Many-body theory and density functional theory

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Overview

Part I : Introduction to nonequilibrium Green's functions

- Second quantization
- Time-propagation and Keldysh contour
- Feynman diagrams and the self-energy
- Kadanoff-Baym equations
- Bethe-Salpeter and double excitations

Part II: Density functionals from many-body theory

- Kohn-Sham equations and the action functional
- Adiabatic connection in TDDFT
- Conserving density functionals and the xc-kernel

(material inspired by
" Nonequilibrium Many-Body Theory and the Keldysh Formalism"
Gianluca Stefanucci and RvL, Cambridge University Press
to be published 2012/2013)

Basic one-particle quantum mechanics

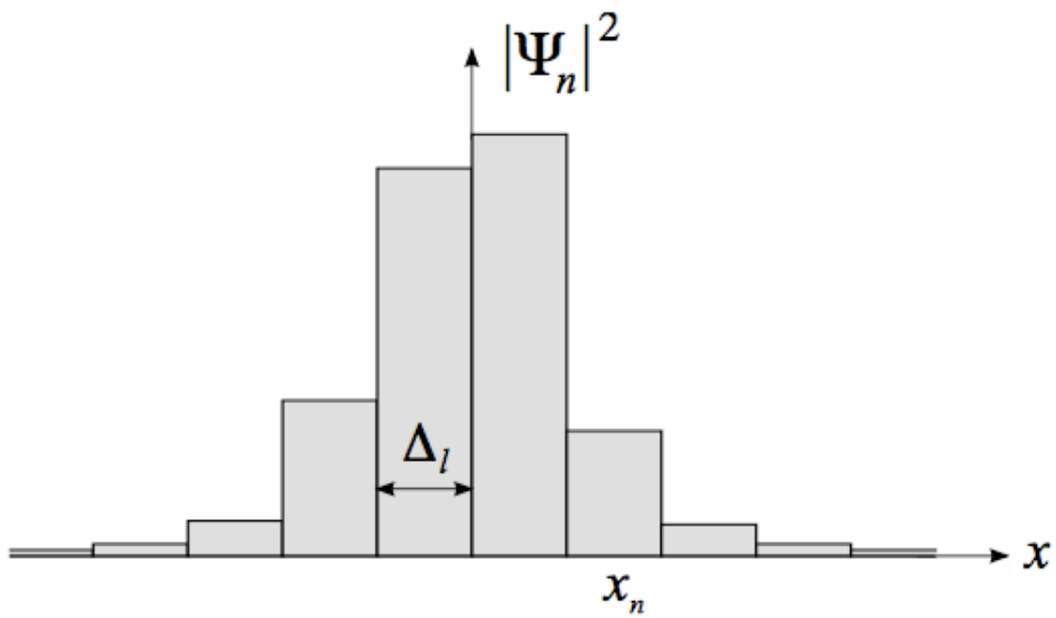
We measure a particle to be in interval Δ_n

Its corresponding state is denoted by

$$|x_n\rangle$$

These states have the property

$$\langle x_n|x_m\rangle = \delta_{nm}$$



and form a complete set

$$|\Psi\rangle = \sum_n |x_n\rangle\langle x_n|\Psi\rangle$$

If the system is in state $|\Psi\rangle$ then the probability to measure state $|x_n\rangle$ is

$$P_n = |\langle x_n|\Psi\rangle|^2 = |\Psi(x_n)|^2$$

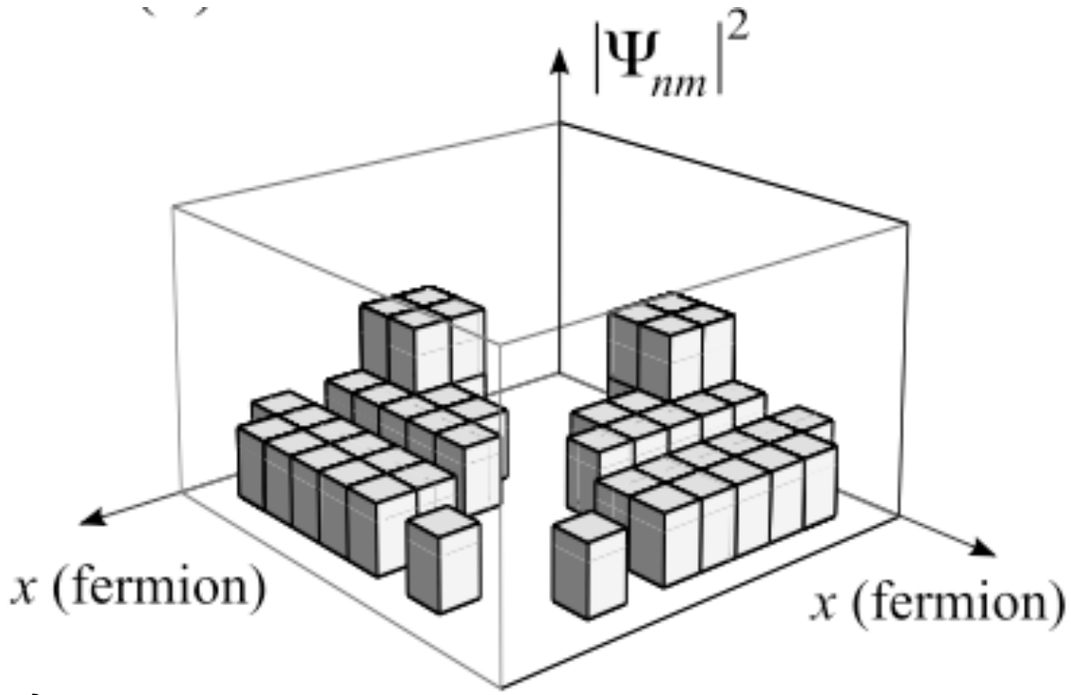
Two particles

If we simultaneously measure a particle in intervals Δ_n and Δ_m the state is

$$|x_n\, x_m\rangle$$

The particles are indistinguishable

$$|x_n\, x_m\rangle = \lambda |x_m\, x_n\rangle = \lambda^2 |x_n\, x_m\rangle \rightarrow \lambda = \pm 1$$



The states are normalized

$$\langle x_n\, x_m | x_{n'}\, x_{m'}\rangle = \delta_{nn'}\delta_{mm'} \pm \delta_{nm'}\delta_{mn'}$$

Let us consider fermions. Only the states with n > m are linearly independent and we have

$$|\Psi\rangle = \sum_{n>m} |x_n\, x_m\rangle\langle x_n\, x_m|\Psi\rangle$$

$$P_{nm} = |\langle x_n\, x_m|\Psi\rangle|^2 = |\Psi(x_n, x_m)|^2$$

Second quantization

For N fermions we have (with P a permutation)

$$|\mathbf{x}_1 \dots \mathbf{x}_N\rangle = (-1)^P \, |\mathbf{x}_{P(1)} \dots \mathbf{x}_{P(N)}\rangle \qquad\qquad \mathbf{x} = \mathbf{r}, \sigma$$

$$\langle \mathbf{x}_1 \dots \mathbf{x}_N | \mathbf{y}_1 \dots \mathbf{y}_N \rangle = \sum_P (-1)^P \prod_{j=1}^{N} \delta(\mathbf{x}_j - \mathbf{y}_{P(j)})$$

There is a unique operator $\hat{\psi}^\dagger(\mathbf{x})$ that generates the position basis. It is defined by

$$\begin{aligned} |\mathbf{x}_1\rangle &= \hat{\psi}^\dagger(\mathbf{x}_1)|0\rangle \\ |\mathbf{x}_1\, \mathbf{x}_2\rangle &= \hat{\psi}^\dagger(\mathbf{x}_2)|\mathbf{x}_1\rangle = \hat{\psi}^\dagger(\mathbf{x}_2)\hat{\psi}^\dagger(\mathbf{x}_1)|0\rangle \\ |\mathbf{x}_1 \dots \mathbf{x}_N\rangle &= \hat{\psi}^\dagger(\mathbf{x}_N)|\mathbf{x}_1 \dots \mathbf{x}_{N-1}\rangle = \hat{\psi}^\dagger(\mathbf{x}_N) \dots \hat{\psi}^\dagger(\mathbf{x}_1)|0\rangle \end{aligned}$$

$\hat{\psi}^\dagger(\mathbf{x})$ is called creation operator

It follows : $$\hat{\psi}^\dagger(\mathbf{x})\hat{\psi}^\dagger(\mathbf{y}) = -\hat{\psi}^\dagger(\mathbf{y})\hat{\psi}^\dagger(\mathbf{x})$$

Remember that the adjoint of an operator $\hat{O}$ is defined by

$$\langle\Phi|\hat{O}^\dagger|\chi\rangle = \langle\chi|\hat{O}|\Phi\rangle^*$$

The adjoint $\hat{\psi}(\mathbf{x})$ of the creation operator therefore satisfies

$$\langle\mathbf{x}_1\ldots\mathbf{x}_{N-1}|\hat{\psi}(\mathbf{x}_N)|\mathbf{y}_1\ldots\mathbf{y}_N\rangle^* = \langle\mathbf{y}_1\ldots\mathbf{y}_N|\hat{\psi}^\dagger(\mathbf{x}_N)|\mathbf{x}_1\ldots\mathbf{x}_{N-1}\rangle$$
$$= \langle\mathbf{y}_1\ldots\mathbf{y}_N|\mathbf{x}_1\ldots\mathbf{x}_N\rangle = \sum_P(-1)^P\prod_{j=1}^N\delta(\mathbf{y}_j-\mathbf{x}_{P(j)})$$

and hence (check yourself!)

$$\hat{\psi}(\mathbf{x})|\mathbf{y}_1\ldots\mathbf{y}_N\rangle = \sum_{k=1}^N(-1)^{N-k}\,\delta(\mathbf{x}-\mathbf{y}_k)\,|\mathbf{y}_1\ldots\mathbf{y}_{k-1}\mathbf{y}_{k+1}\ldots\mathbf{y}_N\rangle$$

For example:

$$
\begin{aligned}
\hat{\psi}(\mathbf{x})|0\rangle &= 0 \\
\hat{\psi}(\mathbf{x})|\mathbf{y}_1\rangle &= \delta(\mathbf{x}-\mathbf{y}_1)|0\rangle \\
\hat{\psi}(\mathbf{x})|\mathbf{y}_1\,\mathbf{y}_2\rangle &= \delta(\mathbf{x}-\mathbf{y}_2)|\mathbf{y}_1\rangle - \delta(\mathbf{x}-\mathbf{y}_1)|\mathbf{y}_2\rangle \\
\hat{\psi}(\mathbf{x})|\mathbf{y}_1\,\mathbf{y}_2\,\mathbf{y}_3\rangle &= \delta(\mathbf{x}-\mathbf{y}_3)|\mathbf{y}_1\,\mathbf{y}_2\rangle - \delta(\mathbf{x}-\mathbf{y}_2)|\mathbf{y}_1\,\mathbf{y}_3\rangle + \delta(\mathbf{x}-\mathbf{y}_1)|\mathbf{y}_2\,\mathbf{y}_3\rangle
\end{aligned}
$$

The operator $\hat{\psi}(\mathbf{x})$ is called annihilation operator

It follows (with anti-commutator $[A,B]_+ = AB + BA$):

$$
\begin{aligned}
\left[\hat{\psi}(\mathbf{x}),\hat{\psi}(\mathbf{y})\right]_+ &= \left[\hat{\psi}^\dagger(\mathbf{x}),\hat{\psi}^\dagger(\mathbf{y})\right]_+ = 0 \\
\left[\hat{\psi}(\mathbf{x}),\hat{\psi}^\dagger(\mathbf{y})\right]_+ &= \delta(\mathbf{x}-\mathbf{y})
\end{aligned}
$$

The density operator is defined by

$$\hat{n}(\mathbf{x}) = \hat{\psi}^\dagger(\mathbf{x})\hat{\psi}(\mathbf{x})$$

and has the property

$$\hat{n}(\mathbf{x})|\mathbf{x}_1 \ldots \mathbf{x}_N\rangle = \sum_{j=1}^{N} \delta(\mathbf{x} - \mathbf{x}_j)\,|\mathbf{x}_1 \ldots \mathbf{x}_N\rangle$$

For example:

$$\begin{aligned}
\hat{\psi}^\dagger(\mathbf{x})\,\hat{\psi}(\mathbf{x})|\mathbf{y}_1\mathbf{y}_2\rangle &= \hat{\psi}^\dagger(\mathbf{x})\ (\delta(\mathbf{x}-\mathbf{y}_2)|\mathbf{y}_1\rangle - \delta(\mathbf{x}-\mathbf{y}_1)|\mathbf{y}_2\rangle) \\
&= \delta(\mathbf{x}-\mathbf{y}_2)|\mathbf{y}_1\mathbf{x}\rangle - \delta(\mathbf{x}-\mathbf{y}_1)|\mathbf{y}_2\mathbf{x}\rangle \\
&= (\delta(\mathbf{x}-\mathbf{y}_1) + \delta(\mathbf{x}-\mathbf{y}_2))|\mathbf{y}_1\mathbf{y}_2\rangle
\end{aligned}$$

The expectation value $n(\mathbf{x}) = \langle\Psi|\hat{n}(\mathbf{x})|\Psi\rangle$

is the particle density of the system in state $|\Psi\rangle$

The Hamiltonian

The time-evolution of a N-particle system is given by the Schrödinger equation

$$i\partial_t|\Psi(t)\rangle = \hat{H}(t)|\Psi(t)\rangle \qquad\qquad |\Psi(t_0)\rangle = |\Psi_0\rangle$$

It has one- and two-body parts

$$\hat{H}(t) = \hat{H}_0(t) + \hat{W}$$

Kinetic energy + external potential

Two-particle interactions

If we use a specific Hamiltonian we have to give its representation in a given basis.

For one particle in position basis we can, for example, define the Hamiltonian

$$\langle \mathbf{x}|\hat{h}|\mathbf{x}'\rangle = (-\frac{1}{2}\nabla^2 + v(\mathbf{x},t))\langle \mathbf{x}|\mathbf{x}'\rangle$$

The Schrödinger equation

$$\hat{h}|\psi(t)\rangle = i\partial_t|\psi(t)\rangle \qquad\qquad \psi(\mathbf{x},t) = \langle \mathbf{x}|\psi(t)\rangle$$

in the position representation then has the form

$$\begin{aligned} i\partial_t\psi(\mathbf{x},t) &= \langle \mathbf{x}|\hat{h}|\psi(t)\rangle = \int d\mathbf{x}'\, \langle \mathbf{x}|\hat{h}|\mathbf{x}'\rangle\langle \mathbf{x}'|\psi(t)\rangle \\ &= \int d\mathbf{x}' \left(-\frac{1}{2}\nabla^2 + v(\mathbf{x},t)\right) \langle \mathbf{x}|\mathbf{x}'\rangle\langle \mathbf{x}'|\psi(t)\rangle \\ &= \left(-\frac{1}{2}\nabla^2 + v(\mathbf{x},t)\right) \psi(\mathbf{x},t) \end{aligned}$$

Similarly for N particles we define the Hamiltonian by

$$\langle \mathbf{x}_1 \dots \mathbf{x}_N | \hat{H} | \mathbf{x}'_1 \dots \mathbf{x}'_N \rangle$$

$$= \left(\sum_j^N -\frac{1}{2}\nabla_j^2 + v(\mathbf{x}_j, t) + \frac{1}{2}\sum_{i \neq j}^N w(\mathbf{x}_i, \mathbf{x}_j) \right) \langle \mathbf{x}_1 \dots \mathbf{x}_N | \mathbf{x}'_1 \dots \mathbf{x}'_N \rangle$$

or equivalently, for any state $|\Psi\rangle$

Many-body wave function

$$\langle \mathbf{x}_1 \dots \mathbf{x}_N | \hat{H} | \Psi \rangle$$

$$= \left(\sum_j^N -\frac{1}{2}\nabla_j^2 + v(\mathbf{x}_j, t) + \frac{1}{2}\sum_{i \neq j}^N w(\mathbf{x}_i, \mathbf{x}_j) \right) \langle \mathbf{x}_1 \dots \mathbf{x}_N | \Psi \rangle$$

Since the one- and two-body potentials are diagonal in the position representation it is easy to express them in second quantization

For the 2-particle interaction we have

$$\hat{W}|\mathbf{x}_1 \ldots \mathbf{x}_N\rangle = \frac{1}{2}\sum_{i\neq j}^{N} w(\mathbf{x}_i, \mathbf{x}_j)|\mathbf{x}_1 \ldots \mathbf{x}_N\rangle$$

Since the density operator has the property

$$\hat{n}(\mathbf{x})|\mathbf{x}_1 \ldots \mathbf{x}_N\rangle = \sum_{j=1}^{N} \delta(\mathbf{x}-\mathbf{x}_j)\,|\mathbf{x}_1 \ldots \mathbf{x}_N\rangle$$

it follows that

$$\begin{aligned}
\hat{W} &= \frac{1}{2}\int d\mathbf{x}d\mathbf{y}\, w(\mathbf{x},\mathbf{y})\hat{n}(\mathbf{x})\hat{n}(\mathbf{y}) - \frac{1}{2}\int d\mathbf{x}\, w(\mathbf{x},\mathbf{x})\hat{n}(\mathbf{x}) \\
&= \frac{1}{2}\int d\mathbf{x}d\mathbf{y}\, w(\mathbf{x},\mathbf{y})\left(\hat{\psi}^\dagger(\mathbf{x})\hat{\psi}(\mathbf{x})\hat{\psi}^\dagger(\mathbf{y})\hat{\psi}(\mathbf{y}) - \delta(\mathbf{x}-\mathbf{y})\hat{\psi}^\dagger(\mathbf{x})\hat{\psi}(\mathbf{x})\right) \\
&= \frac{1}{2}\int d\mathbf{x}d\mathbf{y}\, w(\mathbf{x},\mathbf{y})\,\hat{\psi}^\dagger(\mathbf{x})\hat{\psi}^\dagger(\mathbf{y})\hat{\psi}(\mathbf{y})\hat{\psi}(\mathbf{x})
\end{aligned}$$

$$\hat{W} = \frac{1}{2}\int d\mathbf{x}d\mathbf{y}\, w(\mathbf{x},\mathbf{y})\,\hat{\psi}^\dagger(\mathbf{x})\hat{\psi}^\dagger(\mathbf{y})\hat{\psi}(\mathbf{y})\hat{\psi}(\mathbf{x})$$

Similarly for the one-body potential

$$\hat{V}(t)|\mathbf{x}_1 \ldots \mathbf{x}_N\rangle = \sum_j^N v(\mathbf{x}_j, t)|\mathbf{x}_1 \ldots \mathbf{x}_N\rangle = \int d\mathbf{x}\, \hat{n}(\mathbf{x}) v(\mathbf{x}, t)|\mathbf{x}_1 \ldots \mathbf{x}_N\rangle$$

$$\hat{V}(t) = \int d\mathbf{x}\, \hat{\psi}^\dagger(\mathbf{x})\hat{\psi}(\mathbf{x})\, v(\mathbf{x}, t)$$

The kinetic energy operator is only slightly more difficult. Let's illustrate it for 3 particles. Remember that

$$\hat{\psi}(\mathbf{x})|\mathbf{y}_1\, \mathbf{y}_2\, \mathbf{y}_3\rangle \quad = \quad \delta(\mathbf{x} - \mathbf{y}_3)|\mathbf{y}_1\, \mathbf{y}_2\rangle - \delta(\mathbf{x} - \mathbf{y}_2)|\mathbf{y}_1\, \mathbf{y}_3\rangle + \delta(\mathbf{x} - \mathbf{y}_1)|\mathbf{y}_2\, \mathbf{y}_3\rangle$$

$$\hat{\psi}^\dagger(\mathbf{x})\nabla^2\hat{\psi}(\mathbf{x})\, |\mathbf{y}_1\mathbf{y}_2\mathbf{y}_3\rangle$$

$$= \nabla^2\delta(\mathbf{x} - \mathbf{y}_3)|\mathbf{y}_1\, \mathbf{y}_2\, \mathbf{x}\rangle + \nabla^2\delta(\mathbf{x} - \mathbf{y}_2)|\mathbf{y}_1\mathbf{x}\, \mathbf{y}_3\rangle + \nabla^2\delta(\mathbf{x} - \mathbf{y}_1)|\mathbf{x}\, \mathbf{y}_2\, \mathbf{y}_3\rangle$$

If we therefore define

$$\hat{T} = -\frac{1}{2}\int d\mathbf{x}\,\hat{\psi}^\dagger(\mathbf{x})\nabla^2\hat{\psi}(\mathbf{x})$$

then since T is Hermitian

$$\langle \mathbf{y}_1\mathbf{y}_2\mathbf{y}_3|\hat{T}|\mathbf{x}_1\mathbf{x}_2\mathbf{x}_3\rangle = \langle \mathbf{x}_1\mathbf{x}_2\mathbf{x}_3|\hat{T}|\mathbf{y}_1\mathbf{y}_2\mathbf{y}_3\rangle^*$$

$$= -\frac{1}{2}\left(\nabla^2_{\mathbf{y}_1} + \nabla^2_{\mathbf{y}_2} + \nabla^2_{\mathbf{y}_3}\right)\langle \mathbf{x}_1\mathbf{x}_2\mathbf{x}_3|\mathbf{y}_1\mathbf{y}_2\mathbf{y}_3\rangle^*$$

$$= -\frac{1}{2}\left(\nabla^2_{\mathbf{y}_1} + \nabla^2_{\mathbf{y}_2} + \nabla^2_{\mathbf{y}_3}\right)\langle \mathbf{y}_1\mathbf{y}_2\mathbf{y}_3|\mathbf{x}_1\mathbf{x}_2\mathbf{x}_3\rangle$$

yielding exactly the matrix element of the kinetic energy operator. Hence

$$\hat{H}(t) = \int d\mathbf{x}\,\hat{\psi}^\dagger(\mathbf{x})\left(-\frac{1}{2}\nabla^2 + v(\mathbf{x},t)\right)\hat{\psi}(\mathbf{x})$$

$$+\frac{1}{2}\int d\mathbf{x}d\mathbf{y}\,w(\mathbf{x},\mathbf{y})\,\hat{\psi}^\dagger(\mathbf{x})\hat{\psi}^\dagger(\mathbf{y})\hat{\psi}(\mathbf{y})\hat{\psi}(\mathbf{x})$$

Often also a discrete representation is used by defining

$$\hat{a}_n^\dagger = \int d\mathbf{x}\, \varphi_n(\mathbf{x}) \hat{\psi}^\dagger(\mathbf{x}) \qquad\qquad \hat{a}_n = \int d\mathbf{x}\, \varphi_n^*(\mathbf{x}) \hat{\psi}(\mathbf{x})$$

where φ_n is an orthonormal set of orbitals

The Hamiltonian then attains the form

$$\hat{H}(t) = \sum_{ij} h_{ij}(t)\, \hat{a}_i^\dagger\, \hat{a}_j + \frac{1}{2} \sum_{ijkl} v_{ijkl}\, \hat{a}_i^\dagger\, \hat{a}_j^\dagger\, \hat{a}_k\, \hat{a}_l$$

where

$$h_{ij}(t) = \int d\mathbf{x}\, \varphi_i^*(\mathbf{x}) h(\mathbf{x}, t) \varphi_j(\mathbf{x})$$

$$v_{ijkl} = \int d\mathbf{x} d\mathbf{y}\, w(\mathbf{x}, \mathbf{y})\, \varphi_i^*(\mathbf{x}) \varphi_j^*(\mathbf{y}) \varphi_k(\mathbf{y}) \varphi_l(\mathbf{x})$$

Time propagation

The next task is to solve the Schrödinger equation $i\partial_t|\Psi(t)\rangle = \hat{H}(t)|\Psi(t)\rangle$

If we divide [t_0 , T] into n intervals Δ then

$$|\Psi(T)\rangle \approx e^{-i\hat{H}(t_n)\Delta}\ldots e^{-i\hat{H}(t_0)\Delta}|\Psi(t_0)\rangle = \mathcal{T}\left\{e^{-i\hat{H}(t_n)\Delta}\ldots e^{-i\hat{H}(t_0)\Delta}\right\}|\Psi(t_0)\rangle$$

$$= \mathcal{T}\left\{e^{-i\sum_j^n \hat{H}(t_j)\Delta}\right\}|\Psi(t_0)\rangle$$

where $\mathcal{T}$ denotes time-ordering that orders the latest operator most left.
We used that operators commute under time-ordering

$$\mathcal{T}\left\{\hat{A}(t_1)\hat{B}(t_2)\right\} = \mathcal{T}\left\{\hat{B}(t_2)\hat{A}(t_1)\right\}$$

and hence, in particular

$$\mathcal{T}\left\{e^{\hat{A}(t_1)}e^{\hat{B}(t_2)}\right\} = \mathcal{T}\left\{e^{\hat{A}(t_1)+\hat{B}(t_2)}\right\}$$

In the limit Δ => 0 then

$$|\Psi(T)\rangle = \mathcal{T}\left\{e^{-i\int_{t_0}^{T} dt\,\hat{H}(t)}\right\}|\Psi(t_0)\rangle = \hat{U}(T,t_0)|\Psi(t_0)\rangle$$

Time-evolution operator

It follows from the Schrödinger equation that

$$i\partial_t\,\hat{U}(t,t') = \hat{H}(t)\hat{U}(t,t')$$

Let us now calculate an expectation value of an operator Ô(t) :

$$\langle\hat{O}(t)\rangle = \langle\Psi(t)|\hat{O}(t)|\Psi(t)\rangle = \langle\Psi_0|\hat{U}(t_0,t)\,\hat{O}(t)\,\hat{U}(t,t_0)|\Psi_0\rangle = \langle\Psi_0|\hat{O}_H(t)|\Psi_0\rangle$$

where

$$\hat{O}_H(t) = \hat{U}(t_0,t)\,\hat{O}(t)\,\hat{U}(t,t_0)$$

defines the Heisenberg form of the operator Ô(t)

It satisfies the equation (check yourself!)

$$\partial_t \hat{O}_H(t) = -i\left[\hat{O}_H(t), \hat{H}_H(t)\right] + \left(\partial_t \hat{O}(t)\right)_H$$

For example, you can check that

$$i\,\partial_t \hat{\psi}_H(\mathbf{x},t) = \left(-\frac{1}{2}\nabla^2 + v(\mathbf{x},t)\right)\hat{\psi}_H(\mathbf{x},t) + \int d\mathbf{y}\, w(\mathbf{x},\mathbf{y})\,\hat{n}_H(\mathbf{y},t)\,\hat{\psi}_H(\mathbf{x},t)$$

It will be useful to extend the concept of expectation value to ensembles

$$\langle \hat{O}_H(t)\rangle = \sum_n w_n \langle \Psi_n|\hat{O}_H(t)|\Psi_n\rangle = \mathrm{Tr}\,\left\{\hat{\rho}\,\hat{O}_H(t)\right\}$$

$$\hat{\rho} = \sum_n w_n |\Psi_n\rangle\langle\Psi_n| \qquad \sum_n w_n = 1 \qquad w_m \geq 0$$

where we defined $\mathrm{Tr}\ \hat{A} = \sum_m \langle \Phi_m|\hat{A}|\Phi_m\rangle$ with $|\Phi_m\rangle$ any complete orthonormal set

An important special case is

$$w_n = \frac{e^{-\beta E_n}}{\sum_m e^{-\beta E_m}} \qquad \hat{H}^M|\Psi_n\rangle = E_n|\Psi_n\rangle \qquad \hat{H}^M = \hat{H}(t_0) - \mu\hat{N}$$

$$\hat{\rho} = \sum_n w_n|\Psi_n\rangle\langle\Psi_n| = \frac{e^{-\beta\hat{H}^M}}{\mathrm{Tr}\left\{e^{-\beta\hat{H}^M}\right\}}$$

This corresponds to an initial system at inverse temperature β and chemical potential μ

$$e^{-\beta\hat{H}^M} = e^{-i[(t_0-i\beta)-t_0]\hat{H}^M} = \hat{U}(t_0 - i\beta, t_0)$$

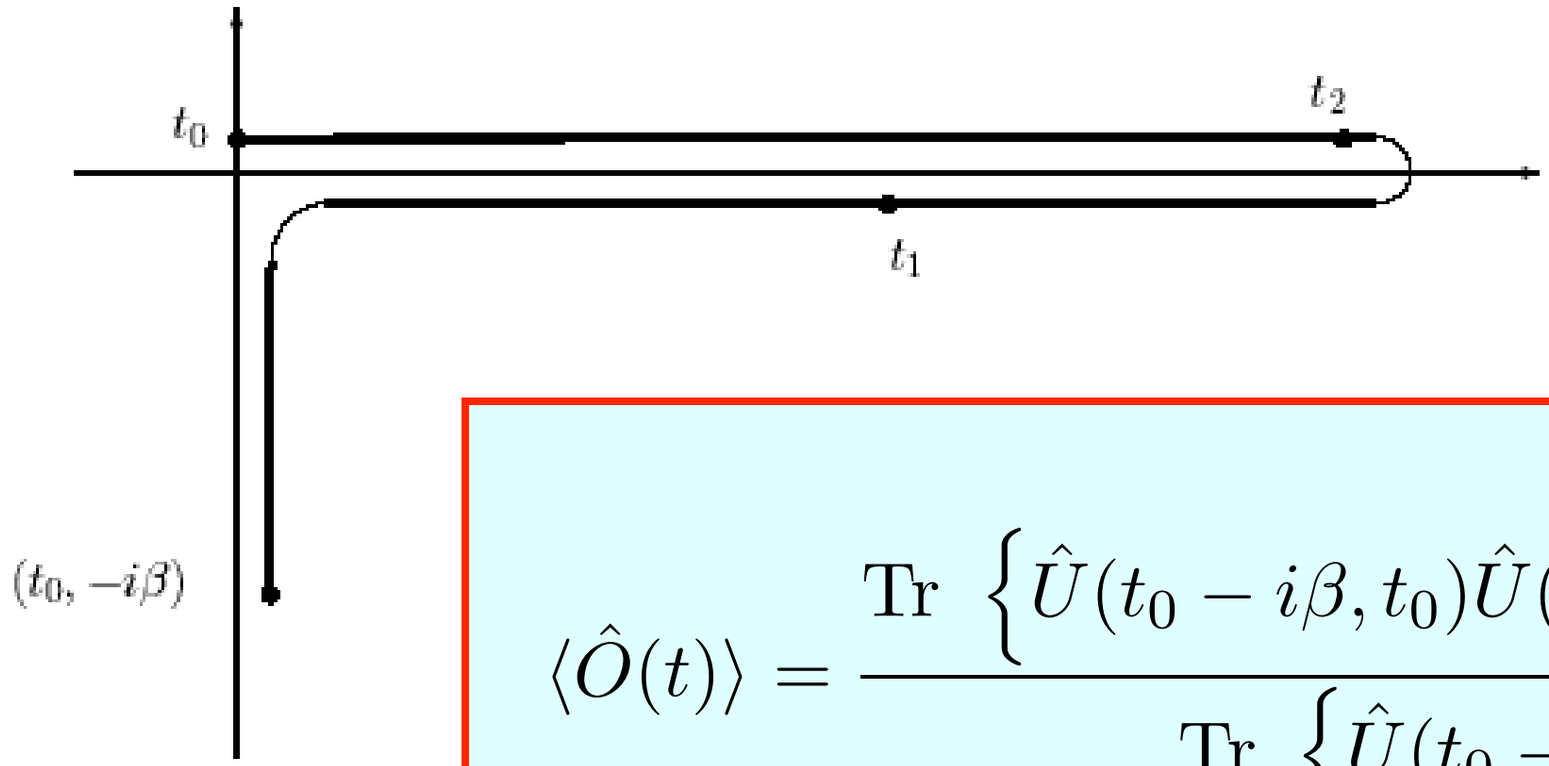
If we therefore define

$$\hat{H}(z) = \begin{cases} \hat{H}(t) & z \in [t_0, \infty[\\ \hat{H}^M & z \in [t_0, t_0 - i\beta] \end{cases}$$

then we can write

Time contour

(L.V.Keldysh, Sov.Phys.JETP20, 1018 (1965))



$$\langle \hat{O}(t) \rangle = \frac{\mathrm{Tr}\ \left\{ \hat{U}(t_0 - i\beta, t_0) \hat{U}(t_0, t) \hat{O}(t) \hat{U}(t, t_0) \right\}}{\mathrm{Tr}\ \left\{ \hat{U}(t_0 - i\beta, t_0) \right\}}$$

$$\langle \hat{O}(t) \rangle = \frac{\mathrm{Tr}\ \mathcal{T} \left\{ e^{-i \int_\gamma dz\, \hat{H}(z)} \hat{O}(t) \right\}}{\mathrm{Tr}\ \mathcal{T} \left\{ e^{-i \int_\gamma dz\, \hat{H}(z)} \right\}}$$

Time ordering is now defined along the Keldysh contour

Perturbation expansion

$$\mathrm{Tr}\ \mathcal{T}\left\{e^{-i\int_\gamma dz\,(\hat{H}_0(z)+\hat{W}(z))}\hat{O}(t)\right\}$$

$$=\sum_{n=0}^{\infty}\frac{(-i)^n}{n!}\int_\gamma dz_1\ldots dz_n\,\mathrm{Tr}\ \mathcal{T}\left\{e^{-i\int_\gamma dz\,\hat{H}_0(z)}\hat{O}(t)\hat{W}(z_1)\ldots\hat{W}(z_n)\right\}$$

The integrand has the form

$$\mathrm{Tr}\ \mathcal{T}\left\{e^{-\beta\hat{H}^M}\hat{O}_{H_0}(t)\hat{W}_{H_0}(z_1)\ldots\hat{W}_{H_0}(z_n)\right\}=$$

$$\left(\prod_{j=1}^{n}\frac{1}{2}\int d\mathbf{x}_j d\mathbf{x}'_j w(\mathbf{x}_j,\mathbf{x}'_j)\right)\mathrm{Tr}\ \mathcal{T}\left\{e^{-\beta\hat{H}^M}\hat{O}_{H_0}(t)\prod_{k=1}^{n}\hat{\psi}^\dagger_{H_0}(\mathbf{x}_k z_k)\hat{\psi}^\dagger_{H_0}(\mathbf{x}'_k z_k)\hat{\psi}_{H_0}(\mathbf{x}'_k z_k)\hat{\psi}_{H_0}(\mathbf{x}_k z_k)\right\}$$

We thus have to deal with time-ordered strings of an equal number of creation and annihilation operators

We therefore define the general correlator $j = \mathbf{x}_j z_j$

$$g_n(1 \dots n, 1' \dots n') = \frac{1}{i^n} \frac{\mathrm{Tr}\ \mathcal{T}\left\{ e^{-i\int_\gamma dz\, \hat{H}_0(z)} \hat{\psi}(1) \dots \hat{\psi}(n) \hat{\psi}^\dagger(n') \dots \hat{\psi}^\dagger(1') \right\}}{\mathrm{Tr}\ \mathcal{T}\left\{ e^{-i\int_\gamma dz\, \hat{H}_0(z)} \right\}}$$

also known as the (noninteracting) n-particle Green's function which has some nice properties (as explained very soon) if we define the time-ordering for field operators such that every interchange yields a minus sign

If we now let $\hat{O}(t)$ be a 1-body operator :

$$\hat{O}(t) = \int d\mathbf{x}\, \hat{\psi}^\dagger(\mathbf{x}) o(\mathbf{x}, t) \hat{\psi}(\mathbf{x})$$

then we can expand its expectation value in terms of g_k

This gives

$$\langle \hat{O}(t) \rangle = \frac{\mathrm{Tr}\ \mathcal{T}\left\{ e^{-i\int_\gamma dz\, \hat{H}(z)} \hat{O}(t) \right\}}{\mathrm{Tr}\ \mathcal{T}\left\{ e^{-i\int_\gamma dz\, \hat{H}(z)} \right\}}$$

$$= \frac{-i\sum_{k=0}^{\infty} \frac{1}{k!}\left(\frac{i}{2}\right)^k \int d\mathbf{x} \int w(1,1')\ldots w(k,k')\, o(\mathbf{x},z) g_{2k+1}(\mathbf{x}z,1,1',\ldots;\mathbf{x}'z^+,1^+,1'^+,\ldots)|_{\mathbf{x}=\mathbf{x}',z=t}}{\sum_{k=0}^{\infty} \frac{1}{k!}\left(\frac{i}{2}\right)^k \int w(1,1')\ldots w(k,k')\, g_{2k}(1,1',\ldots;1^+,1'^+,\ldots)}$$

and can be rewritten as

$$\langle \hat{O}(t) \rangle = -i \int d\mathbf{x}\, o(\mathbf{x},t)\, G(\mathbf{x}z,\mathbf{x}'z^+)|_{\mathbf{x}=\mathbf{x}',z=t}$$

where we defined the (interacting) 1-particle Green's function as

$$G(a,b) = \frac{\sum_{k=0}^{\infty} \frac{1}{k!} \left(\frac{i}{2}\right)^k \int w(1,1') \dots w(k,k')\, g_{2k+1}(a,1,1',\dots;b,1^+,1'^+,\dots)}{\sum_{k=0}^{\infty} \frac{1}{k!} \left(\frac{i}{2}\right)^k \int w(1,1') \dots w(k,k')\, g_{2k}(1,1',\dots;1^+,1'^+,\dots)}$$

$$w(1,1') = w(\mathbf{x}_1,\mathbf{x}_2)\delta(z_1,z_1')$$

It is alternatively defined as

$$G(1,1') = \frac{1}{i} \frac{\mathrm{Tr}\ \mathcal{T}\left\{e^{-i\int_\gamma dz\, \hat{H}(z)} \hat{\psi}(1)\hat{\psi}^\dagger(1')\right\}}{\mathrm{Tr}\ \mathcal{T}\left\{e^{-i\int_\gamma dz\, \hat{H}(z)}\right\}}$$

$$= -i\,\mathrm{Tr}\ \left[\hat{\rho}\,\mathcal{T}\left\{\hat{\psi}_H(1)\hat{\psi}_H^\dagger(1')\right\}\right]$$

It remains to find an explicit simple equation for g_k

Wick's theorem

$$g_n(1\ldots n, 1'\ldots n') = \begin{vmatrix} g(1,1') & \ldots & g(1,n') \\ \vdots & & \vdots \\ g(n,1') & \ldots & g(n,n') \end{vmatrix}$$

where we denoted $g(1,1') = g_1(1,1')$

The proof of this identity is easy: Apply the operators

$$i\,\partial_{z_j} - h(\mathbf{x}_j, z_j) \qquad\qquad h(\mathbf{x}, z) = -\frac{1}{2}\nabla^2 + v(\mathbf{x}, z)$$

on both sides of the equation and check that both sides satisfies the same differential equation and boundary conditions

what you need is that

$$(i\,\partial_{z_j} - h(j))g(j,j') = \delta(j,j') \qquad\qquad (-i\,\partial_{z'_j} - h(j'))g(j,j') = \delta(j,j')$$

$$g_k(\ldots,t_0,\ldots) = -g_k(\ldots,t_0 - i\beta,\ldots)$$

which follow directly from the definition of these quantities (check yourself)
(it is now also clear why the field operators need to anti-commute under the time-ordering operator)

The equations of motion for g(1,1') are simple one-particle equations and we can therefore easily solve them.

In combination with Wick's theorem this leads to an explicit expression for the interacting Green's function as a perturbation series

Perturbation expansion for the Green's function :

$$G(a,b) = \frac{\sum_{k=0}^{\infty} \frac{1}{k!} \left(\frac{i}{2}\right)^k \int w(1,1') \dots w(k,k') \begin{vmatrix} g(a,b) & g(a,1^+) & \dots & g(a,k'^+) \\ g(1,b) & g(1,1^+) & \dots & g(1,k'^+) \\ \vdots & \vdots & & \vdots \\ g(k',b) & g(k',1^+) & \dots & g(k',k'^+) \end{vmatrix}}{\sum_{k=0}^{\infty} \frac{1}{k!} \left(\frac{i}{2}\right)^k \int w(1,1') \dots w(k,k') \begin{vmatrix} g(1,1^+) & g(1,1'^+) & \dots & g(1,k'^+) \\ g(1',1^+) & g(1',1'^+) & \dots & g(1',k'^+) \\ \vdots & \vdots & & \vdots \\ g(k',1^+) & g(k',1'^+) & \dots & g(k',k'^+) \end{vmatrix}}$$

It is now only a technical matter to evaluate these terms

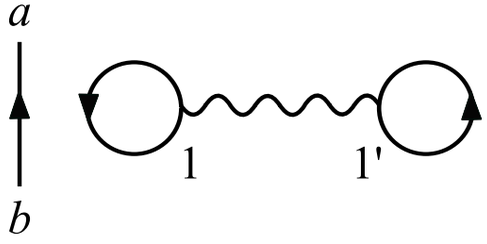
This leads to Feynman diagrams. Let us give an example an expand the numerator N(a,b) to first order

Expanding the 3x3 determinant along the first column we find

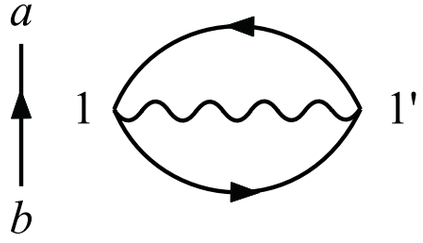
$$N^{(1)}(a;b) = \frac{i}{2} g(a;b) \int d1 d1' w(1,1') \begin{vmatrix} g(1;1^+) & g(1;1'^+) \\ g(1';1^+) & g(1';1'^+) \end{vmatrix}$$

$$\pm \frac{i}{2} \int d1 d1' w(1,1') g(1;b) \begin{vmatrix} g(a;1^+) & g(a;1'^+) \\ g(1';1^+) & g(1';1'^+) \end{vmatrix}$$

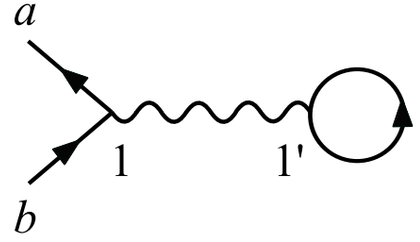
$$+ \frac{i}{2} \int d1 d1' w(1,1') g(1';b) \begin{vmatrix} g(a;1^+) & g(a;1'^+) \\ g(1;1^+) & g(1;1'^+) \end{vmatrix}$$



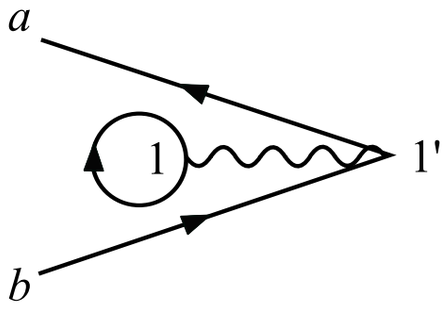
(*b*,1,1')



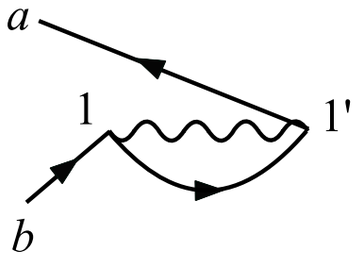
(*b*,1',1)



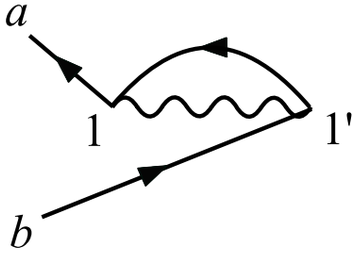
(1,*b*,1')



(1',1,*b*)



(1',*b*,1)

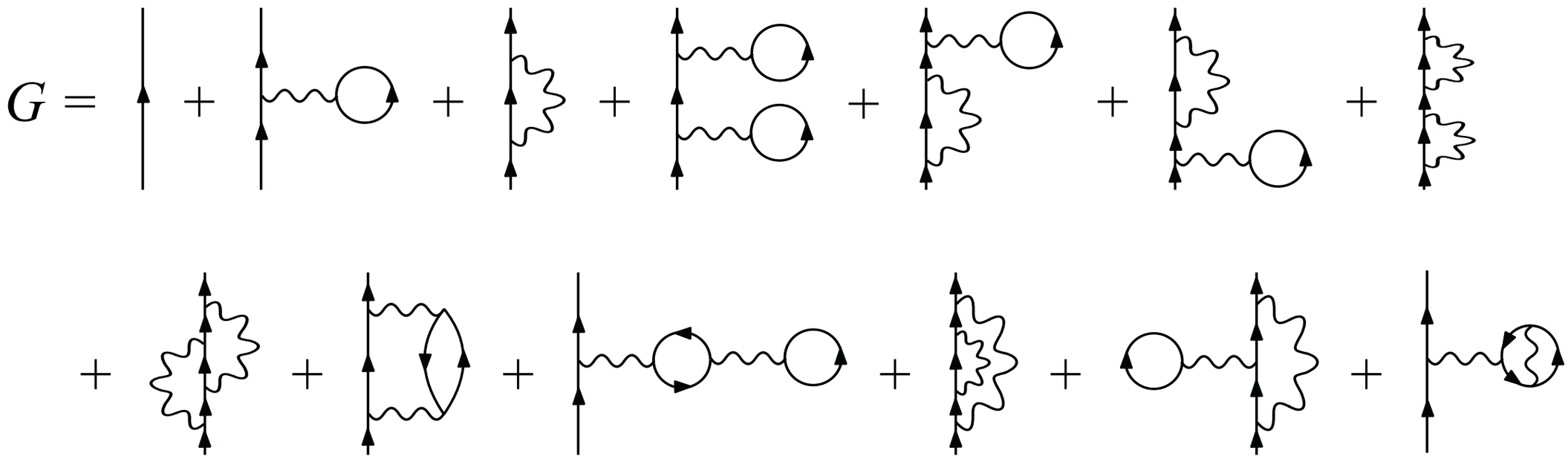


(1,1',*b*)

It is not difficult to prove that the disconnected diagrams from the numerator are cancelled by those of the denominator and we can further simplify to

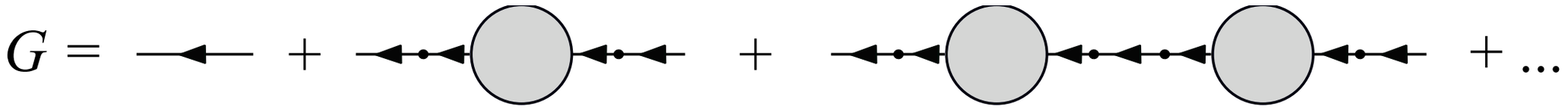
$$G(a,b) = \sum_{k=0}^{\infty} i^k \int w(1,1') \dots w(k,k') \left| \begin{array}{cccc} g(a,b) & g(a,1^+) & \dots & g(a,k'^+) \\ g(1,b) & g(1,1^+) & \dots & g(1,k'^+) \\ \vdots & \vdots & & \vdots \\ g(k',b) & g(k',1^+) & \dots & g(k',k'^+) \end{array} \right|_{CTI}$$

where in the expansion of the determinant we retain only the connected (C) and topologically inequivalent (TI) terms

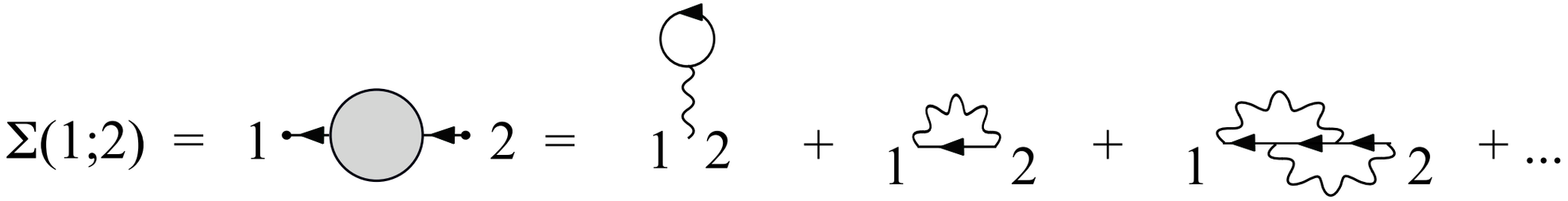


Self energy

The expansion of G has the structure



where the self-energy is defined as the sum over irreducible diagrams
(i.e. can not be cut in two by cutting one g-line)

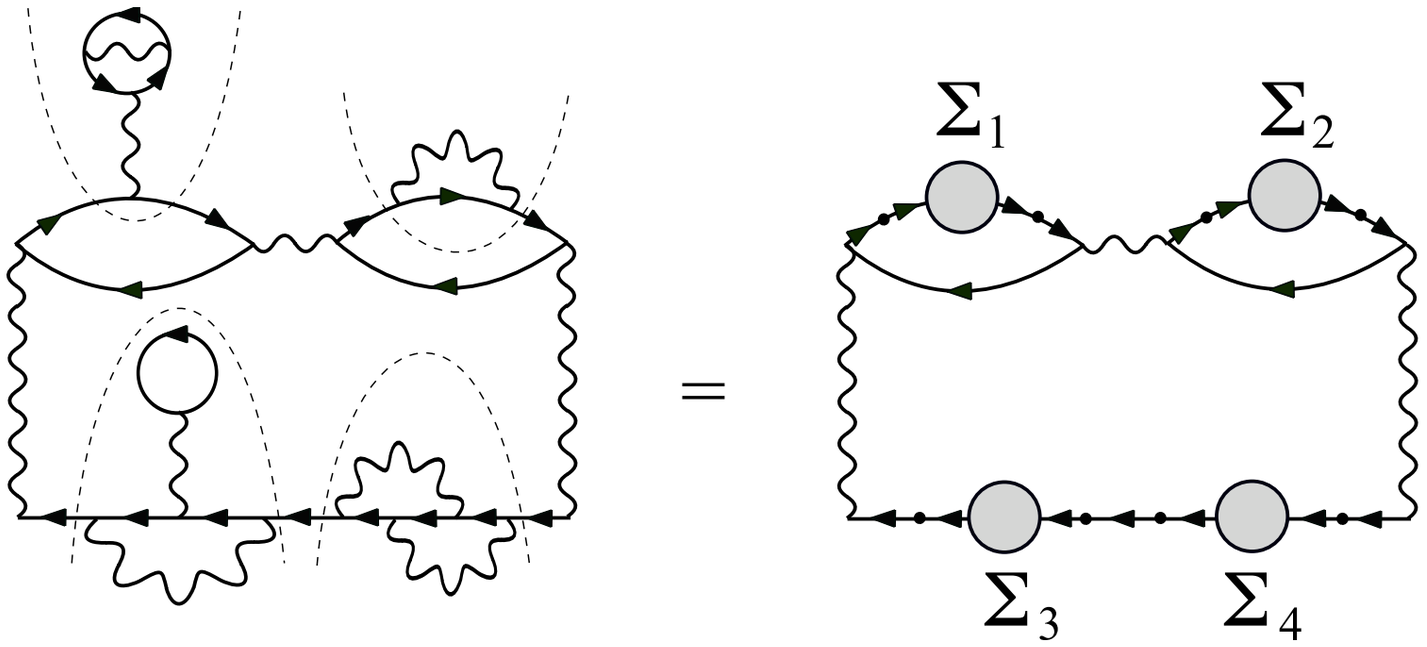


The Green's function thus satisfies the equation

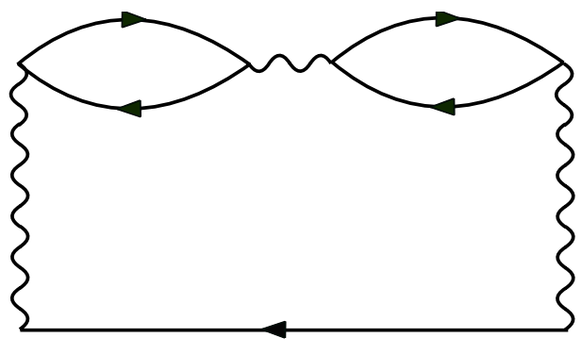
$$G(1,2) = g(1,2) + \int_\gamma d3d4\, g(1,3)\, \Sigma[g](3,4)\, G(4,2)$$

Skeletons

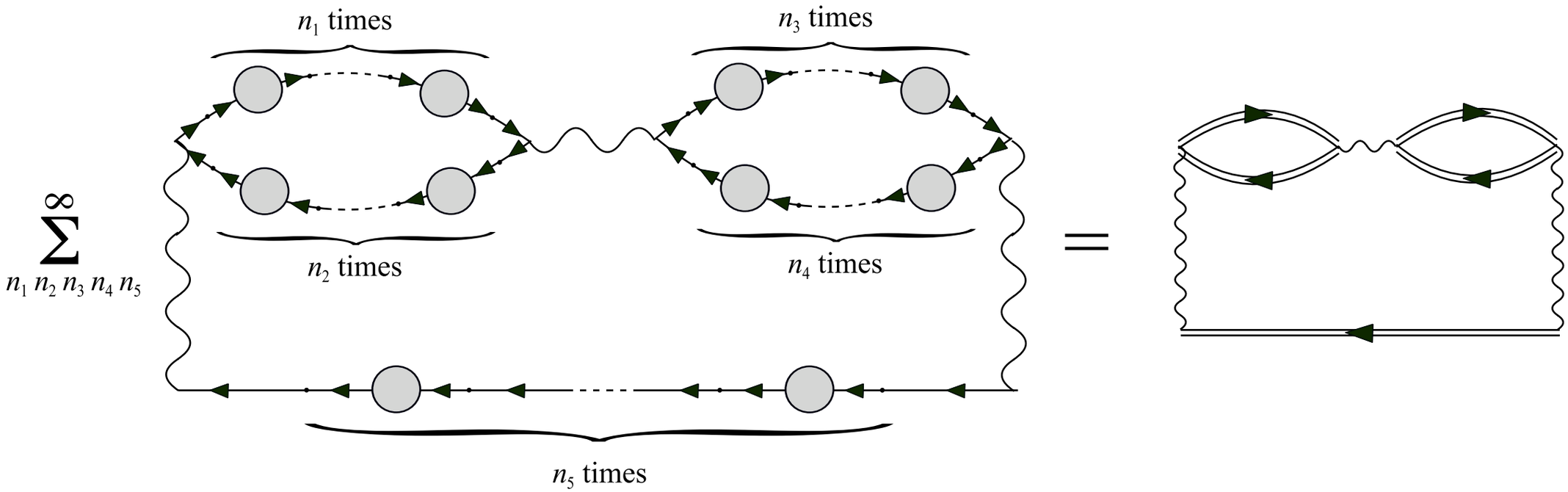
A skeleton diagram is a diagram without self-energy insertions, for example



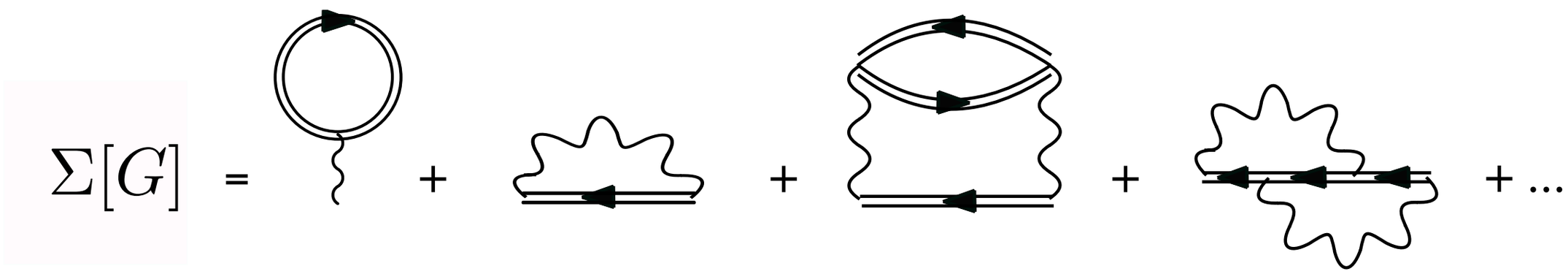
The corresponding skeleton is therefore



By replacing ‘g’ by ‘G’ in the skeleton we sum over all self-energy insertions



It follows that



where we sum over all dressed irreducible skeletons in terms of G

We therefore find the Dyson equation

$$G(1,2) = g(1,2) + \int_\gamma d3d4\, g(1,3)\, \Sigma[G](3,4)\, G(4,2)$$

or, if we use the equation of motion for g : $(i\,\partial_{z_1} - h(1))g(1,2) = \delta(1,2)$

$$(i\partial_{z_1} - h(1))G(1,1') = \delta(1,1') + \int_\gamma d2\, \Sigma[G](1,2)\, G(2,1')$$

This is a self-consistent equation of motion for the Green's function that needs to be solved with the boundary conditions

$$G(\mathbf{x}_1 t_0 - i\beta, 2) = -G(\mathbf{x}_1 t_0, 2)$$

$$G(1, \mathbf{x}_2 t_0) = -G(1, \mathbf{x}_2 t_0 - i\beta)$$

Particle/Hole propagators

If we denote $\langle \hat{A} \rangle = \mathrm{Tr}\ \ \hat{\rho}\hat{A}$ then the Green's function has the structure

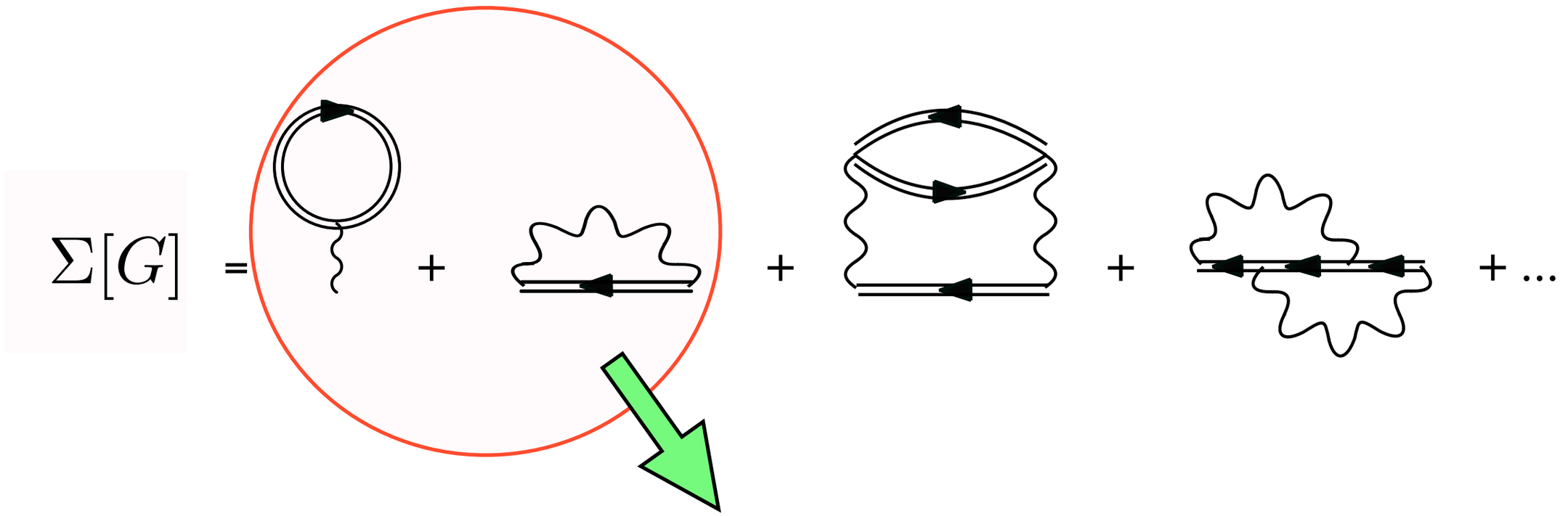
$$G(1,2) = -i\langle \mathcal{T}\left\{\hat{\psi}_H(1)\hat{\psi}_H^\dagger(2)\right\}\rangle = \theta(z_1,z_2)\,G^>(1,2) + \theta(z_1,z_2)\,G^<(1,2)$$

$G^>(1,2) = -i\langle \hat{\psi}_H(1)\hat{\psi}_H^\dagger(2)\rangle$ Propagation of a "particle" (added electron)

$G^<(1,2) = i\langle \hat{\psi}_H^\dagger(2)\hat{\psi}_H(1)\rangle$ Propagation of a "hole" (removed electron)

Natural tool in quantum transport; electrons are continuously added and removed from the central system.

The same is, of course, true for photo-emission



$$\Sigma^{\rm HF}(1,2) \sim \delta(z_1, z_2)$$

Hartree-Fock type diagrams are instantaneous

The self-energy has the structure

$$\Sigma(1,2) = \Sigma^{\rm HF}(1,2) + \theta(z_1, z_2)\,\Sigma^{>}(1,2) + \theta(z_2, z_1)\,\Sigma^{<}(1,2)$$

Putting the structure of the self-energy and the Green's function in the equation of motion for the Green's function we can undo the contour integrals and derive real-time equations for the particle and hole propagators. These are the Kadanoff-Baym equations

Kadanoff-Baym equations

For example, for the hole propagator we have the equation

Time-dependent external field

$$(i\partial_{t_1} - h(1))G^<(1,2) - \int d\mathbf{x}_3 \Sigma^{HF}(1,\mathbf{x}_3 t_1)G^<(\mathbf{x}_3 t_1, 2)$$

$$= \int_{t_0}^{t_1} d3[\Sigma^>(1,3) - \Sigma^<(1,3)]G^<(3,2) - \int_{t_0}^{t_2} d2\,\Sigma^<(1,3)[G^>(3,2) - G^<(3,2)]$$

$$+ \int_{t_0}^{t_0 - i\beta} d3\,\Sigma^\rceil(1,3)G^\lceil(3,2)$$

Collision or electron correlation terms : Memory kernels

Initial correlations

Kadanoff-Baym equations: practical solution

For practical solution the Green function is expanded into one-particle states

$$G(1,2) = \sum_{ij} \varphi_i(\mathbf{x}_1) G_{ij}(t_1, t_2) \varphi_j^*(\mathbf{x}_2)$$

For the one-particle states we can, for instance, use the solutions to the Hartree-Fock or Kohn-Sham equations

The Kadanoff-Baym equations become equations for time-dependent matrices

If we use the notation

$$f \cdot g = \int_{t_0}^{\infty} f(t) g(t)$$

$$f \star g = \int_0^{\beta} d\tau \, f(\tau) g(\tau)$$

then the full set of Kadanoff-Baym equations is compactly given as

$$
\begin{aligned}
i\partial_{t_1} G^{\lessgtr}(t_1,t_2) &= h^{\mathrm{HF}}(t_1)G^{\lessgtr}(t_1,t_2) + \left[\Sigma^{\lessgtr}\cdot G^{A} + \Sigma^{R}\cdot G^{\lessgtr} + \Sigma^{\rceil}\cdot G^{\lceil}\right](t_1,t_2) \\
-i\partial_{t_2} G^{\lessgtr}(t_1,t_2) &= G^{\lessgtr}(t_1,t_2)h^{\mathrm{HF}}(t_2) + \left[G^{\lessgtr}\cdot \Sigma^{A} + G^{R}\cdot \Sigma^{\lessgtr} + G^{\rceil}\cdot \Sigma^{\lceil}\right](t_1,t_2) \\
i\partial_{t} G^{\rceil}(t,\tau) &= \left[\Sigma^{R}\cdot G^{\rceil} + \Sigma^{\rceil}\star G^{M}\right](t,\tau) \\
-i\partial_{t} G^{\lceil}(\tau,t) &= \left[G^{\lceil}\cdot \Sigma^{A} + G^{M}\star \Sigma^{\lceil}\right](t,\tau)
\end{aligned}
$$

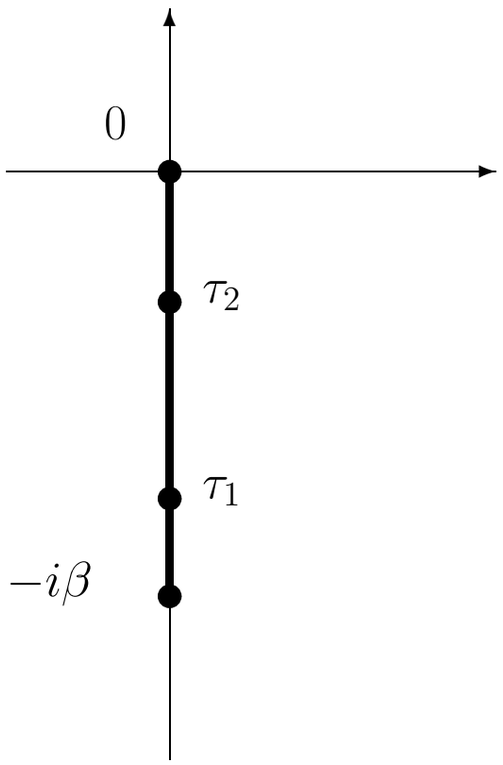
where all products are matrix products and the retarded and advanced functions are defined as

$$k^R(t,t') = \theta(t-t')[k^>(t,t') - k^<(t,t')]$$

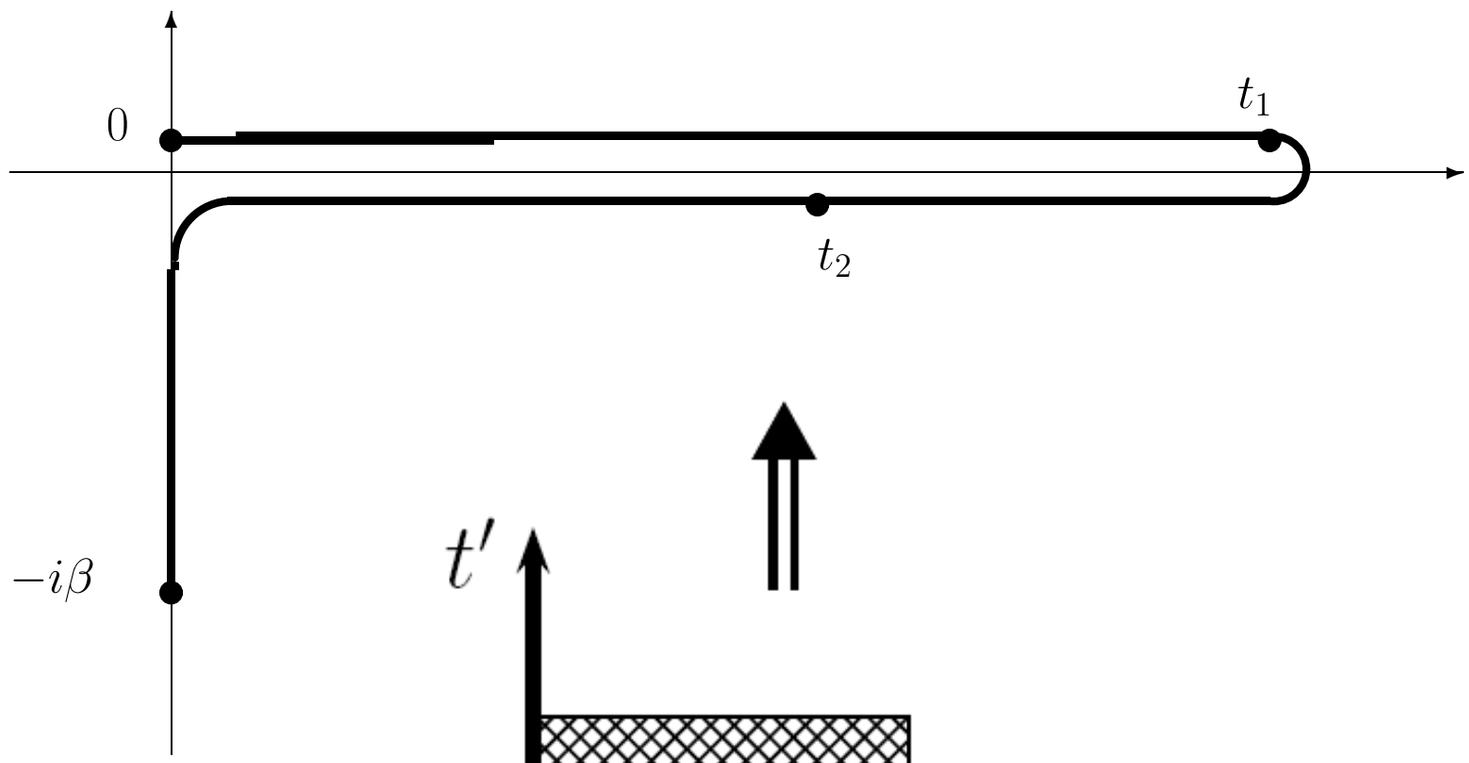
$$k^A(t,t') = -\theta(t'-t)[k^>(t,t') - k^<(t,t')]$$

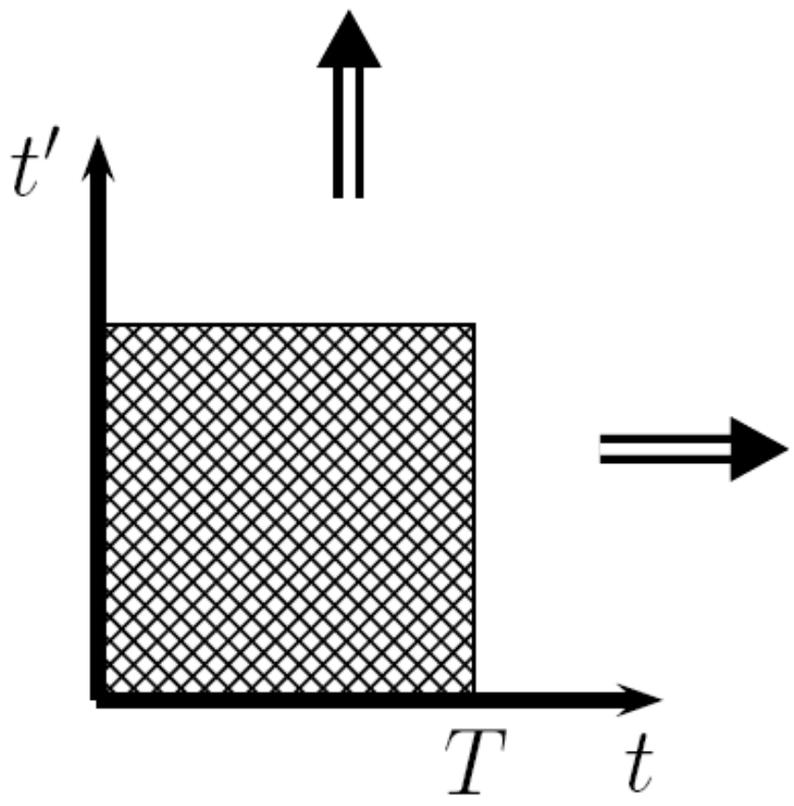
Time propagation of the Kadanoff-Baym equations

Solve equilibrium case on the imaginary axis



Carry out time-stepping in the double-time plane (possibly with external field applied)





(Nils Erik Dahlen, RvL,
Phys.Rev.Lett. 98, 153004 (2007),
A.Stan, N.E.Dahlen, RvL,
J.Chem.Phys.130, 224101 (2009))

The conservation laws

From an approximate Green function we can calculate several observables

$$\langle n(1)\rangle = -iG(1,1^+)$$ ⟸ density

$$\langle \mathbf{j}(1)\rangle = -i\left[\frac{\nabla_1}{2i} - \frac{\nabla_{1'}}{2i} + \mathbf{A}(1)\right] G(1,1')_{1'=1^+}$$ ⟸ current density

$$\langle \mathbf{P}(t_1)\rangle = \int d\mathbf{x}_1 \langle \mathbf{j}(1)\rangle$$ ⟸ momentum

These observables are related by conservation laws such as

$$\partial_{t_1}\langle n(1)\rangle + \nabla_1 \cdot \langle \mathbf{j}(1)\rangle = 0$$ ⟸ number conservation

$$\partial_{t_1}\langle \mathbf{P}(t_1)\rangle = -\int d\mathbf{x}_1 \left[\langle n(1)\rangle \mathbf{E}(1) + \langle \mathbf{j}(1)\rangle \times \mathbf{B}(1)\right]$$ ⟸ momentum conservation

Will these relations be satisfied if the ingredients are calculated from an approximate Green function ?

The conservation laws

(G.Baym, Phys.Rev. 127, 1391 (1962))

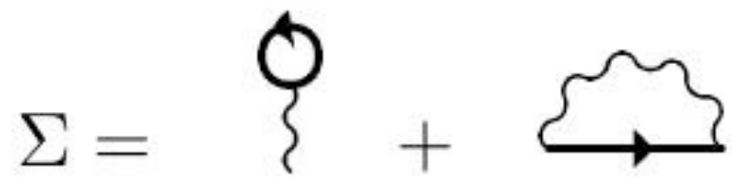
Conservation laws, such as those of energy, momentum, angular momentum and particle number, are automatically obeyed when we use so-called Phi-derivable approximations for the self-energy.

$$\Sigma(1,2) = \frac{\delta\Phi}{\delta G(2,1)}$$

For Phi-derivable approximations the expectation values are independent from the way they are calculated

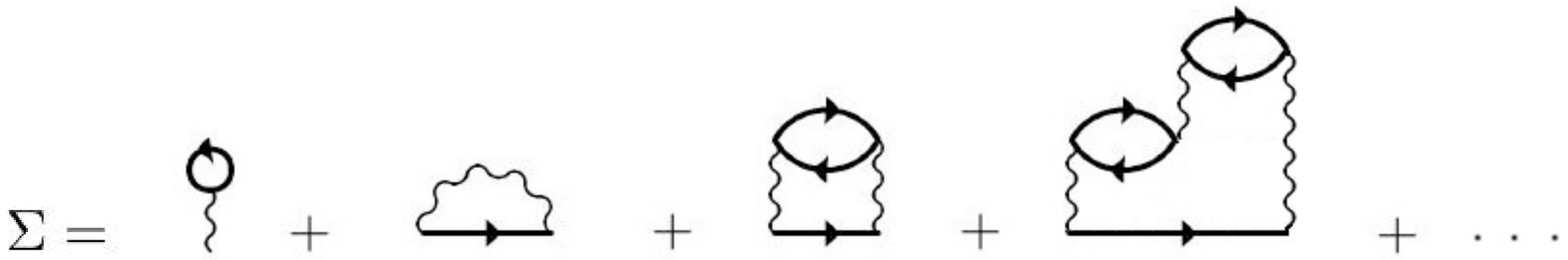
Conserving many-body approximations

Hartree-Fock



2nd Born

GW



The hydrogen molecule in a laser field

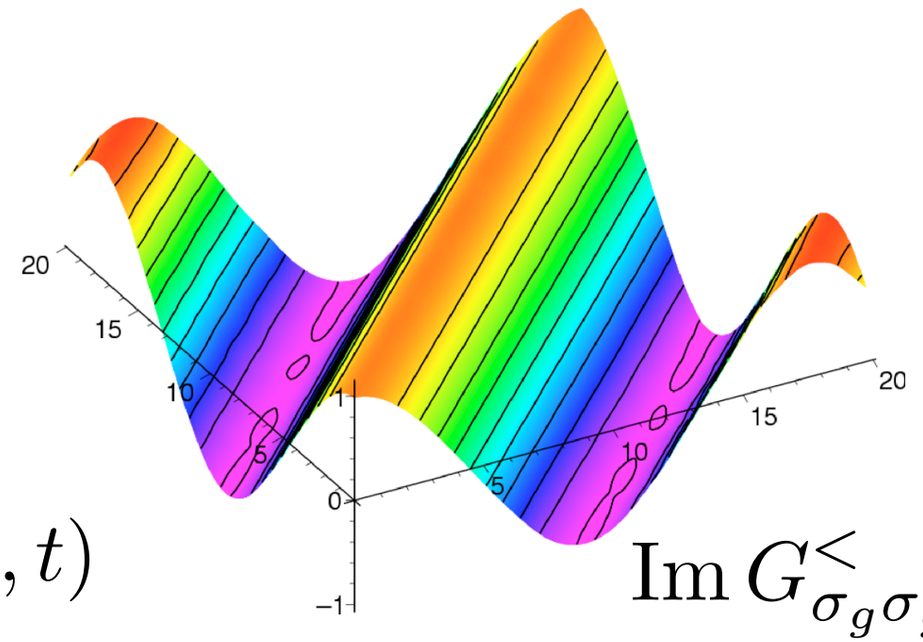
Equilibrium (no field applied)

$$v(\mathbf{r}t) = E(t)z$$

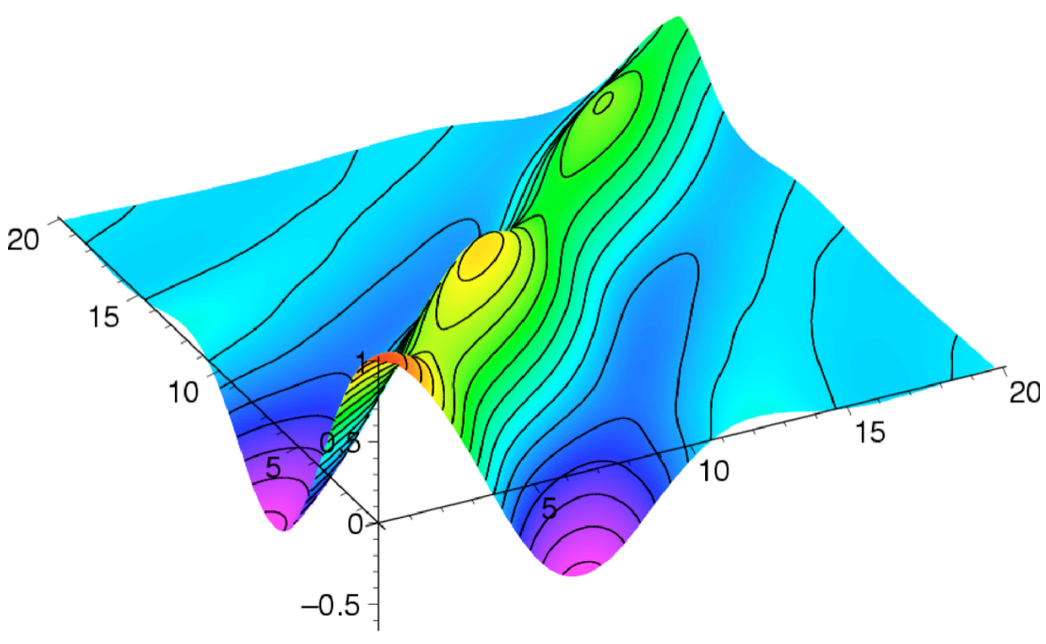
$$E(t) = \theta(t - t_0)E_0$$

On the time diagonal :

$$n_i(t) = \langle \hat{a}^\dagger_{i,H}(t)\hat{a}_{i,H}(t)\rangle = \mathrm{Im}\, G^<_{ii}(t,t)$$

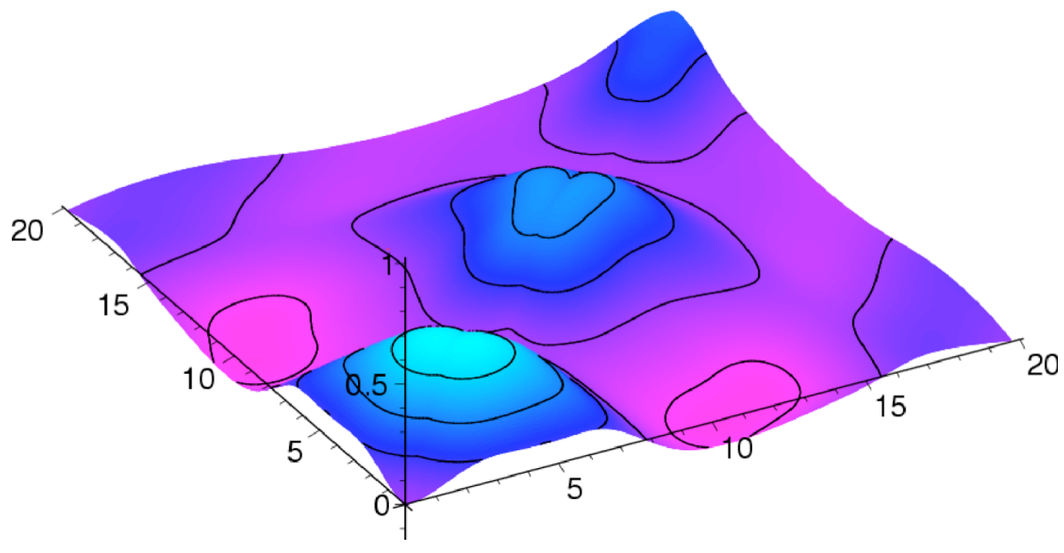


$\mathrm{Im}\, G^<_{\sigma_g\sigma_g}(t_1,t_2)$



$\mathrm{Im}\, G^<_{\sigma_g\sigma_g}(t_1,t_2)$

Nonequilibrium (field applied)

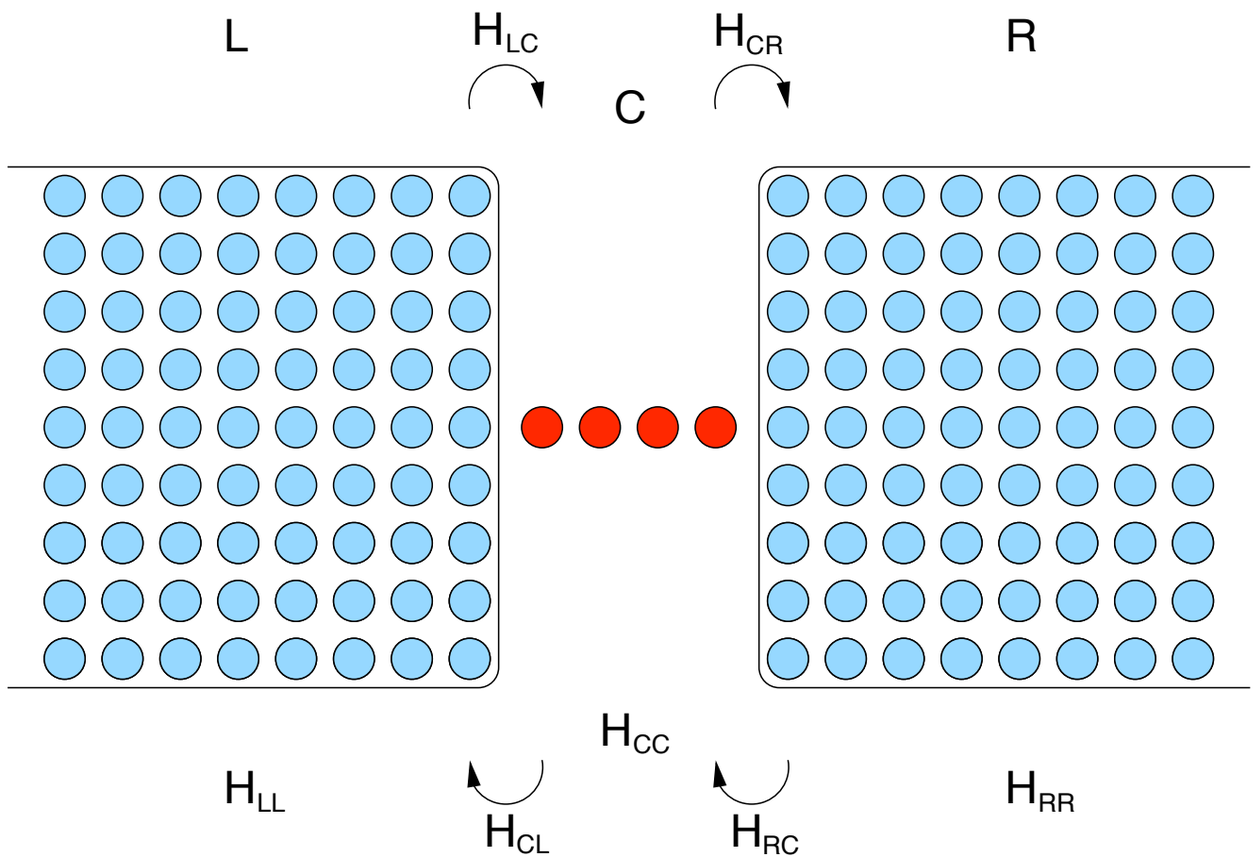


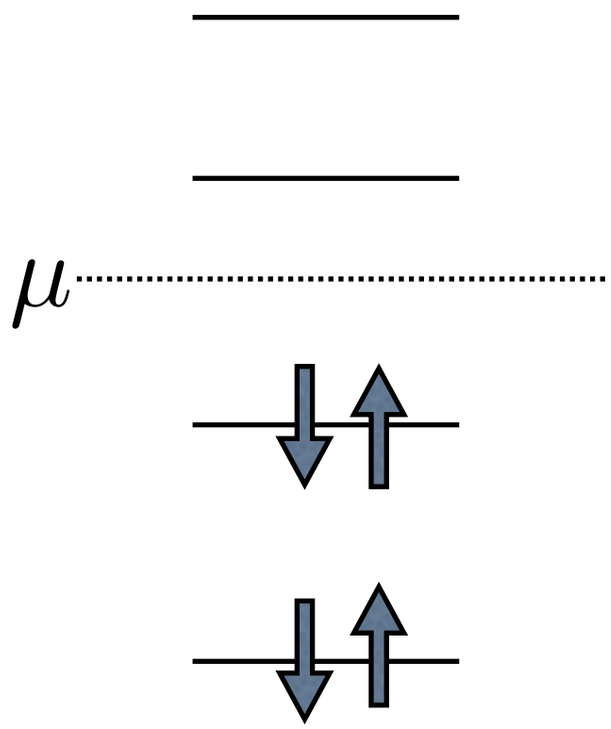
$\mathrm{Im}\, G^<_{\sigma_u\sigma_u}(t_1,t_2)$

Quantum transport

Green's functions are a natural tool in quantum transport; electrons are continuously added and removed from the central system.

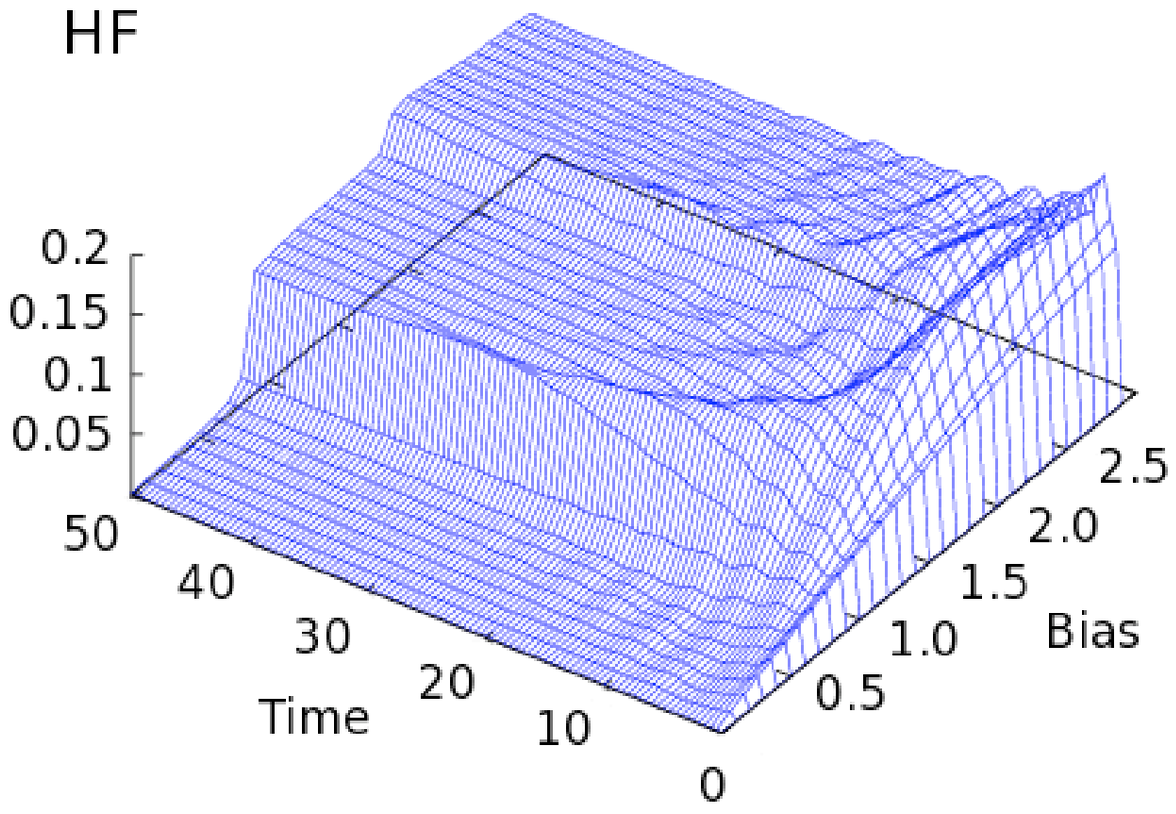
(see e.g. P. Myöhänen et al, Phys.Rev.B80, 115107 (2009))



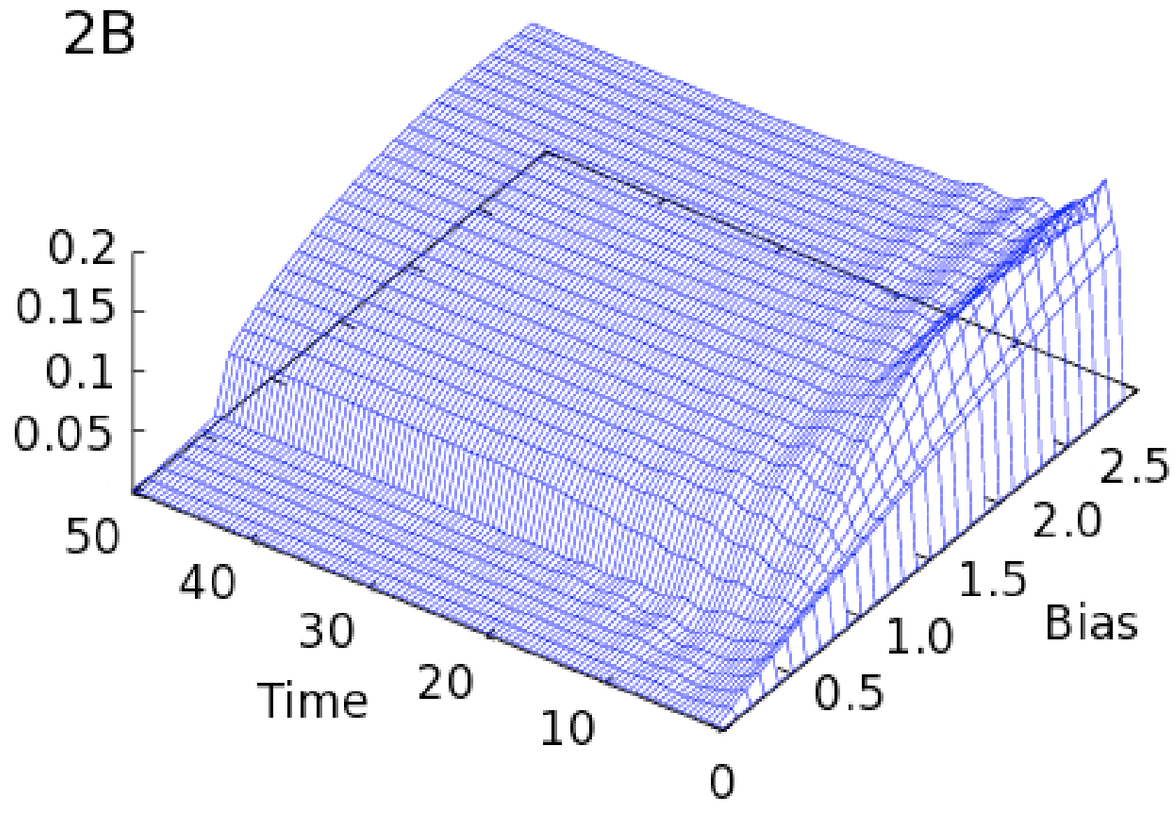


Time-dependent buildup of the I-V curves

Hartree-Fock



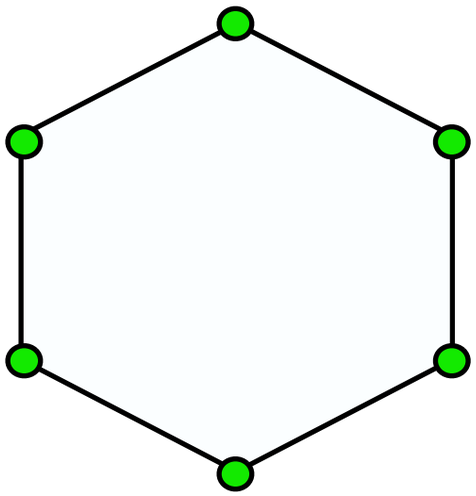
second Born

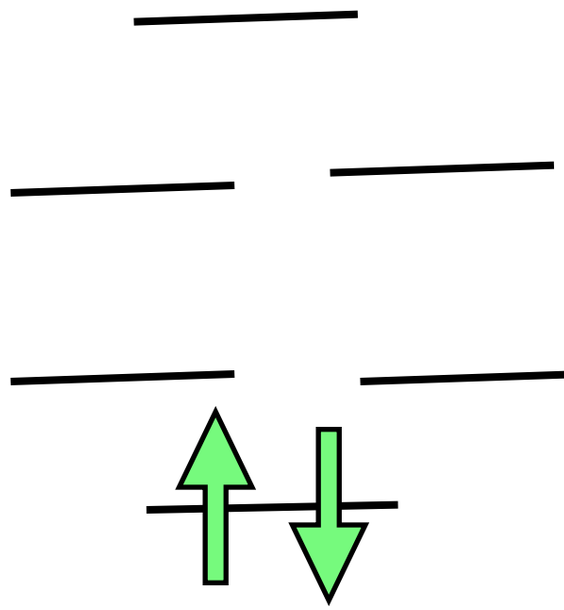


electron correlations beyond mean-field wash out I-V features

Linear response and optical absorption: double excitations

Example: Bench-mark system: 6 site Hubbard ring with 2 electrons





$$\hat{H}(t) = \sum_{ij} h_{ij}(t)\, \hat{a}_i^\dagger\, \hat{a}_j + \frac{1}{2} \sum_{ij} w_{ij}\, \hat{n}_i \hat{n}_j \qquad\qquad w_{ij} = U \delta_{ij}$$

(Niko Säkkinen, M.Manninen, RvL, New.J.Phys. 2012)

Response functions

Let us see how an (in general nonequilibrium) system reacts to a small additional perturbation. For instance

$$\delta n(1) = -i\delta G(1,1^+) = \int d2\,\chi(1,2)\delta v(2)$$

Let us define a generalized response function by

$$\delta G(1,1') = \int d2\Gamma(11';2)\delta v(2)$$

and try to find out its diagrammatic content. We have

$$(i\partial_{t_1} - h(1))\delta G(1,2) - \delta v(1)G(1,2) = \int d3(\Sigma(1,3)\delta G(3,2) + \delta\Sigma(1,3)G(3,2))$$

$$(i\partial_{t_1} - h(1))\delta G(1,2) - \int d3\Sigma(1,3)\delta G(3,2) = \delta v(1)G(1,2) + \int d3d4d5\frac{\delta\Sigma(1,3)}{\delta G(4,5)}\delta G(4,5)G(3,2)$$

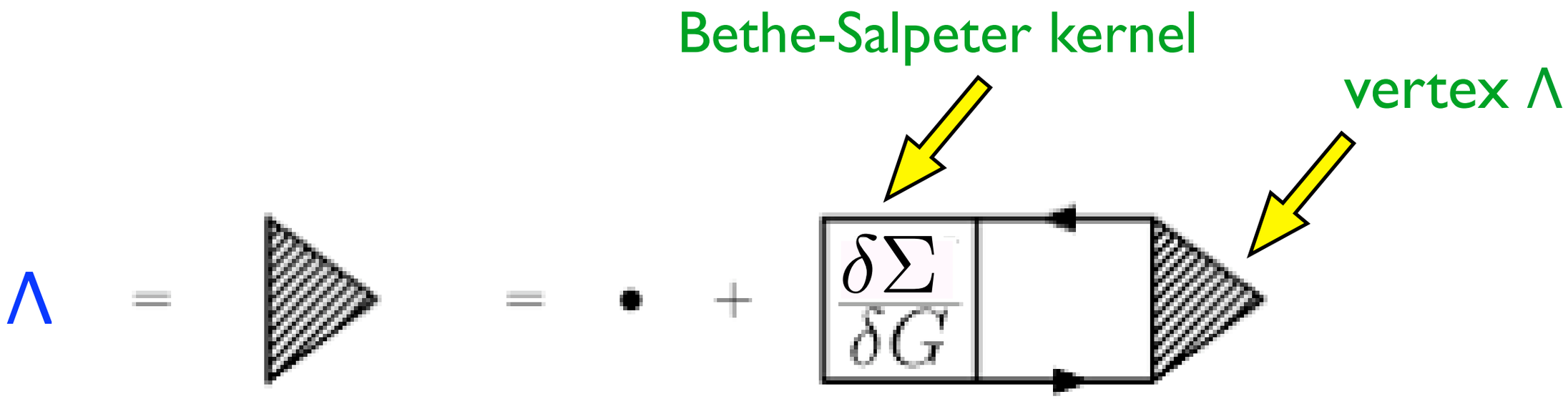
Which gives

$$\delta G(2',2) = \int d1 G(2',1)\delta v(1) G(1,2) + \int d1d3d4d5 G(2',1)\frac{\delta\Sigma(1,3)}{\delta G(4,5)}\delta G(4,5)G(3,2)$$

and finally

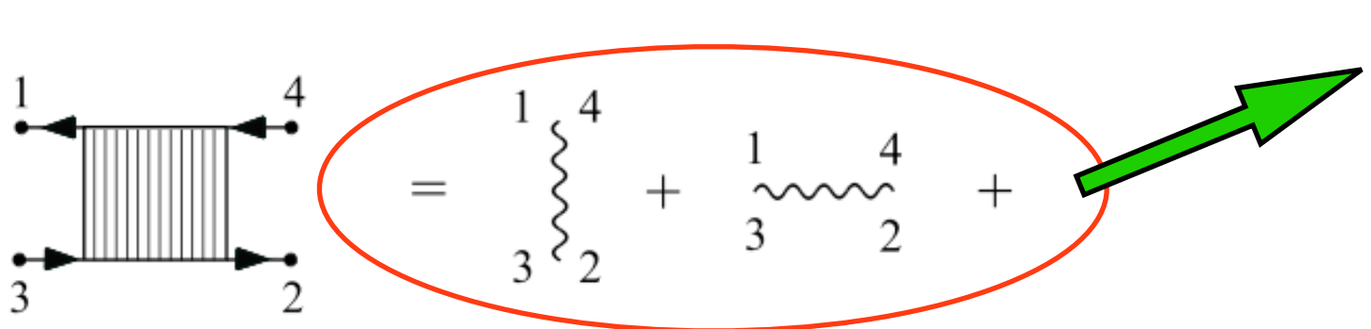
$$\Gamma(2'2;1) = G(2',1)G(1,2) + \int d3d4d5d6 G(2',1)G(3,2)\frac{\delta\Sigma(6,3)}{\delta G(4,5)}\Gamma(45;1)$$

which is diagrammatically given by (writing Γ = GG Λ)

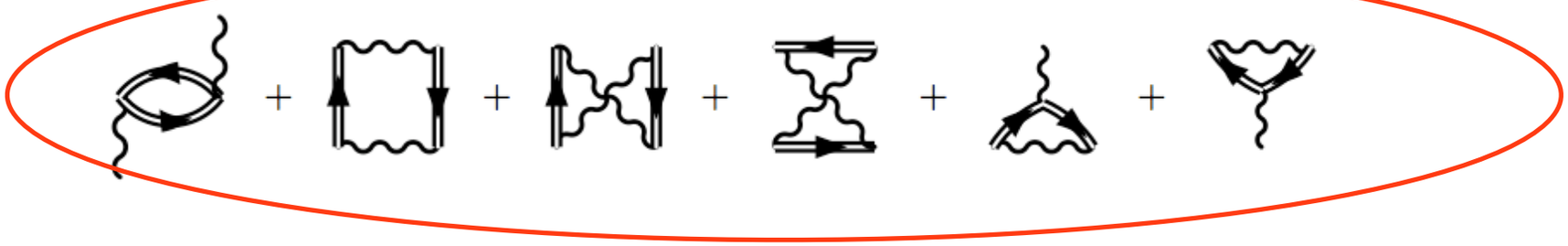


Single and doubly excited states

For instance at 2nd Born level we have the response kernel



TD Hartree-Fock
only singly excited states



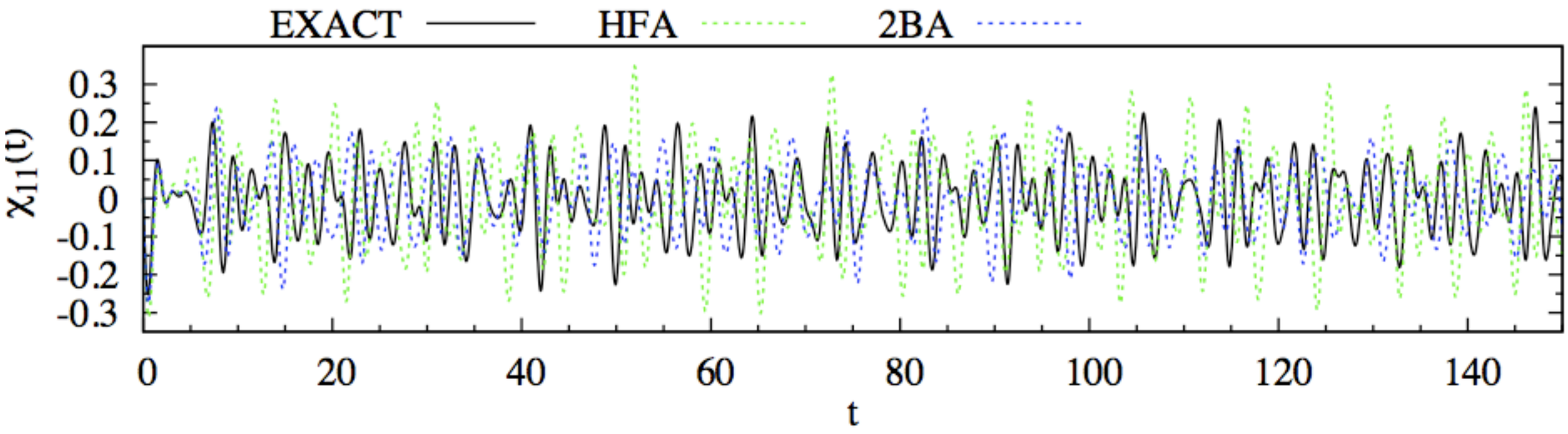
TD 2B containing
doubly excited states

$$\delta n_i(t) = -i\delta G_{ii}(t, t^+) = \sum_j \int_{t_0}^{t} dt'\, \chi_{ij}(t-t')\delta v_j(t')$$

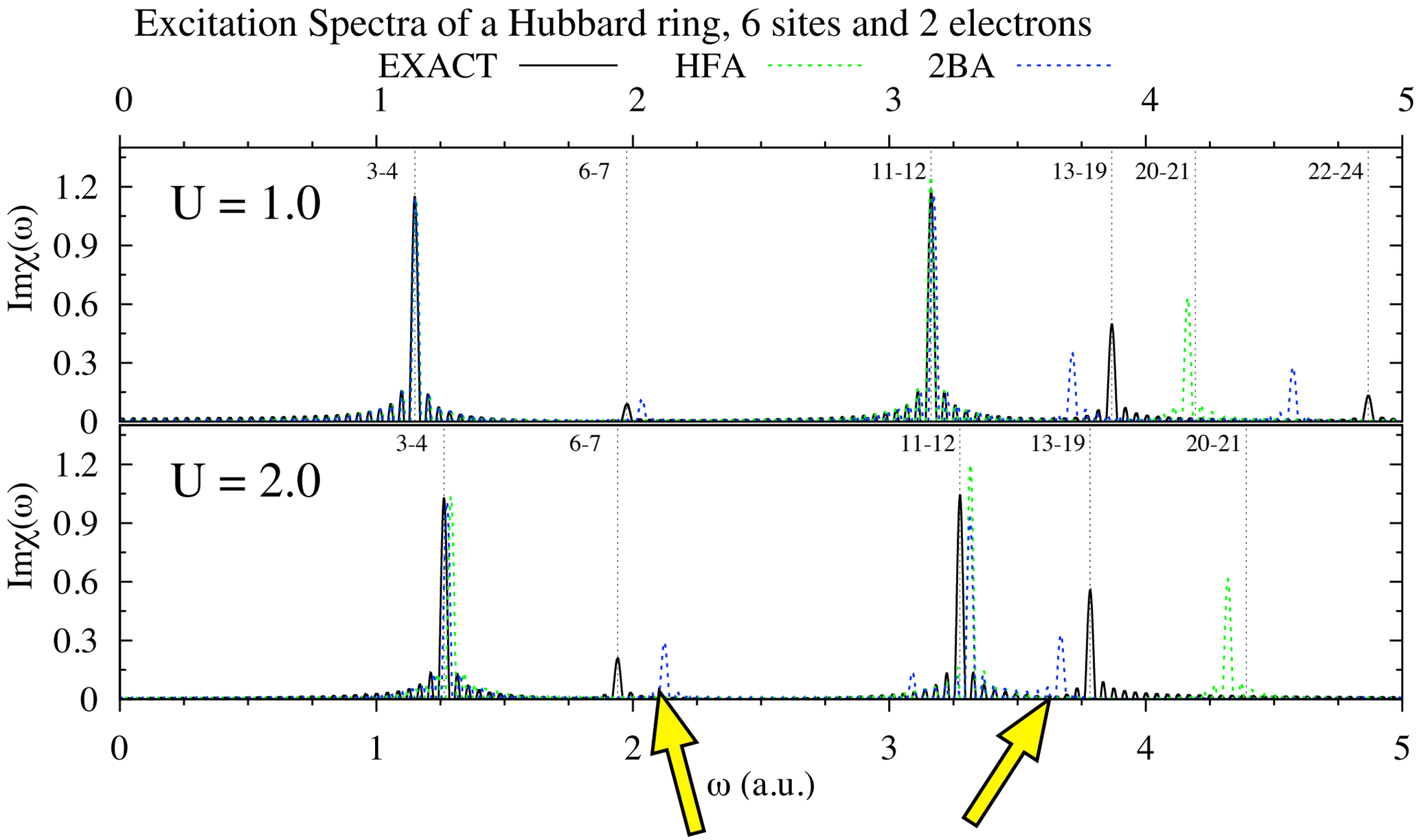
$$\delta v_j(t) = \lambda\, \delta_{1j}\, \delta(t - t_0)$$

$$\chi_{11}(\omega) = \frac{\delta n_1(\omega)}{\lambda}$$

6-site Hubbard, U=2, half-filling



(Niko Säkkinen, Matti Manninen, RvL -New J Phys 2012)



Doubly excited state