# A mathematical study of the $\mathrm{GW}^0$ method for computing electronic excited states of molecules

Éric Cancès, David Gontier, Gabriel Stoltz

Université Paris EST, CERMICS, École des Ponts ParisTech and INRIA
Department of Mathematics, ETH Zürich

GDR DynQua, Grenoble
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Goal: compute the electronic excitation energies of a finite electronic system (molecule).

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

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

Electronic problem with $N$-electrons

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

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

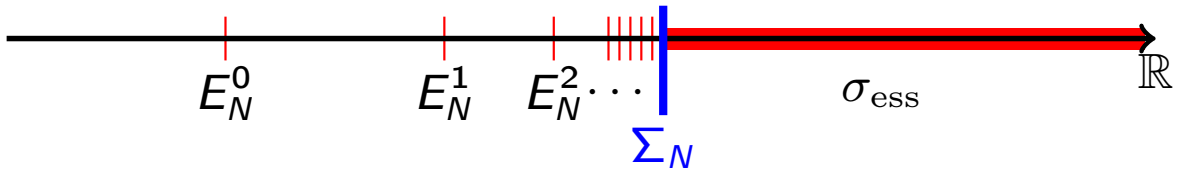
Pauli principle for fermions: $\forall p \in \mathfrak{S}_N,\ \Psi(\mathbf{r}_{p(1)},\ldots\mathbf{r}_{p(N)}) = \epsilon(p)\Psi(\mathbf{r}_1,\ldots\mathbf{r}_N)$.

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 $\left\|\Psi_N^0\right\| = 1$ 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)**

$$H_2 \quad (N = 2) \qquad H_2O \quad (N = 10) \qquad C_8H_{10}N_4O_2 \quad (N = 102)$$

$\Longrightarrow$ Several approximations were proposed in the last decades.

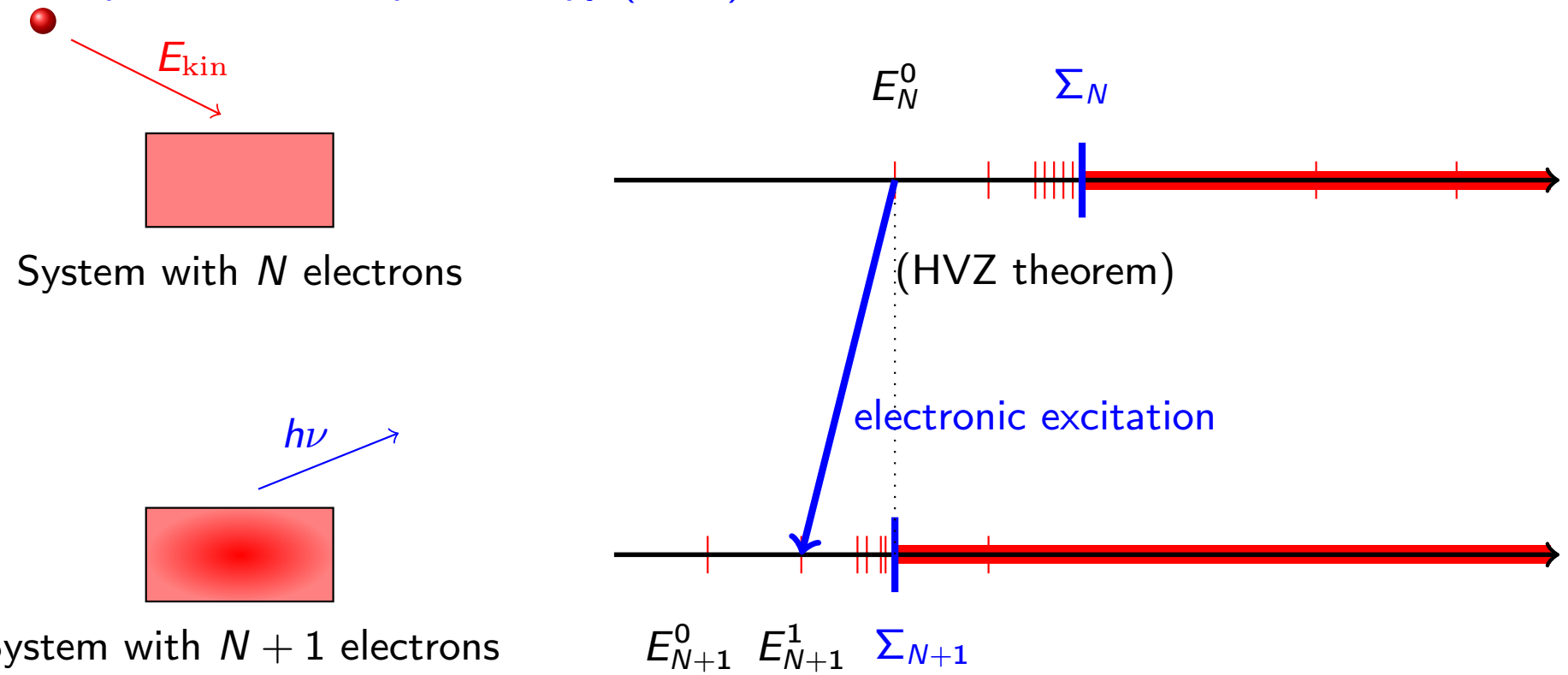
- *Density functional theory (DFT)*: for ground state properties only
- *Quantum Monte Carlo methods*: idem
- *Wavefunction methods*: scales from $N_b^6$ (CISD) to $N_b!$ (full CI)
- *Time-dependent DFT (TDDFT)*: does not work well for extended systems
- *Green's function method*: in this talk, $\mathrm{GW}$.

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

To calculate the electronic excitation energies of a system $\Longrightarrow$ quantities of the form

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

### Inverse photoemission spectroscopy (IPES)

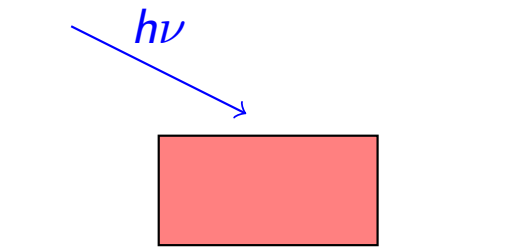


## The GW method (L. Hedin. Phys. Rev. 1965)

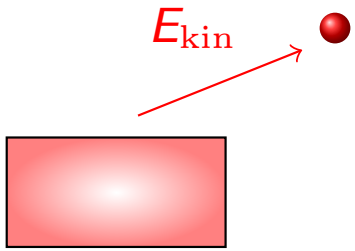
To calculate the electronic excitation energies of a system $\Longrightarrow$ quantities of the form

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

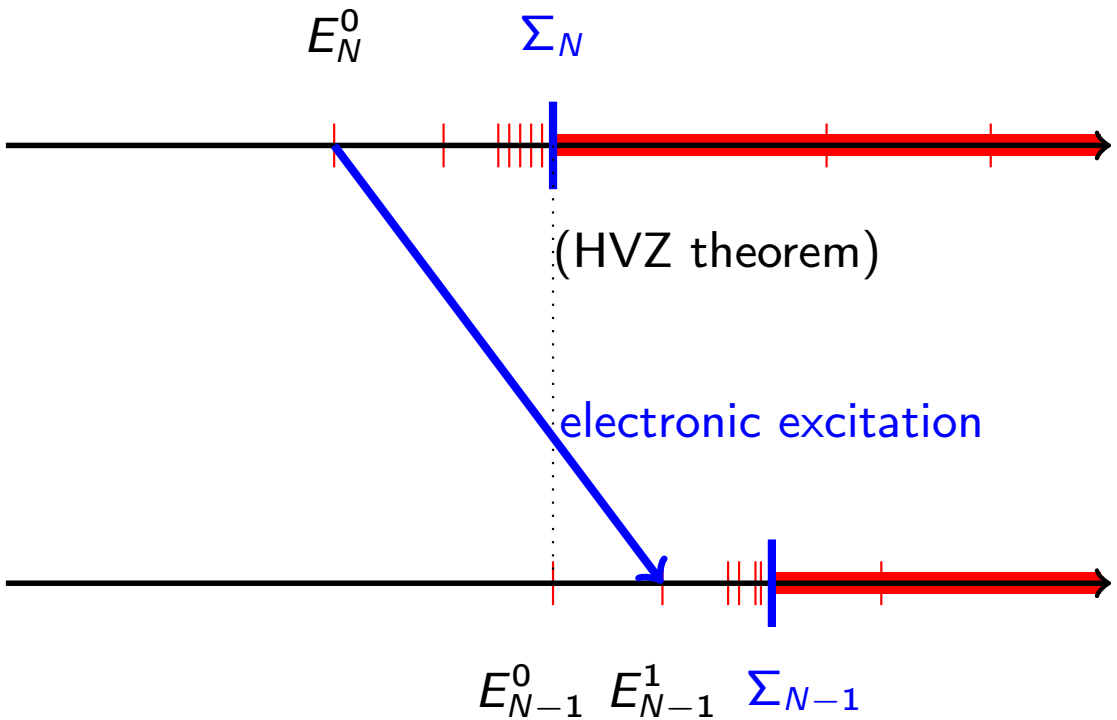
### Photoemission spectroscopy (PES)




System with $N$ electrons




System with $N-1$ electrons



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

## Fock space

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

## Annihilation and creation operators

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

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

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

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

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

## 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)

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

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

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

## Normalization convention for the time-Fourier transform

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

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

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

### Key point

*The support of the distribution* $Im\left(\widehat{G_{\mathrm{p}}}\right)$ *is contained in the particle electronic excitation set* $S_{\mathrm{p}} := \sigma(H_{N+1} - E_N^0)$.

- Particle electronic excited energies can be recovered from $\widehat{G_{\mathrm{p}}}$,
- $\widehat{G_{\mathrm{p}}}$ is highly irregular.

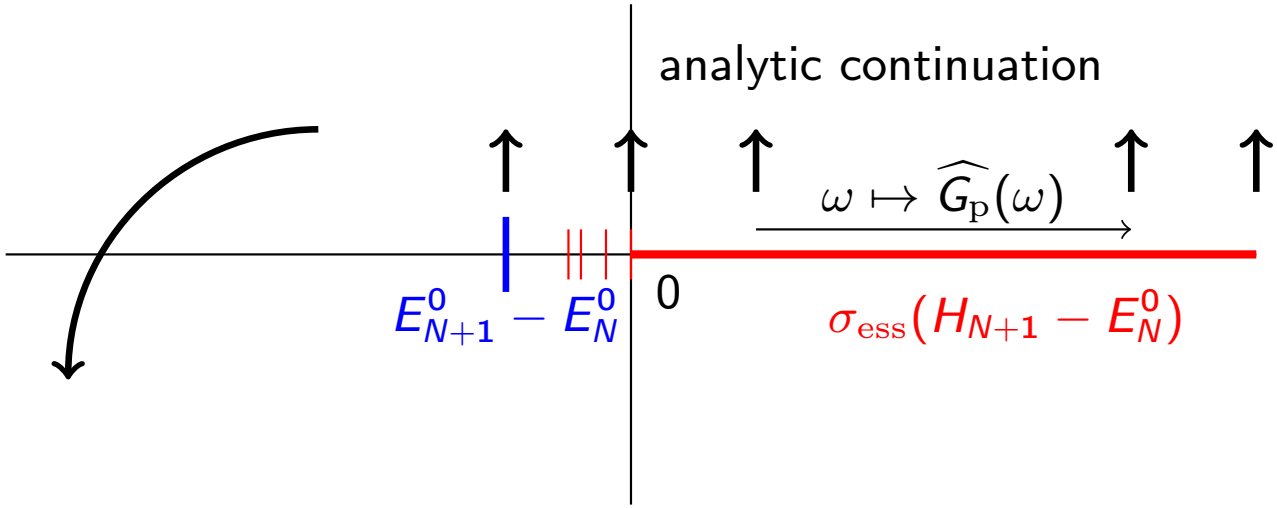
**Laplace transform of the Green's function** For $z \in \mathbb{U} = \{z \in \mathbb{C}, \mathrm{Im}\,(z) > 0\}$, define

$$\widetilde{G_{\mathrm{p}}}(z) := \int_0^\infty G_{\mathrm{p}}(\tau) \mathrm{e}^{\mathrm{i}z\tau} \mathrm{d}\tau.$$

## Remark

- *$\widetilde{G_{\mathrm{p}}}$ is an analytical continuation of $\widehat{G_{\mathrm{p}}}$ on $\mathbb{U}$ (Titchmarsh's theory),*
- *This continuation can be extended to $\mathbb{C} \setminus S_{\mathrm{p}}$.*

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



## Definition of the one-body hole Green's function

### Annihilation and creation operators (ter)

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

### In the time domain

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

### Properties

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

- One-body electronic ground-state density matrix: $\gamma_N^0 = -\mathrm{i}G_{\mathrm{h}}(0^-) = A_-^* A_-$

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

- Electronic ground state density

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

- Ground state energy (Galiskii-Migdal formula)

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

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

## The hole Green's function in the frequency domain

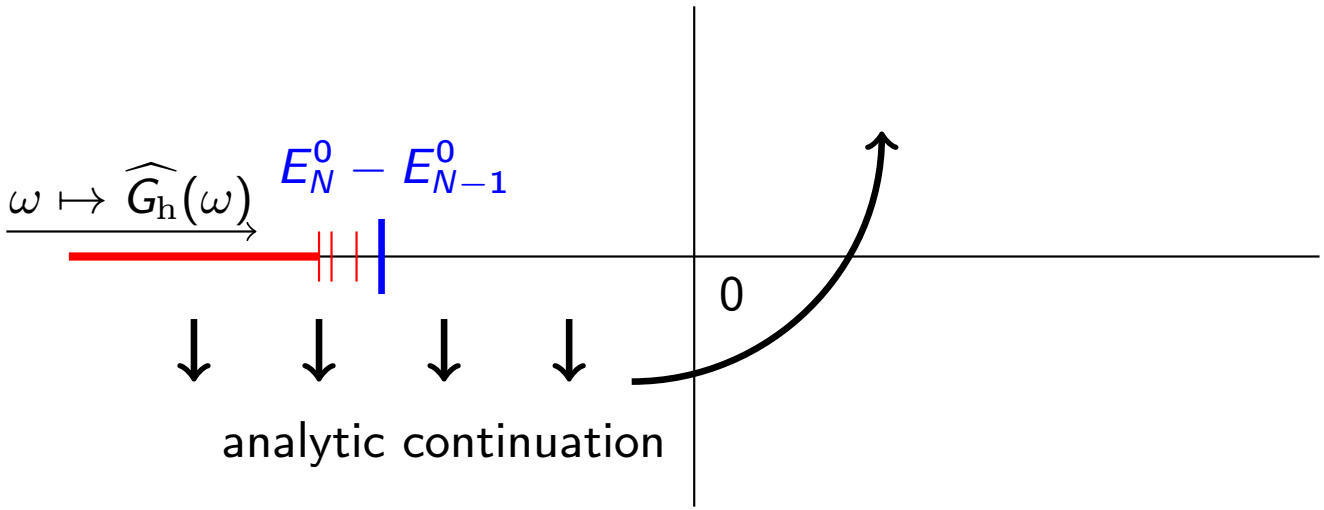
$$\widehat{G_{\mathrm{h}}}(\omega) = \left(\mathcal{F}_T G_{\mathrm{h}}\right)(\omega), \quad \widehat{G_{\mathrm{h}}} \in H^{-1}(\mathbb{R}_\omega, \mathcal{B}(\mathcal{H}_1)).$$

### Key point

*The support of the distribution* $Im\left(\widehat{G_{\mathrm{h}}}\right)$ *is contained in the hole electronic excitation set* $S_{\mathrm{h}} := \sigma(E_N^0 - H_{N-1}^0)$.

## In the complex frequency domain

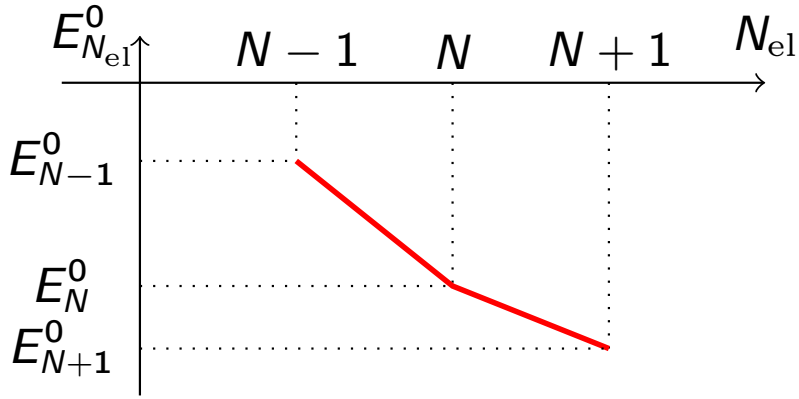
$$\forall z \in \mathbb{C} \setminus S_{\mathrm{h}}, \quad \widetilde{G_{\mathrm{h}}}(z) = A_-^* \left(\frac{1}{z - (E_N^0 - H_{N-1})}\right) A_-.$$



## Definition of the total Green's function

### Assumption: Stability condition

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

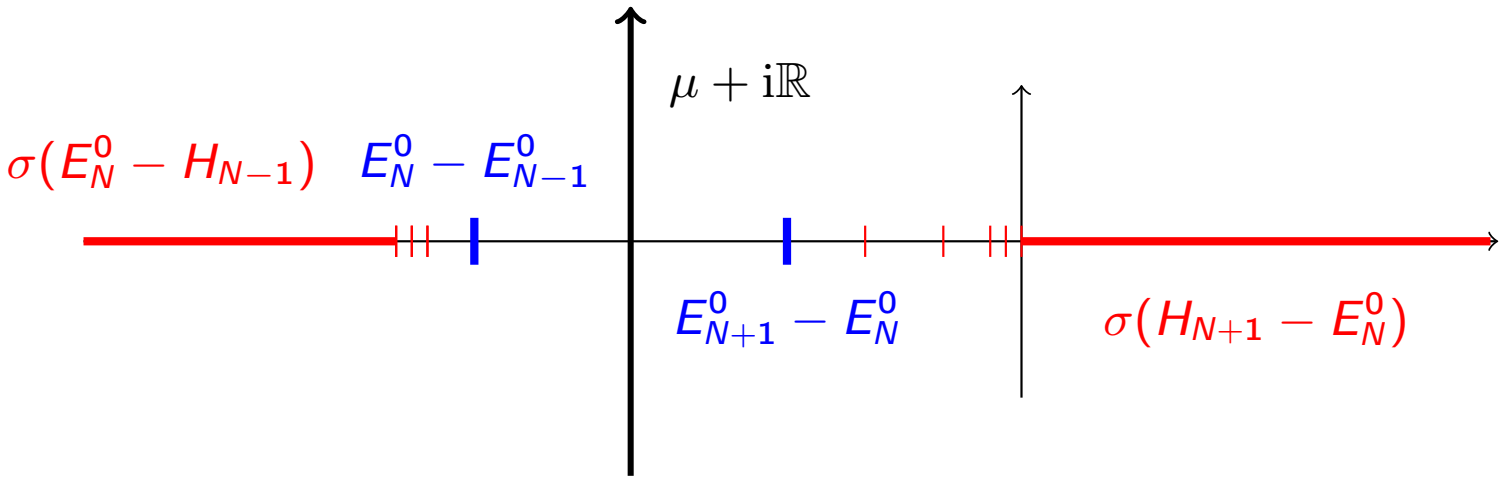



### Chemical potential $\mu$

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

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

$$\forall z \in \mathbb{C} \setminus (S_{\rm h} \cup S_{\rm p}), \quad \widetilde{G}(z) = \widetilde{G_{\rm h}}(z) + \widetilde{G_{\rm p}}(z).$$



## Green's function for non-interacting systems

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

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

## Assumptions

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

## Chemical potential of the non-interacting system $\mu_0$

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

## Ground state of the non-interacting system

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

## Green's function of the non-interaction system

$$\widetilde{G_{0,\mathrm{h}}}(z) = \gamma_{0,N}^0 (z - h_1)^{-1}, \quad \widetilde{G_{0,\mathrm{p}}}(z) = (1 - \gamma_{0,N}^0)(z - h_1)^{-1}, \quad \boxed{\widetilde{G_0}(z) = (z - h_1)^{-1}.}$$

## 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 $z \in \mathbb{C} \setminus (S_{\mathrm{h}} \cup S_{\mathrm{p}})$, $\widetilde{H}(z) = z - G(z)^{-1}$ 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:

$$\boxed{\mu = \mu_0.}$$

## Self-energy

$\forall z \in \mathbb{U} \cup \mathbb{L} \cup (\mu - a, \mu + b)$, $\quad \widetilde{\Sigma}(z) = \widetilde{H}(z) - h_1 = \widetilde{G_0}(z)^{-1} - \widetilde{G}(z)^{-1}$ (Dyson equation).

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

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

$$\boxed{\forall \omega \in \mathbb{R}_\omega, \quad \widetilde{\Sigma}(\mu + \mathrm{i}\omega) = \widetilde{G_0}(\mu + \mathrm{i}\omega)^{-1} - \widetilde{G}(\mu + \mathrm{i}\omega)^{-1}}$$

## Road map

- Construct a good non-interacting model for $\widetilde{G_0}(\mu + \mathrm{i}\omega)$
  - Hartree Hamiltonian (in the original paper)
  - Kohn-Sham Hamiltonian (DFT)
- Use an approximation of the self-energy $\widetilde{\Sigma} \approx \widetilde{\Sigma^{\mathrm{GW}}}$ on the axis $\mu + \mathrm{i}\mathbb{R}$.
- Define $\widetilde{G^{\mathrm{GW}}}(\mu + \mathrm{i}\omega)$ from the Dyson equation with $\widetilde{\Sigma^{\mathrm{GW}}}(\mu + \mathrm{i}\omega)$

$$\widetilde{G^{\mathrm{GW}}}(\mu+\mathrm{i}\omega) = \left(\widetilde{G_0}(\mu + \mathrm{i}\omega)^{-1} - \widetilde{\Sigma^{\mathrm{GW}}}(\mu + \mathrm{i}\omega)\right)^{-1} = \left(\mu + \mathrm{i}\omega - h_1 - \widetilde{\Sigma^{\mathrm{GW}}}(\mu + \mathrm{i}\omega)\right)^{-1}.$$

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

### Kernel of a space-time operator $A$

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

### The Hedin's equations

- Dyson equation

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

- Self-energy

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

- Screened interaction

$$W(12) = v_{\mathrm{c}}(12) + \int \mathrm{d}(34) v_{\mathrm{c}}(13) P(34) W(42),$$

- Irreducible polarization

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

- Vertex function

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

The $\mathrm{GW}^0$ equations:

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

- Dyson equation

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

- Self-energy

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

$W^0$ is the ($\mathrm{GW}^0$ approximation of the) dynamically screened operator.

Flow chart of the self-consistent $\mathrm{GW}^0$ scheme

$$G_0 \xrightarrow{G^{k=0} = G_0} G^{k=0} \longrightarrow W^0$$

Initialization

## The $\mathrm{GW}^0$ equations:

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

- Dyson equation

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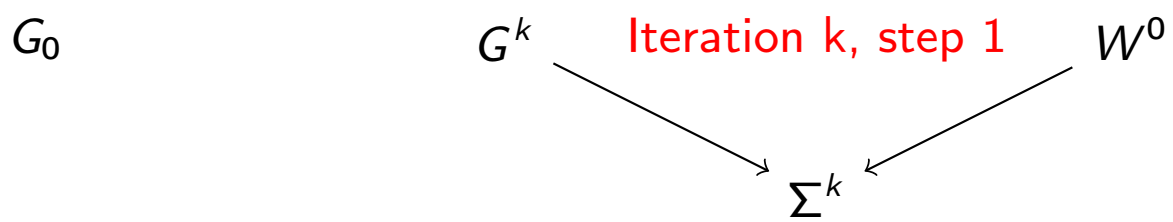

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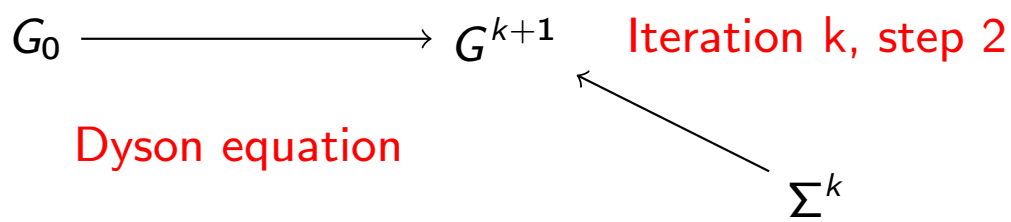

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Find $\left(\Sigma^{\mathrm{GW}^0}, G^{\mathrm{GW}^0}\right)$ such that

- Dyson equation

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- Self-energy

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

$W^0$ is the ($\mathrm{GW}^0$ 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 $\mathrm{GW}^0$ equations on the time axis $\mathbb{R}_\tau$ into formally equivalent $\mathrm{GW}^0$ equations on the imaginary frequency axis $\mu + \mathrm{i}\mathbb{R}_\omega$.

## 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

$$\forall f,g \in \mathcal{H}_1, \quad \langle f|C|g\rangle_{\mathcal{H}_1} = \iint_{\mathbb{R}^2} \overline{f}(\mathbf{r})C(\mathbf{r},\mathbf{r}')g(\mathbf{r}')\mathrm{d}\mathbf{r}\mathrm{d}\mathbf{r}'$$
$$= \iint_{\mathbb{R}^2} A(\mathbf{r},\mathbf{r}')g(\mathbf{r}')B(\mathbf{r}',\mathbf{r})\overline{f}(\mathbf{r})\mathrm{d}\mathbf{r}\mathrm{d}\mathbf{r}' = \mathrm{Tr}_{\mathcal{H}_1}\left(Ag B\overline{f}\right).$$

**Definition**

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

$$\forall f,g \in \mathcal{H}_1, \quad \langle f|A \odot B|g\rangle = \mathrm{Tr}_{\mathcal{H}_1}\left(Ag B\overline{f}\right).$$

**Lemma**

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

$$\forall f,g \in \mathcal{H}_1, \quad gB\overline{f} \in \mathfrak{S}_1(\mathcal{H}_1) \quad \textit{with} \quad \left\|gB\overline{f}\right\|_{\mathfrak{S}_1} \lesssim \|f\|_{\mathcal{H}_1}\|g\|_{\mathcal{H}_1},$$

*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

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

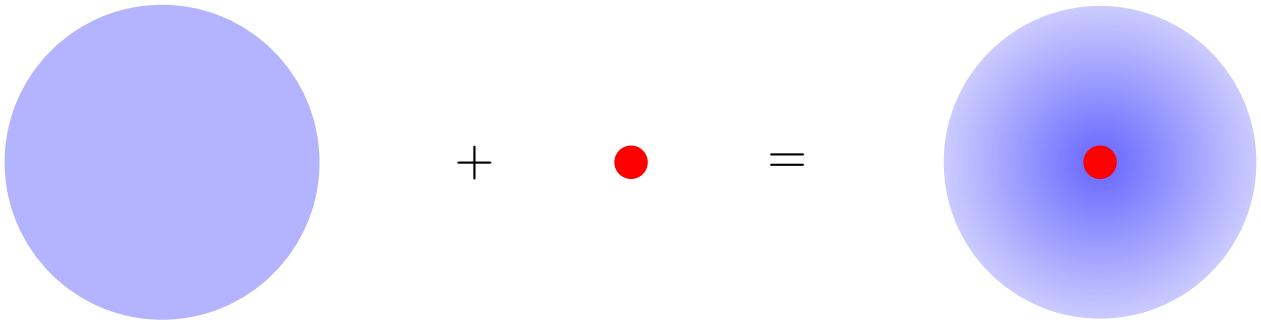
$$\boxed{v_c(\mathbf{r}, \mathbf{r}') = \frac{1}{|\mathbf{r} - \mathbf{r}'|} \quad \text{Coulomb operator.}}$$

### The dynamically screened operator

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

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

### Screening effect



## The dynamically screened operator $W^0$

Calculated from the Hartree Hamiltonian:

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

## $\mathrm{GW}^0$ approximation of the self-energy

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

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

## In practice

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

## Analytical continuation method

Equation

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

is formally equivalent to

$$\widetilde{\Sigma^{\mathrm{app}}}(\mu_0 + \mathrm{i}\omega) = K_x - \frac{1}{2\pi} \int_{-\infty}^{+\infty} \widetilde{G^{\mathrm{app}}}\left(\mu_0 + \mathrm{i}(\omega + \omega')\right) \odot \widetilde{W_c^0}(\mathrm{i}\omega')\, \mathrm{d}\omega'.$$

## The $\mathrm{GW}^0$ equations in the imaginary frequency axis

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

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

with

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

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

**Lemma**

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

$$\widetilde{\Sigma_c^{\mathrm{app}}}(\mu_0 + \mathrm{i}\omega) = -\frac{1}{2\pi} \int_{-\infty}^{+\infty} \widetilde{G^{\mathrm{app}}}\big(\mu_0 + \mathrm{i}(\omega + \omega')\big) \odot \widetilde{W_c^0}(\mathrm{i}\omega')\,\mathrm{d}\omega'$$

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

**Problem**

For $\widetilde{G^{\mathrm{app}}}(\mu_0 + \mathrm{i}\cdot)$ close to $\widetilde{G_0}(\mu_0 + \mathrm{i}\cdot)$ in $L^\infty(\mathbb{R}_\omega, \mathcal{B}(\mathcal{H}_1))$, is the operator

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

invertible?

## The $\mathrm{GW}^0$ approximation in a perturbative regime

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

### Theorem (Éric Cancès, DG, Gabriel Stoltz)

- *There exists $\lambda_* > 0$ such that, for all $0 \leq \lambda \leq \lambda_*$, there exists a unique solution $\widetilde{G^{\mathrm{GW}^0_\lambda}}$ to the problem $(\mathrm{GW}^0_\lambda)$ which is close to $\widetilde{G_0}$.*
- *Moreover, the self-consistent procedure starting from $\widetilde{G_0}$ converges toward $\widetilde{G^{\mathrm{GW}^0_\lambda}}$ in $L^2(\mathbb{R}_\omega, \mathcal{B}(\mathcal{H}_1))$.*

## Current results

- The fundamental objects $(G, G_0, \Sigma, W_0)$ involved in $\mathrm{GW}^0$ formalism are mathematically well-defined.
- Some of their properties have been rigorously proved.
- The $\mathrm{GW}^0$ 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 GW0 method for computing electronic excited energies of molecules* (arXiv 1506.01737).