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Derivations for Personal Learning

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

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

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

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

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

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

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

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

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

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

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

recalling that the bare Coulomb interaction should be independent of frequency. A discussion of how to compute the screened Coulomb interaction can be found in this old work [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 [5]:

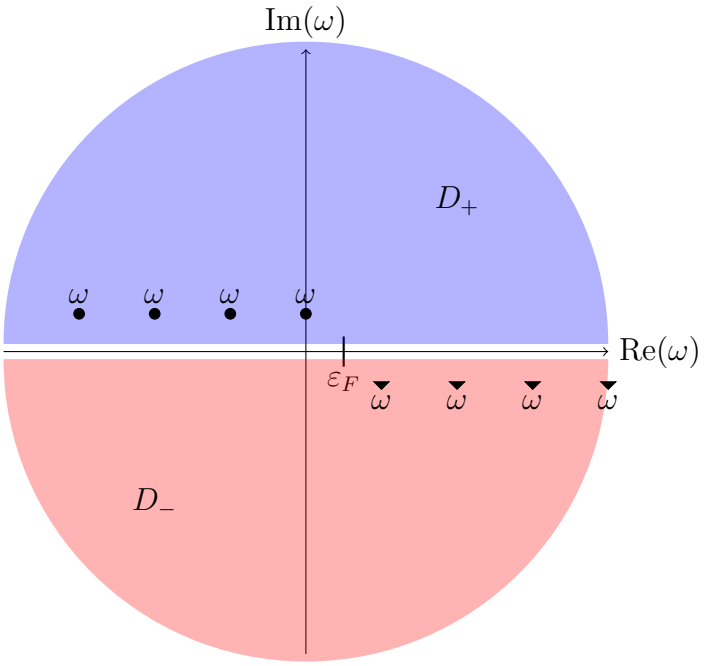

Figure 1.1: Contour for the complex frequency integral. The poles are denoted by the various ω. The Fermi energy is denoted by ε_F. The integration contour D_+ is the semicircle in the upper complex plane, while D_- is the semicircle in the lower complex plane.

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

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

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

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

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

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

1.2.2 Analytic continuation

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

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

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

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

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

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

The noninteracting Green's function has the form:

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

so that the above equation simplifies to:

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

Screened Coulomb Interaction

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

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

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

and

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

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

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

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

with

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

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

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

with

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

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

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

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

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

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

simplifying to

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

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

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

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

with

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

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

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

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

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

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

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

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

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

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

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

1.3 UHF formalism

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

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

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

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

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

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

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

1.4 Deriving linear response: 11/22

1.4.1 The Fundamentals

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

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

to do so, one must understand the reformulation of based on the density matrix as for posed by Furche [2]. 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 7.1 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 7.2 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 7.3. 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 7.4. 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 7.5.

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

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

Chapter 2

Dyson to GQME: 12/13

The Generalized Quantum Master Equation (GQME) is given by

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

where the correlation function is defined as

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

the higher-order moments are

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

with the auxiliary kernels

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

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

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

with $\mathcal{Q} = \mathcal{I} - \mathcal{P}$ being the complementary projection operator. But this becomes complicated, so Wenjie found that we can express $\mathcal{K}_1(t)$ without time evolution using $\hat{f}(0) = \mathcal{Q} i\mathcal{L}\hat{\mu}$ and, we get

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

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

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

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

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

We expect that the higher order auxiliary kernels will decay quickly, so we can truncate the series at some finite n. The moments of the memory kernel are

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

with $\mathcal{L}$ being the Liouville superoperator with $\mathcal{L}\hat{\mu} = \left[\hat{H}, \hat{\mu}\right]$. The construction of the numerator in equation 2.9 can be thought of as the generation of a Krylov subspace up to level n, i.e. we need to build up $\mathcal{K}_n(\mathcal{L}, \hat{\mu}) = \text{span}\{\hat{\mu}, (i\mathcal{L})\hat{\mu}, (i\mathcal{L})^2\hat{\mu}, \ldots, (i\mathcal{L})^{n-1}\hat{\mu}\}$, where $\hat{\mu} = \hat{c}$ or $\hat{c}^\dagger$. In the case if we choose $\hat{\mu} = \hat{c}$, we get the lesser Green's function

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

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

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

Then we can construct the retarded Green's function as

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

Using Krylov subspace methods, one never has to construct the Liouvillian matrix, but instead can directly compute the extremal eigenvalues and eigenvectors of $\mathcal{L}$ by considering the action of $\mathcal{L}$ on the Krylov subspace.

2.1 Explicit Construction of the Liouville Superoperator

Consider that we are working with the upfolded Hamiltonian

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

where we again have a physical space $\mathbf{f}$ and a bath space $\mathbf{d}$, whose coupling is given by $\mathbf{W}$. Tell me what would happened if we considered the action of this on the composite operator vector defined lower? Lets consider making a Krylov subspace, corresponding to repeated applications of the Liouville superoperator to the initial operator $\hat{\boldsymbol{\mu}}$. Now, The idea is to define a composite operator vector

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

where $\hat{c}$ is the annihilation operator and $\hat{c}^\dagger$ is the creation operator. Notice that the equation of motion for the Green's function is

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

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

So our task becomes to figure out how

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

I feel like it should be the case that $-i\hat{H}_0 G(t,t') = \mathcal{C}(t)\Omega_1$. Do you think that this should be the case or no? Because I think we can agree that the equation that comes first should be the same as the equation of motion for the greens function. And then try to apply a decomposed Hamiltonia like $H = H_0 + V$ to the first equation, so that we can see what happens.

To simple by things as much as possible initially consider that we only use the noninteracting Hamiltonian $\hat{H}_0 = \epsilon \hat{c}^\dagger \hat{c}$ in the action of the Liouvillian.

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

If we just consider the numerator, we see that

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

Considering just the first term

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

and the second term

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

which can be summarized as

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

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

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

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

Now come if we consider the higher-order moments

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

where it is implied that we are applying the commutator n times. We want to answer the form for the $\hat{\mathbf{H}}^{G_0 W_0}$ Hamiltonian, which has the super matrix form of

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

and the memory kernel

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

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

Chapter 3

RPA

3.1 RPA Derivations

Here I will enumerate the different routes that can be taken to derive the RPA. See the review [1] for an excellent introduction.

3.1.1 Green's function approach

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

Insertion of these identities into 3.6 gives rise to the equations

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

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

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

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

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

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

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

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

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

and rewriting the equations in matrix form gives

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

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

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

3.1.2 TDHF approach

See the review [1] for the derivation.

3.1.3 Equation of motion approach

The ideas here are based of [4]. The idea is to define an oscillator that satisfies

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

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

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

where m is the maximum number of excitations, which gives

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

where

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

Now define an arbitrary operator R, so

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

and similarly,

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

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

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

and now

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

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

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

Equivalence to what Garnet did

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

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

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

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

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

Plugging 3.34 into 3.33 gives

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

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

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

Particle-hole RPA

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

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

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

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

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

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

and by considering a Hamiltonian of the form

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

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

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

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

we get the RPA form of

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

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

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

Quasiparticle RPA

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

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

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

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

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

where U_ν and V_ν are positive real numbers subject to the normalization $U_\nu^2 + V_\nu^2 = 1$. Plugging in this ansatz for the excitation operator into the equations of motion 3.33 gives

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

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

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

Idea

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

This expands into

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

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

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

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

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

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

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

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

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

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

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

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

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

where Δ_ν is the gap parameter defined by

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

Explicitly,

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

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

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

is given by

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

$$\tag{3.67}$$

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

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

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

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

3.2 Extra

3.2.1 Comments about the correlation energy

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

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

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

$$\hat{O}_\nu^\dagger=\sum_{ia}\left(X_{ai}^\nu a_a^\dagger a_i\right). \tag{3.72}$$

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

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

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

in which the second term cannot be zero.

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

Trying direct evaluation

We know

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

The Lehmann representation for χ_0 is

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

Let's start by considering the right-hand side of equation 3.74. We know that in the particle-hole basis $\chi_0(\omega) = \chi_0^+(\omega) + \chi_0^-(\omega) = \begin{pmatrix}\chi_0^+(\omega) & 0\\ 0 & \chi_0^-(\omega)\end{pmatrix}$ is diagonal, where we define $\chi_0^\pm(\omega) = \frac{1}{\pm\omega+[\epsilon_a-\epsilon_i]}$ as the KS excitation/de-excitations polarizabilities.

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

The Coulomb interaction in the particle-hole basis is

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

Note the permutational symmetries, so $v_{pq,rs}^{++} \equiv (ia|jb) = (ai|bj) \equiv v_{pq,rs}^{--}$ and $v_{pq,rs}^{+-} \equiv (ia|bj) = (ai|jb) \equiv v_{pq,rs}^{-+}$. So the RHS of equation 3.74 is

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

where

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

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

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

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

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

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

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

How to determine the excitations?

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

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

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

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

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

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

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

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

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

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

We know that since $\chi_0^{\pm}(\omega) = \frac{1}{\pm(\omega - [\epsilon_a - \epsilon_i])} \implies \chi_0^+(\omega) = \tilde{\chi}_0(\omega)$ and $\chi_0^-(\omega) = -\tilde{\chi}_0(\omega)$, where $\tilde{\chi}_0(\omega) = \frac{1}{\omega - [\epsilon_a - \epsilon_i]}$. Notice from equation 3.87 that the occupied virtual combination of χ_0

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

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

This implies the system of equations

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

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

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

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

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

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

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

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

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

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

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

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

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

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

Chapter 4

Berkelbach's *GW*

4.1 Formulation for the dTDA

4.1.1 Comparing to Booth's ED

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

$$\boldsymbol{H} = \begin{pmatrix} \boldsymbol{F} & \boldsymbol{W} \\ \boldsymbol{W}^\dagger & \boldsymbol{d} \end{pmatrix} \tag{4.1}$$

where we have the definitions

$$W_{pkv} = \sum_{ia} (pk|ia) X^v_{ia} \quad \text{and} \quad d_{kv,lv'} = (\epsilon_k - \Omega_v)\, \delta_{k,l} \delta_{v,v'} \tag{4.2}$$

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

$$\boldsymbol{H} = \begin{pmatrix} \boldsymbol{F} & \boldsymbol{V}^{\text{2h1p}} \\ \left(\boldsymbol{V}^{\text{2 h1p}}\right)^\dagger & \boldsymbol{C}^{\text{2hlp}} \end{pmatrix} \tag{4.3}$$

where the definitions of the matrix elements are

$$V^{\text{2 h1p}}_{p,k[lc]} = \langle pc|kl\rangle \equiv (pk|lc) \tag{4.4}$$

$$C^{\text{2 h1p}}_{i[ja],k[lc]} = \left[(\epsilon_i + \epsilon_j - \epsilon_a)\, \delta_{jl} \delta_{ac} - \langle jc|al\rangle\right] \delta_{ik} \tag{4.5}$$

and in particular, we have a definition

$$\boldsymbol{C}^{\text{2hlp}} = \epsilon^{\text{1 h}} \oplus (-\boldsymbol{A}) = \epsilon^{\text{1 h}} \otimes \boldsymbol{1} + \boldsymbol{1} \otimes (-\boldsymbol{A}) \tag{4.6}$$

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

$$\boldsymbol{H}' = \boldsymbol{U}^\dagger \boldsymbol{H} \boldsymbol{U} = \begin{pmatrix} \boldsymbol{1} & \boldsymbol{0} \\ \boldsymbol{0} & \boldsymbol{X}^\dagger \end{pmatrix} \begin{pmatrix} \boldsymbol{F} & \boldsymbol{V}^{\text{2h1p}} \\ \left(\boldsymbol{V}^{\text{2 h1p}}\right)^\dagger & \boldsymbol{C}^{\text{2hlp}} \end{pmatrix} \begin{pmatrix} \boldsymbol{1} & \boldsymbol{0} \\ \boldsymbol{0} & \boldsymbol{X} \end{pmatrix} = \begin{pmatrix} \boldsymbol{F} & \boldsymbol{V}^{\text{2h1p}} \boldsymbol{X} \\ \boldsymbol{X}^\dagger \left(\boldsymbol{V}^{\text{2 h1p}}\right)^\dagger & \boldsymbol{X}^\dagger \boldsymbol{C}^{\text{2hlp}} \boldsymbol{X} \end{pmatrix}. \tag{4.7}$$

Now let us evaluate $\boldsymbol{X}^\dagger \boldsymbol{C}^{\text{2hlp}} \boldsymbol{X}$ in the dTDA case. We have

$$\begin{aligned}
\boldsymbol{X}^\dagger \boldsymbol{C}^{\text{2hlp}} \boldsymbol{X} &= \boldsymbol{X}^\dagger \left(\epsilon^{1\ \text{h}} \otimes \mathbf{1} + \mathbf{1} \otimes (-\boldsymbol{A}) \right) \boldsymbol{X} && (4.8)\\
&= \boldsymbol{X}^\dagger \left(\epsilon^{1\ \text{h}} \otimes \mathbf{1} \right) \boldsymbol{X} + \boldsymbol{X}^\dagger \left(\mathbf{1} \otimes (-\boldsymbol{A}) \right) \boldsymbol{X} && (4.9)\\
&= \left(\epsilon^{1\ \text{h}} \underbrace{\boldsymbol{X}^\dagger \boldsymbol{X}}_{\boldsymbol{I}} \right) \otimes \left(\underbrace{\boldsymbol{X}^\dagger \boldsymbol{X}}_{\boldsymbol{I}} \right) + \left(\underbrace{\boldsymbol{X}^\dagger \boldsymbol{X}}_{\boldsymbol{I}} \right) \otimes (- \underbrace{\boldsymbol{X}^\dagger \boldsymbol{A} \boldsymbol{X}}_{\boldsymbol{\Omega}}) && (4.10)\\
&= \epsilon^{1\ \text{h}} \oplus (-\boldsymbol{\Omega}) \equiv \boldsymbol{d}^< && (4.11)
\end{aligned}$$

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

$$\boldsymbol{V}^{2\ \text{h1p}} \boldsymbol{X} = \boldsymbol{W}^< \equiv \sum_{lc} (pk|lc) X^v_{lc} \tag{4.12}$$

$$\tag{4.13}$$

where we have used the definition of the W matrix in Booth's formulation, as given in (4.33).

Downfolding the upfolded Hamiltonian

Application of downfolding on George's supermatrix gave us the expression

$$\boldsymbol{\Sigma}(\omega) = \mathbf{W}^<(\omega \mathbf{I} - \mathbf{d}^<)^{-1} \mathbf{W}^{<,\dagger} + \mathbf{W}^>(\omega \mathbf{I} - \mathbf{d}^>)^{-1} \mathbf{W}^{>,\dagger} \tag{4.14}$$

Meanwhile, downfolding Tim's formulation gives us the expression for the correlation self energy

$$\Sigma(\omega) = \mathbf{V}^{\text{2hlp}} \left[\omega \mathbf{1} - \mathbf{C}^{\text{2hlp}} \right]^{-1} \left[\mathbf{V}^{\text{2hlp}} \right]^\dagger + \mathbf{V}^{\text{2plh}} \left[\omega \mathbf{1} - \mathbf{C}^{\text{2plh}} \right]^{-1} \left[\mathbf{V}^{\text{2plh}} \right]^\dagger \tag{4.15}$$

Above, we showed that the forms are actually equivalent for the TDA case.

4.1.2 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 $\boldsymbol{H}\boldsymbol{R} = \boldsymbol{\sigma}$, where $\boldsymbol{\sigma} = (\sigma_i,\ \sigma_a,\ \sigma_{i[jb]},\ \sigma_{[jb]a})$. Consider

$$\boldsymbol{H}\boldsymbol{R} = \begin{pmatrix} \boldsymbol{F} & \boldsymbol{V}^{\text{2h1p}} & \boldsymbol{V}^{\text{2p1\ h}} \\ \left(\boldsymbol{V}^{2\ \text{h1p}}\right)^\dagger & \boldsymbol{C}^{\text{2hlp}} & \mathbf{0} \\ \left(\boldsymbol{V}^{\text{2plh}}\right)^\dagger & \mathbf{0} & \boldsymbol{C}^{\text{2plh}} \end{pmatrix} \begin{pmatrix} r_i \\ r_a \\ r_{i[jb]} \\ r_{[jb]a} \end{pmatrix} = \begin{pmatrix} \sigma_i \\ \sigma_a \\ \sigma_{i[jb]} \\ \sigma_{[jb]a} \end{pmatrix} \tag{4.16}$$

$$\tag{4.17}$$

Let us enumerate now what we actually will get:

$$\sigma_i = \sum_j f_{ij}\, r_j + \sum_b f_{ib}\, r_b + \sum_{klc} \langle i\, c|k\, l\rangle\, r_{k[lc]} + \sum_{kcd} \langle i\, k|d\, c\rangle\, r_{[kc]d}, \tag{4.18}$$

$$\sigma_a = \sum_j f_{aj}\, r_j + \sum_b f_{ab}\, r_b + \sum_{klc} \langle a\, c|k\, l\rangle\, r_{k[lc]} + \sum_{kcd} \langle a\, k|d\, c\rangle\, r_{[kc]d}, \tag{4.19}$$

$$\sigma_{i[ja]} \sum_k \langle k\, a|i\, j\rangle\, r_k + \sum_b \langle b\, a|i\, j\rangle\, r_b + (\epsilon_i + \epsilon_j - \epsilon_a)\, r_{i[ja]} - \sum_{lc} \langle j\, c|a\, l\rangle\, r_{i[lc]} \tag{4.20}$$

$$\sigma_{[ia]b} = \sum_j \langle j\, i|b\, a\rangle\, r_j + \sum_c \langle c\, i|b\, a\rangle\, r_c + (\epsilon_a + \epsilon_b - \epsilon_i)\, r_{[ia]b} + \sum_{kc} \langle a\, k|i\, c\rangle\, r_{[kc]b}. \tag{4.21}$$

4.2 Formulation for the dRPA

4.2.1 Deriving the dRPA approach as they propose

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

$$\boldsymbol{N}\boldsymbol{M}\underbrace{\boldsymbol{Z}\boldsymbol{Z}^{-1}}_{\mathbf{1}} = \underbrace{\boldsymbol{N}\boldsymbol{N}}_{\mathbf{1}}\boldsymbol{Z} \begin{pmatrix} \boldsymbol{\Omega}_+ & 0 \\ 0 & -\boldsymbol{\Omega}_+ \end{pmatrix} \boldsymbol{Z}^{-1} \implies -\boldsymbol{N}\boldsymbol{M} = -\boldsymbol{Z} \begin{pmatrix} \boldsymbol{\Omega}_+ & 0 \\ 0 & -\boldsymbol{\Omega}_+ \end{pmatrix} \boldsymbol{Z}^{-1} \tag{4.22}$$

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

$$\Theta(-\boldsymbol{N}\boldsymbol{M}) = \boldsymbol{Z} \begin{pmatrix} \Theta(-\boldsymbol{\Omega}_+) & 0 \\ 0 & \Theta(\boldsymbol{\Omega}_+) \end{pmatrix} \boldsymbol{Z}^{-1} = \boldsymbol{Z} \begin{pmatrix} \mathbf{0} & 0 \\ 0 & \mathbf{1} \end{pmatrix} \boldsymbol{Z}^{-1} \tag{4.23}$$

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

$$\tilde{\boldsymbol{M}}\boldsymbol{Z} = \boldsymbol{M}\boldsymbol{Z} + \eta \boldsymbol{N} \Theta(-\boldsymbol{N}\boldsymbol{M})\boldsymbol{Z} = \mathbf{N}\boldsymbol{Z} \begin{pmatrix} \boldsymbol{\Omega}_+ & 0 \\ 0 & -\boldsymbol{\Omega}_+ \end{pmatrix} + \boldsymbol{N}\boldsymbol{Z} \begin{pmatrix} \mathbf{0} & 0 \\ 0 & \boldsymbol{\eta} \end{pmatrix} \underbrace{\boldsymbol{Z}^{-1}\boldsymbol{Z}}_{\mathbf{1}} = \boldsymbol{N}\boldsymbol{Z} \begin{pmatrix} \boldsymbol{\Omega}_+ & 0 \\ 0 & -\boldsymbol{\Omega}_+ + \boldsymbol{\eta} \end{pmatrix} \tag{4.24}$$

Connecting to Booth

Downfolding equivalence

Now they define a super-matrix,

$$\boldsymbol{H} = \begin{pmatrix} \boldsymbol{F} & \boldsymbol{V}^{\mathrm{2h1p}} & \boldsymbol{V}^{\mathrm{2h1p}} & \boldsymbol{V}^{\mathrm{2plh}} & \boldsymbol{V}^{\mathrm{2plh}} \\ \left(\boldsymbol{V}^{\mathrm{2h1p}}\right)^{\dagger} & & & & \\ \left(\boldsymbol{V}^{\mathrm{2h1p}}\right)^{\dagger} & & \boldsymbol{C}^{\mathrm{2hlp}} & & \boldsymbol{0} \\ \left(\boldsymbol{V}^{\mathrm{2plh}}\right)^{\dagger} & & & & \\ \left(\boldsymbol{V}^{\mathrm{2plh}}\right)^{\dagger} & & \boldsymbol{0} & & \boldsymbol{C}^{\mathrm{2plh}} \end{pmatrix} \tag{4.25}$$

where $\mathbf{C}^{\mathrm{2hlp}} = \varepsilon^{1\ \mathrm{h}} \oplus (-\tilde{\mathbf{M}})$ and $\mathbf{C}^{\mathrm{2plh}} = \varepsilon^{\mathrm{1p}} \oplus \tilde{\mathbf{M}}$, which for which we are instructed to use the super-metric

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

and the excitation vector is $\boldsymbol{R} = (\boldsymbol{R}^{\mathrm{1h+1p}}, \boldsymbol{R}^{\mathrm{2h1p}}, \boldsymbol{R}^{\mathrm{2p1h}})^{\dagger}$ with $\boldsymbol{R}^{\mathrm{2h1p}} = (\boldsymbol{r}^{\mathrm{2h1p}}, \bar{\boldsymbol{r}}^{\mathrm{2h1p}})^{\dagger}$ and $\boldsymbol{R}^{\mathrm{2p1h}} = (\boldsymbol{r}^{\mathrm{2p1h}}, \bar{\boldsymbol{r}}^{\mathrm{2p1h}})^{\dagger}$.

Proving ED equivalence

We have the eigenproblem $\boldsymbol{\mathcal{N}HR} = \boldsymbol{RE}$, so we really care about the matrix-vector products $\boldsymbol{\sigma} = \mathcal{N}\boldsymbol{HR}$. The answer they give is:

$$\sigma_i = \sum_j f_{ij}\, r_j + \sum_b f_{ib}\, r_b + \sum_{klc} \langle i\, c | k\, l \rangle\, r_{k[lc]} + \sum_{kcd} \langle i\, k | d\, c \rangle\, r_{[kc]d} + \sum_{klc} \langle i\, c | k\, l \rangle\, \bar{r}_{k[lc]} + \sum_{kcd} \langle i\, k | d\, c \rangle\, \bar{r}_{[kc]d} \tag{4.26}$$

$$\sigma_a = \sum_j f_{aj}\, r_j + \sum_b f_{ab}\, r_b + \sum_{klc} \langle a\, c | k\, l \rangle\, r_{k[lc]} + \sum_{kcd} \langle a\, k | d\, c \rangle\, r_{[kc]d} + \sum_{klc} \langle a\, c | k\, l \rangle\, \bar{r}_{k[lc]} + \sum_{kcd} \langle a\, k | d\, c \rangle\, \bar{r}_{[kc]d} \tag{4.27}$$

$$\sigma_{i[ja]} = \sum_k \langle k\, a | i\, j \rangle\, r_k + \sum_b \langle b\, a | i\, j \rangle\, r_b + \varepsilon_i r_{i[ja]} - \sum_{kb} \left[\mathbf{N}\tilde{\mathbf{M}}\right]^{\mathrm{xx}}_{jakb} r_{i[kb]} - \sum_{kb} \left[\mathbf{N}\tilde{\mathbf{M}}\right]^{\mathrm{xd}}_{jakb} \bar{r}_{i[kb]} \tag{4.28}$$

$$\bar{\sigma}_{i[ja]} = -\sum_k \langle k\, a | i\, j \rangle\, r_k - \sum_b \langle b\, a | i\, j \rangle\, r_b + \varepsilon_i \bar{r}_{i[ja]} - \sum_{kb} \left[\mathbf{N}\tilde{\mathbf{M}}\right]^{\mathrm{dx}}_{ja,kb} r_{i[kb]} - \sum_{kb} \left[\mathbf{N}\tilde{\mathbf{M}}\right]^{\mathrm{dd}}_{ja,kb} \bar{r}_{i[kb]} \tag{4.29}$$

$$\sigma_{[ia]b} = \sum_j \langle j\, i | b\, a \rangle\, r_j + \sum_c \langle c\, i | b\, a \rangle\, r_c + \varepsilon_b r_{[ia]b} + \sum_{jc} \left[\mathbf{N}\tilde{\mathbf{M}}\right]^{\mathrm{xx}}_{ia,jc} r_{[jc]b} + \sum_{jc} \left[\mathbf{N}\tilde{\mathbf{M}}\right]^{\mathrm{xd}}_{ia,jc} \bar{r}_{[jc]b} \tag{4.30}$$

$$\bar{\sigma}_{[ia]b} = -\sum_j \langle j\, i | b\, a \rangle\, r_j - \sum_c \langle c\, i | b\, a \rangle\, r_c + \varepsilon_b \bar{r}_{[ia]b} + \sum_{jc} \left[\mathbf{N}\tilde{\mathbf{M}}\right]^{\mathrm{dx}}_{ia,jc} r_{[jc]b} + \sum_{jc} \left[\mathbf{N}\tilde{\mathbf{M}}\right]^{\mathrm{dd}}_{ia,jc} \bar{r}_{[jc]b} \tag{4.31}$$

It is unclear where these equations come from

I found that these equations give rise to nearly the same spectrum (test on LiH with cc-pvdz basis show up to $10^{-9} Ha$ of agreement) as that of the exact upfolded GW Hamiltonian (Booth's ED), which is given by

$$\boldsymbol{H}^{G_0W_0}_{\text{Upfolded}} = \begin{pmatrix} \boldsymbol{F} & \boldsymbol{W}^{<} & \boldsymbol{W}^{>} \\ \boldsymbol{W}^{<,\dagger} & \boldsymbol{d}^{<} & 0 \\ \boldsymbol{W}^{>,\dagger} & 0 & \boldsymbol{d}^{>} \end{pmatrix} \tag{4.32}$$

where we have the definitions

$$W^{<}_{pkv} >= (\epsilon_k + \Omega_v)\, \delta_{k,l} \delta_{v,v'} \tag{4.33}$$

It concerns me that the agreement isn't exact (below $10^{-13} Ha$). I would want to have this cleared up before I try to reduce the scaling by implementing the Arnoldi procedure they try. Also, I am not able to figure out what motivated the form for this upfolded Hamiltonian for Tim's GW-RPA. Specifically, if one interprets the $\oplus$ as a direct sum, then the shapes of the matrices are not compatible since, for example, $\mathbf{C}^{\text{2hlp}} = \varepsilon^{1\ \text{h}} \oplus (-\tilde{\mathbf{M}})$ has the column dimension $O + 2OV$ which does not equal the width of its upstairs neighbor $\begin{pmatrix} \boldsymbol{V}^{\text{2h1p}} & \boldsymbol{V}^{\text{2h1p}} \end{pmatrix}$, which is $2O^2V$. If one interprets the $\oplus$ as a Kronecker sum, the shapes are compatible, but the energies are wrong. If we assume that the $\oplus$ should actually be the Kronecker product $\otimes$, again the shapes will be compatible, but the energies are wrong. I asked Jinghong, Nemo, and Hamlin and no one was able to figure it out. Can I email Tim to ask him about this?

To figure out how to recreate them consider the matrix multiplication for just the 2h1p channel

$$\boldsymbol{\mathcal{N}}^{\text{2h1p}} \boldsymbol{H}^{\text{2h1p}} \boldsymbol{R}^{\text{2h1p}} \tag{4.34}$$

$$= \begin{pmatrix} \mathbf{1}_{P,P} & 0 \\ 0 & \boldsymbol{X} \end{pmatrix} \begin{pmatrix} \boldsymbol{F}_{P,P} & \boldsymbol{V}^{\text{2h1p}} & \boldsymbol{V}^{\text{2h1p}} \\ (\boldsymbol{V}^{\text{2h1p}})^{\dagger} & & \\ (\boldsymbol{V}^{\text{2h1p}})^{\dagger} & & \boldsymbol{C}^{\text{2hlp}} \end{pmatrix} \begin{pmatrix} r_i \\ r_a \\ r_{i[jb]} \\ \bar{r}_{i[jb]} \end{pmatrix} \tag{4.35}$$

$$= \begin{pmatrix} \mathbf{1}_{P,P} & 0 \\ 0 & \boldsymbol{X} \end{pmatrix} \begin{pmatrix} \boldsymbol{f}_{O,O} r^i_{O,\bar{A}} + \boldsymbol{f}_{O,V} r^a_{V,\bar{A}} + \boldsymbol{v}^{\text{2h1p}}_{O,O^2V} r^{i[jb]}_{O^2V,\bar{A}} + \boldsymbol{v}^{\text{2h1p}}_{O,O^2V} \bar{r}^{i[jb]}_{O^2V,\bar{A}} \\ \boldsymbol{f}_{V,O} r^i_{O,\bar{A}} + \boldsymbol{f}_{V,V} r^a_{V,\bar{A}} + \boldsymbol{v}^{\text{2h1p}}_{V,O^2V} r^{i[jb]}_{O^2V,\bar{A}} + \boldsymbol{v}^{\text{2h1p}}_{V,O^2V} \bar{r}^{i[jb]}_{O^2V,\bar{A}} \\ \boldsymbol{v}^{\text{2h1p},\dagger}_{O^2V,O} r^i_{O,\bar{A}} + \boldsymbol{v}^{\text{2h1p},\dagger}_{O^2V,V} r^a_{V,\bar{A}} + \boldsymbol{c}^{\text{2hlp},xx}_{O^2V,O^2V} r^{i[jb]}_{O^2V,\bar{A}} + \boldsymbol{c}^{\text{2hlp},xd}_{O^2V,O^2V} \bar{r}^{i[jb]}_{O^2V,\bar{A}} \\ \boldsymbol{v}^{\text{2h1p},\dagger}_{O^2V,O} r^i_{O,\bar{A}} + \boldsymbol{v}^{\text{2h1p},\dagger}_{O^2V,V} r^a_{V,\bar{A}} + \boldsymbol{c}^{\text{2hlp},dx}_{O^2V,O^2V} r^{i[jb]}_{O^2V,\bar{A}} + \boldsymbol{c}^{\text{2hlp},dd}_{O^2V,O^2V} \bar{r}^{i[jb]}_{O^2V,\bar{A}} \end{pmatrix} \tag{4.36}$$

$$= \begin{pmatrix} \sigma_i \\ \sigma_a \\ \sigma_{i[ja]} \\ \bar{\sigma}_{i[ja]} \end{pmatrix} = \begin{pmatrix} \sum_j f_{ij}\, r_j + \sum_b f_{ib}\, r_b + \sum_{klc} \langle i\, c | k\, l \rangle\, r_{k[lc]} + \sum_{klc} \langle i\, c | k\, l \rangle\, \bar{r}_{k[lc]} \\ \sum_j f_{aj}\, r_j + \sum_b f_{ab}\, r_b + \sum_{klc} \langle a\, c | k\, l \rangle\, r_{k[lc]} + \sum_{klc} \langle a\, c | k\, l \rangle\, \bar{r}_{k[lc]} \\ \sum_k \langle k\, a | i\, j \rangle\, r_k + \sum_b \langle b\, a | i\, j \rangle\, r_b + \varepsilon_i r_{i[ja]} - \sum_{kb} \big[\mathbf{N}\tilde{\mathbf{M}}\big]^{\text{xx}}_{jakb} r_{i[kb]} - \sum_{kb} \big[\mathbf{N}\tilde{\mathbf{M}}\big]^{\text{xd}}_{jakb} \bar{r}_{i[kb]} \\ -\sum_k \langle k\, a | i\, j \rangle\, r_k - \sum_b \langle b\, a | i\, j \rangle\, r_b + \varepsilon_i \bar{r}_{i[ja]} - \sum_{kb} \big[\mathbf{N}\tilde{\mathbf{M}}\big]^{\text{dx}}_{ja,kb} r_{i[kb]} - \sum_{kb} \big[\mathbf{N}\tilde{\mathbf{M}}\big]^{\text{dd}}_{ja,kb} \bar{r}_{i[kb]} \end{pmatrix} \tag{4.37}$$

They say that $\boldsymbol{V}^{\mathrm{2h1p}}$ has the elements $V^{2\ \mathrm{h1p}}_{p,k[ia]} = \langle pa|ki\rangle \equiv (pk|ia)$ so we say that $\boldsymbol{v}^{\mathrm{2h1p}}_{O,O^2V}$ is the first O rows of $\boldsymbol{V}^{\mathrm{2h1p}}$, while $\boldsymbol{v}^{\mathrm{2h1p}}_{V,O^2V}$ is the latter V rows of $\boldsymbol{V}^{\mathrm{2h1p}}$. $\boldsymbol{C}^{\mathrm{2hlp}}$ is defined as $\varepsilon^{1h} \oplus -\tilde{\boldsymbol{M}}$. They also say that $\boldsymbol{X} = 1 \oplus \boldsymbol{N}$, where $\boldsymbol{N} = \begin{pmatrix} \mathbf{1}_{OV} & 0 \\ 0 & -\mathbf{1}_{OV} \end{pmatrix}$, but I am doubting this because the shapes in the matrix multiplication don't work out then. Define $\begin{pmatrix} \mathbf{1}_{OV} & 0 \\ 0 & -\mathbf{1}_{OV} \end{pmatrix} = \boldsymbol{N}$ and we have $V^{2\ \mathrm{h1p}}_{p,k[ia]} = \langle pa|ki\rangle \equiv (pk|ia)$. To simplify matters, let's just consider the 2h1p sector. Writing this down gives

$$\boldsymbol{\mathcal{N}}\boldsymbol{H}^{\mathrm{2h1p}} \tag{4.38}$$

$$= \begin{pmatrix} \mathbf{1}_{P,P} & 0 \\ 0 & \mathbf{1}_{O,O} \oplus \boldsymbol{N}_{2OV,2OV} \end{pmatrix} \begin{pmatrix} \boldsymbol{F} & \boldsymbol{V}^{\mathrm{2h1p}} & \boldsymbol{V}^{\mathrm{2h1p}} \\ \left(\boldsymbol{V}^{\mathrm{2h1p}}\right)^\dagger & & \\ \left(\boldsymbol{V}^{\mathrm{2h1p}}\right)^\dagger & & \boldsymbol{C}^{\mathrm{2hlp}} \end{pmatrix} \tag{4.39}$$

$$= \begin{pmatrix} \boldsymbol{F}_{P,P} & \mathbf{1}_{P,P}\boldsymbol{V}^{\mathrm{2h1p}}_{P,2O^2V} & \mathbf{1}_{P,P}\boldsymbol{V}^{\mathrm{2h1p}}_{P,2O^2V} \\ \begin{pmatrix} \mathbf{1}_{O,O} & 0 \\ 0 & \boldsymbol{N}_{2OV,2OV} \end{pmatrix} \begin{bmatrix} \left(\boldsymbol{V}^{\mathrm{2h1p}}\right)^\dagger \\ \left(\boldsymbol{V}^{\mathrm{2h1p}}\right)^\dagger \end{bmatrix}_{2O^2V,P} & \begin{pmatrix} \mathbf{1}_{O,O} & 0 \\ 0 & \boldsymbol{N}_{2OV,2OV} \end{pmatrix} \begin{pmatrix} \epsilon^{\mathrm{1h}}_{O,O} & 0 \\ 0 & -\tilde{\mathbf{M}}_{2OV,2OV} \end{pmatrix} \end{pmatrix} \tag{4.40}$$

$$= \begin{pmatrix} \boldsymbol{F}_{P,P} & \mathbf{1}_{P,P}\boldsymbol{V}^{\mathrm{2h1p}}_{P,2O^2V} & \mathbf{1}_{P,P}\boldsymbol{V}^{\mathrm{2h1p}}_{P,2O^2V} \\ \begin{pmatrix} \mathbf{1}_{O,O} & 0 \\ 0 & \boldsymbol{N}_{2OV,2OV} \end{pmatrix} \begin{bmatrix} \left(\boldsymbol{V}^{\mathrm{2h1p}}\right)^\dagger \\ \left(\boldsymbol{V}^{\mathrm{2h1p}}\right)^\dagger \end{bmatrix}_{2O^2V,P} & \begin{pmatrix} \epsilon^{\mathrm{1h}}_{O,O} & 0 \\ 0 & -\mathbf{N}\tilde{\boldsymbol{M}}_{2OV,2OV} \end{pmatrix} \end{pmatrix} \tag{4.41}$$

If we assume that the virtual space is largest, this means that the column width of the excitation vector is $\bar{A}$. The action of the super-metric on the excitation vector is given by $\boldsymbol{\mathcal{N}}\boldsymbol{H}\boldsymbol{R} = \boldsymbol{R}\boldsymbol{E}$ leads to:

$$\begin{pmatrix} \mathbf{1} & 0 & 0 \\ 0 & \mathbf{1} \oplus \boldsymbol{N} & 0 \\ 0 & 0 & \mathbf{1} \oplus \boldsymbol{N} \end{pmatrix} \begin{pmatrix} \boldsymbol{F} & \boldsymbol{V}^{\mathrm{2h1p}} & \boldsymbol{V}^{\mathrm{2h1p}} & \boldsymbol{V}^{\mathrm{2plh}} & \boldsymbol{V}^{\mathrm{2plh}} \\ \left(\boldsymbol{V}^{\mathrm{2h1p}}\right)^\dagger & & & & \\ \left(\boldsymbol{V}^{\mathrm{2h1p}}\right)^\dagger & & \boldsymbol{C}^{\mathrm{2hlp}} & & \mathbf{0} \\ \left(\boldsymbol{V}^{\mathrm{2plh}}\right)^\dagger & & & & \\ \left(\boldsymbol{V}^{\mathrm{2plh}}\right)^\dagger & & \mathbf{0} & & \boldsymbol{C}^{\mathrm{2plh}} \end{pmatrix}_{T,T} \begin{pmatrix} \boldsymbol{r}^{\mathrm{1h+1p}} \\ \boldsymbol{r}^{\mathrm{2h1p}} \\ \bar{\boldsymbol{r}}^{\mathrm{2h1p}} \\ \boldsymbol{r}^{\mathrm{2p1h}} \\ \bar{\boldsymbol{r}}^{\mathrm{2p1h}} \end{pmatrix}_{T,\bar{A}} = E \begin{pmatrix} \boldsymbol{r}^{\mathrm{1h+1p}} \\ \boldsymbol{r}^{\mathrm{2h1p}} \\ \bar{\boldsymbol{r}}^{\mathrm{2h1p}} \\ \boldsymbol{r}^{\mathrm{2p1h}} \\ \bar{\boldsymbol{r}}^{\mathrm{2p1h}} \end{pmatrix}_{T,\bar{A}} \tag{4.42}$$

From this we get:

$$\begin{pmatrix} \mathbf{1}_{P,P} & 0 & 0 \\ 0 & (\mathbf{1}_O \oplus_{\text{kron}} \boldsymbol{N}_{2OV})_{2A,2A} & 0 \\ 0 & 0 & (\mathbf{1}_V \oplus_{\text{kron}} \boldsymbol{N}_{2OV})_{2\bar{A},2\bar{A}} \end{pmatrix}_{T,T} \tag{4.43}$$

$$\begin{pmatrix} \boldsymbol{F}\boldsymbol{r}^{1\text{h}+1\text{p}} + \boldsymbol{V}^{2\text{h}1\text{p}}\boldsymbol{r}^{2\text{h}1\text{p}} + \boldsymbol{V}^{2\text{h}1\text{p}}\bar{\boldsymbol{r}}^{2\text{h}1\text{p}} + \boldsymbol{V}^{2\text{p}1\text{h}}\boldsymbol{r}^{2\text{p}1\text{h}} + \boldsymbol{V}^{2\text{p}1\text{h}}\bar{\boldsymbol{r}}^{2\text{p}1\text{h}} \\ \left(\boldsymbol{V}^{2\text{h}1\text{p}}\right)^\dagger \boldsymbol{r}^{1\text{h}+1\text{p}} + [\tilde{\boldsymbol{C}}^{2\text{hlp}}]^{xx}\boldsymbol{r}^{2\text{h}1\text{p}} + [\tilde{\boldsymbol{C}}^{2\text{hlp}}]^{xd}\bar{\boldsymbol{r}}^{2\text{h}1\text{p}} + \mathbf{0} \\ \left(\boldsymbol{V}^{2\text{h}1\text{p}}\right)^\dagger \boldsymbol{r}^{1\text{h}+1\text{p}} + [\tilde{\boldsymbol{C}}^{2\text{hlp}}]^{dx}\boldsymbol{r}^{2\text{h}1\text{p}} + [\tilde{\boldsymbol{C}}^{2\text{hlp}}]^{dd}\bar{\boldsymbol{r}}^{2\text{h}1\text{p}} + \mathbf{0} \\ \left(\boldsymbol{V}^{2\text{plh}}\right)^\dagger \boldsymbol{r}^{1\text{h}+1\text{p}} + \mathbf{0} + [\tilde{\boldsymbol{C}}^{2\text{plh}}]^{xx}\boldsymbol{r}^{2\text{p}1\text{h}} + [\tilde{\boldsymbol{C}}^{2\text{plh}}]^{xd}\bar{\boldsymbol{r}}^{2\text{p}1\text{h}} \\ \left(\boldsymbol{V}^{2\text{plh}}\right)^\dagger \boldsymbol{r}^{1\text{h}+1\text{p}} + \mathbf{0} + [\tilde{\boldsymbol{C}}^{2\text{plh}}]^{dx}\boldsymbol{r}^{2\text{p}1\text{h}} + [\tilde{\boldsymbol{C}}^{2\text{plh}}]^{dd}\bar{\boldsymbol{r}}^{2\text{p}1\text{h}} \end{pmatrix}_{T,\bar{A}} \tag{4.44}$$

$$= E \begin{pmatrix} \boldsymbol{r}^{1\text{h}+1\text{p}} \\ \boldsymbol{r}^{2\text{h}1\text{p}} \\ \bar{\boldsymbol{r}}^{2\text{h}1\text{p}} \\ \boldsymbol{r}^{2\text{p}1\text{h}} \\ \bar{\boldsymbol{r}}^{2\text{p}1\text{h}} \end{pmatrix}_{T,\bar{A}} \tag{4.45}$$

So notice that the dimensions inside the super-metric must be as indicated. The left hand side becomes

$$\begin{pmatrix} \boldsymbol{F}\boldsymbol{r}^{1\text{h}+1\text{p}} + \boldsymbol{V}^{2\text{h}1\text{p}}\boldsymbol{r}^{2\text{h}1\text{p}} + \boldsymbol{V}^{2\text{h}1\text{p}}\bar{\boldsymbol{r}}^{2\text{h}1\text{p}} + \boldsymbol{V}^{2\text{p}1\text{h}}\boldsymbol{r}^{2\text{p}1\text{h}} + \boldsymbol{V}^{2\text{p}1\text{h}}\bar{\boldsymbol{r}}^{2\text{p}1\text{h}} \\ \left(\boldsymbol{V}^{2\text{h}1\text{p}}\right)^\dagger \boldsymbol{r}^{1\text{h}+1\text{p}} + [\tilde{\boldsymbol{C}}^{2\text{hlp}}]^{xx}\boldsymbol{r}^{2\text{h}1\text{p}} + [\tilde{\boldsymbol{C}}^{2\text{hlp}}]^{xd}\bar{\boldsymbol{r}}^{2\text{h}1\text{p}} + \mathbf{0} \\ \boldsymbol{N}_{A,A}\left(\boldsymbol{V}^{2\text{h}1\text{p}}\right)^\dagger_{A,P} \boldsymbol{r}^{1\text{h}+1\text{p}}_{P,\bar{A}} + \boldsymbol{N}_{A,A}[\tilde{\boldsymbol{C}}^{2\text{hlp}}]^{dx}_{A,A}\boldsymbol{r}^{2\text{h}1\text{p}}_{A,\bar{A}} + \boldsymbol{N}_{A,A}[\tilde{\boldsymbol{C}}^{2\text{hlp}}]^{dd}_{A,A}\bar{\boldsymbol{r}}^{2\text{h}1\text{p}}_{A,\bar{A}} + \mathbf{0} \\ \left(\boldsymbol{V}^{2\text{plh}}\right)^\dagger \boldsymbol{r}^{1\text{h}+1\text{p}} + \mathbf{0} + [\tilde{\boldsymbol{C}}^{2\text{plh}}]^{xx}\boldsymbol{r}^{2\text{p}1\text{h}} + [\tilde{\boldsymbol{C}}^{2\text{plh}}]^{xd}\bar{\boldsymbol{r}}^{2\text{p}1\text{h}} \\ \boldsymbol{N}_{\bar{A},\bar{A}}\left(\boldsymbol{V}^{2\text{plh}}\right)^\dagger_{\bar{A},P} \boldsymbol{r}^{1\text{h}+1\text{p}}_{P,\bar{A}} + \mathbf{0} + \boldsymbol{N}_{\bar{A},\bar{A}}[\tilde{\boldsymbol{C}}^{2\text{plh}}]^{dx}_{\bar{A},\bar{A}}\boldsymbol{r}^{2\text{p}1\text{h}}_{\bar{A},\bar{A}} + \boldsymbol{N}_{\bar{A},\bar{A}}[\tilde{\boldsymbol{C}}^{2\text{plh}}]^{dd}_{\bar{A},\bar{A}}\bar{\boldsymbol{r}}^{2\text{p}1\text{h}}_{\bar{A},\bar{A}} \end{pmatrix}_{T,\bar{A}} \tag{4.46}$$

This is the point at which we encounter issues in the derivation. See the alternate derivation below for a more straightforward approach that highlights this.

$$\begin{pmatrix} \mathbf{1} & 0 & 0 \\ 0 & \mathbf{1} \oplus \boldsymbol{N} & 0 \\ 0 & 0 & \mathbf{1} \oplus \boldsymbol{N} \end{pmatrix} \begin{pmatrix} \boldsymbol{F} & \boldsymbol{V}^{2\text{h}1\text{p}} & \boldsymbol{V}^{2\text{h}1\text{p}} & \boldsymbol{V}^{2\text{plh}} & \boldsymbol{V}^{2\text{plh}} \\ \left(\boldsymbol{V}^{2\text{h}1\text{p}}\right)^\dagger & & & & \\ \left(\boldsymbol{V}^{2\text{h}1\text{p}}\right)^\dagger & & \boldsymbol{C}^{2\text{hlp}} & & \mathbf{0} \\ \left(\boldsymbol{V}^{2\text{plh}}\right)^\dagger & & & & \\ \left(\boldsymbol{V}^{2\text{plh}}\right)^\dagger & & \mathbf{0} & & \boldsymbol{C}^{2\text{plh}} \end{pmatrix} \begin{pmatrix} \boldsymbol{R}^{1\text{h}+1\text{p}} \\ \boldsymbol{R}^{2\text{h}1\text{p}} \\ \boldsymbol{R}^{2\text{p}1\text{h}} \end{pmatrix} = E \begin{pmatrix} \boldsymbol{R}^{1\text{h}+1\text{p}} \\ \boldsymbol{R}^{2\text{h}1\text{p}} \\ \boldsymbol{R}^{2\text{p}1\text{h}} \end{pmatrix} \tag{4.47}$$

The 3 coupled equations can be written as

$$\boldsymbol{F}\boldsymbol{R}^{1\text{h}+1\text{p}} + \boldsymbol{V}^{2\text{h}1\text{p}}\boldsymbol{R}^{2\text{h}1\text{p}} + \boldsymbol{V}^{2\text{plh}}\boldsymbol{R}^{2\text{p}1\text{h}} = E\boldsymbol{R}^{1\text{h}+1\text{p}} \tag{4.48}$$

$$(1 \oplus N)\left(\boldsymbol{V}^{2\text{h}1\text{p}}\right)^\dagger \boldsymbol{R}^{1\text{h}+1\text{p}} + (1 \oplus N)\left(\varepsilon^{1\ \text{h}} \oplus (-\tilde{\boldsymbol{M}})\right)\boldsymbol{R}^{2\text{h}1\text{p}} = E\boldsymbol{R}^{2\text{h}1\text{p}} \tag{4.49}$$

$$(1 \oplus N)\left(\boldsymbol{V}^{2\text{p}1\text{h}}\right)^\dagger \boldsymbol{R}^{1\text{h}+1\text{p}} + (1 \oplus N)\left(\varepsilon^{1\text{p}} \oplus \tilde{\boldsymbol{M}}\right)\tilde{\boldsymbol{C}}^{2\text{p}1\text{h}}\boldsymbol{R}^{2\text{p}1\text{h}} = E\boldsymbol{R}^{2\text{p}1\text{h}} \tag{4.50}$$

and we now define $\tilde{\boldsymbol{C}}^{2\text{hlp}} = (1 \oplus N)\left(\varepsilon^{1\ \text{h}} \oplus (-\tilde{\boldsymbol{M}})\right) = \varepsilon^{1\ \text{h}} \oplus (-\boldsymbol{N}\tilde{\boldsymbol{M}})$ and $\tilde{\boldsymbol{C}}^{2\text{plh}} = (1 \oplus N)\left(\varepsilon^{1\text{p}} \oplus \tilde{\boldsymbol{M}}\right) =$

$\varepsilon^{1\mathrm{p}} \oplus \boldsymbol{N}\tilde{\boldsymbol{M}}$. Now solve the last two equations for $\boldsymbol{R}^{2\mathrm{h1p}}$ and $\bar{\boldsymbol{R}}^{2\mathrm{p1h}}$:

$$\boldsymbol{R}^{2\mathrm{h1p}} = \left(\mathbf{1}E - \tilde{\boldsymbol{C}}^{2\mathrm{hlp}}\right)^{-1} \left((1 \oplus N)\left(\boldsymbol{V}^{2\mathrm{h1p}}\right)^{\dagger} \boldsymbol{R}^{1\mathrm{h}+1\mathrm{p}}\right) \tag{4.51}$$

$$\bar{\boldsymbol{R}}^{2\mathrm{p1h}} = \left(\mathbf{1}E - \tilde{\boldsymbol{C}}^{2\mathrm{plh}}\right)^{-1} \left((1 \oplus N)\left(\boldsymbol{V}^{2\mathrm{plh}}\right)^{\dagger} \boldsymbol{R}^{1\mathrm{h}+1\mathrm{p}}\right) \tag{4.52}$$

Substituting these into the first equation gives us

$$\boldsymbol{F}\boldsymbol{R}^{1\mathrm{h}+1\mathrm{p}} + \boldsymbol{V}^{2\mathrm{h1p}} \left(\mathbf{1}E - \tilde{\boldsymbol{C}}^{2\mathrm{hlp}}\right)^{-1} \left((1 \oplus N)\left(\boldsymbol{V}^{2\mathrm{h1p}}\right)^{\dagger} \boldsymbol{R}^{1\mathrm{h}+1\mathrm{p}}\right) \tag{4.53}$$

$$+ \boldsymbol{V}^{2\mathrm{plh}} \left(\mathbf{1}E - \tilde{\boldsymbol{C}}^{2\mathrm{plh}}\right)^{-1} \left((1 \oplus N)\left(\boldsymbol{V}^{2\mathrm{plh}}\right)^{\dagger} \boldsymbol{R}^{1\mathrm{h}+1\mathrm{p}}\right) = E\boldsymbol{R}^{1\mathrm{h}+1\mathrm{p}} \tag{4.54}$$

This gives us a form for the frequency dependent correlation self energy as

$$\boldsymbol{\Sigma}^{c}(\omega) = \boldsymbol{V}^{2\mathrm{h1p}} \left(\mathbf{1}\omega - \tilde{\boldsymbol{C}}^{2\mathrm{hlp}}\right)^{-1} (1 \oplus N)\left(\boldsymbol{V}^{2\mathrm{h1p}}\right)^{\dagger} + \boldsymbol{V}^{2\mathrm{plh}} \left(\mathbf{1}\omega - \tilde{\boldsymbol{C}}^{2\mathrm{plh}}\right)^{-1} (1 \oplus N)\left(\boldsymbol{V}^{2\mathrm{plh}}\right)^{\dagger} \tag{4.55}$$

The next thing we need to do is to write the spectral decomposition of the $\tilde{\boldsymbol{C}}$ where for the 2h1p sector, this is $\tilde{\boldsymbol{C}}^{2\mathrm{hlp}} = \boldsymbol{U}\left(\mathbf{1}\left(\epsilon_k - \Omega_\nu\right)\right)\boldsymbol{U}^{-1} \implies \left(\mathbf{1}\omega - \tilde{\boldsymbol{C}}^{2\mathrm{hlp}}\right)^{-1} = \boldsymbol{U}\left(\mathbf{1}\left[\omega - \left(\epsilon_k - \Omega_\nu\right)\right]\right)^{-1}\boldsymbol{U}^{-1}$ and $\tilde{\boldsymbol{C}}^{2\mathrm{plh}} = \boldsymbol{U}\left(\mathbf{1}\left(\epsilon_k + \Omega_\nu\right)\right)\boldsymbol{U}^{-1} \implies \left(\mathbf{1}\omega - \tilde{\boldsymbol{C}}^{2\mathrm{plh}}\right)^{-1} = \boldsymbol{U}\left(\mathbf{1}\left[\omega - \left(\epsilon_k + \Omega_\nu\right)\right]\right)^{-1}\boldsymbol{U}^{-1}$. Due to the bioorthonormality of the problem, the columns of $\boldsymbol{U}$ are the left eigenvectors of the $\tilde{\boldsymbol{C}}$ matrices, while the rows are the right eigenvectors. Thus, can we write

$$\boldsymbol{\Sigma}^{c}_{pq}(\omega) = \sum_{\nu}\Bigg[\sum_{k} \frac{\left(\sum_{[ia]} \boldsymbol{V}^{\boldsymbol{2h1p}}_{p,k[ia]} | v^{R,2h1p}_{[ia],\nu}\rangle\right)\left(\sum_{[jb]} \langle v^{L,2h1p}_{[jb],\nu}| \left(\boldsymbol{V}^{\boldsymbol{2h1p}}_{q,k[jb]}\right)^{\dagger}\right)}{\omega - \left(\epsilon_k - \Omega_\nu\right)} \tag{4.56}$$

$$+ \sum_{c} \frac{\left(\sum_{[ia]} \boldsymbol{V}^{\boldsymbol{2plh}}_{p,[ia]c} | v^{R,2plh}_{[ia],\nu}\rangle\right)\left(\sum_{[jb]} \langle v^{L,2plh}_{[jb],\nu}| \left(\boldsymbol{V}^{\boldsymbol{2plh}}_{q,[jb]c}\right)^{\dagger}\right)}{\omega - \left(\epsilon_c + \Omega_\nu\right)}\Bigg] ? \tag{4.57}$$

Deriving matrix vector products for 2h1p sector

The eigenvalue equation is then given by $\boldsymbol{H}\boldsymbol{R} = \boldsymbol{\mathcal{N}}\boldsymbol{R}\boldsymbol{E}$ and then leading to the non-Hermitian eigenvalue equation $\mathcal{N}\boldsymbol{H}\boldsymbol{R} = \boldsymbol{R}\boldsymbol{E}$. Let us carry this matrix multiplication out, just for the 2h1p sector. Collect the relevant components of the excitation vector into a block vector:

$$\boldsymbol{R}_{T,A} = \begin{pmatrix} \boldsymbol{r}_i & \boldsymbol{r}_a & \boldsymbol{r}_{i[jb]} & \bar{\boldsymbol{r}}_{i[jb]} \end{pmatrix}^{\dagger}$$

We will define the total dimension of this excitation vector as $T = P + 2A$, where $P = O + V$ and $A = O^2V$. The super-Hamiltonian decomposes as:

$$\boldsymbol{H} = \begin{pmatrix} \begin{pmatrix} \boldsymbol{F}_{oo} & \boldsymbol{F}_{ov} \\ \boldsymbol{F}_{vo} & \boldsymbol{F}_{vv} \end{pmatrix}_{P,P} & \begin{pmatrix} \boldsymbol{V}^{2\mathrm{h1p}}_{p,i[jb]} & \boldsymbol{V}^{2\mathrm{h1p}}_{p,i[\bar{j}\bar{b}]} \end{pmatrix}_{P,2A} \\ \begin{pmatrix} \boldsymbol{V}^{2\mathrm{h1p}}_{p,k[lc]} & \boldsymbol{V}^{2\mathrm{h1p}}_{p,k[\bar{l}\bar{c}]} \end{pmatrix}^{\dagger}_{2A,P} & \left(\left(\varepsilon^{1h}\right) \oplus_{\mathrm{direct}} -\tilde{\boldsymbol{M}}_{jb,jb;lc,lc}\right)_{2A,2A} \end{pmatrix}_{T,T}$$

The matrix-vector product becomes:

$$\boldsymbol{\sigma}_{T,A} = \boldsymbol{\mathcal{N}}_{T,T} \begin{pmatrix} \begin{pmatrix} \boldsymbol{F}_{oo} & \boldsymbol{F}_{ov} \\ \boldsymbol{F}_{vo} & \boldsymbol{F}_{vv} \end{pmatrix}_{P,P} \begin{pmatrix} \boldsymbol{r}_i \\ \boldsymbol{r}_a \end{pmatrix}_{P,A} + \begin{pmatrix} \boldsymbol{V}^{\text{2h1p}}_{p,i[jb]} & \boldsymbol{V}^{\text{2h1p}}_{p,i[\bar{j}\bar{b}]} \end{pmatrix}_{P,2A} \begin{pmatrix} \boldsymbol{r}_{i[jb]} \\ \bar{\boldsymbol{r}}_{i[\bar{j}\bar{b}]} \end{pmatrix}_{2A,A} \\ \begin{pmatrix} \boldsymbol{V}^{\text{2h1p}}_{p,i[jb]} & \boldsymbol{V}^{\text{2h1p}}_{p,i[\bar{j}\bar{b}]} \end{pmatrix}^{\dagger}_{2A,P} \begin{pmatrix} \boldsymbol{r}_i \\ \boldsymbol{r}_a \end{pmatrix}_{P,A} + \left(\left(\varepsilon^{1h} \right) \oplus_{\text{direct}} -\tilde{\boldsymbol{M}}_{jb,jb;lc,lc} \right)_{2A,2A} \begin{pmatrix} \boldsymbol{r}_{i[jb]} \\ \bar{\boldsymbol{r}}_{i[\bar{j}\bar{b}]} \end{pmatrix}_{2A,A} \end{pmatrix}$$

Now we are left to decide what the super-metric $\boldsymbol{\mathcal{N}}$ is. We can define it as

$$\boldsymbol{\mathcal{N}} = \begin{pmatrix} \boldsymbol{I_{PP}} & 0 \\ 0 & \boldsymbol{N}_{2A,2A} \end{pmatrix}_{T,T}$$

with $\boldsymbol{N}_{2A,2A} \equiv \mathbf{1}_O \oplus_{\text{direct}} \boldsymbol{N}_{\text{2OV}}$.

$$\boldsymbol{\mathcal{N}}\boldsymbol{H}\boldsymbol{R} \tag{4.58}$$

$$= \begin{pmatrix} \mathbf{1}_{P,P} \begin{pmatrix} \boldsymbol{F}_{oo} & \boldsymbol{F}_{ov} \\ \boldsymbol{F}_{vo} & \boldsymbol{F}_{vv} \end{pmatrix}_{P,P} \begin{pmatrix} \boldsymbol{r}_i \\ \boldsymbol{r}_a \end{pmatrix}_{P,A} + \mathbf{1}_{P,P} \begin{pmatrix} \boldsymbol{V}^{\text{2h1p}}_{p,i[jb]} & \boldsymbol{V}^{\text{2h1p}}_{p,i[jb]} \end{pmatrix}_{P,2A} \begin{pmatrix} \boldsymbol{r}_{i[jb]} \\ \bar{\boldsymbol{r}}_{i[\bar{j}\bar{b}]} \end{pmatrix}_{2A,A} \\ \boldsymbol{N}_{2A,2A} \begin{pmatrix} \begin{pmatrix} \boldsymbol{V}^{\text{2h1p}}_{p,i[jb]} \end{pmatrix}^{\dagger} \\ \begin{pmatrix} \boldsymbol{V}^{\text{2h1p}}_{p,i[jb]} \end{pmatrix}^{\dagger} \end{pmatrix}_{2A,P} \begin{pmatrix} \boldsymbol{r}_i \\ \boldsymbol{r}_a \end{pmatrix}_{P,A} + \boldsymbol{N}_{2A,2A} \left(\left(\varepsilon^{1h} \right) \oplus_{\text{direct}} -\tilde{\boldsymbol{M}}_{jb,jb;lc,lc} \right)_{2A,2A} \begin{pmatrix} \boldsymbol{r}_{i[jb]} \\ \bar{\boldsymbol{r}}_{i[\bar{j}\bar{b}]} \end{pmatrix}_{2A,A} \end{pmatrix} \tag{4.59}$$

$$= \begin{pmatrix} \begin{pmatrix} \boldsymbol{F}_{oo}\boldsymbol{r}_i + \boldsymbol{F}_{ov}\boldsymbol{r}_a \\ \boldsymbol{F}_{vo}\boldsymbol{r}_i + \boldsymbol{F}_{vv}\boldsymbol{r}_a \end{pmatrix}_{P,A} + \begin{pmatrix} \boldsymbol{V}^{\text{2h1p}}_{k,i[jb]}\boldsymbol{r}_{i[jb]} + \boldsymbol{V}^{\text{2h1p}}_{k,i[jb]}\bar{\boldsymbol{r}}_{i[\bar{j}\bar{b}]} \\ \boldsymbol{V}^{\text{2h1p}}_{c,i[jb]}\boldsymbol{r}_{i[jb]} + \boldsymbol{V}^{\text{2h1p}}_{c,i[jb]}\bar{\boldsymbol{r}}_{i[jb]} \end{pmatrix}_{P,A} \\ \boldsymbol{N}_{2A,2A} \begin{pmatrix} \boldsymbol{V}^{\text{2h1p}}_{k,i[jb]}\boldsymbol{r}_k + \boldsymbol{V}^{\text{2h1p}}_{a,i[jb]}\boldsymbol{r}_a \\ \boldsymbol{V}^{\text{2h1p}}_{k,i[jb]}\boldsymbol{r}_k + \boldsymbol{V}^{\text{2h1p}}_{a,i[jb]}\boldsymbol{r}_a \end{pmatrix}_{2A,A} + \left(\left(\varepsilon^{1h} \right) \oplus_{\text{direct}} - \begin{pmatrix} \tilde{\boldsymbol{M}}^{xx}_{jb,lc} & \tilde{\boldsymbol{M}}^{xd}_{jb,lc} \\ -\tilde{\boldsymbol{M}}^{dx}_{jb,lc} & -\tilde{\boldsymbol{M}}^{dd}_{jb,lc} \end{pmatrix} \right)_{2A,2A} \begin{pmatrix} \boldsymbol{r}_{i[jb]} \\ \bar{\boldsymbol{r}}_{i[\bar{j}\bar{b}]} \end{pmatrix}_{2A,A} \end{pmatrix} \tag{4.60}$$

$$= \begin{pmatrix} \begin{pmatrix} \sum_j f_{ij}r_j + \sum_b f_{ib}r_b + \sum_{jlc}\langle ic|jl\rangle r_{j[lc]} + \sum_{jlc}\langle ic|jl\rangle \bar{r}_{j[lc]} \\ \sum_j f_{aj}r_j + \sum_b f_{ab}r_b + \sum_{jlc}\langle ac|jl\rangle r_{j[lc]} + \sum_{jlc}\langle ac|jl\rangle \bar{r}_{j[lc]} \end{pmatrix}_{P,A} \\ \begin{pmatrix} ? \\ ? \end{pmatrix}_{2A,A} + \begin{pmatrix} ? \\ ? \end{pmatrix}_{2A,A} \end{pmatrix} \tag{4.61}$$

$$\tag{4.62}$$

4.2.2 Proving ED equivalence to Booth for the dRPA using Z-vector trick

The super matrix that downfolds into the GW self-energy is

$$\begin{pmatrix} \boldsymbol{F} & \boldsymbol{V}^{\text{2h1p}} & \boldsymbol{V}^{\text{2p1 h}} \\ \left(\boldsymbol{V}^{\text{2 h1p}} \right)^{\dagger} & \boldsymbol{C}^{\text{2hlp}} & \mathbf{0} \\ \left(\boldsymbol{V}^{\text{2plh}} \right)^{\dagger} & \mathbf{0} & \boldsymbol{C}^{\text{2plh}} \end{pmatrix} \tag{4.63}$$

For dRPA, we will choose

$$\boldsymbol{C}^{\text{2hlp}} = \epsilon^{1\ \text{h}} \oplus (-\boldsymbol{M}^{1/2}) \implies C^{2\ \text{h1p}}_{i[ja],k[lc]} = \left[\epsilon_i - \boldsymbol{M}^{\mathbf{1/2}}_{ja,lc}\right] \delta_{ik} \tag{4.64}$$

where $\boldsymbol{M}$ is the matrix defined in (4.66). If we choose our unitary transformation to be $\boldsymbol{U'} = \mathbf{1} \oplus \boldsymbol{T}$, where $\boldsymbol{T}$ is the matrix of eigenvectors of the symmetric formulation as

$$\boldsymbol{MT} = \boldsymbol{\lambda T} \tag{4.65}$$

with the matrix $\boldsymbol{M}$ defined as

$$\boldsymbol{M} = (\boldsymbol{A} - \boldsymbol{B})^{1/2}(\boldsymbol{A} + \boldsymbol{B})(\boldsymbol{A} - \boldsymbol{B})^{1/2} \tag{4.66}$$

with the identities $\boldsymbol{\lambda} = \boldsymbol{\Omega}^2$ and $\boldsymbol{T} = \boldsymbol{\Omega}^{1/2} \left[\boldsymbol{A} - \boldsymbol{B}\right]^{-1/2} (\boldsymbol{X} + \boldsymbol{Y})$, where $\boldsymbol{X}$ and $\boldsymbol{Y}$ are the excitation and de-excitation vectors, respectively.

Casida transformation

The matrix problem is:

$$\begin{bmatrix} \mathbf{A} & \mathbf{B} \\ -\mathbf{B} & -\mathbf{A} \end{bmatrix} \begin{bmatrix} \mathbf{X} & \mathbf{Y} \\ \mathbf{Y} & \mathbf{X} \end{bmatrix} = \begin{bmatrix} \mathbf{X} & \mathbf{Y} \\ \mathbf{Y} & \mathbf{X} \end{bmatrix} \begin{bmatrix} \mathbf{\Omega} & 0 \\ 0 & -\mathbf{\Omega} \end{bmatrix}. \tag{4.67}$$

which becomes equivalent to the pair of linear equations for each excitation mode

$$\begin{aligned} (\mathbf{A} + \mathbf{B})\,(X + Y)_\nu &= \Omega_\nu\,(X - Y)_\nu \\ (\mathbf{A} - \mathbf{B})\,(X - Y)_\nu &= \Omega_\nu\,(X + Y)_\nu \end{aligned} \tag{4.68}$$

We know we have the symmetric eigenproblem $\boldsymbol{M}T_\nu = \lambda_\nu T_\nu$, where $\boldsymbol{M} = (\boldsymbol{A} - \boldsymbol{B})^{1/2}(\boldsymbol{A} + \boldsymbol{B})(\boldsymbol{A} - \boldsymbol{B})^{1/2}$. Let us make the ansatze

$$\begin{aligned} (X + Y)_\nu &= \Omega_\nu^{-\frac{1}{2}}\,(\mathbf{A} - \mathbf{B})^{\frac{1}{2}}\,T_\nu \\ (X - Y)_\nu &= \Omega_\nu^{\frac{1}{2}}\,(\mathbf{A} - \mathbf{B})^{-\frac{1}{2}}\,T_\nu \end{aligned} \tag{4.69}$$

We know that this satisfies the biorthogonality relation since

$$(X + Y)^\dagger_\nu\,(X - Y)_\nu = \left(\Omega_\nu^{-\frac{1}{2}}\,(\mathbf{A} - \mathbf{B})^{\frac{1}{2}}\,T_\nu\right)^\dagger \left(\Omega_\nu^{\frac{1}{2}}\,(\mathbf{A} - \mathbf{B})^{-\frac{1}{2}}\,T_\nu\right) = T^\dagger_\nu T_\nu = 1 \tag{4.70}$$

Now, we can plug the ansatz 4.69 into the equations 4.68 to get

$$\begin{aligned} (\mathbf{A} + \mathbf{B})\left(\Omega_\nu^{-\frac{1}{2}}\,(\mathbf{A} - \mathbf{B})^{\frac{1}{2}}\,T_\nu\right) &= \Omega_\nu\left(\Omega_\nu^{\frac{1}{2}}\,(\mathbf{A} - \mathbf{B})^{-\frac{1}{2}}\,T_\nu\right) \\ \implies \Omega_\nu^{-\frac{1}{2}}\,(\mathbf{A} + \mathbf{B})\,(\mathbf{A} - \mathbf{B})^{\frac{1}{2}}\,T_\nu &= \Omega_\nu^{\frac{3}{2}}\,(\mathbf{A} - \mathbf{B})^{-\frac{1}{2}}\,T_\nu \\ \implies (\mathbf{A} - \mathbf{B})^{\frac{1}{2}}\,(\mathbf{A} + \mathbf{B})\,(\mathbf{A} - \mathbf{B})^{\frac{1}{2}}\,T_\nu &= \Omega_\nu^2 T_\nu \end{aligned} \tag{4.71}$$

We make the ansatz that the eigenvectors of the symmetric formulation are given by $\mathbf{T} = \mathbf{\Omega}^{\frac{1}{2}} (\mathbf{A} - \mathbf{B})^{-\frac{1}{2}} (\mathbf{X} + \mathbf{Y})$. Plugging into **??** gives us

$$(\mathbf{A} + \mathbf{B}) \left(\mathbf{\Omega}^{-\frac{1}{2}} (\mathbf{A} - \mathbf{B})^{\frac{1}{2}} \boldsymbol{T} \right) = \mathbf{\Omega} (\boldsymbol{X} - \boldsymbol{Y}) \tag{4.72}$$

$$\mathbf{\Omega}^{-\frac{1}{2}} (\mathbf{A} + \mathbf{B}) (\mathbf{A} - \mathbf{B})^{\frac{1}{2}} \boldsymbol{T} = \mathbf{\Omega} (\boldsymbol{X} - \boldsymbol{Y}) \tag{4.73}$$

$$\mathbf{\Omega}^{-\frac{1}{2}} (\mathbf{A} - \mathbf{B})^{-\frac{1}{2}} \boldsymbol{M} \boldsymbol{T} = \mathbf{\Omega} (\boldsymbol{X} - \boldsymbol{Y}) \tag{4.74}$$

$$\tag{4.75}$$

Then, we can apply the unitary transformation to the Hamiltonian in Tim's formulation as

$$\boldsymbol{H'} = \boldsymbol{U'}^{\dagger} \boldsymbol{H} \boldsymbol{U'} = \begin{pmatrix} \mathbf{1} & \mathbf{0} \\ \mathbf{0} & \boldsymbol{T}^{\dagger} \end{pmatrix} \begin{pmatrix} \boldsymbol{F} & \boldsymbol{V}^{\mathrm{2h1p}} \\ \left(\boldsymbol{V}^{2\ \mathrm{h1p}}\right)^{\dagger} & \boldsymbol{C}^{\mathrm{2hlp}} \end{pmatrix} \begin{pmatrix} \mathbf{1} & \mathbf{0} \\ \mathbf{0} & \boldsymbol{T} \end{pmatrix} = \begin{pmatrix} \boldsymbol{F} & \boldsymbol{V}^{\mathrm{2h1p}} \boldsymbol{T} \\ \boldsymbol{T}^{\dagger} \left(\boldsymbol{V}^{2\ \mathrm{h1p}}\right)^{\dagger} & \boldsymbol{T}^{\dagger} \boldsymbol{C}^{\mathrm{2hlp}} \boldsymbol{T} \end{pmatrix}. \tag{4.76}$$

But now let us try evaluating the term $\boldsymbol{T}^{\dagger} \boldsymbol{C}^{\mathrm{2hlp}} \boldsymbol{T}$ in the dRPA case. We have

$$\boldsymbol{T}^{\dagger} \boldsymbol{C}^{\mathrm{2hlp}} \boldsymbol{T} = \boldsymbol{T}^{\dagger} \left(\epsilon^{1\ \mathrm{h}} \otimes \mathbf{1} + \mathbf{1} \otimes (-\boldsymbol{M}^{1/2}) \right) \boldsymbol{T} \tag{4.77}$$

$$= \boldsymbol{T}^{\dagger} \left(\epsilon^{1\ \mathrm{h}} \otimes \mathbf{1} \right) \boldsymbol{T} + \boldsymbol{T}^{\dagger} \left(\mathbf{1} \otimes (-\boldsymbol{M}^{1/2}) \right) \boldsymbol{T} \tag{4.78}$$

$$= \left(\epsilon^{1\ \mathrm{h}} \underbrace{\boldsymbol{T}^{\dagger} \boldsymbol{T}}_{\boldsymbol{I}} \right) \otimes \left(\underbrace{\boldsymbol{T}^{\dagger} \boldsymbol{T}}_{\boldsymbol{I}} \right) + \left(\underbrace{\boldsymbol{T}^{\dagger} \boldsymbol{T}}_{\boldsymbol{I}} \right) \otimes (- \underbrace{\boldsymbol{T}^{\dagger} \boldsymbol{M}^{1/2} \boldsymbol{T}}_{\mathbf{\Omega}}) \tag{4.79}$$

$$\tag{4.80}$$

Next, let us consider the product $\boldsymbol{V}^{2\ \mathrm{h1p}} \boldsymbol{T}$. We have

$$\boldsymbol{V}^{2\ \mathrm{h1p}} \boldsymbol{T} = \sum_{ia} (pk|ia) \left(X^{v}_{ia} + Y^{v}_{ia} \right) \Omega^{1/2}_{ia;v} \underbrace{\sum_{jb} \left(A_{ia,jb} - B_{ia,jb} \right)^{-1/2}}_{\Delta^{-1/2}_{ia}} \tag{4.81}$$

$$\tag{4.82}$$

This would only work if we could assume that $\left(\frac{\Omega_{ia;v}}{\Delta_{ia}} \right)^{1/2} \approx 1$.

4.2.3 Evaluating 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 $\boldsymbol{H'R} = \boldsymbol{\sigma}$, where $\boldsymbol{\sigma} = (\sigma_i,\ \sigma_a,\ \sigma_{i[jb]},\ \sigma_{[jb]a})$. So the one body matrix vector products are the same as in the dTDA case

$$\sigma_i = \sum_j f_{ij}\, r_j + \sum_b f_{ib}\, r_b + \sum_{klc} \langle i\, c | k\, l \rangle\, r_{k[lc]} + \sum_{kcd} \langle i\, k | d\, c \rangle\, r_{[kc]d}, \tag{4.83}$$

$$\sigma_a = \sum_j f_{aj}\, r_j + \sum_b f_{ab}\, r_b + \sum_{klc} \langle a\, c | k\, l \rangle\, r_{k[lc]} + \sum_{kcd} \langle a\, k | d\, c \rangle\, r_{[kc]d}, \tag{4.84}$$

$$\tag{4.85}$$

For the two-body matrix vector products, we have

$$\sigma_{i[ja]} = \sum_k \langle k\, a | i\, j \rangle\, r_k + \sum_b \langle b\, a | i\, j \rangle\, r_b + \sum_{klc} C^{2\ \mathrm{h1p}}_{i[ja],k[lc]} r_{i[lc]} \tag{4.86}$$

Now, consider just

$$\sum_{klc} C^{2\ \mathrm{h1p}}_{i[ja],k[lc]} r_{i[lc]} = \sum_{klc} \left[\left(\epsilon_i - \boldsymbol{M}^{1/2}_{ja,lc} \right) \delta_{ik} r_{i[lc]} \right] = \sum_{lc} \left(\epsilon_i - \boldsymbol{M}^{1/2}_{ja,lc} \right) r_{i[lc]} \tag{4.87}$$

Consider now just the term

$$\sum_{lc} \boldsymbol{M}^{1/2}_{ja,lc} r_{i[lc]} = \sum_{lc} \left[\underbrace{\Delta^{1/2}_{ja} \left(\Delta_{ja} + 2(ja|lc) \right)_{ja,lc} \Delta^{1/2}_{ja}}_{\boldsymbol{D}} \right]^{1/2} r_{i[lc]}. \tag{4.88}$$

Let us consider instead the similarity transformed $\tilde{\boldsymbol{D}} = \Delta^{-1/2} \boldsymbol{D} \Delta^{-1/2} = (\Delta + 2K)$. This is useful because we have $D^{1/2} = \Delta^{1/2} \tilde{D}^{1/2} \Delta^{1/2} = (\Delta + 2K)^{1/2}$ for our SPD D.Now make the change of variables $u = \Delta^{1/2} r \implies r = \Delta^{-1/2} u$. Then we have $(\Delta + 2K)\, \Delta^{-1/2} u = \Delta^{1/2} \left[I + \underbrace{2 \Delta^{-1/2} K \Delta^{-1/2}}_{L} \right] u$. Again, because we are working with weak to moderately correlated systems, we can assume that L is small, and neglect it for now. So we have

$$\sum_{lc} \boldsymbol{M}^{1/2}_{ja,lc} r_{i[lc]} \approx \sum_{lc} \Delta^{1/2} I \Delta^{1/2} r_{i[lc]} \approx \sum_{lc} \Delta r_{i[lc]} \tag{4.89}$$

We can rewrite this as So really we have reduced the scaling to $O(O^3V^2)$. If we do a similar thing for the other term, we have

$$\sigma_{[ia]b} = \sum_j \langle j\, i | b\, a \rangle\, r_j + \sum_c \langle c\, i | b\, a \rangle\, r_c + \sum_{kc} \left[\epsilon_b + \boldsymbol{M}^{1/2}_{ia,kc} \right] r_{[kc]b} \tag{4.90}$$

which gives the scaling of $O(O^2V^3)$.

Chapter 5

Auxiliary-boson GW

5.1 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

$$\hat{H}^{\mathrm{eB}} = \hat{H}^{\mathrm{e}} + \hat{H}^{\mathrm{B}} + \hat{V}^{\mathrm{eB}} \tag{5.1}$$

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

$$\hat{H}^{e} = \sum_{pq} f_{pq} \left\{ \hat{a}_p^\dagger \hat{a}_q \right\} \tag{5.2}$$

$$\hat{H}^{B} = \sum_{\nu\mu} A_{\nu\mu} \hat{b}_\nu^\dagger \hat{b}_\mu + \frac{1}{2} \sum_{\nu\mu} B_{\nu\mu} \left(\hat{b}_\nu^\dagger \hat{b}_\mu^\dagger + \hat{b}_\nu \hat{b}_\mu \right) \tag{5.3}$$

$$\hat{V}^{eB} = \sum_{pq,\nu} V_{pq\nu} \left\{ \hat{a}_p^\dagger \hat{a}_q \right\} \left(\hat{b}_\nu^\dagger + \hat{b}_\nu \right) \tag{5.4}$$

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

$$\begin{aligned} A_{\nu\mu} &= A_{ia,jb} = \delta_{ij}\delta_{ab} \left(\epsilon_a - \epsilon_i \right) + (ia|bj) \\ B_{v\mu} &= B_{ia,jb} = (ia|jb) \end{aligned} \tag{5.5}$$

and the electron-boson coupling term is defined as

$$V_{pq\nu} = V_{pq,ia} = (pq|ia) \tag{5.6}$$

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

$$\hat{U}^\dagger \hat{H}^{\mathrm{eB}} \hat{U} \to \tilde{H}^{\mathrm{eB}}. \tag{5.7}$$

5.1.1 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

$$\hat{H}^{\mathrm{B}}\left(\hat{b}, \hat{b}^\dagger\right) = -\frac{1}{2}\operatorname{tr}\mathbf{A} + \frac{1}{2}\begin{pmatrix} \mathbf{b}^\dagger & \mathbf{b} \end{pmatrix}\begin{pmatrix} \mathbf{A} & \mathbf{B} \\ \mathbf{B} & \mathbf{A} \end{pmatrix}\begin{pmatrix} \mathbf{b} \\ \mathbf{b}^\dagger \end{pmatrix} \tag{5.8}$$

$$= -\frac{1}{2}\operatorname{tr}\mathbf{A} + \frac{1}{2}\begin{pmatrix} \boldsymbol{b}^\dagger & \boldsymbol{b} \end{pmatrix}\begin{pmatrix} \boldsymbol{A}\boldsymbol{b} + \boldsymbol{B}\boldsymbol{b}^\dagger \\ \boldsymbol{B}\boldsymbol{b} + \boldsymbol{A}\boldsymbol{b}^\dagger \end{pmatrix} \tag{5.9}$$

$$= -\frac{1}{2}\operatorname{tr}\mathbf{A} + \frac{1}{2}\left[\boldsymbol{b}^\dagger\boldsymbol{A}\boldsymbol{b} + \boldsymbol{b}^\dagger\boldsymbol{B}\boldsymbol{b}^\dagger + \boldsymbol{b}\boldsymbol{B}\boldsymbol{b} + \boldsymbol{b}\boldsymbol{A}\boldsymbol{b}^\dagger\right] \tag{5.10}$$

$$= \boldsymbol{b}^\dagger\boldsymbol{A}\boldsymbol{b} + \frac{1}{2}\left[\boldsymbol{b}^\dagger\boldsymbol{B}\boldsymbol{b}^\dagger + \boldsymbol{b}\boldsymbol{B}\boldsymbol{b}\right] + \mathbf{0} \tag{5.11}$$

$$= \sum_{\nu\mu} A_{\nu\mu}\hat{b}_\nu^\dagger\hat{b}_\mu + \frac{1}{2}\sum_{\nu\mu} B_{\nu\mu}\left(\hat{b}_\nu^\dagger\hat{b}_\mu^\dagger + \hat{b}_\nu\hat{b}_\mu\right) \tag{5.12}$$

Going from 5.10 to 5.11, we used the fact that the final term needs to be put into normal order so we can do $\boldsymbol{b}\boldsymbol{A}\boldsymbol{b}^\dagger = \sum_{\mu\nu} A_{\mu\nu} b_\mu b_\nu^\dagger = \sum_{\mu\nu} A_{\mu\nu}\left(b_\nu^\dagger b_\mu + \delta_{\mu\nu}\right) = \boldsymbol{b}^\dagger\boldsymbol{A}\boldsymbol{b} + \operatorname{Tr}(\boldsymbol{A})$. In the above we have showed equivalence to the previously defined form in 5.3. Within this representation of the bosonic Hamiltonian in the bosonic basis, in 5.8, we recognize the appearance of the RPA matrix. From 5.8, we can obtain a diagonalized form

$$\hat{H}^{\mathrm{B}}\left(\bar{b}, \bar{b}^\dagger\right) = -\frac{1}{2}\operatorname{tr}\mathbf{A} + \frac{1}{2}\left(\overline{\mathbf{b}}^\dagger \overline{\mathbf{b}}\right)\begin{pmatrix} \Omega\mathbf{1} & 0 \\ 0 & \Omega\mathbf{1} \end{pmatrix}\begin{pmatrix} \overline{\mathbf{b}} \\ \overline{\mathbf{b}}^\dagger \end{pmatrix} \tag{5.13}$$

through a redefinition of the bosonic operators as

$$\begin{pmatrix} \overline{\mathbf{b}} \\ \overline{\mathbf{b}}^\dagger \end{pmatrix} = \begin{pmatrix} \mathbf{X} & -\mathbf{Y} \\ -\mathbf{Y} & \mathbf{X} \end{pmatrix}^T \begin{pmatrix} \mathbf{b} \\ \mathbf{b}^\dagger \end{pmatrix} \quad \text{and} \quad \begin{pmatrix} \mathbf{b} \\ \mathbf{b}^\dagger \end{pmatrix} = \begin{pmatrix} \mathbf{X} & \mathbf{Y} \\ \mathbf{Y} & \mathbf{X} \end{pmatrix}\begin{pmatrix} \overline{\mathbf{b}} \\ \overline{\mathbf{b}}^\dagger \end{pmatrix}. \tag{5.14}$$

Effect on the bosonic Hamiltonian

Now by expanding, we see

$$\hat{H}^{\mathrm{B}}\left(\overline{\mathbf{b}},\overline{\mathbf{b}}^{\dagger}\right)=-\frac{1}{2}\operatorname{tr}\mathbf{A}+\frac{1}{2}\left(\overline{\mathbf{b}}^{\dagger}\overline{\mathbf{b}}\right)\begin{pmatrix}\Omega\mathbf{1} & 0\\ 0 & \Omega\mathbf{1}\end{pmatrix}\begin{pmatrix}\overline{\mathbf{b}}\\ \overline{\mathbf{b}}^{\dagger}\end{pmatrix} \tag{5.15}$$

$$=-\frac{1}{2}\operatorname{tr}\mathbf{A}+\frac{1}{2}\begin{pmatrix}\overline{\mathbf{b}}^{\dagger} & \overline{\mathbf{b}}\end{pmatrix}\begin{pmatrix}\boldsymbol{\Omega}\overline{\mathbf{b}}\\ \boldsymbol{\Omega}\overline{\mathbf{b}}^{\dagger}\end{pmatrix} \tag{5.16}$$

$$=-\frac{1}{2}\operatorname{tr}\mathbf{A}+\frac{1}{2}\left[\overline{\mathbf{b}}^{\dagger}\boldsymbol{\Omega}\overline{\mathbf{b}}+\underbrace{\overline{\mathbf{b}}\boldsymbol{\Omega}\overline{\mathbf{b}}^{\dagger}}_{\bar{b}^{\dagger}\boldsymbol{\Omega}\bar{b}+\mathrm{Tr}(\boldsymbol{\Omega})}\right] \tag{5.17}$$

$$=\overline{\mathbf{b}}^{\dagger}\boldsymbol{\Omega}\overline{\mathbf{b}}+\frac{1}{2}\operatorname{Tr}\left(\boldsymbol{\Omega}-\mathbf{A}\right) \tag{5.18}$$

$$=\sum_{\nu}\Omega_{\nu}\bar{b}_{\nu}^{\dagger}\bar{b}_{\nu}+E_{\mathrm{RPA}}^{c} \tag{5.19}$$

so we removed the non-boson conserving quality of the bosonic Hamiltonian (compare to 5.3).

Effect on the electron-boson coupling term

Originally, the electron-boson coupling term is given as

$$\hat{V}^{\mathrm{eB}}=\sum_{pq,\nu}V_{pq,\nu}\left\{\hat{a}_{p}^{\dagger}\hat{a}_{q}\right\}\left(\hat{b}_{\nu}^{\dagger}+\hat{b}_{\nu}\right) \tag{5.20}$$

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

$$\hat{V}^{\mathrm{eB}}=\sum_{pq,\nu}V_{pq,\nu}\left\{\hat{a}_{p}^{\dagger}\hat{a}_{q}\right\}\left(\sum_{\mu}\left(\mathbf{X}_{\mu}^{\nu}+\mathbf{Y}_{\mu}^{\nu}\right)\right)\left(\hat{\bar{b}}_{\nu}+\hat{\bar{b}}_{\nu}^{\dagger}\right) \tag{5.21}$$

$$=\sum_{pq,\nu}W_{pq,\nu}\left\{\hat{a}_{p}^{\dagger}\hat{a}_{q}\right\}\left(\bar{b}_{\nu}+\bar{b}_{\nu}^{\dagger}\right) \tag{5.22}$$

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

5.2 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

$$\boldsymbol{H}^{G_0W_0} = \begin{pmatrix} \boldsymbol{F} & \boldsymbol{W}^{<} & \boldsymbol{W}^{>} \\ \boldsymbol{W}^{\dagger<} & \boldsymbol{d}^{<} & \boldsymbol{0} \\ \boldsymbol{W}^{\dagger>} & \boldsymbol{0} & \boldsymbol{d}^{>} \end{pmatrix} \tag{5.23}$$

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

$$W^{<}_{pk\nu} = \sum_{ia} (pk|ia)\left(X^{\nu}_{ia} + Y^{\nu}_{ia}\right) \quad \text{and} \quad W^{>}_{pc\nu} = \sum_{ia} (pc|ia)\left(X^{\nu}_{ia} + Y^{\nu}_{ia}\right) \tag{5.24}$$

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

$$d^{<}_{k\nu,l\nu'} = (\epsilon_k - \Omega_\nu)\,\delta_{k,l}\delta_{\nu,\nu'} \quad \text{and} \quad d^{>}_{c\nu,d\nu'} = (\epsilon_c + \Omega_\nu)\,\delta_{c,d}\delta_{\nu,\nu'} \tag{5.25}$$

5.2.1 Derivation of the supermatrices for the 2h1p sector

Overlap

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

$$\boldsymbol{S} = \begin{pmatrix} \delta_{ij} & 0 & 0 & 0 \\ 0 & -\delta_{ab} & 0 & 0 \\ 0 & 0 & \delta_{ij}\delta_{\nu\nu'} & 0 \\ 0 & 0 & 0 & -\delta_{ab}\delta_{\nu\nu'} \end{pmatrix} \tag{5.26}$$

$\boldsymbol{H}$ takes more care.

Physical

$$H_{ij} = \langle 0_\mathrm{F} 0_\mathrm{B}| \left[a_i^\dagger, \left[\hat{H}^\mathrm{eB}, a_j\right]\right] |0_\mathrm{F} 0_\mathrm{B}\rangle = \langle 0_\mathrm{F} 0_\mathrm{B}| \left[a_i^\dagger, \left[\hat{H}^\mathrm{e}, a_j\right]\right] |0_\mathrm{F} 0_\mathrm{B}\rangle \tag{5.27}$$

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

$$[\hat{H}^e,\ a_j] = \sum_{pq} f_{pq} \left[a_p^\dagger a_q,\ a_j\right] = \sum_{pq} f_{pq} \left(a_p^\dagger \left[\, a_q, a_j \,\right] + [a_p^\dagger, a_j] a_q\right) \tag{5.28}$$

$$= \sum_{pq} f_{pq} \left(a_p^\dagger a_q a_j - a_p^\dagger a_j a_q + a_p^\dagger a_j a_q - a_j a_p^\dagger a_q\right) \tag{5.29}$$

$$[a_i^\dagger,\ [\hat{H}^e,\ a_j]] = \sum_{pq} f_{pq} \left[a_i^\dagger, \left(a_p^\dagger a_q a_j - a_j a_p^\dagger a_q\right)\right] \tag{5.30}$$

$$= \sum_{pq} f_{pq} \left([a_i^\dagger, a_p^\dagger a_q a_j] - [a_i^\dagger, a_j a_p^\dagger a_q]\right) \tag{5.31}$$

$$= \sum_{pq} f_{pq} \left(a_i^\dagger a_p^\dagger a_q a_j - a_p^\dagger a_q a_j a_i^\dagger - a_i^\dagger a_j a_p^\dagger a_q + a_j a_p^\dagger a_q a_i^\dagger\right) \tag{5.32}$$

$$a_i^\dagger a_p^\dagger a_q a_j = \overbrace{a_i^\dagger \overbrace{a_p^\dagger a_q} a_j} + \overbrace{a_i^\dagger \overbrace{a_p^\dagger a_q a_j}} = -\delta_{iq}\delta_{jp} + \cancel{\delta_{ij}\delta_{pq}} \tag{5.33}$$

$$a_p^\dagger a_q a_j a_i^\dagger = 0 \tag{5.34}$$

$$a_i^\dagger a_j a_p^\dagger a_q = \overbrace{a_i^\dagger \overbrace{a_j \overbrace{a_p^\dagger a_q}}} + \overbrace{a_i^\dagger \overbrace{a_j a_p^\dagger} a_q} = 0 + \cancel{\delta_{ij}\delta_{pq}} \tag{5.35}$$

$$a_j a_p^\dagger a_q a_i^\dagger = 0 \tag{5.36}$$

$$= -\sum_{pq} f_{pq}\delta_{iq}\delta_{jp} = -f_{ji} \tag{5.37}$$

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

Auxiliary

$$H_{i\nu j\nu'} = \langle 0_\mathrm{F} 0_\mathrm{B}| \left[a_i^\dagger b_\nu, \left[\hat{H}^\mathrm{eB}, a_j b_{\nu'}^\dagger\right]\right] |0_\mathrm{F} 0_\mathrm{B}\rangle = \langle 0_\mathrm{F} 0_\mathrm{B}| \left[a_i^\dagger b_\nu, \left[\hat{H}^\mathrm{e} + \hat{H}^\mathrm{B} + \hat{V}^\mathrm{eB}, a_j b_{\nu'}^\dagger\right]\right] |0_\mathrm{F} 0_\mathrm{B}\rangle \tag{5.38}$$

$$\tag{5.39}$$

First

$$[\hat{H}^e,\ a_j b_\mu^\dagger] = \sum_{pq} f_{pq}\,[a_p^\dagger a_q, a_j b_\mu^\dagger] = \sum_{pq} f_{pq}[a_p^\dagger a_q a_j - a_j a_p^\dagger a_q] b_\mu^\dagger \tag{5.40}$$

$$[a_i^\dagger b_\nu,\ [\hat{H}^e,\ a_j b_\mu^\dagger]] = [a_i^\dagger b_\nu,\ \sum_{pq} f_{pq}[a_p^\dagger a_q a_j - a_j a_p^\dagger a_q] b_\mu^\dagger] = \sum_{pq} f_{pq}[a_i^\dagger, a_p^\dagger a_q a_j - a_j a_p^\dagger a_q][b_\nu, b_\mu^\dagger] \tag{5.41}$$

$$= \delta_{\nu\mu} \sum_{pq} f_{pq} \left(a_i^\dagger a_p^\dagger a_q a_j - a_p^\dagger a_q a_j a_i^\dagger - a_i^\dagger a_j a_p^\dagger a_q + a_j a_p^\dagger a_q a_i^\dagger \right) \tag{5.42}$$

$$a_i^\dagger a_p^\dagger a_q a_j = \overbrace{a_i^\dagger \overbrace{a_p^\dagger a_q} a_j} + \overbrace{a_i^\dagger \overbrace{a_p^\dagger a_q a_j}} = -\underbrace{\delta_{iq}\delta_{jp}}_{q,p\in O} + \cancel{\delta_{ij}\delta_{pq}} \tag{5.43}$$

$$a_p^\dagger a_q a_j a_i^\dagger = 0 \tag{5.44}$$

$$a_i^\dagger a_j a_p^\dagger a_q = \overbrace{a_i^\dagger \overbrace{a_j a_p^\dagger} a_q} + \overbrace{a_i^\dagger a_j \overbrace{a_p^\dagger a_q}} = 0 + \cancel{\delta_{ij}\delta_{pq}} \tag{5.45}$$

$$a_p^\dagger a_j a_q a_i^\dagger = 0 \tag{5.46}$$

$$\tag{5.47}$$

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

$$[\hat{H}^B,\ a_j b_\mu^\dagger] = [\sum_\nu \Omega_\nu b_\nu^\dagger b_\nu + E^c_{\mathrm{RPA}}, a_j b_\mu^\dagger] = \sum_\nu \Omega_\nu a_j [b_\nu^\dagger b_\nu, b_\mu^\dagger] = \sum_\nu \Omega_\nu a_j b_\nu^\dagger [b_\nu, b_\mu^\dagger] = \Omega_\mu a_j b_\mu^\dagger \tag{5.48}$$

$$[a_i^\dagger b_\nu,\ [\hat{H}^B,\ a_j b_\mu^\dagger]] = \Omega_\mu [a_i^\dagger b_\nu, a_j b_\mu^\dagger] = \Omega_\mu [a_i^\dagger, a_j][b_\nu, b_\mu^\dagger] = \delta_{ij}\delta_{\nu\mu}\Omega_\mu \tag{5.49}$$

$$\tag{5.50}$$

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

$$[a_i^\dagger b_\nu,\ [\hat{V}^{eB},\ a_j b_{\nu'}^\dagger]] = 0 \tag{5.51}$$

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

$$H_{i,p\nu} = \langle 0_{\mathrm{F}} 0_{\mathrm{B}}| \left[a_i^\dagger, \left[\hat{H}^{\mathrm{eB}}, a_p b_\nu^\dagger\right]\right] |0_{\mathrm{F}} 0_{\mathrm{B}}\rangle = \langle 0_{\mathrm{F}} 0_{\mathrm{B}}| \left[a_i^\dagger, \left[\hat{V}^{\mathrm{eB}}, a_p b_\nu^\dagger\right]\right] |0_{\mathrm{F}} 0_{\mathrm{B}}\rangle \tag{5.52}$$

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

$$[V^{eB},\ a_p b_\nu^\dagger] = \sum_{rs,\nu'} W_{rs,\nu'} [a_r^\dagger a_s (b_{\nu'} + b_{\nu'}^\dagger), a_p b_\nu^\dagger] = \sum_{rs,\nu'} W_{rs,\nu'} [a_r^\dagger a_s, a_p][b_{\nu'}, b_\nu^\dagger] \tag{5.53}$$

$$= \sum_{rs} W_{rs,\nu} \left(a_r^\dagger a_s a_p - a_p a_r^\dagger a_s \right) \tag{5.54}$$

$$[a_i^\dagger,\ [\hat{V}^{eB},\ a_p b_\nu^\dagger]] = \sum_{rs} W_{rs,\nu} \left[a_i^\dagger \hat{a}_r^\dagger \hat{a}_s a_p - \hat{a}_r^\dagger \hat{a}_s a_p a_i^\dagger - \left(a_i^\dagger a_p a_r^\dagger a_s - a_p a_r^\dagger a_s a_i^\dagger \right) \right] \tag{5.55}$$

$$a_i^\dagger \hat{a}_r^\dagger \hat{a}_s a_p = \overbrace{a_i^\dagger \overbrace{a_r^\dagger a_s} a_p} + \overbrace{a_i^\dagger \overbrace{a_r^\dagger a_s a_p}} = -\underbrace{\delta_{is}\delta_{rp}}_{s \in O} + \cancel{\delta_{ip}\delta_{rs}} \tag{5.56}$$

$$\hat{a}_r^\dagger \hat{a}_s a_p a_i^\dagger = \overbrace{a_r^\dagger \overbrace{a_s a_p} a_i^\dagger} + \overbrace{a_r^\dagger a_s \overbrace{a_p a_i^\dagger}} = 0 \tag{5.57}$$

$$a_i^\dagger a_p a_r^\dagger a_s = \overbrace{a_i^\dagger a_p} \overbrace{a_r^\dagger a_s} + \overbrace{a_i^\dagger \overbrace{a_p a_r^\dagger} a_s} = \cancel{\delta_{ip}\delta_{rs}} + 0 \tag{5.58}$$

$$a_p a_r^\dagger a_s a_i^\dagger = 0 \tag{5.59}$$

$$\tag{5.60}$$

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

Chapter 6

BSE Notes

6.1 The standard canon

To get the particle-hole response function L, we need to solve the Dyson equation, which reads

$$\frac{\partial G(1,1')}{\partial U(2',2)} \equiv L\left(1,2;1',2'\right) = L_0\left(1,2;1',2'\right) + \int \mathrm{d}\left(3456\right) L_0\left(1,4;1',3\right) \Xi^{\mathrm{eh}}\left(3,5;4,6\right) L\left(6,2;5,2'\right) \tag{6.1}$$

G is the one-particle Green's function and U is the fictitious nonlocal potential due to Schwinger. $L_0\left(1,2;1',2'\right) = G\left(1,2'\right) G\left(2,1'\right)$ is the non-interacting eh propagator and the eh kernel Ξ^{eh} is defined as

$$i\Xi^{\mathrm{eh}}\left(3,5;4,6\right) = v(3,6)\delta(3,4)\delta(5,6) + i\frac{\delta\Sigma\left(3,4\right)}{\delta G\left(6,5\right)} \tag{6.2}$$

6.1.1 TD-DFT Similarity

In the TD-DFT framework, we have the Dyson equation for the density-density response function χ:

$$\frac{\partial \rho(1)}{\partial U(2)} \equiv \chi(1,2) = \chi_0(1,2) + \int \mathrm{d}34 \chi_0(1,3) \Xi^{\mathrm{DFT}}(3,4) \chi(4,2) \tag{6.3}$$

ρ is the density. χ_0 is the non-interacting density-density response function and Ξ^{DFT} is the DFT kernel given by

$$\Xi^{\mathrm{DFT}}(3,4) = v(3,4) + \frac{\partial V^{\mathrm{xc}}(3)}{\partial \rho(4)} \tag{6.4}$$

It is worth noting that $\chi(1,2) = -iL(1,2;1^+,2^+)$ with $\rho(1) = -iG(1,1^+)$, with the $+$ indicating a slightly shifted time to preserve causality. So the Dyson equation for L reduces to the Dyson equation for χ once the appropriate contractions have been performed. Earlier in the year, I was able to show that

$$\chi_{RPA}(\omega) = \left[\begin{pmatrix} \mathbf{A} & \mathbf{B} \\ \mathbf{B} & \mathbf{A} \end{pmatrix} + \omega \begin{pmatrix} \mathbf{I} & 0 \\ 0 & -\mathbf{I} \end{pmatrix} \right]^{-1} \tag{6.5}$$

$$\tag{6.6}$$

So presumably, we can also write

$$L(\omega) = \left[\begin{pmatrix} \tilde{\mathbf{A}} & \tilde{\mathbf{B}} \\ \tilde{\mathbf{B}} & \tilde{\mathbf{A}} \end{pmatrix} + \omega \begin{pmatrix} \mathbf{I} & 0 \\ 0 & -\mathbf{I} \end{pmatrix} \right]^{-1} \tag{6.7}$$

where now the matrices $\tilde{\mathbf{A}}$ and $\tilde{\mathbf{B}}$ are defined in the direct approximation as

$$\tilde{A}_{\mu\nu} \equiv \tilde{A}_{ai,bj} = \left(\epsilon_a^{GW} - \epsilon_i^{GW}\right) \delta_{ab}\delta_{ij} + (ai|jb) - \Xi^c_{ab,ji}(\omega) \tag{6.8}$$

$$\tilde{B}_{\mu\nu} \equiv \tilde{B}_{ai,bj} = (ai|bj) - \Xi^c_{bi,aj}(\omega) \tag{6.9}$$

So we know that we want to solve for the eigenvalues of the matrix

$$\begin{pmatrix} \tilde{\boldsymbol{A}} & \tilde{\boldsymbol{B}} \\ \tilde{\boldsymbol{B}} & \tilde{\boldsymbol{A}} \end{pmatrix} = \begin{pmatrix} \boldsymbol{X} & -\boldsymbol{Y} \\ -\boldsymbol{Y} & \boldsymbol{X} \end{pmatrix} \begin{pmatrix} \Omega\mathbf{1} & 0 \\ 0 & \Omega\mathbf{1} \end{pmatrix} \begin{pmatrix} \boldsymbol{X} & -\boldsymbol{Y} \\ -\boldsymbol{Y} & \boldsymbol{X} \end{pmatrix} \tag{6.10}$$

6.1.2 The GW formulation

In the GW approximation, eh kernel takes on the simpler form

$$i\Xi^{\text{eh}}_{GW}(3,5;4,6) = v(3,6)\delta(3,4)\delta(5,6) - W(3^+,4)\delta(3,6)\delta(4,5) \tag{6.11}$$

This follows when we approximate Σ by the GW self-energy:

$$\Sigma(1,2) \approx \Sigma^{GW}(1,2) = iG(1,2)W(2,1^+) \implies i\frac{\delta\Sigma\,(3,4)}{\delta G\,(6,5)} \approx i\frac{\delta\Sigma^{GW}\,(3,4)}{\delta G\,(6,5)} = -W(3^+,4)\delta(3,6)\delta(4,5) \tag{6.12}$$

The $\boldsymbol{A}$ and $\boldsymbol{B}$ matrices become:

$$A_{ai,bj} = (\epsilon_a - \epsilon_i)\,\delta_{ab}\delta_{ij} + (ai|jb) - W_{ab,ji}(\omega) \tag{6.13}$$

$$B_{ai,bj} = (ai|bj) - W_{bi|aj}(\omega) \tag{6.14}$$

It is customary to make the static approximation to the screened Coulomb potentitial, i.e. $W_{ab,ji}(\omega) \approx W_{ab,ji}(\omega = 0)$. Because the super matrix formulation for GW was so successful at obtaining all QPEs without having to solve a QP equation, I wonder if formulating the BSE in a supermatrix form will enable us to discard this static approximation.

6.2 Berkelbach TDA BSE

Here the BSE is defined as

$$\mathcal{A}(\omega) \equiv A_{ia,jb} - K^{(p)}_{ab,ij}(\omega) \tag{6.15}$$

$$\tag{6.16}$$

where

$$A_{ia,jb} = (E_a - E_i)\,\delta_{ij}\delta_{ab} + \kappa(ia|jb) - (ab|ij) \tag{6.17}$$

$$K^{(\text{p})}_{abij}(\omega) = 2\sum_m^{\Omega_m>0} (ij|\rho_m)\,(ab|\rho_m)\left[\frac{1}{\omega - (E_b - E_i) - \Omega_m} + \frac{1}{\omega - (E_a - E_j) - \Omega_m}\right] \tag{6.18}$$

$$\tag{6.19}$$

with κ set to 2 for singlets and 0 for triplets.

We want to show that the spectrum of the upfolded matrix $\boldsymbol{\mathcal{H}}$ is equivalent to that of the Bethe-Salpeter equation (BSE) in the Tamm-Dancoff approximation (TDA). The upfolded Hamiltonian is given by

$$\mathcal{H} = \begin{pmatrix} \mathbf{A} & -\mathbf{V}^{\mathrm{e}} & -\mathbf{V}^{\mathrm{h}} \\ (\mathbf{V}^{\mathrm{h}})^{\dagger} & \mathbf{D} & \mathbf{0} \\ (\mathbf{V}^{\mathrm{e}})^{\dagger} & \mathbf{0} & \mathbf{D} \end{pmatrix} \tag{6.20}$$

The physical block has already been defined; the rest is:

$$\mathbf{D} = [-\boldsymbol{E}_{\mathrm{occ}}] \oplus_{\mathrm{kron}} \boldsymbol{E}_{\mathrm{vir}} \oplus_{\mathrm{kron}} \mathbf{S} \tag{6.21}$$

$$V^{\mathrm{h}}_{ia,ldkc} = \sqrt{2}\,(il|kc)\,\delta_{ad} \tag{6.22}$$

$$V^{\mathrm{e}}_{ia,ldkc} = \sqrt{2}\,(kc|ad)\,\delta_{il} \tag{6.23}$$

Here, $\mathbf{S}$ is the direct RPA matrix in the TDA, defined as

$$S_{ia,jb} = (\epsilon_a - \epsilon_i)\,\delta_{ij}\delta_{ab} + (ia|jb), \tag{6.24}$$

$\boldsymbol{E}_{\mathrm{occ}}$ and $\boldsymbol{E}_{\mathrm{vir}}$ are diagonal matrices containing the GW QPEs of the occupied and virtual orbitals, respectively. The dimensions of the blocks are as follows: $\mathbf{A}$ is $OV \times OV$, $\mathbf{V}^{\mathrm{e}}$ is $OV \times O^2V^2$, $\mathbf{V}^{\mathrm{h}}$ is $OV \times O^2V^2$, and $\mathbf{D}$ is $O^2V^2 \times O^2V^2$, where O and V are the numbers of occupied and virtual orbitals, respectively.

Comment on system-bath distinction here

The idea is that here we are effectively treating the $\boldsymbol{A}$ as the physical space that has only the single excitations, while $\boldsymbol{D}$ is the bath space that has the double excitations. Just as in their frequency free implementation for GW in the TDA, the couplings between the physical and bath spaces, are just defined in terms of the two-electron integrals.

By downfolding the double excitations into the space of single excitations, we obtain the frequency-dependent effective matrix:

$$\mathcal{A}(\omega) = \mathbf{A} - \mathbf{V}^{\mathrm{e}}(\omega\mathbf{I} - \mathbf{D})^{-1}(\mathbf{V}^{\mathrm{h}})^{\dagger} - \mathbf{V}^{\mathrm{h}}(\omega\mathbf{I} - \mathbf{D})^{-1}(\mathbf{V}^{\mathrm{e}})^{\dagger} \tag{6.25}$$

Start by working out the eigenvalues of $\boldsymbol{D}$.

$$\boldsymbol{D} = -\boldsymbol{E}_O \otimes \boldsymbol{I}_V \otimes \boldsymbol{I}_{OV} + \boldsymbol{I}_O \otimes \boldsymbol{E}_V \otimes \boldsymbol{I}_{OV} + \boldsymbol{I}_O \otimes \boldsymbol{I}_V \otimes \boldsymbol{A}_{OV} \tag{6.26}$$

Now define the unitary transformation $\tilde{\boldsymbol{X}} = \boldsymbol{I}_O \otimes \boldsymbol{I}_V \otimes \boldsymbol{X}_{OV}$, where $\boldsymbol{X}_{OV}$ diagonalizes $\boldsymbol{A}_{OV}$.

The transformation is applied to the matrix $\boldsymbol{D}$ as follows:

$$\tilde{\boldsymbol{X}}^\dagger \boldsymbol{D} \tilde{\boldsymbol{X}} = \tilde{\boldsymbol{X}}^\dagger \left(-\boldsymbol{E}_O \otimes \boldsymbol{I}_V \otimes \boldsymbol{I}_{OV} + \boldsymbol{I}_O \otimes \boldsymbol{E}_V \otimes \boldsymbol{I}_{OV} + \boldsymbol{I}_O \otimes \boldsymbol{I}_V \otimes \boldsymbol{A}_{OV}\right) \tilde{\boldsymbol{X}} \tag{6.27}$$

$$= \tilde{\boldsymbol{X}}^\dagger \left(-\boldsymbol{E}_O \otimes \boldsymbol{I}_V \otimes \boldsymbol{I}_{OV}\right) \tilde{\boldsymbol{X}} + \tilde{\boldsymbol{X}}^\dagger \left(\boldsymbol{I}_O \otimes \boldsymbol{E}_V \otimes \boldsymbol{I}_{OV}\right) \tilde{\boldsymbol{X}} + \tilde{\boldsymbol{X}}^\dagger \left(\boldsymbol{I}_O \otimes \boldsymbol{I}_V \otimes \boldsymbol{A}_{OV}\right) \tilde{\boldsymbol{X}} \tag{6.28}$$

$$= -\boldsymbol{E}_O \underbrace{\boldsymbol{I}_O^\dagger \boldsymbol{I}_O}_{\boldsymbol{I}_O} \otimes \underbrace{\boldsymbol{I}_V^\dagger \boldsymbol{I}_V}_{\boldsymbol{I}_V} \otimes \underbrace{\boldsymbol{X}^\dagger \boldsymbol{X}}_{\boldsymbol{I}_{OV}} + \underbrace{\boldsymbol{I}_O^\dagger \boldsymbol{I}_O}_{\boldsymbol{I}_O} \otimes \boldsymbol{E}_V \underbrace{\boldsymbol{I}_V^\dagger \boldsymbol{I}_V}_{\boldsymbol{I}_V} \otimes \underbrace{\boldsymbol{X}^\dagger \boldsymbol{X}}_{\boldsymbol{I}_{OV}} + \underbrace{\boldsymbol{I}_O^\dagger \boldsymbol{I}_O}_{\boldsymbol{I}_O} \otimes \underbrace{\boldsymbol{I}_V^\dagger \boldsymbol{I}_V}_{\boldsymbol{I}_V} \otimes \underbrace{\boldsymbol{X}^\dagger \boldsymbol{A} \boldsymbol{X}}_{\boldsymbol{\Omega}_{OV}} \tag{6.29}$$

$$= -\boldsymbol{E}_O \oplus \boldsymbol{E}_V \oplus \boldsymbol{\Omega}_{OV} \tag{6.30}$$

$$\implies \boldsymbol{D} = \tilde{\boldsymbol{X}} \left(-\boldsymbol{E}_O \oplus \boldsymbol{E}_V \oplus \boldsymbol{\Omega}_{OV}\right) \tilde{\boldsymbol{X}}^\dagger \tag{6.31}$$

$$\tag{6.32}$$

Now we can write the spectral representation of the resolvent as

$$(\omega \mathbf{I} - \boldsymbol{D})^{-1} = \tilde{\boldsymbol{X}} \left[(\omega \mathbf{I} - (-\boldsymbol{E}_O \oplus \boldsymbol{E}_V \oplus \boldsymbol{\Omega}_{OV}))^{-1}\right] \tilde{\boldsymbol{X}}^\dagger \tag{6.33}$$

This leads to

$$K^{(\mathrm{p})}_{abij}(\omega) = \mathbf{V}^{\mathrm{e}}(\omega \mathbf{I} - \mathbf{D})^{-1}(\mathbf{V}^{\mathrm{h}})^\dagger + \mathbf{V}^{\mathrm{h}}(\omega \mathbf{I} - \mathbf{D})^{-1}(\mathbf{V}^{\mathrm{e}})^\dagger \tag{6.34}$$

$$= \frac{\mathbf{V}^{\mathrm{e}} \tilde{\boldsymbol{X}} (\boldsymbol{V}^{\mathrm{h}} \tilde{\boldsymbol{X}})^\dagger}{\omega \mathbf{I} - (-\boldsymbol{E}_O \oplus \boldsymbol{E}_V \oplus \boldsymbol{\Omega}_{OV})} + \frac{\boldsymbol{V}^{\mathrm{h}} \tilde{\boldsymbol{X}} (\boldsymbol{V}^{\mathrm{e}} \tilde{\boldsymbol{X}})^\dagger}{\omega \mathbf{I} - (-\boldsymbol{E}_O \oplus \boldsymbol{E}_V \oplus \boldsymbol{\Omega}_{OV})} \tag{6.35}$$

$$= 2 \sum_\nu \Big(\frac{\sum_{ldkc} (kc|ad) \delta_{il} \left(e_l \otimes e_d \otimes X_{kc,\nu}\right) \left(\sum_{ldkc} (il|kc) \delta_{ad} \left(e_l \otimes e_d \otimes X_{kc,\nu}\right)\right)^\dagger}{\omega - (E_b - E_i) - \Omega_\nu} \tag{6.36}$$

$$+ \frac{\sum_{ldkc} (il|kc) \delta_{ad} \left(e_l \otimes e_d \otimes X_{kc,\nu}\right) \left(\sum_{ldkc} (kc|ad) \delta_{il} \left(e_l \otimes e_d \otimes X_{kc,\nu}\right)\right)^\dagger}{\omega - (E_a - E_j) - \Omega_\nu} \Big) \tag{6.37}$$

$$= 2 \sum_m^{\Omega_m > 0} (ij|\rho_m) (ab|\rho_m) \left[\frac{1}{\omega - (E_b - E_i) - \Omega_m} + \frac{1}{\omega - (E_a - E_j) - \Omega_m}\right] \tag{6.38}$$

where $(pq|\rho_m) = \sum_{ia} X^m_{ia} (pq|ia)$. Not sure how to derive this. But we can write the upfolded 2p Hamiltonian with RPA screening, noting that

$$B_{ia,jb} = \kappa(ib|aj) \tag{6.39}$$

$$\mathcal{H} = \begin{pmatrix} & -\mathbf{V}^{\mathrm{e}} & -\mathbf{V}^{\mathrm{h}} \\ (\mathbf{V}^{\mathrm{h}})^\dagger & \mathbf{D} & \mathbf{0} \\ (\mathbf{V}^{\mathrm{e}})^\dagger & \mathbf{0} & \mathbf{D} \end{pmatrix} \tag{6.40}$$

$$\tag{6.41}$$

Now we can write the spectral decomposition

$$\implies (\omega I - D)^{-1}_{ia,\nu} = \frac{|ia,\nu\rangle\langle ia,\nu|}{\omega - (E_a - E_i) - \Omega_\nu} \tag{6.42}$$

$$\tag{6.43}$$

where $|ia,\nu\rangle$ is the right eigenvector of $\boldsymbol{D}$ defined by $e_i \otimes e_a \otimes \sum_{jb} X_{jb,\nu}$, with e_i and e_a being unit vectors in the occupied and virtual orbital spaces, respectively, and $\sum_{jb} X_{jb,\nu}$ as the excitation vector for the νth RPA excitation in the TDA and $(pq|\rho_m) = \sum_{ia} X_{ia}^m (pq|ia)$ with

$$K^{(\mathrm{p})}_{abij}(\omega) \equiv \mathbf{V}^{\mathrm{e}}(\omega\mathbf{I} - \mathbf{D})^{-1}(\mathbf{V}^{\mathrm{h}})^\dagger + \mathbf{V}^{\mathrm{h}}(\omega\mathbf{I} - \mathbf{D})^{-1}(\mathbf{V}^{\mathrm{e}})^\dagger \tag{6.44}$$

Explicitly, the matrix elements of $\mathcal{A}(\Omega)$ are given by

$$\mathcal{A}_{ia,jb}(\Omega) = A_{ia,jb} - K^{(\mathrm{p})}_{abij}(\Omega) \tag{6.45}$$

$$A_{ia,jb} = (E_a - E_i)\,\delta_{ij}\delta_{ab} + \kappa(ia|jb) - (ab|ij) \tag{6.46}$$

where the frequency-dependent kernel is

$$K^{(\mathrm{p})}_{abij}(\Omega) = \frac{i}{2\pi}\int d\omega\, e^{-i\omega 0^+} W^{(\mathrm{p})}_{abij}(\omega)\left[\frac{1}{\Omega - \omega - (E_b - E_i) + i\eta} + \frac{1}{\Omega + \omega - (E_a - E_j) + i\eta}\right] \tag{6.47}$$

$$= 2\sum_m^{\Omega_m > 0} (ij|\rho_m)\,(ab|\rho_m)\left[\frac{1}{\Omega - (E_b - E_i) - \Omega_m} + \frac{1}{\Omega - (E_a - E_j) - \Omega_m}\right] \tag{6.48}$$

To prove the equivalence, we need to show that the eigenvalues of the upfolded Hamiltonian $\mathcal{H}$ correspond to the excitation energies obtained from the BSE in the TDA, i.e., the poles of the response function defined by the effective matrix $\mathcal{A}(\omega)$.

$$K^{(\mathrm{p})}_{abij}(\Omega) = 2\sum_m^{\Omega_m > 0} (ij \mid \rho_m)\,(ab \mid \rho_m)\left[\frac{1}{\Omega - (E_b - E_i) - \Omega_m} + \frac{1}{\Omega - (E_a - E_j) - \Omega_m}\right]$$

and we have dropped $i\eta$ terms. The

6.3 A formulation in terms of supermatrices

We know the equation

$$\boldsymbol{L}^{-1} = \boldsymbol{L}_0^{-1} - \boldsymbol{\Xi}^{\mathrm{eh}} \tag{6.49}$$

The excitation energies that we are trying to solve for in the Bethe-Salpeter equation are formally the poles of the reducible eh response function $\boldsymbol{L}$, so we just need to determine the eigenvalues of the RHS of the above equation. This is analogous to how we were able to determine the QPEs by finding the poles of the Green's function, which were the eigenvalues of the upfolded Hamiltonian. First consider

$$\boldsymbol{L}_0 = \boldsymbol{G} \otimes \boldsymbol{G} \tag{6.50}$$

$$\implies \boldsymbol{L}_0^{-1} = \boldsymbol{G}^{-1} \otimes \boldsymbol{G}^{-1} \tag{6.51}$$

$$= (\boldsymbol{H}^{GW}) \otimes (\boldsymbol{H}^{GW}) \tag{6.52}$$

where

$$\boldsymbol{H}^{GW} = \begin{pmatrix} \boldsymbol{F} & \boldsymbol{W}^{<} & \boldsymbol{W}^{>} \\ \boldsymbol{W}^{\dagger <} & \boldsymbol{d}^{<} & \boldsymbol{0} \\ \boldsymbol{W}^{\dagger >} & \boldsymbol{0} & \boldsymbol{d}^{>} \end{pmatrix} \tag{6.53}$$

Note that the irreducible eh response function $\boldsymbol{L}_0$ reduces to the irredubible density-density response function χ_0, when we integrate out one space-time variable.

$$\frac{\delta \boldsymbol{\Sigma}^H}{\delta \boldsymbol{G}} = \boldsymbol{v} \otimes \boldsymbol{I} \tag{6.54}$$

$$\frac{\delta \boldsymbol{\Sigma}^x}{\delta \boldsymbol{G}} = -\boldsymbol{\Pi} \left(\boldsymbol{W} \otimes \boldsymbol{I} \right) \tag{6.55}$$

$$\tag{6.56}$$

where $\boldsymbol{\Pi}$ is a permutation operator with the action of swapping one space-time index betwween the two spaces.

is the so-called BSE kernel.

$$\chi(1,2) = \chi_0(1,2) + \int \mathrm{d}34 \chi_0(1,3) \Xi^{\mathrm{DFT}}(3,4) \chi(4,2)$$

where

$$\Xi^{\mathrm{DFT}}(3,4) = v(3,4) + \frac{\partial V^{\mathrm{xc}}(3)}{\partial \rho(4)}$$

is the TD-DFT kernel. Plugging now the GW self-energy (see eq 7), in a scheme that we label BSE@GW, leads to an approximate version of the BSE kernel

$$\begin{aligned} i\Xi^{\mathrm{BSE}}(3,5;4,6) &= v(3,6)\delta(34)\delta(56) \\ &- W\left(3^{+},4\right)\delta(36)\delta(45) \end{aligned}$$

TODO: check that in the theory we satisfy $\boldsymbol{\chi} = \mathrm{Tr}\, \boldsymbol{L}$, which is the trace of the supermatrix $\boldsymbol{L}$.

Chapter 7

Extraneous derivations

7.1 Density matrix idempotency

Given the orthonormality of the Kohn-Sham orbitals:

$$\int d\mathbf{r}\, \varphi_j^*(t,\mathbf{r})\varphi_k(t,\mathbf{r}) = \delta_{jk},$$

we can expand $\gamma^2(t)$ as follows:

$$\begin{aligned}
\gamma^2(t,\mathbf{r},\mathbf{r}') &= \int d\mathbf{r}_1\, \gamma(t,\mathbf{r},\mathbf{r}_1)\gamma(t,\mathbf{r}_1,\mathbf{r}') \\
&= \int d\mathbf{r}_1 \left(\sum_j \varphi_j(t,\mathbf{r})\varphi_j^*(t,\mathbf{r}_1)\right)\left(\sum_k \varphi_k(t,\mathbf{r}_1)\varphi_k^*(t,\mathbf{r}')\right) \\
&= \sum_{j,k} \varphi_j(t,\mathbf{r})\left(\int d\mathbf{r}_1\, \varphi_j^*(t,\mathbf{r}_1)\varphi_k(t,\mathbf{r}_1)\right)\varphi_k^*(t,\mathbf{r}') \\
&= \sum_{j,k} \varphi_j(t,\mathbf{r})\delta_{jk}\varphi_k^*(t,\mathbf{r}') \\
&= \sum_j \varphi_j(t,\mathbf{r})\varphi_j^*(t,\mathbf{r}') \\
&= \gamma(t,\mathbf{r},\mathbf{r}')
\end{aligned}$$

Thus, $\gamma^2(t) = \gamma(t)$, confirming idempotency.

7.2 Density matrix time evolution

First, we take the time derivative of both sides of equation 1.89:

$$i\frac{\partial}{\partial t}\gamma(t,\mathbf{r},\mathbf{r}') = i\frac{\partial}{\partial t}\left(\sum_{j=1}^{N}\varphi_j(t,\mathbf{r})\varphi_j^*(t,\mathbf{r}')\right) \tag{7.1}$$

$$= \sum_{j=1}^{N}\left[i\frac{\partial\varphi_j(t,\mathbf{r})}{\partial t}\varphi_j^*(t,\mathbf{r}') + i\varphi_j(t,\mathbf{r})\frac{\partial\varphi_j^*(t,\mathbf{r}')}{\partial t}\right] \tag{7.2}$$

We know that the TDKS equations for the orbitals $\varphi_j(t,\mathbf{r})$ and their complex conjugates $\varphi_j^*(t,\mathbf{r}')$ are:

$$i\frac{\partial}{\partial t}\varphi_j(t,\mathbf{r}) = H[\rho](t,\mathbf{r})\varphi_j(t,\mathbf{r}) \tag{7.3}$$

$$-i\frac{\partial}{\partial t}\varphi_j^*(t,\mathbf{r}') = \varphi_j^*(t,\mathbf{r}')H[\rho](t,\mathbf{r}') \tag{7.4}$$

where $H[\rho](t,\mathbf{r})$ is the effective one-particle Hamiltonian.

Substituting these into the time derivative of $\gamma(t)$:

$$i\frac{\partial}{\partial t}\gamma(t,\mathbf{r},\mathbf{r}') = \sum_{j=1}^{N}\left[H[\rho](t,\mathbf{r})\varphi_j(t,\mathbf{r})\varphi_j^*(t,\mathbf{r}') - \varphi_j(t,\mathbf{r})\varphi_j^*(t,\mathbf{r}')H[\rho](t,\mathbf{r}')\right]$$

Notice that the right-hand side can be written in terms of the density matrix $\gamma(t)$:

$$\sum_{j=1}^{N}H[\rho](t,\mathbf{r})\varphi_j(t,\mathbf{r})\varphi_j^*(t,\mathbf{r}') = H[\rho](t,\mathbf{r})\gamma(t,\mathbf{r},\mathbf{r}')$$

$$\sum_{j=1}^{N}\varphi_j(t,\mathbf{r})\varphi_j^*(t,\mathbf{r}')H[\rho](t,\mathbf{r}') = \gamma(t,\mathbf{r},\mathbf{r}')H[\rho](t,\mathbf{r}')$$

Therefore, the equation becomes:

$$i\frac{\partial}{\partial t}\gamma(t,\mathbf{r},\mathbf{r}') = H[\rho](t,\mathbf{r})\gamma(t,\mathbf{r},\mathbf{r}') - \gamma(t,\mathbf{r},\mathbf{r}')H[\rho](t,\mathbf{r}')$$

7.3 Fourier Transform Symmetry for Real Functions

In the context of response theory, it is essential to ensure that external perturbations are represented by real-valued functions. This requirement imposes a specific symmetry on their Fourier transforms. Specifically, for any real-valued function $f(t)$, its Fourier transform $F(\omega)$ must satisfy the condition:

$$F(-\omega) = [F(\omega)]^* \tag{7.5}$$

This subsection provides a four-step derivation of this important property.

Step 1: Definition of the Fourier Transform

The Fourier transform of a real-valued function $f(t)$ is defined as:

$$F(\omega) = \int_{-\infty}^{\infty} f(t)e^{i\omega t}\,dt \tag{7.6}$$

Step 2: Taking the Complex Conjugate

Since $f(t)$ is real, we have $f(t) = f^*(t)$. Taking the complex conjugate of both sides of the Fourier transform yields:

$$\begin{aligned}[F(\omega)]^* &= \left(\int_{-\infty}^{\infty} f(t)e^{i\omega t}\,dt\right)^* \\ &= \int_{-\infty}^{\infty} f^*(t)e^{-i\omega t}\,dt \\ &= \int_{-\infty}^{\infty} f(t)e^{-i\omega t}\,dt \end{aligned} \tag{7.7}$$

Step 3: Evaluating $F(-\omega)$

Substituting $-\omega$ into the Fourier transform definition:

$$\begin{aligned}F(-\omega) &= \int_{-\infty}^{\infty} f(t)e^{i(-\omega)t}\,dt \\ &= \int_{-\infty}^{\infty} f(t)e^{-i\omega t}\,dt \end{aligned} \tag{7.8}$$

Step 4: Establishing the Symmetry

Comparing equations (7.7) and (7.8), we observe that:

$$F(-\omega) = [F(\omega)]^*$$

Thus, for any real-valued function $f(t)$, its Fourier transform satisfies the Hermitian symmetry condition as stated in equation (7.5).

Conclusion

This symmetry ensures that when constructing real-valued external potentials from their Fourier components, the contributions from positive and negative frequencies are related through complex conjugation. Specifically, in equations (11) and (12) of the response theory framework, the inclusion of both $e^{i\omega_\alpha t}$ and $e^{-i\omega_\alpha t}$ terms with appropriately related spatial components guarantees that the external potentials $v_{\text{ext}}(t,x)$ and $\mathbf{A}_{\text{ext}}(t,x)$ remain real-valued functions of time and space.

$$v^{(\alpha)}(-\omega_\alpha, x) = [v^{(\alpha)}(\omega_\alpha, x)]^*, \quad \mathbf{A}^{(\alpha)}(-\omega_\alpha, x) = [\mathbf{A}^{(\alpha)}(\omega_\alpha, x)]^*$$

This property is fundamental in ensuring the physical relevance and mathematical consistency of the perturbations applied in density matrix-based response theory.

7.4 First-Order Response of an Observable to External Perturbations

In the context of density matrix-based response theory, we are interested in how an observable $f_\lambda(t)$ responds to external perturbations characterized by coupling constants λ_α. Specifically, we aim to derive the first-order response given by:

$$\frac{\partial}{\partial \lambda_\alpha} f_\lambda(t)\bigg|_{\lambda=0} = f^{(\alpha)}(\omega_\alpha)e^{i\omega_\alpha t} + f^{(\alpha)}(-\omega_\alpha)e^{-i\omega_\alpha t} \tag{7.9}$$

Here, $f^{(\alpha)}(\omega_\alpha)$ represents the response of the observable at frequency ω_α, and $f^{(\alpha)}(-\omega_\alpha)$ is its counterpart at the negative frequency.

Step 1: Expansion of the Observable in Powers of Coupling Constants

Assume that the observable $f_\lambda(t)$ depends on the coupling strengths $\boldsymbol{\lambda} = \{\lambda_\alpha\}$. We can expand $f_\lambda(t)$ in a Taylor series around $\boldsymbol{\lambda} = \mathbf{0}$ as follows:

$$f_\lambda(t) = f^{(0)}(t) + \sum_\alpha \lambda_\alpha f^{(\alpha)}(t) + \sum_{\alpha,\beta} \lambda_\alpha \lambda_\beta f^{(\alpha\beta)}(t) + \cdots$$

Where:

- $f^{(0)}(t)$ is the unperturbed (zeroth-order) value of the observable.
- $f^{(\alpha)}(t)$ is the first-order response to the perturbation λ_α.
- Higher-order terms represent responses to multiple perturbations and their interactions.

Step 2: Representation of External Perturbations

The external scalar potential is given by Equation (11):

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

Similarly, the external vector potential is given by Equation (12):

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

These perturbations are **monochromatic** and ensure that the external potentials remain real by including both positive and negative frequency components.

Step 3: Taking the First Derivative with Respect to λ_α

To obtain the first-order response of the observable $f_\lambda(t)$ to the perturbation λ_α, we differentiate the Taylor expansion with respect to λ_α and evaluate at $\boldsymbol{\lambda} = \mathbf{0}$:

$$\frac{\partial}{\partial \lambda_\alpha} f_\lambda(t)\bigg|_{\lambda=0} = f^{(\alpha)}(t)$$

However, due to the form of the external perturbations in Equations (11) and (12), the response $f^{(\alpha)}(t)$ inherits the time dependence from the perturbations. Specifically, each perturbation λ_α introduces oscillations at frequencies ω_α and $-\omega_\alpha$. Therefore, the first-order response can be expressed as a sum of contributions from these frequencies:

$$f^{(\alpha)}(t) = f^{(\alpha)}(\omega_\alpha)e^{i\omega_\alpha t} + f^{(\alpha)}(-\omega_\alpha)e^{-i\omega_\alpha t}$$

Substituting this into the derivative, we obtain:

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

7.5 Taylor Expansion of Idempotency Constraint in Perturbation Strength λ to first order

In Time-Dependent Density Functional Theory (TDDFT), the **one-particle density matrix** $\gamma(t)$ satisfies the **idempotency condition**:

$$\gamma(t) = \gamma(t)\gamma(t) \tag{7.10}$$

When external perturbations characterized by coupling constants λ_α are applied, the density matrix becomes dependent on these perturbations:

$$\gamma_\lambda(t) = \gamma(t; \{\lambda_\alpha\}) \tag{7.11}$$

Our goal is to expand $\gamma_\lambda(t)$ in powers of λ_α and derive the equation of motion for the first-order response $\gamma^{(\alpha)}$.

Step 1: Taylor Expansion of the Density Matrix and Hamiltonian Assume that the density matrix $\gamma_\lambda(t)$ and the Hamiltonian $H_\lambda(t)$ can be expanded in a Taylor series around $\lambda = 0$:

$$\gamma_\lambda(t) = \gamma^{(0)}(t) + \sum_\alpha \lambda_\alpha \gamma^{(\alpha)}(t) + \sum_{\alpha\leq\beta} \lambda_\alpha\lambda_\beta \gamma^{(\alpha\beta)}(t) + \cdots \tag{7.12}$$

$$H_\lambda(t) = H^{(0)} + \sum_\alpha \lambda_\alpha H^{(\alpha)}(t) + \sum_{\alpha\leq\beta} \lambda_\alpha\lambda_\beta H^{(\alpha\beta)}(t) + \cdots \tag{7.13}$$

where:

- $\gamma^{(0)}(t)$ is the **zeroth-order** (unperturbed) density matrix.

- $\gamma^{(\alpha)}(t)$ is the **first-order** response to the perturbation λ_α.
- $\gamma^{(\alpha\beta)}(t)$ is the **second-order** response involving perturbations λ_α and λ_β.
- Similarly for the Hamiltonian terms.

Step 2: Applying the Idempotency Condition Substitute the expansion from Equation (A) into both sides of the idempotency condition (8):

$$\gamma_\lambda(t) = \gamma_\lambda(t)\gamma_\lambda(t)$$

$$\gamma^{(0)} + \sum_\alpha \lambda_\alpha \gamma^{(\alpha)} + \sum_{\alpha\leq\beta} \lambda_\alpha\lambda_\beta \gamma^{(\alpha\beta)} + \cdots = \left(\gamma^{(0)} + \sum_\alpha \lambda_\alpha \gamma^{(\alpha)} + \sum_{\alpha\leq\beta} \lambda_\alpha\lambda_\beta \gamma^{(\alpha\beta)} + \cdots\right)\left(\gamma^{(0)} + \sum_\gamma \lambda_\gamma \gamma^{(\gamma)} + \sum_\gamma\right.$$

Expanding the right-hand side (RHS) and collecting terms up to second order:

$$\begin{aligned}\gamma_\lambda(t)\gamma_\lambda(t) = {} & \gamma^{(0)}\gamma^{(0)} \\ & + \sum_\alpha \lambda_\alpha \left(\gamma^{(0)}\gamma^{(\alpha)} + \gamma^{(\alpha)}\gamma^{(0)}\right) \\ & + \sum_{\alpha\leq\beta} \lambda_\alpha\lambda_\beta \left(\gamma^{(0)}\gamma^{(\alpha\beta)} + \gamma^{(\alpha)}\gamma^{(\beta)} + \gamma^{(\beta)}\gamma^{(\alpha)} + \gamma^{(\alpha\beta)}\gamma^{(0)}\right) \\ & + \cdots \end{aligned} \tag{7.14}$$

Step 3: Equating Terms Order by Order To satisfy the idempotency condition at each order of λ, equate the coefficients of corresponding powers of λ on both sides (Left-Hand Side and Right-Hand Side).

1. **Zeroth Order (λ^0):**
$$\gamma^{(0)} = \gamma^{(0)}\gamma^{(0)} \tag{7.15}$$
2. **First Order (λ^1):**
$$\gamma^{(\alpha)} = \gamma^{(0)}\gamma^{(\alpha)} + \gamma^{(\alpha)}\gamma^{(0)} \tag{7.16}$$
3. **Second Order (λ^2):**
$$\gamma^{(\alpha\beta)} = \gamma^{(0)}\gamma^{(\alpha\beta)} + \gamma^{(\alpha)}\gamma^{(\beta)} + \gamma^{(\beta)}\gamma^{(\alpha)} + \gamma^{(\alpha\beta)}\gamma^{(0)} \tag{7.17}$$

These equations ensure that the density matrix remains idempotent at each order of perturbation.

Step 4: Expanding the Equation of Motion Up to First Order Consider the **equation of motion** for the density matrix:

$$i\frac{\partial}{\partial t}\gamma_\lambda(t) = [H_\lambda(t), \gamma_\lambda(t)] \tag{7.18}$$

Substitute the expansions from Equations (A) and (B) into this equation:

$$\begin{aligned} i\frac{\partial}{\partial t}\left(\gamma^{(0)}+\sum_\alpha \lambda_\alpha \gamma^{(\alpha)}+\cdots\right) &= \left(H^{(0)}+\sum_\alpha \lambda_\alpha H^{(\alpha)}+\cdots\right)\left(\gamma^{(0)}+\sum_\alpha \lambda_\alpha \gamma^{(\alpha)}+\cdots\right) \\ &\quad -\left(\gamma^{(0)}+\sum_\alpha \lambda_\alpha \gamma^{(\alpha)}+\cdots\right)\left(H^{(0)}+\sum_\alpha \lambda_\alpha H^{(\alpha)}+\cdots\right) \\ &= [H^{(0)},\gamma^{(0)}]+\sum_\alpha \lambda_\alpha \left([H^{(0)},\gamma^{(\alpha)}]+[H^{(\alpha)},\gamma^{(0)}]\right)+\cdots \end{aligned} \tag{7.19}$$

Step 5: Equating First-Order Terms Collecting first-order terms in λ_α, we obtain:

$$i\frac{\partial}{\partial t}\gamma^{(\alpha)}(t) = [H^{(0)},\gamma^{(\alpha)}(t)]+[H^{(\alpha)}(t),\gamma^{(0)}] \tag{7.20}$$

Step 6: Frequency Domain Representation Assume that the first-order response $\gamma^{(\alpha)}(t)$ oscillates harmonically at frequency ω_α:

$$\gamma^{(\alpha)}(t) = \gamma^{(\alpha)}(\omega_\alpha)e^{-i\omega_\alpha t}+\gamma^{(\alpha)}(-\omega_\alpha)e^{i\omega_\alpha t} \tag{7.21}$$

Taking the time derivative:

$$i\frac{\partial}{\partial t}\gamma^{(\alpha)}(t) = \omega_\alpha\gamma^{(\alpha)}(\omega_\alpha)e^{-i\omega_\alpha t}-\omega_\alpha\gamma^{(\alpha)}(-\omega_\alpha)e^{i\omega_\alpha t} \tag{7.22}$$

Step 7: Substituting into the Equation of Motion Substitute Equations (G) and (H) into Equation (F):

$$\begin{aligned} \omega_\alpha\gamma^{(\alpha)}(\omega_\alpha)e^{-i\omega_\alpha t}-\omega_\alpha\gamma^{(\alpha)}(-\omega_\alpha)e^{i\omega_\alpha t} &= [H^{(0)},\gamma^{(\alpha)}(\omega_\alpha)e^{-i\omega_\alpha t}+\gamma^{(\alpha)}(-\omega_\alpha)e^{i\omega_\alpha t}] \\ &\quad +[H^{(\alpha)}(\omega_\alpha)e^{-i\omega_\alpha t}+H^{(\alpha)}(-\omega_\alpha)e^{i\omega_\alpha t},\gamma^{(0)}] \\ &= [H^{(0)},\gamma^{(\alpha)}(\omega_\alpha)]e^{-i\omega_\alpha t}+[H^{(0)},\gamma^{(\alpha)}(-\omega_\alpha)]e^{i\omega_\alpha t} \\ &\quad +[H^{(\alpha)}(\omega_\alpha),\gamma^{(0)}]e^{-i\omega_\alpha t}+[H^{(\alpha)}(-\omega_\alpha),\gamma^{(0)}]e^{i\omega_\alpha t} \\ &= \left([H^{(0)},\gamma^{(\alpha)}(\omega_\alpha)]+[H^{(\alpha)}(\omega_\alpha),\gamma^{(0)}]\right)e^{-i\omega_\alpha t} \\ &\quad +\left([H^{(0)},\gamma^{(\alpha)}(-\omega_\alpha)]+[H^{(\alpha)}(-\omega_\alpha),\gamma^{(0)}]\right)e^{i\omega_\alpha t} \end{aligned}$$

Step 8: Matching Frequency Components By matching the coefficients of $e^{-i\omega_\alpha t}$ and $e^{i\omega_\alpha t}$ on both sides, we obtain two separate equations:

$$\omega_\alpha\gamma^{(\alpha)}(\omega_\alpha) = [H^{(0)},\gamma^{(\alpha)}(\omega_\alpha)]+[H^{(\alpha)}(\omega_\alpha),\gamma^{(0)}] \tag{7.23}$$

$$-\omega_\alpha\gamma^{(\alpha)}(-\omega_\alpha) = [H^{(0)},\gamma^{(\alpha)}(-\omega_\alpha)]+[H^{(\alpha)}(-\omega_\alpha),\gamma^{(0)}] \tag{7.24}$$

Step 9: Rearranging to Obtain Equation (20) Focusing on Equation (H1), which corresponds to the positive frequency component:

$$\omega_\alpha \gamma^{(\alpha)}(\omega_\alpha) = [H^{(0)}, \gamma^{(\alpha)}(\omega_\alpha)] + [H^{(\alpha)}(\omega_\alpha), \gamma^{(0)}] \tag{7.25}$$

This matches **Equation (20)** from your paper:

$$\omega_\alpha \gamma^{(\alpha)} = [H^{(0)}, \gamma^{(\alpha)}] + [H^{(\alpha)}, \gamma^{(0)}] \tag{7.26}$$

Note: In Equation (20), the frequency dependence is implicit. Here, $\gamma^{(\alpha)}$ is understood to be associated with the frequency ω_α.

Summary of the Derivation 1. **Expansion:** The density matrix $\gamma_\lambda(t)$ and Hamiltonian $H_\lambda(t)$ are expanded in powers of the perturbation parameters λ_α.

2. **Idempotency Condition:** The idempotency condition $\gamma_\lambda(t) = \gamma_\lambda(t)\gamma_\lambda(t)$ is applied, leading to Equations (16)-(18).

3. **Equation of Motion:** The time-dependent equation of motion is expanded and matched order by order in λ.

4. **Frequency Components:** By assuming harmonic time dependence for the first-order response, the equation of motion yields a linear equation for $\gamma^{(\alpha)}(\omega_\alpha)$, resulting in Equation (20).

Implications - **Linear Equation for $\gamma^{(\alpha)}$:** Equation (20) is a linear equation that can be solved to find the first-order response of the density matrix to the perturbation λ_α.

- **Frequency Dependence:** The factor ω_α arises from the time derivative, indicating that the response oscillates at the frequency ω_α.

- **Commutators:** The commutators involve the unperturbed Hamiltonian $H^{(0)}$ and the first-order perturbation $H^{(\alpha)}$, showing how these operators influence the response.

Conclusion Through this systematic expansion and application of the idempotency condition, we derive Equation (20), which governs the first-order response of the density matrix in the presence of external perturbations. This equation is fundamental for calculating how observables respond to external fields within the density matrix-based response theory framework.

If you have any further questions or need additional clarification on specific steps, feel free to ask!

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