsymbol{pq}\nu}\right)\left(\omega-\operatorname{Re}\epsilon^{\text{occ-sat}}_{\boldsymbol{pq}\nu}-i\left(\eta-\operatorname{Im}\epsilon^{\text{occ-sat}}_{\boldsymbol{pq}\nu}\right)\right)}{\left(\omega-\operatorname{Re}\epsilon^{\text{occ-sat}}_{\boldsymbol{pq}\nu}\right)^2+\left(\operatorname{Im}\epsilon^{\text{occ-sat}}_{\boldsymbol{pq}\nu}\right)^2}+\dots\right] \tag{3.65}$$

$$= -\frac{1}{\pi}\left[\frac{\left(\operatorname{Re} Z^{QP}_{\boldsymbol{p}}\right)\left(\operatorname{Im}\epsilon^{QP}_{\boldsymbol{p}}\right)+\left(\operatorname{Im} Z^{QP}_{\boldsymbol{p}}\right)\left(\omega-\operatorname{Re}\epsilon^{QP}_{\boldsymbol{p}}\right)}{\left(\omega-\operatorname{Re}\epsilon^{QP}_{\boldsymbol{p}}\right)^2+\left(\operatorname{Im}\epsilon^{QP}_{\boldsymbol{p}}\right)^2}\right. \tag{3.66}$$

$$\left.+\sum_{\boldsymbol{q}\nu}\frac{\left(\operatorname{Re} Z^{\text{occ-sat}}_{\boldsymbol{pq}\nu}\right)\left(\operatorname{Im}\epsilon^{\text{occ-sat}}_{\boldsymbol{pq}\nu}\right)+\left(\operatorname{Im} Z^{\text{occ-sat}}_{\boldsymbol{pq}\nu}\right)\left(\omega-\operatorname{Re}\epsilon^{\text{occ-sat}}_{\boldsymbol{pq}\nu}\right)}{\left(\omega-\operatorname{Re}\epsilon^{\text{occ-sat}}_{\boldsymbol{pq}\nu}\right)^2+\left(\operatorname{Im}\epsilon^{\text{occ-sat}}_{\boldsymbol{pq}\nu}\right)^2}+\dots\right] \tag{3.67}$$

Chapter 4

TDVP

We start with the definition of the action functional:

$$S = \int_{t_1}^{t_2} dt L(\psi, \bar{\psi}) \tag{4.1}$$

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

$$L(\psi, \bar{\psi}) = \frac{i}{2}\frac{\langle \psi \mid \dot{\psi}\rangle - \langle \dot{\psi} \mid \psi\rangle}{\langle \psi \mid \psi\rangle} - \frac{\langle \psi|H|\psi\rangle}{\langle \psi \mid \psi\rangle} \tag{4.2}$$

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,

$$0 = \delta S = \int \delta L dt = \int dt \left(\frac{1}{2}\frac{\{\langle \delta\psi \mid \dot{\psi}\rangle + \langle \psi \mid \delta\dot{\psi}\rangle - \langle \delta\dot{\psi} \mid \psi\rangle - \langle \dot{\psi} \mid \delta\psi\rangle\}}{\langle \psi \mid \psi\rangle} \right. \tag{4.3}$$

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

$$= \int dt \left(\frac{i\langle \delta\psi \mid \dot{\psi}\rangle - \langle \delta\psi|H|\psi\rangle}{\langle \psi \mid \psi\rangle} - \frac{\langle \psi|i\partial/\partial t - H|\psi\rangle}{\langle \psi \mid \psi\rangle^2}\langle \delta\psi \mid \psi\rangle \right) + \text{c.c.} \tag{4.4}$$

$$\implies \left(i\frac{\partial}{\partial t} - H \right)|\psi\rangle = \frac{\langle \psi|i\partial/\partial t - H|\psi\rangle}{\langle \psi \mid \psi\rangle}|\psi\rangle \tag{4.5}$$

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

$$|\phi(t)\rangle = |\psi(t)\rangle \exp\left[i\int^t d\tau \,\frac{\langle\psi|i\partial_\tau - H|\psi\rangle}{\langle\psi|\psi\rangle}\right] \tag{4.6}$$

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

$$i\frac{\partial}{\partial t}|\phi\rangle = i\frac{\partial}{\partial t}\Big(|\psi\rangle\, e^{i\int^t \frac{\langle\psi|i\partial_\tau - H|\psi\rangle}{\langle\psi|\psi\rangle}d\tau}\Big) \tag{4.7}$$

$$= i(\partial_t|\psi\rangle)e^{i\int^t\cdots} + |\psi\rangle \underbrace{i\partial_t e^{i\int^t\cdots}}_{-\frac{\langle\psi|i\partial_t - H|\psi\rangle}{\langle\psi|\psi\rangle}e^{i\int^t\cdots}} \tag{4.8}$$

$$= e^{i\int^t\cdots}\left[i\partial_t|\psi\rangle - \frac{\langle\psi|i\partial_t - H|\psi\rangle}{\langle\psi|\psi\rangle}|\psi\rangle\right] \tag{4.9}$$

$$= e^{i\int^t\cdots}[H|\psi\rangle] = H|\phi\rangle \tag{4.10}$$

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