

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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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:

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

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

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

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

$$\phi(x) = \int dx_0 G(x, x_0)S(x_0) \quad (3)$$

Green's function for the Laplacian

Consider Laplace's (3D) equation with right-hand 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 $\hat{U}$

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

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): $\hat{U}(t + dt, t)\hat{U}^\dagger(t + dt, t) = 1$.

The operator $\hat{U}(t + dt, t)$ is unitary so that $\hat{U}(t', t)$ is unitary. In particular, it conserves the scalar product.

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

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:

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

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 $\psi(\mathbf{r}_2 t_2)$.

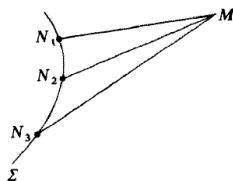


Figure. Huygens principle of the field in M as the contribution from secondary sources on surface Σ . From Quantum Mechanics, Chap. III, Complement J_{III} , Cohen-Tannoudji, Diu, Lalo  .

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:

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

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**):

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

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 define the quantum retarded Green's function as:

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

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.

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 :

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

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:

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

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":

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

$$[i\partial_t - H_0(r, \nabla_r)] \psi_0(\mathbf{r}t) = 0$$

and the corresponding Green's function:

$$[i\partial_t - H_0(r, \nabla_r) - V(r)] G(\mathbf{r}t, \mathbf{r}'t') = \delta(\mathbf{r} - \mathbf{r}')\delta(t - t')$$

$$[i\partial_t - H_0(r, \nabla_r)] G_0(\mathbf{r}t, \mathbf{r}'t') = \delta(\mathbf{r} - \mathbf{r}')\delta(t - t').$$

Then (Exercise):

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

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

Perturbation theory and the Dyson equation

From the previous equations (dropping the integration variables) :

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

which lays the fundamentals 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 $V(34) = V(\mathbf{r}_3)\delta(\mathbf{r}_3 - \mathbf{r}_4)\delta(t_3 - t_4)$:

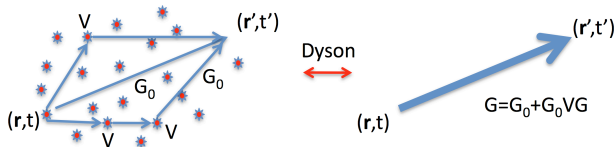
$$G(12) = G_0(12) + \int \int d3d4 G_0(13)V(34)G(42),$$

The quantum billiard

We have seen that:

$$G = G_0 + G_0 V G = G_0 + G_0 V G_0 + G_0 V G_0 V G_0 + \dots$$

This represents the amplitude of probability of going from $(\mathbf{r}, t)$ to $(\mathbf{r}', t')$ 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, interaction 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 Feynman Diagrams in the Many-Body Problem, (McGraw-Hill, 1976) [reprinted by Dover, 1992].

Creation/destruction operators

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

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

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

To preserve the anti-symmetry of fermionic wavefunctions:

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

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: $c_i^\dagger c_i |n_1, n_2, \dots, n_i, \dots\rangle = n_i |n_1, n_2, \dots, n_i, \dots\rangle$.

$c_i^\dagger c_i = \hat{n}_i$ 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:

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

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

$$|\dots n_i \dots\rangle = \prod_i (c_i^\dagger)^{n_i} |0\rangle$$

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):

$$c_{\beta}^{\dagger} = \sum_{\alpha} \langle\alpha|\beta\rangle c_{\alpha}^{\dagger} \quad \text{and:} \quad c_{\beta} = \sum_{\alpha} \langle\beta|\alpha\rangle c_{\alpha}.$$

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 $(\mathbf{r}')$:

$$\langle \mathbf{r}' | \hat{\psi}^\dagger(\mathbf{r}) | 0 \rangle = \langle \mathbf{r}' | \sum_{\alpha} \phi_{\alpha}^*(\mathbf{r}) c_{\alpha}^{\dagger} | 0 \rangle = \sum_{\alpha} \phi_{\alpha}^*(\mathbf{r}) \langle \mathbf{r}' | \alpha \rangle = \delta(\mathbf{r} - \mathbf{r}').$$

The field operator $\hat{\psi}^\dagger(\mathbf{r})$ adds a particle in the "state" $|\mathbf{r}\rangle$, 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:

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

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:

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

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

The Heisenberg representation

We now define the eigenstates in the Heisenberg representation:

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

Concerning the operators in such a representation:

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

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

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

The time-ordered single-particle Green's function

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

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

where:

- ▶ $|\psi_H^0\rangle$ 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:

$$\begin{aligned} i\hbar G(\mathbf{r}t, \mathbf{r}'t') &= \frac{\langle \psi_H^0 | \hat{\psi}_H(\mathbf{r}t) \hat{\psi}_H^\dagger(\mathbf{r}'t') | \psi_H^0 \rangle}{\langle \psi_H^0 | \psi_H^0 \rangle} \quad t \geq t', \\ &= - \frac{\langle \psi_H^0 | \hat{\psi}_H^\dagger(\mathbf{r}'t') \hat{\psi}_H(\mathbf{r}t) | \psi_H^0 \rangle}{\langle \psi_H^0 | \psi_H^0 \rangle} \quad t < t'. \end{aligned}$$

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

$$\begin{aligned} i\hbar G(\mathbf{r}t, \mathbf{r}'t') &= \theta(t - t') \langle \psi_S^0(t) | \hat{\psi}_S(\mathbf{r}) e^{-i\hat{H}(t-t')/\hbar} \hat{\psi}_S^\dagger(\mathbf{r}') | \psi_S^0(t') \rangle \\ &\quad - \theta(t' - t) \langle \psi_S^0(t') | \hat{\psi}_S^\dagger(\mathbf{r}') e^{-i\hat{H}(t'-t)/\hbar} \hat{\psi}_S(\mathbf{r}) | \psi_S^0(t) \rangle, \end{aligned}$$

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

The electron-propagator

Can we understand the following term (case $t > t'$) ?

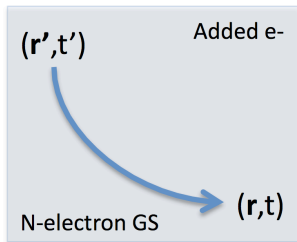
$$i\hbar G(\mathbf{r}t, \mathbf{r}'t') = \theta(t - t') \langle \psi_S^0(t) | \hat{\psi}_S(\mathbf{r}) e^{-i\hat{H}(t-t')/\hbar} \hat{\psi}_S^\dagger(\mathbf{r}') | \psi_S^0(t') \rangle$$

- ▶ $\hat{\psi}_S^\dagger(\mathbf{r}') | \psi_S^0(t') \rangle$ 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 remove one electron in $\mathbf{r}$ at time (t) and see how much this N-electron system overlaps with the N-electron ground-state.

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

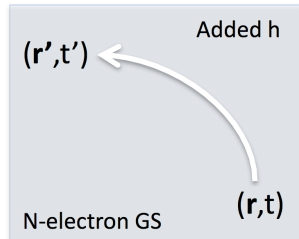
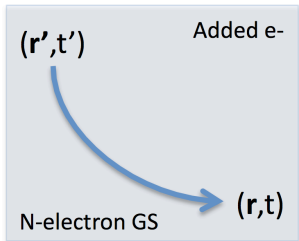
The electron-propagator (II)

Remember that a wave function $\psi(\mathbf{r}_1, \mathbf{r}_2, \dots)$ represents the amplitude of probability of finding an 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 $t < t'$.

$$i\hbar G(\mathbf{r}t, \mathbf{r}'t') = -\theta(t' - t) \times$$

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

Here we create a hole in $(\mathbf{r})$ 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 $(\mathbf{r}')$. 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:

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

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

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

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

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

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

$f_n^{N+1}(\mathbf{r}) = \langle \psi_H^0 | \hat{\psi}_S(\mathbf{r}) | \psi_H^{n,N+1} \rangle$ 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:

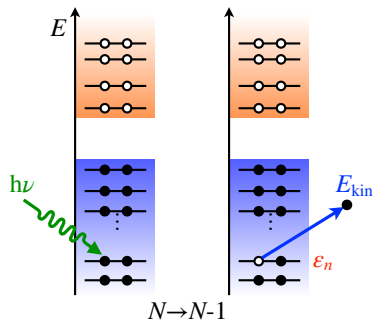
$$\begin{aligned} i\hbar G(\mathbf{r}t, \mathbf{r}'t') = & \theta(t - t') \sum_n f_n^{N+1}(\mathbf{r}) \bar{f}_n^{N+1}(\mathbf{r}') e^{-i\varepsilon_n^{N+1}(t-t')/\hbar} \\ & - \theta(t' - t) \sum_n f_n^{N-1}(\mathbf{r}) \bar{f}_n^{N-1}(\mathbf{r}') e^{-i\varepsilon_n^{N-1}(t-t')/\hbar} \end{aligned}$$

where we have introduced 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

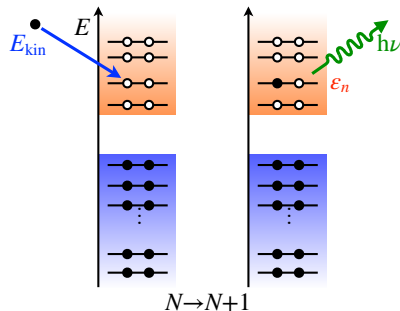


Energy conservation:

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

Identify:

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



Energy conservation:

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

Identify:

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

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):

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

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

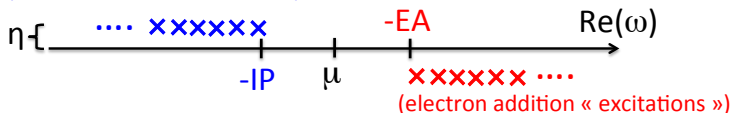
where the ϕ_n and ε_n are the addition/removal Lehman amplitudes and energies depending on the sign of $(\varepsilon_n - \mu)$.

Poles of the time-ordered Green's function in the complex plane

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": $\hbar\omega = (E_0^N - E_n^{N-1}) + i\eta$.

(hole addition « excitations »)



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 .

Retarded Green's function

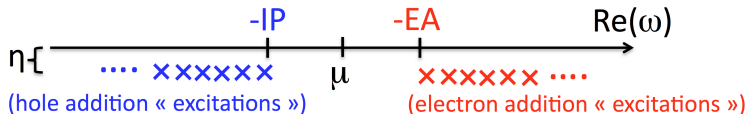
We define the retarded single-particle Green's function as follows:

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

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": $\hbar\omega = (E_0^N - E_n^{N-1}) - i\eta$.



Advanced Green's function

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

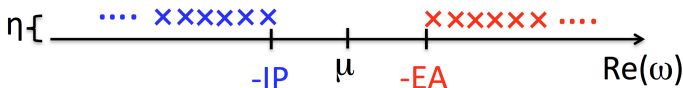
$$i\hbar G^A(\mathbf{r}t, \mathbf{r}'t') = -\theta(t' - t) \langle \psi_H^0 | \hat{\psi}_H(\mathbf{r}t) \hat{\psi}_H^\dagger(\mathbf{r}'t') | \psi_H^0 \rangle$$

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": $\hbar\omega = (E_0^N - E_n^{N-1}) + i\eta$.

(hole addition « excitations »)

(electron addition « excitations »)



Spectral functions

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

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

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

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

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.

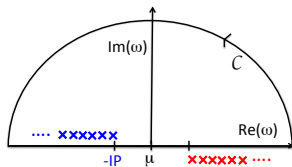
Complement: The charge density

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

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

Using now the frequency domain and the residue theorem again:

$$\begin{aligned}
 \frac{1}{2i\pi} \int_C d\omega e^{i\omega\eta} G^T(\mathbf{r}, \mathbf{r}; \omega) &= n(\mathbf{r}) \\
 &= \sum_n \langle \psi_0^N | \hat{\psi}_S^\dagger(\mathbf{r}') | \psi_n^{N-1} \rangle \langle \psi_n^{N-1} | \hat{\psi}_S(\mathbf{r}) | \psi_0^N \rangle \\
 &= \langle \psi_0^N | \hat{\psi}_S^\dagger(\mathbf{r}) \hat{\psi}_S(\mathbf{r}) | \psi_0^N \rangle = \langle \psi_0^N | \hat{n}(\mathbf{r}) | \psi_0^N \rangle
 \end{aligned}$$

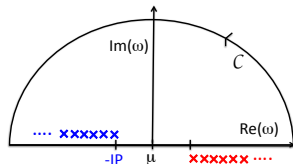


To conclude: $\Sigma^X = iGV^C$ as an introduction to GW

Let's consider the integral:

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

with (η) 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:

$$\begin{aligned} \frac{i}{2\pi} \int_{\mathcal{C}} d\omega e^{i\omega\eta} G^T(\mathbf{r}, \mathbf{r}'; \omega) V^C(\mathbf{r}, \mathbf{r}') &= \frac{i}{2\pi} (2i\pi) \sum_n^{\text{occupied}} \phi_n(\mathbf{r}) \phi_n^*(\mathbf{r}') V^C(\mathbf{r}, \mathbf{r}') \\ &= - \sum_n^{\text{occupied}} \frac{\phi_n(\mathbf{r}) \phi_n^*(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} \end{aligned}$$

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