Contents

Patryk's Notes

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Chapter 1

G_0W_0 Derivations: 11/9

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 [5]. We want to solve for the self-energy whose form along the real axis is:

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

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:

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

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 $W_0=v+v\chi_0v+v\chi_0v\chi_0v+\cdots=v\left(1+\chi_0v+\chi_0v\chi_0v+\cdots\right)=v\left(1-\chi_0v\right)^{-1}$, where we recognize the dielectric function as $\epsilon_0=1-\chi_0v$ so we can express the screened Coulomb interaction as

$$W_0(\mathbf{r},\mathbf{r}',\omega)=\frac{v(\mathbf{r},\mathbf{r}')}{1-\left(\chi_0v\right)\left(\mathbf{r},\mathbf{r}',\omega\right)} \tag{1.44}$$

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 [3]. To simplify notation let us define a polarizability $\mathbf{\Pi}\left(\mathbf{r},\mathbf{r}',\omega\right)=\left(\chi_0v\right)\left(\mathbf{r},\mathbf{r}',\omega\right)$, 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:

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

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

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

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:

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

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 [4]:

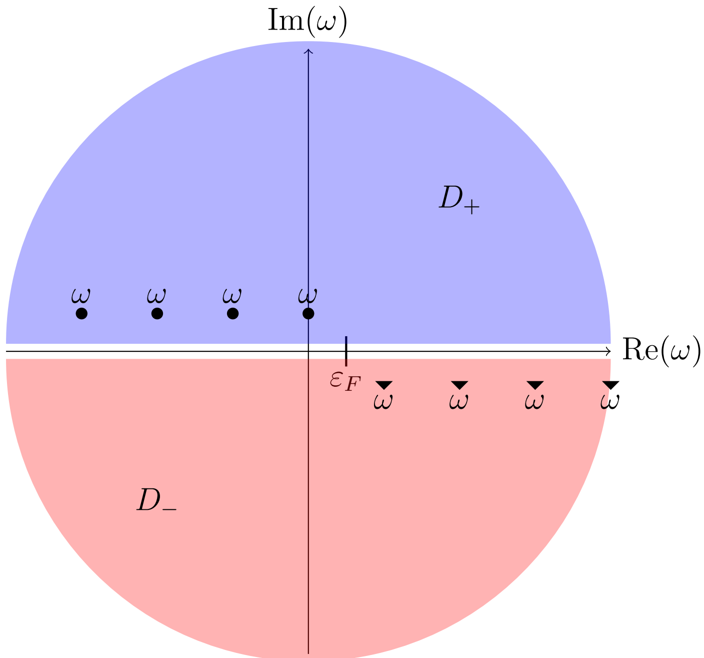

Figure 1.1: Contour for the complex frequency integral. The poles are denoted by the various ω. The Fermi energy is denoted by ε_F. The integration contour D_+ is the semicircle in the upper complex plane, while D_- is the semicircle in the lower complex plane.

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

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_{xc}^λ 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:

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

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

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

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:

$$\begin{aligned} W_0 &= v + v\chi_0 v + v\chi_0 v\chi_0 v + \cdots && (1.64)\\ &= v(1 + \chi_0 v + \chi_0 v \chi_0 v + \cdots) && (1.65)\\ &= v^{1/2}\,(1-\chi_0)^{-1}\, v^{1/2} && (1.66) \end{aligned}$$

simplifying to

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

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

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

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

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. $\Pi\left(\mathbf{q}, i\omega'\right)$ in Eq. 22 is an auxiliary density response function:

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

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.

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

to do so, one must understand the reformulation of based on the density matrix as for posed by Furche [1]. 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

$$\begin{aligned} G &= G_0 + G_0\Sigma G && (1.78) \\ \left(I - G_0\Sigma\right) G &= G_0 && (1.79) \\ G &= \left(I - G_0\Sigma\right)^{-1} G_0 && (1.80) \\ G &= \left(G_0\left(G_0^{-1} - \Sigma\right)\right)^{-1} G_0 && (1.81) \\ G &= \left(G_0^{-1} - \Sigma\right)^{-1} && (1.82) \end{aligned}$$

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

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

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,

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

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

$$\tag{1.96}$$

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 [2].

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 [5].

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 [5].

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

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

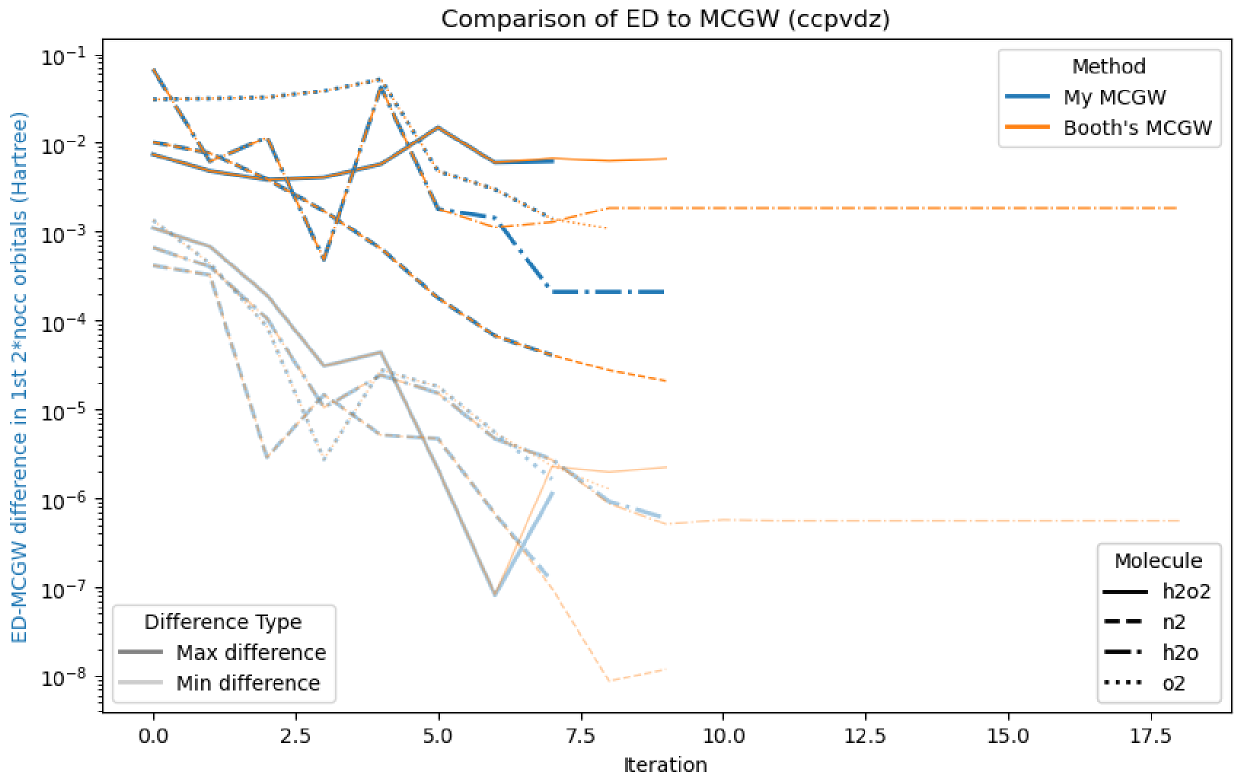

Figure 1.2: From the first $2N_{occ}$ orbitals, representing the space of interest, the maximum and minimum differences between the Ritz values and the exact eigenvalues are plotted as a function of the number of Lanczos iterations used. A cc-pvdz basis is used. An exact match between the blue (my implementation) 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 [**?**]. 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 [**?**]. 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 [**?**] is exploited in [**?**] 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 [**?**], 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 [**?**] 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

Moment-Conserving *GW*

2.1 Löwdin Downfolding: 2/2/2025

We know that the definition of a Green's function associated with some Hamiltonian $\boldsymbol{H}$ is given by:

$$(\omega - \boldsymbol{H})\,\boldsymbol{G} = \boldsymbol{I} \tag{2.1}$$

where we can consider both cases to be fully interacting. The downfolding tells us to separate into a system $\mathcal{S}$ and auxiliary space $\mathcal{L}$, so we have:

$$\left(\omega - \begin{pmatrix} \boldsymbol{H}_{\mathcal{SS}} & \boldsymbol{H}_{\mathcal{SL}} \\ \boldsymbol{H}_{\mathcal{LS}} & \boldsymbol{H}_{\mathcal{LL}} \end{pmatrix}\right) \begin{pmatrix} \boldsymbol{G}_{\mathcal{SS}} & \boldsymbol{G}_{\mathcal{SL}} \\ \boldsymbol{G}_{\mathcal{LS}} & \boldsymbol{G}_{\mathcal{LL}} \end{pmatrix} = \begin{pmatrix} \boldsymbol{I}_{\mathcal{SS}} & \boldsymbol{0} \\ \boldsymbol{0} & \boldsymbol{I}_{\mathcal{LL}} \end{pmatrix}.$$

or:

$$\begin{pmatrix} \omega - \boldsymbol{H}_{\mathcal{SS}} & -\boldsymbol{H}_{\mathcal{SL}} \\ -\boldsymbol{H}_{\mathcal{LS}} & \omega - \boldsymbol{H}_{\mathcal{LL}} \end{pmatrix} \begin{pmatrix} \boldsymbol{G}_{\mathcal{SS}} & \boldsymbol{G}_{\mathcal{SL}} \\ \boldsymbol{G}_{\mathcal{LS}} & \boldsymbol{G}_{\mathcal{LL}} \end{pmatrix} = \begin{pmatrix} \boldsymbol{I}_{\mathcal{SS}} & \boldsymbol{0} \\ \boldsymbol{0} & \boldsymbol{I}_{\mathcal{LL}} \end{pmatrix}.$$

Multiplying out the matrices, the $\mathcal{S}$ block gives:

$$(\omega - \boldsymbol{H}_{\mathcal{SS}})\,\boldsymbol{G}_{\mathcal{SS}} - \boldsymbol{H}_{\mathcal{SL}}\,\boldsymbol{G}_{\mathcal{LS}} = \boldsymbol{I}_{\mathcal{SS}}\,. \tag{2.2}$$

Similarly, the $\mathcal{L}$ block gives:

$$-\boldsymbol{H}_{\mathcal{LS}}\,\boldsymbol{G}_{\mathcal{SS}} + (\omega - \boldsymbol{H}_{\mathcal{LL}})\,\boldsymbol{G}_{\mathcal{LS}} = \boldsymbol{0}\,. \tag{2.3}$$

Assuming $(\omega - \boldsymbol{H}_{\mathcal{LL}})$ is invertible, from the second equation we obtain:

$$\boldsymbol{G}_{\mathcal{LS}} = (\omega - \boldsymbol{H}_{\mathcal{LL}})^{-1}\,\boldsymbol{H}_{\mathcal{LS}}\,\boldsymbol{G}_{\mathcal{SS}}\,.$$

Substituting this into the first equation:

$$(\omega - \boldsymbol{H}_{\mathcal{SS}})\,\boldsymbol{G}_{\mathcal{SS}} - \boldsymbol{H}_{\mathcal{SL}}\,(\omega - \boldsymbol{H}_{\mathcal{LL}})^{-1}\,\boldsymbol{H}_{\mathcal{LS}}\,\boldsymbol{G}_{\mathcal{SS}} = \boldsymbol{I}_{\mathcal{SS}}\,.$$

Factorizing $\boldsymbol{G}_{\mathcal{SS}}$:

$$\left[(\omega - \boldsymbol{H}_{\mathcal{SS}}) - \boldsymbol{H}_{\mathcal{SL}}\,(\omega - \boldsymbol{H}_{\mathcal{LL}})^{-1}\,\boldsymbol{H}_{\mathcal{LS}}\right]\,\boldsymbol{G}_{\mathcal{SS}} = \boldsymbol{I}_{\mathcal{SS}}\,.$$

Thus:

$$\boldsymbol{G}_{\mathcal{SS}} = \left[(\omega - \boldsymbol{H}_{\mathcal{SS}}) - \boldsymbol{H}_{\mathcal{SL}}\left(\omega - \boldsymbol{H}_{\mathcal{LL}}\right)^{-1}\boldsymbol{H}_{\mathcal{LS}}\right]^{-1}.$$

Now, notice that:

$$[\boldsymbol{G}^{0}_{\mathcal{SS}}(\omega)]^{-1} \equiv \omega - \boldsymbol{H}_{\mathcal{SS}} = \omega - (\boldsymbol{F} + \boldsymbol{\Sigma}(\infty)), \implies \boldsymbol{H}_{\mathcal{SS}} = \boldsymbol{F} + \boldsymbol{\Sigma}(\infty).$$

where $\boldsymbol{\Sigma}(\infty)$ is the static self-energy (0 for a HF mean-field reference), and $\boldsymbol{F}$ is the Fock matrix. Identifying the coupling matrices:

$$\boldsymbol{H}_{\mathcal{SL}} = \boldsymbol{W}, \quad \boldsymbol{H}_{\mathcal{LS}} = \boldsymbol{W}^{\dagger}.$$

and

$$\boldsymbol{H}_{\mathcal{LL}} = \boldsymbol{d},$$

Now let us make an ansatz for the upfolded Hamiltonian:

$$\boldsymbol{H}_{\text{Upfolded}} = \begin{pmatrix} \boldsymbol{F} + \boldsymbol{\Sigma}(\infty) & \boldsymbol{W} \\ \boldsymbol{W}^{\dagger} & \boldsymbol{d} \end{pmatrix}.$$

Then, the resolvent is given by:

$$(\omega - \boldsymbol{H}_{\text{Upfolded}}) = \begin{pmatrix} \omega - \boldsymbol{F} - \boldsymbol{\Sigma}(\infty) & -\boldsymbol{W} \\ -\boldsymbol{W}^{\dagger} & \omega - \boldsymbol{d} \end{pmatrix} \tag{2.4}$$

Because we are interested in $\boldsymbol{G}_{\mathcal{SS}}(\omega)$, we care about $(\omega - \boldsymbol{H}_{\text{Upfolded}})^{-1}$ in the upper left block, which is the Schur complement of $(\omega - \boldsymbol{H}_{\text{Upfolded}})$ with respect to $\omega - \boldsymbol{d}$, defined as:

$$\boldsymbol{G}_{\mathcal{SS}}(\omega) = \left(\frac{(\omega - \boldsymbol{H}_{\text{Upfolded}})}{\omega - \boldsymbol{d}}\right)^{-1}_{\mathcal{SS}} = \left(\omega - (\boldsymbol{F} + \boldsymbol{\Sigma}(\infty)) - \boldsymbol{W}\left[\omega - \boldsymbol{d}\right]^{-1}\boldsymbol{W}^{\dagger}\right)^{-1} \tag{2.5}$$

so the ansatz is correct.

2.2 Cumulant Idea

The definition of the cumulant ansatz for the Green's function is given by:

$$\boldsymbol{G}_{\mathcal{SS}}(t) = \boldsymbol{G}^{0}_{\mathcal{SS}}(t)e^{\boldsymbol{C}(t)} \tag{2.6}$$

where $\boldsymbol{C}(t)$ is the cumulant and $\boldsymbol{G}^{0}_{\mathcal{SS}}(t)$ is the HF Green's function. By relating the Dyson equation to the Taylor series expansion of the exponential, we can write:

$$\boldsymbol{G}^{0}_{\mathcal{SS}}(t)\boldsymbol{C}(t) = \iint \mathrm{d}t_1\mathrm{d}t_2\boldsymbol{G}^{0}_{\mathcal{SS}}(t-t_1)\boldsymbol{\Sigma}^{c}(t_1-t_2)\boldsymbol{G}^{0}_{\mathcal{SS}}(t_2) \tag{2.7}$$

Projecting to the spin-orbital basis and inserting the resolution of the identity, we get:

$$\sum_r \langle p| \boldsymbol{G}^0_{\mathcal{SS}}(t) |r\rangle \langle r| \boldsymbol{C}(t) |q\rangle = \sum_{rs} \iint \mathrm{d}t_1 \mathrm{d}t_2 \langle p| \boldsymbol{G}^0_{\mathcal{SS}}(t-t_1) |r\rangle \langle r| \boldsymbol{\Sigma}^c(t_1-t_2) |s\rangle \langle s| \boldsymbol{G}^0_{\mathcal{SS}}(t_2) |q\rangle \tag{2.8}$$

$$\sum_r \boldsymbol{G}^0_{pr}(t)\boldsymbol{C}_{rq}(t) = \sum_{rs} \iint \mathrm{d}t_1 \mathrm{d}t_2 \boldsymbol{G}^0_{ps}(t-t_1)\boldsymbol{\Sigma}^c_{sr}(t_1-t_2)\boldsymbol{G}^0_{rq}(t_2) \tag{2.9}$$

$$\boldsymbol{G}^0_{pp}(t)\boldsymbol{C}_{pq}(t) = \underbrace{\iint \mathrm{d}t_1 \mathrm{d}t_2 \boldsymbol{G}^0_{pp}(t-t_1)\boldsymbol{\Sigma}^c_{pq}(t_1-t_2)\boldsymbol{G}^0_{qq}(t_2)}_{*} \tag{2.10}$$

where $\boldsymbol{G}^0_{\mathcal{SS}}(t) \equiv \boldsymbol{G}^0(t)$ and in the last step we used the fact that the HF Green's function is diagonal in the spin-orbital basis, specifically $\boldsymbol{G}^0_{pp}(t) = -i\Theta(t)e^{-i\epsilon_p t}$, where ϵ_p is the HF energy of the p-th spin-orbital. The formula for the inverse Fourier transform is given by:

$$f(t) = \int \frac{\mathrm{d}\omega}{2\pi} e^{-i\omega t} f(\omega) \tag{2.11}$$

which implies that

$$\boldsymbol{G}^0_{pp}(t-t_1) = \int \frac{\mathrm{d}\omega}{2\pi} e^{-i\omega(t-t_1)} \boldsymbol{G}^0_{pp}(\omega) \tag{2.12}$$

$$\boldsymbol{\Sigma}^c_{pq}(t_1-t_2) = \int \frac{\mathrm{d}\omega'}{2\pi} e^{-i\omega'(t_1-t_2)} \boldsymbol{\Sigma}^c_{pq}(\omega') \tag{2.13}$$

$$\boldsymbol{G}^0_{qq}(t_2) = \int \frac{\mathrm{d}\omega''}{2\pi} e^{-i\omega'' t_2} \boldsymbol{G}^0_{qq}(\omega'') \tag{2.14}$$

and plugging into the double time integral *, we get:

$$* = \iint \mathrm{d}t_1 \mathrm{d}t_2 \left[\int \frac{\mathrm{d}\omega}{2\pi} e^{-i\omega(t-t_1)} \boldsymbol{G}^0_{pp}(\omega)\right] \left[\int \frac{\mathrm{d}\omega'}{2\pi} e^{-i\omega'(t_1-t_2)} \boldsymbol{\Sigma}^c_{pq}(\omega')\right] \left[\int \frac{\mathrm{d}\omega''}{2\pi} e^{-i\omega'' t_2} \boldsymbol{G}^0_{qq}(\omega'')\right] \tag{2.15}$$

$$= \underbrace{\int \mathrm{d}t_1 e^{-i(\omega'-\omega)t_1} \int \mathrm{d}t_2 e^{-i(\omega''-\omega')t_2}}_{4\pi^2\delta(\omega'-\omega)\delta(\omega''-\omega')} \iiint \mathrm{d}\omega \mathrm{d}\omega' \mathrm{d}\omega'' \frac{e^{-i\omega t}}{8\pi^3} \boldsymbol{G}^0_{pp}(\omega)\boldsymbol{\Sigma}^c_{pq}(\omega')\boldsymbol{G}^0_{qq}(\omega'') \tag{2.16}$$

$$= \int \frac{\mathrm{d}\omega}{2\pi} e^{-i\omega t} \boldsymbol{G}^0_{pp}(\omega)\boldsymbol{\Sigma}^c_{pq}(\omega)\boldsymbol{G}^0_{qq}(\omega) \tag{2.17}$$

But now note that from the left hand side of eqn. 5.36, we can divide out the HF Green's function to get:

$$\boldsymbol{C}_{pq}(t) = i \int \frac{\mathrm{d}\omega}{2\pi} e^{-i(\omega-\epsilon_p)t} \boldsymbol{G}^0_{pp}(\omega)\boldsymbol{\Sigma}^c_{pq}(\omega)\boldsymbol{G}^0_{qq}(\omega) \tag{2.18}$$

Now, we insert the upfolded form for the self-energy, which is frequency independent as $\boldsymbol{\Sigma}^c_{pq}(\omega) \equiv \boldsymbol{\Sigma}^c_{pq} = \begin{pmatrix} \boldsymbol{\Sigma}(\infty) & \boldsymbol{W}^< & \boldsymbol{W}^> \\ \boldsymbol{W}^{\dagger<} & \boldsymbol{d}^< & \boldsymbol{0} \\ \boldsymbol{W}^{\dagger>} & \boldsymbol{0} & \boldsymbol{d}^> \end{pmatrix}_{pq}$. *Customarily this is the point where the diagonal* *approximation for the self-energy is introduced instead.* We also know that $\boldsymbol{G}^0_{pp}(\omega) = \frac{\boldsymbol{I}}{\omega - \epsilon_p}$. We can then write:

$$\boldsymbol{C}_{pq}(t) = i\boldsymbol{\Sigma}^c_{pq} \int \frac{\mathrm{d}\omega}{2\pi} \frac{e^{-i(\omega-\epsilon_p)t}}{(\omega - \epsilon_p)(\omega - \epsilon_q)} \tag{2.19}$$

$$= i\frac{\boldsymbol{\Sigma}^c_{pq}}{\epsilon_q - \epsilon_p} \left[\underbrace{\int \frac{\mathrm{d}\omega}{2\pi} \frac{e^{-i(\omega-\epsilon_p)t}}{\omega - \epsilon_p}}_{-i\Theta(t)} - \underbrace{\int \frac{\mathrm{d}\omega}{2\pi} \frac{e^{-i(\omega-\epsilon_q)t}}{\omega - \epsilon_q}}_{e^{-i(\epsilon_q-\epsilon_p)t}(-i\Theta(t))} \right] \tag{2.20}$$

$$= \frac{\boldsymbol{\Sigma}^c_{pq}}{\epsilon_q - \epsilon_p} \Theta(t) \left[1 - e^{-i(\epsilon_q-\epsilon_p)t}\right] \tag{2.21}$$

$$\tag{2.22}$$

So now we insert this expression into our original ansatz for the cumulant, and we get:

$$G(t) = G^0(t) e^{\frac{\boldsymbol{\Sigma}^c_{pq}}{\epsilon_q - \epsilon_p}\Theta(t)\left[1 - e^{-i(\epsilon_q-\epsilon_p)t}\right]} \tag{2.23}$$

2.3 Lanczos Iteration

The block tridiagonal form can be expressed as:

$$\tilde{\mathbf{H}}_{\text{tri}} = \tilde{\mathbf{q}}^{(j),\dagger} \begin{bmatrix} \mathbf{f} + \boldsymbol{\Sigma}_\infty & \mathbf{W} \\ \mathbf{W}^\dagger & \mathbf{d} \end{bmatrix} \tilde{\mathbf{q}}^{(j)} \tag{2.24}$$

$$= \begin{bmatrix} \mathbf{f} + \boldsymbol{\Sigma}_\infty & \mathbf{L} & & & & \mathbf{0} \\ \mathbf{L}^\dagger & \mathbf{H}_1 & \mathbf{C}_1 & & & \\ & \mathbf{C}_1^\dagger & \mathbf{H}_2 & \mathbf{C}_2 & & \\ & & \mathbf{C}_2^\dagger & \mathbf{H}_3 & \ddots & \\ & & & \ddots & \ddots & \mathbf{C}_{j-1} \\ \mathbf{0} & & & & \mathbf{C}_{j-1}^\dagger & \mathbf{H}_j \end{bmatrix} \tag{2.25}$$

where we define $\tilde{\mathbf{q}}^{(j)}$ as

$$\tilde{\mathbf{q}}^{(j)} = \begin{bmatrix} \mathbf{I} & \mathbf{0} \\ \mathbf{0} & \mathbf{q}^{(j)} \end{bmatrix} \tag{2.26}$$

This formulation becomes exact when the level j equals N, the dimension of the original hamiltonian; this corresponds to considering up to the highest moment of the self-energy, i.e. n france from $1, \ldots, N$. in practice, however, we always truncate the Krylov subspace to some $j < N$. Note that the tridiagonal form never actually forces us to compute $\mathbf{W}$ or $\mathbf{d}$, as desired.

2.3.1 Creation of Krylov Subspace

Formally, the Krylov subspace of level j is given as $\mathbf{q}^{(j)} = [\mathbf{q}_1, \mathbf{q}_2, \cdots, \mathbf{q}_j]$, where the projection of the full Hamiltonian onto this subspace gives the tridiagonal form of equation 2.25. To start building up the subspace, we need to determine $\mathbf{q}_1$ via QR decomposition of the exact GW couplings as $\mathbf{W}^\dagger = \mathbf{q}_1\mathbf{L}^\dagger \to \mathbf{q}_1 = \mathbf{W}^\dagger\mathbf{L}^{\dagger,-1}$. $\mathbf{L}$ is defined in terms of just the 0th order self-energy moment as $\mathbf{L}^\dagger = \left(\mathbf{\Sigma}^{(0)}\right)^{\frac{1}{2}}$. We build up the subsequent q_i vectors through a three-term recurrence

$$\mathbf{q}_{i+1}\mathbf{C}_i^\dagger = \left[\mathbf{d}\mathbf{q}_i - \mathbf{q}_i\mathbf{H}_i - \mathbf{q}_{i-1}\mathbf{C}_{i-1}\right], \tag{2.27}$$

where the on-diagonal blocks are defined as

$$\mathbf{H}_i = \mathbf{q}_i^\dagger\mathbf{d}\mathbf{q}_i \tag{2.28}$$

Notice that to form the initial vector $\mathbf{q}_1$ we would need $\mathbf{W}^\dagger$ and to continue building the subspace, we would need $\mathbf{d}$, so to avoid this, we introduce the self-energy moments.

2.3.2 A sketch of the implicit Lanczos method

Due to Garnet's paper on the quasi-boson G_0W_0 method, we know that we have a form for an upfolded G_0W_0 Hamiltonian as

$$\boldsymbol{H}^{G_0W_0}_{\text{Upfolded}} = \begin{pmatrix} \boldsymbol{F} + \boldsymbol{\Sigma}(\infty) & \boldsymbol{W}^< & \boldsymbol{W}^> \\ \boldsymbol{W}^{<,\dagger} & \boldsymbol{d}^< & 0 \\ \boldsymbol{W}^{>,\dagger} & 0 & \boldsymbol{d}^> \end{pmatrix} \tag{2.29}$$

with quantities defined separately for lesser and greater parts. But we will just focus on the lesser part for now, where matrix elements of the screened interaction $\boldsymbol{W}^<$ are given by

$$W^<_{pkv} = \sum_{ia}(pk|ia)\left(X^v_{ia} + Y^v_{ia}\right) \tag{2.30}$$

and

$$d^<_{kv,lv'} = \left(\epsilon_k - \Omega_v\right)\delta_{k,l}\delta_{v,v'} \tag{2.31}$$

Note that we get the factor of $\sqrt{2}$ accompanying all ERIs in RHF because we are considering the expectation value of the form

$$\frac{1}{2}\sum_{pqrs}\langle pq||rs\rangle \langle\Psi_0| \left(\hat{T}_i^{a,\alpha} + \hat{T}_i^{a,\beta}\right)^\dagger \left(a_p^\dagger a_q^\dagger a_s a_r \left(\hat{T}_i^{a,\alpha} + \hat{T}_i^{a,\beta}\right)\right)|\Psi_0\rangle \tag{2.32}$$

where we have the excitation operator for a given spin channel as $\hat{T}_i^{a,\sigma} = a_a^{\dagger,\sigma}a_i^\sigma$ and a singlet state for the RHF ground state carrying a factor of $\frac{1}{\sqrt{2}}$. If we apply Wick's theorem to this string, we get a contribution from both the α and β channels, so $\frac{1}{\sqrt{2}} + \frac{1}{\sqrt{2}} = \sqrt{2}$.
Through the introduction of a Krylov subspace as

$$\tilde{\boldsymbol{H}}^{G_0W_0}_{\text{Upfolded}} = \tilde{\boldsymbol{Q}}^{(n,\dagger)}\boldsymbol{H}^{G_0W_0}_{\text{Upfolded}}\tilde{\boldsymbol{Q}}^{(n)} \tag{2.33}$$

where $\boldsymbol{Q}^{(n)} \equiv \begin{pmatrix} \boldsymbol{q}_1 & \boldsymbol{q}_2 & \cdots & \boldsymbol{q}_n \end{pmatrix}$ is the block Krylov subspace spanned by the Lanczos vectors, but we want to preserve the physical space of $\boldsymbol{F} + \boldsymbol{\Sigma}(\infty)$ so we are really interested in the projection matrix

$$\tilde{\boldsymbol{Q}}^{(n)} = \begin{pmatrix} \boldsymbol{I} & \boldsymbol{0} \\ \boldsymbol{0} & \boldsymbol{Q}^{(n)} \end{pmatrix} \tag{2.34}$$

To get a gist of what the block Lanczos will do, let's just consider the case where we have two Lanczos vectors, so that we have a projection matrix of the form

$$\tilde{\boldsymbol{Q}}^{(2)} = \begin{pmatrix} \boldsymbol{I} & \boldsymbol{0} \\ \boldsymbol{0} & \boldsymbol{Q}^{(2)} \end{pmatrix} \tag{2.35}$$

So

$$\begin{aligned}
\tilde{\boldsymbol{H}}^{\text{Lanczos Iter 2}}_{\text{upfolded}} &= \tilde{\boldsymbol{Q}}^{(2,\dagger)} \boldsymbol{H}^{G_0W_0}_{\text{Upfolded}} \tilde{\boldsymbol{Q}}^{(2)} && (2.36)\\
&= \begin{pmatrix} \boldsymbol{I} & \boldsymbol{0} \\ \boldsymbol{0} & \boldsymbol{Q}^{(2)\dagger} \end{pmatrix} \begin{pmatrix} \boldsymbol{F} + \boldsymbol{\Sigma}(\infty) & \boldsymbol{W} \\ \boldsymbol{W}^\dagger & \boldsymbol{d} \end{pmatrix} \begin{pmatrix} \boldsymbol{I} & \boldsymbol{0} \\ \boldsymbol{0} & \boldsymbol{Q}^{(2)} \end{pmatrix} && (2.37)\\
&= \begin{pmatrix} \boldsymbol{I} & \boldsymbol{0} \\ \boldsymbol{0} & [\boldsymbol{q}_1^\dagger \quad \boldsymbol{q}_2^\dagger] \end{pmatrix} \begin{pmatrix} \boldsymbol{F} + \boldsymbol{\Sigma}(\infty) & \boldsymbol{W} \\ \boldsymbol{W}^\dagger & \boldsymbol{d} \end{pmatrix} \begin{pmatrix} \boldsymbol{I} & \boldsymbol{0} \\ \boldsymbol{0} & [\boldsymbol{q}_1 \quad \boldsymbol{q}_2] \end{pmatrix} && (2.38)\\
&= \begin{pmatrix} \boldsymbol{F} + \boldsymbol{\Sigma}(\infty) & \boldsymbol{W} \\ [\boldsymbol{q}_1^\dagger \quad \boldsymbol{q}_2^\dagger]\boldsymbol{W}^\dagger & [\boldsymbol{q}_1^\dagger \quad \boldsymbol{q}_2^\dagger]\boldsymbol{d} \end{pmatrix} \begin{pmatrix} \boldsymbol{I} & \boldsymbol{0} \\ \boldsymbol{0} & [\boldsymbol{q}_1 \quad \boldsymbol{q}_2] \end{pmatrix} && (2.39)\\
&= \begin{pmatrix} \boldsymbol{F} + \boldsymbol{\Sigma}(\infty) & [\underbrace{\boldsymbol{W}\boldsymbol{q}_1}_{\boldsymbol{\mathcal{R}}\boldsymbol{\mathcal{Q}}^\dagger\boldsymbol{\mathcal{Q}} = \boldsymbol{\mathcal{R}}} \quad \underbrace{\boldsymbol{W}\boldsymbol{q}_2}_{\boldsymbol{0}}] \\ [\underbrace{\boldsymbol{q}_1^\dagger\boldsymbol{W}^\dagger}_{\boldsymbol{\mathcal{Q}}^\dagger\boldsymbol{\mathcal{Q}}\boldsymbol{\mathcal{R}}^\dagger = \boldsymbol{\mathcal{R}}^\dagger} \quad \underbrace{\boldsymbol{q}_2^\dagger\boldsymbol{W}^\dagger}_{\boldsymbol{0}}] & \begin{pmatrix} \underbrace{\boldsymbol{q}_1^\dagger\boldsymbol{d}\boldsymbol{q}_1}_{\boldsymbol{M}_1} & \underbrace{\boldsymbol{q}_1^\dagger\boldsymbol{d}\boldsymbol{q}_2}_{\boldsymbol{C}_1} \\ \underbrace{\boldsymbol{q}_2^\dagger\boldsymbol{d}\boldsymbol{q}_1}_{\boldsymbol{C}_1^\dagger} & \underbrace{\boldsymbol{q}_2^\dagger\boldsymbol{d}\boldsymbol{q}_2}_{\boldsymbol{M}_2} \end{pmatrix} \end{pmatrix} && (2.40)
\end{aligned}$$

where in the last line we used the fact that we are free to choose our $\boldsymbol{q}_1 \equiv \boldsymbol{\mathcal{Q}}$ as the same orthogonal matrix employed in constructing the QR decomposition of $\boldsymbol{W}^\dagger$ as

$$\boldsymbol{W}^\dagger = \boldsymbol{\mathcal{Q}}\boldsymbol{\mathcal{R}}^\dagger \implies \boldsymbol{q}_1 = \boldsymbol{W}^\dagger\boldsymbol{\mathcal{R}}^{-1,\dagger} \tag{2.41}$$

2.3.3 Physical-auxiliary coupling W

Now consider $\boldsymbol{W}\boldsymbol{W}^\dagger = \boldsymbol{\mathcal{R}}\boldsymbol{\mathcal{Q}}\boldsymbol{\mathcal{Q}}^\dagger\boldsymbol{\mathcal{R}}^\dagger = \boldsymbol{\mathcal{R}}\boldsymbol{\mathcal{R}}^\dagger$. So if we can do a Cholesky decomposition of $\boldsymbol{W}\boldsymbol{W}^\dagger$ we would get access to $\boldsymbol{\mathcal{R}}$. But consider that

$$\Sigma^{(n,<)}_{pq} = \sum_{ia,jb,k} \sum_{\mu} (pk|ia) \left(X^\mu_{ia} + Y^\mu_{ia}\right) \left(X^\mu_{jb} + Y^\mu_{jb}\right) (qk|jb) [(\epsilon_k - \Omega_\mu)]^n \tag{2.42}$$

so it becomes clear that $\boldsymbol{W}\boldsymbol{W}^\dagger = \boldsymbol{\Sigma}^0 \implies \boldsymbol{\mathcal{R}} = \left(\boldsymbol{W}\boldsymbol{W}^\dagger\right)^{1/2} = \left(\boldsymbol{\Sigma}^0\right)^{1/2}$, which we hope to be able to accomplish with the Cholesky decomposition.

2.3.4 Auxiliary-auxiliary space d: the working equations

From above, notice that

$$\boldsymbol{M}_i = \boldsymbol{q}_i^\dagger \boldsymbol{d} \boldsymbol{q}_i \quad \text{and} \quad \boldsymbol{C}_i = \boldsymbol{q}_i^\dagger \boldsymbol{d} \boldsymbol{q}_{i+1} \tag{2.43}$$

To get these, define

$$\boldsymbol{S}_{i,j}^{(n)} = \boldsymbol{q}_i^\dagger \boldsymbol{d}^n \boldsymbol{q}_j \tag{2.44}$$

So it must be that $\boldsymbol{S}_{0,j}^{(n)} = \boldsymbol{S}_{i,0}^{(n)} = 0$ for all i, j, $\boldsymbol{S}_{i,j}^{(0)} = \delta_{ij}\boldsymbol{I}$, and we can demand Hermiticity, so that $\boldsymbol{S}_{i,j}^{(n)} = \boldsymbol{S}_{j,i}^{(n)\dagger}$. We are able to initialize $\boldsymbol{S}$ using

$$\boldsymbol{S}_{1,1}^{(n)} = \boldsymbol{q}_1^\dagger \boldsymbol{d}^n \boldsymbol{q}_1 = \boldsymbol{R}^{-1}\boldsymbol{W}\boldsymbol{d}^n\boldsymbol{W}^\dagger\boldsymbol{R}^{-1,\dagger} = \boldsymbol{R}^{-1}\boldsymbol{\Sigma}^{(n)}\boldsymbol{R}^{-1,\dagger} \tag{2.45}$$

So looking at eqn. 2.117, we see that the on-diagonal elements are $\boldsymbol{M}_i = \boldsymbol{S}_{i,i}^{(1)}$ while the off-diagonal elements are $\boldsymbol{C}_i = \boldsymbol{S}_{i,i+1}^{(1)}$. The familiar three-term Lanczos recurrence is

$$\mathbf{q}_{i+1}\mathbf{C}_i^\dagger = [\mathbf{d}\mathbf{q}_i - \mathbf{q}_i\mathbf{M}_i - \mathbf{q}_{i-1}\mathbf{C}_{i-1}] \implies \mathbf{q}_{i+1} = [\mathbf{d}\mathbf{q}_i - \mathbf{q}_i\mathbf{M}_i - \mathbf{q}_{i-1}\mathbf{C}_{i-1}]\,\boldsymbol{C}_i^{\dagger,-1} \tag{2.46}$$

where the participants are block vectors and we have assumed that $\boldsymbol{C}_i$ is invertible. Let us start by considering the form of

$$\begin{aligned}
\boldsymbol{S}_{i+1,i}^{n} \equiv \boldsymbol{q}_{i+1}^\dagger \boldsymbol{d}^n \boldsymbol{q}_i &= \left[[\mathbf{d}\mathbf{q}_i - \mathbf{q}_i\mathbf{M}_i - \mathbf{q}_{i-1}\mathbf{C}_{i-1}]\,\boldsymbol{C}_i^{\dagger,-1}\right]^\dagger \boldsymbol{d}^n \boldsymbol{q}_i && (2.47)\\
&= \boldsymbol{C}_i^{-1}\left[\underbrace{\boldsymbol{q}_i^\dagger \boldsymbol{d}^{n+1}\boldsymbol{q}_i}_{\boldsymbol{S}_{i,i}^{n+1}} - \boldsymbol{M}_i \underbrace{\boldsymbol{q}_i^\dagger \boldsymbol{d}^n \boldsymbol{q}_i}_{\boldsymbol{S}_{i,i}^{n}} - \boldsymbol{C}_{i-1}^\dagger \underbrace{\boldsymbol{q}_{i-1}^\dagger \boldsymbol{d}^n \boldsymbol{q}_i}_{\boldsymbol{S}_{i-1,i}^{n}}\right] && (2.48)\\
&= \boxed{\boldsymbol{C}_i^{-1}\left[\boldsymbol{S}_{i,i}^{n+1} - \boldsymbol{M}_i\boldsymbol{S}_{i,i}^{n} - \boldsymbol{C}_{i-1}^\dagger\boldsymbol{S}_{i-1,i}^{n}\right]} && (2.49)
\end{aligned}$$

Similarly

$$\boldsymbol{S}_{i+1,i+1}^{n} \equiv \boldsymbol{q}_{i+1}^\dagger \boldsymbol{d}^n \boldsymbol{q}_{i+1} = \left[[\mathbf{d}\mathbf{q}_i - \mathbf{q}_i\mathbf{M}_i - \mathbf{q}_{i-1}\mathbf{C}_{i-1}]\,\boldsymbol{C}_i^{\dagger,-1}\right]^\dagger \boldsymbol{d}^n\,[\mathbf{d}\mathbf{q}_i - \mathbf{q}_i\mathbf{M}_i - \mathbf{q}_{i-1}\mathbf{C}_{i-1}]\,\boldsymbol{C}_i^{\dagger,-1} \tag{2.50}$$

$$\tag{2.51}$$

$$
\begin{aligned}
\boldsymbol{S}^{n}_{i+1,i+1} = \boldsymbol{C}_i^{-1} \Big[& \boldsymbol{S}^{n+2}_{i,i} + \boldsymbol{M}_i \boldsymbol{S}^{n}_{i,i} \boldsymbol{M}_i + \boldsymbol{C}^{\dagger}_{i-1} \boldsymbol{S}^{n}_{i-1,i-1} \boldsymbol{C}_{i-1} \\
& - \underbrace{\boldsymbol{q}_i^{\dagger} \boldsymbol{d}^{n+1} \boldsymbol{q}_i}_{\boldsymbol{S}^{n+1}_{i,i}} \boldsymbol{M}_i - \boldsymbol{M}_i \underbrace{\boldsymbol{q}_i^{\dagger} \boldsymbol{d}^{n+1} \boldsymbol{q}_i}_{\boldsymbol{S}^{n+1}_{i,i}} \\
& - \underbrace{\boldsymbol{q}_i^{\dagger} \boldsymbol{d}^{n+1} \boldsymbol{q}_{i-1}}_{\boldsymbol{S}^{n+1}_{i,i-1}} \boldsymbol{C}_{i-1} - \boldsymbol{C}^{\dagger}_{i-1} \underbrace{\boldsymbol{q}_{i-1}^{\dagger} \boldsymbol{d}^{n+1} \boldsymbol{q}_i}_{\boldsymbol{S}^{n+1}_{i-1,i}} \\
& + \boldsymbol{M}_i \underbrace{\boldsymbol{q}_i^{\dagger} \boldsymbol{d}^{n} \boldsymbol{q}_{i-1}}_{\boldsymbol{S}^{n}_{i,i-1}} \boldsymbol{C}_{i-1} + \boldsymbol{C}^{\dagger}_{i-1} \underbrace{\boldsymbol{q}_{i-1}^{\dagger} \boldsymbol{d}^{n} \boldsymbol{q}_i}_{\boldsymbol{S}^{n}_{i-1,i}} \boldsymbol{M}_i \Big] \boldsymbol{C}_i^{\dagger,-1}
\end{aligned} \tag{2.52}
$$

$$
\begin{aligned}
= \boldsymbol{C}_i^{-1} \Big[& \boldsymbol{S}^{n+2}_{i,i} + \boldsymbol{M}_i \boldsymbol{S}^{n}_{i,i} \boldsymbol{M}_i + \boldsymbol{C}^{\dagger}_{i-1} \boldsymbol{S}^{n}_{i-1,i-1} \boldsymbol{C}_{i-1} \\
& - P(\boldsymbol{S}^{n+1}_{i,i} \boldsymbol{M}_i) - P(\boldsymbol{S}^{n+1}_{i,i-1} \boldsymbol{C}_{i-1}) + P(\boldsymbol{M}_i \boldsymbol{S}^{n}_{i,i-1} \boldsymbol{C}_{i-1}) \Big] \boldsymbol{C}_i^{\dagger,-1}
\end{aligned} \tag{2.53}
$$

where we introduced the permutation operator as $P(\boldsymbol{A}) = \boldsymbol{A} + \boldsymbol{A}^{\dagger}$. Setting $n = 0$ we get

$$
\boldsymbol{I} = \boldsymbol{C}_i^{-1} \left[\boldsymbol{S}^{2}_{i,i} + \boldsymbol{M}_i^2 + \boldsymbol{C}^{\dagger}_{i-1} \boldsymbol{C}_{i-1} - P\left(\boldsymbol{M}_i^2\right) - P\left(\boldsymbol{S}^{1}_{i,i-1} \boldsymbol{C}_{i-1}\right) + 0 \right] \boldsymbol{C}_i^{\dagger,-1} \tag{2.54}
$$

$$
\implies \boldsymbol{C}_i^2 = \boldsymbol{C}_i \boldsymbol{C}_i^{\dagger} = \boxed{\boldsymbol{S}^{2}_{i,i} + \boldsymbol{M}_i^2 + \boldsymbol{C}^{\dagger}_{i-1} \boldsymbol{C}_{i-1} - P\left(\boldsymbol{S}^{1}_{i,i} \boldsymbol{M}_i\right) - P\left(\boldsymbol{S}^{1}_{i,i-1} \boldsymbol{C}_{i-1}\right)} \tag{2.55}
$$

$$
\implies \boldsymbol{C}_i \boldsymbol{C}_i^{\dagger} \equiv \boldsymbol{q}_i^{\dagger} \boldsymbol{d} \boldsymbol{q}_{i+1} \boldsymbol{q}_{i+1}^{\dagger} \boldsymbol{d} \boldsymbol{q}_i = \boldsymbol{q}_i^{\dagger} \boldsymbol{d}^2 \boldsymbol{q}_i \tag{2.56}
$$

The hope is that we can use the Cholesky QR algorithm to take the effective matrix square root to get the $\boldsymbol{C}_i$.

2.4 Efficient generation of the self-energy moments

Since the self-energy is defined as a convolution between the interacting Green's function and the screened Coulomb potential in GW we can use the known formula for the moment distribution of a convolution of two quantities to get

$$
\Sigma^{(n,<)}_{pq} = \sum_{ia,jb,k} \sum_{t=0}^{n} \binom{n}{t} (-1)^t \epsilon_k^{n-t} (pk \mid ia) \eta^{(t)}_{ia,jb} (qk \mid jb), \tag{2.57}
$$

where we have defined the density-density response moment as

$$
\eta^{(n)}_{ia,jb} = \sum_{v} \left(X^v_{ia} + Y^v_{ia}\right) \Omega_v^n \left(X^v_{jb} + Y^v_{jb}\right) \tag{2.58}
$$

2.4.1 An alternative formulation of the RPA polarizability with the density response moments

The Casida equation is given by

$$
\begin{pmatrix} \boldsymbol{A} & \boldsymbol{B} \\ -\boldsymbol{B} & -\boldsymbol{A} \end{pmatrix} \begin{pmatrix} \boldsymbol{X} & \boldsymbol{Y} \\ \boldsymbol{Y} & \boldsymbol{X} \end{pmatrix} \begin{pmatrix} \boldsymbol{\Omega} & \boldsymbol{0} \\ \boldsymbol{0} & -\boldsymbol{\Omega} \end{pmatrix} = \begin{pmatrix} \boldsymbol{X} & \boldsymbol{Y} \\ \boldsymbol{Y} & \boldsymbol{X} \end{pmatrix} \tag{2.59}
$$

where the excitation $\boldsymbol{X}$ and de-excitation $\boldsymbol{Y}$ eigenvectors form the biorthogonal set as

$$(\boldsymbol{X}+\boldsymbol{Y})(\boldsymbol{X}-\boldsymbol{Y})^T = (\boldsymbol{X}+\boldsymbol{Y})^T(\boldsymbol{X}-\boldsymbol{Y}) = \boldsymbol{I} \tag{2.60}$$

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

$$A_{ia,jb} = (\epsilon_a - \epsilon_i)\,\delta_{ij}\delta_{ab} + \mathcal{K}_{ia,bj} \tag{2.61}$$
$$B_{ia,jb} = \mathcal{K}_{ia,jb} \tag{2.62}$$

and I take the direct approximation, so $\mathcal{K}_{ia,jb} = (ia \mid jb) = \mathcal{K}_{ia,bj}$. As I showed earlier this year, these neutral excitation energies $\boldsymbol{\Omega}$ define the poles of the polarizability $\chi_{\text{RPA}}(\omega)$ as

$$\chi_{\text{RPA}}(\omega) = \begin{bmatrix} \boldsymbol{X} & \boldsymbol{Y} \\ \boldsymbol{Y} & \boldsymbol{X} \end{bmatrix} \begin{bmatrix} \omega\boldsymbol{I}-\boldsymbol{\Omega} & \boldsymbol{0} \\ \boldsymbol{0} & -\omega\boldsymbol{I}-\boldsymbol{\Omega} \end{bmatrix}^{-1} \begin{bmatrix} \boldsymbol{X} & \boldsymbol{Y} \\ \boldsymbol{Y} & \boldsymbol{X} \end{bmatrix}^T. \tag{2.63}$$

where $\chi_{\text{RPA}}(\omega) = \left(\chi_0(\omega)^{-1} - \mathcal{K}\right)^{-1}$, where $\chi_0(\omega)$ is the irreducible polarizability of the reference state. Because of the bosonic-like symmetry in equation 2.63, we can write a more compact form of the RPA polarizability as

$$\eta(\omega) = (\mathbf{X}+\mathbf{Y})(\omega\mathbf{I}-\boldsymbol{\Omega})^{-1}(\mathbf{X}+\mathbf{Y})^T. \tag{2.64}$$

However, here we are interested in the spectral moments of the compactified RPA polarizability in equation 2.64 over all RPA excitation energies, which is given as

$$\eta^{(n)}_{ia,jb} = -\frac{1}{\pi}\int_0^\infty \text{Im}\left[\eta_{ia,jb}(\omega)\right]\omega^n d\omega = -\frac{1}{\pi}\left(\boldsymbol{X}+\boldsymbol{Y}\right)\left[\int_0^\infty \text{Im}\left[(\omega\mathbf{I}-\boldsymbol{\Omega})^{-1}\right]\omega^n d\omega\right]\left(\boldsymbol{X}+\boldsymbol{Y}\right)^T. \tag{2.65}$$

where in the final equality we have just factored out the frequency independent piece. Now, we can use the identity from complex analysis that $\frac{1}{-\boldsymbol{\Omega}+\boldsymbol{I}(\omega+i\eta)} = P\left(\frac{1}{\omega\boldsymbol{I}-\boldsymbol{\Omega}}\right) - i\pi\delta(\omega-\boldsymbol{\Omega}) \implies \text{Im}\left[\frac{1}{-\boldsymbol{\Omega}+\boldsymbol{I}(\omega+i\eta)}\right] = -\pi\delta(\omega-\boldsymbol{\Omega})$, where P is the Cauchy principal value, so

$$\int_0^\infty \text{Im}\left[(\omega\mathbf{I}-\boldsymbol{\Omega})^{-1}\right]\omega^n d\omega = -\pi\int_0^\infty \delta(\omega-\boldsymbol{\Omega})\omega^n d\omega = -\pi\boldsymbol{\Omega}^n. \tag{2.66}$$

and plugging back and, we get $\boldsymbol{\eta}^{(n)} = \left(\boldsymbol{X}+\boldsymbol{Y}\right)\left(\boldsymbol{\Omega}^n\right)\left(\boldsymbol{X}+\boldsymbol{Y}\right)^T$.

2.4.2 Getting η with lower scaling

Now we will make use of the symmetric formulation of the RPA problem by Fillip Furche. The RPA eigenvalue problem is given by

$$\begin{pmatrix} \boldsymbol{A} & \boldsymbol{B} \\ -\boldsymbol{B} & -\boldsymbol{A} \end{pmatrix}\begin{pmatrix} \boldsymbol{X} \\ \boldsymbol{Y} \end{pmatrix} = \boldsymbol{\Omega}\begin{pmatrix} \boldsymbol{X} \\ \boldsymbol{Y} \end{pmatrix} \tag{2.67}$$

so we can get the coupled equations

$$\boldsymbol{AX}+\boldsymbol{BY} = \boldsymbol{\Omega X} \tag{2.68}$$
$$-\boldsymbol{BX}-\boldsymbol{AY} = \boldsymbol{\Omega Y} \tag{2.69}$$

Adding and subtracting these two equations, we get

$$(\boldsymbol{A}-\boldsymbol{B})(\boldsymbol{X}-\boldsymbol{Y})=(\boldsymbol{X}+\boldsymbol{Y})\boldsymbol{\Omega} \implies (\boldsymbol{A}-\boldsymbol{B})=(\boldsymbol{X}+\boldsymbol{Y})\boldsymbol{\Omega}(\boldsymbol{X}-\boldsymbol{Y})^{\dagger} \implies \boxed{\boldsymbol{\eta}^{(1)}=\boldsymbol{A}-\boldsymbol{B}} \tag{2.70}$$

$$(\boldsymbol{A}+\boldsymbol{B})(\boldsymbol{X}+\boldsymbol{Y})=(\boldsymbol{X}-\boldsymbol{Y})\boldsymbol{\Omega} \implies (\boldsymbol{A}+\boldsymbol{B})=(\boldsymbol{X}-\boldsymbol{Y})\boldsymbol{\Omega}(\boldsymbol{X}+\boldsymbol{Y})^{\dagger} \tag{2.71}$$

But then also notice that since $\boldsymbol{\eta}^{(0)}=(\boldsymbol{X}+\boldsymbol{Y})(\boldsymbol{X}+\boldsymbol{Y})^{\dagger}$, we can write $\boldsymbol{\eta}^{(1)}=\boldsymbol{\eta}^{(0)}(\boldsymbol{A}+\boldsymbol{B})\boldsymbol{\eta}^{(0)}$. Continuing on, we arrive at Furche's symmetric formulation of the RPA problem as

$$(\boldsymbol{A}-\boldsymbol{B})(\boldsymbol{A}+\boldsymbol{B})(\boldsymbol{X}+\boldsymbol{Y})=(\boldsymbol{X}+\boldsymbol{Y})\boldsymbol{\Omega}^{2} \tag{2.72}$$

By right multiplying by $(\boldsymbol{X}+\boldsymbol{Y})^{\dagger}$, this leads to

$$(\boldsymbol{A}-\boldsymbol{B})(\boldsymbol{A}+\boldsymbol{B})\boldsymbol{\eta}^{(0)}=\boldsymbol{\eta}^{(2)} \tag{2.73}$$

This is suggestive of a recursive relation with the form

$$\boldsymbol{\eta}^{(m)}=(\boldsymbol{A}-\boldsymbol{B})(\boldsymbol{A}+\boldsymbol{B})\boldsymbol{\eta}^{(m-2)} \tag{2.74}$$

$$\tag{2.75}$$

But we have already found that $\boldsymbol{\eta}^{(1)}=\boldsymbol{A}-\boldsymbol{B} \implies \boldsymbol{\eta}^{(2)}=\boldsymbol{\eta}^{(1)}(\boldsymbol{A}+\boldsymbol{B})\boldsymbol{\eta}^{(0)}$. Now plug in $\boldsymbol{\eta}^{(1)}=\boldsymbol{\eta}^{(0)}(\boldsymbol{A}+\boldsymbol{B})\boldsymbol{\eta}^{(0)}$ to get

$$\boldsymbol{\eta}^{(2)}=\boldsymbol{\eta}^{(0)}(\boldsymbol{A}+\boldsymbol{B})\boldsymbol{\eta}^{(0)}(\boldsymbol{A}+\boldsymbol{B})\boldsymbol{\eta}^{(0)}=\left[\boldsymbol{\eta}^{(0)}(\boldsymbol{A}+\boldsymbol{B})\right]^{2}\boldsymbol{\eta}^{(0)} \tag{2.76}$$

Repeating gives

$$\boxed{\boldsymbol{\eta}^{(m)}=\left[\boldsymbol{\eta}^{(0)}(\boldsymbol{A}+\boldsymbol{B})\right]^{m}\boldsymbol{\eta}^{(0)}} \tag{2.77}$$

and then to initialize, consider

$$\boldsymbol{A}-\boldsymbol{B}=\boldsymbol{\eta}^{(0)}(\boldsymbol{A}+\boldsymbol{B})\boldsymbol{\eta}^{(0)} \tag{2.78}$$

$$(\boldsymbol{A}-\boldsymbol{B})(\boldsymbol{A}+\boldsymbol{B})=\boldsymbol{\eta}^{(0)}(\boldsymbol{A}+\boldsymbol{B})\boldsymbol{\eta}^{(0)}(\boldsymbol{A}+\boldsymbol{B})=\left[\boldsymbol{\eta}^{(0)}(\boldsymbol{A}+\boldsymbol{B})\right]^{2} \tag{2.79}$$

$$\implies \boldsymbol{\eta}^{(0)}=\left[(\boldsymbol{A}-\boldsymbol{B})(\boldsymbol{A}+\boldsymbol{B})\right]^{1/2}(\boldsymbol{A}+\boldsymbol{B})^{-1} \tag{2.80}$$

We do assume a lot of things in going to equation 2.80, but I have

```
assert np.all(np.linalg.eigvals(ApB) > 0)
```

2.4.3 Bringing it back to outline an efficient procedure for Computing Self-Energy Moments

The moments of the lesser and greater parts of the self-energy have the form

$$\begin{aligned}\Sigma_{pq}^{(n,<)}&=\sum_{ia,jb,k}\sum_{t=0}^{n}\binom{n}{t}(-1)^{t}\epsilon_{k}^{n-t}(pk\mid ia)\eta_{ia,jb}^{(t)}(qk\mid jb),\\ \Sigma_{pq}^{(n,>)}&=\sum_{ia,jb,c}\sum_{t=0}^{n}\binom{n}{t}\epsilon_{c}^{n-t}(pc\mid ia)\eta_{ia,jb}^{(t)}(qc\mid jb),\end{aligned} \tag{2.81}$$

respectively. The energies ϵ and integrals $(pq \mid rs)$ are known to us from the prior mean-field calculation, but the density-density moments $\eta^{(t)}$ are not, so we need to compute them. We find them to be defined as

$$\boldsymbol{\eta}^{(m)} = \left[\boldsymbol{\eta}^{(0)}(\mathbf{A}+\mathbf{B})\right]^m \boldsymbol{\eta}^{(0)}, \tag{2.82}$$

with the initial

$$\boldsymbol{\eta}^{(0)} = [(\mathbf{A}-\mathbf{B})(\mathbf{A}+\mathbf{B})]^{\frac{1}{2}}(\mathbf{A}+\mathbf{B})^{-1} \tag{2.83}$$

where we have $\mathbf{A}$ and $\mathbf{B}$ with components $A_{ia,jb} = \delta_{ij}\delta_{ab}(\epsilon_a - \epsilon_i) + (ia \mid jb)$ and $B_{ia,jb} = (ia \mid jb)$. Note that the scaling of the above would be improved by introducing low-rank approximations to the electron repulsion integrals (ERIs) via the Cholesky decomposition or tensor hyper-contraction, which express these 4-index quantities as a sum of two 3- or five 2-index tensors, respectively.

2.5 Avoiding auxiliary space

To avoid using the large auxiliary quantities, we introduce an operator which will project onto the block Lanczos space as $\mathbf{S}_{i,j}^{(n)} = \mathbf{q}_i^\dagger \mathbf{d}^n \mathbf{q}_j$. But due to the orthogonality of the Krylov subspace, we have $q_i^\dagger q_j = 0$ for $i \neq j$, so $\mathbf{S}_{i,j}^{(n)} = 0$ for $|i-j| > 1$. Furthermore, due to Hermiticity, $\mathbf{S}_{i,j}^{(n)} = \mathbf{S}_{j,i}^{(n)\dagger}$. We can start with the initial definition $\mathbf{S}_{1,1}^{(n)} = \mathbf{q}_1^\dagger \mathbf{d}^n \mathbf{q}_1 = \mathbf{L}^{-1}\boldsymbol{\Sigma}^{(n)}\mathbf{L}^{-1,\dagger}$.

Then we know that the recurrence relation is given by

$$\mathbf{q}_{i+1}\mathbf{C}_i^\dagger = [\mathbf{d}\mathbf{q}_i - \mathbf{q}_i\mathbf{H}_i - \mathbf{q}_{i-1}\mathbf{C}_{i-1}] \tag{2.84}$$

I will not repeat the algebraic manipulations, but Backhouse shows in his thesis that the following relations follow

$$\begin{aligned}
\mathbf{S}_{i+1,i}^{(n)} =& \mathbf{q}_{i+1}^\dagger \mathbf{d}^n \mathbf{q}_i = \mathbf{C}_i^{-1}\left[\mathbf{S}_{i,i}^{(n+1)} - \mathbf{H}_i\mathbf{S}_{i,i}^{(n)} - \mathbf{C}_{i-1}^\dagger \mathbf{S}_{i-1,i}^{(n)}\right] \\
\mathbf{S}_{i+1,i+1}^{(n)} =& \mathbf{q}_{i+1}^\dagger \mathbf{d}^n \mathbf{q}_{i+1} = \mathbf{C}_i^{-1}\Big[\mathbf{S}_{i,i}^{(n+2)} + \mathbf{H}_i\mathbf{S}_{i,i}^{(n)}\mathbf{H}_i + \mathbf{C}_{i-1}^\dagger\mathbf{S}_{i-1,i-1}^{(n)}\mathbf{C}_{i-1} \\
& -P\left(\mathbf{S}_{i,i}^{(n+1)}\mathbf{H}_i\right) + P\left(\mathbf{H}_i\mathbf{S}_{i,i-1}^{(n)}\mathbf{C}_{i-1}\right) - P\left(\mathbf{S}_{i,i-1}^{(n+1)}\mathbf{C}_{i-1}\right)\Big]\mathbf{C}_i^{-1,\dagger},
\end{aligned} \tag{2.85}$$

and then solving for $\mathbf{C}_i^2$

$$\mathbf{C}_i^2 = \left[\mathbf{S}_{i,i}^{(2)} + \mathbf{H}_i^2 + \mathbf{C}_{i-1}^\dagger\mathbf{C}_{i-1} - P\left(\mathbf{S}_{i,i}^{(1)}\mathbf{H}_i\right) - P\left(\mathbf{S}_{i,i-1}^{(1)}\mathbf{C}_{i-1}\right)\right] \tag{2.86}$$

and we can also find the on-diagonal $\mathbf{H}$ matrices using

$$\mathbf{H}_i = \mathbf{q}_i^\dagger \mathbf{d}\mathbf{q}_i = \mathbf{S}_{i,i}^{(1)}. \tag{2.87}$$

Now, we know how to compute every quantity of equation 2.25.

2.6 Spectral Function

When we diagonalize the upfolded Hamiltonian, the eigenpairs are composed of charged excitation energies E_k (analogous to QP energies from the QP equation, but without a diagonal approximation to the self-energy) and eigenvectors $\boldsymbol{u}_k$, which can be transformed into the Dyson orbitals $\boldsymbol{\psi}_k$ via

$$\boldsymbol{\psi}_k = \boldsymbol{L}\boldsymbol{P}\boldsymbol{u}_k \tag{2.88}$$

where $\boldsymbol{P}$ is the projection operator into the physical space

```
eigvec_phys = extracted_eigvecs[j][:mf.nbsf]
```

and then $\boldsymbol{L}$, depending on whether we have an occupied or virtual state, is

```
        moments_less = [form_moment(i, "lesser", mf) for i in range(2*
    n_initial+2)]
        moments_great = [form_moment(i, "greater", mf) for i in range(2*
    n_initial+2)]
        L_less = np.linalg.cholesky(moments_less[0], upper=False)
        L_great = np.linalg.cholesky(moments_great[0], upper=False)
        L = (L_less, L_great)
```

Then, we can construct the spectral function via

$$A(\omega) = \sum_k ||\boldsymbol{\psi}_k||^2 \underbrace{\frac{1}{\pi}\frac{\eta}{(\omega - E_k)^2 + \eta^2}}_{\text{Lorentzian}} \tag{2.89}$$

where η is a broadening parameter. In general, the spectral function is known to have the form

$$A(\omega) = -\frac{1}{\pi}\mathrm{Im}G\left(\omega\right) \tag{2.90}$$

and the Dyson equation is

$$G(\omega) = G_0(\omega) + G_0(\omega)\Sigma(\omega)G(\omega) = \frac{1}{\underbrace{\omega - \epsilon_0}_{G_0(\omega)^{-1}} - \Sigma(\omega)} \tag{2.91}$$

but then we know that $\Sigma(\omega) = \Sigma_R(\omega) + i\Sigma_I(\omega)$, so we can write

$$G(\omega) = \frac{1}{\omega - \epsilon_0 - \Sigma_R(\omega) - i\Sigma_I(\omega)} \tag{2.92}$$

Defining $x(\omega) = \omega - \epsilon_0 - \Sigma_R(\omega)$ and $y(\omega) = \Sigma_I(\omega)$, we can rewrite the Dyson equation as

$$G(\omega) = \frac{1}{x(\omega) - iy(\omega)} \times \frac{x(\omega) + iy(\omega)}{x(\omega) + iy(\omega)} = \frac{x(\omega) + iy(\omega)}{(x(\omega))^2 + (y(\omega))^2} \implies \mathrm{Im}G(\omega) = \frac{y(\omega)}{(x(\omega))^2 + (y(\omega))^2} \tag{2.93}$$

We have the following fully analytic expression for the self-energy

$$\Sigma_{pp}^{\text{corr}}(\omega) = \sum_\mu^{\text{RPA}} \left(\sum_i^{\text{occupied}} \frac{w_{pi}^\mu w_{ip}^\mu}{\omega - (\epsilon_i - \Omega_\mu) + i\eta} + \sum_a^{\text{virtual}} \frac{w_{pa}^\mu w_{ap}^\mu}{\omega - (\epsilon_a + \Omega_\mu) - i\eta} \right) \tag{2.94}$$

with

$$w_{pq}^{\mu} = \sum_{jb} (pq|jb) \left(X_{jb}^{\mu} + Y_{jb}^{\mu} \right) \tag{2.95}$$

So

$$\Sigma_{pp}^{R}(\omega) = \sum_{\mu}^{\text{RPA}} \left(\sum_{i}^{\text{occupied}} \frac{w_{pi}^{\mu} w_{ip}^{\mu}}{\omega - (\epsilon_i - \Omega_\mu)} + \sum_{a}^{\text{virtual}} \frac{w_{pa}^{\mu} w_{ap}^{\mu}}{\omega - (\epsilon_a + \Omega_\mu)} \right) \tag{2.96}$$

and because $\frac{1}{\omega \pm i\eta} = \mathcal{P}\frac{1}{\omega} \mp i\pi\delta(\omega)$, we can write

$$\Sigma_{pp}^{I}(\omega) = \pi \sum_{\mu}^{\text{RPA}} \left(\sum_{a}^{\text{virtual}} w_{pa}^{\mu} w_{ap}^{\mu} \delta(\omega - (\epsilon_a + \Omega_\mu) - \sum_{i}^{\text{occupied}} w_{pi}^{\mu} w_{ip}^{\mu} \delta(\omega - (\epsilon_i - \Omega_\mu)) \right) \tag{2.97}$$

This brings us back to a Lorentzian

$$A(\omega) = -\frac{1}{\pi} \sum_{p} \frac{\eta(\omega)}{\left(\omega - \epsilon_0 - \Sigma_{pp}^{R}(\omega)\right)^2 + \eta(\omega)^2} \tag{2.98}$$

with $\eta(\omega) \equiv \Sigma_{pp}^{I}(\omega)$. We need to compute

$$\eta(\omega) = \left(\sum_{\mu}^{\text{RPA}} \left(\sum_{a}^{\text{virtual}} w_{pa}^{\mu} w_{ap}^{\mu} \left(\frac{\gamma}{\left(\omega - (\epsilon_a + \Omega_\mu)\right)^2 + \gamma^2} \right) - \sum_{i}^{\text{occupied}} w_{pi}^{\mu} w_{ip}^{\mu} \left(\frac{\gamma}{\left(\omega - (\epsilon_i - \Omega_\mu)\right)^2 + \gamma^2} \right) \right) \right)_p \tag{2.99}$$

at each $\omega = E_{QP}$ that we found in the QP equation. Meanwhile, we know that the QP renormalization factor is given by

$$Z_p = \left(1 - \left. \frac{\partial \Sigma_{pp}^{R}(\omega)}{\partial \omega} \right|_{\omega = E_{QP}} \right)^{-1} \tag{2.100}$$

So I need to prove the equivalence between this form and the one I have above using $\eta(\omega)$.

2.7 6/2 Conclusions

2.7.1 Hypothesis

If one maintains orthogonality in the Krylov subspace, the Ritz eigenpairs will converge to exact diagonalization within numerical precision. However, it is a fact that if the residual of the recurrence relation 2.113 loses full rank, the off-diagonal elements get a high condition number and are no longer invertible. So we have seen that MC-GW can replicate the block Lanczos up until this condition is met, but no longer afterwards. So even though MC-GW enforces orthogonality of the Krylov subspace even after the residual does lose its full rank, the off-diagonal elements are then no longer invertible, which explains the numerical issues that I observe after this point.

2.7.2 Systems of Study

Given my physical dimension n_{nocc}, the auxiliary dimension is of size $n_{\mathrm{channel}} \times n_{\mathrm{virt}} \times n_{\mathrm{occ}}$, where n_{channel} is either n_{occ} or n_{virt}, depending on whether we are dealing with the lesser or greater channel; it becomes clear that the block size, which is determined by the physical dimension, will be $O(n_{\mathrm{occ}})$, whereas the size of the auxiliary dimension will be $O(n_{\mathrm{channel}} \times n_{\mathrm{virt}} \times n_{\mathrm{occ}})$. I have been doing my tests up until now with a minimal basis, where at least one of these ns is small, so I wonder if when I move to a larger basis there will be a noticeable difference with the large discrepancy between n and n^3. Perhaps we will be able to exactly converge the low-lying orbital MO QPEs, but not the higher ones, but this is typically all that is desired of the method.

2.8 6/10 plots

As you probably have seen, in the theory of MC-GW, the equations come in two forms; the first gives the explicit definition of the quantity in terms of a projection on the Krylov subspace and the second gives the recurrence relation that is used in MC-GW.

$$\boldsymbol{S}^n_{i+1,i} \equiv \boldsymbol{q}^\dagger_{i+1}\boldsymbol{d}^n\boldsymbol{q}_i = \boldsymbol{C}_i^{-1}\left[\boldsymbol{S}^{n+1}_{i,i} - \boldsymbol{M}_i\boldsymbol{S}^n_{i,i} - \boldsymbol{C}^\dagger_{i-1}\boldsymbol{S}^n_{i-1,i}\right] \tag{2.101}$$

or

$$\begin{aligned}\boldsymbol{S}^n_{i+1,i+1} \equiv \boldsymbol{q}^\dagger_{i+1}\boldsymbol{d}^n\boldsymbol{q}_{i+1} = \boldsymbol{C}_i^{-1}\Big[&\boldsymbol{S}^{n+2}_{i,i} + \boldsymbol{M}_i\boldsymbol{S}^n_{i,i}\boldsymbol{M}_i + \boldsymbol{C}^\dagger_{i-1}\boldsymbol{S}^n_{i-1,i-1}\boldsymbol{C}_{i-1} \\ &-P(\boldsymbol{S}^{n+1}_{i,i}\boldsymbol{M}_i) - P(\boldsymbol{S}^{n+1}_{i,i-1}\boldsymbol{C}_{i-1}) + P(\boldsymbol{M}_i\boldsymbol{S}^n_{i,i-1}\boldsymbol{C}_{i-1})\Big]\boldsymbol{C}_i^{\dagger,-1}\end{aligned} \tag{2.102}$$

or

$$\boldsymbol{C}_i^2 = \boldsymbol{C}_i\boldsymbol{C}_i^\dagger = \boldsymbol{S}^2_{i,i} + \boldsymbol{M}_i^2 + \boldsymbol{C}^\dagger_{i-1}\boldsymbol{C}_{i-1} - P\left(\boldsymbol{S}^1_{i,i}\boldsymbol{M}_i\right) - P\left(\boldsymbol{S}^1_{i,i-1}\boldsymbol{C}_{i-1}\right) \tag{2.103}$$

$$\tag{2.104}$$

with

$$\boldsymbol{C}_i = \boldsymbol{q}_i^\dagger\boldsymbol{d}\boldsymbol{q}_{i+1} \tag{2.105}$$

The curve that I label as MCGW dense corresponds to the middle equality, MCGW sparse corresponds to the right equality, and the black curve is the standard block Lanczos with matrix vector products. Then, I also display the solution that Booth code gives. There is a reason why I am not able to get the MCGW sparse curve to match the dense curve. Recall that to solve 2.107, we want to perform a Cholesky decomposition of the matrix $\boldsymbol{C}_i^2$ to get $\boldsymbol{C}_i$. So the matrix should be symmetric and also positive semidefinite. I always begin by trying to use the modified Cholesky algorithm to perform this matrix square root. However, even in the exact dense theory, the matrix $\boldsymbol{C}_i^2$ is not always even positive semidefinite (it has negative eigenvalues), so I cannot use the modified Cholesky algorithm to solve in that case. In addition, due to the rise in numerical imprecision, the matrix also becomes non-symmetric, so in these cases I just symmetrize it, get the eigendecomposition, and do the matrix square root that way. But in exact arithmetic, this is a Hermitian theory, so I shouldn't have to symmetrize like this and in doing so I introduce some error. As can be seen, this gives a fairly good match with what Booth codes predict; we are probably doing similar things.

2.9 Canonical orthogonalization

The numerical issue with the theory ofMCGW seems to lie with then obtaining the appropriate off-diagonals from

$$\boldsymbol{C}_i^2 = \boldsymbol{C}_i\boldsymbol{C}_i^\dagger = \boldsymbol{S}_{i,i}^2 + \boldsymbol{M}_i^2 + \boldsymbol{C}_{i-1}^\dagger\boldsymbol{C}_{i-1} - P\left(\boldsymbol{S}_{i,i}^1\boldsymbol{M}_i\right) - P\left(\boldsymbol{S}_{i,i-1}^1\boldsymbol{C}_{i-1}\right) \tag{2.106}$$

$$\tag{2.107}$$

Let us now try to achieve the same result using canonical orthogonalization. Once we build $\boldsymbol{C}_i^2$ we can take the eigendecomposition of the matrix to get

$$\boldsymbol{C}_i^2 = \boldsymbol{U}_i\boldsymbol{\Lambda}_i\boldsymbol{U}_i^\dagger \tag{2.108}$$

2.10 Krylov subspace orthogonality contradiction

2.10.1 Theoretical background

There seems to be a contradiction regarding the orthogonality of the Krylov vectors in MCGW. We know that I am able to see convergence to ED to within machine precision when I explicitly build up a Krylov subspace, taking care to ensure orthogonality between Krylov vectors, by both doing Gram-Schmidt on each new vector with all previous ones and then throwing away the small singular values if there is a lack of new directions. This is the exact block Lanczos with matrix vector products curve that I sent Tuesday. Now, MCGW claims to enforce orthogonality in the Krylov subspace by doing $\boldsymbol{S}_{i,j}^{(0)} = \delta_{ij}\boldsymbol{I}$ with

$$\boldsymbol{S}_{i,j}^{(n)} = \boldsymbol{q}_i^\dagger\boldsymbol{d}^n\boldsymbol{q}_j \tag{2.109}$$

This is what rationalizes the simplification in the rewriting of the coupling block $\boldsymbol{W}$ as $\boldsymbol{R}$ padded with 0s. For a brief refresher, see the flow in the equations below in the example of a Krylov subspace which is containing only two block vectors.

$$\begin{aligned}
\tilde{\boldsymbol{H}}_{\text{upfolded}}^{\text{Lanczos Iter 2}} &= \tilde{\boldsymbol{Q}}^{(2,\dagger)}\boldsymbol{H}_{\text{Upfolded}}^{G_0W_0}\tilde{\boldsymbol{Q}}^{(2)} && (2.110)\\
&= \begin{pmatrix}\boldsymbol{I} & \boldsymbol{0}\\ \boldsymbol{0} & [\boldsymbol{q}_1^\dagger \quad \boldsymbol{q}_2^\dagger]\end{pmatrix}\begin{pmatrix}\boldsymbol{F}+\boldsymbol{\Sigma}(\infty) & \boldsymbol{W}\\ \boldsymbol{W}^\dagger & \boldsymbol{d}\end{pmatrix}\begin{pmatrix}\boldsymbol{I} & \boldsymbol{0}\\ \boldsymbol{0} & [\boldsymbol{q}_1 \quad \boldsymbol{q}_2]\end{pmatrix} && (2.111)\\
&= \begin{pmatrix}\boldsymbol{F}+\boldsymbol{\Sigma}(\infty) & [\underbrace{\boldsymbol{W}\boldsymbol{q}_1}_{\mathcal{R}\mathcal{Q}^\dagger\mathcal{Q}=\mathcal{R}} \quad \underbrace{\boldsymbol{W}\boldsymbol{q}_2}_{\boldsymbol{0}}]\\ [\underbrace{\boldsymbol{q}_1^\dagger\boldsymbol{W}^\dagger}_{\mathcal{Q}^\dagger\mathcal{Q}\mathcal{R}^\dagger=\mathcal{R}^\dagger} \quad \underbrace{\boldsymbol{q}_2^\dagger\boldsymbol{W}^\dagger}_{\boldsymbol{0}}] & \begin{pmatrix}\underbrace{\boldsymbol{q}_1^\dagger\boldsymbol{d}\boldsymbol{q}_1}_{\boldsymbol{M}_1} & \underbrace{\boldsymbol{q}_1^\dagger\boldsymbol{d}\boldsymbol{q}_2}_{\boldsymbol{C}_1}\\ \underbrace{\boldsymbol{q}_2^\dagger\boldsymbol{d}\boldsymbol{q}_1}_{\boldsymbol{C}_1^\dagger} & \underbrace{\boldsymbol{q}_2^\dagger\boldsymbol{d}\boldsymbol{q}_2}_{\boldsymbol{M}_2}\end{pmatrix}\end{pmatrix} && (2.112)
\end{aligned}$$

But now recall that MCGW relies on the three-term Lanczos recurrence of

$$\mathbf{q}_{i+1}\mathbf{C}_i^\dagger = [\mathbf{d}\mathbf{q}_i - \mathbf{q}_i\mathbf{M}_i - \mathbf{q}_{i-1}\mathbf{C}_{i-1}] \implies \mathbf{q}_{i+1} = [\mathbf{d}\mathbf{q}_i - \mathbf{q}_i\mathbf{M}_i - \mathbf{q}_{i-1}\mathbf{C}_{i-1}]\,\boldsymbol{C}_i^{\dagger,-1} \tag{2.113}$$

which is used in the definition of the $\boldsymbol{S}$es. Crucially, orthogonality is never enforced in these relations, so after sufficient iterations we get $\boldsymbol{q}_i^\dagger \boldsymbol{q}_j \neq 0$ for $i \neq j$. This is in contradiction with our initial assumption that the coupling block $\boldsymbol{W}$ can be written as $\boldsymbol{R}$ padded with zeros. So it is perfectly natural to not see MCGW converge to ED to within machine precision as is seen in the MCGW sparse curve of my plots. Recall that the MCGW dense curve was obtained by explicitly plugging in the Krylov vector from the exact block Lanczos with matrix vector products into 2.109; this was done with genuinely orthogonalized Krylov vectors and hence we saw an exact convergence to ED similar to that of the matrix vector product implementation.

2.10.2 Comment about the effect of minimal basis

It is true that the fact that I was experiencing a lack of new directions was an artifact of me using a minimal basis in my calculations. This put the size of the physical space, which scales as $O(O+V)$, on par with the auxiliary space, which scales as $O(O^2V)$ or $O(V^2O)$, depending on whether we are dealing with the lesser or greater channel, respectively. The dimension of the auxiliary space will grow faster than that of the physical space as we move to larger system sizes, so it is expected that this effect would be negligible by using a larger basis in my calculation. However, this does not solve the issue of not being able to maintain orthogonality by doing Gram-Schmidt of a new vector on all previous vectors. But, I did a numerical tests of the effect of a lack of reorthogonalization on the Ritz values a few months ago, and the effect was negligible.

2.10.3 Next steps

Should I run this with double zeta basis in C++? At the end of the day, I have just speculated, and I haven't proven anything, so it would be nice to see if what I hypothesis plays out in practice.

2.11 A hierarchy of approximations to block Lanczos with reorthogonalization

To simplify the discussion, I will just consider a single channel here.

2.11.1 Exact solution

The QP energies are given by diagonalizing the upfolded Hamiltonian

$$\boldsymbol{H}_{\text{upfolded}} = \begin{pmatrix} \boldsymbol{F} & \boldsymbol{W} \\ \boldsymbol{W}^\dagger & \boldsymbol{d} \end{pmatrix} \tag{2.114}$$

We can accomplish the same thing by considering the Ritz values as obtained by projecting the upfolded Hamiltonian, which is called exact $\boldsymbol{d}$, onto an orthonormal Krylov subspace as

$$\tilde{\boldsymbol{H}}_{\text{upfolded}}^{\text{Lanczos Iter 3}} = \tilde{\boldsymbol{Q}}^{(3,\dagger)}\boldsymbol{H}_{\text{upfolded}}\tilde{\boldsymbol{Q}}^{(3)} \tag{2.115}$$

$$= \begin{pmatrix} \boldsymbol{I} & \boldsymbol{0} \\ \boldsymbol{0} & [\boldsymbol{q}_1^\dagger \quad \boldsymbol{q}_2^\dagger \quad \boldsymbol{q}_3^\dagger] \end{pmatrix} \begin{pmatrix} \boldsymbol{F} & \boldsymbol{W} \\ \boldsymbol{W}^\dagger & \boldsymbol{d} \end{pmatrix} \begin{pmatrix} \boldsymbol{I} & \boldsymbol{0} \\ \boldsymbol{0} & [\boldsymbol{q}_1 \quad \boldsymbol{q}_2 \quad \boldsymbol{q}_3] \end{pmatrix} \tag{2.116}$$

$$= \begin{pmatrix} \boldsymbol{F} & [\underbrace{\boldsymbol{W}\boldsymbol{q}_1}_{\boldsymbol{\mathcal{R}}\boldsymbol{q}_1^\dagger\boldsymbol{q}_1=\boldsymbol{\mathcal{R}}} \quad \underbrace{\boldsymbol{W}\boldsymbol{q}_2}_{\boldsymbol{\mathcal{R}}\boldsymbol{q}_1^\dagger\boldsymbol{q}_2=\boldsymbol{0}} \quad \underbrace{\boldsymbol{W}\boldsymbol{q}_3}_{\boldsymbol{\mathcal{R}}\boldsymbol{q}_1^\dagger\boldsymbol{q}_3=\boldsymbol{0}}] \\ [\underbrace{\boldsymbol{q}_1^\dagger\boldsymbol{W}^\dagger}_{\boldsymbol{q}_1^\dagger\boldsymbol{q}_1\boldsymbol{\mathcal{R}}^\dagger=\boldsymbol{\mathcal{R}}^\dagger} \quad \underbrace{\boldsymbol{q}_2^\dagger\boldsymbol{W}^\dagger}_{\boldsymbol{q}_1^\dagger\boldsymbol{q}_2\boldsymbol{\mathcal{R}}^\dagger=\boldsymbol{0}^\dagger} \quad \underbrace{\boldsymbol{q}_3^\dagger\boldsymbol{W}^\dagger}_{\boldsymbol{q}_1^\dagger\boldsymbol{q}_3\boldsymbol{\mathcal{R}}^\dagger=\boldsymbol{0}^\dagger}] & \begin{pmatrix} \underbrace{\boldsymbol{q}_1^\dagger\boldsymbol{d}\boldsymbol{q}_1}_{\boldsymbol{M}_1} & \underbrace{\boldsymbol{q}_1^\dagger\boldsymbol{d}\boldsymbol{q}_2}_{\boldsymbol{C}_1} & \underbrace{\boldsymbol{q}_1^\dagger\boldsymbol{d}\boldsymbol{q}_3}_{\boldsymbol{0}} \\ \underbrace{\boldsymbol{q}_2^\dagger\boldsymbol{d}\boldsymbol{q}_1}_{\boldsymbol{C}_1^\dagger} & \underbrace{\boldsymbol{q}_2^\dagger\boldsymbol{d}\boldsymbol{q}_2}_{\boldsymbol{M}_2} & \underbrace{\boldsymbol{q}_2^\dagger\boldsymbol{d}\boldsymbol{q}_3}_{\boldsymbol{C}_2} \\ \underbrace{\boldsymbol{q}_3^\dagger\boldsymbol{d}\boldsymbol{q}_1}_{\boldsymbol{0}} & \underbrace{\boldsymbol{q}_3^\dagger\boldsymbol{d}\boldsymbol{q}_2}_{\boldsymbol{C}_2^\dagger} & \underbrace{\boldsymbol{q}_3^\dagger\boldsymbol{d}\boldsymbol{q}_3}_{\boldsymbol{M}_3} \end{pmatrix} \end{pmatrix} \tag{2.117}$$

This is what the matrix-vector product and exact $\boldsymbol{d}$ both do when we apply reorthogonalization.

2.11.2 Matrix-vector product without reorthogonalization

This is one step down from the exact answer. The only reason that we are able to set $\boldsymbol{q}_i\boldsymbol{d}\boldsymbol{q}_j = \boldsymbol{0}$ for $i > j+1$ in 2.117 is because we are assuming an orthogonal basis where

$$\boldsymbol{d}\boldsymbol{q}_j = \boldsymbol{C}_{j-1}\boldsymbol{q}_{j-1}+\boldsymbol{M}_j\boldsymbol{q}_j+\boldsymbol{C}_{j+1}\boldsymbol{q}_{j+1} \implies \boldsymbol{q}_{j+2}^\dagger\boldsymbol{d}\boldsymbol{q}_j = \boldsymbol{q}_{j+2}^\dagger\left(\boldsymbol{C}_{j-1}^\dagger\boldsymbol{q}_{j-1} + \boldsymbol{M}_j^\dagger\boldsymbol{q}_j + \boldsymbol{C}_{j+1}^\dagger\boldsymbol{q}_{j+1}\right) = \boldsymbol{0} \tag{2.118}$$

We will call this assumption 1. But in general, with a non-orthogonal basis, we have

$$\boldsymbol{d}\boldsymbol{q}_j = \sum_{\ell=1}^{j+1}\boldsymbol{H}_{j,\ell}\boldsymbol{q}_\ell. \tag{2.119}$$

This becomes the case after a few Lanczos iterations, which I have shown before. However, the fact that we have written the coupling block as $\boldsymbol{R}$ padded with zeros (I will refer to this as assumption 2) is consistent with the way that we have constructed the auxiliary block, so even though we have violated assumption 1, assumption 2 still holds, and we get results one level down from the exact solution.

2.11.3 Exact d without reorthogonalization

Because this is just projecting $\boldsymbol{d}$ onto an increasingly non-orthogonal Krylov subspace, we are no longer making assumption 1. To make it more clear what I mean here, consider that we are no longer assuming a tridiagonal form for the auxiliary block in 2.117, as we are allowing for nonzero $\boldsymbol{q}_i\boldsymbol{d}\boldsymbol{q}_j$ with $i > j+1$. But now we are violating assumption 2, which is why this gives different results than 2.11.2. **Do we want to understand under what conditions approximation 1 seems to do better than 2, and if so, then how? It doesn't seem to matter in the context of MC-GW, but maybe you have a broader vision.**

2.11.4 MCGW with recurrence relation

In our derivation of the extended recurrence relation, there were 3 instances where we assumed that we could substitute in our expression for $\boldsymbol{q}_{j+1}$ from 2.118 as

$$\mathbf{q}_{i+1} = \left[\mathbf{d}\mathbf{q}_i - \mathbf{q}_i\mathbf{M}_i - \mathbf{q}_{i-1}\mathbf{C}_{i-1}\right] \boldsymbol{C}_i^{\dagger,-1} \tag{2.120}$$

2 were when defined a $\boldsymbol{S}^n_{i+1,i+1}$ and 1 was when we defined $\boldsymbol{S}^n_{i+1,i}$. This uses more approximations than 2.11.3, so it makes sense that we get worse results.

2.12 Next steps

I have a C++ code that I can run now for the dzvp basis, but it is still to slow, which was why I was only able to show you a limited amount of results last time. I will talk to people in the group about how to make it faster. I guess you want me to generate plots like this one for the larger system sizes.

Chapter 3

Berkelbach's *GW*

3.1 Formulation for the TDA

3.1.1 Definitions

For simplicity, we will just work with a single channel, the lesser one. In the dTDA case, Booth's formulation for the upfolded Hamiltonian is

$$\boldsymbol{H} = \begin{pmatrix} \boldsymbol{F} & \boldsymbol{W} \\ \boldsymbol{W}^\dagger & \boldsymbol{d} \end{pmatrix} \tag{3.1}$$

where we have the definitions

$$W_{pkv} = \sum_{ia} (pk|ia) X_{ia}^{v} \quad \text{and} \quad d_{kv,lv'} = (\epsilon_k - \Omega_v)\,\delta_{k,l}\delta_{v,v'} \tag{3.2}$$

Now, Tim's version of the Hamiltonian is given by

$$\boldsymbol{H} = \begin{pmatrix} \boldsymbol{F} & \boldsymbol{V}^{\text{2h1p}} \\ \left(\boldsymbol{V}^{\text{2 h1p}}\right)^\dagger & \boldsymbol{C}^{\text{2hlp}} \end{pmatrix} \tag{3.3}$$

where the definitions of the matrix elements are

$$V_{p,k[lc]}^{\text{2 h1p}} = \langle pc|kl\rangle \equiv (pk|lc) \tag{3.4}$$

$$C_{i[ja],k[lc]}^{\text{2 h1p}} = \left[(\epsilon_i + \epsilon_j - \epsilon_a)\,\delta_{jl}\delta_{ac} - \langle jc|al\rangle\right]\delta_{ik} \tag{3.5}$$

and in particular, we have a definition

$$\boldsymbol{C}^{\text{2hlp}} = \epsilon^{\text{1 h}} \oplus (-\boldsymbol{A}) = \epsilon^{\text{1 h}} \otimes \boldsymbol{1} + \boldsymbol{1} \otimes (-\boldsymbol{A}) \tag{3.6}$$

Let us show how 5.21 comes from 3.6. If $A_{[ja],[lc]} = (\epsilon_j - \epsilon_a)\,\delta_{jl}\delta_{ac} + \langle jc|al\rangle$, then we can write

$$\begin{aligned} C_{i[ja],k[lc]}^{\text{2 h1p}} &= \left[\epsilon_i \delta_{ik}\delta_{jl}\delta_{ac} + (-A)_{[ja],[lc]}\right] && (3.7) \\ &= \delta_{ik}\left[\epsilon_i\,\delta_{jl}\delta_{ac} + (-A)_{[ja],[lc]}\right] && (3.8) \\ &= \delta_{ik}\left[(\epsilon_i + \epsilon_j - \epsilon_a)\,\delta_{jl}\delta_{ac} - \langle jc|al\rangle\right] && (3.9) \end{aligned}$$

3.1.2 Similarity transformation

Let us define a unitary rotation $\boldsymbol{U} = \mathbf{1}_P \oplus_{\text{diag}} (\mathbf{1}_O \otimes \boldsymbol{X}_{OV})$. Application of this unitary to the Hamiltonian will not change the spectrum and actually transforms the problem into

$$\boldsymbol{H}^{2h1p,\prime} = \boldsymbol{U}^\dagger \boldsymbol{H}^{2h1p} \boldsymbol{U} = \begin{pmatrix} \mathbf{1}_P & \mathbf{0} \\ \mathbf{0} & (\mathbf{1}_O \otimes \boldsymbol{X}_{OV}) \end{pmatrix}^\dagger \begin{pmatrix} \boldsymbol{F}_P & \boldsymbol{V}^{\text{2h1p}}_{P,O^2V} \\ \left(\boldsymbol{V}^{\text{2 h1p}}\right)^\dagger_{O^2V,P} & \boldsymbol{C}^{\text{2hlp}}_{O^2V,O^2V} \end{pmatrix} \begin{pmatrix} \mathbf{1}_P & \mathbf{0} \\ \mathbf{0} & (\mathbf{1}_O \otimes \boldsymbol{X}_{OV}) \end{pmatrix} \tag{3.10}$$

$$= \begin{pmatrix} \boldsymbol{F}_P & \boldsymbol{V}^{\text{2h1p}}_{P,O^2V} (\mathbf{1} \otimes \boldsymbol{X})_{O^2V,O^2V} \\ \left(\boldsymbol{V}^{\text{2h1p}}_{P,O^2V} (\mathbf{1} \otimes \boldsymbol{X})_{O^2V,O^2V}\right)^\dagger & \left((\mathbf{1} \otimes \boldsymbol{X})_{O^2V,O^2V}\right)^\dagger \boldsymbol{C}^{\text{2hlp}}_{O^2V,O^2V} \left((\mathbf{1} \otimes \boldsymbol{X})_{O^2V,O^2V}\right) \end{pmatrix}. \tag{3.11}$$

Now let us evaluate $(\mathbf{1} \otimes \boldsymbol{X})^\dagger \boldsymbol{C}^{\text{2hlp}} (\mathbf{1} \otimes \boldsymbol{X})$ in the TDA case. We have

$$\begin{aligned}
(\mathbf{1} \otimes \boldsymbol{X})^\dagger \boldsymbol{C}^{\text{2hlp}} (\mathbf{1} \otimes \boldsymbol{X}) &= (\mathbf{1} \otimes \boldsymbol{X})^\dagger \left[\epsilon^{\text{1 h}} \otimes \mathbf{1} + \mathbf{1} \otimes (-\boldsymbol{A})\right] (\mathbf{1} \otimes \boldsymbol{X}) && (3.12)\\
&= \left(\mathbf{1} \otimes \boldsymbol{X}^\dagger\right) \left[\boldsymbol{\epsilon}^{\text{1 h}} \otimes \mathbf{1}\right] (\mathbf{1} \otimes \boldsymbol{X}) + \left(\mathbf{1} \otimes \boldsymbol{X}^\dagger\right) [\mathbf{1} \otimes (-\boldsymbol{A})] (\mathbf{1} \otimes \boldsymbol{X}) && (3.13)\\
&= \mathbf{1}\boldsymbol{\epsilon}^{\text{1 h}}\mathbf{1} \otimes \boldsymbol{X}^\dagger \mathbf{1} \boldsymbol{X} + \mathbf{111} \otimes (-\boldsymbol{X}^\dagger \boldsymbol{A} \boldsymbol{X}) && (3.14)\\
&= \boldsymbol{\epsilon}^{\text{1 h}} \otimes \mathbf{1} + \mathbf{1} \otimes (-\boldsymbol{X}^\dagger \boldsymbol{A} \boldsymbol{X}) && (3.15)\\
&= \boldsymbol{\epsilon}^{\text{1 h}} \otimes \mathbf{1} + \mathbf{1} \otimes (-\boldsymbol{\Omega}) && (3.16)\\
&= \boldsymbol{\epsilon}^{\text{1 h}} \oplus (-\boldsymbol{\Omega}) && (3.17)
\end{aligned}$$

where we have used the fact that $\boldsymbol{X}^\dagger \boldsymbol{X} = \mathbf{1}$, since $\boldsymbol{X}$ is unitary. Similarly, we can evaluate the other term

$$\begin{aligned}
\boldsymbol{V}^{\text{2h1p}}_{P,O^2V} (\mathbf{1} \otimes \boldsymbol{X})_{O^2V,O^2V} &= \sum_{k'lc} (pk|lc) X^v_{lc} \delta_{kk'} && (3.18)\\
&= \sum_{lc} (pk|lc) X^v_{lc} \equiv \boldsymbol{W}^< && (3.19)\\
& && (3.20)
\end{aligned}$$

So because Booth's and Tim's forms for TDA are related by a similarity transformation, we know that they have the same spectrum.

3.1.3 Deriving the matrix vector products

Now, we can define a vector $\boldsymbol{R} = (r_i,\ r_a,\ r_{i[jb]},\ r_{[jb]a})$. Application of the Hamiltonian to this vector gives us the matrix-vector product $\boldsymbol{HR} = \boldsymbol{\sigma}$, where $\boldsymbol{\sigma} = (\sigma_i,\ \sigma_a,\ \sigma_{i[jb]},\ \sigma_{[jb]a})$. Consider

$$\boldsymbol{HR} = \begin{pmatrix} \boldsymbol{F} & \boldsymbol{V}^{\text{2h1p}} & \boldsymbol{V}^{\text{2p1 h}} \\ \left(\boldsymbol{V}^{\text{2 h1p}}\right)^\dagger & \boldsymbol{C}^{\text{2hlp}} & \mathbf{0} \\ \left(\boldsymbol{V}^{\text{2plh}}\right)^\dagger & \mathbf{0} & \boldsymbol{C}^{\text{2plh}} \end{pmatrix} \begin{pmatrix} r_i \\ r_a \\ r_{i[jb]} \\ r_{[jb]a} \end{pmatrix} = \begin{pmatrix} \sigma_i \\ \sigma_a \\ \sigma_{i[jb]} \\ \sigma_{[jb]a} \end{pmatrix} \tag{3.21}$$

$$\tag{3.22}$$

Let us enumerate now what we actually will get:

$$\sigma_i = \sum_j f_{ij}\, r_j + \sum_b f_{ib}\, r_b + \sum_{klc} \langle i\, c|k\, l\rangle\, r_{k[lc]} + \sum_{kcd} \langle i\, k|d\, c\rangle\, r_{[kc]d}, \tag{3.23}$$

$$\sigma_a = \sum_j f_{aj}\, r_j + \sum_b f_{ab}\, r_b + \sum_{klc} \langle a\, c|k\, l\rangle\, r_{k[lc]} + \sum_{kcd} \langle a\, k|d\, c\rangle\, r_{[kc]d}, \tag{3.24}$$

$$\sigma_{i[ja]} \sum_k \langle k\, a|i\, j\rangle\, r_k + \sum_b \langle b\, a|i\, j\rangle\, r_b + (\epsilon_i + \epsilon_j - \epsilon_a)\, r_{i[ja]} - \sum_{lc} \langle j\, c|a\, l\rangle\, r_{i[lc]} \tag{3.25}$$

$$\sigma_{[ia]b} = \sum_j \langle j\, i|b\, a\rangle\, r_j + \sum_c \langle c\, i|b\, a\rangle\, r_c + (\epsilon_a + \epsilon_b - \epsilon_i)\, r_{[ia]b} + \sum_{kc} \langle a\, k|i\, c\rangle\, r_{[kc]b}. \tag{3.26}$$

3.2 Formulation for the dRPA

Exact form

The exact form is

$$\boldsymbol{H}^{G_0W_0}_{\text{Upfolded}} = \begin{pmatrix} \boldsymbol{F} & \boldsymbol{W}^{<} & \boldsymbol{W}^{>} \\ \boldsymbol{W}^{<,\dagger} & \boldsymbol{d}^{<} & 0 \\ \boldsymbol{W}^{>,\dagger} & 0 & \boldsymbol{d}^{>} \end{pmatrix} \tag{3.27}$$

where $\boldsymbol{F}$ is the HF Fock matrix

$$\boldsymbol{W}^{<}_{pk\nu} = \sum_{ia} (pk|ia)\, (X^{\nu}_{ia} + Y^{\nu}_{ia}) \quad \text{and} \quad \boldsymbol{W}^{>}_{pc\nu} = \sum_{ia} (pc|ia)\, (X^{\nu}_{ia} + Y^{\nu}_{ia}) \tag{3.28}$$

and

$$\boldsymbol{d}^{<}_{k\nu,l\nu'} = (\epsilon_k - \Omega_\nu)\, \delta_{k,l}\delta_{\nu,\nu'} \quad \text{and} \quad \boldsymbol{d}^{>}_{c\nu,d\nu'} = (\epsilon_c + \Omega_\nu)\, \delta_{c,d}\delta_{\nu,\nu'}. \tag{3.29}$$

Downfolding exercise

Let us confirm that this downfolds to the correct result. First, we can define a excitation vector $\boldsymbol{R}$ as

$$\boldsymbol{R} = \begin{pmatrix} \boldsymbol{R}^{\text{1h+1p}} \\ \boldsymbol{R}^{\text{2h1p}} \\ \boldsymbol{R}^{\text{2p1h}} \end{pmatrix} \tag{3.30}$$

and we can write

$$\begin{pmatrix} \boldsymbol{F} & \boldsymbol{W}^{<} & \boldsymbol{W}^{>} \\ \boldsymbol{W}^{<,\dagger} & \boldsymbol{d}^{<} & 0 \\ \boldsymbol{W}^{>,\dagger} & 0 & \boldsymbol{d}^{>} \end{pmatrix} \begin{pmatrix} \boldsymbol{R}^{\text{1h+1p}} \\ \boldsymbol{R}^{\text{2h1p}} \\ \boldsymbol{R}^{\text{2p1h}} \end{pmatrix} = E \begin{pmatrix} \boldsymbol{R}^{\text{1h+1p}} \\ \boldsymbol{R}^{\text{2h1p}} \\ \boldsymbol{R}^{\text{2p1h}} \end{pmatrix} \tag{3.31}$$

$$\begin{pmatrix} \boldsymbol{F}\boldsymbol{R}^{\text{1h+1p}} + \boldsymbol{W}^{<}\boldsymbol{R}^{\text{2h1p}} + \boldsymbol{W}^{>}\boldsymbol{R}^{\text{2p1h}} \\ \boldsymbol{W}^{<,\dagger}\boldsymbol{R}^{\text{1h+1p}} + \boldsymbol{d}^{<}\boldsymbol{R}^{\text{2h1p}} \\ \boldsymbol{W}^{>,\dagger}\boldsymbol{R}^{\text{1h+1p}} + \boldsymbol{d}^{>}\boldsymbol{R}^{\text{2p1h}} \end{pmatrix} = E \begin{pmatrix} \boldsymbol{R}^{\text{1h+1p}} \\ \boldsymbol{R}^{\text{2h1p}} \\ \boldsymbol{R}^{\text{2p1h}} \end{pmatrix} \tag{3.32}$$

This implies three coupled equations

$$\boldsymbol{F}\boldsymbol{R}^{\text{1h+1p}} + \boldsymbol{W}^{<}\boldsymbol{R}^{\text{2h1p}} + \boldsymbol{W}^{>}\boldsymbol{R}^{\text{2p1h}} = E\boldsymbol{R}^{\text{1h+1p}} \tag{3.33}$$

$$\boldsymbol{W}^{<,\dagger}\boldsymbol{R}^{\text{1h+1p}} + \boldsymbol{d}^{<}\boldsymbol{R}^{\text{2h1p}} = E\boldsymbol{R}^{\text{2h1p}} \tag{3.34}$$

$$\boldsymbol{W}^{>,\dagger}\boldsymbol{R}^{\text{1h+1p}} + \boldsymbol{d}^{>}\boldsymbol{R}^{\text{2p1h}} = E\boldsymbol{R}^{\text{2p1h}} \tag{3.35}$$

Solving the latter two equations gives

$$\boldsymbol{R}^{\text{2h1p}} = \left(E\mathbf{1} - \boldsymbol{d}^{<}\right)^{-1} \boldsymbol{W}^{<,\dagger}\boldsymbol{R}^{\text{1h+1p}} \tag{3.36}$$

$$\boldsymbol{R}^{\text{2p1h}} = \left(E\mathbf{1} - \boldsymbol{d}^{>}\right)^{-1} \boldsymbol{W}^{>,\dagger}\boldsymbol{R}^{\text{1h+1p}} \tag{3.37}$$

Substituting these into the first equation gives us

$$\boldsymbol{F}\boldsymbol{R}^{\text{1h+1p}} + \boldsymbol{W}^{<}\left(E\mathbf{1} - \boldsymbol{d}^{<}\right)^{-1} \boldsymbol{W}^{<,\dagger}\boldsymbol{R}^{\text{1h+1p}} + \boldsymbol{W}^{>}\left(E\mathbf{1} - \boldsymbol{d}^{>}\right)^{-1} \boldsymbol{W}^{>,\dagger}\boldsymbol{R}^{\text{1h+1p}} = E\boldsymbol{R}^{\text{1h+1p}} \tag{3.38}$$

from which we can get the eigenvalue equation

$$\left(\boldsymbol{F} + \boldsymbol{W}^{<}\left(E\mathbf{1} - \boldsymbol{d}^{<}\right)^{-1} \boldsymbol{W}^{<,\dagger} + \boldsymbol{W}^{>}\left(E\mathbf{1} - \boldsymbol{d}^{>}\right)^{-1} \boldsymbol{W}^{>,\dagger}\right)\boldsymbol{R}^{\text{1h+1p}} = E\boldsymbol{R}^{\text{1h+1p}} \tag{3.39}$$

so we can identify that the correlation self energy in this approach is

$$\boldsymbol{\Sigma}_c = \boldsymbol{W}^{<}\left(\omega\mathbf{1} - \boldsymbol{d}^{<}\right)^{-1} \boldsymbol{W}^{<,\dagger} + \boldsymbol{W}^{>}\left(\omega\mathbf{1} - \boldsymbol{d}^{>}\right)^{-1} \boldsymbol{W}^{>,\dagger} \tag{3.40}$$

which is the same as the known frequency dependent form for the real part of the correlation self energy:

$$\Sigma^{\text{corr}}_{pq}(\omega) = \sum_{\mu}^{\text{RPA}} \left(\sum_{i}^{\text{occupied}} \frac{w^{\mu}_{pi} w^{\mu}_{iq}}{\omega - (\epsilon_i - \Omega_\mu)} + \sum_{a}^{\text{virtual}} \frac{w^{\mu}_{pa} w^{\mu}_{aq}}{\omega - (\epsilon_a + \Omega_\mu)} \right) \tag{3.41}$$

with $w^{\mu}_{pq} = \sum_{ia} (pq|ia) \left(X^{\mu}_{ia} + Y^{\mu}_{ai}\right)$.

Showing equivalence between excitation energies of M and Mtilde

So we start with this generalized eigenvalue equation

$$\mathbf{M}\boldsymbol{Z} = \mathbf{N}\boldsymbol{Z}\begin{pmatrix} \boldsymbol{\Omega}_+ & 0 \\ 0 & -\boldsymbol{\Omega}_+ \end{pmatrix}$$

where

$$\mathbf{M} = \begin{pmatrix} \mathbf{A} & \mathbf{B} \\ \mathbf{B} & \mathbf{A} \end{pmatrix} \quad \mathbf{N} = \begin{pmatrix} \mathbf{1} & \mathbf{0} \\ \mathbf{0} & -\mathbf{1} \end{pmatrix} \quad \boldsymbol{Z} = \begin{pmatrix} \boldsymbol{X} & \boldsymbol{Y} \\ \boldsymbol{Y} & \boldsymbol{X} \end{pmatrix}$$

and $\boldsymbol{\Omega}_+$is a diagonal matrix of positive excitation energies. Left multiplying both sides by $\boldsymbol{N}$ and right multiplying by $\boldsymbol{Z}^{-1}$ gives us

$$\boldsymbol{N}\boldsymbol{M}\underbrace{\boldsymbol{Z}\boldsymbol{Z}^{-1}}_{\mathbf{1}} = \underbrace{\boldsymbol{N}\boldsymbol{N}}_{\mathbf{1}}\boldsymbol{Z}\begin{pmatrix} \boldsymbol{\Omega}_+ & 0 \\ 0 & -\boldsymbol{\Omega}_+ \end{pmatrix}\boldsymbol{Z}^{-\mathbf{1}} \implies -\boldsymbol{N}\boldsymbol{M} = -\boldsymbol{Z}\begin{pmatrix} \boldsymbol{\Omega}_+ & 0 \\ 0 & -\boldsymbol{\Omega}_+ \end{pmatrix}\boldsymbol{Z}^{-1} \tag{3.42}$$

Now we can use the fact that the action of a scalar function f, such as the step function, on a diagonalizable matrix $\boldsymbol{X} \equiv \boldsymbol{Y}\boldsymbol{\Lambda}\boldsymbol{Y}^{-1}$ can be expressed as

$$f(\boldsymbol{X}) = \boldsymbol{Y}f(\boldsymbol{\Lambda})\boldsymbol{Y}^{-1}$$

so we can write

$$\Theta(-\boldsymbol{N}\boldsymbol{M}) = \boldsymbol{Z}\begin{pmatrix} \Theta(-\boldsymbol{\Omega}_+) & 0 \\ 0 & \Theta(\boldsymbol{\Omega}_+) \end{pmatrix}\boldsymbol{Z}^{-1} = \boldsymbol{Z}\begin{pmatrix} \mathbf{0} & 0 \\ 0 & \mathbf{1} \end{pmatrix}\boldsymbol{Z}^{-1} \tag{3.43}$$

and so it becomes clear that if we define $\tilde{\boldsymbol{M}} = \boldsymbol{M} + \eta\boldsymbol{N}\Theta(-\boldsymbol{N}\boldsymbol{M})$, we can write

$$\tilde{\boldsymbol{M}}\boldsymbol{Z} = \boldsymbol{M}\boldsymbol{Z}+\eta\boldsymbol{N}\Theta(-\boldsymbol{N}\boldsymbol{M})\boldsymbol{Z} = \mathrm{N}\boldsymbol{Z}\begin{pmatrix} \boldsymbol{\Omega}_+ & 0 \\ 0 & -\boldsymbol{\Omega}_+ \end{pmatrix}+\boldsymbol{N}\boldsymbol{Z}\begin{pmatrix} \mathbf{0} & 0 \\ 0 & \boldsymbol{\eta} \end{pmatrix}\underbrace{\boldsymbol{Z}^{-1}\boldsymbol{Z}}_{\mathbf{1}} = \boldsymbol{N}\boldsymbol{Z}\begin{pmatrix} \boldsymbol{\Omega}_+ & 0 \\ 0 & -\boldsymbol{\Omega}_+ + \boldsymbol{\eta} \end{pmatrix} \tag{3.44}$$

3.2.1 Considering the supermatrices they give

It is understood that the notations <,> and 2h1p, 2p1h can be used interchangeably, respectively. Tim's supermatrix is given by

$$\boldsymbol{H} = \begin{pmatrix} \boldsymbol{F} & \boldsymbol{V}^{\text{2h1p}} & \boldsymbol{V}^{\text{2h1p}} & \boldsymbol{V}^{\text{2plh}} & \boldsymbol{V}^{\text{2plh}} \\ \left(\boldsymbol{V}^{\text{2h1p}}\right)^\dagger & & & & \\ \left(\boldsymbol{V}^{\text{2h1p}}\right)^\dagger & & \boldsymbol{C}^{\text{2hlp}} & & \mathbf{0} \\ \left(\boldsymbol{V}^{\text{2plh}}\right)^\dagger & & & & \\ \left(\boldsymbol{V}^{\text{2plh}}\right)^\dagger & & \mathbf{0} & & \boldsymbol{C}^{\text{2plh}} \end{pmatrix} \tag{3.45}$$

We are told that $\mathbf{C}^{\text{2hlp}} = \varepsilon^{1\ \text{h}}\oplus(-\tilde{\mathbf{M}})$ and $\mathbf{C}^{\text{2plh}} = \varepsilon^{1\text{p}}\oplus\tilde{\mathbf{M}}$ and further, that the super-metric is

$$\boldsymbol{\mathcal{N}} = \begin{pmatrix} \mathbf{1} & 0 & 0 \\ 0 & \mathbf{1}\oplus\boldsymbol{N} & 0 \\ 0 & 0 & \mathbf{1}\oplus\boldsymbol{N} \end{pmatrix} \tag{3.46}$$

Let's just focus on the 2h1p sector for now, so the supermatrices are

$$\boldsymbol{H}^{\text{2hlp}} = \begin{pmatrix} \boldsymbol{F}_{P,P} & \boldsymbol{V}^{\text{2h1p}}_{P,O^2V} & \boldsymbol{V}^{\text{2h1p}}_{P,O^2V} \\ \left(\boldsymbol{V}^{\text{2h1p}}_{P,O^2V}\right)^\dagger & & \\ \left(\boldsymbol{V}^{\text{2h1p}}_{P,O^2V}\right)^\dagger & & \boldsymbol{C}^{\text{2hlp}}_{2O^2V,2O^2V} \end{pmatrix}, \quad \boldsymbol{\mathcal{N}}^{\text{2hlp}} = \begin{pmatrix} \mathbf{1}_{P,P} & 0 \\ 0 & \mathbf{1}_O \oplus \boldsymbol{N}_{2OV} \end{pmatrix}, \quad \boldsymbol{R}^{\text{2hlp}} = \begin{pmatrix} r_i \\ r_a \\ r_{i[jb]} \\ \bar{r}_{i[jb]} \end{pmatrix} \tag{3.47}$$

In the following, we might sometimes use the notation $P = O + V$, $A = O^2V$ and T as the column dimension of the excitation vector.

Multiplication of the Hamiltonian by the excitation vector

First, we can take

$$\boldsymbol{H}^{\text{2hlp}}\boldsymbol{R}^{\text{2hlp}} \tag{3.48}$$

$$= \begin{pmatrix} \boldsymbol{F}_{P,P} & \boldsymbol{V}^{\text{2h1p}}_{P,O^2V} & \boldsymbol{V}^{\text{2h1p}}_{P,O^2V} \\ \left(\boldsymbol{V}^{\text{2h1p}}_{P,O^2V}\right)^\dagger & & \\ \left(\boldsymbol{V}^{\text{2h1p}}_{P,O^2V}\right)^\dagger & & \boldsymbol{C}^{\text{2hlp}}_{2O^2V,2O^2V} \end{pmatrix} \begin{pmatrix} r_i \\ r_a \\ r_{i[jb]} \\ \bar{r}_{i[jb]} \end{pmatrix} \tag{3.49}$$

$$= \begin{pmatrix} \begin{pmatrix} \boldsymbol{F}_{OO} & \boldsymbol{F}_{OV} \\ \boldsymbol{F}_{VO} & \boldsymbol{F}_{VV} \end{pmatrix}_{P,P} \begin{pmatrix} \boldsymbol{r}_i \\ \boldsymbol{r}_a \end{pmatrix}_{P,T} + \begin{pmatrix} \boldsymbol{V}^{\text{2h1p}}_{O,i[jb]} & \boldsymbol{V}^{\text{2h1p}}_{O,i[jb]} \\ \boldsymbol{V}^{\text{2h1p}}_{V,i[jb]} & \boldsymbol{V}^{\text{2h1p}}_{V,i[jb]} \end{pmatrix}_{P,2A} \begin{pmatrix} \boldsymbol{r}_{i[jb]} \\ \bar{\boldsymbol{r}}_{i[\bar{j}b]} \end{pmatrix}_{2A,T} \\ \begin{pmatrix} \left(\boldsymbol{V}^{\text{2h1p}}_{O,i[jb]}\right)^\dagger & \left(\boldsymbol{V}^{\text{2h1p}}_{V,i[jb]}\right)^\dagger \\ \left(\boldsymbol{V}^{\text{2h1p}}_{O,i[jb]}\right)^\dagger & \left(\boldsymbol{V}^{\text{2h1p}}_{V,i[jb]}\right)^\dagger \end{pmatrix}_{2A,P} \begin{pmatrix} \boldsymbol{r}_i \\ \boldsymbol{r}_a \end{pmatrix}_{P,T} + \left[\boldsymbol{\epsilon}^{1\text{ h}}_{O,O} \otimes \mathbf{1}_{2OV,2OV} + \mathbf{1}_{O,O} \otimes -\tilde{\boldsymbol{M}}_{2OV,2OV}\right]_{2A,2A} \begin{pmatrix} \boldsymbol{r}_{i[jb]} \\ \bar{\boldsymbol{r}}_{i[\bar{j}b]} \end{pmatrix}_{2A,T} \end{pmatrix} \tag{3.50}$$

Just evaluate

$$\left[\boldsymbol{\epsilon}^{1\text{ h}}_{O,O} \otimes \mathbf{1}_{2OV,2OV} + \mathbf{1}_{O,O} \otimes -\tilde{\boldsymbol{M}}_{2OV,2OV}\right]_{2A,2A} \begin{pmatrix} \boldsymbol{r}_{i[jb]} \\ \bar{\boldsymbol{r}}_{i[\bar{j}b]} \end{pmatrix}_{2A,T} \tag{3.51}$$

$$\tag{3.52}$$

First, use the definition of the tensor product and also notice that $\boldsymbol{\epsilon}^{1\text{ h}}_{O,O}$ is a matrix with the hole energies on the diagonal and zeros elsewhere

$$\boldsymbol{\epsilon}^{1\text{ h}}_{O,O} \otimes \mathbf{1}_{2OV,2OV} = \begin{pmatrix} \epsilon^{1\text{ h}}_{11}\mathbf{1}_{2OV,2OV} & \epsilon^{1\text{ h}}_{12}\mathbf{1}_{2OV,2OV} & \dots & \epsilon^{1\text{ h}}_{1O}\mathbf{1}_{2OV,2OV} \\ \epsilon^{1\text{ h}}_{21}\mathbf{1}_{2OV,2OV} & \epsilon^{1\text{ h}}_{22}\mathbf{1}_{2OV,2OV} & \dots & \epsilon^{1\text{ h}}_{2O}\mathbf{1}_{2OV,2OV} \\ \vdots & \vdots & \ddots & \vdots \\ \epsilon^{1\text{ h}}_{O1}\mathbf{1}_{2OV,2OV} & \epsilon^{1\text{ h}}_{O2}\mathbf{1}_{2OV,2OV} & \dots & \epsilon^{1\text{ h}}_{OO}\mathbf{1}_{2OV,2OV} \end{pmatrix}_{2A,2A} \tag{3.53}$$

$$= \begin{pmatrix} \epsilon^{1\text{ h}}_{11}\mathbf{1}_{2OV,2OV} & \mathbf{0} & \dots & \mathbf{0} \\ \mathbf{0} & \epsilon^{1\text{ h}}_{22}\mathbf{1}_{2OV,2OV} & \dots & \mathbf{0} \\ \vdots & \vdots & \ddots & \vdots \\ \mathbf{0} & \mathbf{0} & \dots & \epsilon^{1\text{ h}}_{OO}\mathbf{1}_{2OV,2OV} \end{pmatrix}_{2A,2A} \tag{3.54}$$

$$\implies \left(\boldsymbol{\epsilon}^{1\text{ h}}_{O,O} \otimes \mathbf{1}_{2OV,2OV}\right)_{2A,2A} \begin{pmatrix} \boldsymbol{r}_{i[jb]} \\ \bar{\boldsymbol{r}}_{i[\bar{j}\bar{b}]} \end{pmatrix}_{2A,T} \tag{3.55}$$

$$= \begin{pmatrix} \epsilon^{1\text{ h}}_{11}\mathbf{1}_{2OV,2OV} & \mathbf{0} & \dots & \mathbf{0} \\ \mathbf{0} & \epsilon^{1\text{ h}}_{22}\mathbf{1}_{2OV,2OV} & \dots & \mathbf{0} \\ \vdots & \vdots & \ddots & \vdots \\ \mathbf{0} & \mathbf{0} & \dots & \epsilon^{1\text{ h}}_{OO}\mathbf{1}_{2OV,2OV} \end{pmatrix}_{2A,2A} \begin{pmatrix} \boldsymbol{r}_{i[jb]} \\ \bar{\boldsymbol{r}}_{i[\bar{j}\bar{b}]} \end{pmatrix}_{2A,T} \tag{3.56}$$

$$\tag{3.57}$$

For these, we can use the formula

$$(A \otimes B) = \begin{pmatrix} a_{11}B & a_{12}B & \dots & a_{1n}B \\ a_{21}B & a_{22}B & \dots & a_{2n}B \\ \vdots & \vdots & \ddots & \vdots \\ a_{m1}B & a_{m2}B & \dots & a_{mn}B \end{pmatrix} \implies (A \otimes B)\, K = \begin{bmatrix} \sum_{j=1}^{n} a_{1j} B K^{(j)} \\ \sum_{j=1}^{n} a_{2j} B K^{(j)} \\ \vdots \\ \sum_{j=1}^{n} a_{mj} B K^{(j)} \end{bmatrix} \tag{3.58}$$

where the $K^{(j)}$ are the rows of the matrix K. To simplify the notation let us define $t = O//2$. First, with

$$\boldsymbol{K} = \begin{pmatrix} \boldsymbol{r}_{i[jb]} \\ \bar{\boldsymbol{r}}_{i[jb]} \end{pmatrix} = \begin{pmatrix} r_{1[jb]} \\ \vdots \\ r_{O[jb]} \\ \bar{r}_{1[jb]} \\ \vdots \\ \bar{r}_{O[jb]} \end{pmatrix} = \begin{pmatrix} K^{(1)} \\ \vdots \\ K^{(t)} \\ \vdots \\ K^{(O)} \end{pmatrix} \in \mathbb{R}^{2O^2V}, \tag{3.59}$$

$$K^{(m)} = \begin{pmatrix} r_{(2m-1)[jb]} \\ r_{(2m)[jb]} \end{pmatrix} \in \mathbb{R}^{2OV} \forall m \leq t, \quad K^{(m)} = \begin{pmatrix} \bar{r}_{(m-1-t)[jb]} \\ \bar{r}_{(m-t)[jb]} \end{pmatrix} \in \mathbb{R}^{2OV} \forall m > t+1 \tag{3.60}$$

Depending on whether O is even or odd, $K^{(t)}$ will be $\begin{pmatrix} r_{(O-1)[jb]} \\ r_{O[jb]} \end{pmatrix}$ or $\begin{pmatrix} r_{O[jb]} \\ \bar{r}_{1[jb]} \end{pmatrix}$, respectively. This version seems correct, but I am unsure about how to proceed. Next, I will consider a modification to lead to a familiar form, but I am not sure if it is correct.

Incorrect but suggestive form

$$\boldsymbol{K} = \begin{pmatrix} \boldsymbol{r}_{i[jb]} \\ \bar{\boldsymbol{r}}_{i[jb]} \end{pmatrix} \stackrel{?}{=} \begin{pmatrix} r_{1[jb]} \\ \bar{r}_{1[jb]} \\ r_{2[jb]} \\ \bar{r}_{2[jb]} \\ \vdots \\ r_{O[jb]} \\ \bar{r}_{O[jb]} \end{pmatrix} = \begin{pmatrix} K^{(1)} \\ K^{(2)} \\ \vdots \\ K^{(O)} \end{pmatrix} \in \mathbb{R}^{2O^2V}, \quad K^{(i)} = \begin{pmatrix} r_{i[jb]} \\ \bar{r}_{i[jb]} \end{pmatrix} \in \mathbb{R}^{2OV} \tag{3.61}$$

$$
\implies \left(\boldsymbol{\epsilon}^{1\text{ h}}_{O,O} \otimes \mathbf{1}_{2OV,2OV}\right)_{2A,2A} \begin{pmatrix} \boldsymbol{r}_{i[jb]} \\ \bar{\boldsymbol{r}}_{i[\bar{j}\bar{b}]} \end{pmatrix}_{2A,T} \overset{?}{=} \begin{pmatrix} \epsilon^{1\text{h}}_{11} K^{(1)} + \epsilon^{1\text{h}}_{12} K^{(2)} + \cdots + \epsilon^{1\text{h}}_{1O} K^{(O)} \\ \epsilon^{1\text{h}}_{21} K^{(1)} + \epsilon^{1\text{h}}_{22} K^{(2)} + \cdots + \epsilon^{1\text{h}}_{2O} K^{(O)} \\ \vdots \\ \epsilon^{1\text{h}}_{O1} K^{(1)} + \epsilon^{1\text{h}}_{O2} K^{(2)} + \cdots + \epsilon^{1\text{h}}_{OO} K^{(O)} \end{pmatrix} \tag{3.62}
$$

$$
= \begin{pmatrix} \epsilon^{1\text{h}}_{11} K^{(1)} + \cdots + 0 \\ 0 + \epsilon^{1\text{h}}_{22} K^{(2)} + \cdots + 0 \\ \vdots \\ 0 + \cdots + \epsilon^{1\text{h}}_{OO} K^{(O)} \end{pmatrix} = \begin{pmatrix} \epsilon^{1\text{h}}_{11} \begin{pmatrix} r_{1[jb]} \\ \bar{r}_{1[jb]} \end{pmatrix} \\ \epsilon^{1\text{h}}_{22} \begin{pmatrix} r_{2[jb]} \\ \bar{r}_{2[jb]} \end{pmatrix} \\ \vdots \\ \epsilon^{1\text{h}}_{OO} \begin{pmatrix} r_{O[jb]} \\ \bar{r}_{O[jb]} \end{pmatrix} \end{pmatrix} = \begin{pmatrix} \boldsymbol{\epsilon}^{1\text{h}} \boldsymbol{r}_{i[jb]} \\ \boldsymbol{\epsilon}^{1\text{h}} \bar{\boldsymbol{r}}_{i[jb]} \end{pmatrix} \tag{3.63}
$$

where we have used the fact that $\boldsymbol{\epsilon}^{1\text{h}}$ is a diagonal matrix with the hole energies. Next, it is useful to define (where the composite index $\mu \equiv OV$; it implies that the occupied-virtual pair is fixed)

$$
\boldsymbol{K} = \begin{pmatrix} \boldsymbol{r}_{i[jb]} \\ \bar{\boldsymbol{r}}_{i[jb]} \end{pmatrix} \overset{?}{=} \begin{pmatrix} r_{i[\mu_1]} \\ \bar{r}_{i[\mu_2]} \\ r_{i[\mu_3]} \\ \bar{r}_{i[\mu_4]} \\ \vdots \\ r_{i[\mu_{2OV-1}]} \\ \bar{r}_{i[\mu_{2OV}]} \end{pmatrix} = \begin{pmatrix} K^{(1)} \\ K^{(2)} \\ \vdots \\ K^{(2OV)} \end{pmatrix} \in \mathbb{R}^{2O^2V}, \quad K^{(i)} = \left(r_{i[OV]} / \bar{r}_{i[OV]}\right) \in \mathbb{R}^{O} \tag{3.64}
$$

$$\Longrightarrow \left(\mathbf{1}_{O,O} \otimes \tilde{\boldsymbol{M}}_{2OV,2OV}\right)_{2A,2A} \begin{pmatrix} \boldsymbol{r}_{i[jb]} \\ \bar{\boldsymbol{r}}_{i[\bar{j}\bar{b}]} \end{pmatrix}_{2A,T} \stackrel{?}{=} \left(\tilde{\boldsymbol{M}}_{2OV,2OV} \otimes \mathbf{1}_{O,O}\right)_{2A,2A} \begin{pmatrix} \boldsymbol{r}_{i[jb]} \\ \bar{\boldsymbol{r}}_{i[\bar{j}\bar{b}]} \end{pmatrix}_{2A,T} \tag{3.65}$$

$$\stackrel{?}{=} \begin{pmatrix} \tilde{M}_{11}K^{(1)} + \cdots + \tilde{M}_{1,OV}K^{(OV)} + \tilde{M}_{1,OV+1}K^{(OV+1)} + \cdots + \tilde{M}_{1,2OV}K^{(2OV)} \\ \tilde{M}_{2,1}K^{(1)} + \cdots + \tilde{M}_{2,OV}K^{(OV)} + \tilde{M}_{2,OV+1}K^{(OV+1)} + \cdots + \tilde{M}_{2,2OV}K^{(2OV)} \\ \vdots \\ \tilde{M}_{OV,1}K^{(1)} + \cdots + \tilde{M}_{OV,OV}K^{(OV)} + \tilde{M}_{OV,OV+1}K^{(OV+1)} + \cdots + \tilde{M}_{OV,2OV}K^{(2OV)} \\ \tilde{M}_{OV+1,1}K^{(1)} + \cdots + \tilde{M}_{OV+1,OV}K^{(OV)} + \tilde{M}_{OV+1,OV+1}K^{(OV+1)} + \cdots + \tilde{M}_{OV+1,2OV}K^{(2OV)} \\ \vdots \\ \tilde{M}_{2OV,1}K^{(1)} + \cdots + \tilde{M}_{2OV,OV}K^{(OV)} + \tilde{M}_{2OV,OV+1}K^{(OV+1)} + \cdots + \tilde{M}_{2OV,2OV}K^{(2OV)} \end{pmatrix} \tag{3.66}$$

$$= \begin{pmatrix} \tilde{\boldsymbol{M}}_{xx}\boldsymbol{K}_{1\to OV} + \tilde{\boldsymbol{M}}_{xd}\boldsymbol{K}_{OV+1\to 2OV} \\ \tilde{\boldsymbol{M}}_{dx}\boldsymbol{K}_{1\to OV} + \tilde{\boldsymbol{M}}_{dd}\boldsymbol{K}_{OV+1\to 2OV} \end{pmatrix} \tag{3.67}$$

where $\tilde{\boldsymbol{M}}_{xx}$, $\tilde{\boldsymbol{M}}_{xd}$, $\tilde{\boldsymbol{M}}_{dx}$, and $\tilde{\boldsymbol{M}}_{dd}$ are the excitation-excitation, excitation-de-excitation, de-excitation-excitation, and de-excitation-de-excitation blocks of the matrix $\tilde{\boldsymbol{M}}$ respectively. $\boldsymbol{K}_{1\to OV}$ and $\boldsymbol{K}_{OV+1\to 2OV}$ are defined as

$$\boldsymbol{K}_{1\to OV} = \begin{pmatrix} K^{(1)} & K^{(2)} & \ldots & K^{(OV)} \end{pmatrix} = \begin{pmatrix} r_{i[\mu_1]} & \bar{r}_{i[\mu_2]} & \ldots & r_{i[\mu_{OV}]} \end{pmatrix} \tag{3.68}$$

$$\boldsymbol{K}_{OV+1\to 2OV} = \begin{pmatrix} K^{(OV+1)} & K^{(OV+2)} & \ldots & K^{(2OV)} \end{pmatrix} = \begin{pmatrix} r_{i[\mu_{OV+1}]} & \bar{r}_{i[\mu_{OV+2}]} & \ldots & r_{i[\mu_{2OV}]} \end{pmatrix} \tag{3.69}$$

$$\boldsymbol{H}^{\text{2h1p}}\boldsymbol{R}^{\text{2h1p}} \tag{3.70}$$

$$\stackrel{?}{=} \begin{pmatrix} \boldsymbol{F}_{OO}\boldsymbol{r}_i + \boldsymbol{F}_{OV}\boldsymbol{r}_a + \boldsymbol{V}^{\text{2h1p}}_{O,i[jb]}\boldsymbol{r}_{i[jb]} + \boldsymbol{V}^{\text{2h1p}}_{O,i[jb]}\bar{\boldsymbol{r}}_{i[\bar{j}\bar{b}]} \\ \boldsymbol{F}_{VO}\boldsymbol{r}_i + \boldsymbol{F}_{VV}\boldsymbol{r}_a + \boldsymbol{V}^{\text{2h1p}}_{V,i[jb]}\boldsymbol{r}_{i[jb]} + \boldsymbol{V}^{\text{2h1p}}_{V,i[jb]}\bar{\boldsymbol{r}}_{i[\bar{j}\bar{b}]} \\ \left(\boldsymbol{V}^{\text{2h1p}}_{O,i[jb]}\right)^{\dagger}\boldsymbol{r}_i + \left(\boldsymbol{V}^{\text{2h1p}}_{O,i[jb]}\right)^{\dagger}\boldsymbol{r}_a + \boldsymbol{\epsilon}^{1\ \text{h}}_{O,O}\boldsymbol{r}_{i[jb]} - \tilde{\boldsymbol{M}}_{xx}\boldsymbol{K}_{1\to OV} - \tilde{\boldsymbol{M}}_{xd}\boldsymbol{K}_{OV+1\to 2OV} \\ \left(\boldsymbol{V}^{\text{2h1p}}_{V,i[jb]}\right)^{\dagger}\boldsymbol{r}_i + \left(\boldsymbol{V}^{\text{2h1p}}_{V,i[jb]}\right)^{\dagger}\boldsymbol{r}_a + \boldsymbol{\epsilon}^{1\ \text{h}}_{O,O}\bar{\boldsymbol{r}}_{i[jb]} - \tilde{\boldsymbol{M}}_{dx}\boldsymbol{K}_{1\to OV} - \tilde{\boldsymbol{M}}_{dd}\boldsymbol{K}_{OV+1\to 2OV} \end{pmatrix}_{P+2A,T} \tag{3.71}$$

$$= \begin{pmatrix} \sum_j f_{ij}\, r_j + \sum_b f_{ib}\, r_b + \sum_{klc}\langle i\, c|k\, l\rangle\, r_{k[lc]} + \sum_{klc}\langle i\, c|k\, l\rangle\, \bar{r}_{k[lc]} \\ \sum_j f_{aj}\, r_j + \sum_b f_{ab}\, r_b + \sum_{klc}\langle a\, c|k\, l\rangle\, r_{k[lc]} + \sum_{klc}\langle a\, c|k\, l\rangle\, \bar{r}_{k[lc]} \\ \vdots \end{pmatrix}_{P+2A,T} \tag{3.72}$$

Multiplying the supermetric by the Hamiltonian

Alternatively, we can consider the LHS matrix multiplication

$$\boldsymbol{\mathcal{N}}^{\text{2hlp}}\boldsymbol{H}^{\text{2hlp}} = \begin{pmatrix} \mathbf{1}_{P,P} & 0 \\ 0 & \mathbf{1}_{O,O} \oplus_{\text{kron}} \boldsymbol{N}_{2OV,2OV} \end{pmatrix} \begin{pmatrix} \boldsymbol{F}_{P,P} & \boldsymbol{V}^{\text{2h1p}}_{P,O^2V} & \boldsymbol{V}^{\text{2h1p}}_{P,O^2V} \\ \left(\boldsymbol{V}^{\text{2h1p}}_{P,O^2V}\right)^\dagger & & \\ \left(\boldsymbol{V}^{\text{2h1p}}_{P,O^2V}\right)^\dagger & & \boldsymbol{C}^{\text{2hlp}}_{2O^2V,2O^2V} \end{pmatrix} \tag{3.73}$$

$$= \begin{pmatrix} \boldsymbol{F}_{P,P} & \begin{pmatrix} \boldsymbol{V}^{\text{2h1p}} & \boldsymbol{V}^{\text{2h1p}} \end{pmatrix}_{P,2O^2V} \\ \left(\mathbf{1} \oplus_{\text{kron}} \boldsymbol{N}\right)_{2O^2V,2O^2V} \begin{pmatrix} \left(\boldsymbol{V}^{\text{2h1p}}\right)^\dagger \\ \left(\boldsymbol{V}^{\text{2h1p}}\right)^\dagger \end{pmatrix}_{2O^2V,P} & \left(\mathbf{1} \oplus_{\text{kron}} \boldsymbol{N}\right)_{2O^2V,2O^2V} \boldsymbol{C}^{\text{2hlp}}_{2O^2V,2O^2V} \end{pmatrix} \tag{3.74}$$

$$\tag{3.75}$$

First, we can consider the off diagonal term

$$\left(\mathbf{1} \oplus_{\text{kron}} \boldsymbol{N}_{2OV,2OV}\right) \begin{pmatrix} \left(\boldsymbol{V}^{\text{2h1p}}\right)^\dagger \\ \left(\boldsymbol{V}^{\text{2h1p}}\right)^\dagger \end{pmatrix}_{2O^2V,P} = \left(\mathbf{1}_O \otimes \mathbf{1}_{2OV} + \mathbf{1}_O \otimes \boldsymbol{N}_{2OV}\right) \begin{pmatrix} \left(\boldsymbol{V}^{\text{2h1p}}\right)^\dagger \\ \left(\boldsymbol{V}^{\text{2h1p}}\right)^\dagger \end{pmatrix}_{2O^2V,P} \tag{3.76}$$

$$= \begin{pmatrix} \left(\boldsymbol{V}^{\text{2h1p}}\right)^\dagger \\ \left(\boldsymbol{V}^{\text{2h1p}}\right)^\dagger \end{pmatrix}_{2O^2V,P} + \begin{pmatrix} \left(\boldsymbol{V}^{\text{2h1p}}\right)^\dagger \\ -\left(\boldsymbol{V}^{\text{2h1p}}\right)^\dagger \end{pmatrix}_{2O^2V,P} \tag{3.77}$$

$$= \begin{pmatrix} 2\left(\boldsymbol{V}^{\text{2h1p}}\right)^\dagger \\ 0 \end{pmatrix}_{2O^2V,P} \tag{3.78}$$

Next, we can consider the auxiliary block

$$\left(\mathbf{1} \oplus_{\text{kron}} \boldsymbol{N}\right) \boldsymbol{C}^{\text{2hlp}} = \left(\mathbf{1}_O \oplus_{\text{kron}} \boldsymbol{N}_{2OV}\right) \left(\boldsymbol{\epsilon}^{1\text{ h}}_O \oplus_{\text{kron}} (-\tilde{\boldsymbol{M}})_{2OV}\right) \tag{3.79}$$

$$= \left(\mathbf{1}_O \otimes \mathbf{1}_{2OV} + \mathbf{1}_O \otimes \boldsymbol{N}_{2OV}\right) \left(\boldsymbol{\epsilon}^{1\text{ h}}_O \otimes \mathbf{1}_{2OV} + \mathbf{1}_O \otimes (-\tilde{\boldsymbol{M}})_{2OV}\right) \tag{3.80}$$

$$= \boldsymbol{\epsilon}^{1\text{ h}}_O \otimes \mathbf{1}_{2OV} + \underbrace{\mathbf{1}_O \otimes -\tilde{\boldsymbol{M}}_{2OV} + \boldsymbol{\epsilon}^{1\text{ h}}_O \otimes \boldsymbol{N}_{2OV}}_{\text{cross terms}} + \mathbf{1}_O \otimes -\boldsymbol{N}\tilde{\boldsymbol{M}}_{2OV} \tag{3.81}$$

$$= \begin{pmatrix} \epsilon_1^{1\ \mathrm{h}} \mathbf{1}_{2OV} & 0 & \dots & 0 \\ 0 & \epsilon_2^{1\ \mathrm{h}} \mathbf{1}_{2OV} & \dots & 0 \\ \vdots & \vdots & \ddots & \vdots \\ 0 & 0 & \dots & \epsilon_O^{1\ \mathrm{h}} \mathbf{1}_{2OV} \end{pmatrix} - \begin{pmatrix} 1\tilde{\boldsymbol{M}}_{2OV} & 0 & \dots & 0 \\ 0 & 1\tilde{\boldsymbol{M}}_{2OV} & \dots & 0 \\ \vdots & \vdots & \ddots & \vdots \\ 0 & 0 & \dots & 1\tilde{\boldsymbol{M}}_{2OV} \end{pmatrix} \tag{3.82}$$

$$+ \begin{pmatrix} \epsilon_1^{1\ \mathrm{h}} \boldsymbol{N}_{2OV} & 0 & \dots & 0 \\ 0 & \epsilon_2^{1\ \mathrm{h}} \boldsymbol{N}_{2OV} & \dots & 0 \\ \vdots & \vdots & \ddots & \vdots \\ 0 & 0 & \dots & \epsilon_O^{1\ \mathrm{h}} \boldsymbol{N}_{2OV} \end{pmatrix} - \begin{pmatrix} 1\left(\boldsymbol{N}\tilde{\boldsymbol{M}}\right)_{2OV} & 0 & \dots & 0 \\ 0 & 1\left(\boldsymbol{N}\tilde{\boldsymbol{M}}\right)_{2OV} & \dots & 0 \\ \vdots & \vdots & \ddots & \vdots \\ 0 & 0 & \dots & 1\left(\boldsymbol{N}\tilde{\boldsymbol{M}}\right)_{2OV} \end{pmatrix} \tag{3.83}$$

$$= \begin{pmatrix} \epsilon_1^{1\ \mathrm{h}} \left(\mathbf{1} + \boldsymbol{N}\right)_{2OV} & \dots & 0 \\ \vdots & \ddots & \vdots \\ 0 & \dots & \epsilon_O^{1\ \mathrm{h}} \left(\mathbf{1} + \boldsymbol{N}\right)_{2OV} \end{pmatrix} - \begin{pmatrix} 1\left(\tilde{\boldsymbol{M}} + \boldsymbol{N}\tilde{\boldsymbol{M}}\right)_{2OV} & \dots & 0 \\ \vdots & \ddots & \vdots \\ 0 & \dots & 1\left(\tilde{\boldsymbol{M}} + \boldsymbol{N}\tilde{\boldsymbol{M}}\right)_{2OV} \end{pmatrix} \tag{3.84}$$

$$= \begin{pmatrix} \epsilon_1^{1\ \mathrm{h}} \left(\mathbf{1} + \boldsymbol{N}\right)_{2OV} - \left(\tilde{\boldsymbol{M}} + \boldsymbol{N}\tilde{\boldsymbol{M}}\right)_{2OV} & \dots & 0 \\ \vdots & \ddots & \vdots \\ 0 & \dots & \epsilon_O^{1\ \mathrm{h}} \left(\mathbf{1} + \boldsymbol{N}\right)_{2OV} - \left(\tilde{\boldsymbol{M}} + \boldsymbol{N}\tilde{\boldsymbol{M}}\right)_{2OV} \end{pmatrix} \tag{3.85}$$

$$= \begin{pmatrix} \epsilon_1^{1\ \mathrm{h}} \left(\mathbf{1} + \boldsymbol{N}\right)_{2OV} - \left[\left(\mathbf{1} + \boldsymbol{N}\right)\tilde{\boldsymbol{M}}\right]_{2OV} & \dots & 0 \\ \vdots & \ddots & \vdots \\ 0 & \dots & \epsilon_O^{1\ \mathrm{h}} \left(\mathbf{1} + \boldsymbol{N}\right)_{2OV} - \left[\left(\mathbf{1} + \boldsymbol{N}\right)\tilde{\boldsymbol{M}}\right]_{2OV} \end{pmatrix} \tag{3.86}$$

I have plotted 3 different data points from each molecular calculation. The blue bar shows the average deviation of the Ritz values from the exact solution using the expressions for the matrix vector products given in the main paper. The orange bar shows the average deviation of the Ritz values from the exact solution using the expressions for the matrix vector products given in the supplemental material (Supp. MV), where we set B=0. The green bar is just showing the norm of the final residual (when I reach the maximum number of iterations) I get when I run the Davidson iteration using Supp. MV. I am running for up to 75 iterations without doing any restarting. I interpret this as there not being a bug in my implementation since I see the same behavior across different molecules, but perhaps the expressions for the matrix vector products that he proposes in the supplemental material are just not exact. Do you have a different opinion?

Reverse engineering

We have the problem $\boldsymbol{\sigma} = \boldsymbol{\mathcal{N}} \boldsymbol{H} \boldsymbol{R}$. I know that $\boldsymbol{\sigma}$ is given by

$$\sigma_i = \sum_j f_{ij}\, r_j + \sum_b f_{ib}\, r_b + \sum_{klc} \langle i\, c | k\, l \rangle\, r_{k[lc]} + \sum_{kcd} \langle i\, k | d\, c \rangle\, r_{[kc]d} + \sum_{klc} \langle i\, c | k\, l \rangle\, \bar{r}_{k[lc]} + \sum_{kcd} \langle i\, k | d\, c \rangle\, \bar{r}_{[kc]d} \tag{3.87}$$

$$\sigma_a = \sum_j f_{aj}\, r_j + \sum_b f_{ab}\, r_b + \sum_{klc} \langle a\, c | k\, l \rangle\, r_{k[lc]} + \sum_{kcd} \langle a\, k | d\, c \rangle\, r_{[kc]d} + \sum_{klc} \langle a\, c | k\, l \rangle\, \bar{r}_{k[lc]} + \sum_{kcd} \langle a\, k | d\, c \rangle\, \bar{r}_{[kc]d} \tag{3.88}$$

$$\sigma_{i[ja]} = \sum_k \langle k\, a | i\, j \rangle\, r_k + \sum_b \langle b\, a | i\, j \rangle\, r_b + \varepsilon_i r_{i[ja]} - \sum_{kb} [\mathbf{N}\tilde{\mathbf{M}}]^{\mathrm{xx}}_{jakb} r_{i[kb]} - \sum_{kb} [\mathbf{N}\tilde{\mathbf{M}}]^{\mathrm{xd}}_{jakb} \bar{r}_{i[kb]} \tag{3.89}$$

$$\bar{\sigma}_{i[ja]} = -\sum_k \langle k\, a | i\, j \rangle\, r_k - \sum_b \langle b\, a | i\, j \rangle\, r_b + \varepsilon_i \bar{r}_{i[ja]} - \sum_{kb} [\mathbf{N}\tilde{\mathbf{M}}]^{\mathrm{dx}}_{ja,kb} r_{i[kb]} - \sum_{kb} [\mathbf{N}\tilde{\mathbf{M}}]^{\mathrm{dd}}_{ja,kb} \bar{r}_{i[kb]} \tag{3.90}$$

$$\sigma_{[ia]b} = \sum_j \langle j\, i | b\, a \rangle\, r_j + \sum_c \langle c\, i | b\, a \rangle\, r_c + \varepsilon_b r_{[ia]b} + \sum_{jc} [\mathbf{N}\tilde{\mathbf{M}}]^{\mathrm{xx}}_{ia,jc} r_{[jc]b} + \sum_{jc} [\mathbf{N}\tilde{\mathbf{M}}]^{\mathrm{xd}}_{ia,jc} \bar{r}_{[jc]b} \tag{3.91}$$

$$\bar{\sigma}_{[ia]b} = -\sum_j \langle j\, i | b\, a \rangle\, r_j - \sum_c \langle c\, i | b\, a \rangle\, r_c + \varepsilon_b \bar{r}_{[ia]b} + \sum_{jc} [\mathbf{N}\tilde{\mathbf{M}}]^{\mathrm{dx}}_{ia,jc} r_{[jc]b} + \sum_{jc} [\mathbf{N}\tilde{\mathbf{M}}]^{\mathrm{dd}}_{ia,jc} \bar{r}_{[jc]b} \tag{3.92}$$

$\boldsymbol{R}^{2h1p} = \begin{pmatrix} r_i \\ r_a \\ r_{i[jb]} \\ \bar{r}_{i[\bar{j}b]} \end{pmatrix}$ is the excitation vector. We will assume the form $\boldsymbol{\mathcal{N}}^{2h1p} = \begin{pmatrix} \mathbf{1} & 0 \\ 0 & \boldsymbol{X} \end{pmatrix}$. We assume that $\boldsymbol{H}^{2h1p}$ is given by

$$\boldsymbol{H}^{2h1p} = \begin{pmatrix} \boldsymbol{F} & \boldsymbol{V}^{\mathrm{2h1p}} & \boldsymbol{V}^{\mathrm{2h1p}} \\ \left(\boldsymbol{V}^{\mathrm{2h1p}}\right)^{\dagger} & & \\ \left(\boldsymbol{V}^{\mathrm{2h1p}}\right)^{\dagger} & & \boldsymbol{C}^{\mathrm{2hlp}} \end{pmatrix} \tag{3.93}$$

In our notation, $P = O + V$ is the number of molecular orbitals, $A = O^2V$ and T is the column dimension of our excitation vector.

$$\boldsymbol{\mathcal{N}}^{2h1p}\boldsymbol{H}^{2h1p}\boldsymbol{R}^{2h1p} \tag{3.94}$$

$$= \begin{pmatrix} \mathbf{1}_{P,P} & 0 \\ 0 & \boldsymbol{X}_{2A,2A} \end{pmatrix}_{P+2A,P+2A} \begin{pmatrix} \boldsymbol{F}_{P,P} & \boldsymbol{V}^{\text{2h1p}}_{P,A} & \boldsymbol{V}^{\text{2h1p}}_{P,A} \\ \left(\boldsymbol{V}^{\text{2h1p}}\right)^{\dagger}_{A,P} & & \\ \left(\boldsymbol{V}^{\text{2h1p}}\right)^{\dagger}_{A,P} & & \boldsymbol{C}^{\text{2hlp}}_{2A,2A} \end{pmatrix}_{P+2A,P+2A} \begin{pmatrix} \boldsymbol{r}_i \\ \boldsymbol{r}_a \\ \boldsymbol{r}_{i[jb]} \\ \bar{\boldsymbol{r}}_{i[\bar{j}\bar{b}]} \end{pmatrix}_{P+2A,T} \tag{3.95}$$

$$= \begin{pmatrix} \mathbf{1}_{P,P} \begin{pmatrix} \boldsymbol{F}_{OO} & \boldsymbol{F}_{OV} \\ \boldsymbol{F}_{VO} & \boldsymbol{F}_{VV} \end{pmatrix}_{P,P} \begin{pmatrix} \boldsymbol{r}_i \\ \boldsymbol{r}_a \end{pmatrix}_{P,T} + \mathbf{1}_{P,P} \begin{pmatrix} \boldsymbol{V}^{\text{2h1p}}_{O,i[jb]} & \boldsymbol{V}^{\text{2h1p}}_{O,i[jb]} \\ \boldsymbol{V}^{\text{2h1p}}_{V,i[jb]} & \boldsymbol{V}^{\text{2h1p}}_{V,i[jb]} \end{pmatrix}_{P,2A} \begin{pmatrix} \boldsymbol{r}_{i[jb]} \\ \bar{\boldsymbol{r}}_{i[\bar{j}\bar{b}]} \end{pmatrix}_{2A,T} \\ \boldsymbol{X}_{2A,2A} \begin{pmatrix} \left(\boldsymbol{V}^{\text{2h1p}}_{O,i[jb]}\right)^{\dagger} & \left(\boldsymbol{V}^{\text{2h1p}}_{V,i[jb]}\right)^{\dagger} \\ \left(\boldsymbol{V}^{\text{2h1p}}_{O,i[jb]}\right)^{\dagger} & \left(\boldsymbol{V}^{\text{2h1p}}_{V,i[jb]}\right)^{\dagger} \end{pmatrix}_{2A,P} \begin{pmatrix} \boldsymbol{r}_i \\ \boldsymbol{r}_a \end{pmatrix}_{P,T} + \boldsymbol{X}_{2A,2A}\boldsymbol{C}^{\text{2hlp}}_{2A,2A} \begin{pmatrix} \boldsymbol{r}_{i[jb]} \\ \bar{\boldsymbol{r}}_{i[\bar{j}\bar{b}]} \end{pmatrix}_{2A,T} \end{pmatrix} \tag{3.96}$$

$$= \begin{pmatrix} \boldsymbol{F}_{OO}\boldsymbol{r}_i + \boldsymbol{F}_{OV}\boldsymbol{r}_a + \boldsymbol{V}^{\text{2h1p}}_{O,i[jb]}\boldsymbol{r}_{i[jb]} + \boldsymbol{V}^{\text{2h1p}}_{O,i[jb]}\bar{\boldsymbol{r}}_{i[\bar{j}\bar{b}]} \\ \boldsymbol{F}_{VO}\boldsymbol{r}_i + \boldsymbol{F}_{VV}\boldsymbol{r}_a + \boldsymbol{V}^{\text{2h1p}}_{V,i[jb]}\boldsymbol{r}_{i[jb]} + \boldsymbol{V}^{\text{2h1p}}_{V,i[jb]}\bar{\boldsymbol{r}}_{i[\bar{j}\bar{b}]} \\ ? \end{pmatrix}_{P+2A,T} \tag{3.97}$$

$$= \begin{pmatrix} \sum_j f_{ij}r_j + \sum_b f_{ib}r_b + \sum_{klc}\langle i\,c|k\,l\rangle r_{k[lc]} + \sum_{klc}\langle i\,c|k\,l\rangle \bar{r}_{k[lc]} \\ \sum_j f_{aj}r_j + \sum_b f_{ab}r_b + \sum_{klc}\langle a\,c|k\,l\rangle r_{k[lc]} + \sum_{klc}\langle a\,c|k\,l\rangle \bar{r}_{k[lc]} \\ ? \end{pmatrix} \tag{3.98}$$

$$\tag{3.99}$$

Now let's consider that $\boldsymbol{X}_{2A,2A} = \mathbf{1}_O \otimes \boldsymbol{N}_{2OV,2OV} = \mathbf{1}_O \otimes \begin{pmatrix} \mathbf{1}_{OV,OV} & 0 \\ 0 & -\mathbf{1}_{OV,OV} \end{pmatrix}$.Then, it becomes true that

$$(\mathbf{1}_O \otimes \boldsymbol{N}_{2OV,2OV}) \begin{pmatrix} \left(\boldsymbol{V}^{\text{2h1p}}_{O,i[jb]}\right)^{\dagger} & \left(\boldsymbol{V}^{\text{2h1p}}_{V,i[jb]}\right)^{\dagger} \\ \left(\boldsymbol{V}^{\text{2h1p}}_{O,i[jb]}\right)^{\dagger} & \left(\boldsymbol{V}^{\text{2h1p}}_{V,i[jb]}\right)^{\dagger} \end{pmatrix}_{2A,P} \begin{pmatrix} \boldsymbol{r}_i \\ \boldsymbol{r}_a \end{pmatrix}_{P,T} \tag{3.100}$$

$$= \begin{pmatrix} \left(\boldsymbol{V}^{\text{2h1p}}_{O,i[jb]}\right)^{\dagger} & \left(\boldsymbol{V}^{\text{2h1p}}_{V,i[jb]}\right)^{\dagger} \\ \left(-\boldsymbol{V}^{\text{2h1p}}_{O,i[jb]}\right)^{\dagger} & -\left(\boldsymbol{V}^{\text{2h1p}}_{V,i[jb]}\right)^{\dagger} \end{pmatrix}_{2A,P} \begin{pmatrix} \boldsymbol{r}_i \\ \boldsymbol{r}_a \end{pmatrix}_{P,T} \tag{3.101}$$

$$= \begin{pmatrix} \sum_k \langle k\,a|i\,j\rangle\, r_k + \sum_b \langle b\,a|i\,j\rangle\, r_b \\ -\sum_k \langle k\,a|i\,j\rangle\, r_k - \sum_b \langle b\,a|i\,j\rangle\, r_b \end{pmatrix}_{2A,T} \tag{3.102}$$

But it is still unclear how terms like 3.89, arising from the auxiliary space, come about.

3.2.2 My hypothesis for the supermatrix

By reverse engineering from the matrix vector products given in the supplemental material, I have found the form (we have defined $P = O + V$)

$$\boldsymbol{H} = \begin{pmatrix} \boldsymbol{F}_{P,P} & \begin{pmatrix}\boldsymbol{V}^{\text{2h1p}} & \boldsymbol{V}^{\text{2h1p}}\end{pmatrix}_{P,2O^2V} & \begin{pmatrix}\boldsymbol{V}^{\text{2p1h}} & \boldsymbol{V}^{\text{2p1h}}\end{pmatrix}_{P,2OV^2} \\ \begin{pmatrix} \left(\boldsymbol{V}^{\text{2h1p}}\right)^\dagger \\ -\left(\boldsymbol{V}^{\text{2h1p}}\right)^\dagger \end{pmatrix}_{2O^2V,P} & \boldsymbol{C}^{\text{2hlp}}_{2O^2V,2O^2V} & \boldsymbol{0} \\ \begin{pmatrix} \left(\boldsymbol{V}^{\text{2p1h}}\right)^\dagger \\ -\left(\boldsymbol{V}^{\text{2p1h}}\right)^\dagger \end{pmatrix}_{2OV^2,P} & \boldsymbol{0} & \boldsymbol{C}^{\text{2plh}}_{2OV^2,2OV^2} \end{pmatrix} \tag{3.103}$$

with

$$V^{2h1p}_{p,k[ia]} = \langle pa|ki\rangle \equiv (pk|ia) \tag{3.104}$$
$$V^{2p1h}_{p,[ia]c} = \langle pi|ac\rangle \equiv (pc|ia) \tag{3.105}$$
$$\tag{3.106}$$

and

$$C^{\text{2hlp}}_{i[ka],j[lb]} = \begin{pmatrix} \varepsilon^{1h}_{ij}\delta_{kl}\delta_{ab} - [\mathbf{N}\tilde{\mathbf{M}}]^{\text{xx}}_{ka,lb}\delta_{ij} & -[\mathbf{N}\tilde{\mathbf{M}}]^{\text{xd}}_{ka,lb}\delta_{ij} \\ -[\mathbf{N}\tilde{\mathbf{M}}]^{\text{dx}}_{ka,lb}\delta_{ij} & \varepsilon^{1h}_{ij}\delta_{kl}\delta_{ab} - [\mathbf{N}\tilde{\mathbf{M}}]^{\text{dd}}_{ja,lb}\delta_{ij} \end{pmatrix} = \delta_{kl}\delta_{ab}\left(\boldsymbol{\varepsilon}^{1h} \oplus_{\text{diag}} \boldsymbol{\varepsilon}^{1h}\right) - \delta_{ij}\boldsymbol{N}\tilde{\mathbf{M}} \tag{3.107}$$

$$C^{\text{2plh}}_{[kc]a,[ld]b} = \begin{pmatrix} \varepsilon^{1p}_{ab}\delta_{kl}\delta_{cd} + [\mathbf{N}\tilde{\mathbf{M}}]^{\text{xx}}_{kc,ld}\delta_{ab} & [\mathbf{N}\tilde{\mathbf{M}}]^{\text{xd}}_{kc,ld}\delta_{ab} \\ [\mathbf{N}\tilde{\mathbf{M}}]^{\text{dx}}_{kc,ld}\delta_{ab} & \varepsilon^{1p}_{ab}\delta_{kl}\delta_{cd} + [\mathbf{N}\tilde{\mathbf{M}}]^{\text{dd}}_{kc,ld}\delta_{ab} \end{pmatrix} = \delta_{kl}\delta_{cd}\left(\boldsymbol{\varepsilon}^{1p} \oplus_{\text{diag}} \boldsymbol{\varepsilon}^{1p}\right) + \delta_{ab}\boldsymbol{N}\tilde{\mathbf{M}} \tag{3.108}$$

with $\boldsymbol{\varepsilon}^{1h}$ and $\boldsymbol{\varepsilon}^{1p}$ diagonal matrices with the 1h and 1p energies on the diagonal, so actually $\varepsilon^{1h}_{ij} = \varepsilon^{1h}_{ii}\delta_{ij}$ and $\varepsilon^{1p}_{ab} = \varepsilon^{1p}_{aa}\delta_{ab}$, respectively and $\tilde{\boldsymbol{M}} = \boldsymbol{M} + \eta\boldsymbol{N}\Theta(-\boldsymbol{N}\boldsymbol{M})$ where

$$\boldsymbol{M} = \begin{pmatrix} \boldsymbol{A} & \boldsymbol{B} \\ \boldsymbol{B} & \boldsymbol{A} \end{pmatrix}_{2OV,2OV} \qquad \boldsymbol{N} = \begin{pmatrix} \mathbf{1} & \mathbf{0} \\ \mathbf{0} & -\mathbf{1} \end{pmatrix}_{2OV,2OV} \tag{3.109}$$

and η is some very large number.

Connecting to the exact form of GW-RPA

We know the eigendecomposition $\boldsymbol{N}\tilde{\mathbf{M}} = \boldsymbol{Z}\begin{pmatrix} \boldsymbol{\Omega}_+ & 0 \\ 0 & -\boldsymbol{\Omega}_+ + \boldsymbol{\eta} \end{pmatrix}\boldsymbol{Z}^{-1}$. This means we can rewrite 3.107 and 3.108 as

$$C^{\text{2hlp}}_{i[ka],j[lb]} = \delta_{kl}\delta_{ab}\left(\boldsymbol{\varepsilon}^{1h} \oplus_{\text{diag}} \boldsymbol{\varepsilon}^{1h}\right) - \delta_{ij}\boldsymbol{Z}\begin{pmatrix} \boldsymbol{\Omega}_+ & 0 \\ 0 & -\boldsymbol{\Omega}_+ + \boldsymbol{\eta} \end{pmatrix}\boldsymbol{Z}^{-1} \tag{3.110}$$

$$C^{\text{2plh}}_{[kc]a,[ld]b} = \delta_{kl}\delta_{cd}\left(\boldsymbol{\varepsilon}^{1p} \oplus_{\text{diag}} \boldsymbol{\varepsilon}^{1p}\right) + \delta_{ab}\boldsymbol{Z}\begin{pmatrix} \boldsymbol{\Omega}_+ & 0 \\ 0 & -\boldsymbol{\Omega}_+ + \boldsymbol{\eta} \end{pmatrix}\boldsymbol{Z}^{-1} \tag{3.111}$$

Why would we want an Mtilde of this form?

Now, we know the following identity to be true

$$\boldsymbol{MZ} = \boldsymbol{NZ}\begin{pmatrix} \boldsymbol{\Omega}_+ & 0 \\ 0 & -\boldsymbol{\Omega}_+ \end{pmatrix} \tag{3.112}$$

with eigenvectors $\boldsymbol{Z} = \begin{pmatrix} \boldsymbol{X} & \boldsymbol{Y} \\ \boldsymbol{Y} & \boldsymbol{X} \end{pmatrix}_{2OV,2OV}$ and eigenvalues $\begin{pmatrix} \boldsymbol{\Omega}_+ & 0 \\ 0 & -\boldsymbol{\Omega}_+ \end{pmatrix}$. Now we can use the fact that the action of a scalar function f, such as the step function, on a diagonalizable matrix $\boldsymbol{X} \equiv \boldsymbol{Y}\boldsymbol{\Lambda}\boldsymbol{Y}^{-1}$ can be expressed as $f(\boldsymbol{X}) = \boldsymbol{Y}f(\boldsymbol{\Lambda})\boldsymbol{Y}^{-1}$ so we can write

$$\Theta(-\boldsymbol{NM}) = \boldsymbol{Z}\left(\begin{array}{cc} \Theta(-\boldsymbol{\Omega}_+) & 0 \\ 0 & \Theta(\boldsymbol{\Omega}_+) \end{array}\right)\boldsymbol{Z}^{-1} = \boldsymbol{Z}\left(\begin{array}{cc} \boldsymbol{0} & 0 \\ 0 & \boldsymbol{1} \end{array}\right)\boldsymbol{Z}^{-1} \tag{3.113}$$

$$\implies \tilde{\boldsymbol{M}}\boldsymbol{Z} = \boldsymbol{NZ}\left(\begin{array}{cc} \boldsymbol{\Omega}_+ & 0 \\ 0 & -\boldsymbol{\Omega}_+ + \boldsymbol{\eta} \end{array}\right) \quad \text{and} \quad \tilde{\boldsymbol{M}} = \boldsymbol{ZN}\left(\begin{array}{cc} \boldsymbol{\Omega}_+ & 0 \\ 0 & -\boldsymbol{\Omega}_+ + \boldsymbol{\eta} \end{array}\right)\boldsymbol{Z}^{-1} \tag{3.114}$$

So now the purpose of the η becomes clear; it is removing the influence of the negative RPA roots, so that in the GW supermatrix we can easily disregard the portion of its spectrum which inherits from the negative RPA roots. After all, the expression for the GW correlation self-energy is

$$\Sigma^c_{pq}(\omega) = \sum_{\mu}^{RPA}\left[\underbrace{\sum_i^{occ}\frac{\rho^\mu_{pi}\rho^\mu_{qi}}{\omega - (\epsilon_i - \Omega_\mu) - i\eta}}_{2h1p} + \underbrace{\sum_a^{virt}\frac{\rho^n_{pa}\rho^n_{qa}}{\omega - (\epsilon_a + \Omega_\mu) + i\eta}}_{1h2p}\right] \tag{3.115}$$

with the transition densities $\rho^\nu_{rs} = \sum_{ia}(rs|ia)\,(X^\nu_{ia} + Y^\nu_{ia})$, where ν is the RPA index. The standard way to show that this maps to GW-RPA is via similarity transformations, like we did with GW-TDA in 3.1.2, but we can't do this her because $\boldsymbol{N}\tilde{\boldsymbol{M}}$ is not a Hermitian.

Avoid constructing Theta

Right now in order to construct $\Theta(-\boldsymbol{NM})$, I have to diagonalize $\boldsymbol{NM}$ first, which is $O(N^6)$ cost. To avoid this, we can approximate the step function by Chebyshev polynomials. But we don't want to form this Chebyshev polynomial at the beginning of the Davidson iteration, but rather just make an approximation, that will keep improving as we iterate. It is true, though, that we can efficiently estimate the bounds of the spectrum of $\boldsymbol{NM}$ using a few iterations of Arnoldi, getting $\lambda_{\max}$ (because this is RPA, we know that $\lambda_{\min} = -\lambda_{\max}$). So we can rescale the matrix so that its spectrum lies within the interval $[-1, 1]$; this is accomplished by dividing by $\lambda_{\max}$. Then, at each iteration of Davidson, we can apply this polynomial to the current guess vectors. This will be $O(N^4)$ cost per iteration, which is not too bad. The hope is that as we iterate, the guess vectors will span more and more of the space spanned by the negative eigenvalues of $\boldsymbol{NM}$, so that we are effectively applying the step function to the relevant subspace.

Attempting to transform to a Hermitian matrix

The supermatrix 3.103 is not pseudohermitian, or Hermitian under the super metric, so it really is just a similarity transform

$$\boldsymbol{\mathcal{N}} = \begin{pmatrix} \mathbf{1}_{P,P} & \mathbf{0} & \mathbf{0} \\ \mathbf{0} & \mathbf{1}_{O,O} \otimes \boldsymbol{N}_{2OV,2OV} & \mathbf{0} \\ \mathbf{0} & \mathbf{0} & \mathbf{1}_{V,V} \otimes \boldsymbol{N}_{2OV,2OV} \end{pmatrix} \tag{3.116}$$

$$\implies \boldsymbol{H}^\dagger = \boldsymbol{\mathcal{N}} \boldsymbol{H} \boldsymbol{\mathcal{N}}^{-1} \tag{3.117}$$

$$= \begin{pmatrix} \mathbf{1} & \mathbf{0} & \mathbf{0} \\ \mathbf{0} & \mathbf{1} \otimes \boldsymbol{N} & \mathbf{0} \\ \mathbf{0} & \mathbf{0} & \mathbf{1} \otimes \boldsymbol{N} \end{pmatrix} \begin{pmatrix} \boldsymbol{F} & \begin{pmatrix} \boldsymbol{V}^{2\text{h1p}} & \boldsymbol{V}^{2\text{h1p}} \end{pmatrix} & \begin{pmatrix} \boldsymbol{V}^{2\text{p1h}} & \boldsymbol{V}^{2\text{p1h}} \end{pmatrix} \\ \begin{pmatrix} \left(\boldsymbol{V}^{2\text{h1p}}\right)^\dagger \\ -\left(\boldsymbol{V}^{2\text{h1p}}\right)^\dagger \end{pmatrix} & \boldsymbol{C}^{2\text{hlp}} & \mathbf{0} \\ \begin{pmatrix} \left(\boldsymbol{V}^{2\text{p1h}}\right)^\dagger \\ -\left(\boldsymbol{V}^{2\text{p1h}}\right)^\dagger \end{pmatrix} & \mathbf{0} & \boldsymbol{C}^{2\text{plh}} \end{pmatrix} \begin{pmatrix} \mathbf{1} & \mathbf{0} & \mathbf{0} \\ \mathbf{0} & \mathbf{1} \otimes \boldsymbol{N} & \mathbf{0} \\ \mathbf{0} & \mathbf{0} & \mathbf{1} \otimes \boldsymbol{N} \end{pmatrix} \tag{3.118}$$

$$= \begin{pmatrix} \boldsymbol{F} & \begin{pmatrix} \boldsymbol{V}^{2\text{h1p}} & \boldsymbol{V}^{2\text{h1p}} \end{pmatrix} & \begin{pmatrix} \boldsymbol{V}^{2\text{p1h}} & \boldsymbol{V}^{2\text{p1h}} \end{pmatrix} \\ (\mathbf{1} \otimes \boldsymbol{N}) \begin{pmatrix} \left(\boldsymbol{V}^{2\text{h1p}}\right)^\dagger \\ -\left(\boldsymbol{V}^{2\text{h1p}}\right)^\dagger \end{pmatrix} & (\mathbf{1} \otimes \boldsymbol{N})\, \boldsymbol{C}^{2\text{hlp}} & \mathbf{0} \\ (\mathbf{1} \otimes \boldsymbol{N}) \begin{pmatrix} \left(\boldsymbol{V}^{2\text{p1h}}\right)^\dagger \\ -\left(\boldsymbol{V}^{2\text{p1h}}\right)^\dagger \end{pmatrix} & \mathbf{0} & (\mathbf{1} \otimes \boldsymbol{N})\, \boldsymbol{C}^{2\text{plh}} \end{pmatrix} \begin{pmatrix} \mathbf{1} & \mathbf{0} & \mathbf{0} \\ \mathbf{0} & \mathbf{1} \otimes \boldsymbol{N} & \mathbf{0} \\ \mathbf{0} & \mathbf{0} & \mathbf{1} \otimes \boldsymbol{N} \end{pmatrix} \tag{3.119}$$

$$\tag{3.120}$$

To simplify notation, from here on, we will just consider the 2h1p sector

$$\boldsymbol{\mathcal{N}}^{2\text{h1p}} \boldsymbol{H}^{2\text{h1p}} \left(\boldsymbol{\mathcal{N}}^{2\text{h1p}}\right)^{-1} \tag{3.121}$$

$$= \begin{pmatrix} \boldsymbol{F}_P & \left[\begin{pmatrix} \boldsymbol{V}^{2\text{h1p}} & \boldsymbol{V}^{2\text{h1p}} \end{pmatrix} (\mathbf{1} \otimes \boldsymbol{N})\right]_{P,2O^2V} \\ \left[(\mathbf{1} \otimes \boldsymbol{N}) \begin{pmatrix} \left(\boldsymbol{V}^{2\text{h1p}}\right)^\dagger \\ -\left(\boldsymbol{V}^{2\text{h1p}}\right)^\dagger \end{pmatrix}\right]_{2O^2V,P} & (\mathbf{1} \otimes \boldsymbol{N})_{2O^2V}\, \boldsymbol{C}^{2\text{hlp}}_{2O^2V}\, (\mathbf{1} \otimes \boldsymbol{N})_{2O^2V} \end{pmatrix} \tag{3.122}$$

Consider just the multiplication

$$\begin{pmatrix} \boldsymbol{V}^{2\text{h1p}} & \boldsymbol{V}^{2\text{h1p}} \end{pmatrix} (\mathbf{1} \otimes \boldsymbol{N}) = \begin{pmatrix} \boldsymbol{V}^{2\text{h1p}} & -\boldsymbol{V}^{2\text{h1p}} \end{pmatrix} \tag{3.123}$$

$$\tag{3.124}$$

and

$$(\mathbf{1} \otimes \boldsymbol{N}) \begin{pmatrix} \left(\boldsymbol{V}^{2\text{h1p}}\right)^\dagger \\ -\left(\boldsymbol{V}^{2\text{h1p}}\right)^\dagger \end{pmatrix} = \begin{pmatrix} \left(\boldsymbol{V}^{2\text{h1p}}\right)^\dagger \\ \left(\boldsymbol{V}^{2\text{h1p}}\right)^\dagger \end{pmatrix} \tag{3.125}$$

But now we are left to evaluate

$$(\mathbf{1}\otimes\boldsymbol{N})_{2O^2V,2O^2V}\,\boldsymbol{C}^{\text{2hlp}}_{2O^2V,2O^2V}\,(\mathbf{1}\otimes\boldsymbol{N})_{2O^2V,2O^2V} \tag{3.126}$$

$$= \sum_{i'[k'a']}\sum_{j'[l'b']}(\delta_{ii'}N_{k'a',ka})\left[\begin{pmatrix}\varepsilon^{1h}_{i'j'}\delta_{k'l'}\delta_{a'b'} & 0\\ 0 & \varepsilon^{1h}_{i'j'}\delta_{k'l'}\delta_{a'b'}\end{pmatrix}-\begin{pmatrix}\delta_{i'j'}[\mathbf{N}\tilde{\mathbf{M}}]^{\text{xx}}_{k'a',l'b'} & \delta_{i'j'}[\mathbf{N}\tilde{\mathbf{M}}]^{\text{xd}}_{k'a',l'b'}\\ \delta_{i'j'}[\mathbf{N}\tilde{\mathbf{M}}]^{\text{dx}}_{k'a',l'b'} & \delta_{i'j'}[\mathbf{N}\tilde{\mathbf{M}}]^{\text{dd}}_{k'a',l'b'}\end{pmatrix}\right] \tag{3.127}$$

$$\times(\delta_{jj'}N_{lb,l'b'}) \tag{3.128}$$

$$= \sum_{i'[k'a']}\sum_{j'[l'b']}\begin{pmatrix}\delta_{ii'}\delta_{k'k}\delta_{a'a} & 0\\ 0 & -\delta_{ii'}\delta_{k'k}\delta_{a'a}\end{pmatrix}\left[\begin{pmatrix}\varepsilon^{1h}_{i'j'}\delta_{k'l'}\delta_{a'b'} & 0\\ 0 & \varepsilon^{1h}_{i'j'}\delta_{k'l'}\delta_{a'b'}\end{pmatrix}-\begin{pmatrix}\delta_{i'j'}[\mathbf{N}\tilde{\mathbf{M}}]^{\text{xx}}_{k'a',l'b'} & \delta_{i'j'}[\mathbf{N}\tilde{\mathbf{M}}]^{\text{xd}}_{k'a',l'b'}\\ \delta_{i'j'}[\mathbf{N}\tilde{\mathbf{M}}]^{\text{dx}}_{k'a',l'b'} & \delta_{i'j'}[\mathbf{N}\tilde{\mathbf{M}}]^{\text{dd}}_{k'a',l'b'}\end{pmatrix}\right. \tag{3.129}$$

$$\times\begin{pmatrix}\delta_{jj'}\delta_{ll'}\delta_{aa'} & 0\\ 0 & -\delta_{jj'}\delta_{ll'}\delta_{aa'}\end{pmatrix} \tag{3.130}$$

$$= \left[\begin{pmatrix}\varepsilon^{1h}_{ij}\delta_{kl}\delta_{ab} & 0\\ 0 & \varepsilon^{1h}_{ij}\delta_{kl}\delta_{ab}\end{pmatrix}-\sum_{i'[k'a']}\sum_{j'[l'b']}\begin{pmatrix}\delta_{ii'}\delta_{k'k}\delta_{a'a} & 0\\ 0 & -\delta_{ii'}\delta_{k'k}\delta_{a'a}\end{pmatrix}\begin{pmatrix}\delta_{i'j'}[\mathbf{N}\tilde{\mathbf{M}}]^{\text{xx}}_{k'a',l'b'} & \delta_{i'j'}[\mathbf{N}\tilde{\mathbf{M}}]^{\text{xd}}_{k'a',l'b'}\\ \delta_{i'j'}[\mathbf{N}\tilde{\mathbf{M}}]^{\text{dx}}_{k'a',l'b'} & \delta_{i'j'}[\mathbf{N}\tilde{\mathbf{M}}]^{\text{dd}}_{k'a',l'b'}\end{pmatrix}\right. \tag{3.131}$$

$$\left.\times\begin{pmatrix}\delta_{jj'}\delta_{ll'}\delta_{aa'} & 0\\ 0 & -\delta_{jj'}\delta_{ll'}\delta_{aa'}\end{pmatrix}\right] \tag{3.132}$$

$$= \left[\begin{pmatrix}\varepsilon^{1h}_{ij}\delta_{kl}\delta_{ab} & 0\\ 0 & \varepsilon^{1h}_{ij}\delta_{kl}\delta_{ab}\end{pmatrix}-\delta_{ij}\begin{pmatrix}[\mathbf{N}\tilde{\mathbf{M}}]^{\text{xx}}_{ka,lb} & -[\mathbf{N}\tilde{\mathbf{M}}]^{\text{xd}}_{ka,lb}\\ -[\mathbf{N}\tilde{\mathbf{M}}]^{\text{dx}}_{ka,lb} & [\mathbf{N}\tilde{\mathbf{M}}]^{\text{dd}}_{ka,lb}\end{pmatrix}\right] \tag{3.133}$$

This is nothing new, but I have left it here in case it becomes useful.

Identification analysis

Some explanation of the terminology is in order. When I talk about a priori identification, I mean that I identify eigenvalues within the spectrum as QPEs by identifying the eigenpair whose eigenvector has the largest overlap with the MO. This is what I have and still am always doing to identify QPEs in the exact ED spectrum; mathematically, it seemed like the most straightforward approach. However, because there is not a unitary transformation to relate the Supp. supermatrix to the exact one, I suspect that this method may not work for the Supp. supermatrix. In a posteriori identification, I choose which eigenvalue of Supp. supermatrix is closest to the exact QPE, by computing all the differences after both diagonalizations have proceeded. Note that this is not a sustainable approach, but I have included it to highlight that my a priori identification method is not working for the Supp. supermatrix. Alternatively, I have seen in this GW supermatrix literature sometimes people adopt different methods for selecting QPEs from the spectrum, so maybe I can try out some other ones. Attached is a screenshot from Tim's paper. Maybe I can try one of the alternatives he proposes. So I see two things that I need to do:

1. Explore different methods for selecting QPEs from the spectrum of the Supp. supermatrix, like the ones proposed in Tim's paper.

2. Find a way to mathematically bound the difference of the Supp. supermatrix with the exact one. From Googling, I see that there are some different ways, for instance, from the idea for the pseudospectrum.

The first plot that I have attached has the exact same format as what I sent you earlier today, but with CO included, as you requested. The following plots look through all the roots for certain molecule/parameter pairings for CO and N2; these are the parameters that seem to be presenting me with the most identification trouble.

What to do next?

I find numerically that all the eigenvalues of the Supp. supermatrix 3.103 are real. This implies that there is some metric with respect to which the matrix is pseudo-Hermitian. I have not been able to find it yet. I have tried

$$\boldsymbol{\mathcal{N}} = \begin{pmatrix} \mathbf{1}_{P,P} & \mathbf{0} & \mathbf{0} \\ \mathbf{0} & \mathbf{1}_{O,O} \otimes \boldsymbol{N}_{2OV,2OV} & \mathbf{0} \\ \mathbf{0} & \mathbf{0} & \mathbf{1}_{V,V} \otimes \boldsymbol{N}_{2OV,2OV} \end{pmatrix} \tag{3.134}$$

but this doesn't work (see 3.2.2). I probably want to inverstigate this further first, before I move on to a non-Hermitian Davidson, because if I can find the metric, I can use a Hermitian Davidson, which is simpler.

3.2.3 Alternate possibilities (assuming a typo was made)

Supermetric: Kronecker product, Auxiliary: Kronecker sum

Note that it makes the most sense for the auxiliary block to be a Kronecker sum, because this was the case for TDA as can be seen in 3.9. So here, I tried the case where the supermetric is a Kronecker product

$$\boldsymbol{\mathcal{N}}^{\text{2hlp}} = \begin{pmatrix} \mathbf{1}_{P,P} & 0 \\ 0 & \mathbf{1}_{O,O} \otimes \boldsymbol{N}_{2OV,2OV} \end{pmatrix} \tag{3.135}$$

and the auxiliary block is a Kronecker sum. Now we can consider the matrix multiplication

$$\boldsymbol{\mathcal{N}}^{\text{2hlp}} \boldsymbol{H}^{\text{2hlp}} = \begin{pmatrix} \mathbf{1}_{P,P} & 0 \\ 0 & \mathbf{1}_{O,O} \otimes \boldsymbol{N}_{2OV,2OV} \end{pmatrix} \begin{pmatrix} \boldsymbol{F}_{P,P} & \boldsymbol{V}^{\text{2h1p}}_{P,O^2V} & \boldsymbol{V}^{\text{2h1p}}_{P,O^2V} \\ \left(\boldsymbol{V}^{\text{2h1p}}_{P,O^2V}\right)^\dagger & & \\ \left(\boldsymbol{V}^{\text{2h1p}}_{P,O^2V}\right)^\dagger & & \boldsymbol{C}^{\text{2hlp}}_{2O^2V,2O^2V} \end{pmatrix} \tag{3.136}$$

$$= \begin{pmatrix} \boldsymbol{F}_{P,P} & \begin{pmatrix} \boldsymbol{V}^{\text{2h1p}} & \boldsymbol{V}^{\text{2h1p}} \end{pmatrix}_{P,2O^2V} \\ (\mathbf{1} \otimes \boldsymbol{N})_{2O^2V,2O^2V} \begin{pmatrix} \left(\boldsymbol{V}^{\text{2h1p}}\right)^\dagger \\ \left(\boldsymbol{V}^{\text{2h1p}}\right)^\dagger \end{pmatrix}_{2O^2V,P} & (\mathbf{1} \otimes \boldsymbol{N})_{2O^2V,2O^2V}\, \boldsymbol{C}^{\text{2hlp}}_{2O^2V,2O^2V} \end{pmatrix} \tag{3.137}$$

$$\tag{3.138}$$

Evaluating the off-diagonal term, we have ($\boldsymbol{V}^{2\text{h1p}}$ has the elements $V^{2\text{ h1p}}_{p,k[ia]} = \langle pa|ki\rangle \equiv (pk|ia)$ and $\boldsymbol{N}_{2OV,2OV} = \mathbf{1}_{OV,OV} \oplus_{\text{direct}} -\mathbf{1}_{OV,OV}$):

$$\left(\mathbf{1}_{O,O} \otimes \boldsymbol{N}_{2OV,2OV}\right) \begin{pmatrix} \left(\boldsymbol{V}^{2\text{h1p}}\right)^{\dagger} \\ \left(\boldsymbol{V}^{2\text{h1p}}\right)^{\dagger} \end{pmatrix}_{2O^2V,P} = \begin{pmatrix} \left(\boldsymbol{V}^{2\text{h1p}}\right)^{\dagger} \\ -\left(\boldsymbol{V}^{2\text{h1p}}\right)^{\dagger} \end{pmatrix}_{2O^2V,P} \tag{3.139}$$

Evaluating the auxiliary term with $\boldsymbol{C}^{2\text{hlp}}_{2O^2V,2O^2V} = \epsilon^{1\text{ h}} \oplus_{\text{kron}} (-\tilde{\boldsymbol{M}}) = \boldsymbol{\epsilon}^{1\text{ h}}_{O,O} \otimes \mathbf{1}_{2OV,2OV} + \mathbf{1}_{O,O} \otimes (-\tilde{\boldsymbol{M}})_{2OV,2OV}$ we have

$$\begin{aligned}
\left(\mathbf{1} \otimes \boldsymbol{N}\right) \boldsymbol{C}^{2\text{hlp}} &= \left(\mathbf{1}_{O,O} \otimes \boldsymbol{N}_{2OV,2OV}\right) \left(\boldsymbol{\epsilon}^{1\text{ h}}_{O,O} \otimes \mathbf{1}_{2OV,2OV} + \mathbf{1}_{O,O} \otimes (-\tilde{\boldsymbol{M}})_{2OV,2OV}\right) && (3.140)\\
&= \boldsymbol{\epsilon}^{1\text{ h}}_{O,O} \otimes \boldsymbol{N}_{2OV,2OV} + \mathbf{1}_{O,O} \otimes -\boldsymbol{N}_{2OV,2OV} \tilde{\boldsymbol{M}}_{2OV,2OV} && (3.141)\\
&= \left[\left(\boldsymbol{\epsilon}^{1\text{ h}}_{O,O} \otimes \mathbf{1}_{OV,OV}\right) \oplus_{\text{direct}} - \left(\boldsymbol{\epsilon}^{1\text{ h}}_{O,O} \otimes \mathbf{1}_{OV,OV}\right)\right] + \left(\mathbf{1}_{O,O} \otimes -\boldsymbol{N}_{2OV,2OV} \tilde{\boldsymbol{M}}_{2OV,2OV}\right) && (3.142)\\
&= \begin{pmatrix} \boldsymbol{\epsilon}^{1\text{ h}} \otimes \mathbf{1} & \mathbf{0} \\ \mathbf{0} & -\left(\boldsymbol{\epsilon}^{1\text{ h}} \otimes \mathbf{1}\right) \end{pmatrix}_{2O^2V} + \left(\mathbf{1}_O \otimes -\boldsymbol{Z}_{2OV} \begin{pmatrix} \boldsymbol{\Omega} & \mathbf{0} \\ \mathbf{0} & \eta - \boldsymbol{\Omega} \end{pmatrix}_{2OV} \boldsymbol{Z}^{-1}_{2OV}\right)_{2O^2V} && (3.143)\\
&= \begin{pmatrix} \boldsymbol{\epsilon}^{1\text{ h}} \otimes \mathbf{1} & \mathbf{0} \\ \mathbf{0} & -\left(\boldsymbol{\epsilon}^{1\text{ h}} \otimes \mathbf{1}\right) \end{pmatrix}_{2O^2V} - \left[\left(\mathbf{1} \otimes \boldsymbol{Z}\right) \begin{pmatrix} \mathbf{1} \otimes \boldsymbol{\Omega} & \mathbf{0} \\ \mathbf{0} & \mathbf{1} \otimes (\eta - \boldsymbol{\Omega}) \end{pmatrix} \left(\mathbf{1} \otimes \boldsymbol{Z}^{-1}\right)\right]_{2O^2V} && (3.144)\\
&= \left(\mathbf{1} \otimes \boldsymbol{Z}\right) \begin{pmatrix} \boldsymbol{\epsilon}^{1\text{ h}} \otimes \mathbf{1} + \mathbf{1} \otimes -\boldsymbol{\Omega} & \mathbf{0} \\ \mathbf{0} & -\left(\boldsymbol{\epsilon}^{1\text{ h}} \otimes \mathbf{1}\right) - \left(\mathbf{1} \otimes (\eta - \boldsymbol{\Omega})\right) \end{pmatrix} \left(\mathbf{1} \otimes \boldsymbol{Z}^{-1}\right) && (3.145)\\
& && (3.146)
\end{aligned}$$

where $\boldsymbol{Z} = \begin{pmatrix} \boldsymbol{X} & \boldsymbol{Y} \\ \boldsymbol{Y} & \boldsymbol{X} \end{pmatrix}$ is the eigenvector matrix and $\boldsymbol{\Omega}$ is the diagonal matrix of positive excitation energies.

Similarity transformation

Now let us define the rotation $\boldsymbol{\zeta} = \begin{pmatrix} \mathbf{1} & 0 \\ 0 & \mathbf{1}\otimes \boldsymbol{Z} \end{pmatrix}$. We can left multiply by $\boldsymbol{\zeta}^{-1}$ and right multiply by $\boldsymbol{\zeta}$ to get

$$\boldsymbol{\zeta}^{-1}\boldsymbol{\mathcal{N}}^{\text{2hlp}}\boldsymbol{H}^{\text{2hlp}}\boldsymbol{\zeta} = \begin{pmatrix} \mathbf{1} & 0 \\ 0 & \mathbf{1}\otimes \boldsymbol{Z}^{-1} \end{pmatrix} \begin{pmatrix} \boldsymbol{F} & \begin{pmatrix} \boldsymbol{V}^{\text{2h1p}} & \boldsymbol{V}^{\text{2h1p}} \end{pmatrix} \\ \begin{pmatrix} \left(\boldsymbol{V}^{\text{2h1p}}\right)^{\dagger} \\ -\left(\boldsymbol{V}^{\text{2h1p}}\right)^{\dagger} \end{pmatrix} & \left(\mathbf{1}\otimes \boldsymbol{N}\right)\boldsymbol{C}^{\text{2hlp}} \end{pmatrix} \begin{pmatrix} \mathbf{1} & 0 \\ 0 & \mathbf{1}\otimes \boldsymbol{Z} \end{pmatrix} \tag{3.147}$$

$$= \begin{pmatrix} \boldsymbol{F} & \begin{pmatrix} \boldsymbol{V}^{\text{2h1p}} & \boldsymbol{V}^{\text{2h1p}} \end{pmatrix}\left(\mathbf{1}\otimes \boldsymbol{Z}\right) \\ \left(\mathbf{1}\otimes \boldsymbol{Z}^{-1}\right)\begin{pmatrix} \left(\boldsymbol{V}^{\text{2h1p}}\right)^{\dagger} \\ -\left(\boldsymbol{V}^{\text{2h1p}}\right)^{\dagger} \end{pmatrix} & \left(\mathbf{1}\otimes \boldsymbol{Z}^{-1}\boldsymbol{Z}\right)\begin{pmatrix} \boldsymbol{\epsilon}^{1\text{ h}} \oplus_{\text{kron}} -\boldsymbol{\Omega} & \mathbf{0} \\ \mathbf{0} & -\boldsymbol{\epsilon}^{1\text{ h}} \oplus_{\text{kron}} [\eta - \boldsymbol{\Omega}] \end{pmatrix}\left(\mathbf{1}\otimes \boldsymbol{Z}^{-1}\boldsymbol{Z}\right) \end{pmatrix} \tag{3.148}$$

$$= \begin{pmatrix} \boldsymbol{F} & \begin{pmatrix} \boldsymbol{V}^{\text{2h1p}} & \boldsymbol{V}^{\text{2h1p}} \end{pmatrix}\left(\mathbf{1}\otimes \begin{pmatrix} \boldsymbol{X} & \boldsymbol{Y} \\ \boldsymbol{Y} & \boldsymbol{X} \end{pmatrix}\right) \\ \left(\mathbf{1}\otimes \begin{pmatrix} \boldsymbol{X} & \boldsymbol{Y} \\ \boldsymbol{Y} & \boldsymbol{X} \end{pmatrix}^{-1}\right)\left(\mathbf{1}\otimes \boldsymbol{N}\right)\begin{pmatrix} \left(\boldsymbol{V}^{\text{2h1p}}\right)^{\dagger} \\ \left(\boldsymbol{V}^{\text{2h1p}}\right)^{\dagger} \end{pmatrix} & \begin{pmatrix} \boldsymbol{\epsilon}^{1\text{ h}} \oplus_{\text{kron}} -\boldsymbol{\Omega} & \mathbf{0} \\ \mathbf{0} & -\boldsymbol{\epsilon}^{1\text{ h}} \oplus_{\text{kron}} [\eta - \boldsymbol{\Omega}] \end{pmatrix} \end{pmatrix} \tag{3.149}$$

$$= \begin{pmatrix} \boldsymbol{F} & \begin{pmatrix} \boldsymbol{V}^{\text{2h1p}}\left(\boldsymbol{X}+\boldsymbol{Y}\right) & \boldsymbol{V}^{\text{2h1p}}\left(\boldsymbol{X}+\boldsymbol{Y}\right) \end{pmatrix} \\ \left(\mathbf{1}\otimes \begin{pmatrix} \boldsymbol{X} & \boldsymbol{Y} \\ \boldsymbol{Y} & \boldsymbol{X} \end{pmatrix}^{-1}\right)\begin{pmatrix} \left(\boldsymbol{V}^{\text{2h1p}}\right)^{\dagger} \\ -\left(\boldsymbol{V}^{\text{2h1p}}\right)^{\dagger} \end{pmatrix} & \begin{pmatrix} \boldsymbol{\epsilon}^{1\text{ h}} \oplus_{\text{kron}} -\boldsymbol{\Omega} & \mathbf{0} \\ \mathbf{0} & -\boldsymbol{\epsilon}^{1\text{ h}} \oplus_{\text{kron}} [\eta - \boldsymbol{\Omega}] \end{pmatrix} \end{pmatrix} \tag{3.150}$$

But because it is true that $\boldsymbol{Z}$ are the eigenvectors of a non-Hermitian eigenproblem, it is not true that $\boldsymbol{Z}^{-1} = \boldsymbol{Z}^{\dagger}$, so we cannot simplify the lower left block any further. Accordingly, doing ED of this form for the supermatrices gives the wrong spectrum, but I have included this derivation of the similarity transformation because it seems like the most promising approach I have considered so far.

Supermetric: Kronecker sum, Auxiliary: Kronecker product

Let us try the alternate case where $\boldsymbol{C}^{\text{2hlp}} = \left(\boldsymbol{\epsilon}^{1\text{ h}} \otimes -\tilde{\boldsymbol{M}}\right)$, which gives

$$\left(\mathbf{1}\oplus_{\text{kron}}\boldsymbol{N}\right)\boldsymbol{C}^{\text{2hlp}} = \left(\mathbf{1}_{O,O}\oplus_{\text{kron}}\boldsymbol{N}_{2OV,2OV}\right)\left(\boldsymbol{\epsilon}^{1\text{ h}}_{O,O}\otimes(-\tilde{\boldsymbol{M}})_{2OV,2OV}\right) \tag{3.151}$$

$$= \left(\mathbf{1}_{O}\otimes\mathbf{1}_{2OV} + \mathbf{1}_{O}\otimes\boldsymbol{N}_{2OV}\right)\left(\boldsymbol{\epsilon}^{1\text{ h}}_{,O}\otimes(-\tilde{\boldsymbol{M}})_{2OV,}\right) \tag{3.152}$$

$$= \boldsymbol{\epsilon}^{1\text{ h}}\otimes -\tilde{\boldsymbol{M}} + \boldsymbol{\epsilon}^{1\text{ h}}\otimes -\boldsymbol{N}\tilde{\boldsymbol{M}} \tag{3.153}$$

$$\tag{3.154}$$

This is not what we want and the form for the off-diagonal term is the same as in the previous subsubsection.

They say that $\boldsymbol{V}^{\text{2h1p}}$ has the elements $V^{2\text{ h1p}}_{p,k[ia]} = \langle pa|ki\rangle \equiv (pk|ia)$ so we say that $\boldsymbol{v}^{\text{2h1p}}_{O,O^2V}$ is the first O rows of $\boldsymbol{V}^{\text{2h1p}}$, while $\boldsymbol{v}^{\text{2h1p}}_{V,O^2V}$ is the latter V rows of $\boldsymbol{V}^{\text{2h1p}}$.

Chapter 4

Auxiliary-boson *GW*

4.1 Constructing the Hamiltonian

The idea of this method is not to work in the MO basis, but rather to work in a basis of particle-hole excitations, which are approximated as bosons. So $\hat{a}_a^\dagger \hat{a}_i \approx \hat{b}_\nu^\dagger$ and $\hat{a}_i^\dagger \hat{a}_a \approx \hat{b}_\nu$, where in second quantization $\hat{a}$ are fermionic and $\hat{b}$ are bosonic operators, respectively. The drawback is that these bosonic operators no longer obey the Pauli exclusion principle; what was done above is known as the quasi-boson approximation. Then we define the electron-boson Hamiltonian as

$$\hat{H}^{\mathrm{eB}} = \hat{H}^{\mathrm{e}} + \hat{H}^{\mathrm{B}} + \hat{V}^{\mathrm{eB}} \tag{4.1}$$

where $\hat{H}^{\mathrm{e}}$ is the electronic Hamiltonian, $\hat{H}^{\mathrm{B}}$ is the bosonic Hamiltonian, and $\hat{V}^{\mathrm{eB}}$ is the electron-boson coupling term, given as

$$\hat{H}^e = \sum_{pq} f_{pq} \left\{ \hat{a}_p^\dagger \hat{a}_q \right\} \tag{4.2}$$

$$\hat{H}^B = \sum_{\nu\mu} A_{\nu\mu} \hat{b}_\nu^\dagger \hat{b}_\mu + \frac{1}{2} \sum_{\nu\mu} B_{\nu\mu} \left(\hat{b}_\nu^\dagger \hat{b}_\mu^\dagger + \hat{b}_\nu \hat{b}_\mu \right) \tag{4.3}$$

$$\hat{V}^{eB} = \sum_{pq,\nu} V_{pq\nu} \left\{ \hat{a}_p^\dagger \hat{a}_q \right\} \left(\hat{b}_\nu^\dagger + \hat{b}_\nu \right) \tag{4.4}$$

$A_{\nu\mu}$ and $B_{\nu\mu}$ denote the dRPA matrices, as

$$\begin{aligned} A_{\nu\mu} &= A_{ia,jb} = \delta_{ij}\delta_{ab} \left(\epsilon_a - \epsilon_i \right) + (ia|bj) \\ B_{v\mu} &= B_{ia,jb} = (ia|jb) \end{aligned} \tag{4.5}$$

and the electron-boson coupling term is defined as

$$V_{pq\nu} = V_{pq,ia} = (pq|ia) \tag{4.6}$$

As we will see shortly, this formalism has the ability to introduce the desired RPA screening. But the connection to Booth's ED is already clear; the physical space is represented by the electronic Hamiltonian, the auxiliary space by the bosonic Hamiltonian, and the coupling between them by the electron-boson coupling term. Right now the bosonic Hamiltonian (specifically its second term) does not conserve the boson number. To remedy this, we perform a unitary transformation

$$\hat{U}^{\dagger}\hat{H}^{\mathrm{eB}}\hat{U} \to \tilde{H}^{\mathrm{eB}}. \tag{4.7}$$

4.1.1 Nature of the unitary transformation

First consider what the bosonic Hamiltonian looks like when expressed in the bosonic basis $\boldsymbol{b} = \left(\hat{b}_1, \hat{b}_2, \ldots\right)$ as

$$\hat{H}^{\mathrm{B}}\left(\hat{b}, \hat{b}^{\dagger}\right) = -\frac{1}{2}\operatorname{tr}\mathbf{A} + \frac{1}{2}\begin{pmatrix} \mathbf{b}^{\dagger} & \mathbf{b} \end{pmatrix}\begin{pmatrix} \mathbf{A} & \mathbf{B} \\ \mathbf{B} & \mathbf{A} \end{pmatrix}\begin{pmatrix} \mathbf{b} \\ \mathbf{b}^{\dagger} \end{pmatrix} \tag{4.8}$$

$$= -\frac{1}{2}\operatorname{tr}\mathbf{A} + \frac{1}{2}\begin{pmatrix} \boldsymbol{b}^{\dagger} & \boldsymbol{b} \end{pmatrix}\begin{pmatrix} \boldsymbol{A}\boldsymbol{b} + \boldsymbol{B}\boldsymbol{b}^{\dagger} \\ \boldsymbol{B}\boldsymbol{b} + \boldsymbol{A}\boldsymbol{b}^{\dagger} \end{pmatrix} \tag{4.9}$$

$$= -\frac{1}{2}\operatorname{tr}\mathbf{A} + \frac{1}{2}\left[\boldsymbol{b}^{\dagger}\boldsymbol{A}\boldsymbol{b} + \boldsymbol{b}^{\dagger}\boldsymbol{B}\boldsymbol{b}^{\dagger} + \boldsymbol{b}\boldsymbol{B}\boldsymbol{b} + \boldsymbol{b}\boldsymbol{A}\boldsymbol{b}^{\dagger}\right] \tag{4.10}$$

$$= \boldsymbol{b}^{\dagger}\boldsymbol{A}\boldsymbol{b} + \frac{1}{2}\left[\boldsymbol{b}^{\dagger}\boldsymbol{B}\boldsymbol{b}^{\dagger} + \boldsymbol{b}\boldsymbol{B}\boldsymbol{b}\right] + \mathbf{0} \tag{4.11}$$

$$= \sum_{\nu\mu} A_{\nu\mu}\hat{b}_{\nu}^{\dagger}\hat{b}_{\mu} + \frac{1}{2}\sum_{\nu\mu} B_{\nu\mu}\left(\hat{b}_{\nu}^{\dagger}\hat{b}_{\mu}^{\dagger} + \hat{b}_{\nu}\hat{b}_{\mu}\right) \tag{4.12}$$

Going from 4.10 to 4.11, we used the fact that the final term needs to be put into normal order so we can do $\boldsymbol{b}\boldsymbol{A}\boldsymbol{b}^{\dagger} = \sum_{\mu\nu} A_{\mu\nu} b_{\mu} b_{\nu}^{\dagger} = \sum_{\mu\nu} A_{\mu\nu}\left(b_{\nu}^{\dagger} b_{\mu} + \delta_{\mu\nu}\right) = \boldsymbol{b}^{\dagger}\boldsymbol{A}\boldsymbol{b} + \operatorname{Tr}(\boldsymbol{A})$. In the above we have showed equivalence to the previously defined form in 5.20. Within this representation of the bosonic Hamiltonian in the bosonic basis, in 4.8, we recognize the appearance of the RPA matrix. From 4.8, we can obtain a diagonalized form

$$\hat{H}^{\mathrm{B}}\left(\bar{b}, \bar{b}^{\dagger}\right) = -\frac{1}{2}\operatorname{tr}\mathbf{A} + \frac{1}{2}\left(\overline{\mathbf{b}}^{\dagger}\overline{\mathbf{b}}\right)\begin{pmatrix} \Omega\mathbf{1} & 0 \\ 0 & \Omega\mathbf{1} \end{pmatrix}\begin{pmatrix} \overline{\mathbf{b}} \\ \overline{\mathbf{b}}^{\dagger} \end{pmatrix} \tag{4.13}$$

through a redefinition of the bosonic operators as

$$\begin{pmatrix} \overline{\mathbf{b}} \\ \overline{\mathbf{b}}^{\dagger} \end{pmatrix} = \begin{pmatrix} \mathbf{X} & -\mathbf{Y} \\ -\mathbf{Y} & \mathbf{X} \end{pmatrix}^{T}\begin{pmatrix} \mathbf{b} \\ \mathbf{b}^{\dagger} \end{pmatrix} \quad \text{and} \quad \begin{pmatrix} \mathbf{b} \\ \mathbf{b}^{\dagger} \end{pmatrix} = \begin{pmatrix} \mathbf{X} & \mathbf{Y} \\ \mathbf{Y} & \mathbf{X} \end{pmatrix}\begin{pmatrix} \overline{\mathbf{b}} \\ \overline{\mathbf{b}}^{\dagger} \end{pmatrix}. \tag{4.14}$$

Effect on the bosonic Hamiltonian

Now by expanding, we see

$$\hat{H}^{\mathrm{B}}\left(\overline{\mathbf{b}},\overline{\mathbf{b}}^{\dagger}\right)=-\frac{1}{2}\operatorname{tr}\mathbf{A}+\frac{1}{2}\left(\overline{\mathbf{b}}^{\dagger}\overline{\mathbf{b}}\right)\left(\begin{array}{cc}\Omega\mathbf{1} & 0\\ 0 & \Omega\mathbf{1}\end{array}\right)\begin{pmatrix}\overline{\mathbf{b}}\\ \overline{\mathbf{b}}^{\dagger}\end{pmatrix} \tag{4.15}$$

$$=-\frac{1}{2}\operatorname{tr}\mathbf{A}+\frac{1}{2}\begin{pmatrix}\overline{\mathbf{b}}^{\dagger} & \overline{\mathbf{b}}\end{pmatrix}\begin{pmatrix}\mathbf{\Omega}\overline{\mathbf{b}}\\ \mathbf{\Omega}\overline{\mathbf{b}}^{\dagger}\end{pmatrix} \tag{4.16}$$

$$=-\frac{1}{2}\operatorname{tr}\mathbf{A}+\frac{1}{2}\left[\overline{\mathbf{b}}^{\dagger}\mathbf{\Omega}\overline{\mathbf{b}}+\underbrace{\overline{\mathbf{b}}\mathbf{\Omega}\overline{\mathbf{b}}^{\dagger}}_{\overline{b}^{\dagger}\mathbf{\Omega}\overline{b}+\mathrm{Tr}(\mathbf{\Omega})}\right] \tag{4.17}$$

$$=\overline{\mathbf{b}}^{\dagger}\mathbf{\Omega}\overline{\mathbf{b}}+\frac{1}{2}\operatorname{Tr}\left(\mathbf{\Omega}-\mathbf{A}\right) \tag{4.18}$$

$$=\sum_{\nu}\Omega_{\nu}\overline{b}_{\nu}^{\dagger}\overline{b}_{\nu}+E^{c}_{\mathrm{RPA}} \tag{4.19}$$

so we removed the non-boson conserving quality of the bosonic Hamiltonian (compare to 5.20).

Effect on the electron-boson coupling term

Originally, the electron-boson coupling term is given as

$$\hat{V}^{\mathrm{eB}}=\sum_{pq,\nu}V_{pq,\nu}\left\{\hat{a}_p^{\dagger}\hat{a}_q\right\}\left(\hat{b}_{\nu}^{\dagger}+\hat{b}_{\nu}\right) \tag{4.20}$$

Here, we will use that the redefinition of the bosonic operators such that $\hat{b_{\nu}}=\sum_{\mu}\left(\mathbf{X}_{\mu}^{\nu}\hat{\overline{b}}_{\nu}+\mathbf{Y}_{\mu}^{\nu}\hat{\overline{b}}_{\nu}^{\dagger}\right)$ and $\hat{b_{\nu}}^{\dagger}=\sum_{\mu}\left(\mathbf{X}_{\mu}^{\nu}\hat{\overline{b}}_{\nu}^{\dagger}+\mathbf{Y}_{\mu}^{\nu}\hat{\overline{b}}_{\nu}\right)$, which gives $\hat{b}_{\nu}+\hat{b}_{\nu}^{\dagger}=\sum_{\mu}\left(\mathbf{X}_{\mu}^{\nu}+\mathbf{Y}_{\mu}^{\nu}\right)\left(\hat{\overline{b}}_{\nu}+\hat{\overline{b}}_{\nu}^{\dagger}\right)$, so after we plug in

$$\hat{V}^{\mathrm{eB}}=\sum_{pq,\nu}V_{pq,\nu}\left\{\hat{a}_p^{\dagger}\hat{a}_q\right\}\left(\sum_{\mu}\left(\mathbf{X}_{\mu}^{\nu}+\mathbf{Y}_{\mu}^{\nu}\right)\right)\left(\hat{\overline{b}}_{\nu}+\hat{\overline{b}}_{\nu}^{\dagger}\right) \tag{4.21}$$

$$=\sum_{pq,\nu}W_{pq,\nu}\left\{\hat{a}_p^{\dagger}\hat{a}_q\right\}\left(\overline{b}_{\nu}+\overline{b}_{\nu}^{\dagger}\right) \tag{4.22}$$

where now we had identified the RPA screened Coulomb interaction $W_{pq,\nu}=V_{pq,\nu}\sum_{\mu}\left(\mathbf{X}_{\mu}^{\nu}+\mathbf{Y}_{\mu}^{\nu}\right)$.

4.2 Connection to Booth supermatrix

We then build the supermatrices $\mathbf{H}$ and $\mathbf{S}$ with matrix elements,

$$H_{IJ}=\langle 0_{\mathrm{F}}0_{\mathrm{B}}|\left[C_I,\left[\tilde{H}^{\mathrm{eB}},C_J^{\dagger}\right]\right]|0_{\mathrm{F}}0_{\mathrm{B}}\rangle$$

$$S_{IJ}=\langle 0_{\mathrm{F}}0_{\mathrm{B}}|\left[C_I,C_J^{\dagger}\right]|0_{\mathrm{F}}0_{\mathrm{B}}\rangle$$

where $\left\{C_I^\dagger\right\} = \left\{\underbrace{a_i}_{1h}, \underbrace{a_a}_{1p}, \underbrace{a_i b_\nu^\dagger}_{2h1p}, \underbrace{a_a b_\nu}_{1p2p}\right\}$ and $|0\rangle_\mathrm{F}$ and $|0\rangle_\mathrm{B}$ are the Fermi and boson vacuums. Then constructing $-\boldsymbol{S}^{-1}\boldsymbol{H}$ yields Booth's ED, which is

$$\boldsymbol{H}^{G_0W_0} = \begin{pmatrix} \boldsymbol{F} & \boldsymbol{W}^< & \boldsymbol{W}^> \\ \boldsymbol{W}^{\dagger<} & \boldsymbol{d}^< & \boldsymbol{0} \\ \boldsymbol{W}^{\dagger>} & \boldsymbol{0} & \boldsymbol{d}^> \end{pmatrix} \tag{4.23}$$

where $\boldsymbol{F}$ is the Fock matrix, $\boldsymbol{W}^<$ and $\boldsymbol{W}^>$ are the lesser and greater components of the RPA screened Coulomb interaction, defined as

$$W^<_{pk\nu} = \sum_{ia} (pk|ia)\left(X_{ia}^\nu + Y_{ia}^\nu\right) \quad \text{and} \quad W^>_{pc\nu} = \sum_{ia} (pc|ia)\left(X_{ia}^\nu + Y_{ia}^\nu\right) \tag{4.24}$$

and the auxiliary blocks $\boldsymbol{d}^<$ and $\boldsymbol{d}^>$ are defined as

$$d^<_{k\nu,l\nu'} = \left(\epsilon_k - \Omega_\nu\right)\delta_{k,l}\delta_{\nu,\nu'} \quad \text{and} \quad d^>_{c\nu,d\nu'} = \left(\epsilon_c + \Omega_\nu\right)\delta_{c,d}\delta_{\nu,\nu'} \tag{4.25}$$

4.2.1 Derivation of the supermatrices for the 2h1p sector

Overlap

Computing the matrix elements of the $\boldsymbol{S}$ gives:

$$\boldsymbol{S} = \begin{pmatrix} \delta_{ij} & 0 & 0 & 0 \\ 0 & -\delta_{ab} & 0 & 0 \\ 0 & 0 & \delta_{ij}\delta_{\nu\nu'} & 0 \\ 0 & 0 & 0 & -\delta_{ab}\delta_{\nu\nu'} \end{pmatrix} \tag{4.26}$$

$\boldsymbol{H}$ takes more care.

Physical

$$H_{ij} = \langle 0_{\mathrm{F}} 0_{\mathrm{B}} | \left[a_i^\dagger, \left[\hat{H}^{\mathrm{eB}}, a_j \right] \right] | 0_{\mathrm{F}} 0_{\mathrm{B}} \rangle = \langle 0_{\mathrm{F}} 0_{\mathrm{B}} | \left[a_i^\dagger, \left[\hat{H}^{\mathrm{e}}, a_j \right] \right] | 0_{\mathrm{F}} 0_{\mathrm{B}} \rangle \tag{4.27}$$

We can make this simplification because the electronic operators commute with all bosonic operators. Now

$$\begin{aligned}
[\hat{H}^e,\ a_j] &= \sum_{pq} f_{pq}\, [a_p^\dagger a_q,\ a_j] = \sum_{pq} f_{pq} \left(a_p^\dagger \,[\, a_q, a_j \,] + [a_p^\dagger, a_j] a_q \right) && (4.28)\\
&= \sum_{pq} f_{pq} \left(a_p^\dagger a_q a_j - a_p^\dagger a_j a_q + a_p^\dagger a_j a_q - a_j a_p^\dagger a_q \right) && (4.29)\\
[a_i^\dagger,\ [\hat{H}^e,\ a_j]] &= \sum_{pq} f_{pq}\, [a_i^\dagger, \left(a_p^\dagger a_q a_j - a_j a_p^\dagger a_q \right)] && (4.30)\\
&= \sum_{pq} f_{pq} \left([a_i^\dagger, a_p^\dagger a_q a_j] - [a_i^\dagger, a_j a_p^\dagger a_q] \right) && (4.31)\\
&= \sum_{pq} f_{pq} \left(a_i^\dagger a_p^\dagger a_q a_j - a_p^\dagger a_q a_j a_i^\dagger - a_i^\dagger a_j a_p^\dagger a_q + a_j a_p^\dagger a_q a_i^\dagger \right) && (4.32)\\
a_i^\dagger a_p^\dagger a_q a_j &= a_i^\dagger a_p^\dagger a_q a_j + a_i^\dagger a_p^\dagger a_q a_j = -\delta_{iq}\delta_{jp} + \cancel{\delta_{ij}\delta_{pq}} && (4.33)\\
a_p^\dagger a_q a_j a_i^\dagger &= 0 && (4.34)\\
a_i^\dagger a_j a_p^\dagger a_q &= a_i^\dagger a_j a_p^\dagger a_q + a_i^\dagger a_j a_p^\dagger a_q = 0 + \cancel{\delta_{ij}\delta_{pq}} && (4.35)\\
a_j a_p^\dagger a_q a_i^\dagger &= 0 && (4.36)\\
&= -\sum_{pq} f_{pq} \delta_{iq} \delta_{jp} = -f_{ji} && (4.37)
\end{aligned}$$

So $H_{ij} = -f_{ji}$ and then $\boxed{(-S^{-1}H)_{ij} = +\delta_{ij} f_{ji} = f_{ii} = \epsilon_i}$.

Auxiliary

$$H_{i\nu j\nu'} = \langle 0_{\mathrm{F}} 0_{\mathrm{B}} | \left[a_i^\dagger b_\nu, \left[\hat{H}^{\mathrm{eB}}, a_j b_{\nu'}^\dagger \right] \right] | 0_{\mathrm{F}} 0_{\mathrm{B}} \rangle = \langle 0_{\mathrm{F}} 0_{\mathrm{B}} | \left[a_i^\dagger b_\nu, \left[\hat{H}^{\mathrm{e}} + \hat{H}^{\mathrm{B}} + \hat{V}^{\mathrm{eB}}, a_j b_{\nu'}^\dagger \right] \right] | 0_{\mathrm{F}} 0_{\mathrm{B}} \rangle \tag{4.38}$$

$$\tag{4.39}$$

First

$$[\hat{H}^e,\ a_j b_\mu^\dagger] = \sum_{pq} f_{pq}\,[a_p^\dagger a_q, a_j b_\mu^\dagger] = \sum_{pq} f_{pq}[a_p^\dagger a_q a_j - a_j a_p^\dagger a_q] b_\mu^\dagger \tag{4.40}$$

$$[a_i^\dagger b_\nu,\ [\hat{H}^e,\ a_j b_\mu^\dagger]] = [a_i^\dagger b_\nu,\ \sum_{pq} f_{pq}[a_p^\dagger a_q a_j - a_j a_p^\dagger a_q] b_\mu^\dagger] = \sum_{pq} f_{pq}[a_i^\dagger, a_p^\dagger a_q a_j - a_j a_p^\dagger a_q][b_\nu, b_\mu^\dagger] \tag{4.41}$$

$$= \delta_{\nu\mu} \sum_{pq} f_{pq} \left(a_i^\dagger a_p^\dagger a_q a_j - a_p^\dagger a_q a_j a_i^\dagger - a_i^\dagger a_j a_p^\dagger a_q + a_j a_p^\dagger a_q a_i^\dagger \right) \tag{4.42}$$

$$a_i^\dagger a_p^\dagger a_q a_j = a_i^\dagger a_p^\dagger a_q a_j + a_i^\dagger a_p^\dagger a_q a_j = -\underbrace{\delta_{iq}\delta_{jp}}_{q,p\in O} + \cancel{\delta_{ij}\delta_{pq}} \tag{4.43}$$

$$a_p^\dagger a_q a_j a_i^\dagger = 0 \tag{4.44}$$

$$a_i^\dagger a_j a_p^\dagger a_q = a_i^\dagger a_j a_p^\dagger a_q + a_i^\dagger a_j a_p^\dagger a_q = 0 + \cancel{\delta_{ij}\delta_{pq}} \tag{4.45}$$

$$a_p^\dagger a_j a_q a_i^\dagger = 0 \tag{4.46}$$

$$\tag{4.47}$$

So $[a_i^\dagger b_\nu,\ [\hat{H}^e,\ a_j b_\mu^\dagger]] = -\delta_{\nu\mu} f_{ji}$. Next

$$[\hat{H}^B,\ a_j b_\mu^\dagger] = [\sum_\nu \Omega_\nu b_\nu^\dagger b_\nu + E^c_{\mathrm{RPA}}, a_j b_\mu^\dagger] = \sum_\nu \Omega_\nu a_j [b_\nu^\dagger b_\nu, b_\mu^\dagger] = \sum_\nu \Omega_\nu a_j b_\nu^\dagger [b_\nu, b_\mu^\dagger] = \Omega_\mu a_j b_\mu^\dagger \tag{4.48}$$

$$[a_i^\dagger b_\nu,\ [\hat{H}^B,\ a_j b_\mu^\dagger]] = \Omega_\mu [a_i^\dagger b_\nu, a_j b_\mu^\dagger] = \Omega_\mu [a_i^\dagger, a_j][b_\nu, b_\mu^\dagger] = \delta_{ij}\delta_{\nu\mu}\Omega_\mu \tag{4.49}$$

$$\tag{4.50}$$

So $[a_i^\dagger b_\nu,\ [\hat{H}^B,\ a_j b_\mu^\dagger]] = \delta_{ij}\delta_{\nu\mu}\Omega_\mu$. last

$$[a_i^\dagger b_\nu,\ [\hat{V}^{eB},\ a_j b_{\nu'}^\dagger]] = 0 \tag{4.51}$$

because we notice that in the coupling term, the number of bosons is not conserved. So $H_{i\nu j\nu'} = \delta_{\nu\nu'}\left(\delta_{ij}\Omega_{\nu'} - f_{ji}\right)$ and then $\boxed{(-S^{-1}H)_{i\nu j\nu'} = -\delta_{ij}\left(\delta_{\nu\nu'}\left(\delta_{ij}\Omega_\nu - f_{ji}\right)\right) = \delta_{ij}\delta_{\nu\nu'}\left(\epsilon_i - \Omega_\nu\right)}$.

Coupling

$$H_{i,p\nu} = \langle 0_{\mathrm{F}} 0_{\mathrm{B}} | \left[a_i^\dagger, \left[\hat{H}^{\mathrm{eB}}, a_p b_\nu^\dagger\right]\right] | 0_{\mathrm{F}} 0_{\mathrm{B}} \rangle = \langle 0_{\mathrm{F}} 0_{\mathrm{B}} | \left[a_i^\dagger, \left[\hat{V}^{\mathrm{eB}}, a_p b_\nu^\dagger\right]\right] | 0_{\mathrm{F}} 0_{\mathrm{B}} \rangle \tag{4.52}$$

Note that we have neglected the electronic and bosonic Hamiltonians, because using them in this arrangement will not conserve the number of bosons. So we have

$$[V^{eB},\ a_p b_\nu^\dagger] = \sum_{rs,\nu'} W_{rs,\nu'}[a_r^\dagger a_s(b_{\nu'} + b_{\nu'}^\dagger), a_p b_\nu^\dagger] = \sum_{rs,\nu'} W_{rs,\nu'}[a_r^\dagger a_s, a_p][b_{\nu'}, b_\nu^\dagger] \tag{4.53}$$

$$= \sum_{rs} W_{rs,\nu}\left(a_r^\dagger a_s a_p - a_p a_r^\dagger a_s\right) \tag{4.54}$$

$$[a_i^\dagger,\ [\hat{V}^{eB},\ a_p b_\nu^\dagger]] = \sum_{rs} W_{rs,\nu}\left[a_i^\dagger \hat{a}_r^\dagger \hat{a}_s a_p - \hat{a}_r^\dagger \hat{a}_s a_p a_i^\dagger - \left(a_i^\dagger a_p a_r^\dagger a_s - a_p a_r^\dagger a_s a_i^\dagger\right)\right] \tag{4.55}$$

$$a_i^\dagger \hat{a}_r^\dagger \hat{a}_s a_p = a_i^\dagger a_r^\dagger a_s a_p + a_i^\dagger a_r^\dagger a_s a_p = -\underbrace{\delta_{is}\delta_{rp}}_{s\in O} + \cancel{\delta_{ip}\delta_{rs}} \tag{4.56}$$

$$\hat{a}_r^\dagger \hat{a}_s a_p a_i^\dagger = a_r^\dagger a_s a_p a_i^\dagger + a_r^\dagger a_s a_p a_i^\dagger = 0 \tag{4.57}$$

$$a_i^\dagger a_p a_r^\dagger a_s = a_i^\dagger a_p a_r^\dagger a_s + a_i^\dagger a_p a_r^\dagger a_s = \cancel{\delta_{ip}\delta_{rs}} + 0 \tag{4.58}$$

$$a_p a_r^\dagger a_s a_i^\dagger = 0 \tag{4.59}$$

$$\tag{4.60}$$

So we can write $H_{i,p\nu} = -W_{pi,\nu} = -W_{ip,\nu}$ because of the permutational symmetry of the ERIs. Then $\boxed{(-S^{-1}H)_{p,i\nu} = +W_{pi,\nu}}$.

4.3 Implementation for periodic systems

4.3.1 RI

We know the periodic integrals can be expressed as:

$$(i\mathbf{k}_1, a\mathbf{k}_2 \mid j\mathbf{k}_3, b\mathbf{k}_4) = \delta_{\mathbf{k}_1+\mathbf{k}_2,\mathbf{k}_3+\mathbf{k}_4+\mathbf{G}}(ia \mid jb)_{\mathbf{q}'} \tag{4.61}$$

where $\mathbf{q}' = \mathbf{k}_1 - \mathbf{k}_3$ and $\mathbf{G}$ is a reciprocal lattice vector. The RI coefficients are then given by

$$R_{jb}^L(\mathbf{q}) = \sum_Q \left[\mathbf{V}^{-1/2}(\mathbf{q})\right]_{LQ}(Q\mathbf{q} \mid j\mathbf{k}_j, b\mathbf{k}_b) \tag{4.62}$$

It is understood that we must have $\boldsymbol{q} = \mathbf{k}_j - \mathbf{k}_b$ to ensure momentum conservation and $\mathbf{V}(\mathbf{q})$ is the Coulomb metric in the auxiliary basis for that $\mathbf{q}$:

$$V_{PQ}(\mathbf{q}) = (P\mathbf{q} \mid Q\mathbf{q}) = \sum_{\mathbf{R}} e^{-i\mathbf{q}\cdot\mathbf{R}} \int d\mathbf{r}d\mathbf{r}'\chi_P(\mathbf{r})\frac{1}{|\mathbf{r}-\mathbf{r}'|}\chi_Q(\mathbf{r}'-\mathbf{R}) \tag{4.63}$$

So we can recover the ERIs as

$$(ia \mid jb)_{\mathbf{q}} = \sum_L \left(R^L_{ia}(\mathbf{q})\right)^\dagger R^L_{jb}(\mathbf{q}) \tag{4.64}$$

$$= \sum_L \left(\sum_Q (i\mathbf{k}_i, a\mathbf{k}_a \mid Q\mathbf{q})[\mathbf{V}^{-1/2}(\mathbf{q})]_{QL} \right) \left(\sum_R [\mathbf{V}^{-1/2}(\mathbf{q})]_{LR}(R\mathbf{q} \mid j\mathbf{k}_j, b\mathbf{k}_b) \right) \tag{4.65}$$

$$= \sum_{QR} (i\mathbf{k}_i, a\mathbf{k}_a \mid Q\mathbf{q}) \left(\sum_L [\mathbf{V}^{-1/2}(\mathbf{q})]_{QL}[\mathbf{V}^{-1/2}(\mathbf{q})]_{LR} \right) (R\mathbf{q} \mid j\mathbf{k}_j, b\mathbf{k}_b) \tag{4.66}$$

$$= \sum_{QR} (i\mathbf{k}_i, a\mathbf{k}_a \mid Q\mathbf{q})[\mathbf{V}^{-1}(\mathbf{q})]_{QR}(R\mathbf{q} \mid j\mathbf{k}_j, b\mathbf{k}_b) \tag{4.67}$$

$$= (i\mathbf{k}_i, a\mathbf{k}_a \mid j\mathbf{k}_j, b\mathbf{k}_b)_{\mathbf{q}}. \tag{4.68}$$

where in the last step we used the definition of 4.63 to make the appropriate cancellation. Then, we can define a basis of auxiliary bosons as

$$\hat{b}_\nu(\mathbf{q}) = \sum_Q^{N_{AB}} C^Q_\nu(\mathbf{q})\hat{b}_Q(\mathbf{q}) \tag{4.69}$$

where we define the expansion coefficients as

$$C^Q_\nu(\mathbf{q}) = \sum_L R^L_\nu(\mathbf{q}) \left[\boldsymbol{S}^{-1/2}(\mathbf{q})\right]_{LM} P^Q_M \tag{4.70}$$

where $S_{LM}(\mathbf{q}) = \sum_\nu R^L_\nu(\mathbf{q})R^M_\nu(\mathbf{q}) = \sum_Q P^Q_L(\mathbf{q})E_Q(\mathbf{q})P^Q_M(\mathbf{q})$ can be thought of as the overlap matrix in this AB basis where the final expression employs its eigendecomposition. Even though the axillary bases already is small, we can obtain a further truncated basis by only choosing the eigenvalues over a certain threshhold $E_Q(\mathbf{q}) > \epsilon_{AB}$. This is a similar idea to the one that was used to identify rank deficiency in Lanczos.

Scaling comments

Getting the RI coefficients into the MO basis scales as $O(N^3_{\text{orb}}N_{\text{aux}}N_{\mathbf{k}})$, the determination of the overlap matrix scales as $O(N_oN_vN^2_{\text{aux}}N^2_{\mathbf{k}})$, and then computing the AB basis will cost $O(N_{\text{AB}}N^2_{\text{aux}}N_{\mathbf{k}})$. In order to construct the transformed electron boson Hamiltonian in the AB basis we first need to solve the symmetrized dRPA eigenvalue problem

Chapter 5

Cumulant expansion

5.1 Background

5.1.1 The qualitative interpretation

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. 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

$$G(t) = G_0(t)e^{C(t)} \tag{5.1}$$

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

$$C(t) = \int d\omega \frac{\beta(\omega)}{\omega^2}\left[e^{-i\omega t} + i\omega t - 1\right] \tag{5.2}$$

where the cumulant kernel is defined as

$$\beta(\omega) = -\frac{1}{\pi}\operatorname{Im}\Sigma^{\mathrm{c}}(\omega) \tag{5.3}$$

This form is amenable to physical interpretation if we partition into

$$C(t) = -a + i\Delta t + \tilde{C}(t) \tag{5.4}$$

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.

5.1.2 Alternate derivation starting from Dyson equation

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

$$G_u(1,1') = G^0(1,1') + G^0(1,\overline{2})\left\{\left[u(\overline{2}) + v_{Hu}(\overline{2})\right]G_u\left(\overline{2},1'\right) + iv_c(\overline{2},\overline{3})\frac{\delta G_u\left(\overline{2},1'\right)}{\delta u\left(\overline{3}^+\right)}\right\} \tag{5.5}$$

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

$$u_{\text{cl}}(1) = u(1) + v_{Hu}(1) \tag{5.6}$$

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

$$G_u(1,1') = G^0(1,1') + G^0(1,\overline{2})u_{\text{cl}}(\overline{2})G_u\left(\overline{2},1'\right) + iG^0(1,\overline{2})v_c(\overline{2},\overline{3})\frac{\delta G_u\left(\overline{2},1'\right)}{\delta u\left(\overline{3}^+\right)} \tag{5.7}$$

$$= G^0(1,1') + G^0(1,\overline{2})u_{\text{cl}}(\overline{2})G_u\left(\overline{2},1'\right) + iG^0(1,\overline{2})W_u(\overline{2},\overline{3})\frac{\delta G_u\left(\overline{2},1'\right)}{\delta u_{\text{cl}}\left(\overline{3}^+\right)} \tag{5.8}$$

where we have defined the screened Coulomb interaction $W_u = \epsilon_u^{-1}v_c$ with the time-ordered inverse dielectric function $\epsilon_u^{-1} = \delta u_{\text{cl}}/\delta u$. 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

$$G_{ij}^{u_{cl}}(t_{12}) = G_{ij}^0(t_{12}) + G_{im}^0(t_{13})\,u_{\text{cl},mk}(t_3)\,G_{kj}^{u_{cl}}(t_{32}) + iG_{ik}^0(t_{13})\,W_{klmn}(t_{34})\,\frac{\partial G_{nj}^{u_{cl}}(t_{32})}{\partial u_{\text{cl},lm}(t_4)} \tag{5.9}$$

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

$$\frac{\partial G_{nj}^u(t_{32})}{\partial u_{\text{cl},lm}(t_4)} \approx G_{nl}(t_{34})\,G_{mj}(t_{42}) \tag{5.10}$$

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

$$\Sigma_{im}^{GW}(t_{34}) = v_{H,im} + iG_{nl}(t_{34})\,W_{ilmn}(t_{34})\,. \tag{5.11}$$

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

$$\left[G^{QP,u}\right]^{-1}_{ij} = \left[G_0^{-1}\right]_{ij} - \left[u_{\text{cl}}\right]_{ij} - \Sigma^{GW}_{ij}\left(\frac{\varepsilon_i+\varepsilon_j}{2}\right) \tag{5.12}$$

$$\implies \left[G_0\right]_{ij} = G^{QP,u}_{ij} - G^{QP,u}_{im}\left(u_{\text{cl},mk} + \Sigma^{GW}_{mk}\left(\frac{\varepsilon_m+\varepsilon_k}{2}\right)\right)\left[G_0\right]_{kj} \tag{5.13}$$

Plugging this into 5.9 (suppressing the time and orbital indices for ease of notation) gives

$$\begin{aligned}
G^u &= G^{QP,u} - G^{QP,u}\left(u_{\text{cl}}+\Sigma\right)G_0 \\
&\quad + \left(G^{QP,u} - G^{QP,u}\left(u_{\text{cl}}+\Sigma\right)G_0\right)u_{\text{cl}}G^u \\
&\quad + i\left(G^{QP,u} - G^{QP,u}\left(u_{\text{cl}}+\Sigma\right)G_0\right)W\frac{\partial G^u}{\partial u_{\text{cl}}} \\
&= G^{QP,u} + G^{QP,u}u_{\text{cl}}G^u + iG^{QP,u}W\frac{\partial G^u}{\partial u_{\text{cl}}} \\
&\quad - G^{QP,u}\left(u_{\text{cl}}+\Sigma\right)\left[\underbrace{G_0 + G_0 u_{\text{cl}}G^u + iG_0W\frac{\partial G^u}{\partial u_{\text{cl}}}}_{G^u}\right]
\end{aligned} \tag{5.14}$$

$$= G^{QP,u} + iG^{QP,u}W\frac{\partial G^u}{\partial u_{\text{cl}}} - G^{QP,u}\Sigma G^u \tag{5.15}$$

$$\implies G^u_{ij}(t_{12}) = G^{QP,u}_{ij}(t_{12}) + iG^{QP,u}_{ik}(t_{13})W_{klmn}(t_{34})\frac{\partial G^u_{mj}(t_{32})}{\partial u_{\text{cl},lm}(t_4)} - G^{QP,u}_{ik}(t_{13})\Sigma^{GW}_{kl}\left(\frac{\varepsilon_k+\varepsilon_l}{2}\right)G^u_{lj}(t_{32}) \tag{5.16}$$

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 $u_{\text{cl},ij} \to u_{\text{cl},ii} \equiv u$. This is a strong assumption, but nevertheless, it allows us to get to the conventional form for the cumulant expansion. The resulting equation is

$$\mathcal{G}^u(t_{12}) = \mathcal{G}^{QP,u}(t_{12}) + i\mathcal{G}^{QP,u}(t_{13})\mathcal{W}(t_{34})\frac{\partial \mathcal{G}^u(t_{32})}{\partial u(t_4)} - \mathcal{G}^{QP,u}(t_{13})\tilde{\Sigma}^{GW}\mathcal{G}^u(t_{32}) \tag{5.17}$$

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

$$\mathcal{G}\left(t_{12}\right) = \mathcal{G}^0_{QP}\left(t_{12}\right)e^{i(t_1-t_2)\Sigma^{GW}_{ii}(\varepsilon_i)}\exp\left[-i\int_{t_1}^{t_2}dt'\int_{t'}^{t_2}dt''\mathcal{W}\left(t'-t''\right)\right]. \tag{5.18}$$

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

$$-i\int_{t_1}^{t_2} dt' \int_{t'}^{t_2} dt'' \mathcal{W}\left(t'-t''\right) = -\frac{i}{2\pi}\int d\omega\, \mathcal{W}(\omega) \int_{t_1}^{t_2} dt' \int_{t'}^{t_2} dt''\, e^{-i\omega(t'-t'')} \tag{5.19}$$

$$= -\frac{1}{2\pi}\int d\omega\, \frac{\mathcal{W}(\omega)}{\omega} \int_{t_1}^{t_2} dt' \Big(e^{i\omega(t_2-t')} - 1\Big) \tag{5.20}$$

$$= -\frac{1}{2\pi}\int d\omega\, \frac{\mathcal{W}(\omega)}{\omega} \left[\frac{e^{i\omega(t_2-t_1)} - 1}{i\omega} - (t_2-t_1)\right] \tag{5.21}$$

$$= -\left(t_1-t_2\right)\frac{1}{2\pi}\int d\omega \frac{\mathcal{W}(\omega)}{\omega} + \frac{i}{2\pi}\int d\omega \frac{\mathcal{W}(\omega)}{\omega^2}\left(e^{-i\omega(t_1-t_2)} - 1\right) \tag{5.22}$$

where in going from Eq. (5.19) to Eq. (5.20) 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. (5.20) to Eq. (5.21) we have used $\int_{t_1}^{t_2} dt'(e^{i\omega(t_2-t')}-1) = \frac{e^{i\omega\Delta}-1}{i\omega} - \Delta$ with $\Delta = t_2 - t_1$. Let us first examine the term proportional to (t_1-t_2) in Eq. (5.22), by comparing it to a GW quasi-particle shift. In the decoupling approximation, $\Sigma_{kk}^{GW} \approx iG_{kk}W_{kkkk}$. 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 $e^{i(t_1-t_2)\Sigma_{ii}^{GW}(\varepsilon_i)}$, and we are left with

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

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

$$\mathcal{G}(t_{12}) = \mathcal{G}^{QP}(t_{12}) + i\mathcal{G}^{QP}(t_{13})\mathcal{W}(t_{34})\mathcal{G}(t_{34})\mathcal{G}(t_{42}) - \mathcal{G}^{QP}(t_{13})\tilde{\Sigma}^{GW}\mathcal{G}(t_{32}) \tag{5.23}$$

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

$$\begin{aligned}\tilde{\mathcal{G}}(t_{12}) = e^{i(t_1-t_2)\tilde{\Sigma}^{GW}}\mathcal{G}^{QP}(t_{12}) + ie^{i(t_1-t_2)\tilde{\Sigma}^{GW}}\mathcal{G}^{QP}(t_{13})\mathcal{W}(t_{34})e^{-i(t_3-t_4)\tilde{\Sigma}^{GW}}\tilde{\mathcal{G}}(t_{34})e^{-i(t_4-t_2)\tilde{\Sigma}^{GW}}\tilde{\mathcal{G}}(t_{42}) \\ - e^{i(t_1-t_2)\tilde{\Sigma}^{GW}}\mathcal{G}^{QP}(t_{13})\tilde{\Sigma}^{GW}e^{-i(t_3-t_2)\tilde{\Sigma}^{GW}}\tilde{\mathcal{G}}(t_{32})\end{aligned} \tag{5.24}$$

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

$$C(u)\frac{\partial \mathcal{G}^u}{\partial u} + A(u)\mathcal{G}^u = B(u). \tag{5.25}$$

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

$$\frac{\partial \mathcal{G}^u}{\partial u} + \frac{A(u)}{C(u)}\mathcal{G}^u = \frac{B(u)}{C(u)}. \tag{5.26}$$

So our integrating factor is

$$\mu(u) = \exp\left(\int^u \frac{A(s)}{C(s)}ds\right) = \exp\left(+i\int^u ds\frac{\tilde{\Sigma}^{GW}}{\mathcal{W}}\right) \tag{5.27}$$

and the solution is

$$\begin{aligned}\mathcal{G}^u &= \frac{1}{\mu(u)}\left[C_0 + \int^u \mu(s)\frac{B(s)}{C(s)}ds\right] && (5.28)\\ &= \exp\left(-i\int^u ds\frac{\tilde{\Sigma}^{GW}}{\mathcal{W}}\right)\left[C_0 + \int^u ds\exp\left(+i\int^s ds'\frac{\tilde{\Sigma}^{GW}}{\mathcal{W}}\right)\frac{\mathcal{G}^{QP,s}}{i\mathcal{G}^{QP,s}\mathcal{W}}\right] && (5.29)\\ &= \exp\left(-i\int^u ds\frac{\tilde{\Sigma}^{GW}}{\mathcal{W}}\right)\left[C_0 + \int^u ds\exp\left(+i\int^s ds'\frac{\tilde{\Sigma}^{GW}}{\mathcal{W}}\right)\frac{-i}{\mathcal{W}}\right] && (5.30)\end{aligned}$$

(5.31)

5.2 Cumulant expansion for electronic structure

5.2.1 Annotation of Loos paper

The definition of the cumulant ansatz for the retarded Green's function is given by:

$$\boldsymbol{G}(t) = \boldsymbol{G}^0(t)e^{\boldsymbol{C}(t)} \tag{5.32}$$

where $\boldsymbol{C}(t)$ is the retarded cumulant and $\boldsymbol{G}^0(t)$ is the retarded HF Green's function. By relating the Dyson equation to the Taylor series expansion of the exponential (both to first order), we can write:

$$\boldsymbol{G}^0(t)\boldsymbol{C}(t) = \iint \mathrm{d}t_1\mathrm{d}t_2\boldsymbol{G}^0(t-t_1)\boldsymbol{\Sigma}^c(t_1-t_2)\boldsymbol{G}^0(t_2) \tag{5.33}$$

This first order expansion is exact up to the first order in the screened Coulomb interaction W. If we choose instead to use a second order self-energy, now the cumulant will be exact to second order in the bare Coulomb interaction v. Projecting to the spin-orbital basis and inserting the resolution of the identity, we get:

$$\sum_r \langle p|\,\boldsymbol{G}^0(t)\,|r\rangle\,\langle r|\,\boldsymbol{C}(t)\,|q\rangle = \sum_{rs}\iint \mathrm{d}t_1\mathrm{d}t_2\,\langle p|\,\boldsymbol{G}^0(t-t_1)\,|r\rangle\,\langle r|\,\boldsymbol{\Sigma}^c(t_1-t_2)\,|s\rangle\,\langle s|\,\boldsymbol{G}^0(t_2)\,|q\rangle \tag{5.34}$$

$$\sum_r \boldsymbol{G}^0_{pr}(t)\boldsymbol{C}_{rq}(t) = \sum_{rs}\iint \mathrm{d}t_1\mathrm{d}t_2\boldsymbol{G}^0_{ps}(t-t_1)\boldsymbol{\Sigma}^c_{sr}(t_1-t_2)\boldsymbol{G}^0_{rq}(t_2) \tag{5.35}$$

$$\boldsymbol{G}^0_{pp}(t)\boldsymbol{C}_{pq}(t) = \underbrace{\iint \mathrm{d}t_1\mathrm{d}t_2\boldsymbol{G}^0_{pp}(t-t_1)\boldsymbol{\Sigma}^c_{pq}(t_1-t_2)\boldsymbol{G}^0_{qq}(t_2)}_{*} \tag{5.36}$$

where $\boldsymbol{G}^0(t)$ is the retarded HF Green's function, which is diagonal in the spin-orbital basis, specifically $\boldsymbol{G}^0_{pp}(t) = -i\Theta(t)e^{-i\epsilon_p t}$, where ϵ_p is the HF energy of the p-th spin-orbital. The formula for the inverse Fourier transform is given by:

$$f(t) = \int \frac{\mathrm{d}\omega}{2\pi}e^{-i\omega t}f(\omega) \tag{5.37}$$

which implies that

$$\boldsymbol{G}^0_{pp}(t-t_1) = \int \frac{\mathrm{d}\omega}{2\pi}e^{-i\omega(t-t_1)}\boldsymbol{G}^0_{pp}(\omega) \tag{5.38}$$

$$\boldsymbol{\Sigma}^c_{pq}(t_1-t_2) = \int \frac{\mathrm{d}\omega'}{2\pi}e^{-i\omega'(t_1-t_2)}\boldsymbol{\Sigma}^c_{pq}(\omega') \tag{5.39}$$

$$\boldsymbol{G}^0_{qq}(t_2) = \int \frac{\mathrm{d}\omega''}{2\pi}e^{-i\omega'' t_2}\boldsymbol{G}^0_{qq}(\omega'') \tag{5.40}$$

and plugging into the double time integral *, we get:

$$* = \iint \mathrm{d}t_1 \mathrm{d}t_2 \left[\int \frac{\mathrm{d}\omega}{2\pi} e^{-i\omega(t-t_1)} \boldsymbol{G}^0_{pp}(\omega)\right] \left[\int \frac{\mathrm{d}\omega'}{2\pi} e^{-i\omega'(t_1-t_2)} \boldsymbol{\Sigma}^c_{pq}(\omega')\right] \left[\int \frac{\mathrm{d}\omega''}{2\pi} e^{-i\omega'' t_2} \boldsymbol{G}^0_{qq}(\omega'')\right] \tag{5.41}$$

$$= \underbrace{\int \mathrm{d}t_1 e^{-i(\omega'-\omega)t_1} \int \mathrm{d}t_2 e^{-i(\omega''-\omega')t_2}}_{4\pi^2\delta(\omega'-\omega)\delta(\omega''-\omega')} \iiint \mathrm{d}\omega \mathrm{d}\omega' \mathrm{d}\omega'' \frac{e^{-i\omega t}}{8\pi^3} \boldsymbol{G}^0_{pp}(\omega) \boldsymbol{\Sigma}^c_{pq}(\omega') \boldsymbol{G}^0_{qq}(\omega'') \tag{5.42}$$

$$= \int \frac{\mathrm{d}\omega}{2\pi} e^{-i\omega t} \boldsymbol{G}^0_{pp}(\omega) \boldsymbol{\Sigma}^c_{pq}(\omega) \boldsymbol{G}^0_{qq}(\omega) \tag{5.43}$$

Multiplying both sides of eqn. 5.36 by $ie^{\epsilon_p t}$ and recalling that we are dealing with retarded quantities that vanish for negative times, we get: *We are also interested in what happens if we use an exact self-energy in 5.44 instead of the GW one. Also can we get away with not using the diagonal approximation?*

5.2.2 Standard route: diagonal cumulant with GW self-energy

$$C_{pp}(t) = i \int \frac{d\omega}{2\pi} \frac{\Sigma^c_{pp}\left(\omega + \epsilon^{HF}_p\right)}{(\omega + i\eta)^2} e^{-i\omega t} \tag{5.44}$$

$$= i \int \frac{d\omega}{2\pi} \frac{1}{(\omega + i\eta)^2} e^{-i\omega t} \left[\sum_{i\nu} \frac{M^2_{pi\nu}}{\omega + \underbrace{\epsilon^{HF}_p - \epsilon_i + \Omega_\nu + i\eta}_{-\Delta_{pi\nu}}} + \sum_{a\nu} \frac{M^2_{pa\nu}}{\omega + \underbrace{\epsilon^{HF}_p - \epsilon_a - \Omega_\nu + i\eta}_{-\Delta_{pa\nu}}}\right] \tag{5.45}$$

$$= \mathrm{i} \sum_{iv} M^2_{piv} \int \frac{\mathrm{d}\omega}{2\pi} e^{-\mathrm{i}\omega t} \frac{1}{[\omega + \mathrm{i}\eta]^2} \frac{1}{\omega - \Delta_{piv}} + \mathrm{i} \sum_{av} M^2_{pav} \int \frac{\mathrm{d}\omega}{2\pi} e^{-\mathrm{i}\omega t} \frac{1}{[\omega + \mathrm{i}\eta]^2} \frac{1}{\omega - \Delta_{pav}} \tag{5.46}$$

$$= \sum_{i\nu} \zeta_{pi\nu} \left[e^{-i\Delta_{pi\nu} t} - 1 + i\Delta_{pi\nu} t\right] + \sum_{a\nu} \zeta_{pa\nu} \left[e^{-i\Delta_{pa\nu} t} - 1 + i\Delta_{pa\nu} t\right] \tag{5.47}$$

where in going from eqn. 5.318 to eqn. 5.44, where we made a diagonal approximation for the self-energy and introduced the frequency shift $\omega \to \omega + \epsilon^{HF}_p$, and then from eqn. 5.46 to eqn. 5.47, we have evaluated a contour integral. For the final expression, we have defined $\zeta_{pi\nu} = \left(\frac{M_{pi\nu}}{\Delta_{pi\nu}}\right)^2$ and $\zeta_{pa\nu} = \left(\frac{M_{pa\nu}}{\Delta_{pa\nu}}\right)^2$. This allows us to arrive at the something similar to the Landau form of the cumulant.

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

$$\int \frac{\mathrm{d}\omega}{2\pi} e^{-\mathrm{i}\omega t} \frac{1}{(\omega-\omega_1)^2} \frac{1}{\omega-\omega_2} = (-\mathrm{i}) \left\{ \left[\partial_\omega \left(\frac{e^{-\mathrm{i}\omega t}}{\omega-\omega_2} \right) \right]_{\omega=\omega_1} + \left[\frac{e^{-\mathrm{i}\omega t}}{(\omega-\omega_1)^2} \right]_{\omega=\omega_2} \right\} \tag{5.48}$$

$$= \frac{(-\mathrm{i})}{(\omega_1-\omega_2)^2} \left\{ \left[(-\mathrm{i}t)(\omega_1-\omega_2) - 1 \right] e^{-\mathrm{i}\omega_1 t} + e^{-\mathrm{i}\omega_2 t} \right\} \tag{5.49}$$

$$\implies \int \frac{\mathrm{d}\omega}{2\pi} e^{-i\omega t} \frac{1}{[\omega-(0-\mathrm{i}\eta)]^2} \frac{1}{\omega-\Delta} = \frac{-\mathrm{i}}{\Delta^2} \left(e^{-\mathrm{i}\Delta t} + \mathrm{i}\Delta t - 1 \right) \tag{5.50}$$

Now we plug in our derived expression for $C_{pp}(t)$ into the cumulant ansatz for the retarded Green's function:

$$G_{pp}(t) = G_{pp}^{HF}(t) e^{C_{pp}(t)} \tag{5.51}$$

$$= -i\Theta(t) e^{-i\epsilon_p^{HF} t + C_{pp}(t)} \tag{5.52}$$

$$= -i\Theta(t) e^{-i\epsilon_p^{HF} t + \sum_{i\nu} \zeta_{pi\nu} \left(e^{-i\Delta_{pi\nu} t} + i\Delta_{pi\nu} t - 1 \right) + \sum_{a\nu} \zeta_{pa\nu} \left(e^{-i\Delta_{pa\nu} t} + i\Delta_{pa\nu} t - 1 \right)} \tag{5.53}$$

$$= -i\Theta(t) \underbrace{e^{-\sum_{i\nu} \zeta_{pi\nu} - \sum_{a\nu} \zeta_{pa\nu}}}_{Z_p^{QP}} e^{-i \overbrace{\left(\epsilon_p^{HF} - \sum_{i\nu} \zeta_{pi\nu} \Delta_{pi\nu} - \sum_{a\nu} \zeta_{pa\nu} \Delta_{pa\nu} \right)}^{\epsilon_p^{QP}} t} e^{\sum_{i\nu} \zeta_{pi\nu} e^{-i\Delta_{pi\nu} t} + \sum_{a\nu} \zeta_{pa\nu} e^{-i\Delta_{pa\nu} t}} \tag{5.54}$$

$$= -i\Theta(t) Z_p^{QP} e^{-i\epsilon_p^{QP} t} e^{\sum_{i\nu} \zeta_{pi\nu} e^{-i\Delta_{pi\nu} t} + \sum_{a\nu} \zeta_{pa\nu} e^{-i\Delta_{pa\nu} t}} \tag{5.55}$$

$$\tag{5.56}$$

where we have the weight of the quasiparticle peak $Z_p^{QP} = \exp\left(-\sum_{i\nu} \zeta_{pi\nu} - \sum_{a\nu} \zeta_{pa\nu}\right)$ and the quasiparticle energy $\epsilon_p^{QP} = \epsilon_p^{HF} - \left(\sum_{i\nu} \zeta_{pi\nu} \Delta_{pi\nu} + \sum_{a\nu} \zeta_{pa\nu} \Delta_{pa\nu}\right)$.

We pause to make some important connections. Notice

$$\epsilon_p^{QP} = \epsilon_p^{HF} - \left(\sum_{i\nu} \zeta_{pi\nu}\Delta_{pi\nu} + \sum_{a\nu} \zeta_{pa\nu}\Delta_{pa\nu}\right) \tag{5.57}$$

$$= \epsilon_p^{HF} - \left(\sum_{i\nu} \frac{M_{pi\nu}^2}{\Delta_{pi\nu}} + \sum_{a\nu} \frac{M_{pa\nu}^2}{\Delta_{pa\nu}}\right) \tag{5.58}$$

$$= \epsilon_p^{HF} + \Sigma_{pp}^c\left(\epsilon_p^{HF}\right) \tag{5.59}$$

and

$$Z_p^{QP} = \exp\left(-\sum_{i\nu} \zeta_{pi\nu} - \sum_{a\nu} \zeta_{pa\nu}\right) \tag{5.60}$$

$$= \exp\left(-\sum_{i\nu} \left(\frac{M_{pi\nu}}{\Delta_{pi\nu}}\right)^2 - \sum_{a\nu} \left(\frac{M_{pa\nu}}{\Delta_{pa\nu}}\right)^2\right) \tag{5.61}$$

$$= \exp\left(\left[\frac{\partial \Sigma_{pp}^c(\omega)}{\partial \omega}\right]_{\omega=\epsilon_p^{HF}}\right) \tag{5.62}$$

$$\tag{5.63}$$

where we have used the fact that $\Sigma_{pp}^c(\omega) = \sum_{i\nu} \frac{M_{pi\nu}^2}{\omega-\epsilon_i+\Omega_\nu} + \sum_{a\nu} \frac{M_{pa\nu}^2}{\omega-\epsilon_a-\Omega_\nu} \implies \left[\frac{\partial \Sigma_{pp}^c(\omega)}{\partial \omega}\right]_{\omega=\epsilon_p^{HF}} = -\sum_{i\nu} \left(\frac{M_{pi\nu}}{\Delta_{pi\nu}}\right)^2 - \sum_{a\nu} \left(\frac{M_{pa\nu}}{\Delta_{pa\nu}}\right)^2$.

Next, we want to perform a Fourier transform.

$$G_{pp}(\omega) = \int_{-\infty}^{\infty} dt e^{i\omega t} G_{pp}(t) \tag{5.64}$$

$$= -iZ_p^{QP} \int_0^{\infty} dt e^{i(\omega-\epsilon_p^{QP})t} e^{\sum_{i\nu} \zeta_{pi\nu} e^{-i\Delta_{pi\nu}t} + \sum_{a\nu} \zeta_{pa\nu} e^{-i\Delta_{pa\nu}t}} \tag{5.65}$$

$$= -iZ_p^{QP} \int_0^{\infty} dt\, e^{i(\omega-\epsilon_p^{QP})t} \left(1 + \sum_{i\nu} \zeta_{pi\nu} e^{-i\Delta_{pi\nu}t} + \sum_{a\nu} \zeta_{pa\nu} e^{-i\Delta_{pa\nu}t} 4\right) \tag{5.66}$$

$$= -iZ_p^{QP} \int_0^{\infty} dt\, e^{[-\eta + i(\omega-\epsilon_p^{QP})t]} \tag{5.67}$$

$$- iZ_p^{QP} \sum_{i\nu} \zeta_{pi\nu} \int_0^{\infty} dt\, e^{[-\eta + i(\omega-\epsilon_p^{QP}-\Delta_{pi\nu})t]} \tag{5.68}$$

$$- iZ_p^{QP} \sum_{a\nu} \zeta_{pa\nu} \int_0^{\infty} dt\, e^{[-\eta + i(\omega-\epsilon_p^{QP}-\Delta_{pa\nu})t]} + \ldots \tag{5.69}$$

$$= \frac{Z_p^{QP}}{\omega - \epsilon_p^{QP} + i\eta} + \sum_{i\nu} \frac{Z_p^{QP}\zeta_{pi\nu}}{\omega - \epsilon_p^{QP} - \Delta_{pi\nu} + i\eta} + \sum_{a\nu} \frac{Z_p^{QP}\zeta_{pa\nu}}{\omega - \epsilon_p^{QP} - \Delta_{pa\nu} + i\eta} + \ldots \tag{5.70}$$

$$= \frac{Z_p^{QP}}{\omega - \epsilon_p^{QP} + i\eta} + \sum_{i\nu} \frac{Z_{pi\nu}^{sat}}{\omega - \epsilon_{pi\nu}^{sat} + i\eta} + \sum_{a\nu} \frac{Z_{pa\nu}^{sat}}{\omega - \epsilon_{pa\nu}^{sat} + i\eta} + \ldots \tag{5.71}$$

In going from eqn. 5.64 to eqn. 5.65, we used the step function to restrict the lower bound of the integral to 0 and then we end by defining the satellite energies $\epsilon_{pi\nu}^{sat} = \epsilon_p^{QP} + \Delta_{pi\nu}$ and $\epsilon_{pa\nu}^{sat} = \epsilon_p^{QP} + \Delta_{pa\nu}$, as well as the satellite weights $Z_{pi\nu}^{sat} = Z_p^{QP}\zeta_{pi\nu}$ and $Z_{pa\nu}^{sat} = Z_p^{QP}\zeta_{pa\nu}$. *What happens when we treat the exponential more than just up to the first order? Is this useful?*

Spectral function

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

$$
\begin{align}
A_{pp}^{GW+C}(\omega) &= -\frac{1}{\pi}\operatorname{Im} G_{pp}(\omega) \tag{5.72}\\
&= -\frac{1}{\pi}\operatorname{Im}\left[\frac{Z_p^{QP}}{\omega-\epsilon_p^{QP}+i\eta}+\sum_{i\nu}\frac{Z_{pi\nu}^{sat}}{\omega-\epsilon_{pi\nu}^{sat}+i\eta}+\sum_{a\nu}\frac{Z_{pa\nu}^{sat}}{\omega-\epsilon_{pa\nu}^{sat}+i\eta}\right] \tag{5.73}\\
&= -\frac{1}{\pi}\operatorname{Im}\left[\frac{\operatorname{Re} Z_p^{QP}+i\operatorname{Im} Z_p^{QP}}{\omega-\operatorname{Re}\epsilon_p^{QP}+i\left(\eta-\operatorname{Im}\epsilon_p^{QP}\right)}+\sum_{i\nu}\frac{\operatorname{Re} Z_{pi\nu}^{sat}+i\operatorname{Im} Z_{pi\nu}^{sat}}{\omega-\operatorname{Re}\epsilon_{pi\nu}^{sat}+i\left(\eta-\operatorname{Im}\epsilon_{pi\nu}^{sat}\right)}+\dots\right] \tag{5.74}\\
&= -\frac{1}{\pi}\operatorname{Im}\left[\frac{\left(\operatorname{Re} Z_p^{QP}+i\operatorname{Im} Z_p^{QP}\right)\left(\omega-\operatorname{Re}\epsilon_p^{QP}-i\left(\eta-\operatorname{Im}\epsilon_p^{QP}\right)\right)}{\left(\omega-\operatorname{Re}\epsilon_p^{QP}\right)^2+\left(\operatorname{Im}\epsilon_p^{QP}\right)^2}\right. \tag{5.75}\\
&\left.+\sum_{i\nu}\frac{\left(\operatorname{Re} Z_{pi\nu}^{sat}+i\operatorname{Im} Z_{pi\nu}^{sat}\right)\left(\omega-\operatorname{Re}\epsilon_{pi\nu}^{sat}-i\left(\eta-\operatorname{Im}\epsilon_{pi\nu}^{sat}\right)\right)}{\left(\omega-\operatorname{Re}\epsilon_{pi\nu}^{sat}\right)^2+\left(\operatorname{Im}\epsilon_{pi\nu}^{sat}\right)^2}+\dots\right] \tag{5.76}\\
&= -\frac{1}{\pi}\left[\frac{\left(\operatorname{Re} Z_p^{QP}\right)\left(\operatorname{Im}\epsilon_p^{QP}\right)+\left(\operatorname{Im} Z_p^{QP}\right)\left(\omega-\operatorname{Re}\epsilon_p^{QP}\right)}{\left(\omega-\operatorname{Re}\epsilon_p^{QP}\right)^2+\left(\operatorname{Im}\epsilon_p^{QP}\right)^2}\right. \tag{5.77}\\
&\left.+\sum_{i\nu}\frac{\left(\operatorname{Re} Z_{pi\nu}^{sat}\right)\left(\operatorname{Im}\epsilon_{pi\nu}^{sat}\right)+\left(\operatorname{Im} Z_{pi\nu}^{sat}\right)\left(\omega-\operatorname{Re}\epsilon_{pi\nu}^{sat}\right)}{\left(\omega-\operatorname{Re}\epsilon_{pi\nu}^{sat}\right)^2+\left(\operatorname{Im}\epsilon_{pi\nu}^{sat}\right)^2}+\dots\right] \tag{5.78}
\end{align}
$$

5.2.3 Annotation of CC Cumulant Green's function paper

Cumulant from second order self-energy

The second order self-energy, which uses a HF reference, can be written as

$$
\begin{align}
\Sigma_{pq}^{(2)}(\omega) &= \frac{1}{2}\sum_{iab}\frac{\langle pi||ab\rangle\langle ab||qi\rangle}{\omega+\epsilon_i-\epsilon_a-\epsilon_b}+\frac{1}{2}\sum_{ija}\frac{\langle pa||ij\rangle\langle ij||qa\rangle}{\omega+\epsilon_a-\epsilon_i-\epsilon_j} \tag{5.79}\\
\implies \Sigma_{pp}^{(2)}(\omega+\epsilon_p) &= \frac{1}{2}\sum_{iab}\frac{\langle pi\,||\,ab\rangle^2}{\omega-\epsilon_{pi}^{ab}}+\frac{1}{2}\sum_{ija}\frac{\langle pa\,||\,ij\rangle^2}{\omega-\epsilon_{pa}^{ij}} \tag{5.80}
\end{align}
$$

where $\epsilon_{pi}^{ab} = \epsilon_a + \epsilon_b - \epsilon_p - \epsilon_i$ and $\epsilon_{pa}^{ij} = \epsilon_i + \epsilon_j - \epsilon_p - \epsilon_a$. So we can write the diagonal cumulant[1] as

$$C_{pp}(t) \equiv i \int \frac{d\omega}{2\pi} \frac{\Sigma_{pp}^{c}\left(\omega+\epsilon_p\right)}{(\omega+i\eta)^2} e^{-i\omega t} \tag{5.81}$$

$$\implies C_{pp}^{(2)}(t) = \frac{1}{2}\sum_{iab} \langle pi \,||\, ab\rangle^2 \int \frac{d\omega}{2\pi} \frac{ie^{-i\omega t}}{\omega^2\left(\omega-\epsilon_{pi}^{ab}\right)} + \frac{1}{2}\sum_{ija} \langle pa \,||\, ij\rangle^2 \int \frac{d\omega}{2\pi} \frac{ie^{-i\omega t}}{\omega^2\left(\omega-\epsilon_{pa}^{ij}\right)} \tag{5.82}$$

$$= \frac{1}{2}\sum_{iab} \frac{\langle pi \,||\, ab\rangle^2}{\left(\epsilon_{pi}^{ab}\right)^2}\left(e^{-i\epsilon_{pi}^{ab}t} + i\epsilon_{pi}^{ab}t - 1\right) + \frac{1}{2}\sum_{ija} \frac{\langle pa \,||\, ij\rangle^2}{\left(\epsilon_{pa}^{ij}\right)^2}\left(e^{-i\epsilon_{pa}^{ij}t} + i\epsilon_{pa}^{ij}t - 1\right) \tag{5.83}$$

$$= \frac{1}{2}\sum_{iab} \langle pi\|ab\rangle^2 f\left(\epsilon_{pi}^{ab}\right) + \frac{1}{2}\sum_{ija} \langle pa\|ij\rangle^2 f\left(\epsilon_{pa}^{ij}\right) \tag{5.84}$$

$$= \int d\omega\, \beta(\omega) f(\omega) \tag{5.85}$$

where $f(\omega) \equiv \frac{e^{-i\omega t}+i\omega t-1}{\omega^2}$ and we identify the cumulant kernel as [2]

$$\beta(\omega) = -\frac{1}{\pi}\operatorname{Im}\Sigma_{pp}^{(2)}\left(\omega+\epsilon_p\right) \tag{5.86}$$

$$\tag{5.87}$$

$$= \frac{1}{2}\sum_{iab} \langle pi\|ab\rangle^2 \delta\left(\omega-\epsilon_{pi}^{ab}\right) + \frac{1}{2}\sum_{ija} \langle pa\|ij\rangle^2 \delta\left(\omega-\epsilon_{pa}^{ij}\right) \tag{5.88}$$

A connection can be made between the cumulant kernel $\beta(\omega) = \sum_q g_q^2 \delta(\omega-\omega_q)$ for the 2nd-order self energy to that for electrons coupled to bosonic excitations at the frequencies $\omega_q \equiv \epsilon_{pq}^{rs}$ in the quasi-boson approximation with coupling coefficients $g_q \equiv \langle pq\|rs\rangle$.

Equivalence between the second order self-energy and the CC retarded Green's function

When both the IP and EA branches are included, the CC GF can be written in frequency space as [3]

[1] Note that in order to get from eqn. 5.82 to eqn. 5.83 we have used the identity $\int \frac{d\omega}{2\pi}\frac{ie^{-i\omega t}}{\omega^2(\omega-\epsilon)} = \frac{1}{\epsilon^2}\left(e^{-i\epsilon t}+i\epsilon t-1\right)\operatorname{sgn}(t)$, and since we are dealing with retarded quantities, we only care about $t > 0$ so $\operatorname{sgn}(t) = 1$.

[2] To get from eqn. 5.86 to eqn. 5.88, we have used the identity $\operatorname{Im}\frac{1}{x+i\eta} = -\pi\delta(x)$ as $\eta \to 0^+$.

[3] A diagrammatic analysis shows that only three non-zero terms when $p, q \in occ$ survive, which allows us to move from eqn. 5.96 to eqn. 5.97.

The retarded single-particle Green's function in the time domain is defined as

$$G^R_{pq}(t-t') = -i\,\Theta(t-t')\langle 0|\{a_p(t), a^\dagger_q(t')\}|0\rangle. \tag{5.89}$$

Fourier transforming and inserting a resolution of identity over $(N\pm1)$-electron eigenstates gives the Lehmann representation for both the IP and EA parts:

$$G^R_{pq}(\omega) = \sum_n \frac{\langle 0|a_p(t)|n^{N+1}\rangle\langle n^{N+1}|a^\dagger_q(t')|0\rangle}{\omega - (E^{N+1}_n - E^N_0) + i\delta} + \sum_m \frac{\langle 0|a^\dagger_q(t')|m^{N-1}\rangle\langle m^{N-1}|a_p(t)|0\rangle}{\omega + (E^{N-1}_m - E^N_0) + i\delta}. \tag{5.90}$$

In coupled-cluster theory, the exact, correlated ground state can be written as $|\Psi_0\rangle = e^T|\Phi\rangle$ and $\langle\Psi_0| = \langle\Phi|(1+\Lambda)e^{-T}$ and defining the similarity-transformed operators

$$\bar{H}_N = e^{-T}H_N e^T, \qquad \bar{a}_p(t) = e^{-T}a_p(t)e^T, \qquad \bar{a}^\dagger_q(t') = e^{-T}a^\dagger_q(t')e^T. \tag{5.91}$$

we can write

$$G^R_{pq}(\omega) = \langle\Phi|(1+\Lambda)\,\bar{a}^\dagger_q(t')\,\frac{1}{\omega + i\delta + \bar{H}_N}\,\bar{a}_p(t)|\Phi\rangle + \langle\Phi|(1+\Lambda)\,\bar{a}_p(t)\,\frac{1}{\omega + i\delta - \bar{H}_N}\,\bar{a}^\dagger_q(t')|\Phi\rangle. \tag{5.92}$$

Now, if we start again with Eqn. 5.89 and decide just to consider the retarded Green's function for one core orbital c, it is just diagonal and reads

$$G^R_c(t) = -i\Theta(t)e^{iE_0t}\left\langle 0\left|a_c e^{-iHt}a^\dagger_c\right|0\right\rangle - i\Theta(t)e^{-iE_0t}\left\langle 0\left|a^\dagger_c e^{iHt}a_c\right|0\right\rangle \tag{5.93}$$

$$= -i\Theta(t)e^{-iE_0t}\left\langle N-1\left|e^{iHt}\right|N-1\right\rangle \tag{5.94}$$

Note that we could only do this because we were able to make the separable approximation to the ground state $|0\rangle \simeq a^\dagger_c\,|N-1\rangle$, where $|N-1\rangle$ is the exact $N-1$ wavefunction with the core electron separated from it. We are just able to make this approximation for core states because they are localized and thus weakly correlated, so their removal won't relax the exact wavefunction too much. This is not the case for valence states, which are highly correlated, so the separable approximation would not make sense.

$$G^R_{pq}(\omega) = \left\langle \Phi \left| (1+\Lambda)\bar{a}^\dagger_q(\omega + \bar{H}_N + i\delta \right.\right.$$

(5.95)

$$\langle\Phi|(1+\Lambda_2)\left(a^\dagger_q + \left(a^\dagger_q T_2\right)_C\right) X_p(\omega)|\Phi\rangle + \langle\Phi|(1+\Lambda_2)\left(a_p + \left(a_p T_2\right)_C\right) Y_q(\omega)|\Phi\rangle \quad (5.96)$$

$$= \langle\Phi|a^\dagger_q X_{1,p}(\omega)|\Phi\rangle + \langle\Phi|\Lambda_2 \left(a\right.$$

(5.97)

$$= x^q(\omega)_p - \frac{1}{2}\sum_{ijab}\lambda^{ab}_{ij}t^{qj}_{ab}x^i(\omega)_p$$

(5.98)

where to get eqn. 5.96 we limited the CC expansion to doubles, i.e. $T \approx T_2 = \frac{1}{4}\sum_{ijab} t^{ab}_{ij}a^\dagger_a a^\dagger_b a_j a_i$ and $\Lambda \approx \Lambda_2 = \frac{1}{4}\sum_{ijab}\lambda^{ab}_{ij}a^\dagger_i a^\dagger_j a_b a_a$, and expanded the $\bar{a}_p = a_p + [a_p, T_2]$ and $\bar{a}^\dagger_q = a^\dagger_q + [a^\dagger_q, T_2]$ operators into their connected forms. We also defined the $X_p(\omega) \equiv (\omega + \bar{H}_N + i\delta)^{-1}\bar{a}_p$ and $Y_q(\omega) \equiv (\omega - \bar{H}_N + i\delta)^{-1}\bar{a}_q{}^\dagger$ operators that have the components

$$X_p(\omega) = \sum_i x^i(\omega)_p a_i + \frac{1}{2!}\sum_{ij,a} x^{ij}_a(\omega)_p a^\dagger_a a_j a_i = X_{1,p}(\omega) + X_{2,p}(\omega) \quad (5.99)$$

$$Y_q(\omega) = \sum_a y_a(\omega)_q a^\dagger_a + \frac{1}{2!}\sum_{i,ab} y^i_{ab}(\omega)_q a^\dagger_a a^\dagger_b a_i = Y_{1,q}(\omega) + Y_{2,q}(\omega) \quad (5.100)$$

This seems similar to second RPA theory, probably because it is. At this point, we can form a perturbation series defined by a perturbation parameter ξ, e.g. $t^{rs}_{pq} = t^{(0)rs}_{pq} + \xi t^{(1)rs}_{pq} + \xi^2 t^{(2)rs}_{pq}$, etc. By keeping only terms up to second order we get:

$$G^{(2)R}_{pq}(\omega) = x^{(2)q}(\omega)_p - \frac{1}{2}\sum_{ijab}\lambda^{(1)ab}_{ij}t^{(1)qj}_{ab}x^{(0)i}(\omega)_p - \frac{1}{2}\sum_{iab}\left(\lambda^{(1)ab}_{pi}y^{(1)i}_{ab}(\omega)_q + \lambda^{(2)ab}_{pi}y^{(0)i}_{ab}(\omega)_q\right)$$

(5.101)

$$= x^{(0)p}(\omega)_p\delta_{pq} + x^{(2)q}(\omega)_p - \frac{1}{2}\sum_{iab}\lambda^{(1)ab}_{pi}\left(t^{(1)qi}_{ab}x^{(0)p}(\omega)_p + y^{(1)i}_{ab}(\omega)_q\right) \quad (5.102)$$

$$= \frac{\delta_{pq}}{(\omega-\epsilon_p)} + \frac{1}{(\omega-\epsilon_p)}\left[\frac{1}{2}\sum_{ija}\frac{v^{qa}_{ij}v^{pa}_{ij}}{(\omega+\epsilon_a-\epsilon_i-\epsilon_j)} + \frac{1}{2}\sum_{iab}\frac{v^{pi}_{ab}v^{qi}_{ab}}{(\omega+\epsilon_i-\epsilon_a-\epsilon_b)}\right]\frac{1}{(\omega-\epsilon_q)}$$

(5.103)

$$\equiv G^{R(0)}_{pq}(\omega) + G^{R(0)}_{pq}(\omega)\Sigma^{(2)}_{pq}(\omega)G^{R(0)}_{pq}(\omega) \quad (5.104)$$

where we used the simplifications $x^{(1)q}(\omega)_p = 0$ and $x^{(0)q}(\omega)_p = x^{(0)p}(\omega)_p\delta_{pq}$ and in the perturbation analysis, we identified that $G^{(0)R}_{pq}(\omega) = x^{(0)q}(\omega)_p = \frac{1}{(\omega-\epsilon_q)}$.

Real-time EOM-CC Cumulant GF

We restrict the discussion to the retarded core-hole Green's function for a given deep core level $p = c$, $G_c^R = G_{cc}$ given by

$$
\begin{aligned}
G_c^R(t) &= -i\Theta(t-t') \left\langle 0 \left| \left\{ a_c(t), a_c^\dagger(t') \right\} \right| 0 \right\rangle && (5.105)\\
&= -i\Theta(t) e^{iE_0 t} \left\langle 0 \left| a_c e^{-iHt} a_c^\dagger \right| 0 \right\rangle + -i\Theta(t) e^{-iE_0 t} \left\langle 0 \left| a_c^\dagger e^{iHt} a_c \right| 0 \right\rangle && (5.106)\\
&= -i\Theta(t) e^{iE_0 t} \left\langle N-1 \left| a_c a_c e^{-iHt} a_c^\dagger a_c^\dagger \right| N-1 \right\rangle + -i\Theta(t) e^{-iE_0 t} \left\langle N-1 \left| a_c a_c^\dagger e^{iHt} a_c a_c^\dagger \right| N-1 \right\rangle && (5.107)\\
&= -i\Theta(t) e^{-iE_0 t} \left\langle N-1 \left| e^{iHt} \right| N-1 \right\rangle && (5.108)\\
&= -i\Theta(t) e^{-iE_0 t} \langle N-1 | N-1, t \rangle && (5.109)
\end{aligned}
$$

where we have used the separable approximation to the ground state $|0\rangle \simeq a_c^\dagger |N-1\rangle$, which is reasonable for core excitations. And then at the end we have defined $|N-1,t\rangle = e^{iHt}|N-1\rangle$, which is a solution to $-i\frac{d|N-1,t\rangle}{dt} = H|N-1,t\rangle$. The next step is to assume a time-dependent, CC ansatz for $|N-1,t\rangle = N(t)e^{T(t)}|\phi\rangle$, where $|\phi\rangle = a_c|N\rangle$ is the reference determinant with a core hole, $N(t)$ is a *scalar* normalization factor, and $T(t)$ is the time-dependent cluster operator acting only on the $N-1$ electron Fock space. Inserting this ansatz into the differential equation for $|N-1,t\rangle$ and left multiplying by $e^{-T(t)}$, we obtain the coupled EOM [4]

$$
\begin{aligned}
-i\frac{d\left[N(t)e^{T(t)}|\phi\rangle\right]}{dt} &= HN(t)e^{T(t)}|\phi\rangle && (5.110)\\
-ie^{-T(t)}\frac{d\left[N(t)e^{T(t)}\right]}{dt}|\phi\rangle &= N(t)\underbrace{e^{-T(t)}He^{T(t)}}_{\bar{H}(t)}|\phi\rangle && (5.111)\\
-iN(t)\left(\frac{d\ln N(t)}{dt} + \frac{dT(t)}{dt}\right)|\phi\rangle &= N(t)\bar{H}(t)|\phi\rangle && (5.112)\\
-i\left(\frac{d\ln N(t)}{dt} + \frac{dT(t)}{dt}\right)|\phi\rangle &= \left(\bar{H}_N(t) + E^{N-1}\right)|\phi\rangle && (5.113)
\end{aligned}
$$

where we have defined a normal-order, similarity transformed Hamiltonian as $\bar{H}_N(t) = \bar{H}(t) - E^{N-1}$, where $E^{N-1} = \left\langle\phi|\bar{H}|\phi\right\rangle$. Projecting on the reference $\langle\phi|$ and excited de-

[4] In going eqn. 5.111 to eqn. 5.112, we used:

$$
\begin{aligned}
e^{-T(t)}\frac{d}{dt}\left(N(t)e^{T(t)}\right) &= e^{-T(t)}\left(\dot{N}(t)e^{T(t)} + N(t)\dot{T}(t)e^{T(t)}\right)\\
&= \dot{N}(t)e^{-T(t)}e^{T(t)} + N(t)\left(\dot{T}(t) + \frac{1}{2!}[\dot{T}(t),T(t)] + \frac{1}{3!}[[\dot{T}(t),T(t)],T(t)] + \ldots\right)\\
&\approx \dot{N}(t) + N(t)\dot{T}(t)\\
&= N(t)\left(\frac{\dot{N}(t)}{N(t)} + \dot{T}(t)\right)\\
&= N(t)\left(\frac{d}{dt}\ln N(t) + \dot{T}(t)\right)
\end{aligned}
$$

where we have used the Baker-Campbell-Hausdorff expansion and the truncation is consistent with CCSD.

terminants $\left\langle\phi_{ij}^{ab}\right|$, respectively, we obtain the coupled EOMs for the normalization factor and the cluster amplitudes, respectively:

$$-i\frac{d\ln N(t)}{dt} = \left\langle\phi\left|\bar{H}_N(t)\right|\phi\right\rangle + E^{N-1} \tag{5.114}$$

$$\implies N(t) = e^{iE^{N-1}t}e^{i\int_0^t\left\langle\phi\left|\bar{H}_N(t')\right|\phi\right\rangle dt'} \tag{5.115}$$

$$-i\left\langle\phi_{ij\ldots}^{ab\ldots}\left|\frac{dT(t)}{dt}\right|\phi\right\rangle = \langle\phi_{ij\ldots}^{ab\ldots}\left|\bar{H}_N(t)\right|\phi\rangle. \tag{5.116}$$

In order to further evaluate, we need to introduce some additional approximations. First, we assume that the ground state is uncorrelated, i.e. $|N-1\rangle \simeq a_c\,|\Phi\rangle = |\phi\rangle$, so that

$$\begin{aligned}\langle N-1|\, N-1,t\rangle =&N(t)\left\langle N-1\left|e^{iHt}\right|\phi\right\rangle\\ =&N(t)\left\langle\phi\left|\left(1+iHt+\frac{(iHt)^2}{2!}+\ldots\right)\right|\phi\right\rangle\\ =&N(t)\left(1+\langle\phi\left|R(t)\right|\phi\rangle\right)\\ =&N(t).\end{aligned} \tag{5.117}$$

where $R(t)$ is the excitation operator that collects all excited terms in the series expansion, so it has expectation value $\langle\phi\left|R(t)\right|\phi\rangle = 0$. Now, if we insert eqn. 5.115 into eqn. 5.109, we see that the Green's function is given by

$$G_c^R(t) = -i\Theta(t)e^{-iE_0t}N(t) \tag{5.118}$$

$$= -i\Theta(t)e^{-i(E_0-E^{N-1})t}e^{i\int_0^t\left\langle\phi\left|\bar{H}_N(t')\right|\phi\right\rangle dt'} \tag{5.119}$$

$$= -i\Theta(t)e^{-i\epsilon_ct}e^{C_c^R(t)} \tag{5.120}$$

In the last line, we take $E_0 \equiv E_{HF}$ as the reference energy of the N electron system and so we have $E_0 - E^{N-1} \simeq \epsilon_c$, as expected from Koopmans' theorem. And importantly, we have identified the cumulant as

$$C_c^R(t) = i\int_0^t\left\langle\phi\left|\bar{H}_N(t)\right|\phi\right\rangle dt'. \tag{5.121}$$

Now, the known Landau form for the cumulant is

$$C_L(t) = \int d\omega \frac{\beta(\omega)}{\omega^2}\left(e^{-i\omega t} + i\omega t - 1\right) \tag{5.122}$$
$$\implies C_L''(t) = -\int d\omega \beta(\omega) e^{-i\omega t} \tag{5.123}$$
$$\tag{5.124}$$

But now if we do the same thing by differentiating eqn. 5.121 twice, we have

$$C_c''(t) = i\frac{d}{dt}\left\langle \phi \left| \bar{H}_N(t) \right| \phi \right\rangle \tag{5.125}$$
$$\tag{5.126}$$

So we can identify that

$$\int d\omega \beta(\omega) e^{-i\omega t} = -i\frac{d}{dt}\left\langle \phi \left| \bar{H}_N(t) \right| \phi \right\rangle \tag{5.127}$$

Taking the inverse Fourier transform, we find a form for the CC cumulant kernel as

$$\beta(\omega) = \frac{1}{2\pi}\int_{-\infty}^{\infty} dt e^{i\omega t}\left[-i\frac{d}{dt}\left\langle \phi \left| \bar{H}_N(t) \right| \phi \right\rangle\right] \tag{5.128}$$
$$= \frac{1}{\pi}\mathrm{Re}\int_{0}^{\infty} dt e^{-i\omega t}\left[-i\frac{d}{dt}\left\langle \phi \left| \bar{H}_N(t) \right| \phi \right\rangle\right] \tag{5.129}$$

The above relation is not derived yet. Recall, that in the GW+C approach, we had $\beta(\omega) = \frac{1}{\pi}\left|\mathrm{Im}\,\Sigma_{pp}(\omega + \epsilon_p)\right|$. *Therefore, we can identify that there is a connection, but it is unclear currently how to explore it.*

So given the differential equation for the logarithm of the normalization factor in eqn. 5.114 and comparing with eqn. 5.120, we see that the cumulant obeys the differential equation

$$\begin{aligned} -i\frac{dC_c^R(t)}{dt} &= \left\langle \phi \left| \bar{H}_N(t) \right| \phi \right\rangle \\ &= \sum_{ia} f_{ia} t_i^a + \frac{1}{2}\sum_{ijab} v_{ij}^{ab} t_j^b t_i^a, \end{aligned} \tag{5.130}$$

The above relation is not derived yet. Supposedly it requires some tedious algebra and diagrammatic analysis. We can also use eqn. 5.116 to write the equation of motion for the cluster amplitudes, where for the singles, it is given by

$$-i\dot{t}_i^a(t) \equiv -i\left\langle \phi_i^a \left| \frac{dT(t)}{dt} \right| \phi \right\rangle = \left\langle \phi_i^a \right| \bar{H}_N(t) \left| \phi \right\rangle. \tag{5.131}$$

I choose to not continue further for now.

5.3 Cumulant expansion for electron-phonon interactions

5.3.1 Annotating PJ's SC-CE paper

The time-ordered form of the electron Green's function for one electron can be written as the power series expansion of an exponential ansatz

$$\mathcal{G}_k(t) = \mathcal{G}_k^{(0)}(t)\left\langle a_k T e^{-i\int_0^t d\tau V(\tau)} a_k^\dagger \right\rangle \tag{5.132}$$

$$= \mathcal{G}_k^{(0)}(t)\left\langle T e^{-i\int_0^t d\tau V(\tau)} \right\rangle \tag{5.133}$$

$$= \mathcal{G}_k^{(0)}(t)\left\langle \sum_{n=0}^{\infty} \frac{(-i)^n}{n!}\int_0^t dt_1 \cdots \int_0^t dt_n T\left[V(t_1)\cdots V(t_n)\right] \right\rangle \tag{5.134}$$

$$= \mathcal{G}_k^{(0)}(t)\left\langle \sum_{n=0}^{\infty} \frac{(-i)^n}{n!}\int_0^t dt_1 \cdots \int_0^t dt_n T\left[\prod_{j=1}^{n}\sum_{q_j} g_{q_j,k_j} a^\dagger_{k_j+q_j}(t_j)\, a_{k_j}(t_j)\, A_{q_j}(t_j)\right] \right\rangle \tag{5.135}$$

$$= \mathcal{G}_k^{(0)}(t)\left\langle \sum_{n=0}^{\infty} T\left[\frac{(-i)^n}{n!}\int_0^t dt_1 \cdots \int_0^t dt_n \prod_{j=1}^{n}\sum_{q_j} g_{q_j,k_j} a^\dagger_{k_j+q_j} a_{k_j} e^{-it_j(\epsilon_{k_j}-\epsilon_{k_j+q_j})} A_{q_j}(t_j)\right] \right\rangle \tag{5.136}$$

where $k_j = k + \sum_{i=j+1}^{n} q_i$ and $\sum_i q_i = 0$. The interpretation of the above expression is that the electron starts in state k at time 0, and then scatters off n phonons, each with momentum q_j, before returning to state k at time t. $A_q(t) = b_q e^{-i\omega_q t} + b^\dagger_{-q} e^{i\omega_q t}$, where b_q and $b_q^\dagger$ are the annihilation and creation operators for a phonon of momentum q and frequency ω_q with $[b_q, b^\dagger_{q'}] = \delta_{qq'}$. If we define 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,

$$\mathcal{G}_k(t) = \mathcal{G}_k^{(0)}(t)\left\langle T e^{-i\sum_q \int_0^t d\tau \Gamma_{qk}(\tau) A_q(\tau)} \right\rangle \tag{5.137}$$

where the remaining trace is only over the bosonic degrees of freedom. Assuming harmonic bosons, we can use $\langle e^B \rangle = e^{\langle B^2 \rangle/2}$ with the definition

$$B = -i\sum_q \int_0^t d\tau \Gamma_{qk}(\tau) A_q(\tau) \tag{5.138}$$

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

$$\langle Te^S \rangle \equiv \langle Te^B \rangle = \exp\left(\frac{1}{2}\langle TB^2\rangle\right) \tag{5.139}$$

$$\implies S = \frac{1}{2}\langle TB^2\rangle \tag{5.140}$$

$$= \frac{1}{2}(-i)^2 \sum_{qq'} \int_0^t d\tau \int_0^t d\tau' \Gamma_{qk}(\tau)\Gamma_{q'k}(\tau') \langle TA_q(\tau)A_{q'}(\tau')\rangle \tag{5.141}$$

$$= -\frac{1}{2} \sum_{qq'} \int_0^t d\tau \int_0^t d\tau' \Gamma_{qk}(\tau)\Gamma_{q'k}(\tau') \left[iD_q^{(0)}(\tau-\tau')\,\delta_{q,-q'}\right] \tag{5.142}$$

$$= -i \sum_{q} \int_0^t d\tau \int_0^t d\tau' D_q^{(0)}(\tau-\tau')\,\Gamma_{-qk}(\tau)\Gamma_{qk}(\tau') \tag{5.143}$$

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 $F[\hat{A}(\tau), \hat{B}(\tau), \ldots]$ with $\tau \in [0, t]$, which in our case is $e^{S[\Gamma(\tau)]}$, and with a unitary operator of the form $\hat{U}(\tau') = T\exp\left[\int_0^{\tau'} d\tau \hat{P}(\tau)\right]$, then

$$\hat{U}(t)F[\hat{A}(\tau), \hat{B}(\tau), \ldots] = T\left[\exp\left(\int_0^t d\tau \hat{P}(\tau)\right) F\left[\hat{U}(\tau)\hat{A}(\tau)\hat{U}^{-1}(\tau), \ldots\right]\right]. \tag{5.144}$$

We choose $\hat{P}(\tau) = -i\left[\epsilon_k + \frac{d}{d\tau}\phi_k(\tau)\right]$ and so the transformed S is given by

$$\bar{S} = -i\int_0^t d\tau \left(\epsilon_k + \frac{d}{d\tau}\phi_k(\tau)\right) - i\sum_q \int_0^t d\tau \int_0^\tau d\tau' D_q^{(0)}(\tau-\tau')\,\bar{\Gamma}_{-qk}(\tau)\bar{\Gamma}_{qk}(\tau') \tag{5.145}$$

with the transformed vertex operators $\bar{\Gamma}_{qk}(\tau) \equiv \hat{U}(\tau)\Gamma_{qk}(\tau)\hat{U}^{-1}(\tau) = g_{qk}e^{-i\phi_k(\tau)}e^{q\cdot\frac{d}{dk}}e^{+i\phi_k(\tau)}$. The Green's function can then be written as

$$\begin{aligned}\mathcal{G}_k(t) &= i\Theta(t)e^{i\phi_k(t)}T\left[\exp\left(-i\int_0^t d\tau(\epsilon_k + \frac{d}{d\tau}\phi_k(\tau))\right)\right. \qquad (5.146)\\ &\qquad \left.\times \exp\left(-i\sum_q \int_0^t d\tau \int_0^\tau d\tau' D_q^{(0)}(\tau-\tau')\,\bar{\Gamma}_{-qk}(\tau)\bar{\Gamma}_{qk}(\tau')\right)\right]\\ &= i\Theta(t)e^{i\phi_k(t)}\exp\left(\sum_{n=1}^\infty \frac{1}{n!}T\left[\bar{S}^n\right]_c\right) \qquad (5.147)\\ &= i\Theta(t)e^{C_k(t)} \qquad (5.148)\end{aligned}$$

where

$$C_k(t) = i\phi_k(t) + \sum_{n=1}^\infty \frac{1}{n!}T\left[\bar{S}^n\right]_c \tag{5.149}$$

where the notation $[\cdots]_c$ denotes the cumulant of an operator, and $T[\bar{S}]_c = T[\bar{S}]$ with subsequent terms given by $T\left[\bar{S}^n\right]_c = T\left[\bar{S}^n\right] - \sum_{m=1}^{n-1} \frac{(n-1)!}{m!(n-m-1)!} T\left[\bar{S}^m\right] T\left[\bar{S}^{n-m}\right]_c$. Then, evaluating 5.149 with $\phi_k(t) = C_k(t)$ to leading order produces

$$C_k(t) = -i\epsilon_k t - i\frac{g^2}{N}\sum_q \int_0^t d\tau \int_0^\tau d\tau' D_q^{(0)}\left(\tau - \tau'\right) e^{-C_k(\tau)+C_{k-q}(\tau)-C_{k-q}(\tau')+C_k(\tau')} \tag{5.150}$$

$$\implies \dot{C}_k(t) = -i\epsilon_k - i\frac{g^2}{N}\sum_q \int_0^t d\tau D_q^{(0)}(t-\tau) e^{-C_k(t)+C_{k-q}(t)-C_{k-q}(\tau)+C_k(\tau)} \tag{5.151}$$

with the bare 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 the Bose occupation factor $N_q = \left[\exp\left(\beta\omega_q\right) - 1\right]^{-1}$. Eqn 5.150 can be recast as a self-consistent equation for the interacting Green's function by considering

$$\frac{d\mathcal{G}_k(t)}{dt} = \frac{d}{dt}\left[-i\Theta(t)e^{C_k(t)}\right] \tag{5.152}$$

$$= \dot{C}_k(t)\mathcal{G}_k(t) \tag{5.153}$$

$$= -i\epsilon_k\mathcal{G}_k(t) - i\frac{g^2}{N}\sum_q\int_0^t d\tau\mathcal{G}_k(t)D_q^{(0)}(t-\tau)e^{-C_k(t)+C_{k-q}(t)-C_{k-q}(\tau)+C_k(\tau)} \tag{5.154}$$

$$= -i\epsilon_k\mathcal{G}_k(t) - i\frac{g^2}{N}\sum_q\int_0^t d\tau\mathcal{G}_k(t)D_q^{(0)}(t-\tau)\frac{\mathcal{G}_{k-q}(t)\mathcal{G}_k(\tau)}{\mathcal{G}_{k-q}(\tau)\mathcal{G}_k(t)} \tag{5.155}$$

$$= -i\epsilon_k\mathcal{G}_k(t) - i\frac{g^2}{N}\sum_q\int_0^t d\tau D_q^{(0)}(t-\tau)\frac{\mathcal{G}_k(\tau)\mathcal{G}_{k-q}(t)}{\mathcal{G}_{k-q}(\tau)} \tag{5.156}$$

$$\implies \frac{1}{\mathcal{G}_k(t)}\frac{d\mathcal{G}_k(t)}{dt} = -i\epsilon_k - i\frac{g^2}{N}\sum_q\int_0^t d\tau D_q^{(0)}(t-\tau)\frac{\mathcal{G}_{k-q}(t)}{\mathcal{G}_{k-q}(\tau)}\frac{\mathcal{G}_k(\tau)}{\mathcal{G}_k(t)} \tag{5.157}$$

$$\implies \frac{d\ln\mathcal{G}_k(t)}{dt} - \frac{d\ln\mathcal{G}_k^{(0)}(t)}{dt} = -i\frac{g^2}{N}\sum_q\int_0^t d\tau D_q^{(0)}(t-\tau)\frac{\mathcal{G}_{k-q}(t)}{\mathcal{G}_{k-q}(\tau)}\frac{\mathcal{G}_k(\tau)}{\mathcal{G}_k(t)} \tag{5.158}$$

$$\implies \frac{d\ln\left[\mathcal{G}_k(t)/\mathcal{G}_k^{(0)}(t)\right]}{dt} = -i\frac{g^2}{N}\sum_q\int_0^t d\tau D_q^{(0)}(t-\tau)\frac{\mathcal{G}_{k-q}(t)}{\mathcal{G}_{k-q}(\tau)}\frac{\mathcal{G}_k(\tau)}{\mathcal{G}_k(t)} \tag{5.159}$$

$$\implies ln\left[\mathcal{G}_k(t)/\mathcal{G}_k^{(0)}(t)\right] = -i\frac{g^2}{N}\sum_q\int_0^t d\sigma\int_0^\sigma d\tau D_q^{(0)}(\sigma-\tau)\frac{\mathcal{G}_{k-q}(\sigma)}{\mathcal{G}_{k-q}(\tau)}\frac{\mathcal{G}_k(\tau)}{\mathcal{G}_k(\sigma)} \tag{5.160}$$

$$\implies \mathcal{G}_k(t) = \mathcal{G}_k^{(0)}(t)\exp\left[i\sum_q\int_0^t d\sigma\int_0^\sigma d\tau\,|g_{qk}|^2\,D_q^{(0)}(\sigma-\tau)\frac{\mathcal{G}_{k-q}(\sigma)}{\mathcal{G}_{k-q}(\tau)}\frac{\mathcal{G}_k(\tau)}{\mathcal{G}_k(\sigma)}\right] \tag{5.161}$$

$$\implies \mathcal{G}_k^{(n+1)}(t) = \mathcal{G}_k^{(0)}(t)\exp\left[i\sum_q\int_0^t d\sigma\int_0^\sigma d\tau\;|g_{qk}|^2\,D_q^{(0)}(\sigma-\tau)\frac{\mathcal{G}_{k-q}^{(n)}(\sigma)}{\mathcal{G}_{k-q}^{(n)}(\tau)}\frac{\mathcal{G}_k^{(n)}(\tau)}{\mathcal{G}_k^{(n)}(\sigma)}\right] \tag{5.162}$$

where the last equation admits a form for an iterative solution of this self-consistent equation. For $n = 0$, we insert the bare Green's function, and get the second order cumulant,

$$\mathcal{G}_k^{(1)}(t) = \mathcal{G}_k^{(0)}(t)\exp\left[i\sum_q\int_0^t d\sigma\int_0^\sigma d\tau\,|g_{qk}|^2\,D_q^{(0)}(\sigma-\tau)\frac{\mathcal{G}_{k-q}^{(0)}(\sigma)}{\mathcal{G}_{k-q}^{(0)}(\tau)}\frac{\mathcal{G}_k^{(0)}(\tau)}{\mathcal{G}_k^{(0)}(\sigma)}\right] \tag{5.163}$$

$$= \mathcal{G}_k^{(0)}(t)\exp\left[i\sum_q\int_0^t d\sigma\int_0^\sigma d\tau\,|g_{qk}|^2\,D_q^{(0)}(\sigma-\tau)e^{-i\left(\epsilon_{k-q}-\epsilon_k\right)(\sigma-\tau)}\right] \tag{5.164}$$

$$\equiv \mathcal{G}_k^{(0)}(t)\exp\left[C_2(k,t)\right] \tag{5.165}$$

For $n = 1$, we have

$$\mathcal{G}_k^{(2)}(t) = \mathcal{G}_k^{(0)}(t) \exp \left[i \sum_q \int_0^t d\sigma \int_0^\sigma d\tau \, |g_{qk}|^2 \, D_q^{(0)}(\sigma - \tau) \frac{\mathcal{G}_{k-q}^{(1)}(\sigma)}{\mathcal{G}_{k-q}^{(1)}(\tau)} \frac{\mathcal{G}_k^{(1)}(\tau)}{\mathcal{G}_k^{(1)}(\sigma)} \right] \tag{5.166}$$

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

$$\left. \times e^{C_2(k,\tau) + C_2(k-q,\sigma) - C_2(k,\sigma) - C_2(k-q,\tau)} \right] \tag{5.167}$$

$$= \mathcal{G}_k^{(0)}(t) \exp \left[\sum_{n=0}^{\infty} \frac{-i}{n!} \sum_q \int_0^t d\sigma \int_0^\sigma d\tau \, |g_{qk}|^2 \, D_q^{(0)}(\sigma - \tau) \mathcal{G}_{k-q}^{(0)}(\sigma - \tau) \mathcal{G}_k^{(0)}(\tau - \sigma) \right. \tag{5.168}$$

$$\left. \times \left[C_2(k,\tau) + C_2(k-q,\sigma) - C_2(k,\sigma) - C_2(k-q,\tau) \right]^n \right]$$

$$= \mathcal{G}_k^{(0)}(t) \exp \left(\sum_{m=1}^{\infty} C_{2n}^{(2)}(k,t) \right) \tag{5.169}$$

where $C_{2n}^{(2)}(k,t)$ is the approximation to the $2n$th cumulant produced by the second iteration. Because the second iteration produces cumulants of all orders, further iterations require expanding the exponent into moments. For iterations $n \geq 2$, we use

$$\mathcal{G}_{\mathbf{k}}^{(n+1)}(t) = \mathcal{G}_{\mathbf{k}}^{(0)}(t) \exp \left(-i \sum_{\mathbf{q}} \int_0^t d\sigma \int_0^\sigma d\tau \, |g_{qk}|^2 \right. \tag{5.170}$$

$$\left. \times D_{\mathbf{q}}^0(\sigma - \tau) \mathcal{G}_{\mathbf{k}}^{(0)}(\tau - \sigma) \mathcal{G}_{\mathbf{k-q}}^{(0)}(\sigma - \tau) e^{F^{(n)}(\mathbf{k},\mathbf{q},\sigma,\tau)} \right)$$

introducing the notation

$$F^{(n)}(\mathbf{k},\mathbf{q},\sigma,\tau) = F_2^{(n)}(\mathbf{k},\mathbf{q},\sigma,\tau) + F_4^{(n)}(\mathbf{k},\mathbf{q},\sigma,\tau) + \cdots \tag{5.171}$$

where

$$F_i^{(n)}(\mathbf{k},\mathbf{q},\sigma,\tau) = C_i^{(n)}(\mathbf{k}-\mathbf{q},\sigma) - C_i^{(n)}(\mathbf{k}-\mathbf{q},\tau) - C_i^{(n)}(\mathbf{k},\sigma) + C_i^{(n)}(\mathbf{k},\tau) \tag{5.172}$$

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

$$\sum_{m=0}^{\infty} \lambda^{2m} W_{2m}^{(n)}(\mathbf{k},\mathbf{q},\sigma,\tau) = \exp \left(\sum_{m=1}^{\infty} \lambda^{2m} F_{2m}^{(n)}(\mathbf{k},\mathbf{q},\sigma,\tau) \right) \tag{5.173}$$

where we can get explicit expressions by matching the orders of λ on both sides. Our experience with equation (5.168) suggests that each iteration introduces another power of g^2 to all of the approximated cumulants, and since the nth-order cumulant is defined as being proportional to g^n, 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. So alternatively, we can write

$$C_{2n}^{\mathrm{SC-CE}}(\mathbf{k},t) = -i\sum_{\mathbf{q}}\int_0^t d\sigma\int_0^{\sigma} d\tau\,|g_{qk}|^2\,D_{\mathbf{q}}^{(0)}(\sigma-\tau)\mathcal{G}_{\mathbf{k}}^{(0)}(\tau-\sigma)\mathcal{G}_{\mathbf{k-q}}^{(0)}(\sigma-\tau)W_{2n-2}(\mathbf{k},\mathbf{q},\sigma,\tau) \tag{5.174}$$

To determine what is actually solved, at this point consider again equation (5.156), where, if we define $y_k(t) = e^{C_k(t)}$, we can rewrite it as

$$\frac{dy_k(t)}{dt} = -\,i\sum_q\int_0^t d\tau\,|g_{qk}|^2\,D_q^{(0)}(t-\tau)e^{i(\epsilon_k-\epsilon_{k-q})(t-\tau)}\frac{y_k(\tau)y_{k-q}(t)}{y_{k-q}(\tau)} \tag{5.175}$$

This is a VIDE, which can be solved numerically using the appropriate methods.

5.3.2 Annotation of Littlewood's CE paper

Power series ansatze

They use a power series expansion of the cumulant, instead of the usual exponential ansatz. This has the function of making sure that the term involving the g^{2n} EPI constant can only be found in the nth-order cumulant. So the retarded Green's function is given by

$$G(n,t) = G_o(n,t)\mathcal{P}(n,t) = G_o(n,t)\sum_{k=0}^{\infty} g^{2k}C_k(n,t) \tag{5.176}$$

To properly construct the electron self energy, they replace it by power series ansatz in order to re-introduce self-consistency from the start.

$$\begin{aligned}-i\Sigma(t) &= g^2\sum_{n=\pm}\sum_{N=\pm}\mathcal{D}(N,t)\underbrace{G_0(n,t)\mathcal{P}(n,t)}_{G(n,t)} \\ &= g^2\sum_{n=\pm} -i\Sigma_0(n,t)\mathcal{P}(n,t)\end{aligned} \tag{5.177}$$

where $\Sigma_0(n,t) \equiv -i\mathcal{D}(N,t)G_0(n,t)$.

Plugging into the Dyson equation

Now, we can plug into the temporal Dyson equation:

$$G(m,t-t_0) = G_0(m,t-t_0) + \iint dt_1 dt_2\, G_0(m,t-t_2)\,\Sigma(t_2-t_1)\,G(m,t_1-t_0) \tag{5.178}$$

$$G_0(m,t-t_0)\mathcal{P}(m,t-t_0) = G_0(m,t-t_0) - ig^2 \sum_{n=\pm} \iint dt_1 dt_2\, G_0(m,t-t_2)\,\Sigma_0(n,t_2-t_1) \tag{5.179}$$

$$\times\, \mathcal{P}(n,t_2-t_1)\,G_0(m,t_1-t_0)\,\mathcal{P}(m,t_1-t_0)$$

$$G_0(m,t)\mathcal{P}(m,t) = G_0(m,t) - ig^2 \sum_{n=\pm} \iint dt_1 dt_2\, G_0\,(m,t)\,e^{i\varepsilon_m(t_2-t_1)}\,\Sigma_0(n,t_2-t_1) \tag{5.180}$$

$$\times\, \mathcal{P}(n,t_2-t_1)\mathcal{P}(m,t_1-t_0)$$

$$\mathcal{P}(m,t) = 1 - ig^2 \sum_{n=\pm} \int_0^t dt_2 \int_0^{t_2} d\tau e^{i\varepsilon_m\tau}\,\Sigma_0(n,\tau)\mathcal{P}(n,\tau)\mathcal{P}(m,t_2-\tau) \tag{5.181}$$

where in the final line we have defined $\tau = t_2 - t_1$ and set $t_0 = 0$. Also, the temporal contraction property due to the boundary value dependence on time is used, which is only valid when the diagonal approximation is made. There are two distinct terms in this equation: a self correction term P_{SC} that occurs when $n = m$ and an inter-band scattering term P_{IC} that occurs when $n \neq m$. The contraction property is valid for the former but not the latter. So

$$\mathcal{P}(m,t) = 1 + P_{SC} + P_{IC} \tag{5.182}$$

with

$$P_{SC} = -ig^2 \int_0^t dt_2 \int_0^{t_2} d\tau\, e^{i\varepsilon_m\tau}\Sigma_0(m,\tau)\mathcal{P}(m,t_2) \tag{5.183}$$

$$P_{IC} = -ig^2 \int_0^t dt_2 \int_0^{t_2} d\tau\, e^{i\varepsilon_m\tau}\,\Sigma_0(n,\tau)\mathcal{P}(n,\tau)\mathcal{P}(m,t_2-\tau) \tag{5.184}$$

For numerical solution, they start with an initial guess of $\mathcal{P} = 1$ on the right and self consistently compute better values for $\mathcal{P}$ on the left until it converges. It also might be useful to know that we can write

$$C_k(m,t) = -i \int_0^t dt_2 \int_0^{t_2} d\tau \left[e^{i\varepsilon_m\tau}\,\Sigma_o(m,\tau)C_{k-1}(m,t_2) + \sum_{n\neq m}\sum_{l=0}^{k} e^{i\varepsilon_m\tau}\,\Sigma_o(n,\tau)\,C_l(n,\tau)\,C_{k-1-l}(m,t_2-\tau) \right] \tag{5.185}$$

5.3.3 Annotation of Dunn paper

Time evolution

The given Hamiltonian is

$$H = \sum_k \epsilon_k a_k^\dagger a_k + \frac{1}{2}\sum_q (P_q^\dagger P_q + \omega_q^2 Q_q^\dagger Q_q) + \sum_q \gamma_q Q_q \rho_q^\dagger \tag{5.186}$$

$$= H_{\text{el}} + H_{\text{ph}} + H_{\text{int}} \tag{5.187}$$

$$= \sum_k \epsilon_k a_k^\dagger a_k + \sum_q \omega_q \left(b_q^\dagger b_q + \frac{1}{2}\right) + \sum_{qk} \gamma_q \sqrt{\frac{1}{2\omega_q}} (b_q + b_{-q}^\dagger) a_k^\dagger a_{k+q} \langle k|e^{-iq\cdot r}|k+q\rangle \tag{5.188}$$

$$= \sum_k \epsilon_k a_k^\dagger a_k + \sum_q \omega_q b_q^\dagger b_q + \sum_{qk} g_{qk} (b_q + b_{-q}^\dagger) a_k^\dagger a_{k+q} \tag{5.189}$$

where we have introduced bosonic second quantization operators $Q_q = \sqrt{\frac{1}{2\Omega_q}}\left(b_q + b_{-q}^\dagger\right)$ and $P_q = i\sqrt{\frac{\Omega_q}{2}}\left(b_{-q}^\dagger - b_q\right)$, which respond to the position and momentum, respectively, of a harmonic oscillator with frequency Ω_q. The electron density operator is given by $\rho_q = \sum_k a_{k+q}^\dagger a_k \langle k+q|e^{iq\cdot r}|k\rangle$, where the matrix element is between Bloch states. The electron-boson coupling constant is then given by $g_{qk} = \gamma_q \sqrt{\frac{1}{2\Omega_q}} \langle k|e^{-iq\cdot r}|k+q\rangle$. *Garnet started with search and electron boson he molto nan to start his AB theory, so maybe we want to do something similar.* In the present of this interaction, the EOM for the electron annihilation operator is given by

$$\frac{da_k(t)}{dt} = -i\epsilon_k a_k(t) - i\sum_q g_{qk} Q_q(t) a_{k+q}(t) \tag{5.190}$$

$$\implies a_k(t) = e^{-i\epsilon_k t} T \exp\left[-i\int_0^t d\tau \sum_q Q_q(\tau)\Gamma_{qk}(\tau)\right] a_k \tag{5.191}$$

$$\tag{5.192}$$

So the idea is that as time evolves when we are including the interaction, The electronic and botanic processes become inseparable.

The of both is derived. Start by introducing a rotated operator

$$\tilde{a}_k(t) = e^{i\epsilon_k t} a_k(t) \tag{5.193}$$

$$\implies \frac{d\tilde{a}_k(t)}{dt} = i\epsilon_k e^{i\epsilon_k t} a_k(t) + e^{i\epsilon_k t} \frac{da_k(t)}{dt} \tag{5.194}$$

$$= i\epsilon_k e^{i\epsilon_k t} a_k(t) + e^{i\epsilon_k t} \left(-i\epsilon_k a_k(t) - i \sum_q g_{qk} Q_q(t) a_{k+q}(t) \right) \tag{5.195}$$

$$= -i \sum_q g_{qk} e^{i\epsilon_k t} Q_q(t) a_{k+q}(t) \tag{5.196}$$

$$= -i \sum_q g_{qk} Q_q(t) e^{i\left(\epsilon_k - \epsilon_{k+q}\right)t} \tilde{a}_{k+q}(t) \tag{5.197}$$

$$= -i \sum_q g_{qk} Q_q(t) e^{i\left(\epsilon_k - \epsilon_{k+q}\right)t} e^{q\cdot\frac{d}{dk}} \tilde{a}_k(t) \tag{5.198}$$

$$= -i \sum_q Q_q(t) \Gamma_{qk}(t) \tilde{a}_k(t) \tag{5.199}$$

$$\implies \tilde{a}_k(t) = T \exp\left[-i \int_0^t d\tau \sum_q Q_q(\tau) \Gamma_{qk}(\tau) \right] \tilde{a}_k \tag{5.200}$$

$$\implies a_k(t) = e^{-i\epsilon_k t} T \exp\left[-i \int_0^t d\tau \sum_q Q_q(\tau) \Gamma_{qk}(\tau) \right] a_k \tag{5.201}$$

where we defined the vertex operator $\Gamma_{qk}(t) = g_{qk} e^{i\epsilon_k t} e^{q\cdot\frac{d}{dk}} e^{-i\epsilon_k t} = g_{qk} e^{i\left(\epsilon_k - \epsilon_{k+q}\right)t} e^{q\cdot\frac{d}{dk}}$, which uses $f(k+q) = \sum_{n=0}^{\infty} \frac{(q\cdot\nabla_k)^n}{n!} f(k) = e^{q\cdot\nabla_k} f(k)$ so thatt $e^{q\cdot\frac{d}{dk}}$ can be understood as a translation operator in k-space.

Retarded green's function

At this point, they specialized to a greens function for a single electron, which can be simplified as

$$G_k(t) = -i\Theta(t) \langle \{a_k(t), a_k^\dagger\} \rangle \tag{5.202}$$

$$= -i\Theta(t) \langle a_k(t) a_k^\dagger \rangle \tag{5.203}$$

$$= -i\Theta(t) e^{-i\epsilon_k t} \langle T \exp\left[-i \int_0^t d\tau \sum_q Q_q(\tau) \Gamma_{qk}(\tau) \right] a_k a_k^\dagger \rangle \tag{5.204}$$

$$= -i\Theta(t) e^{-i\epsilon_k t} \langle T \exp\left[-i \int_0^t d\tau \sum_q Q_q(\tau) \Gamma_{qk}(\tau) \right] \rangle \tag{5.205}$$

$$= -i\Theta(t) e^{-i\epsilon_k t} \exp\left[i \sum_q \int_0^t d\tau \int_0^\tau d\tau' D_q(\tau - \tau') \Gamma_{qk}(\tau) \Gamma_{-qk}(\tau') \right] \tag{5.206}$$

5.4 My derivations

5.4.1 Taking advantage of connection between EOMs

We use the formula $\mathcal{L}\{(f*g)(t)\}(s) = \mathcal{L}\{f(t)\}(s)\mathcal{L}\{g(t)\}(s)$ for the Laplace transform of a convolution in the below.

EOM with the retarded self energy

We know the retarded Green's function satisfies the equation of motion in the time domain:

$$(i\partial_t - \epsilon_0)G^R(t) - \int_0^t d\tau\, \Sigma^R(t-\tau)\, G^R(\tau) = 0 \tag{5.207}$$

$$\implies i\mathcal{L}\{\partial_t G^R(t)\}(s) - \epsilon_0\mathcal{L}\{G^R(t)\}(s) - \mathcal{L}\left\{\int_0^t d\tau\, \Sigma^R(t-\tau)\, G^R(\tau)\right\}(s) = 0 \tag{5.208}$$

$$i\left(s\mathcal{L}\{G^R(t)\}(s) - G^R(0)\right) - \epsilon_0\mathcal{L}\{G^R(t)\}(s) - \mathcal{L}\{\Sigma^R(t)\}(s)\mathcal{L}\{G^R(t)\}(s) = 0 \tag{5.209}$$

$$\left[s + i\epsilon_0 + i\mathcal{L}\{\Sigma^R(t)\}(s)\right]\mathcal{L}\{G^R(t)\}(s) = -i \tag{5.210}$$

$$\tag{5.211}$$

where we used the boundary condition $G^R(0) = -i$. This implies that

$$\mathcal{L}\{G^R(t)\}(s) = \frac{-i}{s + i\epsilon_0 + i\mathcal{L}\{\Sigma^R(t)\}(s)}. \tag{5.212}$$

With the standard analytic continuation $s \to -i\omega + \eta$, we find

$$G^R(-i\omega+\eta) = \frac{-i}{-i\omega + \eta + i\epsilon_0 + i\mathcal{L}\{\Sigma^R(t)\}(-i\omega+\eta)} \times \frac{i}{i} \tag{5.213}$$

$$= \frac{1}{\omega - \epsilon_0 - \mathcal{L}\{\Sigma^R(t)\}(-i\omega+\eta) + i\eta} \tag{5.214}$$

$$\implies G^R(\omega) = \frac{1}{\omega - \epsilon_0 - \Sigma^R(\omega) + i0^+} \tag{5.215}$$

EOM with the retarded cumulant

It is also valid to replace the convolution term in (5.207) with the time derivative of the cumulant. Considering the Laplace transform of just this term, we have

$$\mathcal{L}\left\{\dot{C}^R(t)G^R(t)\right\}(s) = \int_0^\infty dt\, e^{-st}\dot{C}^R(t)\left(-ie^{-i\epsilon_0 t}e^{C^R(t)}\right) \tag{5.216}$$

$$= -i\int_0^\infty e^{-t(s+i\epsilon_0)}\frac{d}{dt}(e^{C^R(t)})\,dt \tag{5.217}$$

$$= i - i(s+i\epsilon_0)\int_0^\infty e^{t(s+i\epsilon_0)}e^{C^R(t)}\,dt \tag{5.218}$$

$$= i - i(s+i\epsilon_0)\mathcal{L}\{G^R(t)\}(s) \tag{5.219}$$

where we used integration by parts. [5]

EOM from Nakajima-Zwanzig

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

$$\dot{\mathcal{A}}(t) = \mathcal{A}(t)\Omega_1 - \int_0^t d\tau\, \mathcal{A}(t-\tau)\mathcal{K}_1(\tau) + D(t) \tag{5.222}$$

So it is useful to consider the term involving the memory kernel. Its Laplace transform is

$$\mathcal{L}\left\{\mathcal{A}(t) * \mathcal{K}_1(t)\right\}(s) = \mathcal{L}\{\mathcal{A}(t)\}(s)\mathcal{L}\{\mathcal{K}_1(t)\}(s) \tag{5.223}$$

In order to make more progress, we would want to equate

$$\mathcal{L}\left\{\mathcal{A}(t) * \mathcal{K}_1(t)\right\}(s) = \mathcal{L}\left\{\dot{C}^R(t)G^R(t)\right\}(s) \tag{5.224}$$

$$\implies \mathcal{L}\{\mathcal{A}(t)\}(s)\mathcal{L}\{\mathcal{K}_1(t)\}(s) = i - i(s+i\epsilon_0)\mathcal{L}\{G^R(t)\}(s) \tag{5.225}$$

It would be nice to solve for $\mathcal{L}\{G^R(t)\}(s)$ in terms of $\mathcal{L}\{\mathcal{K}_1(t)\}(s)$ now, but to do so, we would need to establish a relationship between $\mathcal{L}\{G^R(t)\}(s)$ and $\mathcal{L}\{\mathcal{A}(t)\}(s)$. We know that the relationship between the fermionic retarded Green function $G^R(t) = -i\theta(t)\langle\{\hat{\mu}(t), \hat{\mu}(0)\}\rangle$ and the autocorrelation function $\mathcal{A}(t) = \langle\hat{\mu}(t)\hat{\mu}(0)\rangle$ of Nakajima-Zwanzig is given by

$$G^R(t) = -i\theta(t)\left[\mathcal{A}(t) + \mathcal{A}(-t)\right] \tag{5.226}$$

$$\implies \mathcal{L}\{G^R(t)\}(s) = -i\mathcal{L}\{[\mathcal{A}(t) + \mathcal{A}(-t)]\}(s) \tag{5.227}$$

$$= -i\left[\mathcal{L}\{\mathcal{A}(t)\}(s) + \mathcal{L}\{\mathcal{A}(-t)\}(s)\right] \tag{5.228}$$

$$\stackrel{?}{=} -i\mathcal{L}\{[\mathcal{A}(t) + \mathcal{A}^*(t)]\}(s) \tag{5.229}$$

$$= -2i\mathcal{L}\{\Re[\mathcal{A}(t)]\}(s) \tag{5.230}$$

The last two equalities only hold if the operators $\hat{\mu}(t)$ that make up the autocorrelation function $\mathcal{A}(t)$ are Hermitian. The fermionic second quantization operators are not Hermitian though. Only observables are Hermitian, which is why they were able to use the property leading to equation (5.229) in Eq. 35-36 of *Any type of spectroscopy can be efficiently simulated on a quantum computer.*

5.4.2 SC-CE

My derivation

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

$$G^R(t) = \underbrace{-i\theta(t)e^{-i\epsilon_0 t}}_{G_0^R(t)} e^{C^R(t)}. \tag{5.231}$$

5

$$\int_0^\infty e^{-t(s+i\epsilon_0)}\frac{d}{dt}e^{C^R(t)}\,dt = \left[e^{-t(s+i\epsilon_0)}e^{C^R(t)}\right]_0^\infty + (s+i\epsilon_0)\int_0^\infty e^{-t(s+i\epsilon_0)}e^{C^R(t)}\,dt \tag{5.220}$$

$$= -1 + (s+i\epsilon_0)\int_0^\infty e^{-t(s+i\epsilon_0)}e^{C^R(t)}\,dt \tag{5.221}$$

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:

$$\partial_t G^R(t) = -i\partial_t \left(e^{-i\epsilon_0 t} e^{C^R(t)}\right) \tag{5.232}$$

$$= -i\epsilon_0 G^R(t) - i\dot{C}^R(t) G^R(t) \tag{5.233}$$

Now, the equation of motion [6] for the retarded Green's function in the Dyson formulation with the self energy Σ is given by

$$\partial_t G^R(t) = -i\epsilon_0 G^R(t) - i \int_0^t d\tau G^R(t-\tau)\Sigma^R(\tau) \tag{5.235}$$

Equating the two gives an expression for the cumulant derivative:

$$\dot{C}^R(t) G^R(t) = \int_0^t d\tau G^R(t-\tau)\Sigma^R(\tau) \tag{5.236}$$

From here there are two directions I have in mind. Firstly, the Kowalski paper gave the EOM for the retarded core-hole cumulant as $-i\frac{dC_c^R(t)}{dt} = \left\langle \phi \left| \bar{H}_N(t) \right| \phi \right\rangle = \sum_{ia} f_{ia} t_i^a + \frac{1}{2}\sum_{ijab} v_{ij}^{ab} t_j^b t_i^a$. I could plug this in and see.

Secondly, we also know that

$$i\dot{C}^R(t) G^R(t) = \int_0^t d\tau\, \mathcal{A}(t-\tau)\mathcal{K}_1(\tau) \tag{5.237}$$

$$\implies \mathcal{L}\left\{i\dot{C}^R(t) G^R(t)\right\}(s) = \mathcal{L}\left\{\int_0^t d\tau\, \mathcal{A}(t-\tau)\mathcal{K}_1(\tau)\right\}(s) \tag{5.238}$$

where the RHS comes from the Nakajima-Zwanzig equation (5.234) and $\mathcal{L}\left\{i\dot{C}^R(t) G^R(t)\right\}(s)$ has a known analytical form. [7] . This Laplace transform might be promising because the RHS is a convolution ($(f * g)(t) = \int_0^t d\tau f(t-\tau) g(\tau)$, with $f(t) = G^R(t)$ and $g(t) = \Sigma^R(t)$)

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

$$\dot{\mathcal{A}}(t) = \mathcal{A}(t)\Omega_1 - \int_0^t d\tau\, \mathcal{A}(t-\tau)\mathcal{K}_1(\tau) + D(t) \tag{5.234}$$

Since we know the connection $\int_0^t d\tau\, \mathcal{A}(t-\tau)\mathcal{K}_1(\tau) = i\dot{C}^R(t) G^R(t) = \int_0^t d\tau G^R(t-\tau)\Sigma^R(\tau)$ and the outer definitions involve convolutions, we might be able to make some progress by demanding equality of their Laplace transforms.

[7]

$$\mathcal{L}\left\{\dot{C}^R(t) G^R(t)\right\}(s) = \int_0^\infty dt\, e^{-st} \dot{C}^R(t) \left(-ie^{-i\epsilon_0 t} e^{C^R(t)}\right) \tag{5.239}$$

$$= -i \int_0^\infty e^{-t(s+i\epsilon_0)} \frac{d}{dt}(e^{C^R(t)})\, dt \tag{5.240}$$

$$= i - i(s+i\epsilon_0) \int_0^\infty e^{-t(s+i\epsilon_0)} e^{C^R(t)}\, dt \tag{5.241}$$

$$= i - i(s+i\epsilon_0)\mathcal{L}\{G^R(t)\}(s) \tag{5.242}$$

and we know that there is a nice formula for the Laplace transform of a convolution as $\mathcal{L}\{(f*g)(t)\}(s) = \mathcal{L}\{f(t)\}(s)\mathcal{L}\{g(t)\}(s)$. From here on out, we will interchange with the notation that $\mathcal{L}\{f(t)\}(s) = \tilde{f}(s)$. Then

$$\mathcal{L}\left\{\text{RHS}\right\}(s) = \tilde{G}^R(s)\tilde{\Sigma}^R(s). \tag{5.247}$$

We already know the form of $\tilde{G}^R(s)$, but we need to find $\tilde{\Sigma}^R(s)$. We can start by taking the Laplace transform of $\Sigma^R(t)$:

$$\begin{aligned}\mathcal{L}\{\Sigma^R(t)\}(s) &= \int_0^\infty dt\, e^{-st}\Sigma^R(t) &(5.248)\\ &= \int_0^\infty dt\, e^{-st}\left[\left(G_0^R(t)\right)^{-1} - \left(G^R(t)\right)^{-1}\right] &(5.249)\end{aligned}$$

Given that it is not simple to invert the Green's function analytically in the time domain, we can stop here. But perhaps you can think of certain limits where this inversion is possible to do numerically? Setting $\mathcal{L}\left\{\text{LHS}\right\}(s) = \mathcal{L}\left\{\text{RHS}\right\}(s)$, we have

$$\begin{aligned}&i - i(s+i\epsilon_0)\tilde{G}^R(s) = \tilde{G}^R(s)\tilde{\Sigma}^R(s) &(5.250)\\ &\implies \tilde{\Sigma}^R(s) = \frac{i}{\tilde{G}^R(s)} - i(s+i\epsilon_0) \quad\iff\quad \tilde{G}^R(s) = \frac{i}{\tilde{\Sigma}^R(s) + i(s+i\epsilon_0)}. &(5.251)\end{aligned}$$

So the relationship of $\tilde{G}^R(s)$ to the $C^R(t)$ becomes clear if we define

$$\begin{aligned}F(z) \equiv \mathcal{L}\{e^{C^R(t)}\}(z) &= \int_0^\infty e^{-zt}\, e^{C^R(t)}\, dt &(5.252)\\ \implies \tilde{G}^R(s) = -i\int_0^\infty dt\, e^{-t(s+i\epsilon_0)}e^{C^R(t)} &= -iF(s+i\epsilon_0) &(5.253)\end{aligned}$$

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where to proceed from (5.240) we take $u' = \frac{d}{dt}(e^{C^R(t)}) \implies u = e^{C^R(t)}$ and $v = e^{-t(s+i\epsilon_0)} \implies v' = -(s+i\epsilon_0)e^{-t(s+i\epsilon_0)}$, so that

$$\begin{aligned}\int_0^\infty e^{-t(s+i\epsilon_0)}\frac{d}{dt}e^{C^R(t)}\, dt &= \left[e^{-t(s+i\epsilon_0)}e^{C^R(t)}\right]_0^\infty + (s+i\epsilon_0)\int_0^\infty e^{-t(s+i\epsilon_0)}e^{C^R(t)}\, dt &(5.243)\\ &= -1 + (s+i\epsilon_0)\int_0^\infty e^{-t(s+i\epsilon_0)}e^{C^R(t)}\, dt &(5.244)\end{aligned}$$

and then in (5.241) we recognize

$$\begin{aligned}\tilde{G}^R(s) &= \int_0^\infty dt\, e^{-st}\left(-ie^{-i\epsilon_0 t}e^{C^R(t)}\right) &(5.245)\\ &= -i\int_0^\infty dt\, e^{-t(s+i\epsilon_0)}e^{C^R(t)} &(5.246)\end{aligned}$$

So with $z = s + i\epsilon_0$ in (5.251), we have

$$-\,i\,F(z) = \frac{i}{\tilde{\Sigma}^R(z - i\epsilon_0) + iz} \tag{5.254}$$

$$\implies F(z) = \mathcal{L}\{e^{C^R(t)}\}(z) = -\,\frac{1}{\tilde{\Sigma}^R(z - i\epsilon_0) + iz} \tag{5.255}$$

$$\implies C^R(t) = \ln\left[\mathcal{L}_z^{-1}\left\{-\frac{1}{\tilde{\Sigma}^R(z - i\epsilon_0) + iz}\right\}(t)\right], \tag{5.256}$$

where $\mathcal{L}_z^{-1}$ is the inverse Laplace transform with respect to z.

If we pass to the frequency domain by setting $z = \eta - i\omega$ (with $\eta \to 0^+$), the boxed relation becomes equivalent to the familiar Dyson form:

$$G^R(\omega) = \frac{1}{\omega - \epsilon_0 - \Sigma^R(\omega)}. \tag{5.257}$$

Thus, the Laplace-space identity is the causal/Laplace version of Dyson's equation combined with the cumulant ansatz.

Under the usual GW+cumulant approximations, one expands around the quasiparticle pole and rewrites $C^R(t)$ in terms of the satellite spectral weight:

$$C^R(t) = \int_{-\infty}^{\infty} \frac{d\omega}{\pi}\, \frac{\Im\,\Sigma^R(\epsilon_0 + \omega)}{\omega^2}(e^{-i\omega t} + i\omega t - 1), \tag{5.258}$$

which can be recovered by (i) expressing the inverse Laplace kernel via a spectral representation of Σ^R, and (ii) performing the Bromwich integral—this uses analyticity and retarded boundary conditions. The result is the well-known closed form used for plasmon satellites and shake-up structures.

Practical use

The compact identity

$$F(z) = -\frac{1}{\tilde{\Sigma}^R(z - i\epsilon_0) + iz} \tag{5.259}$$

is a convenient starting point for controlled approximations:

- **Low-t expansion:** expand the denominator for large z to obtain short-time moments of $C^R(t)$.
- **Long-t (satellite) behavior:** analyze the singularity structure of the denominator (branch cuts from Σ^R) to extract asymptotics and satellite weights.

Maybe the best thing now would be to start with the Landau form of the cumulant and to simplify the notation it is assumed that we deal with retarded quantities only.

$$C(t) = \int d\omega \frac{\beta(\omega)}{\omega^2}\left[e^{-i\omega t} + i\omega t - 1\right] \tag{5.260}$$

where the cumulant kernel is defined as

$$\beta(\omega) = -\frac{1}{\pi}\operatorname{Im}\Sigma(\omega) \tag{5.261}$$

$$= \frac{1}{\pi}\operatorname{Im}\left(G_0^{-1}(\omega) - G^{-1}(\omega)\right) \tag{5.262}$$

$$\tag{5.263}$$

If we partition into a physical and auxiliary space, denoted by $\mathcal{S}$ and $\mathcal{A}$, respectively, $\boldsymbol{G}_0(\omega) = \begin{pmatrix} \boldsymbol{G}^0_{\mathcal{SS}}(\omega) & 0 \\ 0 & \boldsymbol{G}^0_{\mathcal{AA}}(\omega) \end{pmatrix}$ and $\boldsymbol{G}(\omega) = \begin{pmatrix} \boldsymbol{G}_{\mathcal{SS}}(\omega) & \boldsymbol{G}_{\mathcal{SA}}(\omega) \\ \boldsymbol{G}_{\mathcal{AS}}(\omega) & \boldsymbol{G}_{\mathcal{AA}}(\omega) \end{pmatrix}$, and plug in to get an expression for the cumulant kernel in the partitioned space:

$$\beta_{SS}(\omega) = \frac{1}{\pi}\operatorname{Im}\left[\mathbf{G}^{0,-1}_{SS}(\omega) - \left(\mathbf{G}_{SS}(\omega) - \mathbf{G}_{S\mathcal{A}}(\omega)\mathbf{G}^{-1}_{\mathcal{AA}}(\omega)\mathbf{G}_{\mathcal{A}S}(\omega)\right)^{-1}\right] \tag{5.264}$$

I don't know if this form is useful.

One-shot cumulant

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

$$\dot{C}^R_0(t) = \int_0^t d\tau \Sigma^R(\tau) e^{i\epsilon_0 \tau}. \tag{5.265}$$

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

$$\ddot{C}^R_0 = \Sigma^R(t) e^{i\epsilon_0 t}. \tag{5.266}$$

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

$$C^R_0(t) = \int_0^t dt' \int_0^{t'} d\tau \Sigma^R(\tau) e^{i\epsilon_0\tau} = \int_0^t d\tau \Sigma^R(\tau) e^{i\epsilon_0\tau}(t-\tau). \tag{5.267}$$

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

$$C^R_0(\omega) = \int_0^\infty dt\, e^{i\omega t} \int_0^t d\tau\, \Sigma^R(\tau) e^{i\epsilon_0\tau}(t-\tau) \tag{5.268}$$

$$= \int_0^\infty d\tau\, \Sigma^R(\tau) e^{i\epsilon_0\tau} \int_\tau^\infty dt\, e^{i\omega t}(t-\tau) \tag{5.269}$$

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

$$\int_\tau^\infty dt\, e^{i\omega t}(t-\tau) = \int_0^\infty dt'\, e^{i\omega(t'+\tau)} t' \tag{5.270}$$

$$= e^{i\omega\tau} \int_0^\infty dt'\, e^{i\omega t'} t' \tag{5.271}$$

We can evaluate the integral over t' as

$$\int_0^\infty dt'\, e^{i\omega t'} t' = -\frac{1}{(\omega + i\eta)^2} \tag{5.272}$$

where where η is the positive infinitesimal convergence factor.

Putting it all together,

$$C_0^R(\omega) = \int_0^\infty d\tau\, \Sigma^R(\tau) e^{i(\omega+\epsilon_0)\tau} \left(-\frac{1}{(\omega+i\eta)^2}\right) \tag{5.273}$$

$$= -\frac{1}{(\omega+i\eta)^2} \int_0^\infty d\tau\, \Sigma^R(\tau) e^{i(\omega+\epsilon_0)\tau} \tag{5.274}$$

$$= -\frac{\Sigma^R(\omega+\epsilon_0)}{(\omega+i\eta)^2} \tag{5.275}$$

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

$$C_0^R(t) = \int_{-\infty}^\infty d\omega\, e^{-i\omega t} C_0^R(\omega) \tag{5.276}$$

$$= \int_{-\infty}^\infty d\omega\, e^{-i\omega t} \left(-\frac{\Sigma^R(\omega+\epsilon_0)}{(\omega+i\eta)^2}\right) \tag{5.277}$$

5.4.3 Fundamental properties of the cumulant

The interacting Green's function can be written as either a Dyson series

$$G = G_0 + G_0\Sigma G_0 + G_0\Sigma G_0\Sigma G_0 + G_0\Sigma G_0\Sigma G_0\Sigma G_0 + \dots \tag{5.278}$$

or using the cumulant ansatz $G = G_0 e^C$, where we can formally expand the cumulant C in powers of the interaction strength as $C = \lambda C + \lambda^2 C + \lambda^3 C + \mathcal{O}(\lambda^4) \equiv C^{(1)} + C^{(2)} + C^{(3)} + \mathcal{O}(\lambda^4)$. Expanding the exponential gives

$$G = G_0 \left(1 + C + \frac{C^2}{2!} + \frac{C^3}{3!} + \dots\right) \tag{5.279}$$

$$= G_0 \left(1 + C^{(1)} + \frac{1}{2!}\left[\left(C^{(1)}\right)^2 + 2C^{(2)}\right] + \frac{1}{3!}\left[\left(C^{(1)}\right)^3 + 3C^{(1)}C^{(2)} + 3C^{(2)}C^{(1)} + 6C^{(3)}\right] + \mathcal{O}(\lambda^4)\right) \tag{5.280}$$

To form a relationship between the two, we can connect them order by order in powers of λ, where the standard PT convention tells us that a Σ carries with it a λ, to get

Zeroth order:

$$G^{(0)}_{\text{Dyson}} = G^{(0)}_{\text{Cumulant}} \tag{5.281}$$

$$\implies M^{(0)} \equiv G_0 = G_0 \tag{5.282}$$

$$\implies C^{(0)} = 0 \tag{5.283}$$

First order:

$$G^{(1)}_{\text{Dyson}} = G^{(1)}_{\text{Cumulant}} \tag{5.284}$$

$$\implies G_0\Sigma G_0 = G_0 C^{(1)} \tag{5.285}$$

$$\implies C^{(1)} = \Sigma G_0 \equiv M^{(1)} \tag{5.286}$$

Beyond the first order, we will have to consider products of lower-order terms as well.

Second order:

$$G^{(2)}_{\text{Dyson}} = G^{(2)}_{\text{Cumulant}} \tag{5.287}$$

$$\implies G_0\Sigma G_0\Sigma G_0 = G_0\left(C^{(2)} + \frac{1}{2!}(C^{(1)})^2\right) \tag{5.288}$$

$$= G_0\left(C^{(2)} + \frac{1}{2!}M^{(1)}\right) \tag{5.289}$$

$$\implies C^{(2)} = \underbrace{\Sigma G_0\Sigma G_0}_{M^{(2)}} - \frac{1}{2}(M^{(1)})^2 \tag{5.290}$$

Third order:

$$G^{(3)}_{\text{Dyson}} = G^{(3)}_{\text{Cumulant}} \tag{5.291}$$

$$\implies G_0\Sigma G_0\Sigma G_0\Sigma G_0 = G_0\left(C^{(3)} + \frac{1}{2}C^{(1)}C^{(2)} + \frac{1}{2}C^{(2)}C^{(1)} + \frac{1}{6}(C^{(1)})^3\right) \tag{5.292}$$

$$= G_0\left(C^{(3)} + \frac{1}{2}M^{(1)}\left(M^{(2)} - \frac{1}{2}(M^{(1)})^2\right) + \frac{1}{2}\left(M^{(2)} - \frac{1}{2}(M^{(1)})^2\right)M^{(1)} + \frac{1}{6}(M^{(1)})^3\right) \tag{5.293}$$

$$\implies C^{(3)} = \underbrace{\Sigma G_0\Sigma G_0\Sigma G_0}_{M^{(3)}} - \frac{1}{2}\left(M^{(1)}M^{(2)} + M^{(2)}M^{(1)}\right) + \frac{1}{3}(M^{(1)})^3 \tag{5.294}$$

This mirrors the third cumulant in statistics:

$$\kappa_3 = \mu_3' - 3\mu_2'\mu_1' + 2(\mu_1')^3.$$

5.4.4 GW+C

Using exact self-energy

If you give me the exact self-energy, like $\Sigma = G_0^{-1} - G^{-1}$, this means all my terms in the Dyson expansion are exact; i.e. $G = G_0 + G_0\Sigma G_0 + G_0\Sigma G_0\Sigma G_0 + \ldots$ will give the exact G. In other words, I have the exact moments $\mu_{n,k}$ of the interacting Green's function, which in the retarded framework can be written as

$$G_k^R(t) = -i\theta(t)\left\langle\left\{c_k(t), c_k^\dagger(0)\right\}\right\rangle \tag{5.295}$$

$$= -i\theta(t)\left\langle\left\{e^{iHt}c_ke^{-iHt}, c_k^\dagger\right\}\right\rangle \tag{5.296}$$

$$= -i\theta(t)\left\langle\left\{\sum_{n=0}^{\infty}\frac{(-it)^n}{n!}\mathcal{L}^n c_k, c_k^\dagger\right\}\right\rangle \tag{5.297}$$

$$= -i\theta(t)\left(\mu_{0,k} - t\mu_{1,k} + \frac{t^2}{2}\mu_{2,k} + O(t^3)\right) \tag{5.298}$$

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 super-operator $\mathcal{L}O = [H, O]$. Then, it becomes the mathematical exercise of determining the cumulant $C_k(t)$ in terms of the moments, such that the Taylor expansion of the exponential in $G_k^R(t) = G_{0,k}^R(t)e^{C_k(t)}$ matches the Dyson expansion of the exact $G_k^R(t)$ up to order n. Given that the exact 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

$$\kappa_{1,k} = \alpha_{1,k} = -\left(\mu_{1,k} - \mu_{1,k}^0\right) \tag{5.299}$$

$$\kappa_{2,k} = \alpha_{2,k} - \frac{\alpha_{1,k}^2}{2} = \frac{1}{2}\left(\mu_{2,k} - \mu_{2,k}^0\right) - \mu_{1,k}\mu_{1,k}^0 + \left(\mu_{1,k}^0\right)^2 - \frac{1}{2}\left[-\left(\mu_{1,k} - \mu_{1,k}^0\right)\right]^2 \tag{5.300}$$

$$= \frac{1}{2}\left(\mu_{2,k} - \mu_{2,k}^0\right) - \mu_{1,k}\mu_{1,k}^0 + \left(\mu_{1,k}^0\right)^2 - \frac{1}{2}\left(\mu_{1,k} - \mu_{1,k}^0\right)^2 \tag{5.301}$$

$$= \frac{1}{2}\left[\left(\mu_{2,k} - \mu_{2,k}^0\right) + \left(\mu_{1,k}\right)^2 + \left(\mu_{1,k}^0\right)^2\right] \tag{5.302}$$

We know that $\Sigma = G_0^{-1} - G^{-1}$, and inserting this gives
$G_0(\omega)\Sigma(\omega)G_0(\omega) = G_0(\omega)\left(G_0^{-1}(\omega) - G^{-1}(\omega)\right)G_0(\omega) = G_0(\omega) - G_0(\omega)G^{-1}(\omega)G_0(\omega)$

$$C_{pq}(t) = i\int \frac{d\omega}{2\pi} e^{-i(\omega-\epsilon_p^{HF})t}\left[G_0(\omega)\Sigma(\omega)G_0(\omega)\right]_{pq} \tag{5.303}$$

$$= i\int \frac{d\omega}{2\pi} e^{-i(\omega-\epsilon_p^{HF})t}\left[G_0(\omega) - G_0(\omega)G^{-1}(\omega)G_0(\omega)\right]_{pq} \tag{5.304}$$

$$= i\int \frac{d\omega}{2\pi} e^{-i(\omega-\epsilon_p^{HF})t}\left[\frac{1}{\omega - \epsilon_p^{HF} + i\eta} - \left[G_0(\omega)G^{-1}(\omega)G_0(\omega)\right]_{pq}\right] \tag{5.305}$$

$$= \theta(t) - i\int \frac{d\omega}{2\pi} e^{-i(\omega-\epsilon_p^{HF})t}\left[G_0(\omega)G^{-1}(\omega)G_0(\omega)\right]_{pq} \tag{5.306}$$

$$= i\int \frac{d\omega}{2\pi}\left[\frac{e^{-i(\omega-\epsilon_p^{HF})t}}{\omega - \epsilon_p^{HF} + i\eta} - \frac{e^{-i(\omega-\epsilon_p^{HF})t}G_{pq}^{-1}(\omega)}{(\omega - \epsilon_p^{HF} + i\eta)(\omega - \epsilon_q^{HF} + i\eta)}\right] \tag{5.307}$$

$$= \theta(t) - i\int \frac{d\omega}{2\pi} \frac{e^{-i(\omega-\epsilon_p^{HF})t}G_{pq}^{-1}(\omega)}{(\omega - \epsilon_p^{HF} + i\eta)(\omega - \epsilon_q^{HF} + i\eta)} \tag{5.308}$$

Now we plug this into the ansatz for the retarded Green's function:

$$G_{pq}(t) = G_{pp}^{HF}(t)e^{C_{pq}(t)} \tag{5.309}$$

$$= -i\theta(t)e^{-i\epsilon_p^{HF}t}\exp\left[\theta(t) - i\int \frac{d\omega}{2\pi} \frac{e^{-i(\omega-\epsilon_p^{HF})t}G_{pq}^{-1}(\omega)}{(\omega - \epsilon_p^{HF} + i\eta)(\omega - \epsilon_q^{HF} + i\eta)}\right] \tag{5.310}$$

$$\approx -i\theta(t)e^{-i\epsilon_p^{HF}t}\left[1 - i\int \frac{d\omega}{2\pi} \frac{e^{-i(\omega-\epsilon_p^{HF})t}G_{pq}^{-1}(\omega)}{(\omega - \epsilon_p^{HF} + i\eta)(\omega - \epsilon_q^{HF} + i\eta)}\right] \tag{5.311}$$

This doesn't seem useful, so we can start again with eqn. 5.306. We can use a projection technique and split into a HF space where the projector is defined as $\hat{P} = \sum_p^{\mathrm{HF}} |p\rangle\langle p|$, which we can identify with $\begin{pmatrix}1\\0\end{pmatrix}$ and the rest space with projector $\hat{Q} = 1 - \hat{P}$, which we can identify with $\begin{pmatrix} 0 \\ 1 \end{pmatrix}$. Then, using the fact that $G^{-1} = G_0^{-1} - \Sigma$ and assuming the HF reference, we can write:

$$G_{pq}^{-1}(\omega) = \left[\hat{P}G^{-1}(\omega)\hat{P} + \hat{P}G^{-1}(\omega)\hat{Q} + \hat{Q}G^{-1}(\omega)\hat{P} + \hat{Q}G^{-1}(\omega)\hat{Q}\right]_{pq} \tag{5.312}$$

$$= \left(\left[\omega - \epsilon_p^{HF}\right]\delta_{pq} - \Sigma_{pq}(\omega)\right)\hat{P}\otimes\hat{P} - \left(\Sigma_{pQ}^c\right)\hat{P}\otimes\hat{Q} - \left(\Sigma_{Pq}^c\right)\hat{Q}\otimes\hat{P} \tag{5.313}$$

$$+ \left((\omega - \epsilon_P^{HF})\delta_{PQ} - \Sigma_{PQ}(\omega)\right)\hat{Q}\otimes\hat{Q} \tag{5.314}$$

$$= \begin{pmatrix} \left[\omega - \epsilon_p^{HF}\right]\delta_{pq} - \Sigma_{pq}(\omega) & -\Sigma_{pQ}^c \\ -\Sigma_{Pq}^c & (\omega - \epsilon_P^{HF})\delta_{PQ} - \Sigma_{PQ}(\omega) \end{pmatrix} \tag{5.315}$$

$$\implies G_{pq}(\omega) = \tag{5.316}$$

where lowercase letters indicate indices in the physical space, while uppercase letters indicate indices in the rest space.

Off-diagonal cumulant with GW self-energy

We can start with

$$C_{pq}(t) = i\int \frac{d\omega}{2\pi} e^{-i(\omega - \epsilon_p^{HF})t} G_{pp}^{HF}(\omega)\Sigma_{pq}^c(\omega)G_{qq}^{HF}(\omega) \tag{5.317}$$

$$= i\int \frac{d\omega}{2\pi} e^{-i(\omega - \epsilon_p^{HF})t} \frac{\Sigma_{pq}^c(\omega)}{(\omega - \epsilon_p^{HF} + i\eta)(\omega - \epsilon_q^{HF} + i\eta)} \tag{5.318}$$

$$\tag{5.319}$$

At this point we make the frequency shift $\omega \to \omega + \epsilon_p^{HF}$, and then we can write

$$C_{pq}(t) = i\int \frac{d\omega}{2\pi} e^{-i\omega t} \frac{\Sigma_{pq}^c(\omega + \epsilon_p^{HF})}{(\omega + i\eta)(\omega + \underbrace{\epsilon_p^{HF} - \epsilon_q^{HF}}_{\Delta_{pq}} + i\eta)} \tag{5.320}$$

Now using the partial fractions we can write $\frac{1}{(\omega+i\eta)(\omega+\Delta_{pq}+i\eta)} = \frac{1}{\Delta_{pq}}\left(\frac{1}{\omega+i\eta} - \frac{1}{\omega+\Delta_{pq}+i\eta}\right)$ and we can plug in the full form for the retarded GW self-energy as

$$\Sigma_{pq}^{c,\mathrm{G_0\ W_0}}(\omega) = \sum_{i\nu}\left[W_{pi\nu}\frac{1}{\omega - (\epsilon_i - \Omega_\nu) + \mathrm{i}\eta}W_{qi\nu}\right] + \sum_{a\nu}\left[W_{pa\nu}\frac{1}{\omega - (\epsilon_a + \Omega_\nu) + \mathrm{i}\eta}W_{qa\nu}\right] \tag{5.321}$$

to get

$$C_{pq}(t) = \frac{i}{\Delta_{pq}} \int \frac{d\omega}{2\pi} e^{-i\omega t} \left[\sum_{i\nu} \frac{W_{pi\nu} W_{qi\nu}}{\omega + \epsilon_p - (\epsilon_i - \Omega_\nu) + \mathrm{i}\eta} + \sum_{a\nu} \frac{W_{pa\nu} W_{qa\nu}}{\omega + \epsilon_p - (\epsilon_a + \Omega_\nu) + \mathrm{i}\eta} \right] \tag{5.322}$$

$$\left(\frac{1}{\omega + i\eta} - \frac{1}{\omega + (\epsilon_p - \epsilon_q) + i\eta} \right)$$

$$= i \sum_{i\nu} \frac{W_{pi\nu} W_{qi\nu}}{\Delta_{pq}} \int \frac{d\omega}{2\pi} e^{-i\omega t} \times \tag{5.323}$$

$$\left(\frac{1}{(\omega + \epsilon_p - (\epsilon_i - \Omega_\nu) + \mathrm{i}\eta)(\omega + i\eta)} - \frac{1}{(\omega + \epsilon_p - (\epsilon_i - \Omega_\nu) + \mathrm{i}\eta)(\omega + (\epsilon_p - \epsilon_q) + i\eta)} \right)$$

$$+ i \sum_{a\nu} \frac{W_{pa\nu} W_{qa\nu}}{\Delta_{pq}} \int \frac{d\omega}{2\pi} e^{-i\omega t} \times$$

$$\left(\frac{1}{(\omega + \epsilon_p - (\epsilon_a + \Omega_\nu) + \mathrm{i}\eta)(\omega + i\eta)} - \frac{1}{(\omega + \epsilon_p - (\epsilon_a + \Omega_\nu) + \mathrm{i}\eta)(\omega + (\epsilon_p - \epsilon_q) + i\eta)} \right)$$

To evaluate these contour integrals, recall that $\oint d\omega f(\omega) = \int_{-\infty}^{\infty} d\omega f(\omega) + \int_{\text{arc}} d\omega f(\omega)$, so in order to equate the real frequency integral to the contour integral, which will then allow us to use the residue theorem, we need to ensure that the integral over the arc vanishes. This only will happen (due to Jordan's Lemma) if the numerator $e^{-i\omega t}$ vanishes for $\omega \to \infty$ and $\omega \to -\infty$; because we have $t > 0$, this is only true if $\mathrm{Im}(\omega) < 0$, and so we must close the contour in the lower half plane.

$$\int \frac{d\omega}{2\pi} e^{-i\omega t} \frac{1}{(\omega + \epsilon_p - (\epsilon_i - \Omega_\nu) + \mathrm{i}\eta)(\omega + i\eta)} = i \left(\frac{e^{-i(\epsilon_i - \Omega_\nu - \epsilon_p)t} - 1}{\epsilon_i - \Omega_\nu - \epsilon_p} \right) \tag{5.324}$$

$$\int \frac{d\omega}{2\pi} e^{-i\omega t} \frac{1}{(\omega + \epsilon_p - (\epsilon_i - \Omega_\nu) + \mathrm{i}\eta)(\omega + \Delta_{pq} + i\eta)} = i \left(\frac{e^{i(\Delta_{pq})t} - e^{-i(\epsilon_i - \Omega_\nu - \epsilon_p)t}}{-\epsilon_i + \Omega_\nu + \epsilon_p - \Delta_{pq}} \right) \tag{5.325}$$

$$= i \left(\frac{e^{i(\epsilon_p - \epsilon_q)t} - e^{-i(\epsilon_i - \Omega_\nu - \epsilon_p)t}}{-\epsilon_i + \Omega_\nu + \epsilon_q} \right)$$

$$\int \frac{d\omega}{2\pi} e^{-i\omega t} \frac{1}{(\omega + \epsilon_p - (\epsilon_a + \Omega_\nu) + \mathrm{i}\eta)(\omega + i\eta)} = i \left(\frac{e^{-i(\epsilon_a + \Omega_\nu - \epsilon_p)t} - 1}{\epsilon_a + \Omega_\nu - \epsilon_p} \right) \tag{5.326}$$

$$\int \frac{d\omega}{2\pi} e^{-i\omega t} \frac{1}{(\omega + \epsilon_p - (\epsilon_a + \Omega_\nu) + \mathrm{i}\eta)(\omega + \Delta_{pq} + i\eta)} = i \left(\frac{e^{i(\Delta_{pq})t} - e^{-i(\epsilon_a + \Omega_\nu - \epsilon_p)t}}{-\epsilon_a - \Omega_\nu + \epsilon_p - \Delta_{pq}} \right) \tag{5.327}$$

$$= i \left(\frac{e^{i(\epsilon_p - \epsilon_q)t} - e^{-i(\epsilon_a + \Omega_\nu - \epsilon_p)t}}{-\epsilon_a - \Omega_\nu + \epsilon_q} \right)$$

To ease the notation, we can introduce $\Xi_{i\nu} \equiv \epsilon_i - \Omega_\nu$, $\Xi_{a\nu} \equiv \epsilon_a + \Omega_\nu$. Then we can write

As a sanity check at this point, we can consider $\lim_{q\to p} T_{i\nu}(\Delta)$ and see if we recover the diagonal result. We can start by defining $f(\Delta) = \frac{e^{-i(\Xi_{i\nu}-\epsilon_p)t}-1}{\Xi_{i\nu}-\epsilon_p} + \frac{e^{i\Delta t}-e^{-i(\Xi_{i\nu}-\epsilon_p)t}}{\Xi_{i\nu}-\epsilon_q}$ and $g(\Delta) = \Delta$, then $\lim_{q\to p} T_{i\nu}(\Delta) = \lim_{q\to p} \frac{f(\Delta)}{g(\Delta)} = \frac{0}{0}$. So we can use L'Hôpital's rule to get $\lim_{q\to p} T_{i\nu}(\Delta) = \lim_{q\to p} \frac{f'(\Delta)}{g'(\Delta)} = \lim_{\Delta\to 0} \frac{f'(\Delta)}{1} = \lim_{\Delta\to 0} \frac{\left(ite^{i\Delta t}\right)(\Xi_{i\nu}-\epsilon_p+\Delta)-\left(e^{i\Delta t}-e^{-i(\Xi_{i\nu}-\epsilon_p)t}\right)}{(\Xi_{i\nu}-\epsilon_p+\Delta)^2} = \frac{i(\Xi_{i\nu}-\epsilon_p)t-1+e^{-i(\Xi_{i\nu}-\epsilon_p)t}}{(\Xi_{i\nu}-\epsilon_p)^2}$, which is indeed the diagonal result.

$$C_{pq}(t) = i^2 \left[\sum_{i\nu} W_{pi\nu} W_{qi\nu} \left(\underbrace{\frac{1}{\Delta}\left[\frac{e^{-i(\Xi_{i\nu}-\epsilon_p)t}-1}{\Xi_{i\nu}-\epsilon_p} + \frac{e^{i\Delta t}-e^{-i(\Xi_{i\nu}-\epsilon_p)t}}{\Xi_{i\nu}-\epsilon_q} \right]}_{T_{i\nu}(t)} \right) \right. \tag{5.328}$$

$$\left. + \sum_{a\nu} W_{pa\nu} W_{qa\nu} \left(\underbrace{\frac{1}{\Delta}\left[\frac{e^{-i(\Xi_{a\nu}-\epsilon_p)t}-1}{\Xi_{a\nu}-\epsilon_p} + \frac{e^{i\Delta t}-e^{-i(\Xi_{a\nu}-\epsilon_p)t}}{\Xi_{a\nu}-\epsilon_q} \right]}_{T_{a\nu}(t)} \right) \right] \tag{5.329}$$

Now we just work with

$$T_{i\nu}(t) = \frac{(\Xi_{i\nu}-\epsilon_q)\left[e^{-i(\Xi_{i\nu}-\epsilon_p)t}-1\right] + (\Xi_{i\nu}-\epsilon_p)\left[e^{i(\epsilon_p-\epsilon_q)t}-e^{-i(\Xi_{i\nu}-\epsilon_p)t}\right]}{(\epsilon_p-\epsilon_q)(\Xi_{i\nu}-\epsilon_p)(\Xi_{i\nu}-\epsilon_q)} \tag{5.330}$$

$$= \frac{-(\Xi_{i\nu}-\epsilon_q) + (\Xi_{i\nu}-\epsilon_p)e^{i(\epsilon_p-\epsilon_q)t} + (\epsilon_p-\epsilon_q-2\Xi_{i\nu})e^{-i(\Xi_{i\nu}-\epsilon_p)t}}{(\epsilon_p-\epsilon_q)(\Xi_{i\nu}-\epsilon_p)(\Xi_{i\nu}-\epsilon_q)} \tag{5.331}$$

$$= -\frac{1}{(\epsilon_p-\epsilon_q)(\Xi_{i\nu}-\epsilon_p)} + \frac{e^{i(\epsilon_p-\epsilon_q)t}}{(\epsilon_p-\epsilon_q)(\Xi_{i\nu}-\epsilon_q)} + \frac{e^{-i(\Xi_{i\nu}-\epsilon_p)t}}{(\Xi_{i\nu}-\epsilon_p)(\Xi_{i\nu}-\epsilon_q)} - \frac{2\Xi_{i\nu}e^{-i(\Xi_{i\nu}-\epsilon_p)t}}{(\epsilon_p-\epsilon_q)(\Xi_{i\nu}-\epsilon_p)(\Xi_{i\nu}-\epsilon_q)}. \tag{5.332}$$

and we can do the analogous computation to get $T_{a\nu}(t)$. Now we can plug into the expression for the retarded Green's function to get

$$G_{pq}(t) = G_{pq}^{HF}(t)e^{C_{pq}(t)} \tag{5.333}$$

$$= -i\Theta(t)e^{-i\epsilon_p t + C_{pq}(t)} \tag{5.334}$$

$$= -i\Theta(t)\exp\left[-i\epsilon_p t - \sum_{i\nu} W_{pi\nu}W_{qi\nu}T_{i\nu}(t) - \sum_{a\nu} W_{pa\nu}W_{qa\nu}T_{a\nu}(t)\right] \tag{5.335}$$

$$\tag{5.336}$$

The Fourier transform to the frequency domain is given by

$$G_{pq}(\omega) = \int dt e^{i\omega t} G_{pq}(t) \tag{5.337}$$

$$= -i\int_0^\infty dt e^{i(\omega-\epsilon_p)t} \exp\left\{-\sum_{i\nu} W_{pi\nu}W_{qi\nu}T_{i\nu}(t) - \sum_{a\nu} W_{pa\nu}W_{qa\nu}T_{a\nu}(t)\right\} \tag{5.338}$$

$$\approx -i\int_0^\infty dt e^{i(\omega-\epsilon_p)t} \left[1 - \sum_{i\nu} W_{pi\nu}W_{qi\nu}T_{i\nu}(t) - \sum_{a\nu} W_{pa\nu}W_{qa\nu}T_{a\nu}(t)\right] \tag{5.339}$$

$$\tag{5.340}$$

where in the last step we have made a Taylor expansion of the exponential, keeping just the 0th and 1st order terms. This is the right thing to do because in one of our first steps we chose to make the expression exact up to the first order in the screened Coulomb interaction W. If we were to expand beyond the first order, we would be including terms beyond first order in W. So the form for the off-diagonal GW+C spectral function would be

$$A_{pq}(\omega) = -\frac{1}{\pi}\mathrm{Im}G_{pq}(\omega) \tag{5.341}$$

$$\tag{5.342}$$

so we would need to determine

$$\mathrm{Im}\, G_{pq}(\omega) \approx -\,\mathrm{Re}\int_0^\infty dt \left[e^{i(\omega-\epsilon_p)t}\left(1 - \sum_{i\nu} W_{pi\nu}W_{qi\nu}T_{i\nu}(t) - \sum_{a\nu} W_{pa\nu}W_{qa\nu}T_{a\nu}(t)\right)\right] \tag{5.343}$$

$$= -\pi\delta(\omega-\epsilon_p) + \sum_{i\nu} W_{pi\nu}W_{qi\nu}\,\mathrm{Re}\int_0^\infty dt e^{i(\omega-\epsilon_p)t}T_{i\nu}(t) + \sum_{a\nu} W_{pa\nu}W_{qa\nu}\,\mathrm{Re}\int_0^\infty dt e^{i(\omega-\epsilon_p)t}T_{a\nu}(t) \tag{5.344}$$

which leaves us with the task of computing

$$\mathrm{Re}\int_0^\infty dt e^{i(\omega-\epsilon_p)t}T_{i\nu}(t) = -\frac{\pi\delta(\omega-\epsilon_p)}{(\epsilon_p-\epsilon_q)(\Xi_{i\nu}-\epsilon_p)} + \frac{\pi\delta(\omega-\epsilon_q)}{(\epsilon_p-\epsilon_q)(\Xi_{i\nu}-\epsilon_q)} \tag{5.345}$$

$$+\frac{\pi\delta(\omega-\Xi_{i\nu})}{(\Xi_{i\nu}-\epsilon_p)(\Xi_{i\nu}-\epsilon_q)} - \frac{\pi 2\Xi_{i\nu}\delta(\omega-\Xi_{i\nu})}{(\epsilon_p-\epsilon_q)(\Xi_{i\nu}-\epsilon_p)(\Xi_{i\nu}-\epsilon_q)} \tag{5.346}$$

and similarly for $T_{a\nu}(t)$. So

$$A_{pq}(\omega) \approx \delta(\omega-\epsilon_p) - \sum_{i\nu} W_{pi\nu}W_{qi\nu}\left[-\frac{\delta(\omega-\epsilon_p)}{(\epsilon_p-\epsilon_q)(\Xi_{i\nu}-\epsilon_p)} + \frac{\delta(\omega-\epsilon_q)}{(\epsilon_p-\epsilon_q)(\Xi_{i\nu}-\epsilon_q)} + \frac{\delta(\omega-\Xi_{i\nu})}{(\Xi_{i\nu}-\epsilon_p)(\Xi_{i\nu}-\epsilon_q)}\right. \tag{5.347}$$

$$\left.-\frac{2\Xi_{i\nu}\delta(\omega-\Xi_{i\nu})}{(\epsilon_p-\epsilon_q)(\Xi_{i\nu}-\epsilon_p)(\Xi_{i\nu}-\epsilon_q)}\right] - \sum_{a\nu} W_{pa\nu}W_{qa\nu}\left[-\frac{\delta(\omega-\epsilon_p)}{(\epsilon_p-\epsilon_q)(\Xi_{a\nu}-\epsilon_p)} + \frac{\delta(\omega-\epsilon_q)}{(\epsilon_p-\epsilon_q)(\Xi_{a\nu}-\epsilon_q)}\right. \tag{5.348}$$

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

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

5.4.5 Assorted

MKCT

$$\Omega_n = \frac{\Big((\mathrm{i}\mathcal{L})^n \hat{A}, \hat{A}\Big)}{(\hat{A}, \hat{A})}, \tag{5.349}$$

with the corresponding auxiliary kernels

$$K_n(t) = \frac{\Big((\mathrm{i}\mathcal{L})^n \hat{f}(t), \hat{A}\Big)}{(\hat{A}, \hat{A})} \tag{5.350}$$

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

$$\begin{aligned}
\dot{K}_n(t) &= \frac{\Big((\mathrm{i}\mathcal{L})^n \dot{\hat{f}}(t), \hat{A}\Big)}{(\hat{A}, \hat{A})} && (5.351)\\
&= \frac{\Big((\mathrm{i}\mathcal{L})^n \mathrm{i}\mathcal{Q}\mathcal{L}\hat{f}(t), \hat{A}\Big)}{(\hat{A}, \hat{A})} && (5.352)\\
&= \frac{\Big((\mathrm{i}\mathcal{L})^{n+1} \hat{f}(t), \hat{A}\Big)}{(\hat{A}, \hat{A})} - \frac{\Big((\mathrm{i}\mathcal{L})^n \mathrm{i}\mathcal{P}\mathcal{L}\hat{f}(t), \hat{A}\Big)}{(\hat{A}, \hat{A})} && (5.353)\\
&= K_{n+1}(t) - \frac{(\mathrm{i}\mathcal{L}\hat{f}(t), \hat{A})}{(\hat{A}, \hat{A})} \times \frac{\Big((\mathrm{i}\mathcal{L})^n \hat{A}, \hat{A}\Big)}{(\hat{A}, \hat{A})} && (5.354)\\
&= K_{n+1}(t) - K_1(t)\Omega_n, && (5.355)
\end{aligned}$$

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

$$\begin{aligned}
K_n(0) &= \frac{\Big((\mathrm{i}\mathcal{L})^n \mathrm{Q}\mathrm{i}\mathcal{L}\hat{A}, \hat{A}\Big)}{(\hat{A}, \hat{A})} && (5.356)\\
&= \frac{\Big((\mathrm{i}\mathcal{L})^n (\mathrm{i}\mathcal{L}\hat{A} - \mathrm{P}\mathrm{i}\mathcal{L}\hat{A}), \hat{A}\Big)}{(\hat{A}, \hat{A})} && (5.357)\\
&= \frac{\Big((\mathrm{i}\mathcal{L})^{n+1} \hat{A}, \hat{A}\Big)}{(\hat{A}, \hat{A})} - \frac{\Big((\mathrm{i}\mathcal{L})^n \mathrm{P}\mathrm{i}\mathcal{L}\hat{A}, \hat{A}\Big)}{(\hat{A}, \hat{A})} && (5.358)\\
&= \Omega_{n+1} - \Omega_1\Omega_n, && (5.359)
\end{aligned}$$

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

$$K_n^{(m)} = \frac{\Big((\mathrm{i}\mathcal{L})^n(\mathcal{Q}\mathrm{i}\mathcal{L})^{m+1}\hat{A}, \hat{A}\Big)}{(\hat{A}, \hat{A})} \tag{5.360}$$

$$= \frac{\Big((\mathrm{i}\mathcal{L})^n\mathcal{Q}\mathrm{i}\mathcal{L}(\mathcal{Q}\mathrm{i}\mathcal{L})^{m}\hat{A}, \hat{A}\Big)}{(\hat{A}, \hat{A})} \tag{5.361}$$

$$= \frac{\Big((\mathrm{i}\mathcal{L})^n\,(1-\mathcal{P})\,\mathrm{i}\mathcal{L}(\mathcal{Q}\mathrm{i}\mathcal{L})^{m}\hat{A}, \hat{A}\Big)}{(\hat{A}, \hat{A})} \tag{5.362}$$

$$= \frac{\Big((\mathrm{i}\mathcal{L})^{n+1}(\mathcal{Q}\mathrm{i}\mathcal{L})^{m}\hat{A}, \hat{A}\Big)}{(\hat{A}, \hat{A})} - \frac{\Big((\mathrm{i}\mathcal{L})^{n}\mathcal{P}\mathrm{i}\mathcal{L}(\mathcal{Q}\mathrm{i}\mathcal{L})^{m}\hat{A}, \hat{A}\Big)}{(\hat{A}, \hat{A})} \tag{5.363}$$

$$= K_{n+1}^{(m-1)} - \frac{\Big(\mathrm{i}\mathcal{L}(\mathcal{Q}\mathrm{i}\mathcal{L})^{m}\hat{A}, \hat{A}\Big)}{(\hat{A}, \hat{A})} \times \frac{\Big((\mathrm{i}\mathcal{L})^{n}\hat{A}, \hat{A}\Big)}{(\hat{A}, \hat{A})} \tag{5.364}$$

$$= K_{n+1}^{(m-1)} - \bar{\Omega}_m\Omega_n \tag{5.365}$$

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:

$$K_n^{(m)} = K_{n+2}^{(m-2)} - \bar{\Omega}_{m-1}\Omega_{n+1} - \bar{\Omega}_m\Omega_n \tag{5.366}$$

$$= K_{n+m}^{(0)} - \sum_{j=0}^{m-1} \bar{\Omega}_{m-j}\Omega_{n+j} \tag{5.367}$$

$$= \Omega_{n+m+1} - \Omega_1\Omega_{n+m} - \sum_{j=0}^{m-1} \bar{\Omega}_{m-j}\Omega_{n+j} \tag{5.368}$$

$$= \Omega_{n+m+1} - \bar{\Omega}_0\Omega_{n+m} - \sum_{j=0}^{m-1} \bar{\Omega}_{m-j}\Omega_{n+j} \tag{5.369}$$

$$= \Omega_{n+m+1} - \sum_{j=0}^{m} \bar{\Omega}_{m-j}\Omega_{n+j} \tag{5.370}$$

$$\tag{5.371}$$

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

$$\begin{aligned}\tilde{\Omega}_m &= \frac{\Big((\mathrm{i}\mathcal{L}\mathcal{Q})^m \mathrm{i}\mathcal{L}\hat{A}, \hat{A}\Big)}{(\hat{A}, \hat{A})} - \tilde{\Omega}_{m-1}\Omega_1 \\ &= \Omega_{m+1} - \sum_{j=0}^{m-1} \tilde{\Omega}_j \Omega_{m-j}\end{aligned} \tag{5.372}$$

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:

$$K_n(t) \approx \sum_{j=0}^{M} \frac{K_n^{(j)}(0)}{j!} t^j, \tag{5.373}$$

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:

$$K_n(t) \approx \frac{p_{M_1}(t)}{q_{M_2}(t)} = \frac{a_0 + a_1 t + \cdots + a_{M_1} t^{M_1}}{1 + b_1 t + \cdots + b_{M_2} t^{M_2}}, \tag{5.374}$$

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. 5.374 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

$$G_k(t,t') = G_k^0(t,t') + G_k^0(t,t')\Sigma_k^I(t,t')G_k^0(t,t'), \tag{5.375}$$

$$\tag{5.376}$$

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

$$G_k^R(t,t') = G_k^{0,R}(t,t')e^{C_k^R(t,t')} \tag{5.377}$$

$$\implies \frac{G_k^R(t,t')}{G_k^{0,R}(t,t')} = e^{C_k^R(t,t')} \tag{5.378}$$

$$\tag{5.379}$$

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

$$G_k^R(t) = -i\theta(t)\left\langle\left\{c_k(t), c_k^\dagger(0)\right\}\right\rangle \tag{5.380}$$

$$= -i\theta(t)\left\langle\left\{e^{iHt}c_k e^{-iHt}, c_k^\dagger\right\}\right\rangle \tag{5.381}$$

$$= -i\theta(t)\left\langle\left\{\sum_{n=0}^{\infty}\frac{(-it)^n}{n!}\mathcal{L}^n c_k, c_k^\dagger\right\}\right\rangle \tag{5.382}$$

$$= -i\theta(t)\left(\mu_{0,k} - t\mu_{1,k} + \frac{t^2}{2}\mu_{2,k} + O(t^3)\right) \tag{5.383}$$

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

$$G_k^{R,0}(t) = -i\theta(t)\left(\mu_{0,k}^0 - t\mu_{1,k}^0 + \frac{t^2}{2}\mu_{2,k}^0 + O(t^3)\right) \tag{5.384}$$

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

$$\frac{1}{B(t)} = 1 + t\mu_{1,k}^0 + t^2\left[\left(\mu_{1,k}^0\right)^2 - \frac{1}{2}\mu_{2,k}^0\right] + O\left(t^3\right) \tag{5.385}$$

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

$$R_k(t) = \frac{G_k^R(t)}{G_k^{R,0}(t)} = \frac{-i\theta(t)}{-i\theta(t)} \times \frac{A(t)}{B(t)} \tag{5.386}$$

$$= \left(1 - t\mu_{1,k} + \frac{t^2}{2}\mu_{2,k} + O(t^3)\right)\left(1 + t\mu_{1,k}^0 + t^2\left[\left(\mu_{1,k}^0\right)^2 - \frac{1}{2}\mu_{2,k}^0\right] + O\left(t^3\right)\right) \tag{5.387}$$

$$= \left(1 + t\underbrace{\left[-\left(\mu_{1,k} - \mu_{1,k}^0\right)\right]}_{\alpha_{1,k}} + t^2\underbrace{\left[\frac{1}{2}\left(\mu_{2,k} - \mu_{2,k}^0\right) - \mu_{1,k}\mu_{1,k}^0 + \left(\mu_{1,k}^0\right)^2\right]}_{\alpha_{2,k}} + O(t^3)\right) \tag{5.388}$$

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

$$\kappa_{1,k} = \alpha_{1,k} = -\left(\mu_{1,k} - \mu^0_{1,k}\right) \tag{5.389}$$

$$\kappa_{2,k} = \alpha_{2,k} - \frac{\alpha^2_{1,k}}{2} = \frac{1}{2}\left(\mu_{2,k} - \mu^0_{2,k}\right) - \mu_{1,k}\mu^0_{1,k} + \left(\mu^0_{1,k}\right)^2 - \frac{1}{2}\left[-\left(\mu_{1,k} - \mu^0_{1,k}\right)\right]^2 \tag{5.390}$$

$$= \frac{1}{2}\left(\mu_{2,k} - \mu^0_{2,k}\right) - \mu_{1,k}\mu^0_{1,k} + \left(\mu^0_{1,k}\right)^2 - \frac{1}{2}\left(\mu_{1,k} - \mu^0_{1,k}\right)^2 \tag{5.391}$$

$$= \frac{1}{2}\left[\left(\mu_{2,k} - \mu^0_{2,k}\right) + \left(\mu_{1,k}\right)^2 + \left(\mu^0_{1,k}\right)^2\right] \tag{5.392}$$

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:

$$K_1(t) \approx \frac{a_0 + a_1 t + a_2 t^2}{1 + b_1 t + b_2 t^2} \tag{5.393}$$

$$\approx \left(a_0 + a_1 t + a_2 t^2\right)\left(1 - b_1 t + \left(b_1^2 - b_2\right)t^2 + O(t^3)\right) \tag{5.394}$$

$$\approx a_0 + t\left(a_1 - a_0 b_1\right) + t^2\left(a_2 - a_1 b_1 + a_0\left(b_1^2 - b_2\right)\right) + O(t^3) \tag{5.395}$$

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:

$$c_0 = a_0 \tag{5.396}$$

$$c_1 = a_1 - a_0 b_1 \implies a_1 = c_1 + a_0 b_1 \tag{5.397}$$

$$c_2 = a_2 - a_1 b_1 + a_0\left(b_1^2 - b_2\right) \implies a_2 = c_2 + a_1 b_1 - a_0\left(b_1^2 - b_2\right) \tag{5.398}$$

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

$$K_1(0) = \Omega_2 - \Omega_1^2 = \mu_{2,k} - \mu^2_{1,k} \tag{5.399}$$

$$K_1^{(1)}(0) = K_2(0) - \bar{\Omega}_1\Omega_1 = \Omega_3 - \Omega_1\Omega_2 - \bar{\Omega}_1\Omega_1 = \mu_{3,k} - \mu_{1,k}\mu_{2,k} - \bar{\Omega}_1\mu_{1,k} \tag{5.400}$$

$$\tag{5.401}$$

Fundamental starting point

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

$$G^R_k(t) \equiv -i\theta(t)\left\langle\left\{c_k(t), c^\dagger_k(0)\right\}\right\rangle. \tag{5.402}$$

Immediately, we can Fourier transform to the frequency domain:

$$G^R_k(\omega) = \int_{-\infty}^{\infty} dt e^{i\omega t} G^R_k(t). \tag{5.403}$$

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

$$
\begin{aligned}
G_k^R(\omega) &= -i \int_0^\infty dt e^{i\omega t} \left\langle \left\{ c_k(t), c_k^\dagger(0) \right\} \right\rangle && (5.404) \\
&= -i \int_0^\infty dt e^{i\omega t} \sum_{n=0}^{\infty} \frac{(it)^n}{n!} \mu_{n,k} && (5.405) \\
&= -i \sum_{n=0}^{\infty} \frac{i^n}{n!} \mu_{n,k} \int_0^\infty dt e^{i\omega t} t^n && (5.406) \\
&= -i \sum_{n=0}^{\infty} \frac{i^n}{n!} \mu_{n,k} \frac{n!}{(i\omega)^{n+1}} && (5.407) \\
&= -\sum_{n=0}^{\infty} \frac{\mu_{n,k}}{\omega^{n+1}}, && (5.408)
\end{aligned}
$$

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

$$
|f_1\rangle = \mathcal{L}|f_0\rangle - a_0|f_0\rangle, \tag{5.409}
$$

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

$$
|f_{n+1}\rangle = \mathcal{L}|f_n\rangle - a_n|f_n\rangle - b_n^2|f_{n-1}\rangle, \tag{5.410}
$$

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

$$
\begin{aligned}
\mathcal{L}|f_n\rangle &= [H_0 + V, |f_n\rangle] && (5.411) \\
&= \mathcal{L}_0|f_n\rangle + [V, |f_n\rangle] && (5.412) \\
& && (5.413)
\end{aligned}
$$

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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