$O(N^6)$ GW at the Gamma Point

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1 Molecular implementation

We follow the Subotnik paper. The first thing to do is to solve the Casida equation for the polarizability in the direct formulation of the RPA:

$$\begin{pmatrix} \mathbf{A} & \mathbf{B} \\ \mathbf{B}^* & \mathbf{A}^* \end{pmatrix} \begin{pmatrix} \mathbf{X} \\ \mathbf{Y} \end{pmatrix} = \begin{pmatrix} \Omega & 0 \\ 0 & -\Omega \end{pmatrix} \begin{pmatrix} \mathbf{X} \\ \mathbf{Y} \end{pmatrix} \tag{1}$$

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

$$\begin{aligned} \mathbf{A}_{ia,jb}^{\sigma\sigma'} &= \delta_{ij}\delta_{ab}\delta_{\sigma\sigma'}(\varepsilon_a - \varepsilon_i) + (i_\sigma a_\sigma | b_{\sigma'} j_{\sigma'}) \\ \mathbf{B}_{ia,jb}^{\sigma\sigma'} &= (i_\sigma a_\sigma | j_{\sigma'} b_{\sigma'}) \end{aligned} \tag{2}$$

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

$$\begin{pmatrix} \begin{pmatrix} \mathbf{A}_{\alpha\alpha} & \mathbf{A}_{\alpha\beta} \\ \mathbf{A}_{\beta\alpha} & \mathbf{A}_{\beta\beta} \end{pmatrix} & \begin{pmatrix} \mathbf{B}_{\alpha\alpha} & \mathbf{B}_{\alpha\beta} \\ \mathbf{B}_{\beta\alpha} & \mathbf{B}_{\beta\beta} \end{pmatrix} \\ \begin{pmatrix} \mathbf{B}^*_{\alpha\alpha} & \mathbf{B}^*_{\alpha\beta} \\ \mathbf{B}^*_{\beta\alpha} & \mathbf{B}^*_{\beta\beta} \end{pmatrix} & \begin{pmatrix} \mathbf{A}^*_{\alpha\alpha} & \mathbf{A}^*_{\alpha\beta} \\ \mathbf{A}^*_{\beta\alpha} & \mathbf{A}^*_{\beta\beta} \end{pmatrix} \end{pmatrix} \begin{pmatrix} \mathbf{X}_{\alpha\alpha} & \mathbf{X}_{\alpha\beta} \\ \mathbf{X}_{\beta\alpha} & \mathbf{X}_{\beta\beta} \\ \mathbf{Y}_{\alpha\alpha} & \mathbf{Y}_{\alpha\beta} \\ \mathbf{Y}_{\beta\alpha} & \mathbf{Y}_{\beta\beta} \end{pmatrix} = \begin{pmatrix} \Omega & 0 & 0 & 0 \\ 0 & -\Omega & 0 & 0 \\ 0 & 0 & \Omega & 0 \\ 0 & 0 & 0 & -\Omega \end{pmatrix} \begin{pmatrix} \mathbf{X}_{\alpha\alpha} & \mathbf{X}_{\alpha\beta} \\ \mathbf{X}_{\beta\alpha} & \mathbf{X}_{\beta\beta} \\ \mathbf{Y}_{\alpha\alpha} & \mathbf{Y}_{\alpha\beta} \\ \mathbf{Y}_{\beta\alpha} & \mathbf{Y}_{\beta\beta} \end{pmatrix} \tag{3}$$

This implies a way to get the excitation energies Ω^μ and the eigenvectors $\mathbf{X}^\mu$ and $\mathbf{Y}^\mu$ for a certain spin channel σ. Next, for each spin channel, we need to formulate the matrix $\mathbf{M}^\mu$, which is used to form the transition densities.

$$M_{iajb}^\mu = X_{ia}^\mu X_{jb}^\mu + X_{ia}^\mu Y_{jb}^\mu + Y_{ia}^\mu X_{jb}^\mu + Y_{ia}^\mu Y_{jb}^\mu \tag{4}$$

With these quantities, we can then form the self energy for the given spin channel:

$$\Sigma_{pq}^c(\omega) = \sum_{jbkc} \sum_\mu \left(\sum_i \frac{(ip \mid jb)(iq \mid kc)}{\omega - \Omega_\mu - \varepsilon_i^{\mathrm{MF}} - \mathrm{i}\eta} + \sum_a \frac{(ap \mid jb)(aq \mid kc)}{\omega + \Omega_\mu - \varepsilon_a^{\mathrm{MF}} + \mathrm{i}\eta} \right) M_{jbkc}^\mu \tag{5}$$

But in solving the case partial equation, we are just interested in the real, diagonal part of the self energy, so this reduces to:

$$\Sigma_{pp}^c(\omega) = \sum_{jbkc} \sum_\mu \left(\sum_i \frac{(ip \mid jb)(ip \mid kc)}{\omega - \Omega_\mu - \varepsilon_i^{\mathrm{MF}}} + \sum_a \frac{(ap \mid jb)(ap \mid kc)}{\omega + \Omega_\mu - \varepsilon_a^{\mathrm{MF}}} \right) M_{jbkc}^\mu \tag{6}$$