

A mathematical study of the GW^0 method for computing electronic excited states of molecules

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Goal: compute the **electronic excitation energies** of a finite electronic system (molecule).

Nuclear configuration (Born-Oppenheimer approximation): $\{\mathbf{R}_k\}_{1 \leq k \leq N}$:

$$v_{\text{ext}}(\mathbf{r}) := \sum_{k=1}^M \frac{-Z_k}{|\mathbf{r} - \mathbf{R}_k|}.$$

Electronic problem with N -electrons

$$H_N \Psi := \left(-\frac{1}{2} \sum_{i=1}^N \Delta_{\mathbf{r}_i} + \sum_{1 \leq i < j \leq N} \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|} + \sum_{i=1}^N v_{\text{ext}}(\mathbf{r}_i) \right) \Psi(\mathbf{r}_1, \dots, \mathbf{r}_N) = E \Psi(\mathbf{r}_1, \dots, \mathbf{r}_N).$$

$|\Psi(\mathbf{r}_1, \dots, \mathbf{r}_N)|^2$ is the probability density of observing electron 1 at \mathbf{r}_1 , electron 2 at \mathbf{r}_2 , ...

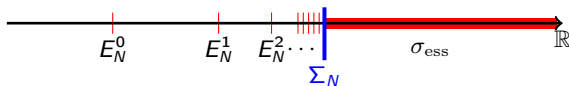
Pauli principle for fermions: $\forall p \in \mathfrak{S}_N, \Psi(\mathbf{r}_{p(1)}, \dots, \mathbf{r}_{p(N)}) = \epsilon(p) \Psi(\mathbf{r}_1, \dots, \mathbf{r}_N)$.

State space

$$\Psi \in \mathcal{H}_N := \bigwedge^N \mathcal{H}_1, \quad \mathcal{H}_1 = L^2(\mathbb{R}^3, \mathbb{C}).$$

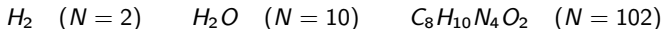
Zhislin's theorem (G.M. Zhislin. Trudy Moskov. Mat. Obsc., 9, 1960)

If $N \leq Z := \sum_{k=1}^M z_k$, then $\sigma(H_N)$ is as follows:



Ground state: $\Psi_N^0 \in \mathcal{H}_N$ such that $\|\Psi_N^0\| = 1$ and $H_N \Psi_N^0 = E_N^0 \Psi_N^0$.

Problem: $\mathcal{H}_N \subset L^2(\mathbb{R}^{3N})$ is a huge space. **(Curse of dimensionality)**



\implies Several approximations were proposed in the last decades.

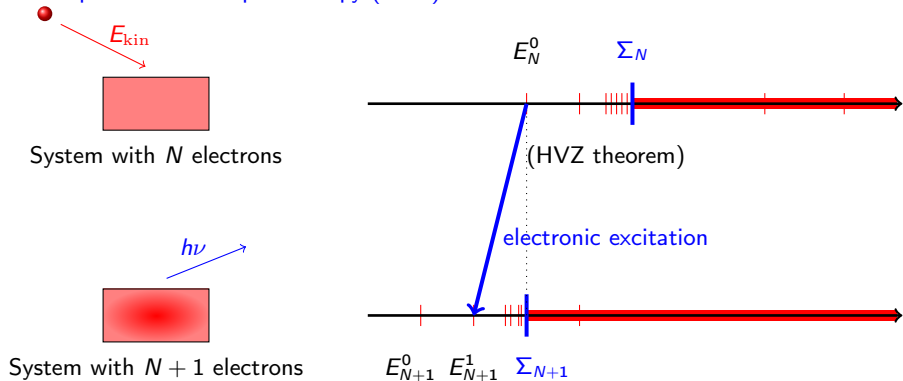
- *Density functional theory (DFT)*: for ground state properties only
- *Quantum Monte Carlo methods*: idem
- *Wavefunction methods*: scales from N_b^6 (CISD) to $N_b!$ (full CI)
- *Time-dependent DFT (TDDFT)*: does not work well for extended systems
- *Green's function method*: in this talk, GW.

The GW method (L. Hedin. Phys. Rev. 1965)

To calculate the **electronic excitation energies** of a system \implies quantities of the form

$$E_N^0 - E_{N+1}^k \quad (\text{gain of an electron})$$

Inverse photoemission spectroscopy (IPES)

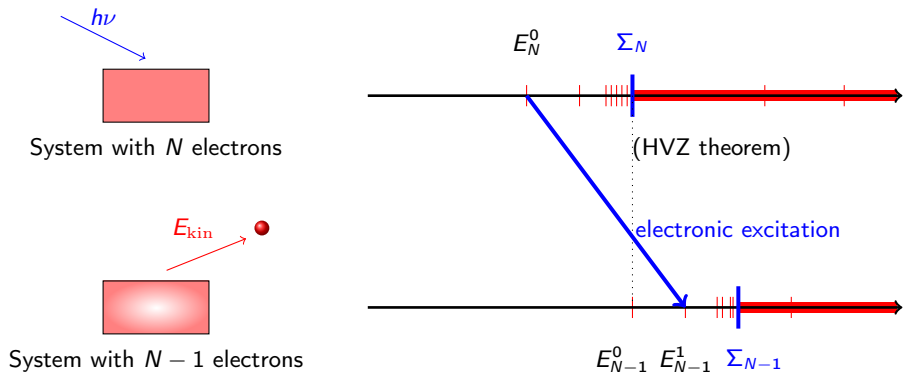


The GW method (L. Hedin. Phys. Rev. 1965)

To calculate the **electronic excitation energies** of a system \implies quantities of the form

$$E_N^0 - E_{N+1}^k \quad (\text{gain of an electron}) \quad \text{and} \quad E_N^0 - E_{N-1}^k \quad (\text{loss of an electron}).$$

Photoemission spectroscopy (PES)



Definition of the Particle Green's function in the time domain

Fock space

$$\mathbb{F} := \bigoplus_{N=0}^{+\infty} \mathcal{H}_N, \quad \mathcal{H}_0 = \mathbb{C}, \quad \mathcal{H}_1 = L^2(\mathbb{R}^3, \mathbb{C}), \quad \mathcal{H}_N = \bigwedge^N \mathcal{H}_1.$$

Annihilation and creation operators

$$a \in \mathcal{B}(\mathcal{H}_1, \mathcal{B}(\mathbb{F})), \quad a^\dagger \in \mathcal{B}(\mathcal{H}_1, \mathcal{B}(\mathbb{F})),$$

$$\forall \phi \in \mathcal{H}_1, \quad a(\phi) : \mathcal{H}_N \rightarrow \mathcal{H}_{N-1}, \quad a^\dagger(\phi) : \mathcal{H}_N \rightarrow \mathcal{H}_{N+1}, \quad a^\dagger(\phi) = (a(\phi))^*,$$

$$\forall \Psi \in \mathcal{H}_N, \quad (a(\phi)\Psi)(\mathbf{r}_1, \dots, \mathbf{r}_{N-1}) = \sqrt{N} \int_{\mathbb{R}^3} \overline{\phi(\mathbf{r})} \Psi(\mathbf{r}, \mathbf{r}_1, \dots, \mathbf{r}_{N-1}) d\mathbf{r}.$$

One-body particle Green's function (in the time domain)

$$\forall \tau \in \mathbb{R}, \forall f, g \in \mathcal{H}_1, \quad \langle g | G_p(\tau) | f \rangle = -i\Theta(\tau) \langle \Psi_N^0 | a(g) e^{-i\tau(H_{N+1} - E_N^0)} a^\dagger(f) | \Psi_N^0 \rangle.$$

Annihilation and creation operators (bis)

$$A_+^* \in \mathcal{B}(\mathcal{H}_1, \mathcal{H}_{N+1}) : f \mapsto a^\dagger(f) | \Psi_N^0 \rangle, \quad A_+ = (A_+^*)^* \in \mathcal{B}(\mathcal{H}_{N+1}, \mathcal{H}_1).$$

One-body particle Green's function (in the time domain) (bis)

$$\forall \tau \in \mathbb{R}, \quad G_p(\tau) = -i\Theta(\tau) A_+ e^{-i\tau(H_{N+1} - E_N^0)} A_+^*.$$

Definition of the Particle Green's function in the frequency domain

$$\forall \tau \in \mathbb{R}, \quad G_p(\tau) = -i\Theta(\tau)A_+e^{-i\tau(H_{N+1}-E_N^0)}A_+^*.$$

Normalization convention for the time-Fourier transform

$$\forall f \in L^1(\mathbb{R}_\tau, X), \quad X \text{ Banach space}, \quad [\mathcal{F}_T f](\omega) = \widehat{f}(\omega) = \int_{-\infty}^{+\infty} f(\tau) e^{i\omega\tau} d\tau.$$

Fourier representation of the one-body particle Green's function

$$\widehat{G}_p(\omega) = (\mathcal{F}_T G_p)(\omega), \quad \widehat{G}_p \in H^{-1}(\mathbb{R}_\omega, \mathcal{B}(\mathcal{H}_1)).$$

Key point

The support of the distribution $\text{Im}(\widehat{G}_p)$ is contained in the particle electronic excitation set $S_p := \sigma(H_{N+1} - E_N^0)$.

- Particle electronic excited energies can be recovered from \widehat{G}_p ,
- \widehat{G}_p is highly irregular.

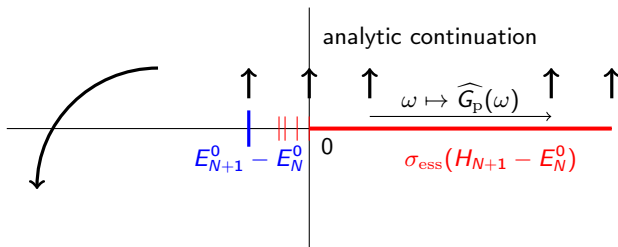
Laplace transform of the Green's function For $z \in \mathbb{U} = \{z \in \mathbb{C}, \text{Im}(z) > 0\}$, define

$$\widetilde{G}_p(z) := \int_0^\infty G_p(\tau) e^{iz\tau} d\tau.$$

Remark

- \widetilde{G}_p is an analytical continuation of \widehat{G}_p on \mathbb{U} (Titchmarsh's theory),
- This continuation can be extended to $\mathbb{C} \setminus S_p$.

$$\forall z \in \mathbb{C} \setminus S_p, \quad \widetilde{G}_p(z) = A_+ \left(\frac{1}{z - (H_{N+1} - E_N^0)} \right) A_+^*.$$



Definition of the one-body hole Green's function

Annihilation and creation operators (ter)

$$A_- \in \mathcal{B}(\mathcal{H}_1, \mathcal{H}_{N-1}) : f \mapsto a(\bar{f})|\Psi_N^0\rangle, \quad A_-^* \in \mathcal{B}(\mathcal{H}_{N-1}, \mathcal{H}_1).$$

In the time domain

$$\forall \tau \in \mathbb{R}, \quad G_h(\tau) = i\Theta(-\tau)A_-^* e^{i\tau(H_{N-1} - E_N^0)} A_-.$$

Properties

From the hole Green's function, we can recover the following quantities:

- One-body electronic ground-state density matrix: $\gamma_N^0 = -iG_h(0^-) = A_-^* A_-$

$$\gamma_N^0(\mathbf{r}, \mathbf{r}') = N \int_{\mathbb{R}^{3(N-1)}} \Psi_N^0(\mathbf{r}, \mathbf{r}_2, \dots, \mathbf{r}_N) \Psi_N^0(\mathbf{r}', \mathbf{r}_2, \dots, \mathbf{r}_N) d\mathbf{r}_2 \cdots d\mathbf{r}_N,$$

- Electronic ground state density

$$\rho_N^0(\mathbf{r}) = N \int_{\mathbb{R}^{3(N-1)}} |\Psi_N^0(\mathbf{r}, \mathbf{r}_2, \dots, \mathbf{r}_N)|^2 d\mathbf{r}_2 \cdots d\mathbf{r}_N,$$

- Ground state energy (Galitskii-Migdal formula)

V.M. Galitskii and A.B. Migdal. Sov. Phys. JETP, 139, 1958.

$$E_N^0 = \frac{1}{2} \text{Tr}_{\mathcal{H}_1} \left[\left(\frac{d}{d\tau} - i \left(-\frac{1}{2} \Delta + v_{\text{ext}} \right) \right) G_h(\tau) \Big|_{\tau=0^-} \right].$$

The hole Green's function in the frequency domain

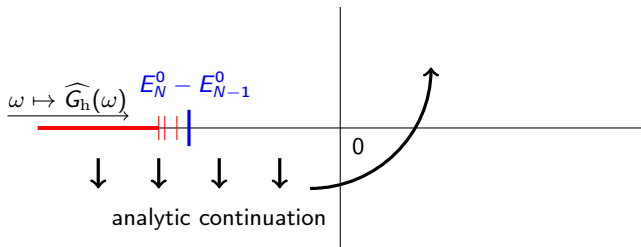
$$\widehat{G}_h(\omega) = (\mathcal{F}_T G_h)(\omega), \quad \widehat{G}_h \in H^{-1}(\mathbb{R}_\omega, \mathcal{B}(\mathcal{H}_1)).$$

Key point

The support of the distribution $\text{Im}(\widehat{G}_h)$ is contained in the hole electronic excitation set $S_h := \sigma(E_N^0 - H_{N-1}^0)$.

In the complex frequency domain

$$\forall z \in \mathbb{C} \setminus S_h, \quad \widetilde{G}_h(z) = A_-^* \left(\frac{1}{z - (E_N^0 - H_{N-1}^0)} \right) A_-.$$



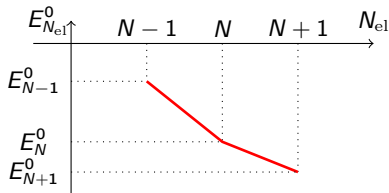
Definition of the total Green's function

Assumption: Stability condition

$$2E_N^0 < E_{N+1}^0 + E_{N-1}^0.$$

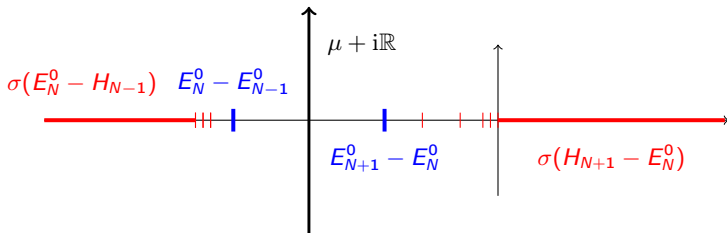
Chemical potential μ

$$E_N^0 - E_{N-1}^0 < \mu < E_{N+1}^0 - E_N^0.$$



One-body total Green's function in the complex frequency domain

$$\forall z \in \mathbb{C} \setminus (S_h \cup S_p), \quad \tilde{G}(z) = \tilde{G}_h(z) + \tilde{G}_p(z).$$



Green's function for non-interacting systems

System of non-interacting electrons subjected to an effective potential V

$$H_{0,N} = \sum_{i=1}^N \left(-\frac{1}{2} \Delta_{\mathbf{r}_i} + V(\mathbf{r}_i) \right) \text{ on } \mathcal{H}_N, \quad h_1 = -\frac{1}{2} \Delta + V \text{ on } \mathcal{H}_1.$$

Assumptions

- h_1 has at least N negative eigenvalues $\varepsilon_1 \leq \varepsilon_2 \leq \dots \leq \varepsilon_N$,
- Stability condition: it holds $\varepsilon_N < \varepsilon_{N+1}$.

Chemical potential of the non-interacting system μ_0

$$\varepsilon_N < \mu_0 < \varepsilon_{N+1}.$$

Ground state of the non-interacting system

$$\Phi_N^0 = \phi_1 \wedge \dots \wedge \phi_N, \quad \gamma_{0,N}^0 = \mathbb{1}_{(-\infty, \mu_0)}(h_1) = \sum_{i=1}^N |\phi_i\rangle\langle\phi_i|.$$

Green's function of the non-interaction system

$$\widetilde{G}_{0,h}(z) = \gamma_{0,N}^0 (z - h_1)^{-1}, \quad \widetilde{G}_{0,p}(z) = (1 - \gamma_{0,N}^0) (z - h_1)^{-1}, \quad \boxed{\widetilde{G}_0(z) = (z - h_1)^{-1}.}$$

Dynamical Hamiltonian

Non-interacting system: $\widetilde{G}_0(z) = (z - h_1)^{-1}$.

Interacting system: $\widetilde{G}(z) = (z - \widetilde{H}(z))^{-1}$, $\widetilde{H}(z)$: dynamical Hamiltonian.

- Eigenvalues = quasi-energies,
- Eigenfunctions = quasi-particles.

Lemma

For all $z \in \mathbb{C} \setminus (S_h \cup S_p)$, $\widetilde{H}(z) = z - G(z)^{-1}$ is a well-defined closed operator on \mathcal{H}_1 , with dense domain $\widetilde{D}(z)$ such that $\widetilde{D}(z) \subset H^2(\mathbb{R}^3)$.

Assumption

- The chemical potential of the interacting system and of the non-interacting system can be chosen equal:

$$\mu = \mu_0.$$

Self-energy

$\forall z \in \mathbb{U} \cup \mathbb{L} \cup (\mu - a, \mu + b)$, $\widetilde{\Sigma}(z) = \widetilde{H}(z) - h_1 = \widetilde{G}_0(z)^{-1} - \widetilde{G}(z)^{-1}$ (Dyson equation).

$$\widetilde{H}(z) = h_1 + \widetilde{\Sigma}(z).$$

Dyson equation on the imaginary axis $\mu + i\mathbb{R}$

$$\forall \omega \in \mathbb{R}_\omega, \quad \widetilde{\Sigma}(\mu + i\omega) = \widetilde{G}_0(\mu + i\omega)^{-1} - \widetilde{G}(\mu + i\omega)^{-1}$$

Road map

- Construct a good non-interacting model for $\widetilde{G}_0(\mu + i\omega)$
 - Hartree Hamiltonian (in the original paper)
 - Kohn-Sham Hamiltonian (DFT)
- Use an approximation of the self-energy $\widetilde{\Sigma} \approx \widetilde{\Sigma}^{\text{GW}}$ on the axis $\mu + i\mathbb{R}$.
- Define $\widetilde{G}^{\text{GW}}(\mu + i\omega)$ from the Dyson equation with $\widetilde{\Sigma}^{\text{GW}}(\mu + i\omega)$

$$\widetilde{G}^{\text{GW}}(\mu + i\omega) = \left(\widetilde{G}_0(\mu + i\omega)^{-1} - \widetilde{\Sigma}^{\text{GW}}(\mu + i\omega) \right)^{-1} = \left(\mu + i\omega - h_1 - \widetilde{\Sigma}^{\text{GW}}(\mu + i\omega) \right)^{-1}.$$

Choice of $(\widetilde{\Sigma}^{GW}, \widetilde{G}^{GW})$? The Hedin's equations (L. Hedin. Phys. Rev., 139, 1965.)

Kernel of a space-time operator A

$$A(12) = A(\mathbf{r}_1, t_1; \mathbf{r}_2, t_2) = [A(t_1 - t_2)](\mathbf{r}_1, \mathbf{r}_2).$$

The Hedin's equations

- Dyson equation

$$G(12) = G_0(12) + \int d(34) G_0(13) \Sigma(34) G(42),$$

- Self-energy

$$\Sigma(12) = i \int d(34) G(13) W(41) \Gamma(32; 4),$$

- Screened interaction

$$W(12) = v_c(12) + \int d(34) v_c(13) P(34) W(42),$$

- Irreducible polarization

$$P(12) = -i \int d(34) G(13) G(41) \Gamma(34; 2),$$

- Vertex function

$$\Gamma(12; 3) = \delta(12)\delta(13) + \int d(4567) \frac{\delta \Sigma(12)}{\delta G(45)} G(46) G(75) \Gamma(67; 3).$$

The GW^0 equations:

Find $(\Sigma^{GW^0}, G^{GW^0})$ such that

- Dyson equation

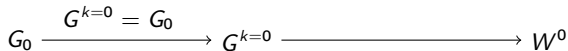
$$G^{GW^0}(12) = G_0(12) + \int d(34) G_0(13) \Sigma^{GW^0}(34) G^{GW^0}(42),$$

- Self-energy

$$\Sigma^{GW^0}(12) = iG^{GW^0}(12)W^0(21).$$

W^0 is the (GW^0 approximation of the) **dynamically screened operator**.

Flow chart of the self-consistent GW^0 scheme



Initialization

The GW^0 equations:

Find $(\Sigma^{GW^0}, G^{GW^0})$ such that

- Dyson equation

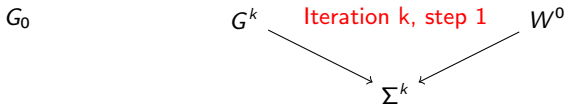
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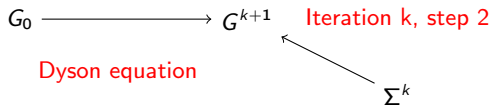
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Flow chart of the self-consistent GW^0 scheme



The GW^0 equations:

Find $(\Sigma^{\text{GW}^0}, G^{\text{GW}^0})$ such that

- Dyson equation

$$G^{\text{GW}^0}(12) = G_0(12) + \int d(34) G_0(13) \Sigma^{\text{GW}^0}(34) G^{\text{GW}^0}(42),$$

- Self-energy

$$\Sigma^{\text{GW}^0}(12) = i G^{\text{GW}^0}(12) W^0(21).$$

W^0 is the (GW^0 approximation of the) **dynamically screened operator**.

Next step: give a sense to these equations

- Define the multiplication $A(12)B(21)$,
- Study the operator W^0 ,
- Transform the GW^0 equations on the **time axis** \mathbb{R}_τ into formally equivalent GW^0 equations on the **imaginary frequency axis** $\mu + i\mathbb{R}_\omega$.

The kernel product (infinite dimensional Hadamard product)

How to define an operator C such that $C(\mathbf{r}, \mathbf{r}') = A(\mathbf{r}, \mathbf{r}')B(\mathbf{r}', \mathbf{r})$?

Associated quadratic form

$$\begin{aligned}\forall f, g \in \mathcal{H}_1, \quad \langle f|C|g \rangle_{\mathcal{H}_1} &= \iint_{\mathbb{R}^2} \bar{f}(\mathbf{r}) C(\mathbf{r}, \mathbf{r}') g(\mathbf{r}') d\mathbf{r} d\mathbf{r}' \\ &= \iint_{\mathbb{R}^2} A(\mathbf{r}, \mathbf{r}') g(\mathbf{r}') B(\mathbf{r}', \mathbf{r}) \bar{f}(\mathbf{r}) d\mathbf{r} d\mathbf{r}' = \text{Tr}_{\mathcal{H}_1} (AgB\bar{f}).\end{aligned}$$

Definition

The kernel-product of A and B is the operator $A \odot B$, defined by the quadratic form

$$\forall f, g \in \mathcal{H}_1, \quad \langle f|A \odot B|g \rangle = \text{Tr}_{\mathcal{H}_1} (AgB\bar{f}).$$

Lemma

If $A \in \mathcal{B}(\mathcal{H}_1)$ and B is such that,

$$\forall f, g \in \mathcal{H}_1, \quad gB\bar{f} \in \mathfrak{S}_1(\mathcal{H}_1) \quad \text{with} \quad \|gB\bar{f}\|_{\mathfrak{S}_1} \lesssim \|f\|_{\mathcal{H}_1} \|g\|_{\mathcal{H}_1},$$

then $A \odot B$ is a well-defined bounded operator on \mathcal{H}_1 .

The dynamically screened operator W

The Coulomb operator

In the **vacuum**, a time-dependent charge $\delta\rho(\mathbf{r}, t)$ creates a potential

$$\delta V(\mathbf{r}', t) = \int_{\mathbb{R}^3} \frac{1}{|\mathbf{r} - \mathbf{r}'|} \delta\rho(\mathbf{r}, t) d\mathbf{r}, \quad \text{or} \quad \delta V = \delta_0(t) v_c(\delta\rho).$$

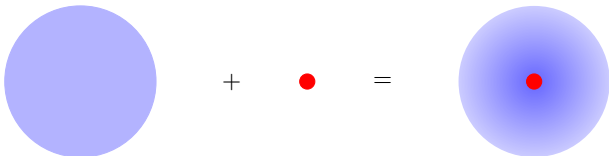
$$v_c(\mathbf{r}, \mathbf{r}') = \frac{1}{|\mathbf{r} - \mathbf{r}'|} \quad \text{Coulomb operator.}$$

The dynamically screened operator

In a **molecule**, a time-dependent charge $\delta\rho(\mathbf{r}, t)$ creates a potential

$$\begin{aligned} \delta V(\mathbf{r}', t) &= \int_{\mathbb{R}^3} \int_{-\infty}^t W(\mathbf{r}t, \mathbf{r}'t') \delta\rho(\mathbf{r}, t') d\mathbf{r} dt' \\ &= \delta_0(t) v_c(\delta\rho) + \int_{\mathbb{R}^3} \int_{-\infty}^t W_c(\mathbf{r}t, \mathbf{r}'t') \delta\rho(\mathbf{r}, t') d\mathbf{r} dt'. \end{aligned}$$

Screening effect



The dynamically screened operator W^0

Calculated from the Hartree Hamiltonian:

$$W^0(\tau) = \delta_0(\tau)v_c + W_c^0(\tau).$$

GW⁰ approximation of the self-energy

$$\Sigma^{\text{app}}(12) = iG^{\text{app}}(12)W^0(21).$$

$$\begin{aligned}\Sigma^{\text{app}}(\mathbf{r}, \mathbf{r}'; \tau) &= i\delta_0(\tau)G_h^{\text{app}}(\mathbf{r}, \mathbf{r}'; 0^-)v_c(\mathbf{r}, \mathbf{r}') + iG^{\text{app}}(\mathbf{r}, \mathbf{r}'; \tau)W_c^0(\mathbf{r}', \mathbf{r}; -\tau) \\ &= \underbrace{-\frac{\gamma_N^{\text{app}}(\mathbf{r}, \mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|}}_{\text{Fock term}}\delta_0(\tau) + iG^{\text{app}}(\mathbf{r}, \mathbf{r}'; \tau)W_c^0(\mathbf{r}', \mathbf{r}; -\tau).\end{aligned}$$

In practice

$$\Sigma^{\text{app}}(\tau) = K_x\delta_0(\tau) + iG^{\text{app}}(\tau) \odot W_c^0(-\tau), \quad \text{with} \quad K_x(\mathbf{r}, \mathbf{r}') := -\frac{\gamma_{0,N}^0(\mathbf{r}, \mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|}.$$

Analytical continuation method

Equation

$$\forall \tau \in \mathbb{R}_\tau, \quad \Sigma^{\text{app}}(\tau) := K_x \delta_0(\tau) + iG^{\text{app}}(\tau) \odot W_c^0(-\tau)$$

is **formally** equivalent to

$$\widetilde{\Sigma}^{\text{app}}(\mu_0 + i\omega) = K_x - \frac{1}{2\pi} \int_{-\infty}^{+\infty} \widetilde{G}^{\text{app}}(\mu_0 + i(\omega + \omega')) \odot \widetilde{W}_c^0(i\omega') d\omega'.$$

The GW^0 equations in the imaginary frequency axis

Find $G^{\text{GW}^0} \in L^\infty(\mathbb{R}_\omega, \mathcal{B}(\mathcal{H}_1))$ solution to the system

$$(\text{GW}^0) \quad \begin{cases} \widetilde{\Sigma}^{\text{GW}^0}(\mu_0 + i\omega) = K_x - \frac{1}{2\pi} \int_{-\infty}^{+\infty} \widetilde{G}^{\text{GW}^0}(\mu_0 + i(\omega + \omega')) \odot \widetilde{W}_c^0(i\omega') d\omega', \\ \widetilde{G}^{\text{GW}^0}(\mu_0 + i\omega) = \left[\mu_0 + i\omega - \left(h_1 + \widetilde{\Sigma}^{\text{GW}^0}(\mu_0 + i\omega) \right) \right]^{-1}, \end{cases}$$

with

$$K_x(\mathbf{r}, \mathbf{r}') = -\frac{\gamma_{0,N}^0(\mathbf{r}, \mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|}.$$

$$(GW^0) \quad \begin{cases} \widetilde{\Sigma}^{GW^0}(\mu_0 + i\omega) = K_x - \frac{1}{2\pi} \int_{-\infty}^{+\infty} \widetilde{G}^{GW^0}(\mu_0 + i(\omega + \omega')) \odot \widetilde{W}_c^0(i\omega') d\omega', \\ \widetilde{G}^{GW^0}(\mu_0 + i\omega) = \left[\mu_0 + i\omega - \left(h_1 + \widetilde{\Sigma}^{GW^0}(\mu_0 + i\omega) \right) \right]^{-1} \end{cases}$$

Lemma

For all $\widetilde{G}^{\text{app}}(\mu_0 + i\cdot) \in L^2(\mathbb{R}_\omega, \mathcal{B}(\mathcal{H}_1))$ and all $\omega \in \mathbb{R}_\omega$, the operator

$$\widetilde{\Sigma}_c^{\text{app}}(\mu_0 + i\omega) = -\frac{1}{2\pi} \int_{-\infty}^{+\infty} \widetilde{G}^{\text{app}}(\mu_0 + i(\omega + \omega')) \odot \widetilde{W}_c^0(i\omega') d\omega'$$

is a well-defined bounded operator on \mathcal{H}_1 .

Problem

For $\widetilde{G}^{\text{app}}(\mu_0 + i\cdot)$ close to $\widetilde{G}_0(\mu_0 + i\cdot)$ in $L^\infty(\mathbb{R}_\omega, \mathcal{B}(\mathcal{H}_1))$, is the operator

$$\mu_0 + i\omega - \left(h_1 + \widetilde{\Sigma}^{\text{app}}(\mu_0 + i\omega) \right)$$

invertible?

The GW^0 approximation in a perturbative regime

$$(\text{GW}_\lambda^0) \quad \begin{cases} \widetilde{\Sigma}^{\text{GW}_\lambda^0}(\mu_0 + i\omega) = K_x - \frac{1}{2\pi} \int_{-\infty}^{+\infty} \widetilde{G}^{\text{GW}_\lambda^0}(\mu_0 + i(\omega + \omega')) \odot \widetilde{W}_c^0(i\omega') d\omega', \\ \widetilde{G}^{\text{GW}_\lambda^0}(\mu_0 + i\omega) = \left[\mu_0 + i\omega - \left(h_1 + \lambda \widetilde{\Sigma}^{\text{GW}_\lambda^0}(\mu_0 + i\omega) \right) \right]^{-1}. \end{cases}$$

Theorem (Éric Cancès, DG, Gabriel Stoltz)

- There exists $\lambda_* > 0$ such that, for all $0 \leq \lambda \leq \lambda_*$, there exists a unique solution $\widetilde{G}^{\text{GW}_\lambda^0}$ to the problem (GW_λ^0) which is close to \widetilde{G}_0 .
- Moreover, the self-consistent procedure starting from \widetilde{G}_0 converges toward $\widetilde{G}^{\text{GW}_\lambda^0}$ in $L^2(\mathbb{R}_\omega, \mathcal{B}(\mathcal{H}_1))$.

Current results

- The fundamental objects (G , G_0 , Σ , W_0) involved in GW^0 formalism are mathematically well-defined.
- Some of their properties have been rigorously proved.
- The GW^0 equations are well-posed in a perturbative regime.

Future work

- Perform the same work for periodic systems.
with Éric Cancès and Gabriel Stoltz
- Study the speed of convergence with respect to numerical parameters.
- Understand the Bethe-Salpeter equations.

Reference

- Éric Cancès, DG and Gabriel Stoltz, *A mathematical analysis of the GW^0 method for computing electronic excited energies of molecules* (arXiv 1506.01737).