Slides for Patryk's Notes

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Outline

1. Why UEG MP2 poles are bad
2. Implementation of QP MP2
3. Comparison to evGW

Outline

Why UEG MP2 poles are bad

The VASP paper by Kresse (2012) proves that QP MP2 consists of terminating the Dyson equation for the χ to lowest order, so MP2 self-energy sets

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So MP2 self-energy is only reliable if the $\chi_0(\omega)$ is small, and thus the MP2 pole at $r_s = 4$ is bad. When we do this large scale study of molecular IP/EAs, we should find a way to quantify the $\chi_0(\omega)$, so we can see if this trend gets reproduced.

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Algorithm for QP MP2

Likely, we want to do:

1. Start with HF reference orbitals and energies.
2. Solve QP equation for each orbital using MP2 self-energy of 2.
3. Update *some* orbital energies in 2, keeping the numerator fixed.
4. Repeat steps 2-3 until convergence in the orbital energies *of interest*.

$$\Sigma^{(2)}_{pp}(\omega) = \sum_{iab} \frac{(pa|ib)\Big(2(qa|ib) - (qb|ia)\Big)}{\omega - \epsilon_a - \epsilon_b + \epsilon_i + i\eta} + \sum_{ija} \frac{(pi|aj)\Big(2(qi|aj) - (qj|ai)\Big)}{\omega - \epsilon_i - \epsilon_j + \epsilon_a + i\eta} \tag{2}$$

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When solving the QP equation, we can linearize, so do

$$\epsilon_p^i = \epsilon_p^{i-1} + Z_p \Sigma^{\mathrm{c}}_{pp}\left(\omega = \epsilon_p^{i-1}\right) \tag{3}$$

where $\epsilon_p^i \equiv \epsilon_p^{HF}$ at $i = 0$ and

$$Z_p = \left[1 - \left.\frac{\partial \Sigma^{\mathrm{c}}_{pp}(\omega)}{\partial \omega}\right|_{\omega=\epsilon_p^{i-1}}\right]^{-1} \tag{4}$$

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3. Is GW100 the right test set? They compare to some $\Delta CCSD(T)$ results. Do we want to use that reference or do something else?

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Note that we can do *evGW* and/or *evGW*$_0$. To understand the difference, consider the GW self-energy

$$\Sigma^{\mathrm{c}}_{pq}(\omega) = \sum_{im} \frac{M_{pi,m} M_{qi,m}}{\omega - \epsilon_i + \Omega_m - \mathrm{i}\eta} + \sum_{am} \frac{M_{pa,m} M_{qa,m}}{\omega - \epsilon_a - \Omega_m + \mathrm{i}\eta} \tag{5}$$

In *evGW*$_0$, we update only green, while in *evGW* we update both green and red.