Slides for Patryk's Notes

Patryk Kozlowski

January 30, 2026

Outline

Outline

How to do larger UEG supercell

- python vs. cpp
- using Choleskies with G=0 included to implement my methods

Outline

Review of what I do with the PT2+C spectral functions

I presented two varieties of cumulants. The Landau form is

$$C_{pp}(t) \equiv i \int \frac{d\omega}{2\pi} \frac{\Sigma_{pp}(\omega + E_p)}{(\omega + i\eta)^2} e^{-i\omega t} \tag{1}$$

and the time domain Green's function in the cumulant ansatz is

$$G_{pp}(t) = \underbrace{-i\Theta(t) e^{-t(iE_p+\eta)}}_{\boldsymbol{G}_0} e^{C_{pp}(t)} \tag{2}$$

In 'G_0 via HF', $E_p \equiv \epsilon_p^{HF}, \{\epsilon_p^{HF}\} \rightarrow \Sigma_{pp}(\omega)$, while in '$G_0$ via SRG', $E_p \equiv \epsilon_p^{SRG-MP2}, \{\epsilon_p^{SRG-MP2}\} \rightarrow \Sigma_{pp}(\omega)$. I understand this through

$$\boldsymbol{G}(\omega) = \boldsymbol{G}_0(\omega) + \boldsymbol{G}_0(\omega)\boldsymbol{\Sigma}(\omega)\boldsymbol{G}(\omega) \tag{3}$$

so in 1 and 2, the former approach sets $\boldsymbol{G}_0 \equiv \boldsymbol{G}_{HF}$ and the latter sets $\boldsymbol{G}_0 \equiv \boldsymbol{G}_{SRG-MP2}$. *Loos found that for small molecules, SRG-GW+C can be worse than G_0W_0+C.*

How SRG-MP2 comes about

Derivation can be done, but the final expression is most relevant:

$$
\begin{aligned}
F_{pq}^{(2)}(s) = \frac{1}{2} \sum_{ija} & \frac{\Delta_{ij}^{pa} + \Delta_{ij}^{qa}}{\left(\Delta_{ij}^{pa}\right)^2 + \left(\Delta_{ij}^{qa}\right)^2} \langle pa|ij\rangle \langle ij|qa\rangle \\
& \times \left[1 - e^{-\left[\left(\Delta_{ij}^{pa}\right)^2 + \left(\Delta_{ij}^{qa}\right)^2\right] s}\right] \\
& + \frac{1}{2} \sum_{abi} \frac{\Delta_{ab}^{pi} + \Delta_{ab}^{qi}}{\left(\Delta_{ab}^{pi}\right)^2 + \left(\Delta_{ab}^{qi}\right)^2} \langle pi|ab\rangle \langle ab|qi\rangle \\
& \times \left[1 - e^{-\left[\left(\Delta_{ab}^{pi}\right)^2 + \left(\Delta_{ab}^{qi}\right)^2\right] s}\right] . \qquad (4)
\end{aligned}
$$

The idea is to add this to your HF Fock matrix and iterate to self-consistency. Tolle found that it is optimal to choose $s = 1e3$ in his IP/EA tests, so that's what I use.

Nooijen's approach

MP2 tells us that we have to diagonalize:

$$A_{pq}^{\mathrm{MP2}}(\omega) = \epsilon_p \delta_{pq} + \frac{1}{2} \sum_{l,c,d} \frac{V_{pl[cd]} V_{cd[ql]}}{\omega + \epsilon_l - \epsilon_c - \epsilon_d} - \frac{1}{2} \sum_{k,l,d} \frac{V_{pd[kl]} V_{kl[qd]}}{\epsilon_k + \epsilon_l - \epsilon_d - \omega} \tag{5}$$

Nooijen starts with CCSD-GF, but then approximates CC amplitudes with MBPT(2) analogues as

$$t_i^a = 0$$

$$t_{ij}^{ab} = \frac{V_{abij}}{\epsilon_i + \epsilon_j - \epsilon_a - \epsilon_b}$$

They call this MBPT(2)-GF and it leads to $A^{\mathrm{MBPT(2)}}(\omega)$. The paper is not about this theory though, but rather they use it as a starting point for further approximations that reduce cost.

Starting point for DSO-GF

They first replace the most demanding 2h1p block of $A^{\mathrm{MBPT(2)}}(\omega)$ by a diagonal form, but this is not size-consistent. But it is when the diagonal is approximated with a MP partitioning as

$$ {}^{\mathrm{DSO}}D^{b}_{ij} = -\epsilon_i - \epsilon_j + \epsilon_b \tag{10}$$

leading to

$$A^{\mathrm{DSO-GF}}_{ij}(\omega) = U_{ij} - \frac{1}{2}\sum_{k,l,d}\frac{W_{id[kl]}W_{kl[jd]}}{\epsilon_k + \epsilon_l - \epsilon_d - \omega} \tag{6}$$

$$= \epsilon_i\delta_{ij} + \sum_{c,d,l} V_{ilcd}\left(2t^{cd}_{jl} - t^{dc}_{jl}\right) - \frac{1}{2}\sum_{k,l,d}\frac{W_{id[kl]}V_{kl[jd]}}{\epsilon_k + \epsilon_l - \epsilon_d - \omega} \tag{7}$$

$$= \epsilon_i\delta_{ij} + \frac{1}{2}\sum_{l,c,d}\frac{V_{il[cd]}V_{cd[jl]}}{\epsilon_j + \epsilon_l - \epsilon_c - \epsilon_d} - \frac{1}{2}\sum_{k,l,d}\frac{W_{id[kl]}V_{kl[jd]}}{\epsilon_k + \epsilon_l - \epsilon_d - \omega} \tag{8}$$

Approximations they propose

The intermediates which are used to get 8 are defined as

$$U_{ki} = \epsilon_i \delta_{ki} + \sum_{c,d,l} V_{klcd} \left(2t_{il}^{cd} - t_{il}^{dc} \right) \tag{9}$$

$$W_{klid} = V_{klid} \tag{10}$$

$$W_{kbij} = V_{kbij} + \sum_{l,d} V_{klid} \left(2t_{lj}^{db} - t_{jl}^{db} \right) - \sum_{l,d} V_{lkid}\, t_{lj}^{db} + \sum_{c,d} V_{bkdc}\, t_{ji}^{dc} - \sum_{l,c} V_{lkjc}\, t_{li}^{bc} \tag{11}$$

As can be seen, 8 has a $W_{id[kl]}$ remaining, which is obtained via 11. They try to approximate this by just the leading term $V_{id[kl]}$ to reduce cost; this is m-DSO-GF in the paper. But their data suggests keeping the full $W_{id[kl]}$ in 8 leads to good results.

Thoughts

- Would it make sense to do self consistency in Nooijen's schemes?
- Would a paper on the full hierarchy of PT2 methods for one-shot cumulant be useful; we have
  - MP2
  - SRG-MP2
  - DSO-GF
  - m-DSO-GF
  - MBPT(2)-GF
  - CCSD-GF
- Is it useful to study UEG for intermediate supercell sizes?