Mathematical contributions to the calculations of electronic structures

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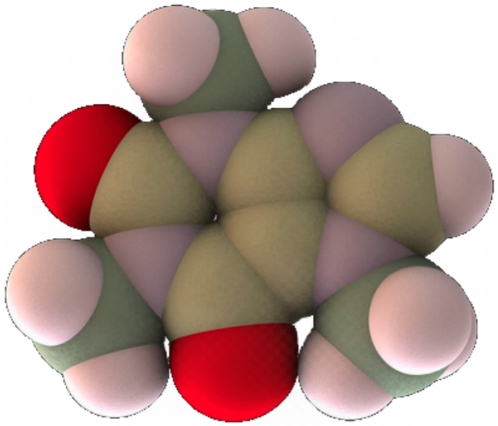
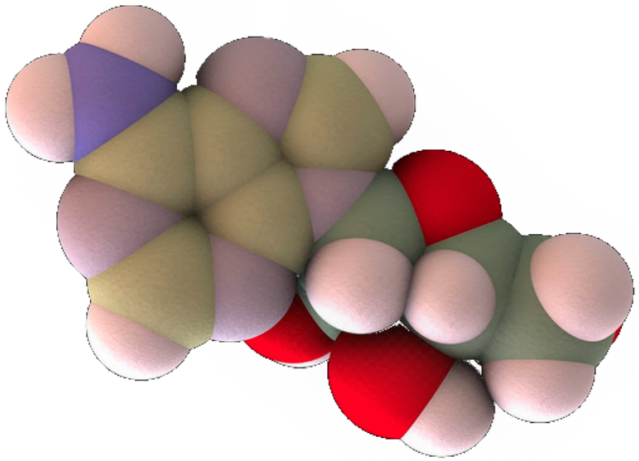
Why does coffee wake you up?



Caffeine molecule

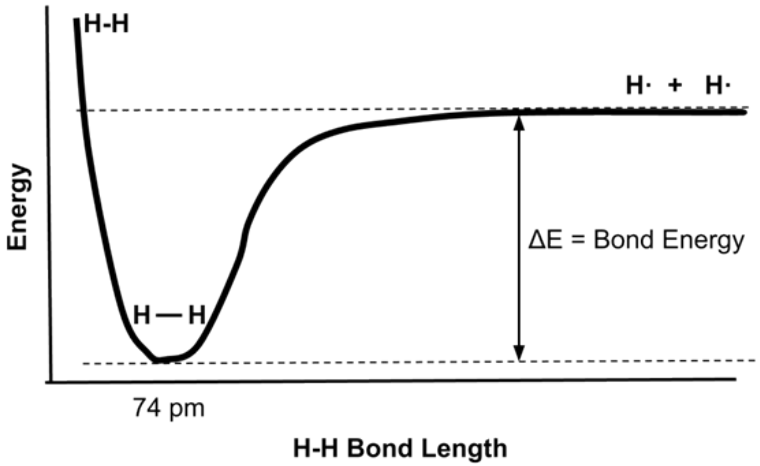


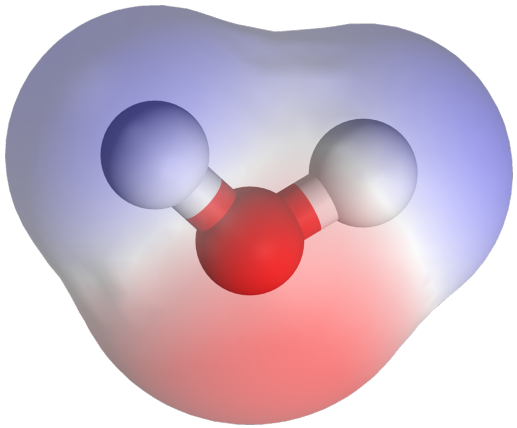
Adenosine molecule
(blocks the production of adrenaline)

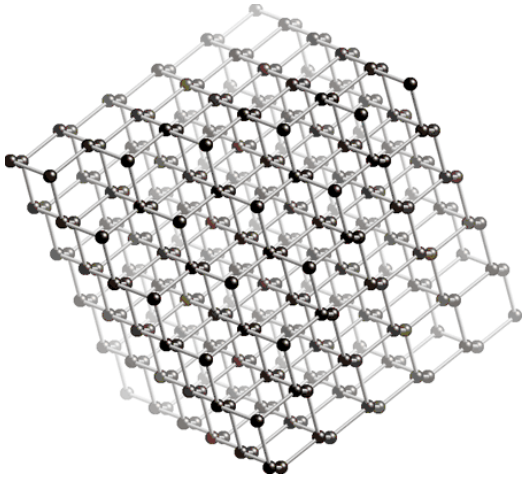
Can we predict the structure of the caffeine molecule?

Geometry optimization problem (within the Born-Oppenheimer approximation):

What is the configuration of the atoms that minimizes the energy of the system?







What is the energy of a given configuration?

- System of M nuclei and N electrons
- Let $\mathbf{R}_k \in \mathbb{R}^3$ be the position of the k-th nucleus, and $z_k \in \mathbb{N}^*$ be its charge.

The energy of the system is well approximated by the quantity

$$\mathcal{E}_{\text{sys}}(\mathbf{R}_1, z_1; \cdots; \mathbf{R}_M, z_M) := \underbrace{\sum_{1 \le k < l \le M} \frac{z_k z_l}{|\mathbf{R}_k - \mathbf{R}_l|}}_{\text{nucleus pair Coulomb repulsion}} + \underbrace{E_{\text{el}}(\mathbf{R}_1, z_1; \cdots; \mathbf{R}_M, z_N)}_{\text{quantum energy of the electrons}},$$

where E_{el} is given by a minimization problem over the set of wave functions.

Quantum representation of N-electrons

N electrons are represented by a wave function $\Psi(\mathbf{r}_1, \ldots, \mathbf{r}_N)$.
$|\Psi(\mathbf{r}_1, \ldots, \mathbf{r}_N)|^2$ is the probability density of observing electron 1 at $\mathbf{r}_1$, electron 2 at $\mathbf{r}_2$, ...

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

$$\mathcal{W}_N := \left\{ \Psi \in L^2(\mathbb{R}^{3N}),\ \|\Psi\|_{L^2} = 1,\ \|\nabla\Psi\|_{L^2} < \infty,\ \Psi \text{ satisfies } (PP) \right\}.$$

Energy of the electronic configuration Ψ:

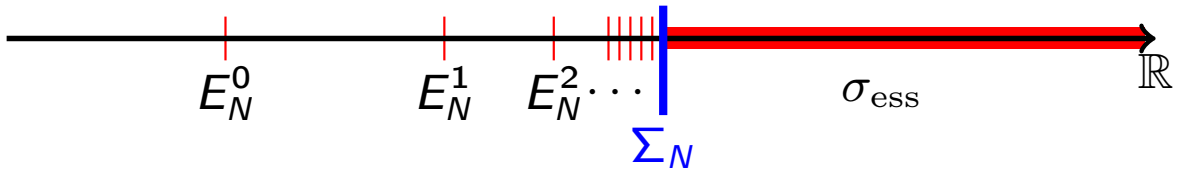
$$\mathcal{E}_{\mathrm{el}}(\Psi) = \left\langle \Psi \middle| \underbrace{\left(-\frac{1}{2}\sum_{i=1}^{N} \Delta_{\mathbf{r}_i} + \sum_{1 \le i < j \le N} \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|} + \sum_{i=1}^{N}\sum_{k=1}^{M} \frac{-z_k}{|\mathbf{r}_i - \mathbf{R}_k|} \right)}_{H_N} \Psi \right\rangle_{L^2(\mathbb{R}^{3N})}.$$

Ground state energy

$$E_{\mathrm{el}} = E_N^0 := \inf\left\{ \mathcal{E}_{\mathrm{el}}(\Psi),\ \Psi \in \mathcal{W}_N \right\} = \inf\left\{ \langle \Psi | H_N \Psi \rangle,\ \Psi \in \mathcal{W}_N \right\}.$$

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: $\Psi_N^0 \in \mathcal{W}_N$ such that $H_N \Psi_N^0 = E_N^0 \Psi_N^0$.

Problem: $\mathcal{W}_N \subset L^2(\mathbb{R}^{3N})$ 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.

The purpose of my thesis was to study mathematically some of these approximations.

Outline of my thesis

- Spin Density Functional Theory
  - *N-Representability in noncollinear spin-polarized density-functional theory* (published in Phys. Rev. Lett. 111 (2013), p. 153001).
  - *Pure-state N-representability in current-spin-density-functional theory* (accepted in CMS, (2015)).
  - *Existence of minimizers for Kohn–Sham within the local spin density approximation* (published in Nonlinearity 28.1 (2015), pp. 57–76).
- The GW method for finite systems
  - (with Éric Cancès and Gabriel Stoltz) *A mathematical analysis of the GW0 method for computing electronic excited energies of molecules* (arXiv 1506.01737).
- Numerical simulation of perfect crystals
  - (with Salma Lahbabi) *Convergence rates of supercell calculations in the reduced Hartree-Fock model* (arXiv 1507.00316).
  - (with Éric Cancès, Virginie Ehrlacher, Antoine Levitt and Damiano Lombardi) *Fast numerical methods for Brillouin-zone integration* (in preparation).

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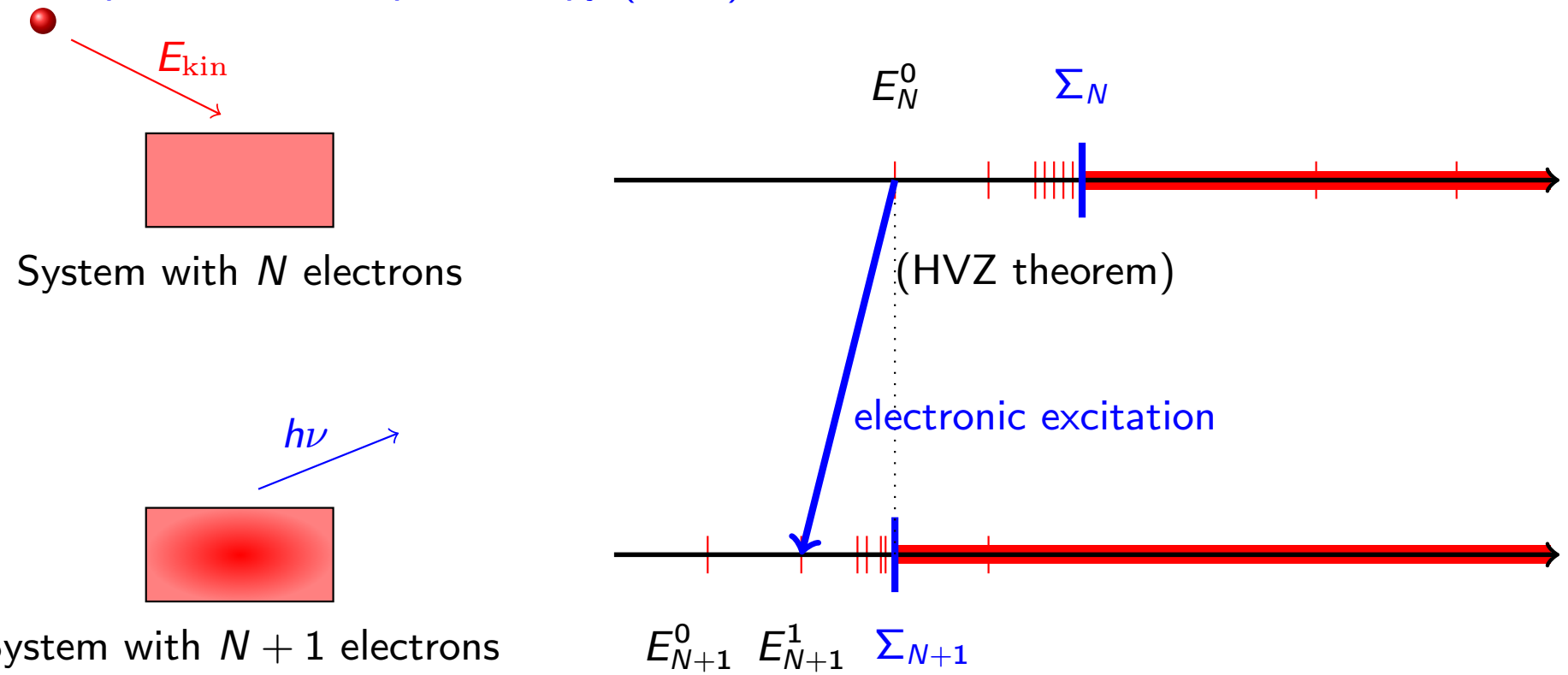
The GW method (L. Hedin. Phys. Rev. 1965)

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)

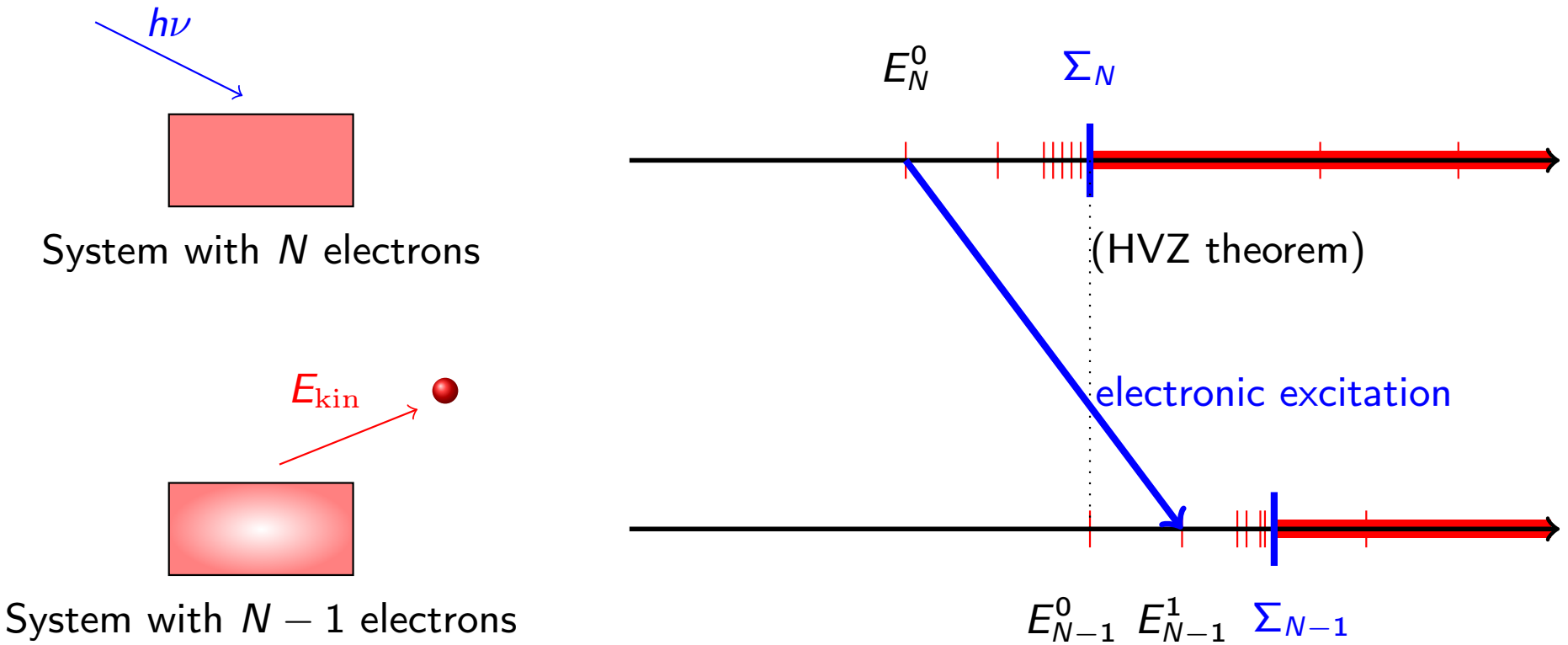


The GW method (L. Hedin. Phys. Rev. 1965)

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)



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)

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

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.

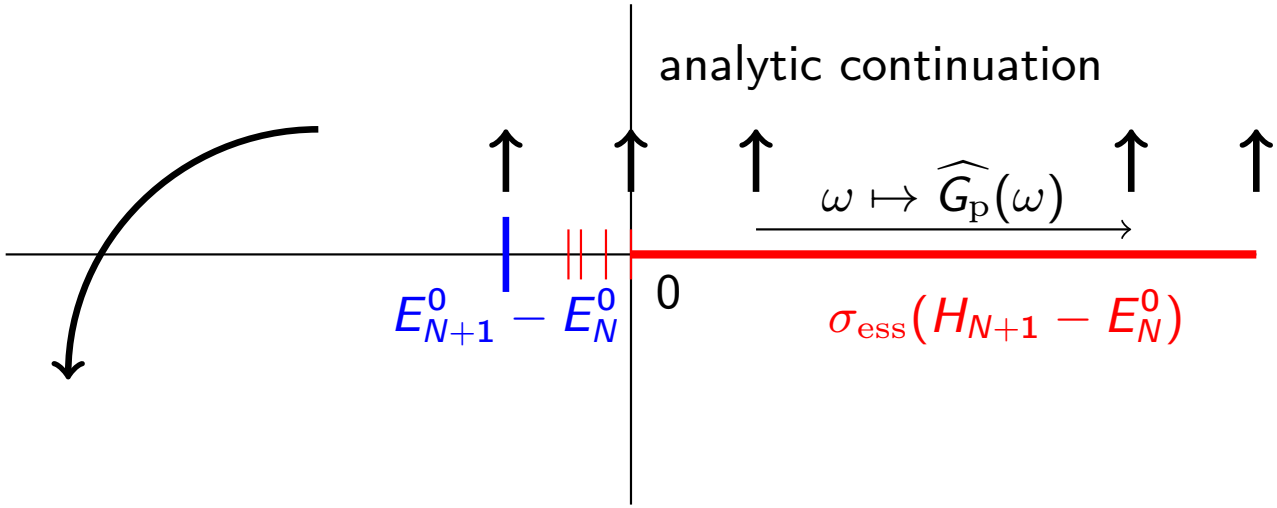
Laplace transform of the Green's function For $z \in \mathbb{U} = \{z \in \mathbb{C}, \mathrm{Im}\,(z) > 0\}$, define

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

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

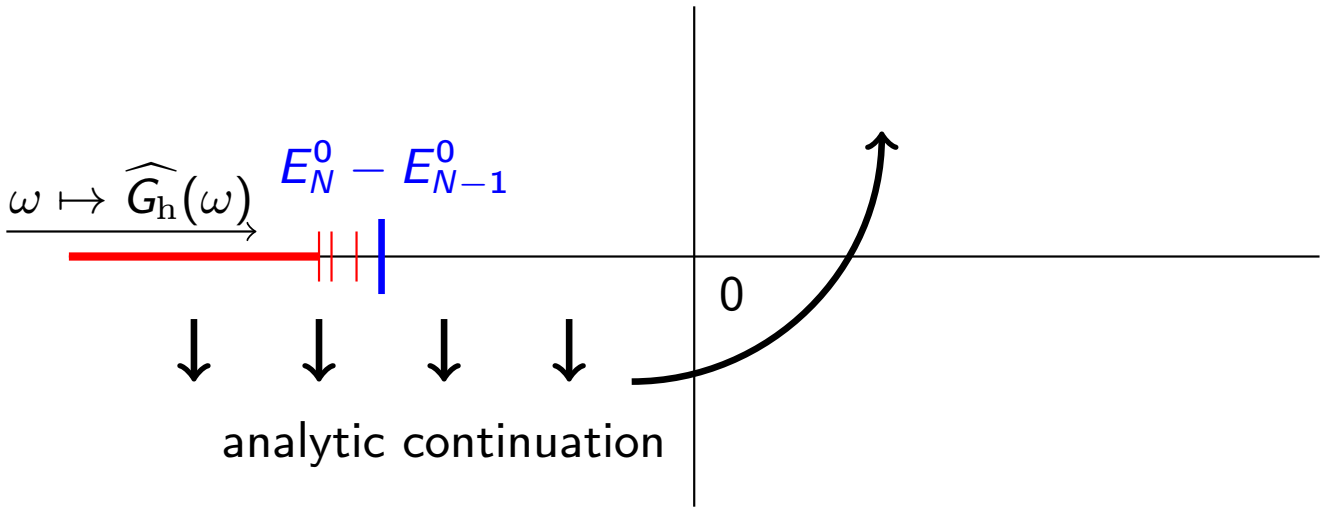
$$\widehat{G_{\mathrm{h}}}(\omega) = \left(\mathcal{F}_T G_{\mathrm{h}}\right)(\omega), \quad \widehat{G_{\mathrm{h}}} \in H^{-1}(\mathbb{R}_\omega, \mathcal{B}(\mathcal{H}_1)).$$

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

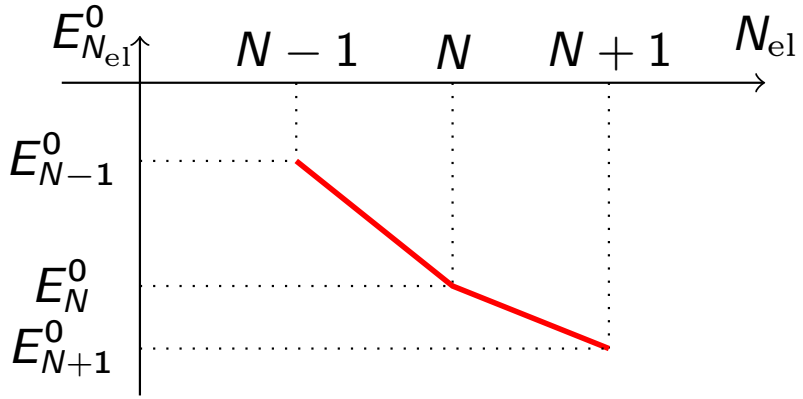
$$\forall z \in \mathbb{C} \setminus S_{\mathrm{h}}, \quad \widetilde{G_{\mathrm{h}}}(z) = A_-^* \left(\frac{1}{z - (E_N^0 - H_{N-1})}\right) A_-.$$



Definition of the total Green's function

Assumption: Stability condition

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

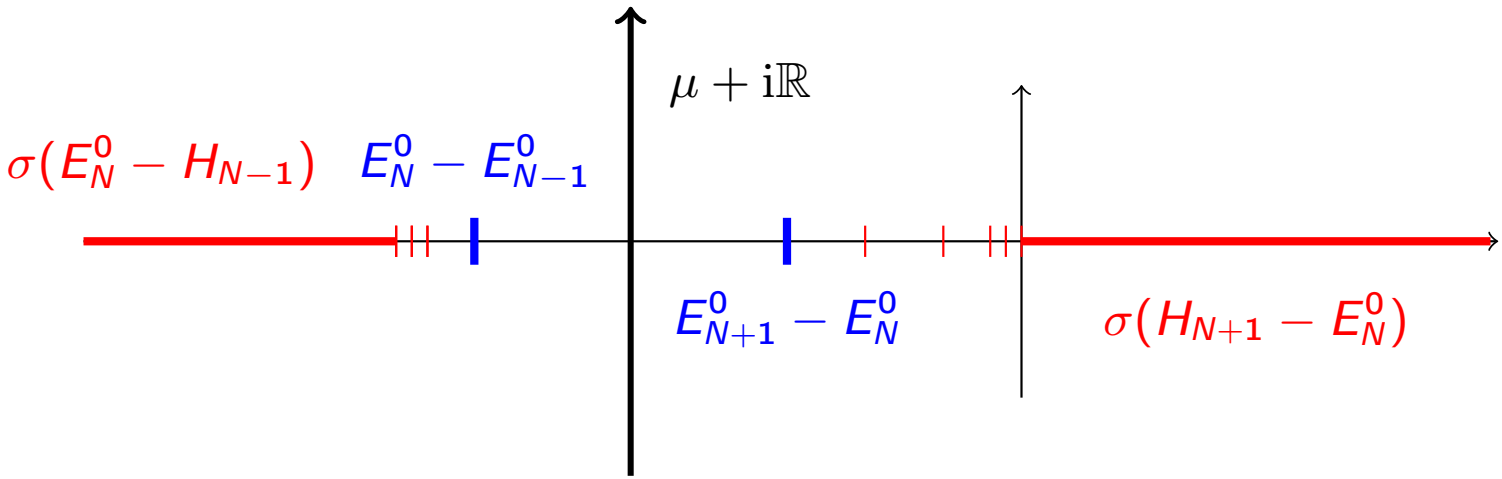


Chemical potential μ

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

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

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



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 μ_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 $\widetilde{\Sigma^{\mathrm{GW}}}(\mu + \mathrm{i}\omega)$

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

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

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

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

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The GW equations

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

- Dyson equation

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

- Self-energy

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

- Screened interaction

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

- Irreducible polarization

$$P^{\mathrm{GW}}(12) = -\mathrm{i} G^{\mathrm{GW}}(12) G^{\mathrm{GW}}(21).$$

Flow chart of the self-consistent GW scheme

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

Initialization

The GW equations

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

- Dyson equation

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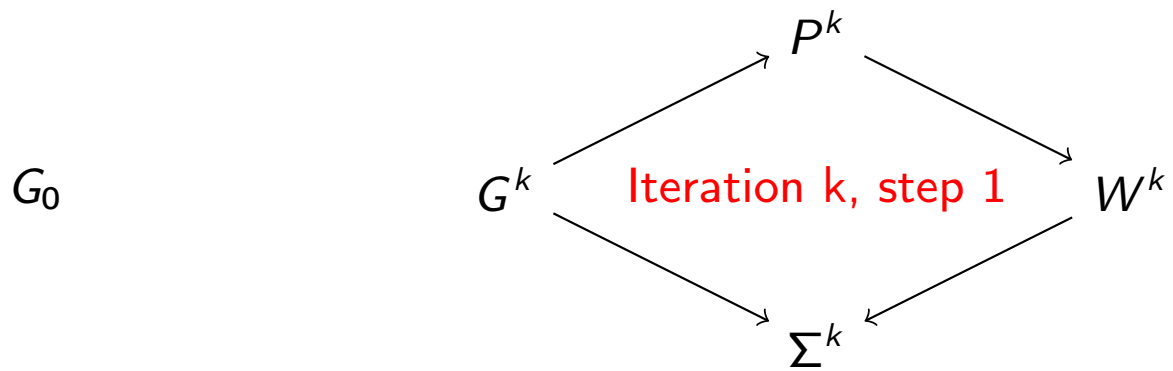

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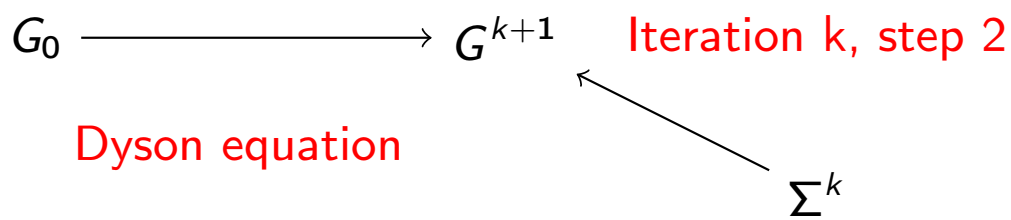
Flow chart of the self-consistent GW scheme



The GW^0 equations:

$$\boxed{\text{Fix } W^k = W^0.}$$

- Numerically faster,
- Accuracy similar to the full GW method.

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

- Dyson equation

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

- Self-energy

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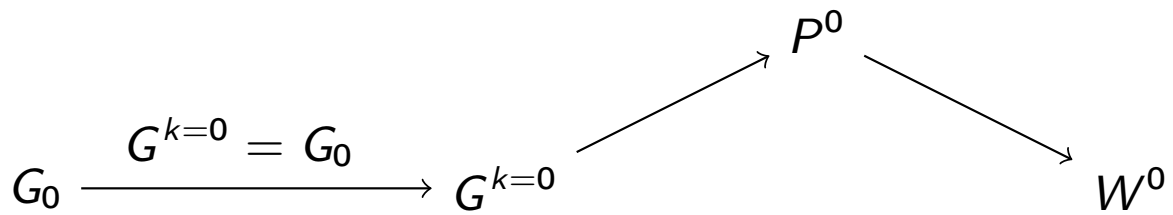
Flow chart of the self-consistent GW^0 scheme



Initialization

The GW^0 equations:

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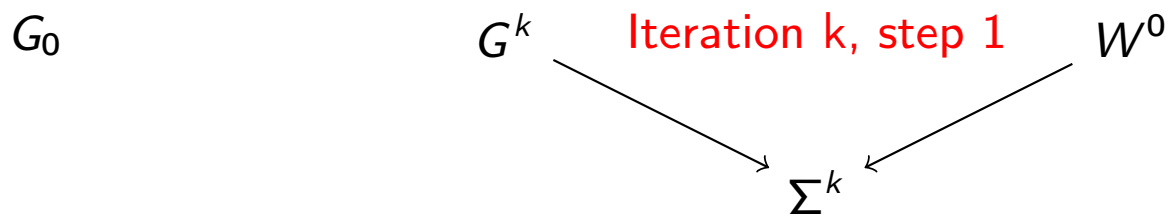

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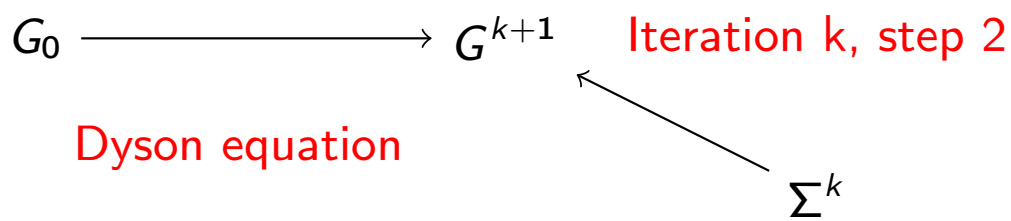

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Next step: give a sense to these equations

- Define the multiplication $A(12)B(21)$,
- Study the operators W and W^0,
- Transform the GW^0 equations on the time axis $\mathbb{R}_\tau$ into formally equivalent 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

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

Definition

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

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

Lemma

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

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

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

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

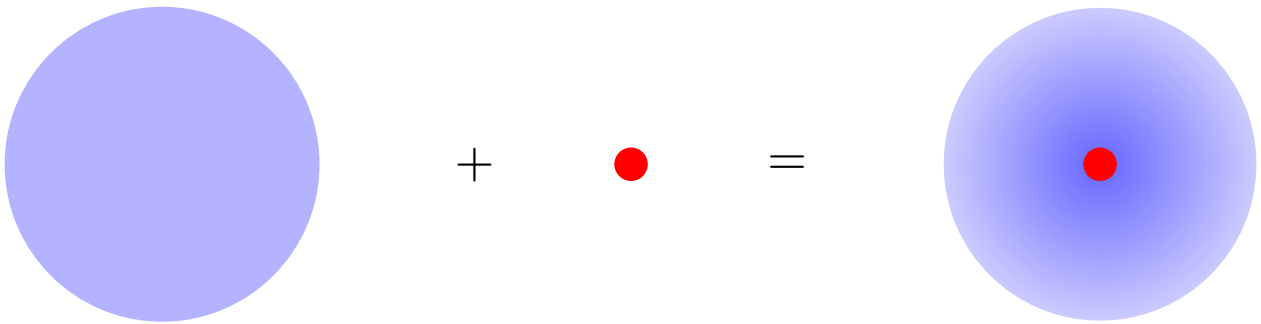
$$\boxed{v_c(\mathbf{r}, \mathbf{r}') = \frac{1}{|\mathbf{r} - \mathbf{r}'|} \quad \text{Coulomb operator.}}$$

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:

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

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

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

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 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 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)

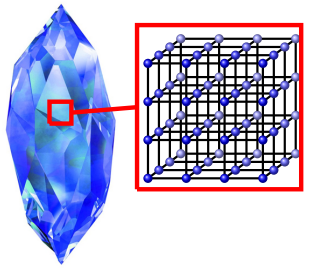
- *There exists $\lambda_* > 0$ such that, for all $0 \leq \lambda \leq \lambda_*$, there exists a unique solution $\widetilde{G^{\mathrm{GW}^0_\lambda}}$ to the problem (GW^0_λ) which is close to $\widetilde{G_0}$.*
- *Moreover, the self-consistent procedure starting from $\widetilde{G_0}$ converges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

Outline of my thesis

- Spin Density Functional Theory
  - *N-Representability in noncollinear spin-polarized density-functional theory* (published in Phys. Rev. Lett. 111 (2013), p. 153001).
  - *Pure-state N-representability in current-spin-density-functional theory* (accepted in CMS, (2015)).
  - *Existence of minimizers for Kohn–Sham within the local spin density approximation* (published in Nonlinearity 28.1 (2015), pp. 57–76).
- The GW method for finite systems
  - (with Éric Cancès and Gabriel Stoltz) *A mathematical analysis of the GW0 method for computing electronic excited energies of molecules* (arXiv 1506.01737).
- Numerical simulation of perfect crystals
  - (with Salma Lahbabi) *Convergence rates of supercell calculations in the reduced Hartree-Fock model* (arXiv 1507.00316).
  - (with Éric Cancès, Virginie Ehrlacher, Antoine Levitt and Damiano Lombardi) *Fast numerical methods for Brillouin-zone integration* (in preparation).

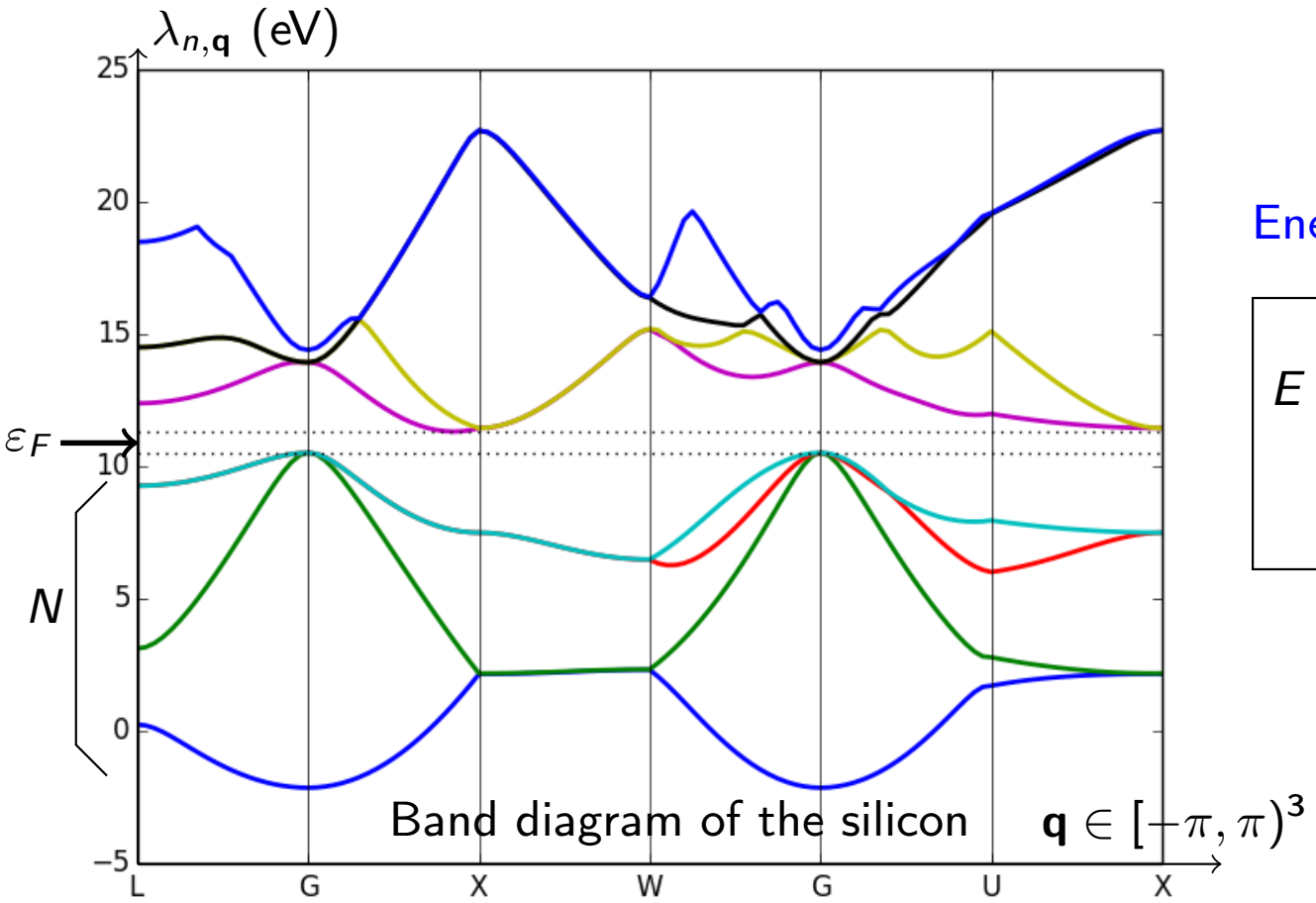
Periodic Hamiltonian Consider V_{per} a real-valued $\mathbb{Z}^3$-periodic function.

$$H_{\mathrm{per}} = -\frac{1}{2}\Delta + V_{\mathrm{per}} \quad \text{acting on} \quad L^2(\mathbb{R}^3).$$



Bloch theory

$$\sigma(H_{\mathrm{per}}) = \bigcup_{\mathbf{q}\in[-\pi,\pi)^3} \sigma(H_{\mathbf{q}}) \quad \text{with} \quad H_{\mathbf{q}} := \frac{1}{2}|-\mathrm{i}\nabla_{\mathrm{per}}+\mathbf{q}|^2+V_{\mathrm{per}} \quad \text{acting on} \quad L^2_{\mathrm{per}}([0,1)^3).$$



Energy per unit volume

$$E = \int_{[-\pi,\pi)^3} \underbrace{\left(\sum_{n=1}^{N} \lambda_{n,\mathbf{q}}\right)}_{e(\mathbf{q})} \mathrm{d}\mathbf{q}.$$

How to calculate E efficiently?

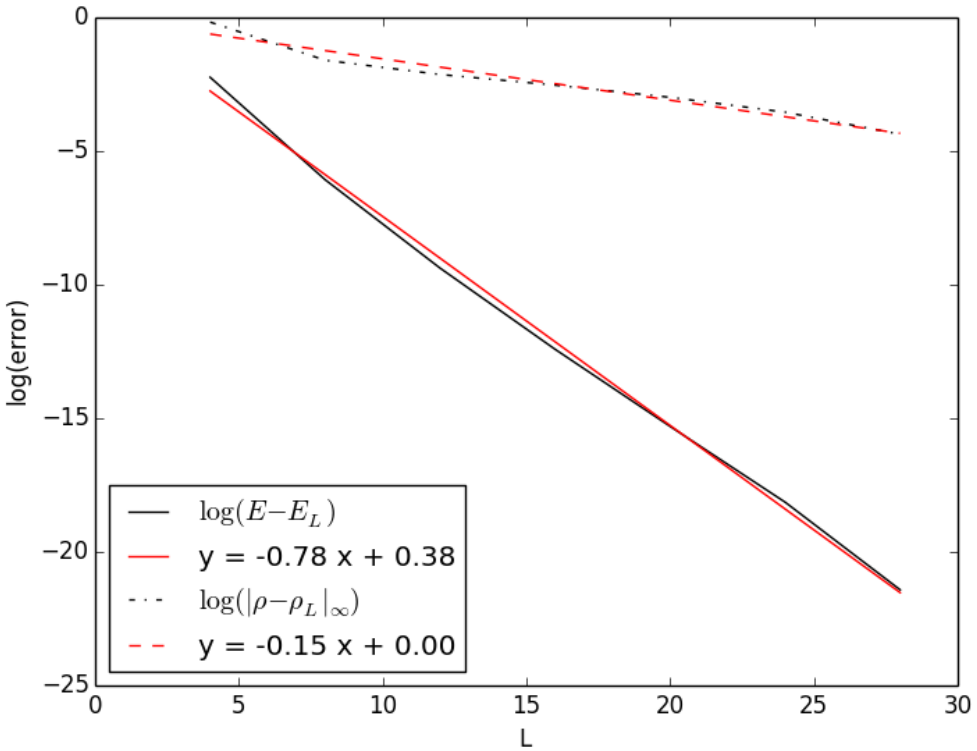
Energy per unit volume for the periodic supercell model. Introduce for $L \in \mathbb{N}^*$

$$E_L := \frac{1}{L^3} \sum_{\mathbf{Q}=[-L/2,L/2)^3} e\left(\frac{2\pi}{L}\mathbf{Q}\right) \quad \text{(Riemann sum)}.$$

$\Longrightarrow$ corresponds to the energy per unit cell for the periodic supercell model.

Theorem (DG, Salma Lahbabi)

- *The function* $\mathbf{q} \mapsto e(\mathbf{q})$ *is analytic on a strip* $\mathbb{R}^3 + \mathrm{i}[-A, A]^3$ *with* $A > 0$.
- *There exists* $C \in \mathbb{R}$ *and* $\alpha > 0$ *such that, for all* $L \in \mathbb{N}^*$, *it holds* $|E - E_L| \leq C\mathrm{e}^{-\alpha L}$.



Future work

- The GW method
  - 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.
- Numerical simulation of crystals
  - Study the speed of convergence of crystals with a local defect.
    with Salma Lahbabi
  - Design new algorithms to calculate the energy for metallic systems.
    with Éric Cancès, Virginie Ehrlacher, Antoine Levitt and Damiano Lombardi