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Derivations for Personal Learning

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Chapter 1

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1.1 Deriving Hedin's equations

1.1.1 Time-Domain Definition of the Green's Function

Start by considering the equation of motion for the field operators

$$i\frac{\partial}{\partial t}\hat{\psi}(\mathbf{x},t) = [\hat{\psi}(\mathbf{x},t), \hat{H}_{elec}] = [\hat{\psi}(\mathbf{x},t), \hat{H}_0 + \hat{H}_{int}] = [\hat{\psi}(\mathbf{x},t), \hat{H}_0] + [\hat{\psi}(\mathbf{x},t), \hat{H}_{int}] \tag{1.1}$$

For the non-interacting part, we have

$$[\hat{\psi}(\mathbf{x},t), \hat{H}_0] = [\hat{\psi}(\mathbf{x},t), \int d\mathbf{x}'\hat{\psi}^\dagger(\mathbf{x}',t)\hat{h}^0(\mathbf{x}')\hat{\psi}(\mathbf{x}',t)] \tag{1.2}$$

$$= \int d\mathbf{x}'[\hat{\psi}(\mathbf{x},t), \hat{\psi}^\dagger(\mathbf{x}',t)\hat{h}^0(\mathbf{x}')\hat{\psi}(\mathbf{x}',t)] \tag{1.3}$$

$$= \int d\mathbf{x}' \left(\underbrace{[\hat{\psi}(\mathbf{x},t), \hat{\psi}^\dagger(\mathbf{x}',t)]}_{\delta(\mathbf{x}-\mathbf{x}')} \hat{h}^0(\mathbf{x}')\hat{\psi}(\mathbf{x}',t) + \hat{\psi}^\dagger(\mathbf{x}',t)\hat{h}^0(\mathbf{x}') \underbrace{[\hat{\psi}(\mathbf{x},t), \hat{\psi}(\mathbf{x}',t)]}_{0} \right) \tag{1.4}$$

$$= h^0(\mathbf{x})\hat{\psi}(\mathbf{x},t). \tag{1.5}$$

For the interacting part, we have

$$[\hat{\psi}(\mathbf{x},t), \hat{H}_{int}] = \frac{1}{2}\int d\mathbf{x}'d\mathbf{x}''v(\mathbf{x},\mathbf{x}')[\hat{\psi}(\mathbf{x},t), \hat{\psi}^\dagger(\mathbf{x}',t)\hat{\psi}^\dagger(\mathbf{x}'',t)\hat{\psi}(\mathbf{x}'',t)\hat{\psi}(\mathbf{x}',t)] \tag{1.6}$$

$$= \frac{1}{2}\int d\mathbf{x}'d\mathbf{x}''v(\mathbf{x},\mathbf{x}') \left(\delta(\mathbf{x}-\mathbf{x}')\hat{\psi}^\dagger(\mathbf{x}'',t)\hat{\psi}(\mathbf{x}'',t)\hat{\psi}(\mathbf{x}',t) + \hat{\psi}^\dagger(\mathbf{x}',t)\delta(\mathbf{x}-\mathbf{x}'')\hat{\psi}(\mathbf{x}'',t)\hat{\psi}(\mathbf{x}',t) \right) \tag{1.7}$$

$$= \int d\mathbf{x}'\hat{\psi}^\dagger(\mathbf{x}',t)v(\mathbf{x},\mathbf{x}')\hat{\psi}(\mathbf{x}',t)\hat{\psi}(\mathbf{x},t) \tag{1.8}$$

so overall we have

$$i\frac{\partial}{\partial t}\hat{\psi}(\mathbf{x},t) = \left(\hat{h}^0(\mathbf{x}) + \int d\mathbf{x}'v(\mathbf{x},\mathbf{x}')\hat{\psi}^\dagger(\mathbf{x}',t)\hat{\psi}(\mathbf{x}',t) \right) \hat{\psi}(\mathbf{x},t) \tag{1.9}$$

Now we can consider the equation of motion for the Green's function, defined as $G(\mathbf{x}t, \mathbf{x}'t') = -i \langle N| \mathcal{T}\left(\hat{\psi}(\mathbf{x},t)\hat{\psi}^\dagger(\mathbf{x}',t')\right)|N\rangle$, where $\mathcal{T}$ is the time-ordering operator.

$$\frac{\partial}{\partial t}G(\mathbf{x}t,\mathbf{x}'t') = -i\langle N|\frac{\partial}{\partial t}\mathcal{T}\left(\hat{\psi}(\mathbf{x},t)\hat{\psi}^\dagger(\mathbf{x}',t')\right)|N\rangle \tag{1.10}$$

$$\tag{1.11}$$

Now,

$$\frac{\partial}{\partial t}\mathcal{T}\left(\hat{\psi}(\mathbf{x},t)\hat{\psi}^\dagger(\mathbf{x}',t')\right) = \frac{\partial}{\partial t}\left(\theta(t-t')\hat{\psi}(\mathbf{x},t)\hat{\psi}^\dagger(\mathbf{x}',t') - \theta(t'-t)\hat{\psi}^\dagger(\mathbf{x}',t')\hat{\psi}(\mathbf{x},t)\right) \tag{1.12}$$

$$= \underbrace{\frac{\partial\theta(t-t')}{\partial t}}_{\delta(t-t')}\hat{\psi}(\mathbf{x},t)\hat{\psi}^\dagger(\mathbf{x}',t') + \theta(t-t')\frac{\partial}{\partial t}\hat{\psi}(\mathbf{x},t)\hat{\psi}^\dagger(\mathbf{x}',t') - \underbrace{\frac{\partial\theta(t'-t)}{\partial t}}_{-\delta(t'-t)}\hat{\psi}^\dagger(\mathbf{x}',t')\hat{\psi}(\mathbf{x},t) - \theta(t'-t)\frac{\partial}{\partial t}\hat{\psi}^\dagger(\mathbf{x}',t \tag{1.13}$$

$$= \underbrace{\delta(t-t')\left\{\hat{\psi}(\mathbf{x},t),\hat{\psi}^\dagger(\mathbf{x}',t')\right\}}_{\delta(\mathbf{x}-\mathbf{x}')\delta(t-t')} + \mathcal{T}\left(\frac{\partial}{\partial t}\hat{\psi}(\mathbf{x},t)\hat{\psi}^\dagger(\mathbf{x}',t')\right) \tag{1.14}$$

$$\tag{1.15}$$

So now consider plugging in the equation of motion for $\hat{\psi}(\mathbf{x},t)$ into the above expression

$$\mathcal{T}\left(\frac{\partial}{\partial t}\hat{\psi}(\mathbf{x},t)\hat{\psi}^\dagger(\mathbf{x}',t')\right) = \mathcal{T}\left(-i\left(\hat{h}^0(\mathbf{x}) + \int d\mathbf{x}''v(\mathbf{x},\mathbf{x}'')\hat{\psi}^\dagger(\mathbf{x}'',t)\hat{\psi}(\mathbf{x}'',t)\right)\hat{\psi}(\mathbf{x},t)\hat{\psi}^\dagger(\mathbf{x}',t')\right) \tag{1.16}$$

$$= -i\hat{h}^0(\mathbf{x})\mathcal{T}\left(\hat{\psi}(\mathbf{x},t)\hat{\psi}^\dagger(\mathbf{x}',t')\right) - i\int d\mathbf{x}''v(\mathbf{x},\mathbf{x}'')\mathcal{T}\left(\hat{\psi}(\mathbf{x},t)\hat{\psi}^\dagger(\mathbf{x}'',t)\hat{\psi}(\mathbf{x}'',t)\hat{\psi}^\dagger(\mathbf{x}',t')\right) \tag{1.17}$$

So we have

$$\left[i\frac{\partial}{\partial t} - \hat{h}^0(\mathbf{x})\right]G(\mathbf{x}t,\mathbf{x}'t') = \delta(\mathbf{x}-\mathbf{x}')\delta(t-t') - i\int d\mathbf{x}''v(\mathbf{x},\mathbf{x}'')\underbrace{G_2(\mathbf{x}t,\mathbf{x}''t,\mathbf{x}'t^+,\mathbf{x}'t')}_{\langle N|\mathcal{T}\left(\hat{\psi}(\mathbf{x},t)\hat{\psi}(\mathbf{x}'',t)\hat{\psi}^\dagger(\mathbf{x}'',t')\hat{\psi}^\dagger(\mathbf{x}',t')\right)|N\rangle} \tag{1.18}$$

and we notice that in order to compute the single-particle Green's function, we need to know the two-particle Green's function, which needs the three-particle Green's function, and so on. So to simplify we introduce a nonlocal, time-dependent self-energy $\Sigma(\mathbf{x}t,\mathbf{x}'t')$ that satisfies

$$-i\int d\mathbf{x}''v(\mathbf{x},\mathbf{x}'')G_2(\mathbf{x}t,\mathbf{x}''t,\mathbf{x}'t^+,\mathbf{x}'t') \equiv \int dt''\int d\mathbf{x}''\overline{\Sigma}(\mathbf{x}t,\mathbf{x}''t'')G(\mathbf{x}''t'',\mathbf{x}'t') \tag{1.19}$$

and further define $\Sigma = \overline{\Sigma} - v_H$ with

$$v_H(\mathbf{x},t) = \int d\mathbf{x}'v(\mathbf{x},\mathbf{x}')\underbrace{\langle N|\hat{\psi}^\dagger(\mathbf{x}')\hat{\psi}(\mathbf{x}')|N\rangle}_{-\frac{1}{i}G(\mathbf{x}'t,\mathbf{x}'t)} = i\int d\mathbf{x}'v(\mathbf{x},\mathbf{x}')G(\mathbf{x}'t,\mathbf{x}'t) \tag{1.20}$$

and we can rewrite the equation of motion as

$$\left[i\frac{\partial}{\partial t} - \hat{h}^0(\mathbf{x}) - v_H(\mathbf{x},t)\right] G(\mathbf{x}t,\mathbf{x}'t') = \delta(\mathbf{x}-\mathbf{x}')\delta(t-t') + \int dt'' \int d\mathbf{x}''\Sigma(\mathbf{x}t,\mathbf{x}''t'')G(\mathbf{x}''t'',\mathbf{x}'t') \tag{1.21}$$

Now consider defining the G_0 of the non-interacting system

$$\left[i\frac{\partial}{\partial t} - \hat{h}^0(\mathbf{x}) - v_H(\mathbf{x},t)\right] G_0(\mathbf{x}t,\mathbf{x}'t') = \delta(\mathbf{x}-\mathbf{x}')\delta(t-t') \tag{1.22}$$

So we can write equations 1.21 and 1.22 symbolically as

$$\hat{O}G = \delta + \Sigma G \quad \text{and} \quad \hat{O}G_0 = \delta \tag{1.23}$$

$$\implies G_0 = \hat{O}^{-1} \implies G = G_0 + G_0\Sigma G \tag{1.24}$$

$$\implies G(1,2) = G_0(1,2) + \int d3d4G_0(1,3)\Sigma(3,4)G(4,2) \tag{1.25}$$

where we use the space-time notation $1 = (\mathbf{x}_1, t_1)$ etc.

1.1.2 Hedin's Equations

Schwinger chose to introduce a potential φ that we will later set to zero, in order to rewrite the two-particle Green's function as

$$G_2(1,3,2,3^+) = G(1,2)\,G(3,3^+) - \frac{\delta G(1,2)}{\delta\varphi(3)}, \tag{1.26}$$

So

$$\bar{\Sigma}(1,2) = -i\int d(3)\; v(1,3)\,G_2(1,3,2,3^+) \tag{1.27}$$

$$= -i\int d(3)\, v(1,3)\left[G(1,2)\,G(3,3^+) - \frac{\delta G(1,2)}{\delta\varphi(3)}\right] \tag{1.28}$$

$$= -i\,G(1,2)\underbrace{\int d(3)\, v(1,3)\,G(3,3^+)}_{-iv_H(1)} + i\int d(3)\, v(1,3)\,\frac{\delta G(1,2)}{\delta\varphi(3)}. \tag{1.29}$$

Now because $\delta G = -G\,(\delta G^{-1})\,G$ we can write the identity

$$\frac{\delta G(1,2)}{\delta\varphi(3)} = -\int d(4)d(5)\; G(1,4)\,\frac{\delta G^{-1}(4,5)}{\delta\varphi(3)}\,G(5,2). \tag{1.30}$$

So the second term in Eq. (1.29) gives

$$i\int d(3)\; v(1,3)\,\frac{\delta G(1,2)}{\delta\varphi(3)} = -i\int d(3)\, v(1,3)\int d(4)d(5)\; G(1,4)\,\frac{\delta G^{-1}(4,5)}{\delta\varphi(3)}\,G(5,2)$$

$$= -i\int d(3,4,5)\; v(1,3)\,G(1,4)\,\frac{\delta G^{-1}(4,5)}{\delta\varphi(3)}\,G(5,2). \tag{1.31}$$

Now we can get rid of a $G(1,2)$ dependence by multiplying with G^{-1}, yielding

$$\overline{\Sigma}(1,2) = -\delta(1,2)\, v_H(1) - i \int d(3,4)\; v(1,3)\, G(1,4)\, \frac{\delta G^{-1}(4,2)}{\delta \varphi(3)}. \tag{1.32}$$

Introduce $V(1) = \varphi(1) + v_H(1)$ as the total potential that electrons experience. Consider

$$\frac{\delta G^{-1}(1,2)}{\delta \varphi(3)} \equiv \underbrace{\frac{\delta G^{-1}(1,2)}{\delta V(5)}}_{-\Gamma(1,2,5)} \underbrace{\frac{\delta V(5)}{\delta \varphi(3)}}_{\varepsilon^{-1}(5,3)}. \tag{1.33}$$

So

$$\overline{\Sigma}(1,2) = -\delta(1,2)\, v_H(1) + i \int d(5) \underbrace{\int d(3) v(1,3)\, \varepsilon^{-1}(3,5)}_{W(1,5)} \int d(4) G(1,4)\, \Gamma(4,5,2). \tag{1.34}$$

and if we further make the GW approximation where $\Gamma(4,5,2) \approx \delta(4,5)\delta(2,5)$ we get

$$\overline{\Sigma}(1,2) = -\delta(1,2)\, v_H(1) + iW(1,2)G(1,2) \tag{1.35}$$

and if we just care about the exchange-correlation part, we can define

$$\Sigma_{xc}(1,2) = \overline{\Sigma}(1,2) + \delta(1,2)\, v_H(1) = iW(1,2)G(1,2) \implies \Sigma_{xc}(\tau) = iW(\tau)G(\tau) \tag{1.36}$$

where $\tau = t_1 - t_2$. Define $G(\tau) = \int \frac{d\omega'}{2\pi} e^{-i\omega'\tau} G(\omega')$ and $W(\tau) = \int \frac{d\omega''}{2\pi} e^{-i\omega''\tau} W(\omega'')$ to get

$$\Sigma_{xc}(\tau) = i \int \frac{d\omega'}{2\pi} \int \frac{d\omega''}{2\pi} e^{-i(\omega'+\omega'')\tau} G(\omega') W(\omega'') \tag{1.37}$$

Taking the inverse Fourier transform of $\Sigma_{xc}(\tau)$ we get

$$\Sigma_{xc}(\omega) = \int \frac{d\tau}{2\pi} e^{i\omega\tau} \Sigma_{xc}(\tau) = i \int \frac{d\omega'}{2\pi} \int \frac{d\omega''}{2\pi} G(\omega') W(\omega'') \underbrace{\int d\tau e^{i(\omega-\omega'-\omega'')\tau}}_{2\pi\delta(\omega-\omega'-\omega'')} = i \int \frac{d\omega'}{2\pi} G(\omega') W(\omega-\omega') \tag{1.38}$$

Now in G_0W_0 one applies the Cauchy residue theorem to solve this convolution integral, yielding the known form.

1.2 Final expressions

1.2.1 Fully analytic

I follow the notation of Tianyu's paper throughout this section [15]. We want to solve for the self-energy whose form along the real axis is:

$$\Sigma(\mathbf{r}, \mathbf{r}', \omega) = \frac{i}{2\pi} \int_{-\infty}^{\infty} e^{i\omega'\eta} d\omega' G_0(\mathbf{r}, \mathbf{r}', \omega + \omega') W_0(\mathbf{r}, \mathbf{r}', \omega') \tag{1.39}$$

In the molecular brutal basis, the self energy is given as:

$$\Sigma_{nn'}(\mathbf{k},\omega) = \iint d\mathbf{r}d\mathbf{r}'\psi^*_{n\mathbf{k}}(\mathbf{r})\Sigma(\mathbf{r},\mathbf{r}',\omega)\psi_{n'\mathbf{k}}(\mathbf{r}') \tag{1.40}$$

Also, recall that the Lehmann representation of the noninteracting Green's function is:

$$G_0\left(\mathbf{r},\mathbf{r}',\omega\right) = \sum_{o\mathbf{q}} \frac{\psi_{o\mathbf{q}}(\mathbf{r})\psi^*_{o\mathbf{q}}\left(\mathbf{r}'\right)}{\omega - \epsilon_{o\mathbf{q}} + i\eta\,\mathrm{sgn}\left(\epsilon_{o\mathbf{q}} - \mu\right)} \tag{1.41}$$

Now plugging both of these back into the original expression, we find:

$$\begin{aligned}
\Sigma_{nn'}(\mathbf{k},\omega) &= \frac{i}{2\pi}\sum_{o\mathbf{q}}\int_{-\infty}^{\infty} d\omega' \frac{e^{i\omega'\eta}}{\omega+\omega'-\epsilon_{o\mathbf{q}}+i\eta\,\mathrm{sgn}\left(\epsilon_{o\mathbf{q}}-\mu\right)} \\
&\quad\times \iint d\mathbf{r}d\mathbf{r}'\psi^*_{n\mathbf{k}}(\mathbf{r})\psi_{o\mathbf{q}}(\mathbf{r})W_0(\mathbf{r},\mathbf{r}',\omega')\psi^*_{o\mathbf{q}}\left(\mathbf{r}'\right)\psi_{n'\mathbf{k}}(\mathbf{r}') \qquad (1.42)\\
&= \frac{i}{2\pi}\sum_{o\mathbf{q}}\int_{-\infty}^{\infty} d\omega' \frac{e^{i\omega'\eta}}{\omega+\omega'-\epsilon_{o\mathbf{k}-\mathbf{q}}+i\eta\,\mathrm{sgn}\left(\epsilon_{o\mathbf{k}-\mathbf{q}}-\mu\right)}(n_{\mathbf{k}}o_{\mathbf{k}-\mathbf{q}}|W_0|o_{\mathbf{k}-\mathbf{q}}n'_{\mathbf{k}}) \qquad (1.43)
\end{aligned}$$

Where we have used the fact that the momentum index $\mathbf{q}$ is the same as $\mathbf{k}-\mathbf{q}$, given that we are looping over both $\mathbf{k}$ and $\mathbf{q}$ anyways.

So the Green's function will bring poles at $\omega' = \epsilon_{0\mathbf{k}-\mathbf{q}} - \omega + i\eta\,\mathrm{sgn}(\mu - \epsilon_{0\mathbf{k}-\mathbf{q}})$. Now, we know that the screened Coulomb interaction has the expansion in terms of the bare Coulomb potential v and the density response function χ_0 as $W_0 = v + v\chi_0 v + v\chi_0 v\chi_0 v + \cdots = v\left(1+\chi_0 v+\chi_0 v\chi_0 v+\cdots\right) = v\left(1-\chi_0 v\right)^{-1}$, where we recognize the dielectric function as $\epsilon_0 = 1-\chi_0 v$ so we can express the screened Coulomb interaction as

$$W_0(\mathbf{r},\mathbf{r}',\omega) = \frac{v(\mathbf{r},\mathbf{r}')}{1-\left(\chi_0 v\right)(\mathbf{r},\mathbf{r}',\omega)} \tag{1.44}$$

recalling that the bare Coulomb interaction should be independent of frequency. A discussion of how to compute the screened Coulomb interaction can be found in this old work [8]. To simplify notation let us define a polarizability $\mathbf{\Pi}\left(\mathbf{r},\mathbf{r}',\omega\right) = \left(\chi_0 v\right)\left(\mathbf{r},\mathbf{r}',\omega\right)$, so that we can rewrite the screened Coulomb interaction as:

$$(n_{\mathbf{k}}o_{\mathbf{k}-\mathbf{q}}|W_0|o_{\mathbf{k}-\mathbf{q}}n'_{\mathbf{k}}) = \iint d\mathbf{r}d\mathbf{r}'\psi^*_{n\mathbf{k}}(\mathbf{r})\psi_{o\mathbf{q}}(\mathbf{r})W_0(\omega)\psi^*_{o\mathbf{q}}\left(\mathbf{r}'\right)\psi_{n'\mathbf{k}}(\mathbf{r}') \tag{1.45}$$

At this point, we recognize the decomposition of the ERIs with the Cholesky vectors as:

$$(p_{\mathbf{k}_p}q_{\mathbf{k}_q}|\frac{1}{|\mathbf{r}-\mathbf{r}'|}|r_{\mathbf{k}_r}s_{\mathbf{k}_s}) = \sum_{PQ} v^{p\mathbf{k_p}q\mathbf{k_q}}_{P\mathbf{q}} v^{r\mathbf{k_r}s\mathbf{k_s}}_{Q(-\mathbf{q})} \tag{1.46}$$

so each Cholesky brings a factor of $\mathbf{J}^{\frac{1}{2}}$. Each Cholesky is defined as:

$$v^{p\mathbf{k_p}q\mathbf{k_q}}_{P\mathbf{q}} = \sum_R \mathbf{J}^{-\frac{1}{2}}_{RP}(\mathbf{q})\left(R\mathbf{q}\mid p\mathbf{k}_p q\mathbf{k}_q\right) \tag{1.47}$$

where

$$\begin{aligned}\mathbf{J}_{PQ}(\mathbf{k}) &= \iint d\mathbf{r}d\mathbf{r}'\phi_{P(-\mathbf{k})}(\mathbf{r})\frac{1}{|\mathbf{r}-\mathbf{r}'|}\phi_{Q\mathbf{k}}(\mathbf{r}') \\ (Q\mathbf{k}_{rs} \mid r\mathbf{k}_r s\mathbf{k}_s) &= \iint d\mathbf{r}d\mathbf{r}'\phi_{Q\mathbf{k}_{rs}}(\mathbf{r})\frac{1}{|\mathbf{r}-\mathbf{r}'|}\phi^*_{r\mathbf{k}_r}(\mathbf{r}')\,\phi_{s\mathbf{k}_s}(\mathbf{r}')\end{aligned} \tag{1.48}$$

So the simplest thing now will be to derive an expression for the columb interaction in terms of an auxiliary basis:

$$W_{0,PQ}(\omega) = \left[\mathbf{J}(\mathbf{I}-\mathbf{\Pi}(\mathbf{q},\omega))^{-1}\right]_{PQ} \tag{1.49}$$

and then we need to contract with the Choleskies to get the matrix element:

$$(n_{\mathbf{k}}o_{\mathbf{k}-\mathbf{q}}|W_0|o_{\mathbf{k}-\mathbf{q}}n'_{\mathbf{k}}) = \sum_{PQ} v_P^{nm}\left[\mathbf{I}-\mathbf{\Pi}(\mathbf{q},\omega)\right]^{-1}_{PQ} v_Q^{mn'} \tag{1.50}$$

So in our quest to find poles of W_0, we are really just looking for poles of the χ_0. χ_0 is given by:

$$\chi_0(\mathbf{r},\mathbf{r}',\omega) = \sum_{r\mathbf{k}s\mathbf{k}'}(f_{r\mathbf{k}}-f_{s\mathbf{k}'})\frac{\psi_{r\mathbf{k}}(\mathbf{r})\psi^*_{r\mathbf{k}}(\mathbf{r}')\,\psi_{s\mathbf{k}'}(\mathbf{r}')\,\psi^*_{s\mathbf{k}'}(\mathbf{r})}{\omega-(\epsilon_{r\mathbf{k}}-\epsilon_{s\mathbf{k}'})+i\eta\,\mathrm{sgn}(\epsilon_{r\mathbf{k}}-\epsilon_{s\mathbf{k}'}-\mu)} \tag{1.51}$$

where the occupations of the KS states $r\mathbf{k}(s\mathbf{k}')$ with energies $\epsilon_{r\mathbf{k}}(\epsilon_{s\mathbf{k}'})$ are given by the Fermi-Dirac distribution $f_{r\mathbf{k}}(f_{s\mathbf{k}'})$, which is just a step function at zero temperature. Notice that the occupation factor will always be 0 unless rs form an occupied-virtual pair. So we can separate the density response into two terms, one where δ_{ri} and δ_{sa} and the other with δ_{ra} and δ_{si}, where i and a are occupied and virtual indices, respectively. This allows us to now combine with the bare Coulomb potential in order to form the polarizability $\Pi \equiv \chi_0 v$ as:

$$\Pi(\mathbf{r},\mathbf{r}',\omega) = \sum_{i\mathbf{k}a\mathbf{k}'}\frac{\psi_{i\mathbf{k}}(\mathbf{r})\psi^*_{i\mathbf{k}}(\mathbf{r}')\frac{1}{|\mathbf{r}-\mathbf{r}'|}\psi_{a\mathbf{k}'}(\mathbf{r}')\,\psi^*_{a\mathbf{k}'}(\mathbf{r})}{\omega+(\Omega_{i\mathbf{k}a\mathbf{k}'})-i\eta} - \sum_{a\mathbf{k}i\mathbf{k}'}\frac{\psi_{a\mathbf{k}}(\mathbf{r})\psi^*_{a\mathbf{k}}(\mathbf{r}')\frac{1}{|\mathbf{r}-\mathbf{r}'|}\psi_{i\mathbf{k}'}(\mathbf{r}')\,\psi^*_{i\mathbf{k}'}(\mathbf{r})}{\omega-(\Omega_{i\mathbf{k}a\mathbf{k}'})+i\eta}, \tag{1.52}$$

where we define the KS eigenvalue differences as $\Omega_{i\mathbf{k}a\mathbf{k}'} = \epsilon_{a\mathbf{k}} - \epsilon_{i\mathbf{k}'}$, which will eventually become the excitation energies from RPA. So sandwiching this operator in between the molecular or brutal bases gives:

$$\langle n\mathbf{k}|\,\Pi(\omega)\,|n'\mathbf{k}\rangle = \sum_{iajb\mathbf{k}\mathbf{k}'}\frac{(ia\mid jb)}{(\omega+\Omega^\mu_{\mathbf{k}})-i\eta} - \sum_{aibj\mathbf{k}\mathbf{k}'}\frac{(ai\mid bj)}{(\omega-\Omega^\mu_{\mathbf{k}})+i\eta} \tag{1.53}$$

So we see that we can get the poles of the screened Coulomb interaction by the poles of the polarizability, which are $\omega = \Omega^\mu_{\mathbf{k}} - i\eta$ and $\omega = \Omega^\mu_{\mathbf{k}} + i\eta$, suggesting that they are in the upper complex plane for excitations and vice versa for deexcitations. See the figure 1.1 for a picture. For a more comprehensive picture, this should be juxtaposed with the figure from Tianyu's paper for CD. In the literature, they talk about approximating the dielectric function by a multiple one or a single pole approximation, so which one would I want to implement? This suggests that the notation in the G_0W_0 literature is confusing because they always say that to solve for the χ_0 in the RPA, but if we are actually dealing with χ_0, which is the Kohn-Sham density response function, then we don't use the RPA, where the density response function is solved for using a Dyson-like equation [10]:

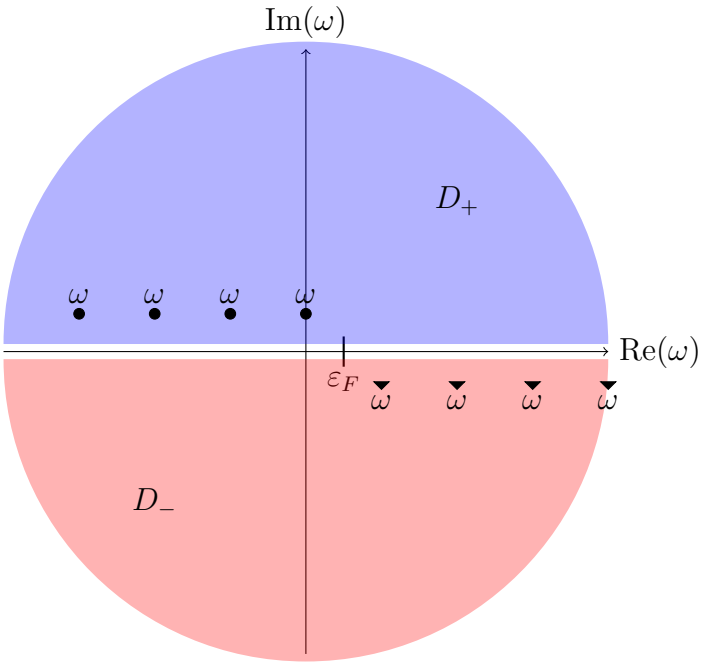

Figure 1.1: Contour for the complex frequency integral. The poles are denoted by the various ω. The Fermi energy is denoted by ε_F. The integration contour D_+ is the semicircle in the upper complex plane, while D_- is the semicircle in the lower complex plane.

$$\chi^{\lambda}\left(\mathbf{r},\mathbf{r}',i\omega\right)=\chi^{0}\left(\mathbf{r},\mathbf{r}',i\omega\right)+\int d\mathbf{r}_1 d\mathbf{r}_2 \chi^{0}\left(\mathbf{r},\mathbf{r}_1,i\omega\right)\left[\frac{\lambda}{|\mathbf{r}_1-\mathbf{r}_2|}+f_{\mathrm{xc}}^{\lambda}\left(\mathbf{r}_1,\mathbf{r}_2,i\omega\right)\right]\chi^{\lambda}\left(\mathbf{r}_2,\mathbf{r}',\omega\right) \tag{1.54}$$

where the parameter λ controls the amount of interaction in the system, ranging from $\lambda = 0$ for the KS reference system to $\lambda = 1$ for the fully interacting system. The $f_{\mathrm{xc}}^{\lambda}$ is the exchange-correlation kernel, which is set to zero for the RPA. But we will proceed with an RPA calculation anyways in order to solve for the excitation energies and their corresponding eigenvectors. So it makes sense that the numerator of the expression for the screened Coulomb interaction should be given a construction of the ERIs with the excitation factors in a transition density defined as:

$$w_{pq}^{\mu}=\sum_{ia}(pq|ia)\left(X_{ia}^{\mu}+Y_{ai}^{\mu}\right) \tag{1.55}$$

where we have defined the excitation and de-excitation vectors at the excitation index μ as X_{ia}^{μ} and Y_{ai}^{μ}, respectively. I am not sure how to connect this with the known expression $v\epsilon^{-1}$; I see the similarities given that we are contracting an ERI with what we get from the RPA calculation that is connected to the polarizability, but can't connect exactly. We want to figure out how this matches with my previous $O(N^6)$ expression, which was

$$\Sigma_{pp}^{\mathrm{corr}}(\omega)=\sum_{\mu}^{\mathrm{RPA}}\left(\sum_{i}^{\mathrm{occupied}}\frac{w_{pi}^{\mu}w_{ip}^{\mu}}{\omega-(\epsilon_i-\Omega_{\mu})}+\sum_{a}^{\mathrm{virtual}}\frac{w_{pa}^{\mu}w_{ap}^{\mu}}{\omega-(\epsilon_a+\Omega_{\mu})}\right) \tag{1.56}$$

for the molecular case. Today I want us to dissect how this equation came about, so that I can understand for my k-point version.

1.2.2 Analytic continuation

We start with the original form for the self-energy along the real axis:

$$\Sigma\left(\mathbf{r},\mathbf{r}',\omega\right)=\frac{i}{2\pi}\int_{-\infty}^{\infty}d\omega' e^{i\omega'\eta}G_0\left(\mathbf{r},\mathbf{r}',\omega+\omega'\right)W_0\left(\mathbf{r},\mathbf{r}',\omega'\right) \tag{1.57}$$

But to avoid the poles, we need to evaluate along the imaginary axis, so the problem becomes:

$$\Sigma\left(\mathbf{r},\mathbf{r}',i\omega\right)=-\frac{1}{2\pi}\int_{-\infty}^{\infty}d\omega' G_0\left(\mathbf{r},\mathbf{r}',i\omega+i\omega'\right)W_0\left(\mathbf{r},\mathbf{r}',i\omega'\right)$$

We are interested in evaluating the matrix elements of this operator in the molecular orbital basis. Note that both molecular orbitals must have the same crystal momentum in order for it to be conserved in this process. We also apply the identity operator:

$$\left\langle n\mathbf{k}\right|\Sigma(i\omega)\left|n'\mathbf{k}\right\rangle=-\frac{1}{2\pi}\sum_{m\mathbf{k}'}\int_{-\infty}^{\infty}d\omega'\left\langle n\mathbf{k}\right|G_0(i\omega+i\omega')\left|m\mathbf{k}'\right\rangle\left\langle m\mathbf{k}'\right|W_0(i\omega')\left|n'\mathbf{k}\right\rangle \tag{1.58}$$

The noninteracting Green's function has the form:

$$G_0\left(\mathbf{r},\mathbf{r}',i\omega\right)=\sum_{m\mathbf{k}_m}\frac{\psi_{m\mathbf{k}_m}(\mathbf{r})\psi^*_{m\mathbf{k}_m}\left(\mathbf{r}'\right)}{i\omega+\epsilon_F-\epsilon_{m\mathbf{k}_m}}\implies G_0\left(\mathbf{k}-\mathbf{q},i\omega+i\omega'\right)=\sum_{m\mathbf{k}-\mathbf{q}}\frac{\psi_{m\mathbf{k}-\mathbf{q}}\psi^*_{m\mathbf{k}-\mathbf{q}}}{i\left(\omega+\omega'\right)+\epsilon_F-\epsilon_{m\mathbf{k}-\mathbf{q}}}$$

so that the above equation simplifies to:

$$\mathbf{\Sigma}_{nn'}(\mathbf{k},i\omega)=-\frac{1}{2\pi N_{\mathbf{k}}}\sum_{m\mathbf{q}}\int_{-\infty}^{\infty}d\omega'\frac{(n\mathbf{k},m\mathbf{k}-\mathbf{q}\mid W_0(\mathbf{q},i\omega)\mid m\mathbf{k}-\mathbf{q},n'\mathbf{k})}{i\left(\omega+\omega'\right)+\epsilon_F-\epsilon_{m\mathbf{k}-\mathbf{q}}} \tag{1.59}$$

Screened Coulomb Interaction

$$(n\mathbf{k},m\mathbf{k}-\mathbf{q}\left|W_0(\mathbf{q},i\omega)\right|m\mathbf{k}-\mathbf{q},n'\mathbf{k})=\int\int d\mathbf{r}_1d\mathbf{r}_2\psi^*_{n\mathbf{k}}(\mathbf{r}_1)\psi_{m\mathbf{k}-\mathbf{q}}(\mathbf{r}_1)W_0(\mathbf{q},\mathbf{r}_1,\mathbf{r}_2,i\omega)\psi^*_{m\mathbf{k}-\mathbf{q}}(\mathbf{r}_2)\psi_{n'\mathbf{k}}(\mathbf{r}_2)$$

We expand the orbital pair product $\psi^*_{n\mathbf{k}}(\mathbf{r})\psi_{m\mathbf{k}-\mathbf{q}}(\mathbf{r})$ in the auxiliary basis

$$\psi^*_{n\mathbf{k}}(\mathbf{r})\psi_{m\mathbf{k}-\mathbf{q}}(\mathbf{r})=\sum_P b^{n\mathbf{k},m\mathbf{k}-\mathbf{q}}_{P\mathbf{q}}\phi_{P\mathbf{q}}(\mathbf{r})$$

and

$$\psi^*_{m\mathbf{k}-\mathbf{q}}(\mathbf{r})\psi_{n'\mathbf{k}}(\mathbf{r})=\sum_Q b^{m\mathbf{k}-\mathbf{q},n'\mathbf{k}}_{Q(-\mathbf{q})}\phi_{Q(-\mathbf{q})}(\mathbf{r}) \tag{1.60}$$

where we have recognized the fact that in the former there is a momentum transfer of $\mathbf{q}$, and in the latter, there is a momentum transfer of $-\mathbf{q}$. Substituting in gives

$$(n\mathbf{k}, m\mathbf{k}-\mathbf{q}\,|W_0(\mathbf{q},i\omega)|\,m\mathbf{k}-\mathbf{q}, n'\mathbf{k}) \tag{1.61}$$

$$= \sum_{PQ} b_{P\mathbf{q}}^{n\mathbf{k},m\mathbf{k}-\mathbf{q}} \left[\iint d\mathbf{r}_1 d\mathbf{r}_2 \phi_{P\mathbf{q}}(\mathbf{r}_1) W_0(\mathbf{q},\mathbf{r}_1,\mathbf{r}_2,i\omega)\phi_{Q(-\mathbf{q})}(\mathbf{r}_2)\right] b_{Q(-\mathbf{q})}^{m\mathbf{k}-\mathbf{q},n'\mathbf{k}} \tag{1.62}$$

with

$$b_{P\mathbf{q}}^{n\mathbf{k},m\mathbf{k}-\mathbf{q}} = \sum_R (n\mathbf{k}, m\mathbf{k}-\mathbf{q} \mid R\mathbf{q}) \cdot \mathbf{J}_{RP}^{-1}(\mathbf{q}) \tag{1.63}$$

Now is a good place to recall their definition of the density fitting where the ERIs are represented as:

$$(p\mathbf{k}_p q\mathbf{k}_q \mid r\mathbf{k}_r s\mathbf{k}_s) = \sum_{PQ} (p\mathbf{k}_p q\mathbf{k}_q \mid P\mathbf{k}_{pq})\, \mathbf{J}_{PQ}^{-1}\, (Q\mathbf{k}_{rs} \mid r\mathbf{k}_r s\mathbf{r}_s)\,,$$

with

$$\mathbf{J}_{PQ}(\mathbf{k}) = \iint d\mathbf{r} d\mathbf{r}' \phi_{P(-\mathbf{k})}(\mathbf{r}) \frac{1}{|\mathbf{r}-\mathbf{r}'|} \phi_{Q\mathbf{k}}(\mathbf{r}')\,,$$

$$(Q\mathbf{k}_{rs} \mid r\mathbf{k}_r s\mathbf{k}_s) = \iint d\mathbf{r} d\mathbf{r}' \phi_{Q\mathbf{k}_{rs}}(\mathbf{r}) \frac{1}{|\mathbf{r}-\mathbf{r}'|} \phi_{r\mathbf{k}_r}^*(\mathbf{r}')\, \phi_{s\mathbf{k}_s}(\mathbf{r}')\,.$$

Note that these b are then not yet our Cholesky vectors, since each one contains $\frac{|\mathbf{r}-\mathbf{r}'|}{|\mathbf{r}-\mathbf{r}'|}$ scaling, i.e., there should be a factor of $\mathbf{J}^{-\frac{1}{2}}$ instead of $\mathbf{J}^{-1}$ in 1.63 if we are to apply the Cholesky vectors. At this point, we use the expansion of the screened Coulomb interaction:

$$W_0 = v + v\chi_0 v + v\chi_0 v\chi_0 v + \cdots \tag{1.64}$$

$$= v(1 + \chi_0 v + \chi_0 v\chi_0 v + \cdots) \tag{1.65}$$

$$= v^{1/2}\,(1-\chi_0)^{-1}\, v^{1/2} \tag{1.66}$$

simplifying to

$$(n\mathbf{k}, m\mathbf{k}-\mathbf{q}\,|W_0(\mathbf{q},i\omega)|\,m\mathbf{k}-\mathbf{q}, n'\mathbf{k}) = \sum_{PQ} b_{P\mathbf{q}}^{n\mathbf{k},m\mathbf{k}-\mathbf{q}} \left[\mathbf{J}^{\frac{\mathbf{1}}{\mathbf{2}}}\,(\mathbf{I}-\mathbf{\Pi}(\mathbf{q},i\omega))\,\mathbf{J}^{\frac{\mathbf{1}}{\mathbf{2}}}\right]_{PQ}^{-1} b_{Q(-\mathbf{q})}^{m\mathbf{k}-\mathbf{q},n'\mathbf{k}} \tag{1.67}$$

$$= \sum_{PQ} v_P^{nm} \left[\mathbf{I}-\mathbf{\Pi}\,(\mathbf{q},i\omega')\right]_{PQ}^{-1} v_Q^{mn'} \tag{1.68}$$

where $\mathbf{J}_{PQ}$ is the Coulomb interaction projected onto the auxiliary basis, and we have defined

$$v_{P\mathbf{q}}^{n\mathbf{k},m\mathbf{k}-\mathbf{q}} = \sum_{pq} C_{pn}(\mathbf{k}) C_{qm}(\mathbf{k}-\mathbf{q}) v_{P\mathbf{q}}^{p\mathbf{k},q\mathbf{k}-\mathbf{q}} \tag{1.69}$$

with

$$v_{P\mathbf{q}}^{p\mathbf{k},q\mathbf{k}-\mathbf{q}} = \sum_R (p\mathbf{k}, q\mathbf{k}-\mathbf{q} \mid R\mathbf{q}) \mathbf{J}_{RP}^{-1/2}(\mathbf{q}) \tag{1.70}$$

If we first rename $\mathbf{k}' = \mathbf{k} - \mathbf{q} \implies \mathbf{k} = \mathbf{k}' + \mathbf{q}$, and then we are free to redefine $\mathbf{q} \to -\mathbf{q}$, so that 1.69 becomes

$$v_{P-\mathbf{q}}^{n\mathbf{k}-\mathbf{q},m\mathbf{k}} = \sum_{pq} C_{pn}(\mathbf{k}-\mathbf{q}) C_{qm}(\mathbf{k}) v_{P-\mathbf{q}}^{p\mathbf{k}-\mathbf{q},q\mathbf{k}} \tag{1.71}$$

but we know that the bare Coulomb potential projected onto the auxiliary basis is given by

$$v_{P\mathbf{q}}^{n\mathbf{k},m\mathbf{k}-\mathbf{q}} = \sum_{pq} C_{pn}(\mathbf{k}) C_{qm}(\mathbf{k}-\mathbf{q}) v_{P\mathbf{q}}^{p\mathbf{k},q\mathbf{k}-\mathbf{q}} \tag{1.72}$$

To ease notation, some momentum labels are suppressed in the above and following equations (e.g., we will use b_P^{nm} to denote $b_{P\mathbf{q}}^{n\mathbf{k},m\mathbf{k}-\mathbf{q}}$). Using Eqs. 19-21, the matrix elements of W_0 are computed as

$$\begin{aligned}
&(n\mathbf{k}, m\mathbf{k}-\mathbf{q} \,|W_0|\, m\mathbf{k}-\mathbf{q}, n'\mathbf{k}) \\
&= \sum_{PQ} b_P^{nm} \left[\iint d\mathbf{r} d\mathbf{r}' \phi_{P\mathbf{q}}(\mathbf{r}) W_0(\mathbf{r}, \mathbf{r}', i\omega') \, \phi_{Q(-\mathbf{q})}(\mathbf{r}') \right] b_Q^{mn'} \\
&= \sum_{PQ} b_P^{nm} \left[\mathbf{J}_{PQ}(\mathbf{q}) + \left(\mathbf{J}^{1/2} \mathbf{\Pi} \mathbf{J}^{1/2} \right)_{PQ}(\mathbf{q}) + \ldots \right] b_Q^{mn'} \\
&= \sum_{PQ} v_P^{nm} \left[\mathbf{I} - \mathbf{\Pi}(\mathbf{q}, i\omega') \right]_{PQ}^{-1} v_Q^{mn'}
\end{aligned}$$

The 3-center 2-electron integral v_P^{nm} between auxiliary basis function P and molecular orbital pairs nm is obtained from an AO to MO transformation of the GDF AO integrals defined in Eq. 15:

$$v_P^{nm} = \sum_p \sum_q C_{pn}(\mathbf{k}) C_{qm}(\mathbf{k}-\mathbf{q}) v_{P\mathbf{q}}^{p\mathbf{k},q\mathbf{k}-\mathbf{q}}$$

where $C(\mathbf{k})$ refers to the MO coefficients in the AO basis. $\Pi(\mathbf{q}, i\omega')$ in Eq. 22 is an auxiliary density response function:

$$\mathbf{\Pi}_{PQ}(\mathbf{q}, i\omega') = \frac{2}{N_{\mathbf{k}}} \sum_{\mathbf{k}} \sum_{i}^{\text{occ}} \sum_{a}^{\text{vir}} v_P^{ia} \frac{\epsilon_{i\mathbf{k}} - \epsilon_{a\mathbf{k}-\mathbf{q}}}{\omega'^2 + \left(\epsilon_{i\mathbf{k}} - \epsilon_{a\mathbf{k}-\mathbf{q}}\right)^2} v_Q^{ai}$$

1.3 UHF formalism

The first thing to do is to solve the Casida equation for the polarizability in the direct formulation of the RPA:

$$\begin{pmatrix} \mathbf{A} & \mathbf{B} \\ \mathbf{B}^* & \mathbf{A}^* \end{pmatrix} \begin{pmatrix} \mathbf{X} \\ \mathbf{Y} \end{pmatrix} = \begin{pmatrix} \Omega & 0 \\ 0 & -\Omega \end{pmatrix} \begin{pmatrix} \mathbf{X} \\ \mathbf{Y} \end{pmatrix} \tag{1.73}$$

with $\mathbf{A}$ and $\mathbf{B}$ given by

$$\begin{aligned}
\mathbf{A}_{ia,jb}^{\sigma\sigma'} &= \delta_{ij}\delta_{ab}\delta_{\sigma\sigma'}(\varepsilon_a - \varepsilon_i) + (i_\sigma a_\sigma | b_{\sigma'} j_{\sigma'}) \\
\mathbf{B}_{ia,jb}^{\sigma\sigma'} &= (i_\sigma a_\sigma | j_{\sigma'} b_{\sigma'})
\end{aligned} \tag{1.74}$$

Therefore, with the different spins we form a super matrix:

$$\begin{pmatrix} \begin{pmatrix} \mathbf{A}_{\alpha\alpha} & \mathbf{A}_{\alpha\beta} \\ \mathbf{A}_{\beta\alpha} & \mathbf{A}_{\beta\beta} \end{pmatrix} & \begin{pmatrix} \mathbf{B}_{\alpha\alpha} & \mathbf{B}_{\alpha\beta} \\ \mathbf{B}_{\beta\alpha} & \mathbf{B}_{\beta\beta} \end{pmatrix} \\ \begin{pmatrix} \mathbf{B}^*_{\alpha\alpha} & \mathbf{B}^*_{\alpha\beta} \\ \mathbf{B}^*_{\beta\alpha} & \mathbf{B}^*_{\beta\beta} \end{pmatrix} & \begin{pmatrix} \mathbf{A}^*_{\alpha\alpha} & \mathbf{A}^*_{\alpha\beta} \\ \mathbf{A}^*_{\beta\alpha} & \mathbf{A}^*_{\beta\beta} \end{pmatrix} \end{pmatrix} \begin{pmatrix} \mathbf{X}_{\alpha\alpha} & \mathbf{X}_{\alpha\beta} \\ \mathbf{X}_{\beta\alpha} & \mathbf{X}_{\beta\beta} \\ \mathbf{Y}_{\alpha\alpha} & \mathbf{Y}_{\alpha\beta} \\ \mathbf{Y}_{\beta\alpha} & \mathbf{Y}_{\beta\beta} \end{pmatrix} = \begin{pmatrix} \Omega & 0 & 0 & 0 \\ 0 & \Omega & 0 & 0 \\ 0 & 0 & -\Omega & 0 \\ 0 & 0 & 0 & -\Omega \end{pmatrix} \begin{pmatrix} \mathbf{X}_{\alpha\alpha} & \mathbf{X}_{\alpha\beta} \\ \mathbf{X}_{\beta\alpha} & \mathbf{X}_{\beta\beta} \\ \mathbf{Y}_{\alpha\alpha} & \mathbf{Y}_{\alpha\beta} \\ \mathbf{Y}_{\beta\alpha} & \mathbf{Y}_{\beta\beta} \end{pmatrix} \tag{1.75}$$

Now, there will be $2OV$ unique excitation energies; we sort them into singlets or triplets as follows: for each excitation we compute the overlap between the α and β excitation. For TDA, this is just the νth column of $\begin{pmatrix} \mathbf{X}_{\alpha\alpha} & \mathbf{X}_{\alpha\beta} \end{pmatrix}$ with the νth row of $\begin{pmatrix} \mathbf{X}_{\beta\alpha} \\ \mathbf{X}_{\beta\beta} \end{pmatrix}$. If greater than 0, we have a singlet excitation, otherwise we have a triplet excitation. For later use in GW, we just want the neutral excitation energies, so we only care about the singlet excitations.

1.4 Deriving linear response: 11/22

1.4.1 The Fundamentals

The motivation for this is to be able to understand why the poles of the screened Coulomb interaction are the same as those of the fully interacting polarizability, which are given by the frequencies of the RPA, obtained by diagonalizing the Casida equation. And then we want to be able to connect why $W_0 = v + v\chi_0 v + \ldots = \frac{v}{1-\chi_0 v}$ where W_0 is the screened Coulomb interaction and χ_0 is the non-interacting polarizability with Lehmann representation.

$$\chi_0\left(\mathbf{r}, \mathbf{r}', \omega\right) = \sum_{ia} \frac{\psi_i(\mathbf{r})\psi_a^*(\mathbf{r}')\psi_i(\mathbf{r}')\psi_a^*(\mathbf{r})}{\omega - (\epsilon_a - \epsilon_i) + i\eta\,\mathrm{sgn}\left(\epsilon_a - \epsilon_i - \mu\right)} \tag{1.76}$$

to do so, one must understand the reformulation of based on the density matrix as for posed by Furche [5]. Alternatively, let us start from the known Dyson equation that relates the fully interacting Green's function to the non-interacting one. We know the integral form of the Dyson equation is

$$G(1,2) = G_0(1,2) + \int d3d4 G_0(1,3)\Sigma(3,4)G(4,2) \tag{1.77}$$

but we proceed symbolically to get

$$G = G_0 + G_0\Sigma G \tag{1.78}$$

$$\left(I - G_0\Sigma\right) G = G_0 \tag{1.79}$$

$$G = \left(I - G_0\Sigma\right)^{-1} G_0 \tag{1.80}$$

$$G = \left(G_0\left(G_0^{-1} - \Sigma\right)\right)^{-1} G_0 \tag{1.81}$$

$$G = \left(G_0^{-1} - \Sigma\right)^{-1} \tag{1.82}$$

Now, we also know the Dyson equation for the polarizability is

$$\begin{aligned} \chi\left(\omega, x_1, x_2\right) =& \chi_0\left(\omega, x_1, x_2\right) + \int dx dx' \chi_0\left(\omega, x_1, x\right) \\ & \times \left(\frac{1}{|\mathbf{r} - \mathbf{r}'|} + f_{\mathrm{xc}}\left(\omega, x, x'\right)\right) \chi\left(\omega, x', x_2\right) \end{aligned} \tag{1.83}$$

In the RPA, we neglect the exchange correlation kernel f_{xc}, so we have

$$\chi_{RPA} = \chi_0 + \chi_0 v \chi_{RPA} = \frac{\chi_0}{1 - v\chi_0} \tag{1.84}$$

where in the final step we used the symbolic manipulation that was used before. So $W_0 = \frac{v}{1-v\chi_0} = v\chi_{RPA}\chi_0^{-1} = v\left(\frac{\chi_0\chi_0^{-1}}{1-v\chi_0}\right) = \frac{v}{1-v\chi_0}$. Therefore, we see why the poles of W_0 are the same as those of χ_{RPA}, since they have a linear relationship. Now, we will proceed to derive the poles of χ_{RPA}. But first we must introduce the density matrix based linear response theory.

1.4.2 Introduction to TDKS

In time-dependent density functional theory (TDDFT), the **Time-Dependent Kohn-Sham (TDKS)** equations describe a system of N noninteracting fermions that reproduce the same time-dependent density $\rho(t, \mathbf{r})$ as the interacting system. The TDKS equations are given by:

$$i\frac{\partial}{\partial t}\varphi_j(t, \mathbf{r}) = H[\rho](t, \mathbf{r})\varphi_j(t, \mathbf{r}) \tag{1.85}$$

where $j = 1, \ldots, N$ indexes the Kohn-Sham orbitals $\varphi_j(t, \mathbf{r})$, and $H[\rho](t, \mathbf{r})$ is the effective one-particle Hamiltonian defined as:

$$H[\rho](t, \mathbf{r}) = \frac{\boldsymbol{\pi}^2(t, \mathbf{r})}{2} + v_{\text{eff}}[\rho](t, \mathbf{r}) \tag{1.86}$$

where $v_{\text{eff}}[\rho](t, \mathbf{r}) = v_{\text{ext}}(t, \mathbf{r}) + v_{\text{H}}[\rho](t, \mathbf{r}) + v_{\text{xc}}[\rho](t, \mathbf{r})$.

The operator $\boldsymbol{\pi}(t, \mathbf{r})$ is known as the **kinetic momentum operator**. In the presence of an electromagnetic field, the kinetic momentum operator is modified from the canonical momentum operator $\mathbf{p}$ to include the effects of the vector potential $\mathbf{A}_{\text{ext}}(t, \mathbf{r})$:

$$\boldsymbol{\pi}(t, \mathbf{r}) = \mathbf{p} + \frac{1}{c}\mathbf{A}_{\text{ext}}(t, \mathbf{r}) \tag{1.87}$$

Here, $\mathbf{p} = -i\hbar\nabla$ is the canonical momentum operator, and c is the speed of light. The vector potential $\mathbf{A}_{\text{ext}}(t, \mathbf{r})$ accounts for the influence of external perturbative electromagnetic fields on the system. *Why it does the influence of the vector potential not just all go into the v_{eff}?*

But we know that under a gauge transformation, the physical observables will be invariant, while the orbits will merely acquire a **phase factor**:

$$\varphi_j(t, \mathbf{r}) \to \varphi_j'(t, \mathbf{r}) = \varphi_j(t, \mathbf{r}) \exp\left(-\frac{i}{c}\psi(t, \mathbf{r})\right) \tag{1.88}$$

Therefore observables, like the density or current density will be unaffected by this gauge transformation.

1.4.3 Density Matrix Formulation in TDKS Theory

In Time-Dependent Density Functional Theory (TDDFT), the **Time-Dependent Kohn-Sham (TDKS)** equations 1.85 describe a system of N noninteracting fermions that reproduce the same time-dependent electron density $\rho(t, \mathbf{r})$ as the interacting system. An alternative formulation of TDKS theory utilizes the one-particle density matrix $\gamma(t, \mathbf{r}, \mathbf{r}')$, which offers advantage because it introduces a basis that one can exploit computationally. The one-particle density matrix is defined as:

$$\gamma(t, \mathbf{r}, \mathbf{r}') = \sum_{j=1}^{N} \varphi_j(t, \mathbf{r}) \varphi_j^*(t, \mathbf{r}') \tag{1.89}$$

and it is idempotent, meaning that

$$\gamma^2(t, \mathbf{r}, \mathbf{r}') = \gamma(t, \mathbf{r}, \mathbf{r}') \tag{1.90}$$

See section **??** for a proof.

Now, we would like to derive an evolution equation for the density matrix in analogy with the one we already have for the KS orbitals in equation 1.85. The result is

$$i\frac{\partial}{\partial t}\gamma(t) = [H[\rho](t), \gamma(t)] \tag{1.91}$$

See section **??** for proof. For the purposes of response theory, it is convenient to consider external scalar potentials,

$$v_{\text{ext}}(t, x) = v^{(0)}(x) + \sum_{\alpha} \lambda_\alpha \left(v^{(\alpha)}(\omega_\alpha, x)\, e^{i\omega_\alpha t} + v^{(\alpha)}(-\omega_\alpha, x)\, e^{-i\omega_\alpha t} \right) \tag{1.92}$$

and longitudinal vector potentials

$$\mathbf{A}_{\text{ext}}(t, x) = \sum_{\alpha} \lambda_\alpha \left(\mathbf{A}^{(\alpha)}(\omega_\alpha, x)\, e^{i\omega_\alpha t} + \mathbf{A}^{(\alpha)}(-\omega_\alpha, x)\, e^{-i\omega_\alpha t} \right) \tag{1.93}$$

Note that we are not considering transverse vector potentials, as we would get if we had a magnetic field. The cemetery of the Fourier component is fate in section **??**. Next, we need to determine the derivatives of the observables with respect to a perturbation. We have Any time-dependent expectation value $f_\lambda(t)$ is a function of the coupling strength vector $\boldsymbol{\lambda}$. Its response to the external perturbation is defined by its derivatives with respect to $\boldsymbol{\lambda}$ at $\boldsymbol{\lambda} = 0$. For monochromatic perturbations, the derivatives exhibit a characteristic time dependence,

$$f_\lambda(t)|_{\boldsymbol{\lambda}=0} = f^{(0)}, \tag{1.94}$$

$$\frac{\partial}{\partial \lambda_\alpha} f_\lambda(t)\bigg|_{\boldsymbol{\lambda}=0} = f^{(\alpha)}(\omega_\alpha)\, e^{i\omega_\alpha t} + f^{(\alpha)}(-\omega_\alpha)\, e^{-i\omega_\alpha t}, \tag{1.95}$$

$$\tag{1.96}$$

Proof of the second expression is given in section **??**. The third expression follows by taking the derivative of the second expression.

$$\frac{\partial^2}{\partial\lambda_\alpha\partial\lambda_\beta}f_\lambda(t)\bigg|_{\boldsymbol{\lambda}=0} = f^{(\alpha\beta)}\left(\omega_\alpha,\omega_\beta\right)e^{i\left(\omega_\alpha+\omega_\beta\right)t} + f^{(\alpha\beta)}\left(\omega_\alpha,-\omega_\beta\right)e^{i\left(\omega_\alpha-\omega_\beta\right)t} \tag{1.97}$$

$$+ f^{(\alpha\beta)}\left(-\omega_\alpha,\omega_\beta\right)e^{i\left(-\omega_\alpha+\omega_\beta\right)t} + f^{(\alpha\beta)}\left(-\omega_\alpha,-\omega_\beta\right)e^{-i\left(\omega_\alpha+\omega_\beta\right)t} \tag{1.98}$$

These expressions define the frequency dependent response of f_λ up to second order. The key step is to realize that when evaluating the expectation value of some observable O, we must consider the coupling to the density matrix, i.e. $f_\lambda(t) = \mathrm{tr}\left(O(t)\gamma_\lambda(t)\right)$.

The route to frequency-dependent response properties is then obvious: (1) Calculate the frequencydependent KS density matrix response by differentiation of Eqs. (8) and (10); (2) Take the trace with O. The interacting response can be calculated from the noninteracting KS system because the TDKS density matrix yields the interacting density and current density as it follows from Eq. (9). **Better understanding needed.**

For the idempotency constraint, expansion up to second order yields, in shorthand notation,

$$\gamma^{(0)} = \gamma^{(0)}\gamma^{(0)}, \tag{16}$$

$$\gamma^{(\alpha)} = \gamma^{(0)}\gamma^{(\alpha)} + \gamma^{(\alpha)}\gamma^{(0)}, \tag{17}$$

$$\gamma^{(\alpha\beta)} = \gamma^{(0)}\gamma^{(\alpha\beta)} + \gamma^{(\alpha)}\gamma^{(\beta)} + \gamma^{(\beta)}\gamma^{(\alpha)} + \gamma^{(\alpha\beta)}\gamma^{(0)}. \tag{18}$$

The equations of motion up to second order read

$$0 = \left[H^{(0)},\gamma^{(0)}\right] \tag{1.99}$$

$$\omega_\alpha\gamma^{(\alpha)} = \left[H^{(0)},\gamma^{(\alpha)}\right] + \left[H^{(\alpha)},\gamma^{(0)}\right] \tag{1.100}$$

$$\left(\omega_\alpha+\omega_\beta\right)\gamma^{(\alpha\beta)} = \left[H^{(0)},\gamma^{(\alpha\beta)}\right] + \left[H^{(\alpha)},\gamma^{(\beta)}\right] + \left[H^{(\beta)},\gamma^{(\alpha)}\right] + \left[H^{(\alpha\beta)},\gamma^{(0)}\right] \tag{1.101}$$

Proof of this series is given in section **??**.

1.5 GW Density Matrix

The expression for the density matrix γ is

$$\gamma\left(\mathbf{r},\mathbf{r}'\right) = -\frac{i}{2\pi}\int_{-\infty}^{+\infty} d\omega e^{i\eta\omega}G\left(\mathbf{r},\mathbf{r}',\omega\right) \tag{1.102}$$

Next, we want to consider the expression for the linearized Dyson equation, which is given by

$$G = G_0 + G_0\left(\Sigma_{xc} - V_{xc}\right)G_0 \tag{1.103}$$

So by inserting this LDE into the expression for the density matrix, we can identify a few different terms. First, consider the term just corresponding to G_0:

$$\gamma^{\mathrm{gKS}}_{\mathbf{k}ij} = 2\delta_{ij}\theta\left(\mu - \epsilon_{\mathbf{k}i}\right) \tag{1.104}$$

We can take a similar approach to treat the static portion of 1.103, i.e., the Hartree-Fock term, which is given by

$$\Delta\gamma^{\mathrm{HF}}_{\mathbf{k}ij} = 2\theta\left(\mu - \epsilon_{\mathbf{k}i}\right)\theta\left(\epsilon_{\mathbf{k}j} - \mu\right)\frac{\langle \mathbf{k}i|\Sigma_x - V_{xc}|\mathbf{k}j\rangle}{\epsilon_{\mathbf{k}i} - \epsilon_{\mathbf{k}j}} \tag{1.105}$$

Note that for a HF noninteracting Green's function, the static term is given by the Hartree-Fock self-energy, but this cancels out exactly with the exchange correlation potential V_{xc}, so this term is zero. Finally we have the most complicated term involving the insertion of $G_0\Sigma_c G_0$. The correlation self energy has a frequency dependence, so what they do is Finally, we get

$$\gamma^{GW} = \gamma^{\mathrm{gKS}} + \Delta\gamma^{\mathrm{HF}} + \Delta\gamma^{GW} \tag{1.106}$$

1.6 Summary of GW-RPA implementations

Note that mainly we will be talking about G_0W_0 implementations, but it will be commented on as to the whether self-consistency is possible. We will also discuss scaling and whether it can be applied to extended systems.

1.6.1 Complex integration approaches

Treatment of extended systems is possible for the below. Self-consistency is also possible in all cases, as there is no restriction for what the reference state can be. For a discussion of all of the below approaches, see [7].

Fully analytic

Here we will perform the frequency integration over the real axis. If we choose the upper or lower contour, we encounter many poles of G and W, so we must apply Cauchy's residue theorem repeatedly. Therefore this method must explicitly calculate the reducible polarizability for all frequencies, or in other words, if the RPA approximation is employed, diagonalize the RPA matrix, which scales as $O(N^6)$. Because of this prohibitive cost, the method is never used.

Analytic continuation (AC)

The idea is to not perform the frequency integration over the real axis in order to avoid the poles of G and W, but instead to perform this integration completely on the imaginary axis. This has positive effects on the scaling, but at the expense of a poor description of core states. For example, to accurately evaluate the QP equation for a core state, we need the self-energy at frequencies close to the core solution, where there is a fine pole structure, which AC cannot capture. By a similar reasoning, satellite features are also not captured.

Scaling analysis for extended systems

It is true that if only G_0W_0 QP energies are required, one only needs to compute the diagonal self-energy matrix elements. The most expensive step is then computing the auxiliary density response function Π, whose cost scales as $O\left(N_{\boldsymbol{k}}^2 N_O N_V N_{\text{aux}}^2\right)$. If the full G_0W_0 Green's function and off-diagonal self-energy matrix at all k-points are sought, computation of Σ^c becomes the most time-consuming step, with a cost scaling of $O\left(N_{\boldsymbol{k}}^2 N_{AO}^2 N_{\text{aux}}^2\right)$. For more detail, see [15].

Note that one must apply a finite size correction to the dielectric function to get a reasonable convergence towards the TDL, known as the head and wings correction. This is a result of the fact that RI is used for this method, where the 3-center integrals have a divergence at $\mathbf{q} = 0$.

Contour deformation (CD)

The real frequency integration is decomposed into an integral over the deformed contour minus an integral over the imaginary axis. By doing so, we avoid all poles of W, but poles of G below the Fermi level remain. This has a negative effect on the scaling if core states are sought, because we will have to evaluate the self-energy at frequencies well below the Fermi level, where we may encounter many of the occupied poles of G, which are positioned above the real axis. However the description of core states is known to be accurate, and the GW satellite structure is well-preserved.

Scaling analysis for extended systems

As is also the case for AC, if only G_0W_0 QP energies are required, one only needs to compute the diagonal self-energy matrix elements. In the decomposition of the real frequency integral in CD, the imaginary integration has a similar computational cost to the G_0W_0-AC scheme. But in the contour integral, we encounter many poles if we want core states, which are far away from the Fermi level, and so we must compute many residues. So for deep core excitations, the scaling becomes $O\left(N_{\boldsymbol{k}}^3 N_{\text{O}}^2 N_{\text{V}} N_{\text{aux}}^2\right)$. For more detail, see [15].

In analogy to AC, we must apply the finite size correction to the dielectric function for reasonable convergence towards the TDL.

1.6.2 Supermatrix approaches

These all make use of Löwdin's partitioning technique to form an upfolded supermatrix, whose eigenpairs are the QP energies and Dyson orbitals. It is given by

$$\boldsymbol{H}_{\text{Upfolded}}^{GW} = \begin{pmatrix} \boldsymbol{F} & \boldsymbol{W}^{<} & \boldsymbol{W}^{>} \\ \boldsymbol{W}^{<,\dagger} & \boldsymbol{d}^{<} & 0 \\ \boldsymbol{W}^{>,\dagger} & 0 & \boldsymbol{d}^{>} \end{pmatrix} \tag{1.107}$$

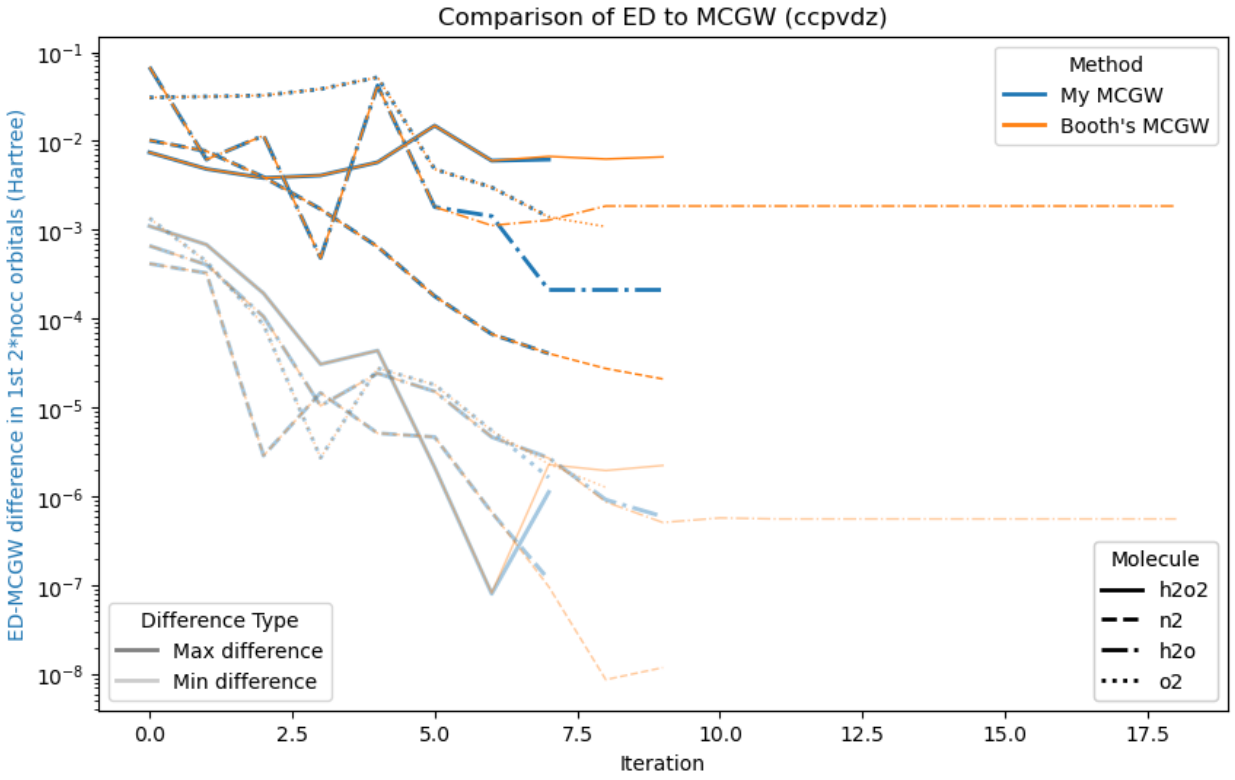

Figure 1.2: From the first $2N_{occ}$ orbitals, representing the space of interest, the maximum and minimum differences between the Ritz values and the exact eigenvalues are plotted as a function of the number of Lanczos iterations used. A cc-pvdz basis is used. An exact match between the blue (my implementation) and the orange curves (George Booth's open source code, momentGW) is shown for all early Lanczos iterations. For later iterations, there start to become no new directions for Lanczos to explore, and so the match no longer is exact, reflecting the different numerical handlings of this limiting case.

where $\boldsymbol{F}$ is the HF Fock matrix, $\boldsymbol{W}^{<}_{pk\nu} = \sum_{ia}(pk|ia)\,(X^{\nu}_{ia} + Y^{\nu}_{ia})$, $\boldsymbol{W}^{>}_{pc\nu} = \sum_{ia}(pc|ia)\,(X^{\nu}_{ia} + Y^{\nu}_{ia})$, $\boldsymbol{d}^{<}_{k\nu,l\nu'} = (\epsilon_k - \Omega_\nu)\,\delta_{k,l}\delta_{\nu,\nu'}$, and $\boldsymbol{d}^{>}_{c\nu,d\nu'} = (\epsilon_c + \Omega_\nu)\,\delta_{c,d}\delta_{\nu,\nu'}$. Recall that the X^{ν}_{ia} and Y^{ν}_{ia} are the RPA eigenvectors and the Ω_ν are the RPA excitation energies. Just constructing this supermatrix requires diagonalizing the RPA matrix, which scales as $O(N^6)$. Therefore, the below methods use Krylov subspace procedures to reduce this scaling. Because the QPs are interior eigenpairs of the supermatrix, the strategy is to identify the QPs by a root-following procedure, where we look to maximize overlap with the mean field eigenvectors.

Moment conserving

Moments of the self-energy are computed, which are then used to power a Lanczos procedure. To learn more, see [11]. Crucially, the Krylov subspace is not reorthogonalized throughout the iteration. If the lack of reorthogonalization did not interfere with the convergence of the Ritz values to the exact solution to within chemical accuracy, this would not be a problem, but as can be seen, it is a problem for some small molecules, invalidating the approach.

The Casida transformation is used in this, so extension to extended systems is not possible. Self-consistency is possible, as shown in [2]. Scaling is $O(N^4)$ with RI. No diagonal approximation to the self-energy must be made.

Auxiliary boson (AB)

The known connection of CC to G_0W_0 discussed in [12] is exploited in [13] to form a supermatrix. Then, a series of matrix-vector products is proposed, which can be used in a Davidson procedure.

The study is done for finite systems so the Casida transformation is used, but it can not be used too, so extension to extended systems is possible. Self-consistency is not possible; in CC, the reference determinant must always be HF, so there can no self-consistency in the exactly related AB method. Scaling is $O(N^4)$ with RI. No diagonal approximation to the self-energy must be made. In principle, the method is exact, but poor convergence with respect to the basis size is observed, likely due to the AB expansion ansatz.

Tim's method

As discussed in [3], this method is exact for the case of TDA screening. The supplementary material proposes an extension to the full RPA screening, by postulating a non-symmetric supermatrix, which can be iteratively diagonalized by a non-symmetric Davidson procedure. I was not able to find a similarity transformation that relates their supermatrix to the exact solution, so the validity of this method is doubtful.

It can be applied to extended systems. Self-consistency is possible. No diagonal approximation to the self-energy must be made. Focusing the discussion here just on finite systems, the scaling could be brought down to $O(N^4)$ with RI, but I already observe the numerical issues with my $O(N^6)$ implementation due to the introduction of a large η parameter, so I did not pursue the scaling reduction. A few words about this potential scaling reduction; the construction of the matrix-vector products requires building a step function, which requires diagonalizing the RPA matrix, conventionally at a $O(N^6)$ cost, but an approximation to the step function with Chebyshev polynomials could be made, reducing the scaling.

Numerical Lanczos

The method described in [6] does not use a supermatrix per se, but it fits better conceptually in this section. This method reformulates the correlation part of the GW self-energy as a resolvent of a Hermitian matrix to which a Lanczos procedure can be applied.

It cannot be applied to extended systems, since the method relies on the Casida transformation. Self-consistency is possible. The diagonal approximation to the self-energy must be made. The scaling is $O(N^4)$ with RI.

Chapter 2

Dyson to GQME: 12/13

The Generalized Quantum Master Equation (GQME) is given by

$$\dot{\mathcal{C}}(t) = \mathcal{C}(t)\Omega_1 - \int_0^t d\tau\, \mathcal{C}(t-\tau)\mathcal{K}_1(\tau) + D(t) \tag{2.1}$$

where the correlation function is defined as

$$\mathcal{C}(t) = (\hat{\mu} \mid \hat{\mu}(t)), \tag{2.2}$$

the higher-order moments are

$$\Omega_n \equiv \left((i\mathcal{L})^n \hat{\mu}, \hat{\mu}\right) / (\hat{\mu}, \hat{\mu}) \tag{2.3}$$

with the auxiliary kernels

$$K_n(t) \equiv \left((i\mathcal{L})^n \hat{f}(t), \hat{\mu}\right) / (\hat{\mu}, \hat{\mu}) \tag{2.4}$$

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

$$\hat{f}(t) \equiv e^{it\mathcal{L}\mathcal{L}} \mathcal{Q} i\mathcal{L}\hat{\mu} \tag{2.5}$$

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

$$K_n(0) = \Omega_{n+1} - \Omega_n \Omega_1 \tag{2.6}$$

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

$$\dot{K}_1(t) = \frac{(i\mathcal{L}\dot{\hat{f}}(t), \hat{\mu})}{(\hat{\mu}, \hat{\mu})} = K_2(t) - \Omega_1 K_1(t) \tag{2.7}$$

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

$$\dot{K}_n(t) = K_{n+1}(t) - \Omega_n K_1(t). \tag{2.8}$$

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

$$\Omega_n = \frac{((i\mathcal{L})^n \hat{\mu}, \hat{\mu})}{(\hat{\mu}, \hat{\mu})}, \tag{2.9}$$

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 2.9 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

$$\mathcal{C}(t) = (\hat{c}, \hat{c}(t)) \equiv \langle \hat{c}^\dagger(0)\hat{c}(t)\rangle = \frac{G^<(t)}{i} \tag{2.10}$$

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

$$\mathcal{C}(t) = (\hat{c}^\dagger, \hat{c}^\dagger(t)) \equiv \langle \hat{c}(0)\hat{c}^\dagger(t)\rangle = -\frac{G^>(t)}{i} \tag{2.11}$$

Then we can construct the retarded Green's function as

$$G_R(t) = \Theta(t)\left(G^<(t) - G^>(t)\right) \tag{2.12}$$

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.

2.1 Explicit Construction of the Liouville Superoperator

Consider that we are working with the upfolded Hamiltonian

$$\mathbf{H} = \begin{pmatrix} \mathbf{f} & \mathbf{W} \\ \mathbf{W}^\dagger & \mathbf{d} \end{pmatrix} \tag{2.13}$$

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

$$\hat{\boldsymbol{\mu}} \equiv \begin{pmatrix} \hat{\mu}_1 \\ \hat{\mu}_2 \end{pmatrix} = \begin{pmatrix} \hat{c} \\ \hat{c}^\dagger \end{pmatrix}, \tag{2.14}$$

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

$$(i\partial_t - \hat{H}_0)G(t,t') = \delta(t-t') + \int_{-\infty}^{\infty} d\tau\, \Sigma(t,\tau)\, G(\tau,t') \tag{2.15}$$

$$\rightarrow G(\dot{t},t') = -i\hat{H}_0 G(t,t') - i\delta(t-t') + \int_{-\infty}^{\infty} d\tau'\, \Sigma(t,\tau')\, G(\tau',t') \tag{2.16}$$

So our task becomes to figure out how

$$-i\hat{H}_0 G(t,t') - i\delta(t-t') + \int_{-\infty}^{\infty} d\tau' \, \Sigma(t,\tau') \, G(\tau',t') = \mathcal{C}(t)\Omega_1 - \int_0^t d\tau \, \mathcal{C}(t-\tau)\mathcal{K}(\tau) + D(t) \quad (2.17)$$

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.

$$\Omega_1 = \frac{((i\mathcal{L})\hat{\boldsymbol{\mu}}, \hat{\boldsymbol{\mu}})}{(\hat{\boldsymbol{\mu}}, \hat{\boldsymbol{\mu}})} = \frac{\Big((i[\hat{H}_0, \hat{\boldsymbol{\mu}}], \hat{\boldsymbol{\mu}}\Big)}{(\hat{\boldsymbol{\mu}}, \hat{\boldsymbol{\mu}})} \quad (2.18)$$

If we just consider the numerator, we see that

$$\Big((i[\hat{H}_0, \hat{\boldsymbol{\mu}}], \hat{\boldsymbol{\mu}}\Big) = \Big(i[\hat{H}_0, \hat{c}], \hat{c}\Big) + \Big(i[\hat{H}_0, \hat{c}^\dagger], \hat{c}^\dagger\Big) \quad (2.19)$$

Considering just the first term

$$\Big(i[\hat{H}_0, \hat{c}], \hat{c}\Big) = -i\epsilon([\hat{c}^\dagger \hat{c}, \hat{c}], \hat{c}) = -i\epsilon(\hat{c}, \hat{c}) = -i\epsilon\,(1 - f(\epsilon)) \quad (2.20)$$

and the second term

$$\Big(i[\hat{H}_0, \hat{c}^\dagger], \hat{c}^\dagger\Big) = -i\epsilon([\hat{c}^\dagger \hat{c}, \hat{c}^\dagger], \hat{c}^\dagger) = -i\epsilon(\hat{c}^\dagger, \hat{c}^\dagger) = -i\epsilon f(\epsilon) \quad (2.21)$$

which can be summarized as

$$\Big(i[\hat{H}_0, \hat{\boldsymbol{\mu}}], \hat{\boldsymbol{\mu}}\Big) = -i\epsilon \implies \Omega_1 = -i\epsilon \quad (2.22)$$

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

$$\left(i\frac{\partial}{\partial t} - h_0\right) G(t,t') = \delta(t-t') + \int dt'' \Sigma(t,t'') G(t'',t') \quad (2.23)$$

$$\frac{\partial}{\partial t} G(t,t') = \underbrace{-ih_0 G(t,t')}_{\Omega_1 C(t)} - i\delta(t-t') + \int dt'' \Sigma(t,t'') G(t'',t') \quad (2.24)$$

Now come if we consider the higher-order moments

$$\Omega_n \equiv \frac{((i\mathcal{L})^n \hat{\boldsymbol{\mu}}, \hat{\boldsymbol{\mu}})}{(\hat{\boldsymbol{\mu}}, \hat{\boldsymbol{\mu}})} = \frac{(i)^n \, (\mathcal{L}^n \hat{\boldsymbol{\mu}}, \hat{\boldsymbol{\mu}})}{(\hat{\boldsymbol{\mu}}, \hat{\boldsymbol{\mu}})} = (i)^n \Big([\hat{H}, [\hat{H}, [\hat{H}, \cdots, \hat{\boldsymbol{\mu}}]]] \cdots\Big) \quad (2.25)$$

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

$$\begin{bmatrix} \mathbf{f} + \boldsymbol{\Sigma}_\infty & \mathbf{W} \\ \mathbf{W}^\dagger & \mathbf{d} \end{bmatrix} \quad (2.26)$$

and the memory kernel

$$\mathcal{K}(t) = \left(\mathbf{A} \left| \mathcal{L}\mathcal{Q} e^{i\mathcal{Q}\mathcal{L}t} \mathcal{Q}\mathcal{L} \right| \mathbf{A}\right), \quad (2.27)$$

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

Chapter 3

RPA

3.1 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.

3.1.1 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

$$\hat{\mathcal{K}}^{\mathrm{RPA}}(1,2,3,4) = \hat{\mathcal{U}}(1,4)\left[\delta(1-2)\,\delta(3-4) - \delta(1-3)\,\delta(2-4)\right] \tag{3.1}$$

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

$$\mathrm{G}(1,2,3,4) = \mathrm{G}^0(1,2,3,4) + \int d5d6d7d8\mathrm{G}^0(1,2,5,6)\,\hat{\mathcal{K}}(5,6,7,8)\,\mathrm{G}(7,8,3,4) \tag{3.2}$$

$$\tilde{\mathrm{G}}(1,2,3,4) = \mathrm{G}^0(1,2,3,4) \tag{3.3}$$

$$+ \int d5d6\mathrm{G}^0(1,2,5,6)\,\hat{\mathcal{U}}(5,6)\,\tilde{\mathrm{G}}(6,5,3,4) \tag{3.4}$$

$$- \int d5d6\mathrm{G}^0(1,2,5,6)\,\hat{\mathcal{U}}(5,6)\,\tilde{\mathrm{G}}(5,6,3,4) \tag{3.5}$$

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

$$\tilde{G}(\nu_1,\nu_2,\nu_3,\nu_4,E) = G^0(\nu_1,\nu_2,\nu_3,\nu_4,E) + \frac{1}{\hbar}\sum_{\bar{1},\bar{2},\bar{3},\bar{4}} G^0(\nu_1,\nu_2,\bar{1},\bar{2},E)\left[\hat{V}_{1234} - \hat{V}_{1423}\right]\tilde{G}(\bar{3},\bar{4},\nu_3,\nu_4,E) \tag{3.6}$$

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:

$$\frac{i}{\hbar}G\left(\nu_1,\nu_2,\nu_3,\nu_4,E\right) = \frac{1}{\langle\Psi_0 \mid \Psi_0\rangle}\sum_n\left[\frac{\langle\Psi_0|\,\hat{a}_{\nu_1}\hat{a}^+_{\nu_3}\,|\Psi_n\rangle\,\langle\Psi_n|\,\hat{a}_{\nu_2}\hat{a}^+_{\nu_4}\,|\Psi_0\rangle}{E-(E_n-E_0)-i\eta} - \frac{\langle\Psi_0|\,\hat{a}_{\nu_2}\hat{a}^+_{\nu_4}\,|\Psi_n\rangle\,\langle\Psi_n|\,\hat{a}_{\nu_1}\hat{a}^+_{\nu_3}\,|\Psi_0\rangle}{E+(E_n-E_0)+i\eta}\right] \tag{3.7}$$

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

$$G^0(m,i,j,n,E) = \hbar\frac{\delta_{ij}\delta_{mn}}{\epsilon_m-\epsilon_i-E-i\eta}, \tag{3.8}$$

$$G^0(i,m,n,j,E) = \hbar\frac{\delta_{ij}\delta_{mn}}{\epsilon_m-\epsilon_i+E-i\eta}, \tag{3.9}$$

$$G^0(m,i,n,j,E) = G^0(i,m,j,n,E) = 0. \tag{3.10}$$

Insertion of these identities into 3.6 gives rise to the equations

$$\sum_{q,l}\left\{\left[A_{miql}-E\delta_{m,q}\delta_{i,l}\right]\tilde{G}(q,l,j,n,E)+B_{miql}\tilde{G}(l,q,j,n,E)\right\} = \delta_{m,n}\delta_{i,j}, \tag{3.11}$$

$$\sum_{q,l}\left\{\left[A^*_{miql}+E\delta_{m,q}\delta_{i,l}\right]\tilde{G}(l,q,j,n,E)+B^*_{miql}\tilde{G}(q,l,j,n,E)\right\} = 0, \tag{3.12}$$

$$\sum_{q,l}\left\{\left[A_{miql}-E\right)\delta_{m,q}\delta_{i,l}\right]\tilde{G}(q,l,n,j,E)+B_{miql}\tilde{G}(l,q,n,j,E)\right\} = 0, \tag{3.13}$$

$$\sum_{q,l}\left\{\left[A^*_{miql}+E\delta_{m,q}\delta_{i,l}\right]\tilde{G}(l,q,n,j,E)+B^*_{miql}\tilde{G}(q,l,n,j)\right\} = \delta_{m,n}\delta_{i,j}, \tag{3.14}$$

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

$$G_1(E) \equiv \tilde{G}(m,i,j,n,E), \tag{3.15}$$

$$G_2(E) \equiv \tilde{G}(m,i,n,j,E), \tag{3.16}$$

$$G_3(E) \equiv \tilde{G}(i,m,j,n,E), \tag{3.17}$$

$$G_4(E) \equiv \tilde{G}(i,m,n,j,E) \tag{3.18}$$

and rewriting the equations in matrix form gives

$$\begin{pmatrix} A-E\mathbb{I} & B \\ B^* & A^*+E\mathbb{I}\end{pmatrix}\begin{pmatrix} G_1(E) & G_2(E) \\ G_3(E) & G_4(E)\end{pmatrix} = \begin{pmatrix}\mathbb{I} & 0 \\ 0 & \mathbb{I}\end{pmatrix} \tag{3.19}$$

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

$$\begin{pmatrix} A-\omega_n\mathbb{I} & B \\ B^* & A^*+\omega_n\mathbb{I}\end{pmatrix}\begin{pmatrix} X_n \\ \\ Y_n\end{pmatrix} = 0. \tag{3.20}$$

3.1.2 TDHF approach

See the review [4] for the derivation.

3.1.3 Equation of motion approach

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

$$[H, O^\dagger] = \omega O^\dagger, \qquad [H, O] = -\omega O, \qquad [O, O^\dagger] = 1 \tag{3.21}$$

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

$$O^\dagger = \sum_{n=0}^{m} (n+1)^{1/2} |n+1\rangle\langle n| + \sum_{p,q>m} C_{pq} |p\rangle\langle q| \tag{3.22}$$

where m is the maximum number of excitations, which gives

$$\left[H, O^\dagger\right] = \omega O^\dagger + P, \qquad [H, O] = -\omega O - P^\dagger, \qquad [O, O^\dagger] = 1 + Q \tag{3.23}$$

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

$$\begin{aligned}
\langle\phi|[R,[H,O^\dagger]]|\phi\rangle &= \langle\phi|R[H,O^\dagger] + R^\dagger[H,O]|\phi\rangle && (3.24)\\
&= \langle\phi|R(\omega O^\dagger + P) + R^\dagger(-\omega O - P^\dagger)|\phi\rangle && (3.25)\\
&= \omega\langle\phi|RO^\dagger|\phi\rangle - \omega\langle\phi|R^\dagger O|\phi\rangle && (3.26)\\
&= \omega\left(\langle\phi|RO^\dagger|\phi\rangle - \langle\phi|R^\dagger O|\phi\rangle\right) && (3.27)\\
&= \omega\left(\langle\phi|RO^\dagger|\phi\rangle - \langle\phi|O^\dagger R|\phi\rangle^*\right) && (3.28)\\
&= \omega\left(\langle\phi|RO^\dagger|\phi\rangle - \langle\phi|O^\dagger R|\phi\rangle\right) && (3.29)\\
&= \omega\langle\phi|[R,O^\dagger]|\phi\rangle && (3.30)
\end{aligned}$$

and similarly,

$$\langle\phi|[R,[H,O]]|\phi\rangle = -\omega\langle\phi|[R,O]|\phi\rangle \tag{3.31}$$

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

$$2\left[R, H, O^\dagger\right] = \left[R, \left[H, O^\dagger\right]\right] + \left[[R, H], O^\dagger\right] \tag{3.32}$$

and now

$$\langle\phi|\left[R, H, O^\dagger\right]|\phi\rangle = \omega\langle\phi|\left[R, O^\dagger\right]|\phi\rangle \tag{3.33}$$

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

$$O_k^\dagger = \sum_\alpha X_\alpha(\kappa)\eta_\alpha^\dagger \tag{3.34}$$

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

$$\hat{b}_\nu^\dagger \approx \sum_Q^{N_{\mathrm{AB}}} C_\nu^Q \hat{b}_Q^\dagger \tag{3.35}$$

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

$$(ia \mid jb) \approx \sum_L R_{ia}^L R_{jb}^L \tag{3.36}$$

$$\implies C_\nu^Q = \sum_{LM} R_\nu^L \left[\mathbf{S}^{-1/2}\right]_{LM} P_M^Q \quad \text{with } S_{LM} = \sum_\nu R_\nu^L R_\nu^M = \sum_Q P_L^Q E_Q P_M^Q \tag{3.37}$$

Plugging 3.34 into 3.33 gives

$$\sum_\beta \underbrace{\langle\phi|\left[\eta_\alpha, H, \eta_\beta^\dagger\right]|\phi\rangle}_{M_{\alpha\beta}} X_\beta(\kappa) = \omega_\kappa \sum_\beta \underbrace{\langle\phi|\left[\eta_\alpha, \eta_\beta^\dagger\right]|\phi\rangle}_{N_{\alpha\beta}} X_\beta(\kappa) \tag{3.38}$$

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

$$\sum_{\beta>0}\langle\alpha|H|\beta\rangle X_\beta(\kappa) = (E_0 + \omega_k)\sum_{\beta>0}\langle\alpha \mid \beta\rangle X_\beta(\kappa) \tag{3.39}$$

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

$$A_{ai,bj} = \langle\phi|\left[a_i^\dagger a_a,\, H,\, a_b^\dagger a_j\right]|\phi\rangle \tag{3.40}$$

$$B_{ai,bj} = -\langle\phi|\left[a_i^\dagger a_a,\, H,\, a_j^\dagger a_b\right]|\phi\rangle \tag{3.41}$$

$$U_{ai,bj} = \langle\phi|\left[a_i^\dagger a_a,\, a_b^\dagger a_j\right]|\phi\rangle \tag{3.42}$$

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

$$\begin{pmatrix} A & B \\ B^\dagger & A^* \end{pmatrix} \begin{pmatrix} Y \\ Z \end{pmatrix} = \omega \begin{pmatrix} U & 0 \\ 0 & -U^* \end{pmatrix} \begin{pmatrix} Y \\ Z \end{pmatrix}. \tag{3.43}$$

and by considering a Hamiltonian of the form

$$H = \sum_{\nu\nu'} T_{\nu\nu'} a_\nu^\dagger a_{\nu'} + \frac{1}{4} \sum_{\mu\nu\mu'\nu'} V_{\mu\nu\mu'\nu'} a_\mu^\dagger a_\nu^\dagger a_{\nu'} a_{\mu'} \tag{3.44}$$

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

$$\langle | a_a \left[H, a_b^\dagger \right] | \rangle = \delta_{ab} \varepsilon_a \tag{3.45}$$

$$\langle | a_i^\dagger \left[H, a_j \right] | \rangle = -\delta_{ij} \varepsilon_i. \tag{3.46}$$

we get the RPA form of

$$A_{aibj} = \delta_{ab}\delta_{ij} \left(\varepsilon_i - \varepsilon_a \right) + V_{ajib} \tag{3.47}$$

$$B_{aibj} = V_{abij} \tag{3.48}$$

$$U_{aibj} = \delta_{ab}\delta_{ij}. \tag{3.49}$$

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

$$O^\dagger = \sum_{\mu\nu} \left(Y_{\mu\nu} \alpha_\mu^\dagger \alpha_\nu^\dagger + Z_{\mu\nu} \alpha_\mu \alpha_\nu \right) \tag{3.50}$$

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

$$\alpha_\nu^\dagger = U_\nu a_\nu^\dagger - V_\nu a_\nu \tag{3.51}$$

$$\alpha_{\bar{\nu}}^\dagger = U_\nu a_{\bar{\nu}}^\dagger + V_\nu a_\nu \tag{3.52}$$

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 3.33 gives

$$A_{\mu\nu\mu'\nu'} = \langle \phi | \left[\alpha_\nu \alpha_\mu, H, \alpha_{\mu'}^\dagger \alpha_{\nu'}^\dagger \right] | \phi \rangle, \tag{3.53}$$

$$B_{\mu\nu\mu'\nu'} = \langle \phi | \left[\alpha_\nu \alpha_\mu, H, \alpha_{\mu'} \alpha_{\nu'} \right] | \phi \rangle, \tag{3.54}$$

$$U_{\mu\nu\mu'\nu'} = \langle \phi | \left[\alpha_\nu \alpha_\mu, \alpha_{\mu'}^\dagger \alpha_{\nu'}^\dagger \right] | \phi \rangle. \tag{3.55}$$

Idea

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

This expands into

$$\begin{aligned}
A_{\mu\nu\mu'\nu'} =& (1-\hat{p}_{\mu\nu})\left[(1+\hat{p}_{\mu\nu}\hat{p}_{\mu'\nu'})\left(\langle\phi|\alpha_\nu\left[H,\alpha^\dagger_{\nu'}\right]|\phi\rangle\delta_{\mu\mu'}\right.\right.\\
&\left.-\langle\phi|\left\{\alpha_\nu,\left[H,\alpha^\dagger_{\nu'}\right]\right\}|\phi\rangle\langle\phi|\alpha^\dagger_{\mu'}\alpha_\mu|\phi\rangle\right)+\mathcal{V}^{(\mathrm{F})}_{\mu\nu\mu'\nu'}\\
&-\frac{1}{2}(1-\hat{p}_{\mu\nu})\langle\phi|\left[\alpha_\mu,\left\{\left[H,\alpha^\dagger_{\mu'}\right],\alpha^\dagger_{\nu'}\right\}\right]\alpha_\nu|\phi\rangle\\
&-\frac{1}{2}(1-\hat{p}_{\mu'\nu'})\langle\phi|\alpha^\dagger_{\nu'}\left[\alpha_\nu,\left\{\alpha_\mu,\left[H,\alpha^\dagger_{\mu'}\right]\right\}\right]|\phi\rangle\\
&-(1+\hat{p}_{\mu\nu}\hat{p}_{\mu'\nu'})\langle\phi|:\alpha^\dagger_{\mu'}\left\{\alpha_\nu,\left[H,\alpha^\dagger_{\nu'}\right]\right\}\alpha_\mu:|\phi\rangle\Big]\\
B_{\mu\nu\mu'\nu'} =& (1-\hat{p}_{\mu\nu})(1+\hat{p}_{\mu\nu}\hat{p}_{\mu'\nu'})\langle\phi|\{\alpha_\mu,[H,\alpha_{\mu'}]\}\rangle\langle\phi|\alpha_\nu\alpha_{\nu'}|\phi\rangle\\
&+\mathcal{V}^{(\mathrm{B})}_{\mu\nu\mu'\nu'}\\
&+\frac{1}{2}(1-\hat{p}_{\mu\nu})\langle\phi|\left[\alpha_\mu,\{[H,\alpha_{\mu'}],\alpha_{\nu'}\}\right]\alpha_\nu|\phi\rangle\\
&+\frac{1}{2}(1-\hat{p}_{\mu'\nu'})\langle\phi|\left[\alpha_\nu,\{\alpha_\mu,[H,\alpha_{\mu'}]\}\right]\alpha_{\nu'}|\phi\rangle\\
&+(1+\hat{p}_{\mu\nu}\hat{p}_{\mu'\nu'})\langle\phi|:\{\alpha_\mu,[H,\alpha_{\mu'}]\}\alpha_\nu\alpha_{\nu'}:|\phi\rangle\Big],\\
U_{\mu\nu\mu'\nu'} =& (1-\hat{p}_{\mu\nu})\left[\delta_{\mu\mu'}\delta_{\nu\nu'}-\delta_{\mu\mu'}\langle\phi|\alpha_{\nu'}\alpha_\nu|\phi\rangle-\delta_{\nu\nu'}\langle\phi|\alpha^\dagger_{\mu'}\alpha_\mu|\phi\rangle\right],
\end{aligned}\tag{3.56}$$

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

$$\mathcal{V}^{(\mathrm{F})}_{\mu\nu\mu'\nu'}=\frac{1}{2}\left\{\alpha_\nu,\left[\alpha_\mu,\left\{\left[H,\alpha^\dagger_{\mu'}\right],\alpha^\dagger_{\nu'}\right\}\right]\right\}\tag{3.57}$$

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

$$\mathcal{V}^{(\mathrm{B})}_{\mu\nu\mu'\nu'}=-\frac{1}{2}\{\alpha_\nu,[\alpha_\mu,\{[H,\alpha_{\mu'}],\alpha_{\nu'}\}]\}\tag{3.58}$$

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

$$|\tilde{\phi}\rangle=\prod_{\nu>0}\left(U_\nu+V_\nu a^\dagger_\nu a^\dagger_{\overline{\nu}}\right)|-\rangle\tag{3.59}$$

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

$$A_{\mu\nu\mu'\nu'}=(1-\hat{p}_{\mu\nu})\left[(1+\hat{p}_{\mu\nu}\hat{p}_{\mu'\nu'})\langle\tilde{\phi}|\alpha_\nu\left[H,\alpha^\dagger_{\nu'}\right]|\tilde{\phi}\rangle\delta_{\mu\mu'}+\mathcal{V}^{(\mathrm{F})}_{\mu\nu\mu'\nu'}\right].\tag{3.60}$$

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

$$\langle\tilde{\phi}|\left\{a_\nu,\left[H,{a_{\nu'}}^\dagger\right]\right\}|\tilde{\phi}\rangle=\delta_{\nu\nu'}(\varepsilon_\nu-\lambda).\tag{3.61}$$

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

$$\langle\tilde{\phi}|\left\{\alpha^\dagger_{\bar{\nu}},\left[H,\alpha^\dagger_{\nu'}\right]\right\}|\tilde{\phi}\rangle = \delta_{\nu'\nu}\left[\left({U_\nu}^2-{V_\nu}^2\right)\Delta_\nu - 2U_\nu V_\nu\left(\varepsilon_\nu-\lambda\right)\right]=0 \tag{3.62}$$

where Δ_ν is the gap parameter defined by

$$\langle\tilde{\phi}|\left\{a_{\bar{\nu}},[H,a_{\nu'}]\right\}|\tilde{\phi}\rangle = \langle\tilde{\phi}|\left\{{a_\nu}^\dagger,\left[H,{a_{\bar{\nu}'}}^\dagger\right]\right\}|\tilde{\phi}\rangle = \delta_{\nu'}\Delta_\nu. \tag{3.63}$$

Explicitly,

$$\Delta_\nu = \frac{1}{2}\sum_\mu V_{\bar{\mu}\mu\bar{\nu}\bar{\nu}}\langle|a^\dagger_{\bar{\mu}}a^\dagger_\mu|\rangle = -\frac{1}{2}\sum_\mu V_{\bar{\mu}\mu\bar{\nu}}U_\mu V_\mu. \tag{3.64}$$

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

$$\langle\tilde{\phi}|\left\{\alpha_\nu,\left[H,{\alpha_{\nu'}}^\dagger\right]\right\}|\tilde{\phi}\rangle = \delta_{\nu\nu'}\langle\tilde{\phi}|\left\{\alpha_\nu,\left[H,{\alpha_\nu}^\dagger\right]\right\}|\tilde{\phi}\rangle = \delta_{\nu\nu'}E_\nu, \tag{3.65}$$

is given by

$$E_\nu = \left(U_\nu^2-V_\nu^2\right)\left(\varepsilon_\nu-\lambda\right)+2U_\nu V_\nu\Delta_\nu \tag{3.66}$$

$$\tag{3.67}$$

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

$$A_{\mu\nu\mu'\nu'} = \left(1-\hat{p}_{\mu\nu}\right)\left[\delta_{\mu\mu'}\delta_{\nu\nu'}\left(E_\mu+E_\nu\right)+\mathcal{V}^{(\mathrm{F})}_{\mu\nu\mu'\nu'}\right], \tag{3.68}$$

$$B_{\mu\nu\mu'\nu'} = \left(1-\hat{p}_{\mu\nu}\right)\mathcal{V}^{(\mathrm{B})}_{\mu\nu\mu'\nu'}, \tag{3.69}$$

$$U_{\mu\nu\mu'\nu'} = \left(1-\hat{p}_{\mu\nu}\right)\delta_{\mu\mu'}\delta_{\nu\nu'}. \tag{3.70}$$

3.2 Extra

3.2.1 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:

$$|\nu\rangle = \hat{O}^\dagger_\nu|\nu_0\rangle \tag{3.71}$$

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

$$\hat{O}^\dagger_\nu = \sum_{ia}\left(X^\nu_{ai}a^\dagger_a a_i\right). \tag{3.72}$$

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

$$\hat{O}_\nu\,|\Phi_0\rangle = \sum_{ia}\left(X_{ai}^\nu a_a a_i^\dagger + Y_{ai}^\nu a_i a_a^\dagger\right)|\Phi_0\rangle \neq 0 \tag{3.73}$$

in which the second term cannot be zero.

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

Trying direct evaluation

We know

$$\chi_{RPA}^{-1}(\omega) = \frac{1-v\chi_0}{\chi_0} = \chi_0^{-1} - \mathbf{v} \tag{3.74}$$

The Lehmann representation for χ_0 is

$$\chi_0\left(\mathbf{r},\mathbf{r}',\omega\right) = \sum_{ia}\frac{\psi_i(\mathbf{r})\psi_a^*(\mathbf{r}')\psi_i(\mathbf{r}')\psi_a^*(\mathbf{r})}{\omega\,\mathrm{sgn}\left(\epsilon_a-\epsilon_i-\mu\right) + \underbrace{\left(\epsilon_a-\epsilon_i\right)}_{\text{KS bare }\Omega_0} + i\eta\,\mathrm{sgn}\left(\epsilon_a-\epsilon_i-\mu\right)} \tag{3.75}$$

Let's start by considering the right-hand side of equation 3.74. 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.

$$\chi_0^{-1}(\omega) = \begin{pmatrix}\frac{1}{\chi_0^+(\omega)} & 0\\ 0 & \frac{1}{\chi_0^-(\omega)}\end{pmatrix} = \begin{pmatrix}\omega+[\epsilon_a-\epsilon_i] & 0\\ 0 & -\omega+[\epsilon_a-\epsilon_i]\end{pmatrix} \tag{3.76}$$

The Coulomb interaction in the particle-hole basis is

$$\mathbf{v} = \begin{pmatrix}\mathbf{v}^{++} & \mathbf{v}^{+-}\\ \mathbf{v}^{-+} & \mathbf{v}^{--}\end{pmatrix} \tag{3.77}$$

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 3.74 is

$$\chi_{RPA}^{-1}(\omega) = \chi_0^{-1}(\omega) - \mathbf{v} = \begin{pmatrix}(\omega+[\epsilon_a-\epsilon_i]) - \mathbf{v}^{++} & -\mathbf{v}^{+-}\\ -\mathbf{v}^{-+} & (-\omega+[\epsilon_a-\epsilon_i]) - \mathbf{v}^{--}\end{pmatrix} = \omega\boldsymbol{\Sigma}_\mathbf{z} + \mathbf{M} \tag{3.78}$$

where

$$\boldsymbol{\Sigma}_\mathbf{z} = \begin{pmatrix}\mathbf{I} & 0\\ 0 & -\mathbf{I}\end{pmatrix} \quad \text{and} \quad \mathbf{M} = \begin{pmatrix}\mathbf{A} & \mathbf{B}\\ \mathbf{B} & \mathbf{A}\end{pmatrix} \tag{3.79}$$

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

$$\chi_{RPA}(\omega) = \left[\begin{pmatrix} \mathbf{A} & \mathbf{B} \\ \mathbf{B} & \mathbf{A} \end{pmatrix} + \omega \begin{pmatrix} \mathbf{I} & 0 \\ 0 & -\mathbf{I} \end{pmatrix}\right]^{-1} \tag{3.80}$$

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

$$\omega\mathbf{\Sigma_z} + \mathbf{M} = \begin{pmatrix} \mathbf{X} \\ \mathbf{Y} \end{pmatrix} \begin{pmatrix} \mathbf{\Omega} - \omega & 0 \\ 0 & \mathbf{\Omega} + \omega \end{pmatrix} \begin{pmatrix} \mathbf{X} \\ \mathbf{Y} \end{pmatrix}^{\dagger} \tag{3.81}$$

$$\chi_{RPA}(\omega) = (\omega\mathbf{\Sigma_z} + \mathbf{M})^{-1} = \begin{pmatrix} \mathbf{X} \\ \mathbf{Y} \end{pmatrix} \begin{pmatrix} \frac{1}{\mathbf{\Omega}-\omega} & 0 \\ 0 & \frac{1}{\mathbf{\Omega}+\omega} \end{pmatrix} \begin{pmatrix} \mathbf{X} \\ \mathbf{Y} \end{pmatrix}^{\dagger} \tag{3.82}$$

$$\chi_{RPA}(\omega) = \sum_{\mathrm{I}} \left[\frac{1}{\Omega_{\mathrm{I}} + \omega} \begin{pmatrix} X^{\mathrm{I}} \\ Y^{\mathrm{I}} \end{pmatrix} \begin{pmatrix} X^{\mathrm{I}} & Y^{\mathrm{I}} \end{pmatrix} + \frac{1}{\Omega_{\mathrm{I}} - \omega} \begin{pmatrix} Y^{\mathrm{I}} \\ X^{\mathrm{I}} \end{pmatrix} \begin{pmatrix} Y^{\mathrm{I}} & X^{\mathrm{I}} \end{pmatrix}\right] \tag{3.83}$$

How to determine the excitations?

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

$$\chi_{RPA} = \chi_0 + \chi_0 v \chi_{RPA} = \frac{\chi_0}{1 - v\chi_0} \tag{3.84}$$

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

$$[\mathbf{I} - \mathbf{v}\chi_{\mathbf{0}}(\omega)]\,\mathbf{F} = 0 \implies \mathbf{v}\chi_{\mathbf{0}}(\omega)\mathbf{F} = \mathbf{F} \tag{3.85}$$

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

$$\langle pq|\,\mathbf{v}\chi_0(\omega)\,|rs\rangle = \sum_{tu} \langle pq|\,\mathbf{v}\,|tu\rangle\,\langle tu|\,\chi_0(\omega)\,|rs\rangle \tag{3.86}$$

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

$$\langle \tilde{pq}|\,\mathbf{v}\chi_0(\omega)\,|\tilde{rs}\rangle = v_{\tilde{pq}\tilde{rs}}\chi_{0,\tilde{rs}}(\omega) \tag{3.87}$$

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:

$$\chi_0(\omega) = \chi_0^+(\omega) + \chi_0^-(\omega) \tag{3.88}$$

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 3.87 that the occupied virtual combination of χ_0

constrains the second index of $\mathbf{v}$, so we can formulate a matrix for equation 3.85 in this pair basis:

$$\begin{pmatrix} \mathbf{v}^{++}\tilde{\chi}_0(\omega) & -\mathbf{v}^{+-}\tilde{\chi}_0(\omega) \\ \mathbf{v}^{-+}\tilde{\chi}_0(\omega) & -\mathbf{v}^{--}\tilde{\chi}_0(\omega) \end{pmatrix} \begin{pmatrix} \mathbf{F}^{+} \\ \mathbf{F}^{-} \end{pmatrix} = \begin{pmatrix} \mathbf{F}^{+} \\ \mathbf{F}^{-} \end{pmatrix} \tag{3.89}$$

This implies the system of equations

$$\left(\mathbf{v}^{++}\tilde{\chi}_0(\omega) - \mathbf{I}\right)\mathbf{F}^{+} - \mathbf{v}^{+-}\tilde{\chi}_0(\omega)\,\mathbf{F}^{-} = 0 \tag{3.90}$$

$$\mathbf{v}^{-+}\tilde{\chi}_0(\omega)\,\mathbf{F}^{+} - \left(\mathbf{v}^{--}\tilde{\chi}_0(\omega) + \mathbf{I}\right)\mathbf{F}^{-} = 0 \tag{3.91}$$

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

$$\mathbf{v}^{++}\mathbf{F}^{+} - \mathbf{v}^{+-}\mathbf{F}^{-} = (\omega - [\epsilon_a - \epsilon_i])\,\mathbf{F}^{+} \tag{3.92}$$

$$\mathbf{v}^{-+}\mathbf{F}^{+} - \mathbf{v}^{--}\mathbf{F}^{-} = -(\omega - [\epsilon_a - \epsilon_i])\,\mathbf{F}^{-} \tag{3.93}$$

$$\begin{pmatrix} \mathbf{v}^{++} & \mathbf{v}^{+-} \\ \mathbf{v}^{-+} & \mathbf{v}^{--} \end{pmatrix} \begin{pmatrix} \mathbf{F}^{+} \\ -\mathbf{F}^{-} \end{pmatrix} = (\omega - [\epsilon_a - \epsilon_i]) \begin{pmatrix} \mathbf{F}^{+} \\ -\mathbf{F}^{-} \end{pmatrix} \tag{3.94}$$

$$\begin{pmatrix} \mathbf{v}^{++} & \mathbf{v}^{+-} \\ \mathbf{v}^{-+} & \mathbf{v}^{--} \end{pmatrix} \begin{pmatrix} \mathbf{F}^{+} \\ -\mathbf{F}^{-} \end{pmatrix} = \omega \begin{pmatrix} \mathbf{F}^{+} \\ -\mathbf{F}^{-} \end{pmatrix} - [\epsilon_a - \epsilon_i] \begin{pmatrix} \mathbf{F}^{+} \\ -\mathbf{F}^{-} \end{pmatrix} \tag{3.95}$$

$$\begin{pmatrix} [\epsilon_a - \epsilon_i] + \mathbf{v}^{++} & \mathbf{v}^{+-} \\ \mathbf{v}^{-+} & [\epsilon_a - \epsilon_i] + \mathbf{v}^{--} \end{pmatrix} \begin{pmatrix} \mathbf{F}^{+} \\ -\mathbf{F}^{-} \end{pmatrix} = \omega \begin{pmatrix} \mathbf{F}^{+} \\ -\mathbf{F}^{-} \end{pmatrix} \tag{3.96}$$

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

$$A_{iajb} = \delta_{ij}\delta_{ab}(\epsilon_a - \epsilon_i) - (ia|jb) \tag{3.97}$$

$$B_{iajb} = (ia|bj) \tag{3.98}$$

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

$$\begin{pmatrix} \mathbf{A} & \mathbf{B} \\ -\mathbf{B} & -\mathbf{A} \end{pmatrix} \begin{pmatrix} \mathbf{F}^{+} \\ \mathbf{F}^{-} \end{pmatrix} = \omega\sigma_{\mathbf{z}} \begin{pmatrix} \mathbf{F}^{+} \\ \mathbf{F}^{-} \end{pmatrix} \tag{3.99}$$

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 4

Down folding methods

4.1 Constrained RPA

See [1] and [14] for useful introductions. I will just sketch the main ideas here. We partition into a target space and a rest space. Accordingly, we can write the total non-interacting polarizability P as

$$P = P^t + P^r \tag{4.1}$$

where P^t and P^r are the non-interacting polarizabilities in the target and rest spaces respectively. Then, after some algebra, we can write the Dyson equation for the total screened interaction W as

$$W = W_r + W_r P^t W_r \tag{4.2}$$

and then with the bare interaction v we can write

$$W_r = v + vP^r W_r. \tag{4.3}$$

Then, W_r is identified with the effective interaction a.k.a Hubbard U, i.e. $U = W_r$.

Why it is useful

It enables us to perform the so called fluctuation diagnostics. By varying which bands we choose to put in the target space, we are able to see how much each contributes to the screening.

4.1.1 cRPA through the lens of CC

In section 3.1.3 we showed how the RPA comes about in the EOM formalism. In order to connect with CC, my idea would be to constrain the second quantization operators involved to be part of the target space or rest space. This may lead us to a potential constrained CC method.

Chapter 5

Non-Symmetric Davidson

5.1 The problem

We are tasked with the nonsymmetric eigenvalue problem

$$\mathbf{A}X_i = \lambda_i X_i \tag{5.1}$$

where $\mathbf{A} \in \mathbb{R}^{n\times n}$ is a real nonsymmetric matrix with right-hand eigenvector corresponding to the eigenvalue λ_i denoted by $\mathbf{X}_i$. Because $\mathbf{A}$ is nonsymmetric, we will also have a left-hand eigenvector $\bar{X}_i$ such that

$$\mathbf{A}^\dagger \bar{X}_i = \lambda_i \bar{X}_i. \tag{5.2}$$

The left-hand eigenvector is related to the right-hand eigenvector by the bi-orthogonality condition

$$\bar{\mathbf{X}}^\dagger \mathbf{X} = \boldsymbol{I}^{(n)} \tag{5.3}$$

with $\boldsymbol{I}^{(n)}$ being the $n \times n$ identity matrix.

5.2 Ritz approximation

Now, to pursue the Ritz approximation, define $N \times m$ matrices

$$\bar{\boldsymbol{B}}^{(m)} = \left(\bar{b}_1, \bar{b}_2, \ldots, \bar{b}_m\right) \quad \text{and} \quad \boldsymbol{B}^{(m)} = (b_1, b_2, \ldots, b_m) \tag{5.4}$$

where $\bar{\boldsymbol{B}}^{(m)}$ contains left-hand trial vectors and $\boldsymbol{B}^{(m)}$ contains right-hand trial vectors. In addition, they satisfy the bi-orthogonality condition

$$\left(\bar{\boldsymbol{B}}^{(m)}\right)^\dagger \boldsymbol{B}^{(m)} = \boldsymbol{I}^{(m)} \tag{5.5}$$

where $\boldsymbol{I}^{(m)}$ is an $m \times m$ unit matrix. The LHS and RHS Ritz vectors are determined simultaneously in order to give a fast convergence to the desired eigenpairs. Since $\boldsymbol{A}$ is nonsymmetric, it is normal for complex Ritz vectors to appear at some stage of the iteration even when one starts initially with real vectors. A projection of $\boldsymbol{A}$ onto the LHS and RHS subspaces gives the interaction matrix

$$\tilde{\boldsymbol{A}}^{(m)} = \left(\bar{\boldsymbol{B}}^{(m)}\right)^\dagger \boldsymbol{A}\boldsymbol{B}^{(m)} \tag{5.6}$$

Assume that $\tilde{\boldsymbol{A}}^{(m)}$ can be diagonalized such that

$$\left(\boldsymbol{C}^{(m)}\right)^{-1} \tilde{\boldsymbol{A}}^{(m)} \boldsymbol{C}^{(m)} = \left(\bar{\boldsymbol{C}}^{(m)}\right)^{\dagger} \tilde{\boldsymbol{A}}^{(m)} \boldsymbol{C}^{(m)} = \boldsymbol{\Lambda}^{(m)} \tag{5.7}$$

where $\boldsymbol{\Lambda}^{(m)}$ is a diagonal matrix containing the collection of Ritz values. Since the LHS and RHS vectors are biorthogonal

$$\left(\boldsymbol{C}^{(m)}\right)^{\dagger} \boldsymbol{C}^{(m)} = \boldsymbol{I}^{(m)} \implies \left(\boldsymbol{C}^{(m)}\right)^{\dagger} = \left(\boldsymbol{C}^{(m)}\right)^{-1}. \tag{5.8}$$

5.7 is equivalent to eigenvalue equations

$$\left(\tilde{\boldsymbol{A}}^{(m)} - \lambda_k^{(m)}\right) C_k^{(m)} = 0, \tag{5.9}$$

$$\left(\left(\tilde{\boldsymbol{A}}^{(m)}\right)^{\dagger} - \lambda_k^{(m)}\right) \bar{C}_k^{(m)} = 0. \tag{5.10}$$

Then, the expansions $\bar{\boldsymbol{B}}^{(m)} \bar{C}_k^{(m)}$ and $\boldsymbol{B}^{(m)} C_k^{(m)}$ will converge to left- and right-hand eigenvectors of $\boldsymbol{A}$, $\bar{X}_k^{(m)}$ and $X_k^{(m)}$, respectively. So the connection to Krylov becomes clear: $\bar{\boldsymbol{B}}^{(m)}$ and $\boldsymbol{B}^{(m)}$ are the left- and right-hand Krylov subspaces, at the m-th step of the iteration, respectively. If we define LHS and RHS residual vectors $\bar{\xi}$ and ξ such that

$$\left(\boldsymbol{A} - \lambda_k^{(m)}\right)\left(X_k^{(m)} + \xi\right) = 0, \tag{5.11}$$

$$\left(\boldsymbol{A}^{\dagger} - \lambda_k^{(m)}\right)\left(\bar{X}_k^{(m)} + \bar{\xi}\right) = 0, \tag{5.12}$$

then we can approximate them at iteration $m+1$ as (where the preconditioner $\left(\lambda_k^{(m)} - A_{II}\right)^{-1}$ is introduced to accelerate convergence)

$$\xi_{I,m+1} = \left(\lambda_k^{(m)} - A_{II}\right)^{-1} q_{I,m}, \tag{5.13}$$

$$\bar{\xi}_{I,m+1} = \left(\lambda_k^{(m)} - A_{II}\right)^{-1} \bar{q}_{I,m}, \quad I = 1, 2, \ldots, N, \tag{5.14}$$

where

$$q_m = \left(\boldsymbol{A} - \lambda_k^{(m)}\right) X_k^{(m)}, \tag{5.15}$$

$$\bar{q}_m = \left(\boldsymbol{A}^{\dagger} - \lambda_k^{(m)}\right) \bar{X}_k^{(m)}. \tag{5.16}$$

so notice that $q_m \approx 0$ if $\lambda_k^{(m)}$ and $X_k^{(m)}$ become good approximations to the exact eigenpair. We want to biorthogonalize our new directions, so do this by defining

$$d_{m+1} = \left[\prod_{i=1}^{m}\left(I - b_i \bar{b}_i^{\dagger}\right)\right] \xi_{m+1}, \tag{5.17}$$

$$\bar{d}_{m+1} = \left[\prod_{i=1}^{m}\left(I - \bar{b}_i b_i^{\dagger}\right)\right] \bar{\xi}_{m+1}. \tag{5.18}$$

and then the new vectors are defined as

$$b_{m+1} = d_{m+1}/g_{m+1}^{1/2}, \tag{5.19}$$

$$\bar{b}_{m+1} = \bar{d}_{m+1}/g_{m+1}^{1/2}, \tag{5.20}$$

where

$$g_{m+1} = \bar{d}_{m+1}^{\dagger} d_{m+1}. \tag{5.21}$$

As previously alluded to, we claim convergence when $\|q_m\|$ and $\|\bar{q}_m\|$ become less than a given threshold. The left- and right-hand eigenvectors obtained are biorthogonal

Chapter 6

Cumulant Expansion

6.1 Mathematical origins

TODO

6.1.1 Alternate derivation starting from Dyson equation

We can start from where Schwinger's fictitious potential u has already been introduced:

$$G_u(1,1') = G^0(1,1') + G^0(1,\overline{2})\left\{\left[u(\overline{2}) + v_{Hu}(\overline{2})\right] G_u\left(\overline{2},1'\right) + iv_c(\overline{2},\overline{3})\frac{\delta G_u\left(\overline{2},1'\right)}{\delta u\left(\overline{3}^+\right)}\right\} \quad (6.1)$$

where G^0 is the non-interacting Green's function and v_c is the bare Coulomb interaction. v_{Hu} is the Hartree potential built with the density $n_u(\mathbf{x}) = -iG_u(\mathbf{x},\mathbf{x},t,t^+)$. One of the complications of the equations is the fact that the density n_u in the Hartree potential introduces a term that is quadratic in G_u for the first term in the above equation. To overcome this problem, we introduce the total classical potential

$$u_{\mathrm{cl}}(1) = u(1) + v_{Hu}(1) \quad (6.2)$$

which allows us to rewrite the equation for $G_u \equiv G_u^{\mathrm{cl}}$ as

$$G_u(1,1') = G^0(1,1') + G^0(1,\overline{2})u_{\mathrm{cl}}(\overline{2})G_u\left(\overline{2},1'\right) + iG^0(1,\overline{2})v_c(\overline{2},\overline{3})\frac{\delta G_u\left(\overline{2},1'\right)}{\delta u\left(\overline{3}^+\right)} \quad (6.3)$$

$$= G^0(1,1') + G^0(1,\overline{2})u_{\mathrm{cl}}(\overline{2})G_u\left(\overline{2},1'\right) + iG^0(1,\overline{2})W_u(\overline{2},\overline{3})\frac{\delta G_u\left(\overline{2},1'\right)}{\delta u_{\mathrm{cl}}\left(\overline{3}^+\right)} \quad (6.4)$$

where we have defined the screened Coulomb interaction $W_u = \epsilon_u^{-1} v_c$ with the time-ordered inverse dielectric function $\epsilon_u^{-1} = \delta u_{\mathrm{cl}}/\delta u$. Note that ϵ_u^{-1} is not the usual linear response dielectric function, since it depends on the perturbing potential. However, since we are interested in the solution for vanishing u, a reasonable approximation is to evaluate the

equation using $\epsilon_u^{-1} \approx \epsilon^{-1}$ at $u = 0$. *This corresponds to a linear-response approximation.* Written in a basis, the resulting equation reads

$$G_{ij}^{u_{cl}}(t_{12}) = G_{ij}^{0}(t_{12}) + G_{im}^{0}(t_{13})\, u_{\mathrm{cl},mk}(t_3)\, G_{kj}^{u_{cl}}(t_{32}) + iG_{ik}^{0}(t_{13})\, W_{klmn}(t_{34}) \frac{\partial G_{nj}^{u_{cl}}(t_{32})}{\partial u_{\mathrm{cl},lm}(t_4)} \quad (6.5)$$

where $t_{12} \equiv (t_1, t_2)$ or $(t_1 - t_2)$ in equilibrium, W_{klmn} is a matrix element of the screened Coulomb interaction W, and we have replaced functional derivatives by partial derivatives, supposing the basis to be discrete, which corresponds to calculations in practice. Repeated indices are summed over.

GW approximation

The GW approximation sets

$$\frac{\partial G_{nj}^{u}(t_{32})}{\partial u_{\mathrm{cl},lm}(t_4)} \approx G_{nl}(t_{34})\, G_{mj}(t_{42}) \quad (6.6)$$

At $u = 0$, this yields the Dyson equation $G = G^0 + G^0 \Sigma^{GW} G$ with the GW approximation for the self-energy,

$$\Sigma_{im}^{GW}(t_{34}) = v_{H,im} + iG_{nl}(t_{34})\, W_{ilmn}(t_{34}). \quad (6.7)$$

But we will take a different route here, in order to obtain the cumulant expression for the Green's function.

Cumulant expansion

The basic idea is to introduce a quasi-particle Green's function $G^{QP,u}$, defined as

$$\left[G^{QP,u}\right]_{ij}^{-1} = \left[G_0^{-1}\right]_{ij} - \left[u_{\mathrm{cl}}\right]_{ij} - \Sigma_{ij}^{GW}\left(\frac{\varepsilon_i + \varepsilon_j}{2}\right) \quad (6.8)$$

$$\implies [G_0]_{ij} = G_{ij}^{QP,u} - G_{im}^{QP,u}\left(u_{\mathrm{cl},mk} + \Sigma_{mk}^{GW}\left(\frac{\varepsilon_m + \varepsilon_k}{2}\right)\right)[G_0]_{kj} \quad (6.9)$$

Plugging this into 6.5 (suppressing the time and orbital indices for ease of notation) gives

$$\begin{aligned} G^u &= G^{QP,u} - G^{QP,u}\left(u_{\mathrm{cl}} + \Sigma\right) G_0 \\ &\quad + \left(G^{QP,u} - G^{QP,u}\left(u_{\mathrm{cl}} + \Sigma\right) G_0\right) u_{\mathrm{cl}} G^u \\ &\quad + i\left(G^{QP,u} - G^{QP,u}\left(u_{\mathrm{cl}} + \Sigma\right) G_0\right) W \frac{\partial G^u}{\partial u_{\mathrm{cl}}} \qquad (6.10) \\ &= G^{QP,u} + G^{QP,u} u_{\mathrm{cl}} G^u + i G^{QP,u} W \frac{\partial G^u}{\partial u_{\mathrm{cl}}} \\ &\quad - G^{QP,u}\left(u_{\mathrm{cl}} + \Sigma\right) \left[\underbrace{G_0 + G_0 u_{\mathrm{cl}} G^u + i G_0 W \frac{\partial G^u}{\partial u_{\mathrm{cl}}}}_{G^u}\right] \\ &= G^{QP,u} + i G^{QP,u} W \frac{\partial G^u}{\partial u_{\mathrm{cl}}} - G^{QP,u} \Sigma G^u \qquad (6.11) \end{aligned}$$

$$\implies G^u_{ij}(t_{12}) = G^{QP,u}_{ij}(t_{12}) + i G^{QP,u}_{ik}(t_{13}) W_{klmn}(t_{34}) \frac{\partial G^u_{mj}(t_{32})}{\partial u_{\mathrm{cl},lm}(t_4)} - G^{QP,u}_{ik}(t_{13}) \Sigma^{GW}_{kl}\left(\frac{\varepsilon_k + \varepsilon_l}{2}\right) G^u_{lj}(t_{32}) \qquad (6.12)$$

We have made use of the *GW* self-energy. It is known that in the *GW* approximation, because of a fortuitous cancellation of errors, it is most wise to use the RPA approximation for the dielectric function that goes into the screened Coloumb interaction. I wonder if this is also the smartest decision for the cumulant expansion; we could try using a more accurate approximation to the dielectric function and see what the effect is. Now one decouples the equations by supposing that G^u and $G^{QP,u}$ are diagonal in the same u-independent basis. So we take the diagonal components of all operators in the above equation, so $G^u_{ij} \to G^u_{ii} \equiv \mathcal{G}^u$, $G^{QP,u}_{ij} \to G^{QP,u}_{ii} \equiv \mathcal{G}^{QP,u}$, $\Sigma^{GW}_{ij}\left(\frac{\varepsilon_i+\varepsilon_j}{2}\right) \to \Sigma^{GW}_{ii}\left(\varepsilon_i\right) \equiv \tilde{\Sigma}^{GW}$, $W_{ijkl} \to W_{iiii} \equiv \mathcal{W}$, and $u_{\mathrm{cl},ij} \to u_{\mathrm{cl},ii} \equiv u$. This is a strong assumption, but nevertheless, it allows us to get to the conventional form for the cumulant expansion. The resulting equation is

$$\mathcal{G}^u(t_{12}) = \mathcal{G}^{QP,u}(t_{12}) + i\mathcal{G}^{QP,u}(t_{13}) \mathcal{W}(t_{34}) \frac{\partial \mathcal{G}^u(t_{32})}{\partial u(t_4)} - \mathcal{G}^{QP,u}(t_{13}) \tilde{\Sigma}^{GW} \mathcal{G}^u(t_{32}) \qquad (6.13)$$

In the paper they claim that the solution for $u \to 0$ is

$$\mathcal{G}\left(t_{12}\right) = \mathcal{G}^0_{QP}\left(t_{12}\right) e^{i(t_1 - t_2)\Sigma^{GW}_{ii}(\varepsilon_i)} \exp\left[-i \int_{t_1}^{t_2} dt' \int_{t'}^{t_2} dt'' \mathcal{W}\left(t' - t''\right)\right]. \qquad (6.14)$$

I have not been able to derive, but my attempts are below, and we will just continue for now. The double integral can be evaluated as

$$-i\int_{t_1}^{t_2}dt'\int_{t'}^{t_2}dt''\mathcal{W}\left(t'-t''\right)=-\frac{i}{2\pi}\int d\omega\,\mathcal{W}(\omega)\int_{t_1}^{t_2}dt'\int_{t'}^{t_2}dt''\,e^{-i\omega(t'-t'')} \tag{6.15}$$

$$=-\frac{1}{2\pi}\int d\omega\,\frac{\mathcal{W}(\omega)}{\omega}\int_{t_1}^{t_2}dt'\Big(e^{i\omega(t_2-t')}-1\Big) \tag{6.16}$$

$$=-\frac{1}{2\pi}\int d\omega\,\frac{\mathcal{W}(\omega)}{\omega}\left[\frac{e^{i\omega(t_2-t_1)}-1}{i\omega}-(t_2-t_1)\right] \tag{6.17}$$

$$=-\left(t_1-t_2\right)\frac{1}{2\pi}\int d\omega\frac{\mathcal{W}(\omega)}{\omega}+\frac{i}{2\pi}\int d\omega\frac{\mathcal{W}(\omega)}{\omega^2}\left(e^{-i\omega(t_1-t_2)}-1\right) \tag{6.18}$$

where in going from Eq. (6.15) to Eq. (6.16) we have used $\int_{t'}^{t_2}dt''\,e^{-i\omega(t'-t'')}=\frac{e^{i\omega(t_2-t')}-1}{i\omega}$, and in going from Eq. (6.16) to Eq. (6.17) we have used $\int_{t_1}^{t_2}dt'\big(e^{i\omega(t_2-t')}-1\big)=\frac{e^{i\omega\Delta}-1}{i\omega}-\Delta$ with $\Delta=t_2-t_1$. Let us first examine the term proportional to (t_1-t_2) in Eq. (6.18), by comparing it to a GW quasi-particle shift. In the decoupling approximation, $\Sigma^{GW}_{kk}\approx iG_{kk}W_{kkkk}$. Evaluated at the quasi-particle energy, this yields exactly the term we are interested in. This means that $e^{-(t_1-t_2)\frac{1}{2\pi}\int d\omega\frac{\mathcal{W}(\omega)}{\omega}}$ approximately cancels with the GW shift in $e^{i(t_1-t_2)\Sigma^{GW}_{ii}(\varepsilon_i)}$, and we are left with

$$\mathcal{G}\left(t_{12}\right)=\mathcal{G}^0_{QP}\left(t_{12}\right)\exp\left[\frac{i}{2\pi}\int d\omega\frac{\mathcal{W}(\omega)}{\omega^2}\left(e^{i\omega(t_1-t_2)}-1\right)\right] \tag{17}$$

Using the functional derivative identity $\frac{\partial \mathcal{G}^u(t_{32})}{\partial u(t_4)}|_{u=0} = \mathcal{G}(t_{34})\mathcal{G}(t_{42})$ and correspondingly setting $\mathcal{G}^u \to \mathcal{G}$, $\mathcal{G}^{QP,u} \to \mathcal{G}^{QP}$ gives

$$\mathcal{G}(t_{12}) = \mathcal{G}^{QP}(t_{12}) + i\mathcal{G}^{QP}(t_{13})\mathcal{W}(t_{34})\mathcal{G}(t_{34})\mathcal{G}(t_{42}) - \mathcal{G}^{QP}(t_{13})\tilde{\Sigma}^{GW}\mathcal{G}(t_{32}) \tag{6.19}$$

Now define $\tilde{\mathcal{G}}(t_{12}) = e^{i(t_1-t_2)\tilde{\Sigma}^{GW}}\mathcal{G}(t_{12}) \implies \mathcal{G}(t_{12}) = e^{-i(t_1-t_2)\tilde{\Sigma}^{GW}}\tilde{\mathcal{G}}(t_{12})$. Plugging this in gives

$$\begin{aligned}\tilde{\mathcal{G}}(t_{12}) = {} & e^{i(t_1-t_2)\tilde{\Sigma}^{GW}}\mathcal{G}^{QP}(t_{12}) + ie^{i(t_1-t_2)\tilde{\Sigma}^{GW}}\mathcal{G}^{QP}(t_{13})\mathcal{W}(t_{34})e^{-i(t_3-t_4)\tilde{\Sigma}^{GW}}\tilde{\mathcal{G}}(t_{34})e^{-i(t_4-t_2)\tilde{\Sigma}^{GW}}\tilde{\mathcal{G}}(t_{42}) \\ & - e^{i(t_1-t_2)\tilde{\Sigma}^{GW}}\mathcal{G}^{QP}(t_{13})\tilde{\Sigma}^{GW}e^{-i(t_3-t_2)\tilde{\Sigma}^{GW}}\tilde{\mathcal{G}}(t_{32})\end{aligned} \tag{6.20}$$

Inegration factor method

Define $A(u) = -\mathcal{G}^{QP,u}(t_{13})\,\tilde{\Sigma}^{GW}, \quad B(u) = \mathcal{G}^{QP,u}(t_{12}), \quad C(u) = i\mathcal{G}^{QP,u}(t_{13})\,\mathcal{W}(t_{34})$. Then the equation can be written as

$$C(u)\frac{\partial \mathcal{G}^u}{\partial u} + A(u)\mathcal{G}^u = B(u). \tag{6.21}$$

Divide through by $C(u)$, we get

$$\frac{\partial \mathcal{G}^u}{\partial u} + \frac{A(u)}{C(u)}\mathcal{G}^u = \frac{B(u)}{C(u)}. \tag{6.22}$$

So our integrating factor is

$$\mu(u) = \exp\left(\int^u \frac{A(s)}{C(s)}ds\right) = \exp\left(+i\int^u ds\frac{\tilde{\Sigma}^{GW}}{\mathcal{W}}\right) \tag{6.23}$$

and the solution is

$$\mathcal{G}^u = \frac{1}{\mu(u)}\left[C_0 + \int^u \mu(s)\frac{B(s)}{C(s)}ds\right] \tag{6.24}$$

$$= \exp\left(-i\int^u ds\frac{\tilde{\Sigma}^{GW}}{\mathcal{W}}\right)\left[C_0 + \int^u ds\exp\left(+i\int^s ds'\frac{\tilde{\Sigma}^{GW}}{\mathcal{W}}\right)\frac{\mathcal{G}^{QP,s}}{i\mathcal{G}^{QP,s}\mathcal{W}}\right] \tag{6.25}$$

$$= \exp\left(-i\int^u ds\frac{\tilde{\Sigma}^{GW}}{\mathcal{W}}\right)\left[C_0 + \int^u ds\exp\left(+i\int^s ds'\frac{\tilde{\Sigma}^{GW}}{\mathcal{W}}\right)\frac{-i}{\mathcal{W}}\right] \tag{6.26}$$

$$\tag{6.27}$$

6.2 Motivation

The cumulant has the ability to enhance spectral features with respect to GW. The prototypical example that is given to motivate its utility is the analysis of the self-consistent GW spectral function by von Barth and Holm for the uniform electron gas. There they show that scGW predicts an unphysical peak, known as the plasmaron, which is off from the expected plasmon frequency, as the only feature in the satellite spectrum. Cumulant plus GW, on the other hand, gives a more accurate answer.

A qualitative interpretation

The way I think about this is as follows. GW (with or without self-consistency) yields similar quasiparticle energies, while self-consistency mostly affects spectral weight distribution. However, GW often produces an artificial plasmaron satellite. The cumulant expansion not only redistributes weight but also corrects the satellite structure, eliminating the spurious plasmaron and aligning the features with the physical plasmon frequency.

As we know, the ansatz for the cumulant $C(t)$ is

$$G(t) = G_0(t)e^{C(t)} \tag{6.28}$$

where we have the non-interacting and fully interacting Green's functions G_0 and G, respectively. After some derivation, we arrive at the Landau form for the cumulant

$$C(t) = \int d\omega \frac{\beta(\omega)}{\omega^2} \left[e^{-i\omega t} + i\omega t - 1\right] \tag{6.29}$$

where the cumulant kernel is defined as

$$\beta(\omega) = -\frac{1}{\pi} \operatorname{Im} \Sigma^{\mathrm{c}}(\omega) \tag{6.30}$$

This form is amenable to physical interpretation if we partition into

$$C(t) = -a + i\Delta t + \tilde{C}(t) \tag{6.31}$$

where $a = \int d\omega \beta(\omega)/\omega^2$ is the net satellite strength, $\Delta = \int d\omega \beta(\omega)/\omega$ is the quasiparticle shift, or core-level "relaxation energy", and $\tilde{C}(t)$ is the remainder of the cumulant, which contains the information about the satellites.

6.3 Current directions in the field

6.3.1 Connection to CC

The conceptual similarities between the cumulant and CC are there; both are exponential ansatzes that attempt to provide a more accurate treatment of many-body correlation. There is a body of literature that seeks to exploit this connection, but if the focus is on a low-scaling ab initio method, then one does not escape the high cost of CC usually.

6.3.2 Non-linear cumulant

TODO

6.3.3 Self-consistent cumulant

My derivation

The cumulant ansatz for the retarded Green's function is:

$$G^R(t) = -i\theta(t)e^{-i\epsilon_0 t}e^{C^R(t)}. \tag{6.32}$$

Note that because this is for the retarded Green's function, we can assume that $t > 0$ when differentiating, so $\theta(t) = 1$. Differentiating with respect to time gives:

$$\partial_t G^R(t) = -i\partial_t \left(e^{-i\epsilon_0 t}e^{C^R(t)}\right) \tag{6.33}$$

$$= -i\epsilon_0 G^R(t) - i\dot{C}^R(t)G^R(t) \tag{6.34}$$

$$\tag{6.35}$$

Now, the equation of motion for the retarded Green's function in the Dyson formulation with the self energy Σ is given by

$$(i\partial_t - H_0)\, G^R(t) - \int_0^t d\tau \Sigma^R(\tau)G^R(t-\tau) = 0 \tag{6.36}$$

$$\implies \partial_t G^R(t) = -i\epsilon_0 G^R(t) - i\int_0^t d\tau G^R(t-\tau)\Sigma^R(\tau) \tag{6.37}$$

COMPARISON

The Nakajima-Zwanzig equation for a correlation function $\mathcal{A}(t)$ is given by

$$\dot{\mathcal{A}}(t) = \mathcal{A}(t)\Omega_1 - \int_0^t d\tau\, \mathcal{A}(t-\tau)\mathcal{K}_1(\tau) + D(t) \tag{6.38}$$

The self-energy, cumulant and the memory kernel are all auxiliary quantities that bridge the mean-field description with the exact solution. Your conjecture is that the memory kernel decays faster than the self-energy, potentially enabling lower scaling methods with high accuracy. I wonder how the cumulant compares in this respect. The linked cluster theorem says that the cumulant performs an exponential resummation of the diagrams so that it is able to treat all higher order diagrams approximately.

Equating the two gives an expression for the cumulant derivative:

$$\dot{C}^R(t)G^R(t) = \int_0^t d\tau G^R(t-\tau)\Sigma^R(\tau) \tag{6.39}$$

$$\implies \dot{C}^R(t) = \int_0^t d\tau \Sigma^R(\tau)\frac{G^R(t-\tau)}{G^R(t)}. \tag{6.40}$$

Using the cumulant ansatz for the Green's function, we can write:

$$\frac{G^R(t-\tau)}{G^R(t)} = e^{i\epsilon_0\tau}e^{C^R(t-\tau)-C^R(t)} = e^{i\epsilon_0\tau}e^{-\int_{t-\tau}^{t} dt'\dot{C}^R(t')}. \tag{6.41}$$

So the final expression for the cumulant derivative is a nonlinear Volterra integro-differential equation (VIDE):

$$\dot{C}^R(t) = \int_0^t d\tau \Sigma^R(\tau) e^{i\epsilon_0\tau} e^{-\int_{t-\tau}^{t} dt'\dot{C}^R(t')} \tag{6.42}$$

$$= i\int_0^t d\tau \int_0^\infty d\tau' \left[G^R(\tau-\tau')W^>(\tau') + G^<(\tau-\tau')W^R(\tau')\right] e^{i\epsilon_0\tau} e^{-\int_0^{\tau} dt'\dot{C}^R(t')} \tag{6.43}$$

A VIDE also appeared in PJ's SC-CE and they solved it using differential equation solvers in the time domain.

One-shot cumulant

In the first iteration, we set the exponential factor to 1, which gives the time-derivative of the one-shot cumulant:

$$\dot{C}_0^R(t) = \int_0^t d\tau \Sigma^R(\tau) e^{i\epsilon_0\tau}. \tag{6.44}$$

Note that we can express the second-derivative of the one-shot retarded cumulant as

$$\ddot{C}_0^R = \Sigma^R(t) e^{i\epsilon_0 t}. \tag{6.45}$$

We integrate with respect to time to get the cumulant itself:

$$C_0^R(t) = \int_0^t dt' \int_0^{t'} d\tau \Sigma^R(\tau) e^{i\epsilon_0\tau} = \int_0^t d\tau \Sigma^R(\tau) e^{i\epsilon_0\tau}(t-\tau). \tag{6.46}$$

Now, we perform a Fourier transform to get the frequency-domain cumulant:

$$C_0^R(\omega) = \int_0^\infty dt\, e^{i\omega t} \int_0^t d\tau\, \Sigma^R(\tau) e^{i\epsilon_0\tau}(t-\tau) \tag{6.47}$$

$$= \int_0^\infty d\tau\, \Sigma^R(\tau) e^{i\epsilon_0\tau} \int_\tau^\infty dt\, e^{i\omega t}(t-\tau) \tag{6.48}$$

Let $t' = t - \tau$, so $dt = dt'$, and when $t = \tau$, $t' = 0$, and as $t \to \infty$, $t' \to \infty$:

$$\int_\tau^\infty dt\, e^{i\omega t}(t-\tau) = \int_0^\infty dt'\, e^{i\omega(t'+\tau)} t' \tag{6.49}$$

$$= e^{i\omega\tau} \int_0^\infty dt'\, e^{i\omega t'} t' \tag{6.50}$$

We can evaluate the integral over t' as

$$\int_0^\infty dt'\, e^{i\omega t'} t' = -\frac{1}{(\omega + i\eta)^2} \tag{6.51}$$

where where η is the positive infinitesimal convergence factor.

Putting it all together,

$$C_0^R(\omega) = \int_0^\infty d\tau\, \Sigma^R(\tau) e^{i(\omega+\epsilon_0)\tau} \left(-\frac{1}{(\omega+i\eta)^2}\right) \tag{6.52}$$

$$= -\frac{1}{(\omega+i\eta)^2} \int_0^\infty d\tau\, \Sigma^R(\tau) e^{i(\omega+\epsilon_0)\tau} \tag{6.53}$$

$$= -\frac{\Sigma^R(\omega+\epsilon_0)}{(\omega+i\eta)^2} \tag{6.54}$$

Now, consider the inverse Fourier transform to get back to the time domain:

$$C_0^R(t) = \int_{-\infty}^\infty d\omega\, e^{-i\omega t} C_0^R(\omega) \tag{6.55}$$

$$= \int_{-\infty}^\infty d\omega\, e^{-i\omega t} \left(-\frac{\Sigma^R(\omega+\epsilon_0)}{(\omega+i\eta)^2}\right) \tag{6.56}$$

Annotating PJ's SC-CE paper

The time-ordered form of the electron Green's function is given by

$$\mathcal{G}_k(t) = \mathcal{G}_k^{(0)}(t) \left\langle a_k T e^{-i\int_0^t d\tau V(\tau)} a_k^\dagger \right\rangle, \tag{6.57}$$

where a_k and $a_k^\dagger$ are the annihilation and creation operators for an electron in state k, T is the time-ordering operator, and $V(t)$ is the interaction picture representation of the electron-boson interaction. The non-interacting Green's function is given by

$$\mathcal{G}_k^{(0)}(t) \equiv -i\Theta(t) e^{-i\epsilon_k t}, \tag{6.58}$$

This can be rewritten as

$$\mathcal{G}_k(t) = \mathcal{G}_k^{(0)}(t) T e^S = -i\Theta(t) e^{C_k(t)}, \tag{6.59}$$

with the differential operator S and cumulant $C_k(t)$. Note that they are actually setting $e^{-i\epsilon_k t} T e^S = e^{C_k(t)}$ as this is supposed to be a self consistent formulation. We can expand the exponential in 6.57 in a power series like $T e^{-i\int_0^t d\tau V(\tau)} = \sum_{n=0}^\infty \frac{(-i)^n}{n!} \int_0^t dt_1 \cdots \int_0^t dt_n T\left[V(t_1)\cdots V\left(t_n\right)\right]$ with $V(t) = \sum_{k,q} g_{q,k} a_{k+q}^\dagger(t) a_k(t) A_q(t)$ where $g_{q,k}$ is the electron-boson coupling constant and $A_q(t) = b_q e^{-i\omega_q t} + b_{-q}^\dagger e^{i\omega_q t}$ (b_q and $b_q^\dagger$ are the annihilation and creation operators for a phonon of momentum q and frequency ω_q so $[b_q, b_{q'}^\dagger] = \delta_{qq'}$). They specialize to the case of a single electron on a lattice, and so the Green's function becomes

$$\mathcal{G}_k(t) = G_k^{(0)}(t) \left\langle \sum_{n=0}^\infty T \left[\frac{(-i)^n}{n!} \sum_{(q)|_{j=1}^n} \int_0^t dt_1 \cdots \int_0^t dt_n \right. \right. \tag{6.60}$$

$$\times g_{q_n,k} e^{-it_n\epsilon_k} e^{it_n\epsilon_{k+q_n}} A_{q_n}\left(t_n\right) \tag{6.61}$$

$$\times g_{q_{n-1},k+q_n} e^{-t_{n-1}\epsilon_{k+q_n}} e^{it_{n-1}\epsilon_{k+q_n+q_{n-1}}} A_{q_{n-1}}\left(t_{n-1}\right) \tag{6.62}$$

$$\left. \left. \times \cdots \times g_{q_1,k+q_2+\cdots+q_n} e^{-it_1\epsilon_{k+q_2+\cdots+q_n}} e^{it_1\epsilon_k} A_{q_1}\left(t_1\right) \right] \right\rangle \tag{6.63}$$

with $\sum_i q_i = 0$. By defining the vertex operator $\Gamma_{qk}(t) = g_{qk} e^{-it\epsilon_k} e^{q\cdot \frac{d}{dk}} e^{it\epsilon_k}$ we can rewrite the electron Green's function as an exponential,

$$\mathcal{G}_k(t) = \mathcal{G}_k^{(0)}(t) \left\langle T e^{-i\sum_q \int_0^t d\tau \Gamma_{qk}(\tau) A_q(\tau)} \right\rangle \tag{6.64}$$

so we can see that in the single electron case $\left\langle a_k T e^{-i\int_0^t d\tau V(\tau)} a_k^\dagger \right\rangle = \left\langle T e^{-i\sum_q \int_0^t d\tau \Gamma_{qk}(\tau) A_q(\tau)} \right\rangle$, where the trace on the RHS is only over the bosonic degrees of freedom. Assuming harmonic bosons, we can use $\left\langle e^B \right\rangle = e^{\langle B^2 \rangle/2}$ with the definition

$$B = -i \sum_q \int_0^t d\tau \Gamma_{qk}(\tau) A_q(\tau) \tag{6.65}$$

where our B is linear in the bosonic operators A_q, so the identity applies. Then,

$$\begin{aligned}
\ln \left\langle T e^B \right\rangle &= \frac{1}{2} \left\langle T B^2 \right\rangle && (6.66)\\
&= \frac{1}{2}(-i)^2 \sum_{qq'} \int_0^t d\tau \int_0^t d\tau' \Gamma_{qk}(\tau) \Gamma_{q'k}(\tau') \left\langle T A_q(\tau) A_{q'}(\tau') \right\rangle && (6.67)\\
&= -\frac{1}{2} \sum_{qq'} \int_0^t d\tau \int_0^t d\tau' \Gamma_{qk}(\tau) \Gamma_{q'k}(\tau') \left[i D_q^{(0)}(\tau - \tau') \delta_{q,-q'} \right] && (6.68)\\
&= -\frac{i}{2} \sum_q \int_0^t d\tau \int_0^t d\tau' D_q^{(0)}(\tau - \tau') \Gamma_{qk}(\tau) \Gamma_{-q,k}(\tau') && (6.69)\\
&= -i \sum_q \int_0^t d\tau \int_0^\tau d\tau' D_q^{(0)}(\tau - \tau') \Gamma_{-qk}(\tau) \Gamma_{qk}(\tau') = S && (6.70)
\end{aligned}$$

To find a self consistent expression for S, we use the Feynman operator ordering theorem, which states that given a functional of time-dependent operators $F[\hat{A}(\tau), \hat{B}(\tau), \ldots]$ where $\tau \in [0, t]$ and with a unitary operator of the form $\hat{U}(\tau') = T \exp\left[\int_0^{\tau'} d\tau \hat{P}(\tau)\right]$, then

$$\hat{U}(t) F[\hat{A}(\tau), \hat{B}(\tau), \ldots] = T \left[\exp\left(\int_0^t d\tau \hat{P}(\tau) \right) F\left[\hat{U}(\tau) \hat{A}(\tau) \hat{U}^{-1}(\tau), \ldots \right] \right]. \tag{6.71}$$

We choose $\hat{P}(\tau) = -i\left[\epsilon_k + \frac{d}{d\tau}\phi_k(\tau)\right]$ and also $\phi_k(t) = -iC_k(t)$, so $\hat{U}(\tau) = e^{-i\epsilon_k \tau} e^{-\phi_k(\tau)}$. This choice of $\phi_k(t)$ emphasizes that at time 0 the noninteracting and fully interacting Green's functions are equal. The transformed vertex functional can be simplified to

$$\begin{aligned}
\bar{\Gamma}_{qk}(\tau) &= \hat{U}(\tau) \Gamma_{qk}(\tau) \hat{U}^{-1}(\tau) && (6.72)\\
&= \left(e^{-i\epsilon_k \tau} e^{-i\phi_k(\tau)} \right) g_{qk} e^{-i\tau\epsilon_k} e^{q\cdot\frac{d}{dk}} e^{i\tau\epsilon_k} \left(e^{i\phi_k(\tau)} e^{i\epsilon_k \tau} \right) && (6.73)\\
&= g_{qk} e^{-i\phi_k(\tau)} e^{-2i\tau\epsilon_k} e^{q\cdot\frac{d}{dk}} e^{2i\tau\epsilon_k} e^{i\phi_k(\tau)} && (6.74)\\
&= g_{qk} e^{-i\phi_k(\tau)} e^{q\cdot\frac{d}{dk}} e^{+i\phi_k(\tau)}, && (6.75)
\end{aligned}$$

and the transformed S is then given by

$$\bar{S} = -i\int_0^t d\tau \left(\epsilon_k + \frac{d}{d\tau}\phi_k(\tau)\right) - i\sum_q \int_0^t d\tau \int_0^\tau d\tau' D_q^{(0)}\left(\tau-\tau'\right)\bar{\Gamma}_{-qk}(\tau)\bar{\Gamma}_{qk}\left(\tau'\right) \tag{6.76}$$

Just as in the standard cumulant expansion, the cumulants of a given order can be computed by evaluating time-ordered powers of S,

$$C_k(t) = \sum_{n=1}^{\infty} \frac{1}{n!} T\left[\bar{S}^n\right]_c \tag{6.77}$$

where the notation $[\cdots]_c$ denotes the cumulant of an operator, and $T[\bar{S}]_c = T[\bar{S}]$. Subsequent terms are given by

$$T\left[\bar{S}^n\right]_c = T\left[\bar{S}^n\right] - \sum_{m=1}^{n-1} \frac{(n-1)!}{m!(n-m-1)!} T\left[\bar{S}^m\right] T\left[\bar{S}^{n-m}\right]_c \tag{6.78}$$

Evaluating 6.77 with $\phi_k(t) = C_k(t)$ to leading order produces

$$C_k(t) = -i\epsilon_k t - i\frac{g^2}{N}\sum_q \int_0^t d\tau \int_0^\tau d\tau' D_q^{(0)}\left(\tau-\tau'\right) e^{-C_k(\tau)+C_{k-q}(\tau)-C_{k-q}(\tau')+C_k(\tau')} \tag{6.79}$$

Here, $D_q^{(0)}(t)$ is the free phonon propagator, $D_q^{(0)}(t) = -i\left[\left(1+N_q\right)e^{-i\omega_q|l|} + N_q e^{|\omega_q|l|}\right]$, and N_q is the Bose occupation factor, $N_q = \left[\exp\left(\beta\omega_q\right)-1\right]^{-1}$. Equation (12) is a difficult integral equation to solve, coupling the solution for a fixed wave vector at time t to all other Green's functions for other momenta and all previous times. It is, however, readily transformed into a self-consistent expression for the interacting Green's functions, which is more convenient for calculations

$$\begin{aligned}\frac{d\mathcal{G}_{\hat{k}}(t)}{dt} =& -i\epsilon_{\hat{k}}\mathcal{G}_{\hat{k}}(t) \\ & -i\frac{g^2}{N}\sum_{\vec{q}}\int_0^t d\tau D_{\vec{q}}^{(0)}(t-\tau)\frac{\mathcal{G}_{\vec{k}}(\tau)\mathcal{G}_{\vec{k}-\vec{q}}(t)}{\mathcal{G}_{\vec{k}-\vec{q}}(\tau)}\end{aligned}$$

The properties of the solutions to Eqs. (12) and (13) are not readily apparent; however, it can be shown by expressing Eq. (12) recursively (Appendix B) that the weak-coupling limit of this SC-CE returns to that of the standard CE. The recursive SC-CE solution demonstrates that the SC-CE approximates higher-order cumulants by screened second-order cumulants.

The recursive expression (13) suggests that SC-CE might suffer from some of the same problems as the fourth-order CE which introduces, e.g., negative spectral weight. However, it is not clear whether terms which appear to be problematic in the recursive formulation are suppressed when Eq. (13) is solved directly. Before taking up the question of the performance of the SC-CE, we first take a detour, exploring Eq. (13) from a different perspective. Here, we illustrate how the lowest-order SC-CE generates the exact second-order CE and approximations to all higherorder CEs. Considering only the lowest order in

Eqs. (A7) and (A8), we can write Eq. (13) for the SC-CE as a selfconsistent equation for the Green's function,

$$\begin{aligned}\mathcal{G}_k(t) =&\mathcal{G}_k^{(0)}(t)\exp\left(i\sum_q\int_0^t d\sigma\int_0^\sigma d\tau\,|g_{qk}|^2\right.\\&\left.\times D_q^{(0)}(\sigma-\tau)\frac{\mathcal{G}_{k-q}(\sigma)\mathcal{G}_k(\tau)}{\mathcal{G}_{k-q}(\tau)\mathcal{G}_k(\sigma)}\right)\end{aligned}$$

In the weak-coupling limit, we find an iterative solution starting with the bare Green's function. The first iteration is straightforward and replicates exactly the second cumulant,

$$\mathcal{G}_k^{(1)}(t)=\mathcal{G}_k^{(0)}(t)\exp\left[C_2(k,t)\right].$$

While the integrals for subsequent iterations may be analytically evaluated, it is more instructive to consider the further iterations as functions of $C_2(k,t)$.

The second and all subsequent iterations now have exponential resummations of the second-order cumulant itself. Explicitly,

$$\begin{aligned}\mathcal{G}_k^{(2)}(t) =&\mathcal{G}_k^{(0)}(t)\exp\left(-i\sum_q\int_0^t d\sigma\int_0^\sigma d\tau\,|g_{qk}|^2\right.\\&\times D_q^{(0)}(\sigma-\tau)\mathcal{G}_{k-q}^{(0)}(\sigma-\tau)\mathcal{G}_k^{(0)}(\tau-\sigma)\\&\left.\times e^{c_2(k,\tau)+c_2(k-q,\sigma)-c_2(k,\sigma)-c_2(k-q,\tau)}\right)\end{aligned}$$

The nth cumulant is defined as being proportional to the nth power of the coupling constant, so by expanding the exponent we find an approximation for all higher-order cumulants,

$$\begin{aligned}\mathcal{G}_k^{(2)}(t) =&\mathcal{G}_k^{(0)}(t)\exp\left(\sum_{n=0}^\infty\frac{-i}{n!}\sum_q\int_0^t d\sigma\int_0^\sigma d\tau\right.\\&\times|g_{qk}|^2\,D_q^{(0)}(\sigma-\tau)\mathcal{G}_{k-q}^{(0)}(\sigma-\tau)\mathcal{G}_k^{(0)}(\tau-\sigma)\\&\times\left[C_2(k,\tau)+C_2(k-q,\sigma)\right.\\&\left.\left.-C_2(k,\sigma)-C_2(k-q,\tau)\right]^n\right)\end{aligned}$$

We can simplify this expression by introducing $C_m^{(n)}(k,t)$, which represents the approximation to the nth iteration of the m th cumulant. This results in

$$\mathcal{G}_k^{(2)}(t)=\mathcal{G}_k^{(0)}(t)\exp\left(\sum_{n=1}^\infty C_{2n}^{(2)}(k,t)\right).$$

Importantly, because the second iteration produces cumulants of all orders, further iterations require expanding the exponent into moments.

After the second iteration, we can generalize to an arbitrary iteration:

$$\begin{aligned}\mathcal{G}_{\mathbf{k}}^{(n+1)}(t) =&\mathcal{G}_{\mathbf{k}}^{(0)}(t)\exp\left(-i\sum_{\mathbf{q}}\int_0^t d\sigma\int_0^\sigma d\tau\,|g_{qk}|^2\right.\\&\left.\times D_{\mathbf{q}}^0(\sigma-\tau)\mathcal{G}_{\mathbf{k}}^{(0)}(\tau-\sigma)\mathcal{G}_{\mathbf{k}-\mathbf{q}}^{(0)}(\sigma-\tau)e^{F(\mathrm{w})(\mathbf{k},\mathbf{q},\sigma,\tau)}\right)\end{aligned}$$

Here, we introduce the notation

$$\begin{aligned} F^{(n)}(\mathbf{k},\mathbf{q},\sigma,\tau) \equiv & F_2^{(n)}(\mathbf{k},\mathbf{q},\sigma,\tau) + F_4^{(n)}(\mathbf{k},\mathbf{q},\sigma,\tau) + \cdots \\ F_i^{(n)}(\mathbf{k},\mathbf{q},\sigma,\tau) \equiv & C_i^{(n)}(\mathbf{k}-\mathbf{q},\sigma) - C_i^{(n)}(\mathbf{k}-\mathbf{q},\tau) \\ & - C_i^{(n)}(\mathbf{k},\sigma) + C_i^{(n)}(\mathbf{k},\tau). \end{aligned}$$

The procedure for constructing the approximation to the nth iteration of the m th cumulant is given by the moment expansion

$$\sum_{m=0}^{\infty} \lambda^{2m} W_{2m}^{(n)}(\mathbf{k},\mathbf{q},\sigma,\tau) = e^{\sum_{m=1}^{\infty} \lambda^{2m} F_m^{(k)}(\mathbf{k},\mathbf{q},\sigma,\tau)},$$

where the first few moments are given by

$$\begin{aligned} W_0^{(n)}(\mathbf{k},\mathbf{q},\sigma,\tau) &= 1, \\ W_2^{(n)}(\mathbf{k},\mathbf{q},\sigma,\tau) &= F_2^{(n)}(\mathbf{k},\mathbf{q},\sigma,\tau), \\ W_4^{(n)}(\mathbf{k},\mathbf{q},\sigma,\tau) &= F_4^{(n)}(\mathbf{k},\mathbf{q},\sigma,\tau) + \frac{1}{2}\left(F_2^{(n)}(\mathbf{k},\mathbf{q},\sigma,\tau)\right)^2. \end{aligned}$$

Because each iteration introduces another power of g^2 to all of the approximated cumulants, and the n th-order cumulant is defined as being proportional to g'', the nth iteration cannot alter any of the approximated cumulants of order lower than n. Because of this, and the fact that the approximate cumulant for a given order is an integral over lower-order approximations, the iterative method is actually recursive. Dropping the superscripts indicating iteration, the general form for the SC-CE approximation to the nth cumulant is

$$\begin{aligned} C_{2n}^{\mathrm{SCCE}}(\mathbf{k},t) = & -i\sum_{\mathbf{q}} \int_0^t d\sigma \int_0^\sigma d\tau \, |g_{q\mathbf{k}}|^2 \, D_{\mathbf{q}}(\sigma-\tau) \\ & \times \mathcal{G}_{\mathbf{k}}^{(0)}(\tau-\sigma)\mathcal{G}_{\mathbf{k}-\mathbf{q}}^{(0)}(\sigma-\tau) W_{2n-2}(\mathbf{k},\mathbf{q},\sigma,\tau) \end{aligned}$$

APPENDIX C: NUMERICAL VIDE SOLUTION Equation (13) is not convenient for numerical calculations. Instead, we define $y_k(t) = e^{C_\lambda(t)}$ and solve directly for $y_k(t)$,

$$\begin{aligned} \frac{dy_k(t)}{dt} = & -i\sum_{q} \int_0^t d\tau \, |g_{qk}|^2 \, D_q^{(0)}(t-\tau) \\ & \times e^{i(\epsilon-\epsilon-\epsilon-q)(t-\tau)} \frac{y_k(\tau) y_{k-q}(t)}{y_{k-q}(\tau)} \end{aligned}$$

Numerical solutions to Eq. (C1) were carried out with a multistep predictor corrector method as derived by Linz [55]. His method is general for first-order Volterra integrodifferential equations (VIDEs) of the form

$$y'(x) = F\left(x, y(x), \int_0^x dt K[x,t,y(t)]\right)$$

The form of Eq. (Cl) implies that F can be written purely as a function of $\int_0^x dt K[x,t,y(t)]$. We used an Adams-Bashforth second-order predictor step and a third-order Adams-Moulton corrector step. Following Linz, for the starting procedure of the Holstein model we applied the self-consistent Simpson's method iterated five times [55].

Annotation of second memory kernel coupling theory

Following Mori's projection approach, [**?**] the correlation function in Eq. **??** satisfies the generalized quantum master equation (GQME):

$$\dot{C}_{AA}(t) = \Omega C_{AA}(t) + \int_0^t \mathrm{d}\tau\, K(t-\tau) C_{AA}(\tau), \tag{6.80}$$

where the scalar Ω and the kernel function $K(t)$ are derived from the Mori-Zwanzig formalism:

$$\Omega = (\mathrm{i}\mathcal{L}\hat{A}, A)(\hat{A}, \hat{A})^{-1}, \tag{6.81}$$

$$K(t) = (\mathrm{i}\mathcal{L}e^{\mathrm{i}t\boldsymbol{\mathcal{Q}}\mathcal{L}}\boldsymbol{\mathcal{Q}}\mathrm{i}\mathcal{L}\hat{A}, \hat{A})(\hat{A}, \hat{A})^{-1}. \tag{6.82}$$

Here, the Mori-product notation $(\hat{A}, \hat{B})$ denotes an appropriate inner product. The Liouville operator acts on an arbitrary operator $\hat{X}$ as $\mathcal{L}\hat{X} \equiv \frac{1}{\hbar}\Big[\hat{H}, \hat{X}\Big]$. The projection operator is defined as $\boldsymbol{\mathcal{P}}\hat{X} = (\hat{X}, \hat{A})\hat{A}(\hat{A}, \hat{A})^{-1}$, and the complementary projection operator is $\boldsymbol{\mathcal{Q}} = \mathbf{1} - \boldsymbol{\mathcal{P}}$. In the first paper on MKCT, they introduced the high order moments

$$\Omega_n = \frac{\Big((\mathrm{i}\mathcal{L})^n \hat{A}, \hat{A}\Big)}{(\hat{A}, \hat{A})}, \tag{6.83}$$

with the corresponding auxiliary kernels

$$K_n(t) = \frac{\Big((\mathrm{i}\mathcal{L})^n \hat{f}(t), \hat{A}\Big)}{(\hat{A}, \hat{A})} \tag{6.84}$$

So we can show the main result of their first paper that the higher-order kernels satisfy the following coupled ordinary differential equation (ODE):

$$\dot{K}_n(t) = \frac{\Big((\mathrm{i}\mathcal{L})^n \dot{\hat{f}}(t), \hat{A}\Big)}{(\hat{A}, \hat{A})} \tag{6.85}$$

$$= \frac{\Big((\mathrm{i}\mathcal{L})^n \mathrm{i}\mathcal{Q}\mathcal{L}\hat{f}(t), \hat{A}\Big)}{(\hat{A}, \hat{A})} \tag{6.86}$$

$$= \frac{\Big((\mathrm{i}\mathcal{L})^{n+1} \hat{f}(t), \hat{A}\Big)}{(\hat{A}, \hat{A})} - \frac{\Big((\mathrm{i}\mathcal{L})^n \mathrm{i}\mathcal{P}\mathcal{L}\hat{f}(t), \hat{A}\Big)}{(\hat{A}, \hat{A})} \tag{6.87}$$

$$= K_{n+1}(t) - \frac{(\mathrm{i}\mathcal{L}\hat{f}(t), \hat{A})}{(\hat{A}, \hat{A})} \times \frac{\Big((\mathrm{i}\mathcal{L})^n \hat{A}, \hat{A}\Big)}{(\hat{A}, \hat{A})} \tag{6.88}$$

$$= K_{n+1}(t) - K_1(t)\Omega_n, \tag{6.89}$$

where we have used the fact that the random fluctuation operator is $\hat{f}(t) = e^{\mathrm{i}t\mathrm{Q}\mathrm{C}}\mathcal{Q}\mathrm{i}\mathcal{L}\hat{A} \Longrightarrow \dot{\hat{f}}(t) = \mathrm{i}\mathcal{Q}\mathcal{L}\hat{f}(t)$ and we can deduce the initial conditions in a similar fashion with $\hat{f}(0) =$

$\mathcal{Q}i\mathcal{L}\hat{A}$, so

$$K_n(0) = \frac{\left((\mathrm{i}\mathcal{L})^n \mathrm{Q}\mathrm{i}\mathcal{L}\hat{A}, \hat{A}\right)}{(\hat{A}, \hat{A})} \tag{6.90}$$

$$= \frac{\left((\mathrm{i}\mathcal{L})^n (\mathrm{i}\mathcal{L}\hat{A} - \mathrm{P}\mathrm{i}\mathcal{L}\hat{A}), \hat{A}\right)}{(\hat{A}, \hat{A})} \tag{6.91}$$

$$= \frac{\left((\mathrm{i}\mathcal{L})^{n+1}\hat{A}, \hat{A}\right)}{(\hat{A}, \hat{A})} - \frac{\left((\mathrm{i}\mathcal{L})^n \mathrm{P}\mathrm{i}\mathcal{L}\hat{A}, \hat{A}\right)}{(\hat{A}, \hat{A})} \tag{6.92}$$

$$= \Omega_{n+1} - \Omega_1 \Omega_n, \tag{6.93}$$

suggesting that the central quantity to compute is the $\{\Omega_n\}$. But an issue with this ODE is that it extends to infinite order, and hard truncation to finite order can lead to numerical instabilities. To this end, they introduce a truncation scheme with Padé approximants. First, they noticed that the m-th derivative of kernel $K_n(t)$ evaluated at $t = 0$ is

$$K_n^{(m)} = \frac{\left((\mathrm{i}\mathcal{L})^n (\mathcal{Q}\mathrm{i}\mathcal{L})^{m+1}\hat{A}, \hat{A}\right)}{(\hat{A}, \hat{A})} \tag{6.94}$$

$$= \frac{\left((\mathrm{i}\mathcal{L})^n \mathcal{Q}\mathrm{i}\mathcal{L}(\mathcal{Q}\mathrm{i}\mathcal{L})^m \hat{A}, \hat{A}\right)}{(\hat{A}, \hat{A})} \tag{6.95}$$

$$= \frac{\left((\mathrm{i}\mathcal{L})^n (1-\mathcal{P})\, \mathrm{i}\mathcal{L}(\mathcal{Q}\mathrm{i}\mathcal{L})^m \hat{A}, \hat{A}\right)}{(\hat{A}, \hat{A})} \tag{6.96}$$

$$= \frac{\left((\mathrm{i}\mathcal{L})^{n+1}(\mathcal{Q}\mathrm{i}\mathcal{L})^m \hat{A}, \hat{A}\right)}{(\hat{A}, \hat{A})} - \frac{\left((\mathrm{i}\mathcal{L})^n \mathcal{P}\mathrm{i}\mathcal{L}(\mathcal{Q}\mathrm{i}\mathcal{L})^m \hat{A}, \hat{A}\right)}{(\hat{A}, \hat{A})} \tag{6.97}$$

$$= K_{n+1}^{(m-1)} - \frac{\left(\mathrm{i}\mathcal{L}(\mathcal{Q}\mathrm{i}\mathcal{L})^m \hat{A}, \hat{A}\right)}{(\hat{A}, \hat{A})} \times \frac{\left((\mathrm{i}\mathcal{L})^n \hat{A}, \hat{A}\right)}{(\hat{A}, \hat{A})} \tag{6.98}$$

$$= K_{n+1}^{(m-1)} - \bar{\Omega}_m \Omega_n \tag{6.99}$$

where we introduced the auxiliary moment $\bar{\Omega}_m = \frac{\left(\mathrm{i}\mathcal{L}(\mathcal{Q}\mathrm{i}\mathcal{L})^m \hat{A}, \hat{A}\right)}{(\hat{A},\hat{A})}$. So recursively applying this expression leads to the relation:

$$
\begin{aligned}
K_n^{(m)} &= K_{n+2}^{(m-2)} - \bar{\Omega}_{m-1}\Omega_{n+1} - \bar{\Omega}_m\Omega_n && (6.100)\\
&= K_{n+m}^{(0)} - \sum_{j=0}^{m-1} \bar{\Omega}_{m-j}\Omega_{n+j} && (6.101)\\
&= \Omega_{n+m+1} - \Omega_1\Omega_{n+m} - \sum_{j=0}^{m-1} \bar{\Omega}_{m-j}\Omega_{n+j} && (6.102)\\
&= \Omega_{n+m+1} - \bar{\Omega}_0\Omega_{n+m} - \sum_{j=0}^{m-1} \bar{\Omega}_{m-j}\Omega_{n+j} && (6.103)\\
&= \Omega_{n+m+1} - \sum_{j=0}^{m} \bar{\Omega}_{m-j}\Omega_{n+j} && (6.104)\\
& && (6.105)
\end{aligned}
$$

that $K_n^{(m)}$ can be expressed with moments and auxiliary moments. Similarly, the auxiliary moments themselves have recursions

$$
\begin{aligned}
\tilde{\Omega}_m &= \frac{\left((\mathrm{i}\mathcal{L}\mathcal{Q})^m \mathrm{i}\mathcal{L}\hat{A}, \hat{A}\right)}{(\hat{A},\hat{A})} - \tilde{\Omega}_{m-1}\Omega_1 \\
&= \Omega_{m+1} - \sum_{j=0}^{m-1} \tilde{\Omega}_j\Omega_{m-j}
\end{aligned}
\qquad (6.106)
$$

which means the auxiliary moments $\{\tilde{\Omega}_m\}$ can be obtained by the moments $\{\Omega_n\}$; it becomes a problem of efficiently computing the moments. The series expansion for the n-th order auxiliary kernel can then be given by Padé approximant. Initially, $K_n(t)$ is expressed as a truncated Taylor series:

$$
K_n(t) \approx \sum_{j=0}^{M} \frac{K_n^{(j)}(0)}{j!} t^j, \qquad (6.107)
$$

which is a good local approximation but lacks accuracy over a broader range of t. A more reliable approximation can be achieved using the Padé approximant:

$$
K_n(t) \approx \frac{p_{M_1}(t)}{q_{M_2}(t)} = \frac{a_0 + a_1 t + \cdots + a_{M_1} t^{M_1}}{1 + b_1 t + \cdots + b_{M_2} t^{M_2}}, \qquad (6.108)
$$

where $p_{M_1}(t)$ and $q_{M_2}(t)$ are polynomials of degrees M_1 and M_2, respectively. The coefficients $\{a_i\}$ and $\{b_i\}$ are computed using the python library SciPy, which implements the standard Padé approximant procedure as described in Ref. [**?**]. Overall, Eq. 6.108 provides a numerically stable truncation for the MKCT Eq. **??**, where *all* coefficients can be evaluated with higher-order moments $\{\Omega_n\}$.

Relation of improper self energy to cumulant

The Dyson equation for the one particle greens function can be written using an improper Σ^I self energy as

$$G_k(t,t') = G_k^0(t,t') + G_k^0(t,t')\Sigma_k^I(t,t')G_k^0(t,t'), \tag{6.109}$$
$$\tag{6.110}$$

instead of using the proper self energy Σ^*, which satisfies $G_k(t,t') = G_k^0(t,t') + G_k^0(t,t')\Sigma_k^*(t,t')G_k(t,t')$. Now, the retarded cumulant ansatz can be written as

$$G_k^R(t,t') = G_k^{0,R}(t,t')e^{C_k^R(t,t')} \tag{6.111}$$
$$\implies \frac{G_k^R(t,t')}{G_k^{0,R}(t,t')} = e^{C_k^R(t,t')} \tag{6.112}$$
$$\tag{6.113}$$

Let's deal directly with this ratio instead of needing to introduce a self energy. The retarded Green's function can be written as

$$G_k^R(t) = -i\theta(t)\left\langle\left\{c_k(t), c_k^\dagger(0)\right\}\right\rangle \tag{6.114}$$
$$= -i\theta(t)\left\langle\left\{e^{iHt}c_k e^{-iHt}, c_k^\dagger\right\}\right\rangle \tag{6.115}$$
$$= -i\theta(t)\left\langle\left\{\sum_{n=0}^{\infty}\frac{(-it)^n}{n!}\mathcal{L}^n c_k, c_k^\dagger\right\}\right\rangle \tag{6.116}$$
$$= -i\theta(t)\left(\mu_{0,k} - t\mu_{1,k} + \frac{t^2}{2}\mu_{2,k} + O(t^3)\right) \tag{6.117}$$

where we have defined the moments $\mu_{n,k} = \left\langle\left\{(i\mathcal{L})^n c_k, c_k^\dagger\right\}\right\rangle$ and the Liouvillian superoperator $\mathcal{L}O = [H, O]$. The non-interacting retarded Green's function is given by

$$G_k^{R,0}(t) = -i\theta(t)\left(\mu_{0,k}^0 - t\mu_{1,k}^0 + \frac{t^2}{2}\mu_{2,k}^0 + O(t^3)\right) \tag{6.118}$$

where the non-interacting moments are $\mu_{n,k}^0 = \left\langle\left\{(i\mathcal{L}_0)^n c_k, c_k^\dagger\right\}\right\rangle$ and $\mathcal{L}_0 O = [H_0, O]$. Defining $A(t) = 1 - t\mu_{1,k} + \frac{t^2}{2}\mu_{2,k} + O(t^3)$ and $B(t) = 1 - t\mu_{1,k}^0 + \frac{t^2}{2}\mu_{2,k}^0 + O(t^3)$ we can use a geometric series to write

$$\frac{1}{B(t)} = 1 + t\mu_{1,k}^0 + t^2\left[\left(\mu_{1,k}^0\right)^2 - \frac{1}{2}\mu_{2,k}^0\right] + O\left(t^3\right) \tag{6.119}$$

Note that the inverse power series coefficients can be computed by Wronski's formula (if one is interested in still higher orders of t). So, we can write the ratio and then group terms by

order in t, to get

$$R_k(t) = \frac{G_k^R(t)}{G_k^{R,0}(t)} = \frac{-i\theta(t)}{-i\theta(t)} \times \frac{A(t)}{B(t)} \tag{6.120}$$

$$= \left(1 - t\mu_{1,k} + \frac{t^2}{2}\mu_{2,k} + O(t^3)\right)\left(1 + t\mu_{1,k}^0 + t^2\left[\left(\mu_{1,k}^0\right)^2 - \frac{1}{2}\mu_{2,k}^0\right] + O\left(t^3\right)\right) \tag{6.121}$$

$$= \left(1 + t\underbrace{\left[-\left(\mu_{1,k} - \mu_{1,k}^0\right)\right]}_{\alpha_{1,k}} + t^2\underbrace{\left[\frac{1}{2}\left(\mu_{2,k} - \mu_{2,k}^0\right) - \mu_{1,k}\mu_{1,k}^0 + \left(\mu_{1,k}^0\right)^2\right]}_{\alpha_{2,k}} + O(t^3)\right) \tag{6.122}$$

Given that the cumulant can be expanded as $C_k^R(t) = \kappa_{1,k}t + \kappa_{2,k}t^2 + O(t^3)$, we can Taylor expand the exponential $e^{C_k^R(t)}$ and then match coefficients with the above expression for $R_k(t)$ to plug into the usual relations between the cumulants $\kappa_{n,k}$ and moments $\alpha_{n,k}$, to get

$$\kappa_{1,k} = \alpha_{1,k} = -\left(\mu_{1,k} - \mu_{1,k}^0\right) \tag{6.123}$$

$$\kappa_{2,k} = \alpha_{2,k} - \frac{\alpha_{1,k}^2}{2} = \frac{1}{2}\left(\mu_{2,k} - \mu_{2,k}^0\right) - \mu_{1,k}\mu_{1,k}^0 + \left(\mu_{1,k}^0\right)^2 - \frac{1}{2}\left[-\left(\mu_{1,k} - \mu_{1,k}^0\right)\right]^2 \tag{6.124}$$

$$= \frac{1}{2}\left(\mu_{2,k} - \mu_{2,k}^0\right) - \mu_{1,k}\mu_{1,k}^0 + \left(\mu_{1,k}^0\right)^2 - \frac{1}{2}\left(\mu_{1,k} - \mu_{1,k}^0\right)^2 \tag{6.125}$$

$$= \frac{1}{2}\left[\left(\mu_{2,k} - \mu_{2,k}^0\right) + \left(\mu_{1,k}\right)^2 + \left(\mu_{1,k}^0\right)^2\right] \tag{6.126}$$

So now we need to determine how to compute the moments for this cumulant approach and potentially for the MKCT approach. But let's begin by discerning the form for the 2/2 Padé approximant to the cumulant for the memory kernel at n=1:

$$K_1(t) \approx \frac{a_0 + a_1 t + a_2 t^2}{1 + b_1 t + b_2 t^2} \tag{6.127}$$

$$\approx \left(a_0 + a_1 t + a_2 t^2\right)\left(1 - b_1 t + \left(b_1^2 - b_2\right)t^2 + O(t^3)\right) \tag{6.128}$$

$$\approx a_0 + t\left(a_1 - a_0 b_1\right) + t^2\left(a_2 - a_1 b_1 + a_0\left(b_1^2 - b_2\right)\right) + O(t^3) \tag{6.129}$$

with the derivatives given by $c_0 = K_1(0)$, $c_1 = K_1^{(1)}(0)$, and $c_2 = \frac{K_1^{(2)}(0)}{2}$. Matching coefficients of t^0, t^1, and t^2 gives us the following system of equations:

$$c_0 = a_0 \tag{6.130}$$

$$c_1 = a_1 - a_0 b_1 \implies a_1 = c_1 + a_0 b_1 \tag{6.131}$$

$$c_2 = a_2 - a_1 b_1 + a_0\left(b_1^2 - b_2\right) \implies a_2 = c_2 + a_1 b_1 - a_0\left(b_1^2 - b_2\right) \tag{6.132}$$

We can find that $a_0 = K_1(0)$, $a_1 = K_1^{(1)}(0) - \frac{K_1(0)K_1^{(2)}(0)}{2K_1^{(1)}(0)}$, and $b_1 = -\frac{K_1^{(2)}(0)/2}{K_1^{(1)}(0)}$. We start by computing

$$K_1(0) = \Omega_2 - \Omega_1^2 = \mu_{2,k} - \mu_{1,k}^2 \tag{6.133}$$

$$K_1^{(1)}(0) = K_2(0) - \bar{\Omega}_1\Omega_1 = \Omega_3 - \Omega_1\Omega_2 - \bar{\Omega}_1\Omega_1 = \mu_{3,k} - \mu_{1,k}\mu_{2,k} - \bar{\Omega}_1\mu_{1,k} \tag{6.134}$$

$$\tag{6.135}$$

Fundamental starting point

We start with the definition of the retarded Green's function in the time domain:

$$G_k^R(t) \equiv -i\theta(t)\left\langle\left\{c_k(t), c_k^\dagger(0)\right\}\right\rangle. \tag{6.136}$$

Immediately, we can Fourier transform to the frequency domain:

$$G_k^R(\omega) = \int_{-\infty}^{\infty} dt e^{i\omega t} G_k^R(t). \tag{6.137}$$

But because $G_k^R(t)$ is already zero for $t < 0$ (by the $\theta(t)$), this integral reduces to

$$G_k^R(\omega) = -i\int_0^{\infty} dt e^{i\omega t}\left\langle\left\{c_k(t), c_k^\dagger(0)\right\}\right\rangle \tag{6.138}$$

$$= -i\int_0^{\infty} dt e^{i\omega t}\sum_{n=0}^{\infty}\frac{(it)^n}{n!}\mu_{n,k} \tag{6.139}$$

$$= -i\sum_{n=0}^{\infty}\frac{i^n}{n!}\mu_{n,k}\int_0^{\infty} dt e^{i\omega t}t^n \tag{6.140}$$

$$= -i\sum_{n=0}^{\infty}\frac{i^n}{n!}\mu_{n,k}\frac{n!}{(i\omega)^{n+1}} \tag{6.141}$$

$$= -\sum_{n=0}^{\infty}\frac{\mu_{n,k}}{\omega^{n+1}}, \tag{6.142}$$

where we have defined the moments $\mu_{n,k} = \left\langle\left\{\mathcal{L}^n c_k, c_k^\dagger\right\}\right\rangle$. This works because $c_k(t) = e^{iHt}c_k e^{-iHt} = e^{i\mathcal{L}t}c_k$, where $\mathcal{L}$ is the Liouvillian superoperator, so the time evolution operator can be expanded in a Taylor series, as $e^{i\mathcal{L}t} = \sum_{n=0}^{\infty}\frac{(it)^n}{n!}\mathcal{L}^n \implies \left\langle\left\{c_k(t), c_k^\dagger(0)\right\}\right\rangle = \sum_{n=0}^{\infty}\frac{(it)^n}{n!}\mu_{n,k}$. The complementary projection operator is $\mathcal{Q} = 1 - \mathcal{P}$. The Liouvillian superoperator acts on an arbitrary operator X as $\mathcal{L}X = [H, X]$. Since we know that Mori's is formally a projector method with $\mathcal{P}X = \frac{(X,c_k)}{(c_k,c_k)}c_k$, where $(A, B) = \langle\{A, B^\dagger\}\rangle$ is the fermionic Mori inner product, so $(c_k, c_k) = \langle\{c_k, c_k^\dagger\}\rangle = 1$. Lanczos is also formally a projection onto the Krylov subspace, so we can try to exploit this by devising a Lanczos procedure. Then we can initiate a Lanczos sequence with $|f_0\rangle = c_k$ and then for $n = 0$, we have

$$|f_1\rangle = \mathcal{L}|f_0\rangle - a_0|f_0\rangle, \tag{6.143}$$

where $a_0 = \frac{(\mathcal{L}f_0, f_0)}{(f_0, f_0)} = \mu_{1,k}$. Then for $n \geq 1$ define

$$|f_{n+1}\rangle = \mathcal{L}|f_n\rangle - a_n|f_n\rangle - b_n^2|f_{n-1}\rangle, \tag{6.144}$$

where the coefficients are given by $a_n = \frac{(\mathcal{L}f_n, f_n)}{(f_n, f_n)}$ and $b_{n+1}^2 = \frac{(f_{n+1}, f_{n+1})}{(f_n, f_n)}$. Let us try to determine the action of the Liouvillian onto a given state $|f_n\rangle$. We can write

$$\mathcal{L}|f_n\rangle = [H_0 + V, |f_n\rangle] \tag{6.145}$$

$$= \mathcal{L}_0|f_n\rangle + [V, |f_n\rangle] \tag{6.146}$$

$$\tag{6.147}$$

where H_0 is the non-interacting Hamiltonian and V is the interaction. We can also define a non-interacting Liouvillian $\mathcal{L}_0$ such that $\mathcal{L}_0 X = [H_0, X]$. So we can write

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