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:

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

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

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

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

recalling that the bare Coulomb interaction should be independent of frequency. A discussion of how to compute the screened Coulomb interaction can be found in this old work [3]. To simplify notation let us define a polarizability $\mathbf{\Pi}\left(\mathbf{r},\mathbf{r}',\omega\right) = \left(\chi_0 v\right)\left(\mathbf{r},\mathbf{r}',\omega\right)$, so that we can rewrite the screened Coulomb interaction as:

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

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

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

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

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

where

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

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

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

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

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

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

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

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

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

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

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

So we see that we can get the poles of the screened Coulomb interaction by the poles of the polarizability, which are $\omega = \Omega^\mu_{\mathbf{k}} - i\eta$ and $\omega = \Omega^\mu_{\mathbf{k}} + i\eta$, suggesting that they are in the upper complex plane for excitations and vice versa for deexcitations. See the figure 1.1 for a picture. For a more comprehensive picture, this should be juxtaposed with the figure from Tianyu's paper for CD. In the literature, they talk about approximating the dielectric function by a multiple one or a single pole approximation, so which one would I want to implement? This suggests that the notation in the G_0W_0 literature is confusing because they always say that to solve for the χ_0 in the RPA, but if we are actually dealing with χ_0, which is the Kohn-Sham density response function, then we don't use the RPA, where the density response function is solved for using a Dyson-like equation [4]:

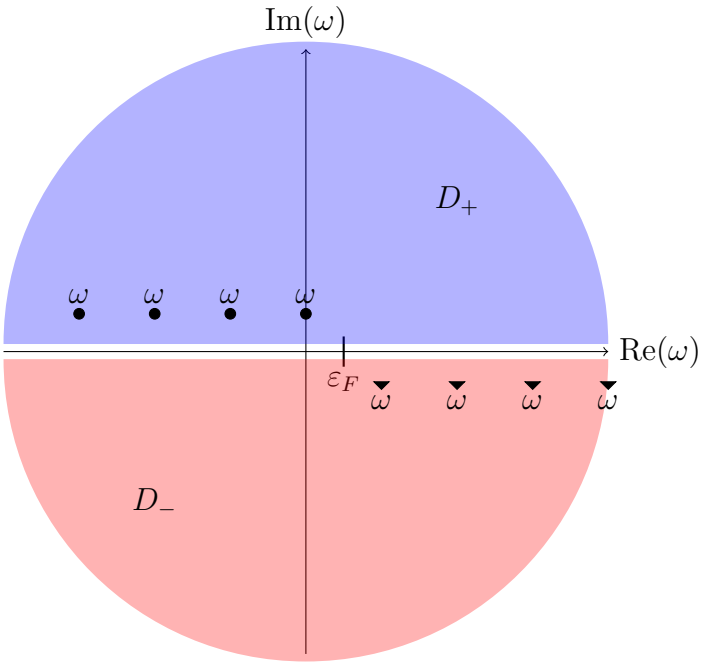

Figure 1.1: Contour for the complex frequency integral. The poles are denoted by the various ω. The Fermi energy is denoted by ε_F. The integration contour D_+ is the semicircle in the upper complex plane, while D_- is the semicircle in the lower complex plane.

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

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

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

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

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

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

1.2.2 Analytic continuation

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

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

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

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

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

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

The noninteracting Green's function has the form:

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

so that the above equation simplifies to:

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

Screened Coulomb Interaction

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

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

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

and

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

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

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

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

with

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

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

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

with

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

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

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

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

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

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

simplifying to

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

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

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

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

with

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

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

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

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

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

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

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

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

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

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

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

1.3 UHF formalism

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

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

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

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

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

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

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

1.4 Deriving linear response: 11/22

1.4.1 The Fundamentals

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

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

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

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

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

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

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

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

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

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

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

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

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

1.4.2 Introduction to TDKS

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

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

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

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

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

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

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

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

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

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

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

1.4.3 Density Matrix Formulation in TDKS Theory

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

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

and it is idempotent, meaning that

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

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

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

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

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

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

and longitudinal vector potentials

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

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

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

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

$$\tag{1.96}$$

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

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

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

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

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

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

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

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

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

The equations of motion up to second order read

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

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

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

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

1.5 GW Density Matrix

The expression for the density matrix γ is

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

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

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

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

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

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

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

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

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

1.6 Summary of GW-RPA implementations

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

1.6.1 Complex integration approaches

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

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

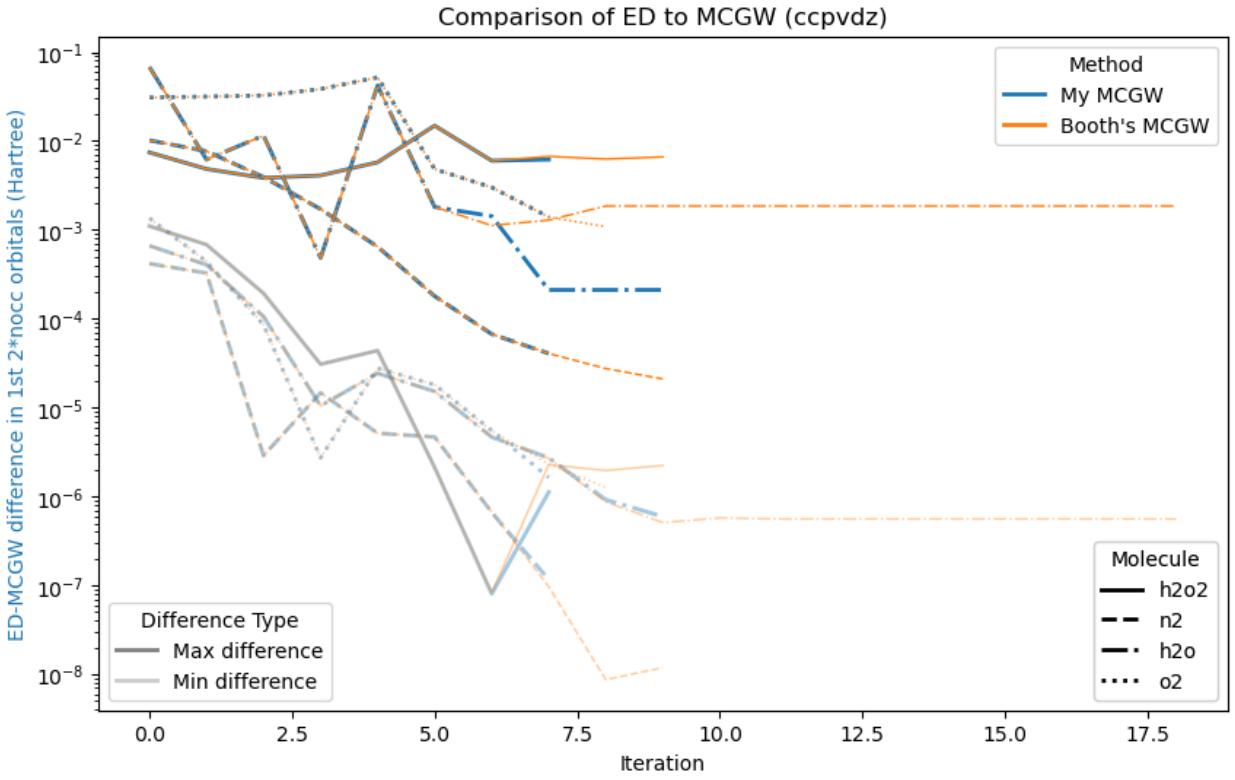

Figure 1.2: From the first $2N_{occ}$ orbitals, representing the space of interest, the maximum and minimum differences between the Ritz values and the exact eigenvalues are plotted as a function of the number of Lanczos iterations used. A cc-pvdz basis is used. An exact match between the blue (my implementation)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

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

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:

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

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. 2.10, 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 $\boldsymbol{\Sigma}^c_{pq}(\omega) \equiv \boldsymbol{\Sigma}^c_{pq} = \begin{pmatrix} \boldsymbol{\Sigma}(\infty) & \boldsymbol{W}^< & \boldsymbol{W}^> \\ \boldsymbol{W}^{\dagger <} & \boldsymbol{d}^< & \mathbf{0} \\ \boldsymbol{W}^{\dagger >} & \mathbf{0} & \boldsymbol{d}^> \end{pmatrix}_{pq}$. *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 $\mathbf{W}^\dagger = \mathbf{q}_1\mathbf{L}^\dagger \rightarrow \mathbf{q}_1 = \mathbf{W}^\dagger\mathbf{L}^{\dagger,-1}$. $\mathbf{L}$ 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

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

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

$$\tilde{\boldsymbol{H}}^{\text{Lanczos Iter 2}}_{\text{upfolded}} = \tilde{\boldsymbol{Q}}^{(2,\dagger)} \boldsymbol{H}^{G_0W_0}_{\text{Upfolded}} \tilde{\boldsymbol{Q}}^{(2)} \tag{2.36}$$

$$= \begin{pmatrix} \boldsymbol{I} & \boldsymbol{0} \\ \boldsymbol{0} & \boldsymbol{Q}^{(2)\dagger} \end{pmatrix} \begin{pmatrix} \boldsymbol{F} + \boldsymbol{\Sigma}(\infty) & \boldsymbol{W} \\ \boldsymbol{W}^\dagger & \boldsymbol{d} \end{pmatrix} \begin{pmatrix} \boldsymbol{I} & \boldsymbol{0} \\ \boldsymbol{0} & \boldsymbol{Q}^{(2)} \end{pmatrix} \tag{2.37}$$

$$= \begin{pmatrix} \boldsymbol{I} & \boldsymbol{0} \\ \boldsymbol{0} & [\boldsymbol{q}_1^\dagger \quad \boldsymbol{q}_2^\dagger] \end{pmatrix} \begin{pmatrix} \boldsymbol{F} + \boldsymbol{\Sigma}(\infty) & \boldsymbol{W} \\ \boldsymbol{W}^\dagger & \boldsymbol{d} \end{pmatrix} \begin{pmatrix} \boldsymbol{I} & \boldsymbol{0} \\ \boldsymbol{0} & [\boldsymbol{q}_1 \quad \boldsymbol{q}_2] \end{pmatrix} \tag{2.38}$$

$$= \begin{pmatrix} \boldsymbol{F} + \boldsymbol{\Sigma}(\infty) & \boldsymbol{W} \\ [\boldsymbol{q}_1^\dagger \quad \boldsymbol{q}_2^\dagger]\boldsymbol{W}^\dagger & [\boldsymbol{q}_1^\dagger \quad \boldsymbol{q}_2^\dagger]\boldsymbol{d} \end{pmatrix} \begin{pmatrix} \boldsymbol{I} & \boldsymbol{0} \\ \boldsymbol{0} & [\boldsymbol{q}_1 \quad \boldsymbol{q}_2] \end{pmatrix} \tag{2.39}$$

$$= \begin{pmatrix} \boldsymbol{F} + \boldsymbol{\Sigma}(\infty) & [\underbrace{\boldsymbol{W}\boldsymbol{q}_1}_{\boldsymbol{\mathcal{R}}\boldsymbol{\mathcal{Q}}^\dagger\boldsymbol{\mathcal{Q}}=\boldsymbol{\mathcal{R}}} \quad \underbrace{\boldsymbol{W}\boldsymbol{q}_2}_{\boldsymbol{0}}] \\ [\underbrace{\boldsymbol{q}_1^\dagger\boldsymbol{W}^\dagger}_{\boldsymbol{\mathcal{Q}}^\dagger\boldsymbol{\mathcal{Q}}\boldsymbol{\mathcal{R}}^\dagger=\boldsymbol{\mathcal{R}}^\dagger} \quad \underbrace{\boldsymbol{q}_2^\dagger\boldsymbol{W}^\dagger}_{\boldsymbol{0}}] & \begin{pmatrix} \underbrace{\boldsymbol{q}_1^\dagger\boldsymbol{d}\boldsymbol{q}_1}_{\boldsymbol{M}_1} & \underbrace{\boldsymbol{q}_1^\dagger\boldsymbol{d}\boldsymbol{q}_2}_{\boldsymbol{C}_1} \\ \underbrace{\boldsymbol{q}_2^\dagger\boldsymbol{d}\boldsymbol{q}_1}_{\boldsymbol{C}_1^\dagger} & \underbrace{\boldsymbol{q}_2^\dagger\boldsymbol{d}\boldsymbol{q}_2}_{\boldsymbol{M}_2} \end{pmatrix} \end{pmatrix} \tag{2.40}$$

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

$$\boldsymbol{S}_{i+1,i}^n \equiv \boldsymbol{q}_{i+1}^\dagger \boldsymbol{d}^n \boldsymbol{q}_i = \left[[\mathbf{d}\mathbf{q}_i - \mathbf{q}_i\mathbf{M}_i - \mathbf{q}_{i-1}\mathbf{C}_{i-1}]\,\boldsymbol{C}_i^{\dagger,-1}\right]^\dagger \boldsymbol{d}^n\boldsymbol{q}_i \tag{2.47}$$

$$= \boldsymbol{C}_i^{-1}\left[\underbrace{\boldsymbol{q}_i^\dagger \boldsymbol{d}^{n+1}\boldsymbol{q}_i}_{\boldsymbol{S}_{i,i}^{n+1}} - \boldsymbol{M}_i\underbrace{\boldsymbol{q}_i^\dagger\boldsymbol{d}^n\boldsymbol{q}_i}_{\boldsymbol{S}_{i,i}^n} - \boldsymbol{C}_{i-1}^\dagger\underbrace{\boldsymbol{q}_{i-1}^\dagger\boldsymbol{d}^n\boldsymbol{q}_i}_{\boldsymbol{S}_{i-1,i}^n}\right] \tag{2.48}$$

$$= \boxed{\boldsymbol{C}_i^{-1}\left[\boldsymbol{S}_{i,i}^{n+1} - \boldsymbol{M}_i\boldsymbol{S}_{i,i}^n - \boldsymbol{C}_{i-1}^\dagger\boldsymbol{S}_{i-1,i}^n\right]} \tag{2.49}$$

Similarly

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

$$\tag{2.51}$$

$$
\begin{aligned}
\boldsymbol{S}^{n}_{i+1,i+1} = \boldsymbol{C}_i^{-1} \Big[& \boldsymbol{S}^{n+2}_{i,i} + \boldsymbol{M}_i \boldsymbol{S}^{n}_{i,i} \boldsymbol{M}_i + \boldsymbol{C}^{\dagger}_{i-1} \boldsymbol{S}^{n}_{i-1,i-1} \boldsymbol{C}_{i-1} \\
& - \underbrace{\boldsymbol{q}_i^{\dagger} \boldsymbol{d}^{n+1} \boldsymbol{q}_i}_{\boldsymbol{S}^{n+1}_{i,i}} \boldsymbol{M}_i - \boldsymbol{M}_i \underbrace{\boldsymbol{q}_i^{\dagger} \boldsymbol{d}^{n+1} \boldsymbol{q}_i}_{\boldsymbol{S}^{n+1}_{i,i}} \\
& - \underbrace{\boldsymbol{q}_i^{\dagger} \boldsymbol{d}^{n+1} \boldsymbol{q}_{i-1}}_{\boldsymbol{S}^{n+1}_{i,i-1}} \boldsymbol{C}_{i-1} - \boldsymbol{C}^{\dagger}_{i-1} \underbrace{\boldsymbol{q}_{i-1}^{\dagger} \boldsymbol{d}^{n+1} \boldsymbol{q}_i}_{\boldsymbol{S}^{n+1}_{i-1,i}} \\
& + \boldsymbol{M}_i \underbrace{\boldsymbol{q}_i^{\dagger} \boldsymbol{d}^{n} \boldsymbol{q}_{i-1}}_{\boldsymbol{S}^{n}_{i,i-1}} \boldsymbol{C}_{i-1} + \boldsymbol{C}^{\dagger}_{i-1} \underbrace{\boldsymbol{q}_{i-1}^{\dagger} \boldsymbol{d}^{n} \boldsymbol{q}_i}_{\boldsymbol{S}^{n}_{i-1,i}} \boldsymbol{M}_i \Big] \boldsymbol{C}_i^{\dagger,-1} \qquad (2.52) \\
= \boldsymbol{C}_i^{-1} \Big[& \boldsymbol{S}^{n+2}_{i,i} + \boldsymbol{M}_i \boldsymbol{S}^{n}_{i,i} \boldsymbol{M}_i + \boldsymbol{C}^{\dagger}_{i-1} \boldsymbol{S}^{n}_{i-1,i-1} \boldsymbol{C}_{i-1} \\
& - P(\boldsymbol{S}^{n+1}_{i,i} \boldsymbol{M}_i) - P(\boldsymbol{S}^{n+1}_{i,i-1} \boldsymbol{C}_{i-1}) + P(\boldsymbol{M}_i \boldsymbol{S}^{n}_{i,i-1} \boldsymbol{C}_{i-1}) \Big] \boldsymbol{C}_i^{\dagger,-1} \qquad (2.53)
\end{aligned}
$$

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

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

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

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

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

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

where we have defined the density-density response moment as

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

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

The Casida equation is given by

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

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 $\chi_{\mathrm{RPA}}(\omega)$ as

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

where $\chi_{\mathrm{RPA}}(\omega)=(\chi_0(\omega)^{-1}-\mathcal{K})^{-1}$, 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

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

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

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

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

$$\boldsymbol{A}\boldsymbol{X}+\boldsymbol{B}\boldsymbol{Y}=\boldsymbol{\Omega}\boldsymbol{X} \tag{2.68}$$
$$-\boldsymbol{B}\boldsymbol{X}-\boldsymbol{A}\boldsymbol{Y}=\boldsymbol{\Omega}\boldsymbol{Y} \tag{2.69}$$

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

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

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 $A_{ia,jb} = \delta_{ij}\delta_{ab}\left(\epsilon_a - \epsilon_i\right) + (ia \mid jb)$ 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 $\mathbf{S}^{(n)}_{i,j} = \mathbf{q}_i^\dagger \mathbf{d}^n \mathbf{q}_j$. But due to the orthogonality of the Krylov subspace, we have $q_i^\dagger q_j = 0$ for $i \neq j$, so $\mathbf{S}^{(n)}_{i,j} = 0$ for $|i-j| > 1$. Furthermore, due to Hermiticity, $\mathbf{S}^{(n)}_{i,j} = \mathbf{S}^{(n)\dagger}_{j,i}$. We can start with the initial definition $\mathbf{S}^{(n)}_{1,1} = \mathbf{q}_1^\dagger \mathbf{d}^n \mathbf{q}_1 = \mathbf{L}^{-1}\boldsymbol{\Sigma}^{(n)}\mathbf{L}^{-1,\dagger}$.

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

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

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

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

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

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

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

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

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

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

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

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

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 $n_{\text{channel}} \times n_{\text{virt}} \times n_{\text{occ}}$, 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 $O(n_{\text{occ}})$, whereas the size of the auxiliary dimension will be $O(n_{\text{channel}} \times n_{\text{virt}} \times n_{\text{occ}})$. 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.

$$\tilde{\boldsymbol{H}}_{\text{upfolded}}^{\text{Lanczos Iter 2}} = \tilde{\boldsymbol{Q}}^{(2,\dagger)}\boldsymbol{H}_{\text{Upfolded}}^{G_0W_0}\tilde{\boldsymbol{Q}}^{(2)} \tag{2.110}$$

$$= \begin{pmatrix} \boldsymbol{I} & \boldsymbol{0} \\ \boldsymbol{0} & [\boldsymbol{q}_1^\dagger \quad \boldsymbol{q}_2^\dagger] \end{pmatrix} \begin{pmatrix} \boldsymbol{F} + \boldsymbol{\Sigma}(\infty) & \boldsymbol{W} \\ \boldsymbol{W}^\dagger & \boldsymbol{d} \end{pmatrix} \begin{pmatrix} \boldsymbol{I} & \boldsymbol{0} \\ \boldsymbol{0} & [\boldsymbol{q}_1 \quad \boldsymbol{q}_2] \end{pmatrix} \tag{2.111}$$

$$= \begin{pmatrix} \boldsymbol{F} + \boldsymbol{\Sigma}(\infty) & [\underbrace{\boldsymbol{W}\boldsymbol{q}_1}_{\boldsymbol{\mathcal{R}}\boldsymbol{\mathcal{Q}}^\dagger\boldsymbol{\mathcal{Q}}=\boldsymbol{\mathcal{R}}} \quad \underbrace{\boldsymbol{W}\boldsymbol{q}_2}_{\boldsymbol{0}}] \\ [\underbrace{\boldsymbol{q}_1^\dagger\boldsymbol{W}^\dagger}_{\boldsymbol{\mathcal{Q}}^\dagger\boldsymbol{\mathcal{Q}}\boldsymbol{\mathcal{R}}^\dagger=\boldsymbol{\mathcal{R}}^\dagger} \quad \underbrace{\boldsymbol{q}_2^\dagger\boldsymbol{W}^\dagger}_{\boldsymbol{0}}] & \begin{pmatrix} \underbrace{\boldsymbol{q}_1^\dagger\boldsymbol{d}\boldsymbol{q}_1}_{\boldsymbol{M}_1} & \underbrace{\boldsymbol{q}_1^\dagger\boldsymbol{d}\boldsymbol{q}_2}_{\boldsymbol{C}_1} \\ \underbrace{\boldsymbol{q}_2^\dagger\boldsymbol{d}\boldsymbol{q}_1}_{\boldsymbol{C}_1^\dagger} & \underbrace{\boldsymbol{q}_2^\dagger\boldsymbol{d}\boldsymbol{q}_2}_{\boldsymbol{M}_2} \end{pmatrix} \end{pmatrix} \tag{2.112}$$

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

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

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

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

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 $\boldsymbol{q}_i d\boldsymbol{q}_j = \boldsymbol{0}$ for $i > j+1$ in 2.117 is because we are assuming an orthogonal basis where

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

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

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

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 $\boldsymbol{q}_i d\boldsymbol{q}_j$ 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

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

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

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

where the definitions of the matrix elements are

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

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

and in particular, we have a definition

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

Let us show how 3.106 comes from 3.6. If $A_{[ja],[lc]} = (\epsilon_j - \epsilon_a)\, \delta_{jl}\delta_{ac} + \langle jc|al\rangle$, then we can write

$$C^{2\ \text{h1p}}_{i[ja],k[lc]} = \left[\epsilon_i \delta_{ik}\delta_{jl}\delta_{ac} + (-A)_{[ja],[lc]}\right] \tag{3.7}$$

$$= \delta_{ik} \left[\epsilon_i\, \delta_{jl}\delta_{ac} + (-A)_{[ja],[lc]}\right] \tag{3.8}$$

$$= \delta_{ik} \left[(\epsilon_i + \epsilon_j - \epsilon_a)\, \delta_{jl}\delta_{ac} - \langle jc|al\rangle\right] \tag{3.9}$$

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

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

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

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

$$(\mathbf{1} \otimes \boldsymbol{X})^\dagger \boldsymbol{C}^{2\text{hlp}} (\mathbf{1} \otimes \boldsymbol{X}) = (\mathbf{1} \otimes \boldsymbol{X})^\dagger \left[\epsilon^{1\text{ h}} \otimes \mathbf{1} + \mathbf{1} \otimes (-\boldsymbol{A})\right] (\mathbf{1} \otimes \boldsymbol{X}) \tag{3.12}$$

$$= \left(\mathbf{1} \otimes \boldsymbol{X}^\dagger\right) \left[\boldsymbol{\epsilon}^{1\text{ h}} \otimes \mathbf{1}\right] (\mathbf{1} \otimes \boldsymbol{X}) + \left(\mathbf{1} \otimes \boldsymbol{X}^\dagger\right) [\mathbf{1} \otimes (-\boldsymbol{A})] (\mathbf{1} \otimes \boldsymbol{X}) \tag{3.13}$$

$$= \mathbf{1}\boldsymbol{\epsilon}^{1\text{ h}}\mathbf{1} \otimes \boldsymbol{X}^\dagger \mathbf{1} \boldsymbol{X} + \mathbf{1}\mathbf{1} \otimes (-\boldsymbol{X}^\dagger \boldsymbol{A} \boldsymbol{X}) \tag{3.14}$$

$$= \boldsymbol{\epsilon}^{1\text{ h}} \otimes \mathbf{1} + \mathbf{1} \otimes (-\boldsymbol{X}^\dagger \boldsymbol{A} \boldsymbol{X}) \tag{3.15}$$

$$= \boldsymbol{\epsilon}^{1\text{ h}} \otimes \mathbf{1} + \mathbf{1} \otimes (-\boldsymbol{\Omega}) \tag{3.16}$$

$$= \boldsymbol{\epsilon}^{1\text{ h}} \oplus (-\boldsymbol{\Omega}) \tag{3.17}$$

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

$$\boldsymbol{V}^{2\text{h1p}}_{P,O^2V} (\mathbf{1} \otimes \boldsymbol{X})_{O^2V,O^2V} = \sum_{k'lc} (pk|lc) X^v_{lc} \delta_{kk'} \tag{3.18}$$

$$= \sum_{lc} (pk|lc) X^v_{lc} \equiv \boldsymbol{W}^< \tag{3.19}$$

$$\tag{3.20}$$

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

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

$$\tag{3.22}$$

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

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

and we can write

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

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

This implies three coupled equations

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

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

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

Solving the latter two equations gives

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

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

Substituting these into the first equation gives us

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

from which we can get the eigenvalue equation

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

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

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

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

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

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

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

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

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

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

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 $\mathbf{C}^{\text{2plh}} = \varepsilon^{\text{1p}} \oplus \tilde{\mathbf{M}}$ 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

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

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

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

Just evaluate

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

$$\tag{3.52}$$

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

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

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

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

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)

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

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

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

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

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

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

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

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

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

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

Multiplying the supermetric by the Hamiltonian

Alternatively, we can consider the LHS matrix multiplication

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

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

$$\tag{3.75}$$

First, we can consider the off diagonal term

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

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

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

Next, we can consider the auxiliary block

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

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

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

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

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

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

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

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

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.

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

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

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

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

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

$$\tag{3.99}$$

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

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

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

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

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 $P = O + V$)

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

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

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

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

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

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

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

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

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

Why would we want an Mtilde of this form?

Now, we know the following identity to be true

$$\boldsymbol{M}\boldsymbol{Z} = \boldsymbol{N}\boldsymbol{Z}\begin{pmatrix}\boldsymbol{\Omega}_+ & 0\\ 0 & -\boldsymbol{\Omega}_+\end{pmatrix} \tag{3.112}$$

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

$$\Theta(-\boldsymbol{N}\boldsymbol{M}) = \boldsymbol{Z}\begin{pmatrix}\Theta(-\boldsymbol{\Omega}_+) & 0\\ 0 & \Theta(\boldsymbol{\Omega}_+)\end{pmatrix}\boldsymbol{Z}^{-1} = \boldsymbol{Z}\begin{pmatrix}\boldsymbol{0} & 0\\ 0 & \boldsymbol{1}\end{pmatrix}\boldsymbol{Z}^{-1} \tag{3.113}$$

$$\implies \tilde{\boldsymbol{M}}\boldsymbol{Z} = \boldsymbol{N}\boldsymbol{Z}\begin{pmatrix}\boldsymbol{\Omega}_+ & 0\\ 0 & -\boldsymbol{\Omega}_+ + \boldsymbol{\eta}\end{pmatrix} \quad \text{and} \quad \tilde{\boldsymbol{M}} = \boldsymbol{Z}\boldsymbol{N}\begin{pmatrix}\boldsymbol{\Omega}_+ & 0\\ 0 & -\boldsymbol{\Omega}_+ + \boldsymbol{\eta}\end{pmatrix}\boldsymbol{Z}^{-1} \tag{3.114}$$

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 $\Theta(-\boldsymbol{N}\boldsymbol{M})$, I have to diagonalize $\boldsymbol{N}\boldsymbol{M}$ 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 $\boldsymbol{N}\boldsymbol{M}$ 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 $\boldsymbol{N}\boldsymbol{M}$, 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

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

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

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

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

$$\tag{3.120}$$

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

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

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

Consider just the multiplication

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

$$\tag{3.124}$$

and

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

But now we are left to evaluate

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

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

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

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

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

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

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

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

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

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

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

$$(\mathbf{1} \otimes \boldsymbol{N})\, \boldsymbol{C}^{\text{2hlp}} = (\mathbf{1}_{O,O} \otimes \boldsymbol{N}_{2OV,2OV}) \left(\boldsymbol{\epsilon}^{1\ \text{h}}_{O,O} \otimes \mathbf{1}_{2OV,2OV} + \mathbf{1}_{O,O} \otimes (-\tilde{\boldsymbol{M}})_{2OV,2OV}\right) \tag{3.140}$$

$$= \boldsymbol{\epsilon}^{1\ \text{h}}_{O,O} \otimes \boldsymbol{N}_{2OV,2OV} + \mathbf{1}_{O,O} \otimes -\boldsymbol{N}_{2OV,2OV}\tilde{\boldsymbol{M}}_{2OV,2OV} \tag{3.141}$$

$$= \left[\left(\boldsymbol{\epsilon}^{1\ \text{h}}_{O,O} \otimes \mathbf{1}_{OV,OV}\right) \oplus_{\text{direct}} - \left(\boldsymbol{\epsilon}^{1\ \text{h}}_{O,O} \otimes \mathbf{1}_{OV,OV}\right)\right] + \left(\mathbf{1}_{O,O} \otimes -\boldsymbol{N}_{2OV,2OV}\tilde{\boldsymbol{M}}_{2OV,2OV}\right) \tag{3.142}$$

$$= \begin{pmatrix} \boldsymbol{\epsilon}^{1\ \text{h}} \otimes \mathbf{1} & \mathbf{0} \\ \mathbf{0} & -\left(\boldsymbol{\epsilon}^{1\ \text{h}} \otimes \mathbf{1}\right) \end{pmatrix}_{2O^2V} + \left(\mathbf{1}_O \otimes -\boldsymbol{Z}_{2OV} \begin{pmatrix} \boldsymbol{\Omega} & \mathbf{0} \\ \mathbf{0} & \eta - \boldsymbol{\Omega} \end{pmatrix}_{2OV} \boldsymbol{Z}^{-1}_{2OV}\right)_{2O^2V} \tag{3.143}$$

$$= \begin{pmatrix} \boldsymbol{\epsilon}^{1\ \text{h}} \otimes \mathbf{1} & \mathbf{0} \\ \mathbf{0} & -\left(\boldsymbol{\epsilon}^{1\ \text{h}} \otimes \mathbf{1}\right) \end{pmatrix}_{2O^2V} - \left[(\mathbf{1} \otimes \boldsymbol{Z}) \begin{pmatrix} \mathbf{1} \otimes \boldsymbol{\Omega} & \mathbf{0} \\ \mathbf{0} & \mathbf{1} \otimes (\eta - \boldsymbol{\Omega}) \end{pmatrix} \left(\mathbf{1} \otimes \boldsymbol{Z}^{-1}\right)\right]_{2O^2V} \tag{3.144}$$

$$= (\mathbf{1} \otimes \boldsymbol{Z}) \begin{pmatrix} \boldsymbol{\epsilon}^{1\ \text{h}} \otimes \mathbf{1} + \mathbf{1} \otimes -\boldsymbol{\Omega} & \mathbf{0} \\ \mathbf{0} & -\left(\boldsymbol{\epsilon}^{1\ \text{h}} \otimes \mathbf{1}\right) - (\mathbf{1} \otimes (\eta - \boldsymbol{\Omega})) \end{pmatrix} \left(\mathbf{1} \otimes \boldsymbol{Z}^{-1}\right) \tag{3.145}$$

$$\tag{3.146}$$

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

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

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

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

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

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

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

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

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

$$\tag{3.154}$$

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

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 4.3. 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

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

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

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

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

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

so we removed the non-boson conserving quality of the bosonic Hamiltonian (compare to 4.3).

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 $\hat{b_{\nu}}=\sum_{\mu}\left(\mathbf{X}_{\mu}^{\nu}\hat{\bar{b}}_{\nu}+\mathbf{Y}_{\mu}^{\nu}\hat{\bar{b}}_{\nu}^{\dagger}\right)$ and $\hat{b_{\nu}}^{\dagger}=\sum_{\mu}\left(\mathbf{X}_{\mu}^{\nu}\hat{\bar{b}}_{\nu}^{\dagger}+\mathbf{Y}_{\mu}^{\nu}\hat{\bar{b}}_{\nu}\right)$, which gives $\hat{b}_{\nu}+\hat{b}_{\nu}^{\dagger}=\sum_{\mu}\left(\mathbf{X}_{\mu}^{\nu}+\mathbf{Y}_{\mu}^{\nu}\right)\left(\hat{\bar{b}}_{\nu}+\hat{\bar{b}}_{\nu}^{\dagger}\right)$, so after we plug in

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

$$=\sum_{pq,\nu}W_{pq,\nu}\left\{\hat{a}_{p}^{\dagger}\hat{a}_{q}\right\}\left(\bar{b}_{\nu}+\bar{b}_{\nu}^{\dagger}\right) \tag{4.22}$$

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

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

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

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

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

$$[\hat{H}^e,\ a_j] = \sum_{pq} f_{pq}\,[a_p^\dagger a_q,\ a_j] = \sum_{pq} f_{pq}\left(a_p^\dagger\,[\,a_q, a_j\,] + [a_p^\dagger, a_j]a_q\right) \tag{4.28}$$

$$= \sum_{pq} f_{pq}\left(a_p^\dagger a_q a_j - a_p^\dagger a_j a_q + a_p^\dagger a_j a_q - a_j a_p^\dagger a_q\right) \tag{4.29}$$

$$[a_i^\dagger,\ [\hat{H}^e,\ a_j]] = \sum_{pq} f_{pq}\,[a_i^\dagger, \left(a_p^\dagger a_q a_j - a_j a_p^\dagger a_q\right)] \tag{4.30}$$

$$= \sum_{pq} f_{pq}\left([a_i^\dagger, a_p^\dagger a_q a_j] - [a_i^\dagger, a_j a_p^\dagger a_q]\right) \tag{4.31}$$

$$= \sum_{pq} f_{pq}\left(a_i^\dagger a_p^\dagger a_q a_j - a_p^\dagger a_q a_j a_i^\dagger - a_i^\dagger a_j a_p^\dagger a_q + a_j a_p^\dagger a_q a_i^\dagger\right) \tag{4.32}$$

$$a_i^\dagger a_p^\dagger a_q a_j = \overbrace{a_i^\dagger a_p^\dagger}\,\overbrace{a_q a_j} + \overbrace{a_i^\dagger a_p^\dagger a_q}\,\overbrace{a_j} = -\delta_{iq}\delta_{jp} + \cancel{\delta_{ij}\delta_{pq}} \tag{4.33}$$

$$a_p^\dagger a_q a_j a_i^\dagger = 0 \tag{4.34}$$

$$a_i^\dagger a_j a_p^\dagger a_q = \overbrace{a_i^\dagger\,\overbrace{a_j a_p^\dagger}\,a_q} + \overbrace{a_i^\dagger}\,\overbrace{a_j}\,\overbrace{a_p^\dagger a_q} = 0 + \cancel{\delta_{ij}\delta_{pq}} \tag{4.35}$$

$$a_j a_p^\dagger a_q a_i^\dagger = 0 \tag{4.36}$$

$$= -\sum_{pq} f_{pq}\delta_{iq}\delta_{jp} = -f_{ji} \tag{4.37}$$

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

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

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

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

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

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

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

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

$$\tag{4.47}$$

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

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

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

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

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

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

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

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

$$\tag{4.60}$$

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 $O(N_o N_v N^2_{\text{aux}} N^2_{\mathbf{k}})$, 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

Contour Deformation

5.1 Equations

After deforming the contour, the real frequency integral for the self-energy is rewritten as the difference of a contour integral and an integral along the imaginary axis:

$$\Sigma\left(\mathbf{r},\mathbf{r}',\omega\right)=\underbrace{\frac{i}{2\pi}\oint\,\mathrm{d}\omega' G_0\left(\mathbf{r},\mathbf{r}',\omega+\omega'\right)W_0\left(\mathbf{r},\mathbf{r}',\omega'\right)}_{\Sigma^C(\mathbf{r},\mathbf{r}',\omega)}-\underbrace{\frac{1}{2\pi}\int_{-\infty}^{\infty}\mathrm{d}\omega' G_0\left(\mathbf{r},\mathbf{r}',\omega+i\omega'\right)W_0\left(\mathbf{r},\mathbf{r}',i\omega'\right)}_{\Sigma^I(\mathbf{r},\mathbf{r}',\omega)} \tag{5.1}$$

$$\tag{5.2}$$

We know the poles of G_0 are located at frequencies

$$\omega'_{m\mathbf{k}_m}=\epsilon_{m\mathbf{k}_m}-\omega+i\eta\,\mathrm{sgn}\left(\epsilon_F-\epsilon_{m\mathbf{k}_m}\right) \tag{5.3}$$

with residues

$$\mathrm{Res}\left\{G_0\left(\mathbf{r},\mathbf{r}',\omega+\omega'\right),\omega'_{m\mathbf{k}_m}\right\}=\psi_{m\mathbf{k}_m}(\mathbf{r})\psi^*_{m\mathbf{k}_m}\left(\mathbf{r}'\right) \tag{5.4}$$

Depending on where the single Portugal energy is in relation to the Fermi level, the poles of G_0 will enter either the upper or lower contour. The contour interval is given by

$$\Sigma^C_{nn'}(\mathbf{k},\omega)=\frac{1}{N_\mathbf{k}}\sum_{m\mathbf{q}}f_{m\mathbf{k}-\mathbf{q}}\left(n\mathbf{k},m\mathbf{k}-\mathbf{q}\left|W\left(\omega'_{m\mathbf{k}-\mathbf{q}}\right)\right|m\mathbf{k}-\mathbf{q},n'\mathbf{k}\right) \tag{5.5}$$

$$=\frac{1}{N_\mathbf{k}}\sum_{m\mathbf{q}}f_{m\mathbf{k}-\mathbf{q}}\left(n\mathbf{k},m\mathbf{k}-\mathbf{q}\left|\left(v+W^C\left(\omega'_{m\mathbf{k}-\mathbf{q}}\right)\right)\right|m\mathbf{k}-\mathbf{q},n'\mathbf{k}\right) \tag{5.6}$$

$$=\frac{1}{N_\mathbf{k}}\sum_{m\mathbf{q}}f_{m\mathbf{k}-\mathbf{q}}\sum_{PQ}v_P^{nm}\left[\mathbf{I}-\mathbf{\Pi}\left(\mathbf{q},\omega'_{m\mathbf{k}-\mathbf{q}}\right)\right]^{-1}_{PQ}v_Q^{mn'} \tag{5.7}$$

$$=\frac{1}{N_\mathbf{k}}\sum_{m\mathbf{q}}f_{m\mathbf{k}-\mathbf{q}}\sum_{PQ}v_P^{nm}\left[\mathbf{I}-\mathbf{\Pi}\left(\mathbf{q},\omega'_{m\mathbf{k}-\mathbf{q}}\right)\right]^{-1}_{PQ}v_Q^{mn'} \tag{5.8}$$

$$\tag{5.9}$$

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