Polarization Propagator and Equation of Motion Methods

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1 Polarization propagator derivation of RPA

When A and B are one-electron number conserving, e.g. creation/annihilation operators are in pairs, we have

$$A = \sum_{rs} A_{rs} a_r^\dagger a_s, \qquad B = \sum_{rs} B_{rs} a_r^\dagger a_s \tag{1}$$

which allow us to define the general polarization propagator. If the elements did not conserve the number of electrons, we could use the same formalism to get the electron propagator, which can describe the attachment/detachment of electrons from a system, thus describing processes such as ionization. In general, it is sufficient to consider the typical elements $A \to a_r^\dagger a_s$ and $B \to a_t^\dagger a_u$. If spin-orbitals of reference are ψ_i, ψ_j,..., then a "particle-hole" basis includes only "excitation" and "de-excitation" operators $a_a^\dagger a_i$ and $a_i^\dagger a_a$, respectively. Thus the basis and its dual:

$$\mathbf{n} = (\mathbf{e} \quad \mathbf{d}), \qquad \mathbf{n}^\dagger = \begin{pmatrix} \mathbf{e}^\dagger \\ \mathbf{d}^\dagger \end{pmatrix}, \qquad e_{ia} = a_a^\dagger a_i = E_{ia}, \qquad d_{ai} = a_i^\dagger a_a = E_{ia}^\dagger \tag{2}$$

This gives, for our resolvent,

$$R(\omega) = \left[\mathbf{n}^\dagger(\hbar\omega\hat{1} - \hat{H})\mathbf{n}\right]^{-1} = \begin{bmatrix} \mathbf{e}^\dagger(\hbar\omega\hat{1} - \hat{H})\mathbf{e} & \mathbf{e}^\dagger(\hbar\omega\hat{1} - \hat{H})\mathbf{d} \\ \mathbf{d}^\dagger(\hbar\omega\hat{1} - \hat{H})\mathbf{e} & \mathbf{d}^\dagger(\hbar\omega\hat{1} - \hat{H})\mathbf{d} \end{bmatrix}^{-1} \tag{3}$$

As an example, we give the elements of the first block:

$$E_{ia}^\dagger(\hbar\omega\hat{1} - \hat{H})E_{jb} = \hbar\omega E_{ia}^\dagger E_{jb} - E_{ia}^\dagger\left[H, E_{jb}\right] \tag{4}$$

with scalar products

$$E_{ia}^\dagger E_{jb} = \langle\psi_0|[E_{ia}^\dagger, E_{jb}]|\psi_0\rangle, \qquad E_{ia}^\dagger\left[H, E_{jb}\right] = \langle\psi_0|[E_{ia}^\dagger, [H, E_{jb}]]|\psi_0\rangle \tag{5}$$

Evaluating these products gives

$$E_{ia}^\dagger E_{jb} = \langle\psi_0|[E_{ia}^\dagger, E_{jb}]|\psi_0\rangle = \langle\psi_0|E_{ia}^\dagger E_{jb}|\psi_0\rangle - \langle\psi_0|E_{jb}E_{ia}^\dagger|\psi_0\rangle = \langle\psi_0|E_{ia}^\dagger E_{jb}|\psi_0\rangle = \delta_{ia,jb} \tag{6}$$

and

$$\begin{aligned} E_{ia}^\dagger\left[H, E_{jb}\right] &= \langle\psi_0|[E_{ia}^\dagger, [H, E_{jb}]]|\psi_0\rangle \\ &= \langle\psi_0|E_{ia}^\dagger H E_{jb}|\psi_0\rangle - \langle\psi_0|E_{ia}^\dagger E_{jb} H|\psi_0\rangle - \langle\psi_0|H E_{jb} E_{ia}^\dagger|\psi_0\rangle + \langle\psi_0|E_{jb} H E_{ia}^\dagger|\psi_0\rangle \\ &= \langle\psi_i^a|H|\psi_j^b\rangle - \delta_{ia}\delta_{jb}\langle\psi_0|H|\psi_0\rangle \qquad \text{* see (11) of Maurice \& Head-Gordon IJQC (1995)} \\ &= E_0\delta_{ij}\delta_{ab} + F_{ab}\delta_{ij} - F_{ij}\delta_{ab} + \langle aj||ib\rangle - \delta_{ia}\delta jb E_0 \\ &= (\epsilon_a - \epsilon_i)\delta_{ia}\delta_{ab} + \langle aj||ib\rangle = \mathbf{A} \end{aligned} \tag{7}$$

Which is precisely the same elements as we have derived earlier for TDHF. Completing the rest, we have:

$$R(\omega) = M(\omega)^{-1} = \begin{bmatrix} \mathbf{A} & \mathbf{B} \\ \mathbf{B}^* & \mathbf{A}^* \end{bmatrix} - \hbar\omega \begin{bmatrix} \mathbf{1} & \mathbf{0} \\ \mathbf{0} & -\mathbf{1} \end{bmatrix} \tag{8}$$

With $\mathbf{B} = \langle ab||ij\rangle$. Now, we saw from the definition of the resolvent that $R(\omega) \to \infty$ at $\omega \to \omega_{0n}$, which are the poles of $R(\omega)$. Therefore, $R(\omega)^{-1} \to 0$ and

$$\begin{bmatrix} \mathbf{A} & \mathbf{B} \\ \mathbf{B}^* & \mathbf{A}^* \end{bmatrix} \begin{bmatrix} \mathbf{X} \\ \mathbf{Y} \end{bmatrix} = \hbar\omega \begin{bmatrix} \mathbf{1} & \mathbf{0} \\ \mathbf{0} & -\mathbf{1} \end{bmatrix} \begin{bmatrix} \mathbf{X} \\ \mathbf{Y} \end{bmatrix} \tag{9}$$

which are the RPA/TDHF equations. The eigencolumns determine the linear combinations of excitation and de-excitation operators that produce corresponding approximate excited states when working on the reference state $|\psi_0\rangle$.