An introduction to Green's function in many-body condensed-matter quantum systems

International summer School in electronic structure Theory: electron correlation in Physics and Chemistry

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June 17, 2015

Part I

Green's functions for non-interacting electrons

By non-interacting electrons, we mean systems described by one-body eigenstates $\{\phi(\mathbf{r})\}$ obeying a one-body Schrödinger equation. This includes mean-field approaches such as density functional theory, Hartree-Fock and hybrids !

- From the evolution operator to the retarded Green's function
- Defining the Green's functions we need: retarded, advanced, time-ordered
- Basics of Green's function perturbation theory

Green's function and inhomogeneous differential equations

(Wikipedia) George Green (14 July 1793 - 31 May 1841) was a British mathematical physicist who wrote An Essay on the Application of Mathematical Analysis to the Theories of Electricity and Magnetism (Green, 1828). In mathematics, a Green's function is the impulse response of an inhomogeneous differential equation, namely:

$$\mathcal{L}(x, d_x, ..)\phi(x) = S(x) \tag{1}$$

where S(x) is known and $\phi(x)$ to be found. We define the Green's function as the solution of:

$$\mathcal{L}(x, d_x, ..)G(x, x_0) = \delta(x - x_0) \tag{2}$$

The importance of the Green's function is that it can yields the solution of the inhomogeneous differential equation for any source S (Exercise):

$$\phi(x) = \int dx_0 \; G(x, x_0)S(x_0) \tag{3}$$

Green's function for the Laplacian

Consider Laplace's (3D) equation with right-end side delta-function:

$$\nabla^2 G(\mathbf{r}, \mathbf{r}_0) = \Delta G(\mathbf{r}, \mathbf{r}_0) = \delta(\mathbf{r} - \mathbf{r}_0).$$

It can be shown that:

$$G(\mathbf{r}, \mathbf{r}_0) = \frac{-1}{4\pi|\mathbf{r} - \mathbf{r}_0|}.$$

The solution of the Poisson equation in electrostatics:

$$\Delta V(\mathbf{r}) = -\rho(\mathbf{r})/\epsilon_0$$

(ρ charge density) is thus as expected:

$$V(\mathbf{r}) = \frac{1}{4\pi\epsilon_0} \int d\mathbf{r}_0 \frac{\rho(\mathbf{r}_0)}{|\mathbf{r} - \mathbf{r}_0|}.$$

Quantum mechanics reminder: the evolution operator U

The time evolution operator relates a quantum state at time (t) with the same quantum state at time (t_0): $\boxed{|\psi(t)\rangle = \hat{U}(t, t_0)|\psi(t_0)\rangle}$.

Plugging $|\psi(t)\rangle$ into Schrödinger equation:

$$i\hbar\frac{\partial}{\partial t}\hat{U}(t, t_0)|\psi(t_0)\rangle = \hat{H}(t)\hat{U}(t, t_0)|\psi(t_0)\rangle \Rightarrow i\hbar\frac{\partial}{\partial t}\hat{U}(t, t_0)| = \hat{H}(t)\hat{U}(t, t_0)$$

This implies using a Taylor expansion:

$$\hat{U}(t + dt, t) = \hat{U}(t, t) - \frac{i}{\hbar}\hat{H}(t)\hat{U}(t, t)dt = 1 - \frac{i}{\hbar}\hat{H}(t)dt$$

One therefore have (Exercise): $\hat{U}(t + dt, t)\hat{U}^{\dagger}(t + dt, t) = 1$ (unitarity).

If the Hamiltonian is time-independent: $\boxed{\hat{U}(t, t_0) = e^{-i\hat{H}(t-t_0)/\hbar}}$.

Quantum mechanics reminder: the propagator K

We look for an operator K such that:

$$\psi(\mathbf{r}_2 t_2) = \int d\mathbf{r}_1 K(\mathbf{r}_2 t_2, \mathbf{r}_1 t_1)\psi(\mathbf{r}_1 t_1)$$

We just need to introduce the closure relation in position representation:

$$\int d\mathbf{r}_1 |\mathbf{r}_1\rangle\langle\mathbf{r}_1| = 1$$

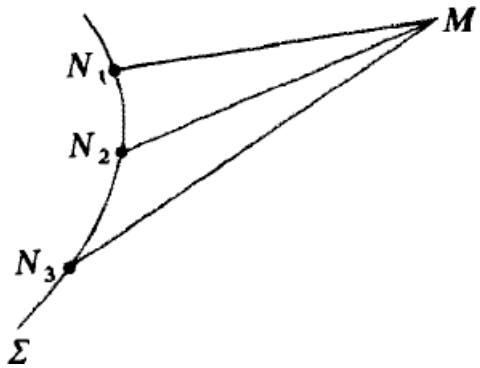


Figure. Huygens principle of the field in M as the contribution from secondary sources on surface Σ. From Quantum Mechanics, Chap. III, Complement J_{III}, Cohen-Tannoudji, Diu, Laloé.

into the definition of $\hat{U}$ to obtain (Exercise):

$$\psi(\mathbf{r}_2 t_2) = \int \langle\mathbf{r}_2|\hat{U}(t_2, t_1)|\mathbf{r}_1\rangle\psi(\mathbf{r}_1 t_1)d\mathbf{r}_1 \Rightarrow K(\mathbf{r}_2 t_2, \mathbf{r}_1 t_1) = \langle\mathbf{r}_2|\hat{U}(t_2, t_1)|\mathbf{r}_1\rangle$$

The propagator K propagates the probability amplitude: if we know the amplitude of probability for the system to be in state $\psi(\mathbf{r}_1 t_1)$ (for all $\mathbf{r}_1$), then we know the amplitude of probability for the system to be in $\psi(\mathbf{r}_2 t_2)$.

The retarded propagator K^r

We now define the retarded propagator, deciding that $\psi(\mathbf{r}_2 t_2)$ can only depend on the $\psi(\mathbf{r}_1 t_1)$ for times $(t_1 \leq t_2)$. We introduce the step (or Heaviside) function: $\theta(t_2 - t_1)$ which is equal to 1 for $(t_1 \leq t_2)$, and zero elsewhere. We then write, with the subscript (r) for retarded:

$$\boxed{K^r(\mathbf{r}_2 t_2, \mathbf{r}_1 t_1) = \theta(t_2 - t_1)\langle \mathbf{r}_2 | \hat{U}(t_2, t_1) | \mathbf{r}_1 \rangle}$$

To study the properties of K^r, we consider the case of a time independent Hamiltonian so that, introducing the closure relation over the $\{\varepsilon_n, \phi_n\}$ Hamiltonian stationary eigenstates:

$$\hat{U}(t_2, t_1) = e^{-i\hat{H}(t_2 - t_1)/\hbar} = \sum_n |\phi_n\rangle\langle\phi_n| e^{-i\varepsilon_n(t_2 - t_1)/\hbar}$$

with the related expression for K^r :

$$K^r(\mathbf{r}_2 t_2, \mathbf{r}_1 t_1) = \theta(t_2 - t_1) \sum_n \phi_n(\mathbf{r}_2)\phi_n^*(\mathbf{r}_1) e^{-i\varepsilon_n(t_2 - t_1)/\hbar}$$

The retarded propagator K^r as a Green's function

An important property of K^r that has been allowed by plugging the $\theta(t_2 - t_1)$ factor is that K^r verifies the following equation (**Exercise**):

$$\boxed{\left(i\hbar\frac{\partial}{\partial t_2} - \hat{H}(\mathbf{r}_2, \nabla_2)\right) K^r(\mathbf{r}_2 t_2, \mathbf{r}_1 t_1) = i\hbar\delta(t_2 - t_1)\delta(\mathbf{r}_2 - \mathbf{r}_1)}$$

where we have used the property: $\partial\theta(t_2 - t_1)/\partial t_2 = \delta(t_2 - t_1)$.

The retarded propagator is thus the solution of the Schrödinger equation with "delta" source terms in the right-hand-side: it is reminiscent of the definition of Green's functions in mathematics. To avoid the $(i\hbar)$ term in the right-hand-side, it is customary to defines the quantum retarded Green's function as:

$$i\hbar G^r(\mathbf{r}_2 t_2, \mathbf{r}_1 t_1) = K^r(\mathbf{r}_2 t_2, \mathbf{r}_1 t_1) = \theta(t_2 - t_1)\langle \mathbf{r}_2 | \hat{U}(t_2, t_1) | \mathbf{r}_1 \rangle$$

Exercise

$$\left(\frac{\partial}{\partial t_2}\theta(t_2-t_1)\right)\sum_n \phi_n(\mathbf{r}_2)\phi_n^*(\mathbf{r}_1)e^{-i\varepsilon_n(t_2-t_1)/\hbar}$$
$$= \delta(t_2-t_1)\sum_n \phi_n(\mathbf{r}_2)\phi_n^*(\mathbf{r}_1)e^{-i\varepsilon_n(t_2-t_1)/\hbar}$$
$$= \delta(t_2-t_1)\sum_n \phi_n(\mathbf{r}_2)\phi_n^*(\mathbf{r}_1)$$
$$= \delta(t_2-t_1)\delta(\mathbf{r}_2-\mathbf{r}_1)$$

and:

$$\left(i\hbar\frac{\partial}{\partial t_2} - \hat{H}(\mathbf{r}_2,\nabla_2)\right)\phi_n(\mathbf{r}_2)e^{-i\varepsilon_n t_2/\hbar} = 0$$

The delta-functions come from the Heaviside term.

Complement: The advanced Green's function

We can also define an advanced Green's function such that:

$$i\hbar G^a(\mathbf{r}_2 t_2, \mathbf{r}_1 t_1) = -\theta(t_1 - t_2)\langle \mathbf{r}_2 | \hat{U}(t_2, t_1) | \mathbf{r}_1 \rangle$$

which is non-zero for $t_1 \geq t_2$. Then:

$$i\hbar G^a(\mathbf{r}_2 t_2, \mathbf{r}_1 t_1) = -\theta(t_1 - t_2) \sum_n \phi_n(\mathbf{r}_2)\phi_n^*(\mathbf{r}_1) e^{-i\varepsilon_n(t_2 - t_1)/\hbar}$$

$$\left(i\hbar \frac{\partial}{\partial t_2} - \hat{H}(\mathbf{r}_2, \nabla_2) \right) G^a(\mathbf{r}_2 t_2, \mathbf{r}_1 t_1) = \delta(t_2 - t_1)\delta(\mathbf{r}_2 - \mathbf{r}_1)$$

G^r and G^a satisfy the very same equation, but with different "boundary conditions" on time.

Complement: The time-ordered Green's function

Let's play a bit to show that we have many choices to define Green's function that can be useful to extract quantities we may need. We define now, introducing the chemical potential μ:

$$i\hbar G^T(\mathbf{r}_2 t_2, \mathbf{r}_1 t_1) = \theta(t_2 - t_1) \sum_n \theta(\varepsilon_n - \mu)\phi_n(\mathbf{r}_2)\phi_n^*(\mathbf{r}_1)e^{-i\varepsilon_n(t_2-t_1)/\hbar} - \theta(t_1 - t_2) \sum_n \theta(\mu - \varepsilon_n)\phi_n(\mathbf{r}_2)\phi_n^*(\mathbf{r}_1)e^{-i\varepsilon_n(t_2-t_1)/\hbar}$$

Then again: $\left(i\hbar\frac{\partial}{\partial t_2} - \hat{H}(\mathbf{r}_2, \nabla_2)\right) G^T(\mathbf{r}_2 t_2, \mathbf{r}_1 t_1) = \delta(t_2 - t_1)\delta(\mathbf{r}_2 - \mathbf{r}_1)$

A nice thing with G^T is that we have separated occupied and unoccupied (virtual) states thanks to the $\theta(\mu - \varepsilon_n)$ factor. As a consequence:

$$-i\hbar G^T(\mathbf{r}_2 t_2, \mathbf{r}_1 t_1) = \theta(\mu - \varepsilon_n) \sum_n \phi_n(\mathbf{r}_2)\phi_n^*(\mathbf{r}_1), \quad \text{for} \quad t_1 = t_2 + 0^+$$

which is nothing but the one-particle density matrix.

Green's function perturbation theory basics

We consider the eigensolutions of the Schrödinger equation with/without a potential V that we consider as the "perturbation":

$$\begin{aligned} [i\partial_t - H_0(r, \nabla_r) - V(\mathbf{r})]\, \psi(\mathbf{r}t) &= 0 \\ [i\partial_t - H_0(r, \nabla_r)]\, \psi_0(\mathbf{r}t) &= 0 \end{aligned}$$

and the corresponding Green's function:

$$\begin{aligned} [i\partial_t - H_0(r, \nabla_r) - V(r)]\, G(\mathbf{r}t, \mathbf{r}'t') &= \delta(\mathbf{r} - \mathbf{r}')\delta(t - t') \\ [i\partial_t - H_0(r, \nabla_r)]\, G_0(\mathbf{r}t, \mathbf{r}'t') &= \delta(\mathbf{r} - \mathbf{r}')\delta(t - t'). \end{aligned}$$

Then (Exercise):

$$\begin{aligned} \psi(\mathbf{r}t) &= \psi_0(\mathbf{r}t) + \int\int d\mathbf{r}'dt'\, G_0(\mathbf{r}t, \mathbf{r}'t')V(\mathbf{r}')\psi(\mathbf{r}'t') \\ \psi(\mathbf{r}t) &= \psi_0(\mathbf{r}t) + \int\int d\mathbf{r}'dt'\, G(\mathbf{r}t, \mathbf{r}'t')V(\mathbf{r}')\psi_0(\mathbf{r}'t') \end{aligned}$$

Perturbation theory and the Dyson equation

From the previous equations (dropping the integration variables) :

$$\begin{aligned}\psi &= \psi_0 + G_0 V(\psi_0 + G_0 V\psi) \\ &= \psi_0 + G_0 V\psi_0 + G_0 V G_0 V(\psi_0 + G_0 V\psi) \\ &= \psi_0 + (G_0 + G_0 V G_0 + G_0 V G_0 V G_0 + ...) V\psi_0\end{aligned}$$

which lays the fundaments of a perturbation theory in terms of successive orders of the "scattering potential" V. Comparing with the last equation of the previous slide, one ends up with the so-called Dyson equation:

$$G = G_0 + G_0 V G \quad \text{or symbolically:} \quad G^{-1} = G_0^{-1} - V.$$

namely, with e.g. $1 = (\mathbf{r}_1 t_1)$ and $V(34) = V(\mathbf{r}_3)\delta(\mathbf{r}_3 - \mathbf{r}_4)\delta(t_3 - t_4)$:

$$G(12) = G_0(12) + \int\int d2d3\ G_0(13) V(34) G(42),$$

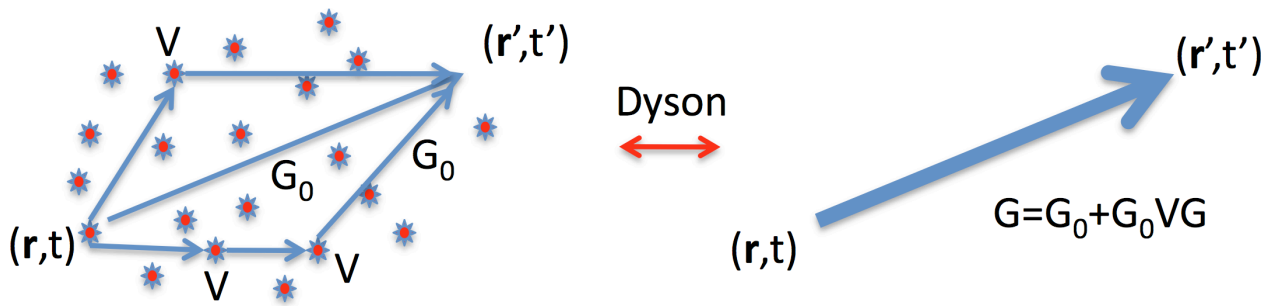
Note that G is known to all orders in V (assuming G_0 and V known) !

The quantum billiard

We have seen that:

$$G = G_0 + G_0 V G = G_0 + G_0 V G_0 + G_0 V G_0 V G_0 + ...$$

This represents the amplitude of probability of going from (**r**t) to (**r**'t') without "collision" (G_0), with one collision ($G_0 V G_0$), with two collisions ($G_0 V G_0 V G_0$).



Note that contrary to a true billiard, the interaction can be long range.

Part II: Green's functions for interacting electrons

- Second quantization: creation/destruction and field operators
- Schrödinger and Heisenberg representation
- Definition: the time-ordered one-particle Green's function

References:

- A. L. Fetter and J. D. Walecka, Quantum Theory of Many-Particle Physics (McGraw-Hill, New York, 1971),
- R. D. Mattuck, A Guide to Feynmnan Diagrams in the Many-Body Problem, (McGraw-Hill, 1976) [reprinted by Dover, 1992].

Creation/destruction operators

We define the "vacuum" state $|0>$ with zero particles.

We then define the "creation operator" $(c_i^\dagger)$ that puts one particle in orbital ϕ_i: $c_i\dagger|0>=|n_i=1>$.

The destruction operator (c_i) can remove the particle from this state: $c_i c_i\dagger|0>=c_i|n_i=1>=|0>$.

To preserve the anti-symmetry of fermionic wavefunctions:

$$\left\{c_i^\dagger, c_j^\dagger\right\}=0 \quad \text{and its adjoint } \{c_i, c_j\}=0, \quad \text{with:} \quad \left\{\hat{A}, \hat{B}\right\}=\hat{A}\hat{B}+\hat{B}\hat{A}.$$

In particular: $c_i^\dagger c_i^\dagger = c_i c_i = 0$ (nul operator) since for fermions one cannot create two particles in the same quantum state.

Creation/destruction operators (II)

Further: $c_i^\dagger c_i | n_1, n_2, ..., n_i, ... >= n_i | n_1, n_2, ..., n_i, ... >$.

$c_i^\dagger c_i = \hat{n}_i$ count the number of particles in orbital (i).

Consequently: $\sum_i \hat{n}_i = \hat{N}$ counts the number of fermions in the system.

Considering all possible cases (n_i or $n_j = 0, 1$ for fermions), one find that:

$$\left\{ c_i^\dagger, c_j \right\} = \delta_{ij} \quad \textit{namely} : \quad c_i^\dagger c_j + c_j c_i^\dagger = \delta_{ij}.$$

which allows e.g. to demonstrate the normalization of:

$$|...n_i...\rangle = \prod_i (c_i^+)^{n_i} |0\rangle$$

Change of basis and the field operator

From the set of (creation/destruction) operators associated with a basis $|\alpha\rangle$, one can by using the closure relation: $\sum_\alpha |\alpha\rangle\langle\alpha| = 1$ obtain the creation/destruction operators in another $|\beta\rangle$ basis:

$$c_\beta^\dagger|0\rangle = |\beta\rangle = \sum_\alpha \langle\alpha|\beta\rangle|\alpha\rangle = \sum_\alpha \langle\alpha|\beta\rangle c_\alpha^\dagger|0\rangle$$

so that (with a similar demonstration for the destruction operator):

$$c_\beta^\dagger = \sum_\alpha < \alpha|\beta > c_\alpha^\dagger \text{ and: } c_\beta = \sum_\alpha < \beta|\alpha > c_\alpha.$$

A special basis is given by the $|\mathbf{r}\rangle$ position representation, yielding the field operators:

$$"c_\mathbf{r}" = \hat{\psi}(\mathbf{r}) = \sum_\alpha \langle\mathbf{r}|\alpha\rangle c_\alpha = \sum_\alpha \phi_\alpha(\mathbf{r}) c_\alpha$$

Field operators: properties and interpretation

They verify the standard (fermionic) commutation relations:

$$\left\{\hat{\psi}(\mathbf{r}), \hat{\psi}(\mathbf{r}')\right\} = 0, \quad \text{and:} \quad \left\{\hat{\psi}(\mathbf{r}), \hat{\psi}^{\dagger}(\mathbf{r}')\right\} = \delta(\mathbf{r} - \mathbf{r}').$$

For an interpretation, let's act with the creation field onto the vacuum state and take the associated probability amplitude in ($\mathbf{r}'$):

$$< \mathbf{r}'|\hat{\psi}^{\dagger}(\mathbf{r})|0 >=< \mathbf{r}'| \sum_{\alpha} \phi^{*}_{\alpha}(\mathbf{r}) c^{\dagger}_{\alpha}|0 >= \sum_{\alpha} \phi^{*}_{\alpha}(\mathbf{r}) < \mathbf{r}'|\alpha >= \delta(\mathbf{r} - \mathbf{r}').$$

The field operator $\hat{\psi}^{\dagger}(\mathbf{r})$ adds a particle in the "state" $|\mathbf{r}>$, namely creates a particle (fermion) in ($\mathbf{r}$) ! The destruction operator $\hat{\psi}(\mathbf{r})$ destroys it. We can also define the number-of-particle operator:

$$\hat{N} = \sum_{\alpha} c^{\dagger}_{\alpha} c_{\alpha} = \int d\mathbf{r}\ \hat{\rho}(\mathbf{r}) \quad \text{with:} \quad \hat{\rho}(\mathbf{r}) = \hat{\psi}^{\dagger}(\mathbf{r})\hat{\psi}(\mathbf{r})$$

which counts the number of particles in the (α) states or as a function of their space location. $\hat{\rho}(\mathbf{r})$ is the density operator.

The (usual) Schrödinger representation

Assume the standard many-body Hamiltonian $\hat{H}$:

$$\hat{H} = \sum_{i=1}^{N} \frac{-\hbar^2 \nabla^2}{2m_e} + \sum_{I,i} \frac{1}{4\pi\epsilon_0} \frac{-Z_I}{|\mathbf{R}_I - \mathbf{r}_i|} + \frac{1}{2} \sum_{i \neq j} \frac{1}{4\pi\epsilon_0} \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|}$$

where $\{\mathbf{R}_I, Z_I\}$ are the ions position and charge, while the $\{\mathbf{r}_i\}$ (i=1,N) indicate the position of the N-electrons in the system. Such an Hamiltonian is time-independent. On the contrary, the eigen-wavefunctions are time-dependent, satisfying the Schrödinger equation:

$$i\hbar \frac{d|\psi_S(t)>}{dt} = \hat{H}\psi_S(t), \quad \Rightarrow |\psi_S(t)> = e^{-i\hat{H}(t-t_0)/\hbar}|\psi_S(t_0)>,$$

where we use the (S)-index for "Schrödinger".

The Heisenberg representation

We now define the eigenstates in the Heisenberg representation:

$$|\psi_H(t)>=\exp(i\hat{H}t/\hbar)|\psi_S(t)> \quad \Rightarrow i\hbar\frac{d|\psi_H(t)>}{dt}=0.$$

Concerning the operators in such a representation:

$$\begin{aligned}<\psi_S^{'}|\hat{O}_S|\psi_S> &=<\psi_H^{'}|\exp(i\hat{H}t/\hbar)\hat{O}_S\exp(-i\hat{H}t/\hbar)|\psi_H> \\ &=<\psi_H^{'}|\hat{O}_H(t)|\psi_H>,\end{aligned}$$

with: $\hat{O}_H(t)=\exp(i\hat{H}t/\hbar)\hat{O}_S\exp(-i\hat{H}t/\hbar)$, so that (Exercice):

$i\hbar\frac{d\hat{O}_H(t)}{dt}=[\hat{O}_H(t),\hat{H}]$. The time evolution is now in the operator !

The time-ordered single-particle Green's function

We DEFINE the time-ordered single-particle Green's function as follows:

$$i\hbar G(\mathbf{r}t,\mathbf{r}'t') = \frac{< \psi_H^0 | T\left[\hat{\psi}_H(\mathbf{r}t)\hat{\psi}_H^\dagger(\mathbf{r}'t')\right] |\psi_H^0 >}{< \psi_H^0 | \psi_H^0 >},$$

where:

- $|\psi_H^0 >$ is the ground-state many-body wave function in the Heisenberg representation (time-independent),
- $\hat{\psi}_H(\mathbf{r}t)$ and $\hat{\psi}_H^\dagger(\mathbf{r}'t')$ are the destruction/creation field operators in the Heisenberg representation (time-dependent),
- T is the time-ordering operator, that orders the operators from left to right according to decreasing time (earliest on the right) with a (-1) factor for each permutation needed (for fermions).

The time-ordered single-particle Green's function (II)

We use the definition of the time-ordering operator:

$$i\hbar G(\mathbf{r}t,\mathbf{r}'t') = \frac{<\psi_H^0|\hat{\psi}_H(\mathbf{r}t)\hat{\psi}_H^\dagger(\mathbf{r}'t')|\psi_H^0>}{<\psi_H^0|\psi_H^0>} \quad t \geq t',$$

$$= -\frac{<\psi_H^0|\hat{\psi}_H^\dagger(\mathbf{r}'t')\hat{\psi}_H(\mathbf{r}t)|\psi_H^0>}{<\psi_H^0|\psi_H^0>} \quad t < t'.$$

or with: $|\psi_H^0>= e^{i\hat{H}t/\hbar}|\psi_S^0(t)>$ and $\hat{O}_H(\mathbf{r}t) = e^{i\hat{H}t/\hbar}\hat{O}_S(\mathbf{r})e^{-i\hat{H}t/\hbar}$:

$$i\hbar G(\mathbf{r}t,\mathbf{r}'t') = \theta(t-t')<\psi_S^0(t)|\hat{\psi}_S(\mathbf{r})e^{-i\hat{H}(t-t')/\hbar}\hat{\psi}_S^\dagger(\mathbf{r}')|\psi_S^0(t')>$$
$$-\theta(t'-t)<\psi_S^0(t')|\hat{\psi}_S^\dagger(\mathbf{r}')e^{-i\hat{H}(t'-t)/\hbar}\hat{\psi}_S(\mathbf{r})|\psi_S^0(t)>,$$

where we have taken $|\psi_H^0>$ to be normalised.

The electron-propagator

Can we understand the following term ?

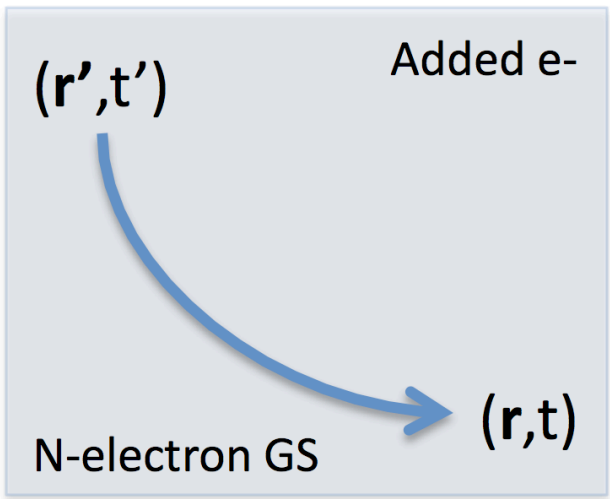
$$i\hbar G(\mathbf{r}t, \mathbf{r}'t') = \theta(t-t') < \psi_S^0(t)|\hat{\psi}_S(\mathbf{r})e^{-i\hat{H}(t-t')/\hbar}\hat{\psi}_S^\dagger(\mathbf{r}')|\psi_S^0(t') >$$

- $\hat{\psi}_S^\dagger(\mathbf{r}')|\psi_S^0(t') >$ represents a state with one electron added in $(\mathbf{r})'$ to the N-electron ground-state at time (t'),
- $e^{i\hat{H}(t-t')/\hbar}$ propagates this state from time (t') to time (t),
- finally, one project this state onto $< \psi_S^0(t)|\hat{\psi}_S(\mathbf{r})|$ that is the bra of the $\hat{\psi}_S^\dagger(\mathbf{r})|\psi_S^0(t) >$ ket, a state with one electron added in $(\mathbf{r})$ to the N-electron ground-state at time (t).

The final projection measures how much the $\hat{\psi}_S^\dagger(\mathbf{r}')|\psi_S^0(t') >$ (N+1)-electron-state overlaps after a (t-t') delay with the $\hat{\psi}_S^\dagger(\mathbf{r})|\psi_S^0(t) >$ (N+1)-electron-state.

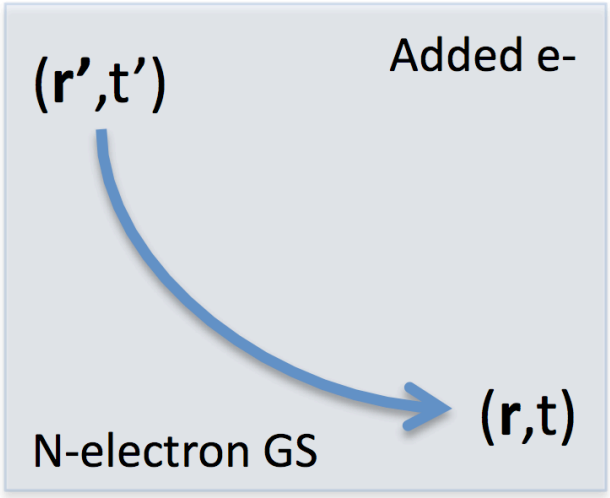
The electron-propagator (II)

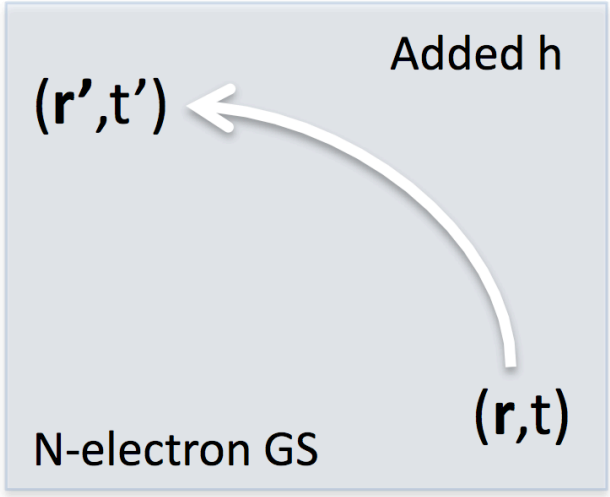
Remember that a wave function $\psi(\mathbf{r}_1, \mathbf{r}_2, ...)$ represents the amplitude of probability of finding en electron in $(\mathbf{r}_1)$, another one in $(\mathbf{r}_2)$, etc. As such, the process described here above can be interpreted as the amplitude of probability of finding an additional electron in $(\mathbf{r}t)$ - additional to the N-electron ground-state - having previously added an additional electron in $(\mathbf{r}'t')$ to the N-electron ground-state.



The one-body Green's function can be interpreted as a propagator of the added electron. Note that while describing the evolution of "one" electron from $(\mathbf{r}'t')$ to $(\mathbf{r}t)$, it is a true many-body quantity accounting for all interactions (including the exchange!)

The hole-propagator





We now examine $G(\mathbf{r}t, \mathbf{r}'t')$ for $t < t'$.

$$i\hbar G(\mathbf{r}t, \mathbf{r}'t') = -\theta(t' - t)\times$$
$$< \psi_S^0(t')|\hat{\psi}_S^\dagger(\mathbf{r}')e^{-i\hat{H}(t'-t)/\hbar}\hat{\psi}_S(\mathbf{r})|\psi_S^0(t) >$$

Here we create a hole in (**r**) at time ($t < t'$) in the N-electron ground-state and propagate this (N-1)-electron state from (t) to (t') where we project it onto the (N-1)-electron state where a hole has been created in (**r**'). Again this is associated with the amplitude of probability for the hole to move from ($\mathbf{r}t$) to ($\mathbf{r}'t'$).

Lehman amplitudes

Let's consider:

$$i\hbar G^{>}(\mathbf{r}t,\mathbf{r}'t') = \boxed{\langle\psi_S^0(t)|\hat{\psi}_S(\mathbf{r})\; e^{-i\hat{H}(t-t')/\hbar}\hat{\psi}_S^{\dagger}(\mathbf{r}')|\psi_S^0(t')\rangle}$$

With $\left\{E_n^{N+1},\psi_H^{n,N+1}\right\}$ the eigenstates of the (N+1) electron system:

$$e^{-i\hat{H}(t-t')/\hbar} = \sum_n e^{-iE_n^{N+1}(t-t')/\hbar}|\psi_H^{n,N+1}\rangle\langle\psi_H^{n,N+1}|$$

$$\text{and}\quad |\psi_S^0(t')\rangle = e^{-iE_0^N t'/\hbar}|\psi_H^0\rangle, \qquad \langle\psi_S^0(t)| = \langle\psi_H^0|e^{iE_0^N t/\hbar}$$

we obtain (with the "overbar" for the complex conjugate) :

$$\langle\psi_S^0(t)|\hat{\psi}_S(\mathbf{r})\; e^{-i\hat{H}(t-t')/\hbar}\hat{\psi}_S^{\dagger}(\mathbf{r}')|\psi_S^0(t')\rangle = \boxed{\sum_n f_n^{N+1}(\mathbf{r})\overline{f}_n^{N+1}(\mathbf{r}')e^{-i\varepsilon_n^{N+1}(t-t')/\hbar}}$$

$f_n^{N+1}(\mathbf{r}) = \langle\psi_H^0|\hat{\psi}_S(\mathbf{r})|\psi_H^{n,N+1}\rangle$ is called an (addition) Lehman amplitude.

$\varepsilon_n^{N+1} = (E_n^{N+1} - E_0^N)$ is an addition energy.

Lehman amplitudes (II)

We can proceed similarly with the hole-related part of the Green's function to obtain:

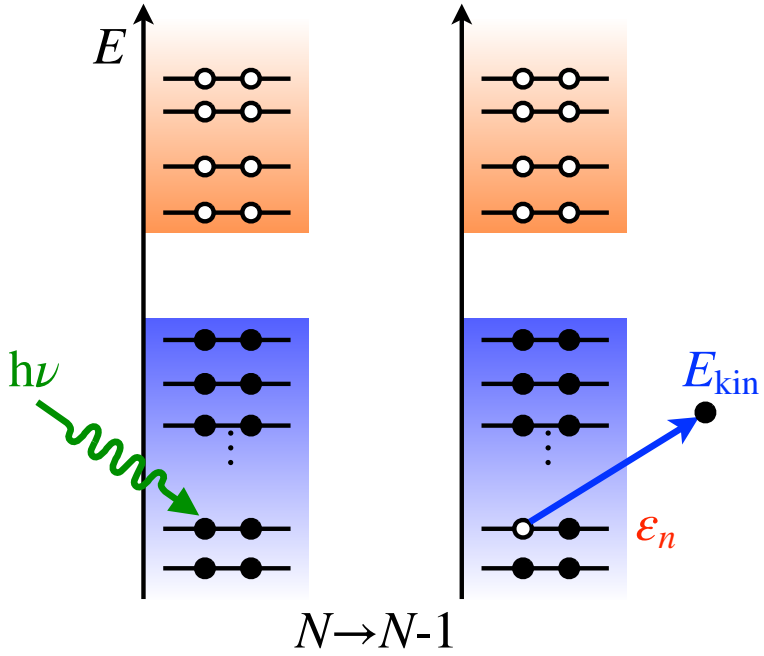
$$i\hbar G(\mathbf{r}t,\mathbf{r}'t') = \theta(t-t')\sum_n f_n^{N+1}(\mathbf{r})\overline{f}_n^{N+1}(\mathbf{r}')e^{-i\varepsilon_n^{N+1}(t-t')/\hbar} - \theta(t'-t)\sum_n f_n^{N-1}(\mathbf{r})\overline{f}_n^{N-1}(\mathbf{r}')e^{-i\varepsilon_n^{N-1}(t-t')/\hbar}$$

where we have introduce the Lehman removal amplitude and removal energies:

$$f_n^{N-1}(\mathbf{r}) = \langle \psi_H^{n,N-1}|\hat{\psi}_S(\mathbf{r})|\psi_H^0\rangle \quad \text{and} \quad \varepsilon_n^{N-1} = (E_0^N - E_n^{N-1})$$

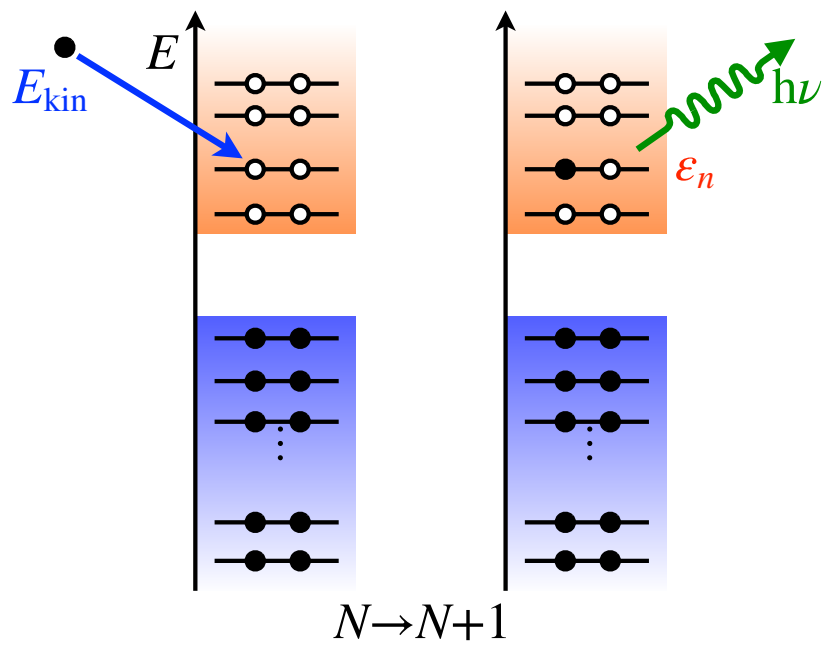
This form is very reminiscent of the independent electron Green's function, but one should not identify the Lehman amplitudes as one-body wavefunctions (except for non-interacting electron systems, see below).

Addition/removal energies and photoemission experiments



Energy conservation:
$h\nu + E_0^N = E_{kin} + E_n^{N-1}$

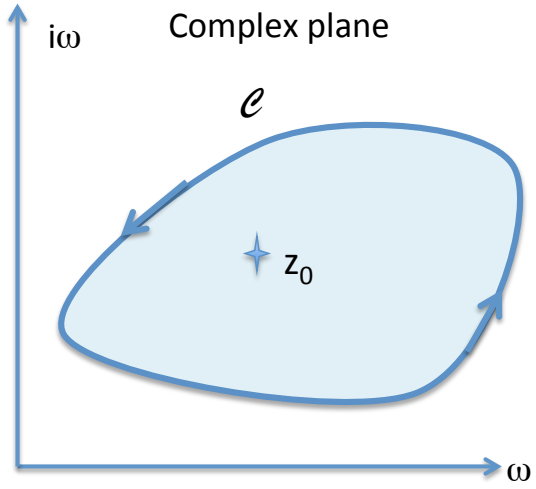
Identify:
$\varepsilon_n^{N-1} = E_0^N - E_n^{N-1} \ \ (< \mu).$



Energy conservation:
$E_{kin} + E_0^N = h\nu + E_n^{N-1}$

Identify:
$\varepsilon_n^{N+1} = E_n^{N+1} - E_0^N \ \ (> \mu).$

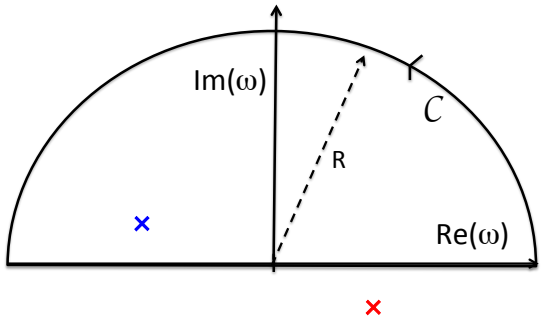
Parenthesis: the residue theorem



If the function of the complex variable $f(z)$ has no poles inside the contour $\mathcal{C}$, then the residue theorem states that:

$$\oint_{\mathcal{C}} dz \frac{f(z)}{(z - z_0)} = 2i\pi f(z_0)$$

Corollary. Consider the function (g) with (a,b,η) positive numbers (A/B spectral weights):



$$g(\omega) = \frac{A}{\omega + a - i\eta} + \frac{B}{\omega - b + i\eta}$$

Then: $\frac{1}{2i\pi} \int_{-\infty}^{\infty} d\omega e^{i\omega 0^+} g(\omega) = A$

With $e^{i\omega 0^+}$, the integrand goes to zero on the $(R \to \infty)$ semi-circle.

Time-ordered Green's function in the frequency domain

Defining the Fourier transform : $g(\omega) = \int d\tau e^{i\omega\tau} g(\tau)$, with (use complex integration and residue theorem):

$$\theta(\pm\tau) = \mp \lim_{\eta\to 0^+} \frac{1}{2i\pi} \int_{-\infty}^{+\infty} d\omega \frac{e^{-i\omega\tau}}{\omega \pm i\eta}, \quad \text{one obtains (Exercise):}$$

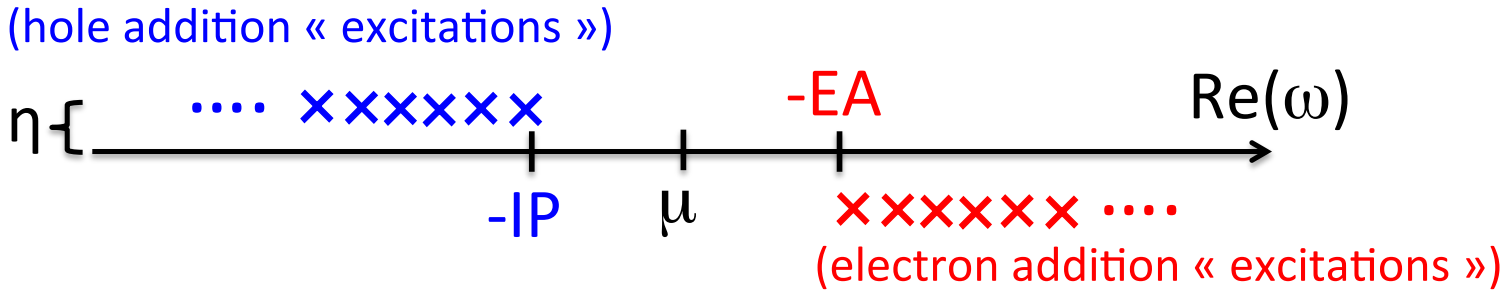
$$\boxed{G(\mathbf{r},\mathbf{r}';\omega) = \sum_n \frac{f_n(\mathbf{r}) f_n^*(\mathbf{r}')}{\hbar\omega - \varepsilon_n + i\eta\hbar \,\mathrm{sgn}(\varepsilon_n - \mu)}}$$

where the ϕ_n and ε_n are the addition/removal Lehman amplitudes and energies depending on the sign of $(\varepsilon_n - \mu)$.

Poles of the time-ordered Green's function

The Green's function has poles at the:

(1) "electron addition energies": $\hbar\omega = (E_n^{N+1} - E_0^N) - i\eta$,
(2) "electron removal energies": $\hbar\omega = (E_0^N - E_n^{N-1}) + i\eta$.



On this graph, we have added:

- the ionisation potential: $IP = (E_0^{N-1} - E_0^N)$,
- the electronic affinity: $AE = (E_0^N - E_0^{N+1})$,
- and the gap in between with the chemical potential μ.

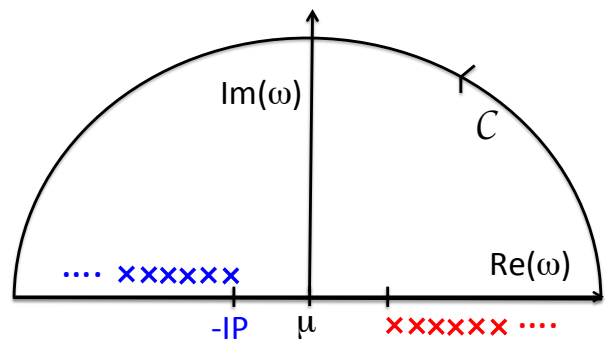
The charge density from G^T

Let's verify a relation demonstrated in the non-interacting case:

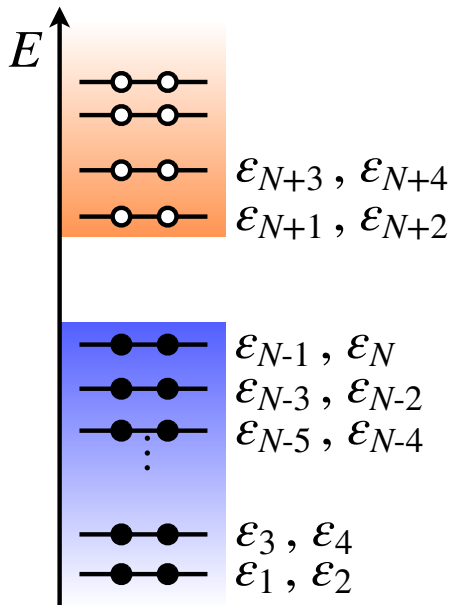
$$-i\hbar G^T(\mathbf{r}t,\mathbf{r}(t+0^+)) = \theta(t'-t)\sum_n f_n^{N-1}(\mathbf{r})\bar{f}_n^{N-1}(\mathbf{r})e^{-i\varepsilon_n^{N-1}(-0^+)/\hbar}$$
$$= \sum_n \langle\psi_H^0|\hat{\psi}_S^\dagger(\mathbf{r})|\psi_H^{n,N-1}\rangle\langle\psi_H^{n,N-1}|\hat{\psi}_S(\mathbf{r})|\psi_H^0\rangle$$
$$= \langle\psi_H^0|\hat{\psi}_S^\dagger(\mathbf{r})\hat{\psi}_S(\mathbf{r})|\psi_H^0\rangle = n(\mathbf{r})$$

Using now the frequency domain and the "residue theorem":

$$\frac{1}{2i\pi}\int_{-\infty}^{\infty} d\omega e^{i\omega 0^+} G^T(\mathbf{r},\mathbf{r};\omega) = n(\mathbf{r})$$
$$= \sum_n < \psi_0^N|\psi_S^\dagger(\mathbf{r}')|\psi_n^{N-1} >< \psi_n^{N-1}|\psi_S(\mathbf{r})|\psi_0^N >$$
$$=< \psi_0^N|\psi_S^\dagger(\mathbf{r})\psi_S(\mathbf{r})|\psi_0^N >=< \psi_0^N|\hat{n}(\mathbf{r})|\psi_0^N >$$



Systems described by a single Slater determinant



$$|\psi_0^N> = |n_1, n_2, n_3, ..., n_N, 0, 0, ... >$$
$$|\psi_n^{N+1}> = |n_1, n_2, n_3, ..., n_N, 0, 0, ..., n_{N+n}, ... >$$
$$\hat{\psi}_S(\mathbf{r}) = \sum_k \phi_k(\mathbf{r})\hat{c}_k$$

where all $\{n_i\}$ are equal to 1 and "populate" the ϕ_i orbitals.

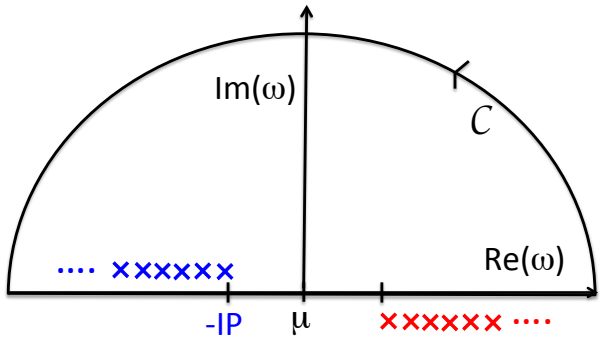
Then: $f_n^{N+1}(\mathbf{r}) =< \psi_0^N|\psi_S(\mathbf{r})|\psi_n^{N+1} >= (-1)^N \phi_{N+n}(\mathbf{r})$.

If the $\{\phi_n\}$ are the one-body Hamiltonian eigenstates then the Lehman amplitudes can be identify to the Hamiltonian eigen-wavefunctions.

To conclude: $\Sigma^X = iGV^C$ as an introduction to GW

Let's consider the integral:

$$\frac{i}{2\pi}\int_{\mathcal{C}} d\omega e^{i\omega 0^+} G^T(\mathbf{r},\mathbf{r}';\omega)V^C(\mathbf{r},\mathbf{r}')$$



with (0^+) an infinitesimal positive and V^C the Coulomb potential, where the contour $\mathcal{C}$ is in the upper half-plane.

We can then use the residue theorem to obtain:

$$\frac{i}{2\pi}\int_{-\infty}^{\infty} d\omega e^{i\omega\eta} G^T(\mathbf{r},\mathbf{r}';\omega)V^C(\mathbf{r},\mathbf{r}') = \frac{i}{2\pi}(2i\pi)\sum_n^{occupied} \phi_n(\mathbf{r})\phi_n^*(\mathbf{r}')V^C(\mathbf{r},\mathbf{r}')$$

$$= -\sum_n^{occupied} \frac{\phi_n(\mathbf{r})\phi_n^*(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}$$

which is the exchange Fock operator (putting back properly the spin !).

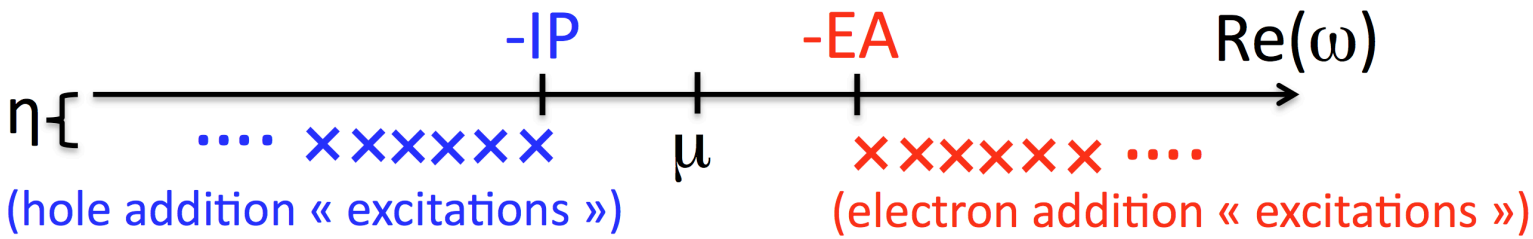
Complement: Retarded Green's function

We define the retarded single-particle Green's function as follows:

$$i\hbar G^R(\mathbf{r}t, \mathbf{r}'t') = \theta(t-t') < \psi_H^0 | \left\{ \hat{\psi}_H(\mathbf{r}t), \hat{\psi}_H^\dagger(\mathbf{r}'t') \right\} | \psi_H^0 >$$

where the time-ordering operator has been removed. The retarded Green's function has all poles in the lower half complex plane:

(1) "electron addition energies": $\hbar\omega = (E_n^{N+1} - E_0^N) - i\eta$,
(2) "electron removal energies": $\hbar\omega = (E_0^N - E_n^{N-1}) - i\eta$.



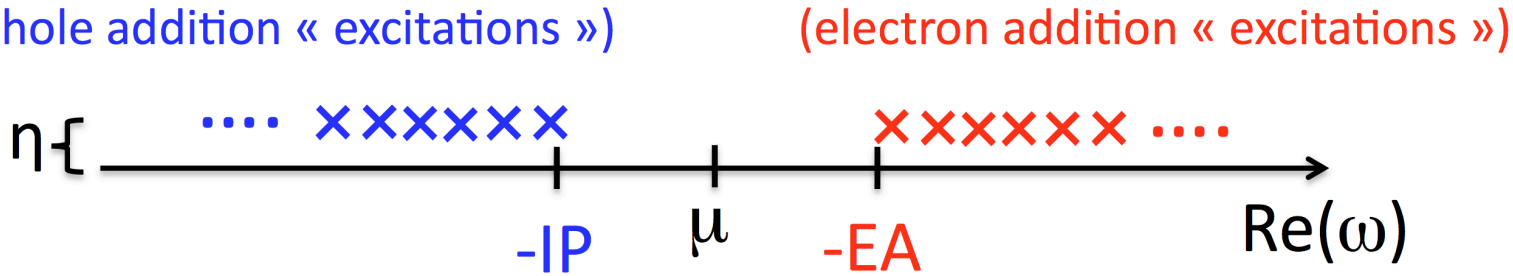
Complement: Advanced Green's function

We define the advanced single-particle Green's function as follows:

$$i\hbar G^A(\mathbf{r}t, \mathbf{r}'t') = -\theta(t'-t) < \psi_H^0 | \left\{ \hat{\psi}_H(\mathbf{r}t), \hat{\psi}_H^\dagger(\mathbf{r}'t') \right\} | \psi_H^0 >$$

The advanced Green's function has all poles in the upper half complex plane:

(1) "electron addition energies": $\hbar\omega = (E_n^{N+1} - E_0^N) + i\eta$,
(2) "electron removal energies": $\hbar\omega = (E_0^N - E_n^{N-1}) + i\eta$.



Complement: Spectral functions

Using the relation: $Im\left(\frac{1}{\omega \pm i\eta}\right) = \mp \pi \delta(\omega)$, one finds:

$$\left(\frac{-1}{\pi}\right) ImG^R(\mathbf{r},\mathbf{r}';\omega) = A(\mathbf{r},\mathbf{r}';\omega) + B(\mathbf{r},\mathbf{r}';\omega) \quad \text{with:}$$

$$A(\mathbf{r},\mathbf{r}';\omega) = \sum_n f_n^{N+1}(\mathbf{r}) \left[f_n^{N+1}(\mathbf{r}')\right]^* \delta(\omega - (E_n^{N+1} - E_O^N))$$

$$B(\mathbf{r},\mathbf{r}';\omega) = \sum_n f_n^{N-1}(\mathbf{r}) \left[f_n^{N-1}(\mathbf{r}')\right]^* \delta(\omega - (E_N^0 - E_n^{N-1}))$$

In return: $G^R(\mathbf{r},\mathbf{r}';\omega) = \int d\omega' \ \frac{[A(\mathbf{r},\mathbf{r}';\omega')+B(\mathbf{r},\mathbf{r}';\omega')]}{\omega-\omega'+i\eta}$. Further:

$$\int d\omega' \ [A(\mathbf{r},\mathbf{r}';\omega') + B(\mathbf{r},\mathbf{r}';\omega')] = \langle \psi_0^N | \{\hat{\psi}(\mathbf{r}), \hat{\psi}^\dagger(\mathbf{r}')\} | \psi_0^N \rangle = \delta(\mathbf{r}-\mathbf{r}')$$

The spectral functions are related to local density of states.