Fall Quarter Report

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1 Notation

In the MO basis, $p, q, r, s, ...$ are used for general orbitals. $i, j, k, l, ...$ are used for occupied orbitals. $a, b, c, d, ...$ are used for virtual orbitals.

2 Theory

There are two main equations that I have been working with this quarter. They are described below.

2.1 Self Energy

$$\Sigma_{pp}^{\text{corr}}(\omega) = \sum_{\mu}^{\text{RPA}} \left(\sum_{i}^{\text{occupied}} \frac{V_{pi}^{\mu} V_{ip}^{\mu}}{\omega - (\varepsilon_i - \Omega_\mu)} + \sum_{a}^{\text{virtual}} \frac{V_{pa}^{\mu} V_{ap}^{\mu}}{\omega - (\varepsilon_a + \Omega_\mu)} \right) \tag{1}$$

I have implemented the diagonal of the real part of the correlation self-energy. The V and Ω are the excitation vectors and energies, respectively, from a previous TD-DFT routine; the direct Tamm-Dancoff approximation (dTDA) and the direct Random Phase Approximation (dRPA) were used here. ω is my input frequency and the ε are the orbital energies from my previous mean-field calculation.

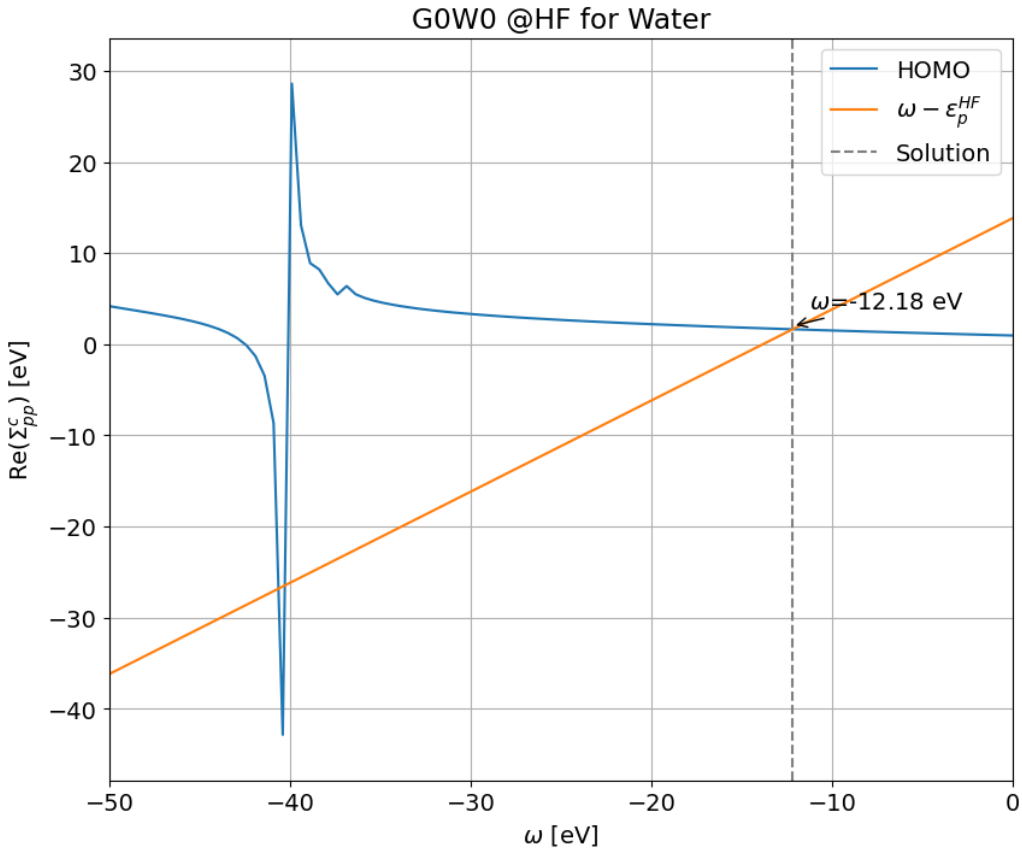
2.2 Iterative G_0W_0 Procedure

$$\delta_{pq} F_{pq}^{HF}[\gamma^{MF}] + \Sigma_{pp}^{corr}(\varepsilon_p^{QP}) = \varepsilon_p^{QP} \tag{2}$$

I have also implemented the iterative procedure to obtain my quasiparticle energies. The first term indicates that I am using the corresponding diagonal element at the orbital index of the HF Fock matrix evaluated at the mean-field density. In the second term, I am inputting quasiparticle energies into the self-energy from equation 1. The output of this equation is a new quasiparticle energy that I use in the next iteration. This process is iterated until convergence. In my very first iteration, the ε_p^{QP} that I input into my Σ_{pp}^{corr} is just the orbital energy from my mean-field calculation.

3 Results

I have been working with the HOMO of the water molecule with HF or DFT@PBE as my mean field object. I have plotted my self-energy computed for a wide range of frequencies. The line at $\omega - \varepsilon^{HF}$ should intersect with my self-energy at the same quasiparticle energy that I get from my iterative procedure, and indeed this is the case. Also, at around ω = -40 eV, one can



observe a pole structure. This is a derivate discontinuity in my self-energy that would pose problems for my iterative procedure if the quasiparticle energy of the orbital that I was looking for was close to this value.