Excited state methods for electronic structure in the Green's function formalism

Patryk Kozlowski

November 13, 2025

Outline

1. GW

2. Cumulant Expansion

Outline

Introduction

The Dyson equation is

$$G = G_0 + G_0 \Sigma G \tag{1}$$

where G is the interacting Green's function, G_0 is the non-interacting Green's function, and $\Sigma = iGW\Gamma$ is the proper self-energy.

Introduction

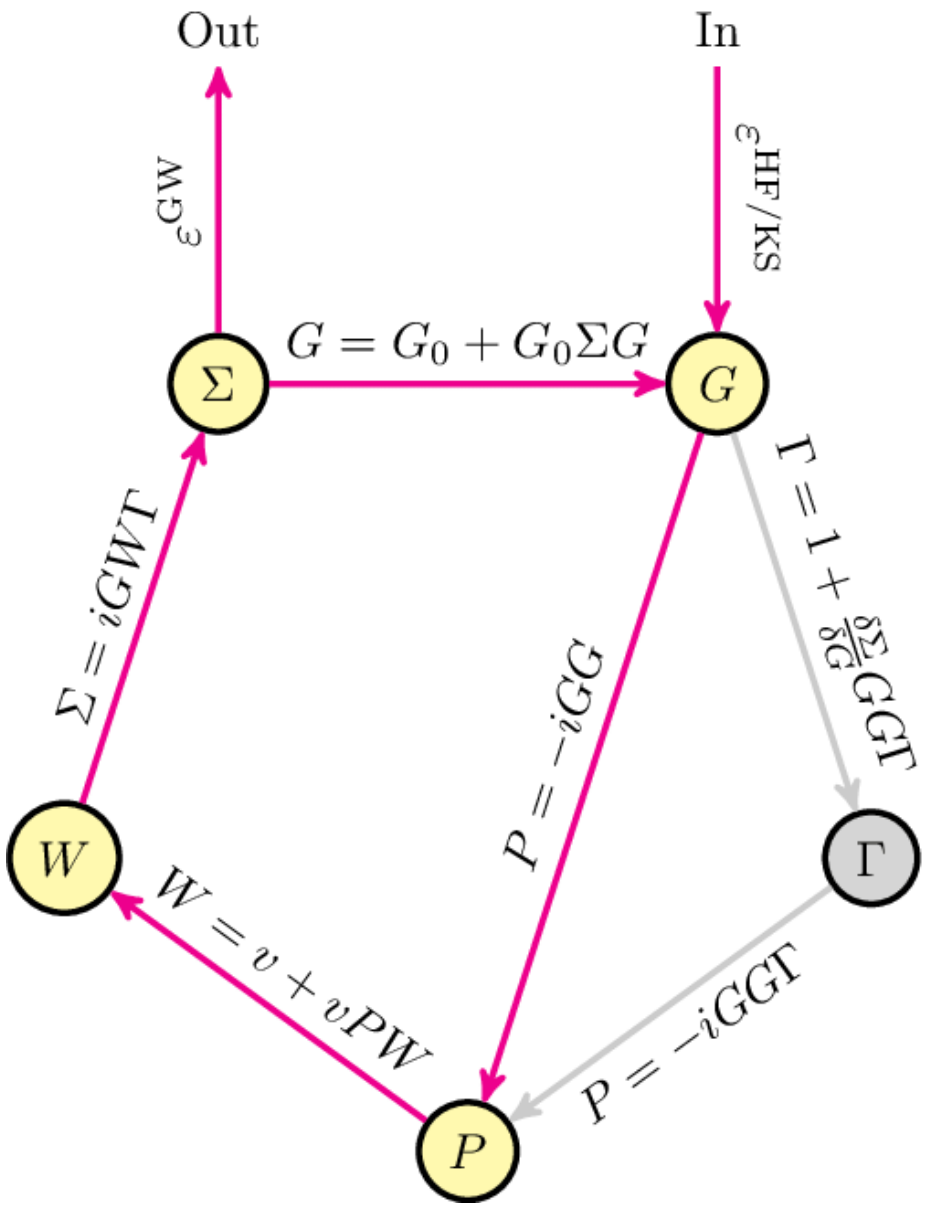
The Dyson equation is

$$G = G_0 + G_0 \Sigma G \tag{1}$$

where G is the interacting Green's function, G_0 is the non-interacting Green's function, and $\Sigma = iGW\Gamma$ is the proper self-energy. The GW approximation for the self-energy is

$$\Sigma \approx iGW \tag{2}$$

Hedin's Equations [1]



Frequency Integral [3]

$$\Sigma^{GW}(\mathbf{r},\mathbf{r}';\omega) = \frac{i}{2\pi}\int_{-\infty}^{\infty} d\omega' G\left(\mathbf{r},\mathbf{r}';\omega+\omega'\right) W\left(\mathbf{r},\mathbf{r}';\omega'\right) \tag{3}$$

$$\equiv \Sigma^{x}(\mathbf{r},\mathbf{r}') + \Sigma^{c}(\mathbf{r},\mathbf{r}';\omega) \tag{4}$$

Frequency Integral [3]

$$\Sigma^{GW}(\mathbf{r},\mathbf{r}';\omega) = \frac{i}{2\pi}\int_{-\infty}^{\infty} d\omega' G\left(\mathbf{r},\mathbf{r}';\omega+\omega'\right) W\left(\mathbf{r},\mathbf{r}';\omega'\right) \tag{3}$$

$$\equiv \Sigma^{x}(\mathbf{r},\mathbf{r}') + \Sigma^{c}(\mathbf{r},\mathbf{r}';\omega) \tag{4}$$

where the exact expression for the correlation self-energy is

$$\Sigma^{c}_{pq}(\omega) = \sum_{\mu}^{\mathrm{RPA}}\left(\sum_{i}^{\mathrm{O}}\frac{w^{\mu}_{pi}w^{\mu}_{iq}}{\omega-(\epsilon_i-\Omega_\mu)+i\eta} + \sum_{a}^{\mathrm{V}}\frac{w^{\mu}_{pa}w^{\mu}_{aq}}{\omega-(\epsilon_a+\Omega_\mu)-i\eta}\right) \tag{5}$$

Frequency Integral [3]

$$\Sigma^{GW}(\mathbf{r},\mathbf{r}';\omega) = \frac{i}{2\pi}\int_{-\infty}^{\infty} d\omega' G\left(\mathbf{r},\mathbf{r}';\omega+\omega'\right) W\left(\mathbf{r},\mathbf{r}';\omega'\right) \tag{3}$$

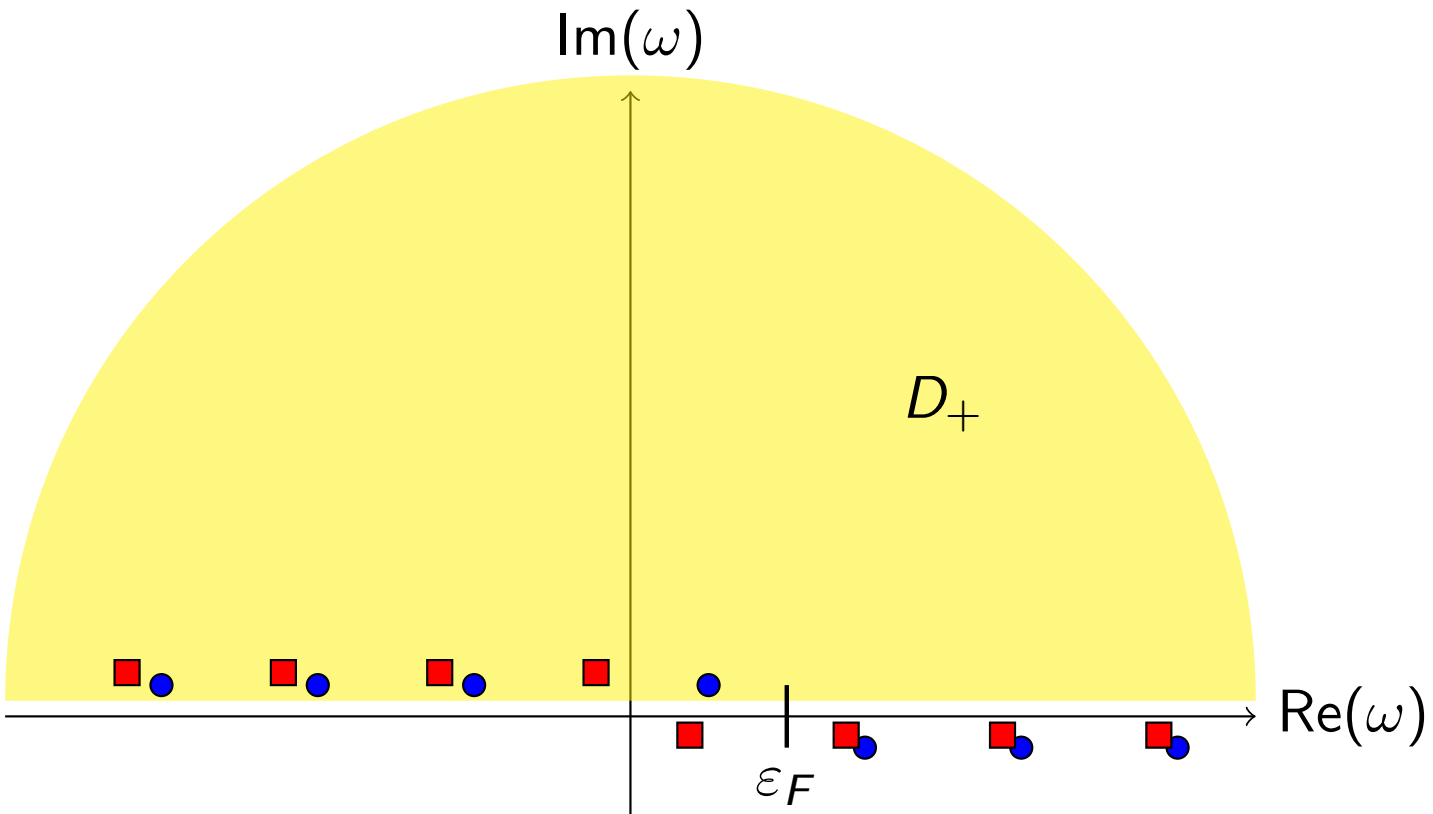
$$\equiv \Sigma^{x}(\mathbf{r},\mathbf{r}') + \Sigma^{c}(\mathbf{r},\mathbf{r}';\omega) \tag{4}$$

where the exact expression for the correlation self-energy is

$$\Sigma^{c}_{pq}(\omega) = \sum_{\mu}^{\mathrm{RPA}}\left(\sum_{i}^{\mathrm{O}}\frac{w^{\mu}_{pi}w^{\mu}_{iq}}{\omega-(\epsilon_i-\Omega_\mu)+i\eta} + \sum_{a}^{\mathrm{V}}\frac{w^{\mu}_{pa}w^{\mu}_{aq}}{\omega-(\epsilon_a+\Omega_\mu)-i\eta}\right) \tag{5}$$

To get the Ω_μ and w^{μ}_{pq}, we solve the RPA eigenvalue problem, which scales as $O(N^6)$.

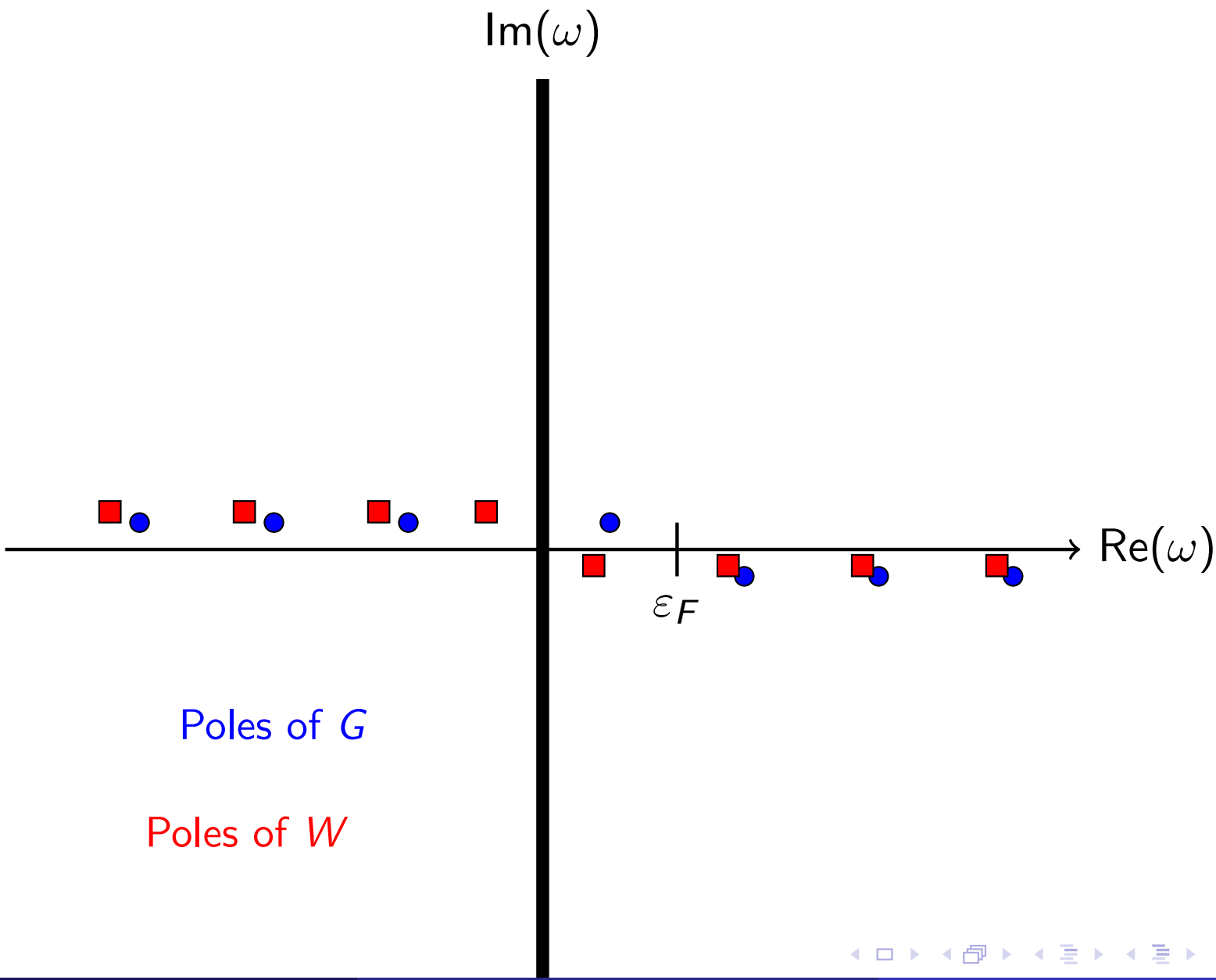
How does this expression come about?



Poles of G

Poles of W

Analytic continuation: the plot



Analytic continuation: the equations

Perform

$$\Sigma^c(\mathbf{r}, \mathbf{r}', i\omega) = -\frac{1}{2\pi} \int_{-\infty}^{\infty} d\omega' G\left(\mathbf{r}, \mathbf{r}', i\omega + i\omega'\right) W\left(\mathbf{r}, \mathbf{r}', i\omega'\right) \tag{6}$$

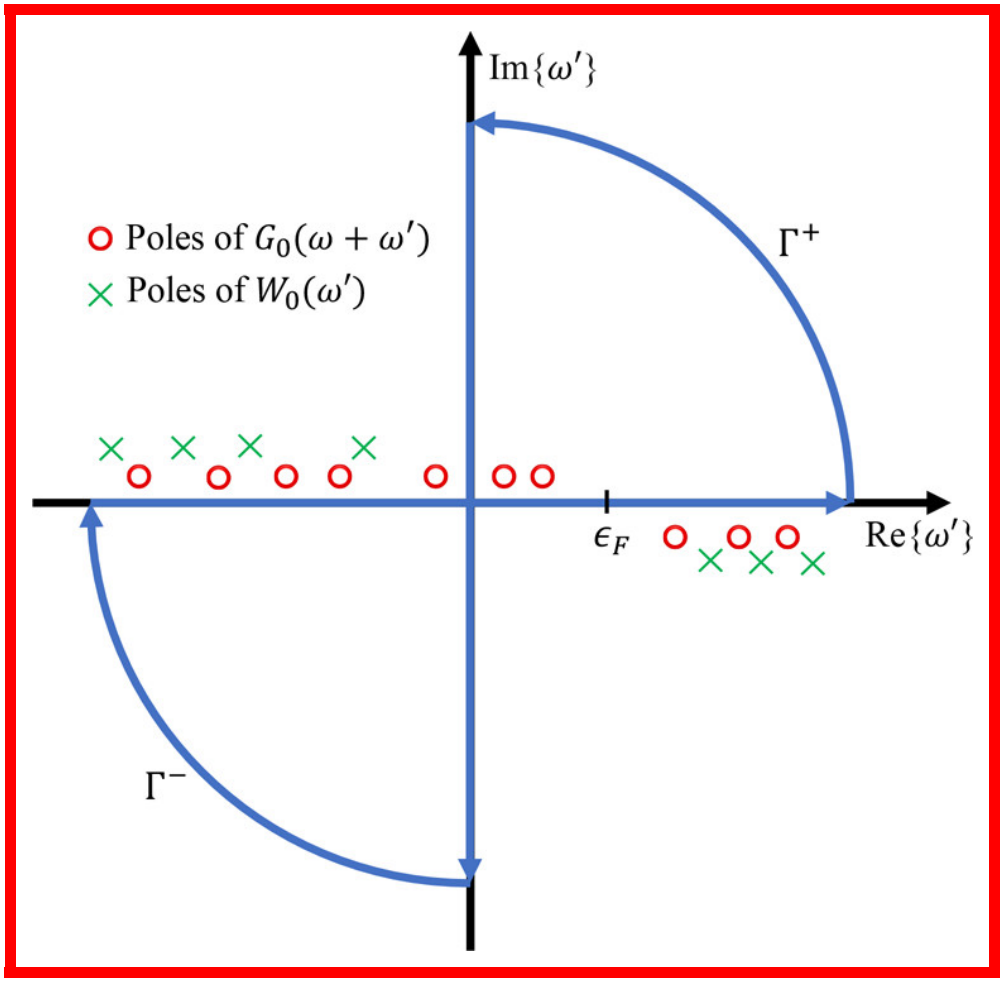
Analytic continuation: the equations

Perform

$$\Sigma^c(\mathbf{r}, \mathbf{r}', i\omega) = -\frac{1}{2\pi} \int_{-\infty}^{\infty} d\omega' G\left(\mathbf{r}, \mathbf{r}', i\omega + i\omega'\right) W\left(\mathbf{r}, \mathbf{r}', i\omega'\right) \tag{6}$$

and then analytically continue to real frequencies, obtaining $\Sigma^c(\mathbf{r}, \mathbf{r}'; \omega)$.

Contour deformation: the plot



Contour deformation: the equations

Split into parts as

$$\oint \cdots = \int_{\mathrm{Re}} \cdots + \int_{\mathrm{Im}} \cdots + \int_{\mathrm{arc}\,\Gamma^{+}} \cdots + \int_{\mathrm{arc}\,\Gamma^{-}} \cdots \tag{7}$$

$$\Longrightarrow \int_{\mathrm{Re}} \cdots = \oint \cdots - \int_{\mathrm{Im}} \cdots \tag{8}$$

A summary of frequency integration schemes

Method	Scaling	Comments
Fully analytic	$O(N^6)$	Evaluate the real frequency integral by integrating over a contour, which spans the positive imaginary axis.

A summary of frequency integration schemes

Method	Scaling	Comments
Fully analytic	$O(N^6)$	Evaluate the real frequency integral by integrating over a contour, which spans the positive imaginary axis.
Analytic continuation	$O(N^4)$	Avoid all poles by integrating along imaginary frequency axis, then analytically continuing to real frequencies.

A summary of frequency integration schemes

Method	Scaling	Comments
Fully analytic	$O(N^6)$	Evaluate the real frequency integral by integrating over a contour, which spans the positive imaginary axis.
Analytic continuation	$O(N^4)$	Avoid all poles by integrating along imaginary frequency axis, then analytically continuing to real frequencies.
Contour deformation	$O(N^5)$	Deform the contour to do the integral in a piecewise fashion.

A summary of frequency integration schemes

Method	Scaling	Comments
Fully analytic	$O(N^6)$	Evaluate the real frequency integral by integrating over a contour, which spans the positive imaginary axis.
Analytic continuation	$O(N^4)$	Avoid all poles by integrating along imaginary frequency axis, then analytically continuing to real frequencies.
Contour deformation	$O(N^5)$	Deform the contour to do the integral in a piecewise fashion.
Frequency-free	$O(N^4)$	Perform convolution without frequency dependence, so we are not constrained by the poles.

Solving the quasi-particle (QP) equation

In *GW*, we can compute QP energies by solving:

$$\epsilon_p^{QP} = \epsilon_p^{HF} + \mathrm{Re}\left(\Sigma_{pq}^c(\omega)\right)\delta_{pq} \tag{9}$$

Solving the quasi-particle (QP) equation

In GW, we can compute QP energies by solving:

$$\epsilon_p^{QP} = \epsilon_p^{HF} + \mathrm{Re}\left(\Sigma_{pq}^c(\omega)\right)\delta_{pq} \tag{9}$$

with

$$\Sigma_{pq}^c(\omega) = \sum_{\mu}^{\mathrm{RPA}} \left(\sum_{i}^{\mathrm{occupied}} \frac{w_{pi}^{\mu} w_{iq}^{\mu}}{\omega - (\epsilon_i - \Omega_\mu) + i\eta} + \sum_{a}^{\mathrm{virtual}} \frac{w_{pa}^{\mu} w_{aq}^{\mu}}{\omega - (\epsilon_a + \Omega_\mu) - i\eta} \right) \tag{10}$$

Solving the quasi-particle (QP) equation

In *GW*, we can compute QP energies by solving:

$$\epsilon_p^{QP} = \epsilon_p^{HF} + \mathrm{Re}\left(\Sigma_{pq}^c(\omega)\right)\delta_{pq} \tag{9}$$

with

$$\Sigma_{pq}^c(\omega) = \sum_{\mu}^{\mathrm{RPA}} \left(\sum_{i}^{\mathrm{occupied}} \frac{w_{pi}^{\mu} w_{iq}^{\mu}}{\omega - (\epsilon_i - \Omega_\mu) + i\eta} + \sum_{a}^{\mathrm{virtual}} \frac{w_{pa}^{\mu} w_{aq}^{\mu}}{\omega - (\epsilon_a + \Omega_\mu) - i\eta} \right) \tag{10}$$

Using Lowdin partitioning we can recast this as a matrix problem

$$\boldsymbol{H}^{GW} = \begin{pmatrix} \boldsymbol{F} & \boldsymbol{W}^{<} & \boldsymbol{W}^{>} \\ \boldsymbol{W}^{<,\dagger} & \boldsymbol{d}^{<} & 0 \\ \boldsymbol{W}^{>,\dagger} & 0 & \boldsymbol{d}^{>} \end{pmatrix} \tag{11}$$

Solving the quasi-particle (QP) equation

In *GW*, we can compute QP energies by solving:

$$\epsilon_p^{QP} = \epsilon_p^{HF} + \mathrm{Re}\left(\Sigma_{pq}^c(\omega)\right)\delta_{pq} \tag{9}$$

with

$$\Sigma_{pq}^c(\omega) = \sum_{\mu}^{\mathrm{RPA}} \left(\sum_{i}^{\mathrm{occupied}} \frac{w_{pi}^{\mu} w_{iq}^{\mu}}{\omega - (\epsilon_i - \Omega_\mu) + i\eta} + \sum_{a}^{\mathrm{virtual}} \frac{w_{pa}^{\mu} w_{aq}^{\mu}}{\omega - (\epsilon_a + \Omega_\mu) - i\eta} \right) \tag{10}$$

Using Lowdin partitioning we can recast this as a matrix problem

$$\boldsymbol{H}^{GW} = \begin{pmatrix} \boldsymbol{F} & \boldsymbol{W}^{<} & \boldsymbol{W}^{>} \\ \boldsymbol{W}^{<,\dagger} & \boldsymbol{d}^{<} & 0 \\ \boldsymbol{W}^{>,\dagger} & 0 & \boldsymbol{d}^{>} \end{pmatrix} \tag{11}$$

The QP energies and Dyson orbitals are the eigenpairs of $\boldsymbol{H}^{GW}$.

Moment-conserving GW [2]

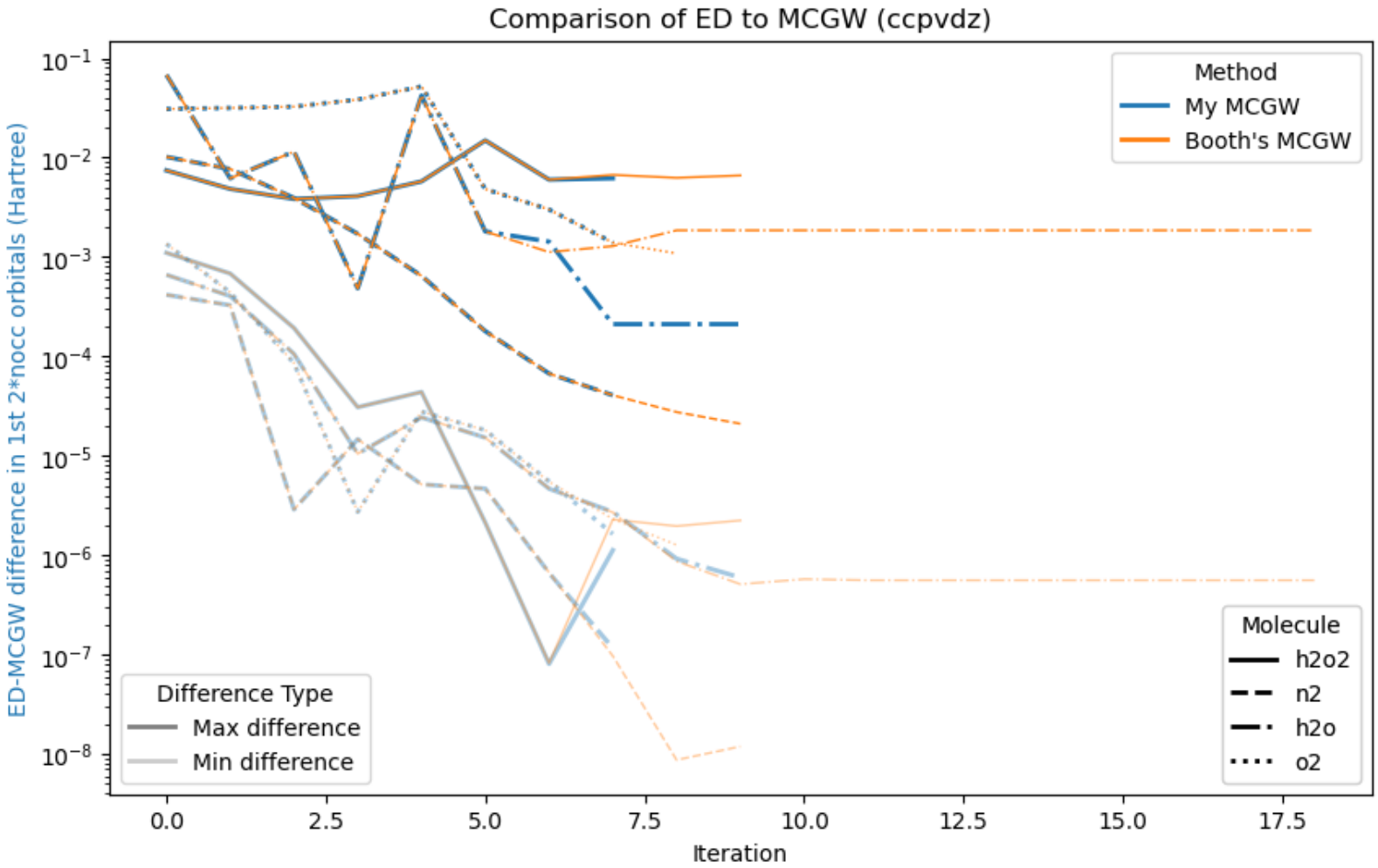
1. Devises a Lanczos procedure to iteratively diagonalize equation 11.

Moment-conserving GW [2]

1. Devises a Lanczos procedure to iteratively diagonalize equation 11.
2. I found that in the limit of a large number of Lanczos iterations, eigenvalues do not converge to the exact answer.

Moment-conserving GW [2]

1. Devises a Lanczos procedure to iteratively diagonalize equation 11.
2. I found that in the limit of a large number of Lanczos iterations, eigenvalues do not converge to the exact answer.



Why?

1. A Krylov subspace is never explicitly constructed.

Why?

1. A Krylov subspace is never explicitly constructed.
2. Therefore, it cannot be reorthogonalized, so there is no guarantee that the Ritz values will converge to the true eigenvalues.

Outline

1. GW

2. Cumulant Expansion

The ansatz

$$G(t) = G_0(t)e^{C(t)} = G_0(t)\left[1 + C(t) + \frac{C(t)^2}{2} + \ldots\right] \tag{12}$$

The ansatz

$$G(t) = G_0(t)e^{C(t)} = G_0(t)\left[1 + C(t) + \frac{C(t)^2}{2} + \ldots\right] \tag{12}$$

vs.

$$G(t) = G_0(t) + G_0(t)\Sigma(t)G_0(t) + G_0(t)\Sigma(t)G_0(t)\Sigma(t)G_0(t) + \ldots \tag{13}$$

The ansatz

$$G(t) = G_0(t)e^{C(t)} = G_0(t)\left[1 + C(t) + \frac{C(t)^2}{2} + \ldots\right] \tag{12}$$

vs.

$$G(t) = G_0(t) + G_0(t)\Sigma(t)G_0(t) + G_0(t)\Sigma(t)G_0(t)\Sigma(t)G_0(t) + \ldots \tag{13}$$

Perturbation series	**Interpretation**
Equation 12	Treats all diagrams approximately
Equation 13	Treats some diagrams exactly, and neglects others entirely.

What is done in popular cumulant schemes for electronic structure?

- Equate 12 and 13 to low order in the interaction.
- Use a known form for the self-energy, most commonly the *GW* form.

What is done in popular cumulant schemes for electronic structure?

- Equate 12 and 13 to low order in the interaction.
- Use a known form for the self-energy, most commonly the *GW* form.

This leads to the famous Landau formula for the cumulant, which is

$$C(t) = \int d\omega \frac{\beta(\omega)}{\omega^2} \left[e^{-i\omega t} + i\omega t - 1 \right] \tag{14}$$

where the cumulant kernel is defined as

$$\beta(\omega) = -\frac{1}{\pi} \operatorname{Im} \Sigma^{c}(\omega) \tag{15}$$

What hasn't been explored?

What hasn't been explored?

1. Studying UEG in a finite basis

What hasn't been explored?

1. Studying UEG in a finite basis
2. Numerical self-consistency

What hasn't been explored?

1. Studying UEG in a finite basis
2. Numerical self-consistency
3. Using second-order self-energy, instead of the *GW* form

Numerical self-consistency scheme

We want

$$G^R_{pp}(t) = -i\Theta(t)e^{-i\epsilon_p t}e^{C^{(2)}_{pp}(t)} \tag{16}$$

with

$$C^{(2)}_{pp}(t) \equiv i\int \frac{d\omega}{2\pi}\frac{\Sigma^{c,(2)}_{pp}(\omega+\epsilon_p)}{(\omega+i\eta)^2}e^{-i\omega t} \tag{17}$$

Numerical self-consistency scheme

We want

$$G^R_{pp}(t) = -i\Theta(t)e^{-i\epsilon_p t}e^{C^{(2)}_{pp}(t)} \tag{16}$$

with

$$C^{(2)}_{pp}(t) \equiv i\int \frac{d\omega}{2\pi}\frac{\Sigma^{c,(2)}_{pp}(\omega+\epsilon_p)}{(\omega+i\eta)^2}e^{-i\omega t} \tag{17}$$

$$= \frac{1}{2}\sum_{iab}\frac{\langle pi \,||\, ab\rangle^2}{\left(\epsilon^{ab}_{pi}\right)^2}\left(e^{-i\epsilon^{ab}_{pi}t} + i\epsilon^{ab}_{pi}t - 1\right) \tag{18}$$

$$+ \frac{1}{2}\sum_{ija}\frac{\langle pa \,||\, ij\rangle^2}{\left(\epsilon^{ij}_{pa}\right)^2}\left(e^{-i\epsilon^{ij}_{pa}t} + i\epsilon^{ij}_{pa}t - 1\right)$$

where $\epsilon^{ab}_{pi} = \epsilon_a + \epsilon_b - \epsilon_p - \epsilon_i$ and $\epsilon^{ij}_{pa} = \epsilon_i + \epsilon_j - \epsilon_p - \epsilon_a$.

Numerical self-consistency scheme (cont.)

So, do:

1. Start with HF orbital energies ϵ_p and coefficients $C_{\mu p}$.

Numerical self-consistency scheme (cont.)

So, do:

1. Start with HF orbital energies ϵ_p and coefficients $C_{\mu p}$.
2. Get $G^R_{pp}(t) = -i\Theta(t)e^{-i\epsilon_p t}e^{C^{(2)}_{pp}(t)}$ with $C^{(2)}_{pp}(t)$ from 18.

Numerical self-consistency scheme (cont.)

So, do:

1. Start with HF orbital energies ϵ_p and coefficients $C_{\mu p}$.
2. Get $G^R_{pp}(t) = -i\Theta(t)e^{-i\epsilon_p t}e^{C^{(2)}_{pp}(t)}$ with $C^{(2)}_{pp}(t)$ from 18.
3. $G^R_{pp}(\omega) = \mathrm{FFT}\left[G^R_{pp}(t)\right]$.

Numerical self-consistency scheme (cont.)

So, do:

1. Start with HF orbital energies ϵ_p and coefficients $C_{\mu p}$.
2. Get $G^R_{pp}(t) = -i\Theta(t)e^{-i\epsilon_p t}e^{C^{(2)}_{pp}(t)}$ with $C^{(2)}_{pp}(t)$ from 18.
3. $G^R_{pp}(\omega) = \mathrm{FFT}\left[G^R_{pp}(t)\right]$.
4. $A_{pp}(\omega) = -\frac{1}{\pi}\,\mathrm{Im}\left[G^R_{pp}(\omega)\right]$.

Numerical self-consistency scheme (cont.)

So, do:

1. Start with HF orbital energies ϵ_p and coefficients $C_{\mu p}$.
2. Get $G^R_{pp}(t) = -i\Theta(t)e^{-i\epsilon_p t}e^{C^{(2)}_{pp}(t)}$ with $C^{(2)}_{pp}(t)$ from 18.
3. $G^R_{pp}(\omega) = \mathrm{FFT}\left[G^R_{pp}(t)\right]$.
4. $A_{pp}(\omega) = -\frac{1}{\pi}\,\mathrm{Im}\left[G^R_{pp}(\omega)\right]$.
5. $n_p = \int_{-\infty}^{\infty} f(\omega-\mu)\,A_{pp}(\omega)\,d\omega$ with $f(\omega-\mu)$ the Fermi–Dirac distribution at chemical potential μ.

Numerical self-consistency scheme (cont.)

So, do:

1. Start with HF orbital energies ϵ_p and coefficients $C_{\mu p}$.
2. Get $G^R_{pp}(t) = -i\Theta(t)e^{-i\epsilon_p t}e^{C^{(2)}_{pp}(t)}$ with $C^{(2)}_{pp}(t)$ from 18.
3. $G^R_{pp}(\omega) = \mathrm{FFT}\left[G^R_{pp}(t)\right]$.
4. $A_{pp}(\omega) = -\frac{1}{\pi}\,\mathrm{Im}\left[G^R_{pp}(\omega)\right]$.
5. $n_p = \int_{-\infty}^{\infty} f(\omega-\mu)\,A_{pp}(\omega)\,d\omega$ with $f(\omega-\mu)$ the Fermi–Dirac distribution at chemical potential μ.
6. $P_{\mu\nu} = 2\sum_p C_{\mu p} n_p C_{\nu p}$.

Numerical self-consistency scheme (cont.)

So, do:

1. Start with HF orbital energies ϵ_p and coefficients $C_{\mu p}$.
2. Get $G^R_{pp}(t) = -i\Theta(t)e^{-i\epsilon_p t}e^{C^{(2)}_{pp}(t)}$ with $C^{(2)}_{pp}(t)$ from 18.
3. $G^R_{pp}(\omega) = \mathrm{FFT}\left[G^R_{pp}(t)\right]$.
4. $A_{pp}(\omega) = -\frac{1}{\pi}\,\mathrm{Im}\left[G^R_{pp}(\omega)\right]$.
5. $n_p = \int_{-\infty}^{\infty} f(\omega-\mu)\,A_{pp}(\omega)\,d\omega$ with $f(\omega-\mu)$ the Fermi–Dirac distribution at chemical potential μ.
6. $P_{\mu\nu} = 2\sum_p C_{\mu p} n_p C_{\nu p}$.
7. $F_{\mu\nu} = h_{\mu\nu} + \sum_{\rho\sigma} P_{\rho\sigma}\left[(\mu\nu \mid \rho\sigma) - \frac{1}{2}(\mu\rho \mid \nu\sigma)\right]$.

Numerical self-consistency scheme (cont.)

So, do:

1. Start with HF orbital energies ϵ_p and coefficients $C_{\mu p}$.
2. Get $G^R_{pp}(t) = -i\Theta(t)e^{-i\epsilon_p t}e^{C^{(2)}_{pp}(t)}$ with $C^{(2)}_{pp}(t)$ from 18.
3. $G^R_{pp}(\omega) = \mathrm{FFT}\left[G^R_{pp}(t)\right]$.
4. $A_{pp}(\omega) = -\frac{1}{\pi}\,\mathrm{Im}\left[G^R_{pp}(\omega)\right]$.
5. $n_p = \int_{-\infty}^{\infty} f(\omega-\mu)\,A_{pp}(\omega)\,d\omega$ with $f(\omega-\mu)$ the Fermi–Dirac distribution at chemical potential μ.
6. $P_{\mu\nu} = 2\sum_p C_{\mu p} n_p C_{\nu p}$.
7. $F_{\mu\nu} = h_{\mu\nu} + \sum_{\rho\sigma} P_{\rho\sigma}\left[(\mu\nu \mid \rho\sigma) - \frac{1}{2}(\mu\rho \mid \nu\sigma)\right]$.
8. Diagonalize $F_{\mu\nu}$ to get new orbital energies ϵ_p and coefficients $C_{\mu p}$.

Numerical self-consistency scheme (cont.)

So, do:

1. Start with HF orbital energies ϵ_p and coefficients $C_{\mu p}$.
2. Get $G^R_{pp}(t) = -i\Theta(t)e^{-i\epsilon_p t}e^{C^{(2)}_{pp}(t)}$ with $C^{(2)}_{pp}(t)$ from 18.
3. $G^R_{pp}(\omega) = \mathrm{FFT}\left[G^R_{pp}(t)\right]$.
4. $A_{pp}(\omega) = -\frac{1}{\pi}\,\mathrm{Im}\left[G^R_{pp}(\omega)\right]$.
5. $n_p = \int_{-\infty}^{\infty} f(\omega-\mu)\,A_{pp}(\omega)\,d\omega$ with $f(\omega-\mu)$ the Fermi–Dirac distribution at chemical potential μ.
6. $P_{\mu\nu} = 2\sum_p C_{\mu p} n_p C_{\nu p}$.
7. $F_{\mu\nu} = h_{\mu\nu} + \sum_{\rho\sigma} P_{\rho\sigma}\left[(\mu\nu \mid \rho\sigma) - \frac{1}{2}(\mu\rho \mid \nu\sigma)\right]$.
8. Diagonalize $F_{\mu\nu}$ to get new orbital energies ϵ_p and coefficients $C_{\mu p}$.
9. Update orbital energies and coefficients within step 2, and repeat until convergence.

Summary of the scheme

Iterate $\Sigma(\omega) \rightarrow C(t) \rightarrow G^R(t) \rightarrow A(\omega) \rightarrow \boldsymbol{F} \rightarrow \Sigma(\omega)$ until convergence.

Thank for listening!

Thanks to the group for the help, Joonho for mentoring, and the National Science Foundation plus the Paul and Daisy Soros Fellowship for New Americans for financial support.

Thank for listening!

Thanks to the group for the help, Joonho for mentoring, and the National Science Foundation plus the Paul and Daisy Soros Fellowship for New Americans for financial support.

Questions?

References I

[1] Pierre-François Loos, Pina Romaniello, and J. Berger. Green functions and self-consistency: Insights from the spherium model. *Journal of Chemical Theory and Computation*, 14, 03 2018. doi: 10.1021/acs.jctc.8b00260.

[2] Charles JC Scott, Oliver J Backhouse, and George H Booth. A "moment-conserving" reformulation of gw theory. *The Journal of chemical physics*, 158(12), 2023.

[3] Tianyu Zhu and Garnet Kin-Lic Chan. All-electron gaussian-based g_0w_0 for valence and core excitation energies of periodic systems. *arXiv [cond-mat.mtrl-sci]*, July 2020.