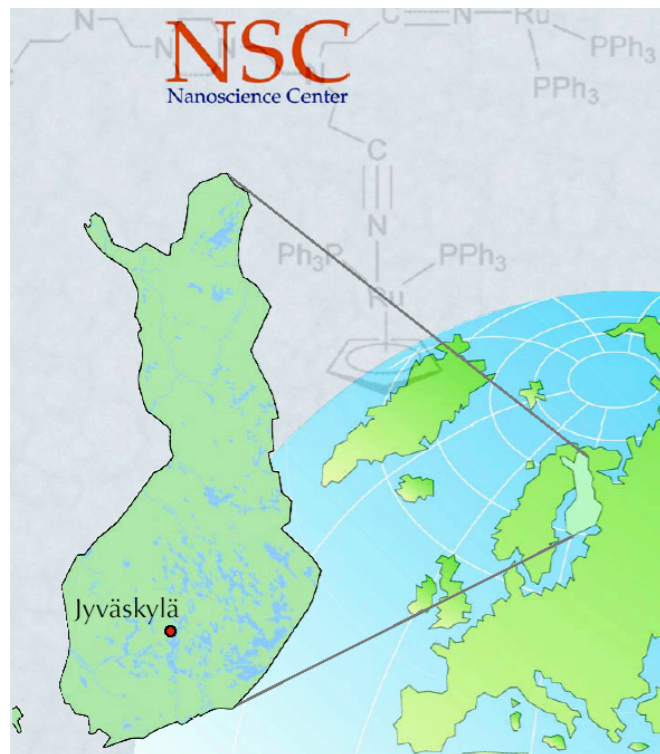# Electron-electron and electron-phonon interactions in time-dependent quantum transport: Nonequilibrium many-body theory

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JYVÄSKYLÄN YLIOPISTO
University of Jyväskylä
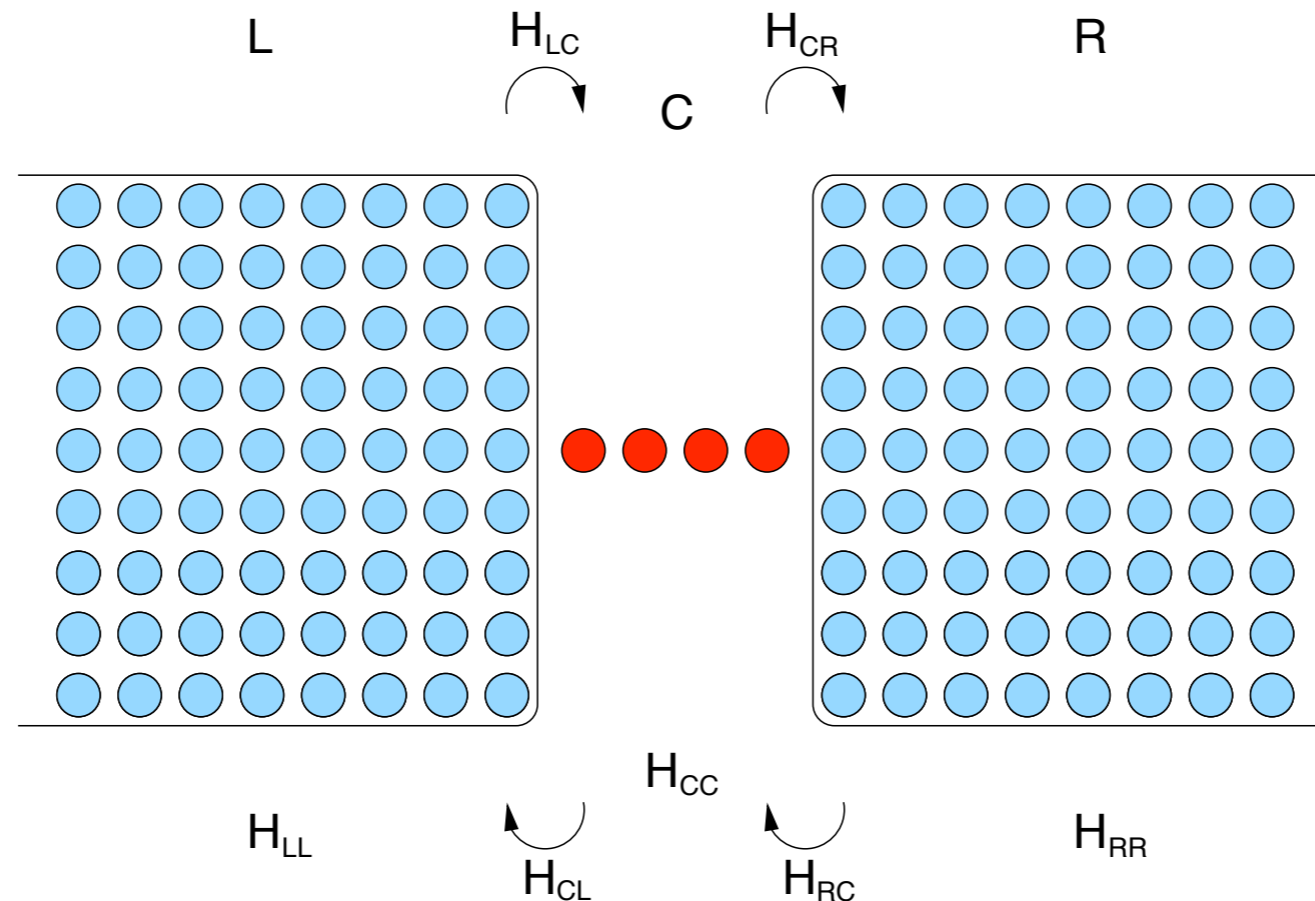
Overview

- Motivation

- Nonequilibrium Green's functions and the Kadanoff-Baym equations

- Illustrative examples
   - Electron-electron interactions
   - Electron-vibron interactions (preliminary results)

The time-dependent quantum transport problem

Consider a molecule (or quantum dot) attached to leads

L H_{LC} H_{CR} R

C

H_{LL} H_{CC} H_{RR}

H_{CL} H_{RC}

Problem:

Calculate the time evolution of observables of this system when a bias is applied.

Fundamental questions in quantum transport

- How long does it take before a steady state is reached (i.e what are the switch times) and how does it depend on e-e and e-ph interactions?

- Are steady states always reached and are they unique ? (bistability)

- What are the current and density distributions in the leads and the molecule (i.e. where in the molecule does the current flow and can we regulate this) ?

- What is the influence of the contact region? (Image charge effect)

- Can we determine the level structure of the molecule from transient spectroscopy?

Challenge for theoretical description, since we deal with :

- Open systems
- Nonequilibrium systems
- Electron-electron and electronic-vibrational interactions

electron-electron interactions

e⁻ e⁻

molecular vibrations
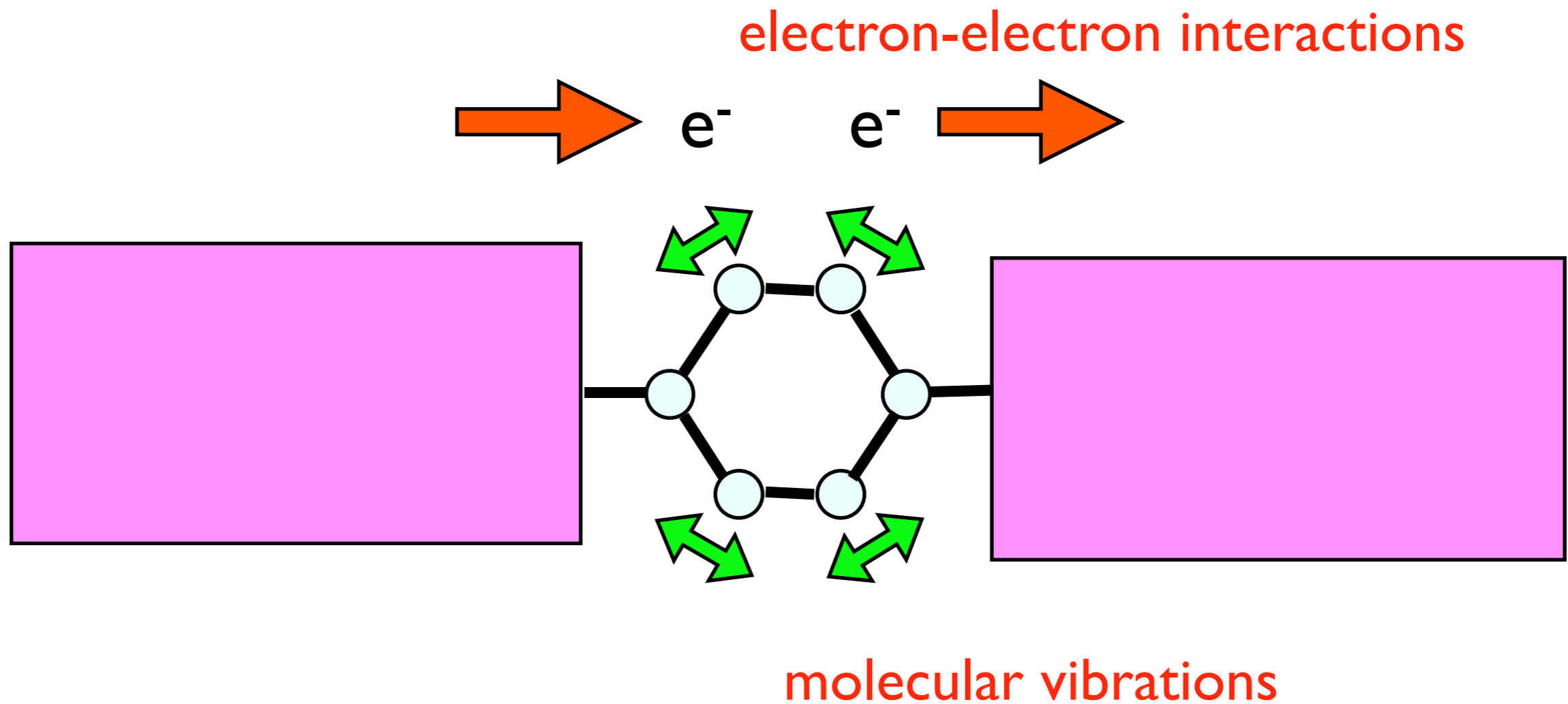
Time evolution of a many-body system

The time-dependent electron-phonon Hamiltonian

$$\hat{H}(t) = \hat{H}_{\mathrm{ph}} + \hat{H}_{\mathrm{el}}(t) + \hat{H}_{\mathrm{e\text{-}ph}}$$

$$\hat{H}_{\mathrm{el}}(t) = \hat{h}(t) + \hat{W}$$

Electron-phonon/vibron interactions

Electron-electron interactions

Kinetic energy
+
time-dependent
external potential
(bias, gate voltage, laser etc.)

The goal is calculate the time-dependent expectation values of observables :

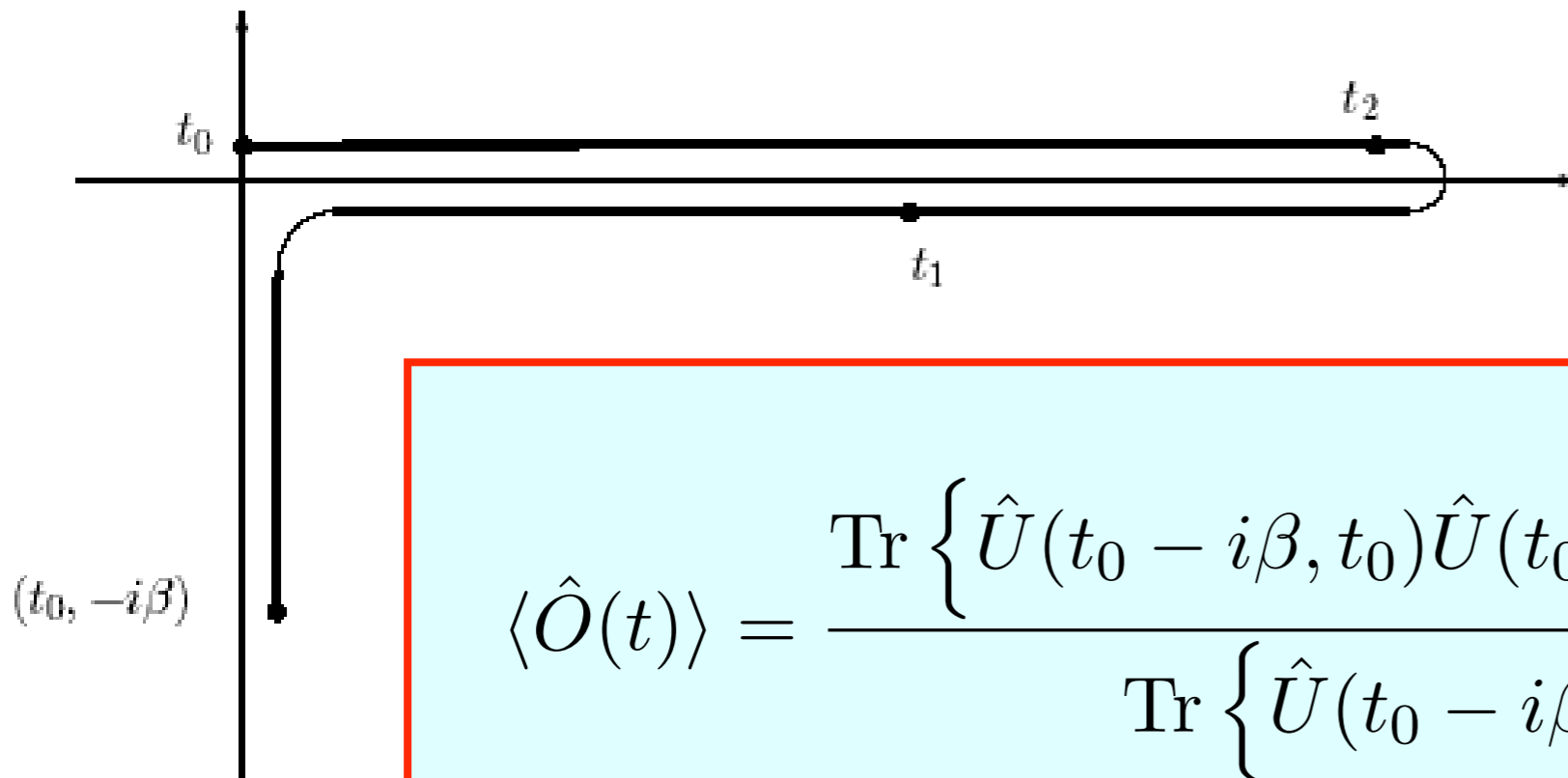$$\langle \hat{O}(t) \rangle = \text{Tr} \left\{ \hat{\rho}\, \hat{O}_H(t) \right\}$$

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

$$\hat{\rho} = \frac{e^{-\beta \hat{H}_0}}{\text{Tr}\, e^{-\beta \hat{H}_0}} \qquad \text{initial correlations} \qquad \hat{H}_0 = \hat{H}(t_0)$$

$$e^{-\beta \hat{H}_0} = e^{-i[(t_0 - i\beta) - t_0]\hat{H}_0} = \hat{U}(t_0 - i\beta, t_0)$$

The time contour

(L.V.Keldysh, Sov.Phys.JETP20, 1018 (1965)
Konstantinov and Perel' , JETP 12,142(1961))

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

$$\langle \hat{O}(t) \rangle = \frac{\mathrm{Tr}\left\{ T_C[\exp(-i\int_C d\bar{t}\hat{H}(\bar{t})\hat{O}(t)] \right\}}{\mathrm{Tr}\left\{ \hat{U}(t_0 - i\beta, t_0) \right\}}$$

We define the Keldysh contour-ordered Green function as :

$$G(1,2) = -i\langle T_C[\hat{\psi}_H(1)\hat{\psi}_H^\dagger(2)]\rangle = \theta(t_1, t_2)G^>(1,2) + \theta(t_2, t_1)G^<(1,2)$$

$$G^>(1,2) = -i\langle \hat{\psi}_H(1)\hat{\psi}_H^\dagger(2)\rangle$$ 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

We define the Keldysh contour-ordered phonon propagator as :

$$D(1,2) = -i\langle T_C[\Delta \hat{u}_H(1)\Delta \hat{u}_H(2)]\rangle = \theta(t_1,t_2)D^>(1,2) + \theta(t_2,t_1)D^<(1,2)$$

$$i = \mu_i t_i$$

$$D^>(1,2) = -i\langle \Delta \hat{u}_H(1)\Delta \hat{u}_H(2)]\rangle$$

$$D^<(1,2) = -i\langle \Delta \hat{u}_H(2)\Delta \hat{u}_H(1)]\rangle$$

Displacement correlation function

Electrons interact via phonon-propagators

The equation of motion for the propagators attain the form

effect of e-e and e-ph interactions
on electronic motion

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

A space-time dependent nonlocal
potential describing the effects of e-e
and e-ph interactions

$$-(\partial_{t_1}^2 + \omega^2)D(1,2) = \delta(1,2) + \int d3\, \Pi[G,D](1,3)D(3,2)$$

effect of e-e and e-ph interactions
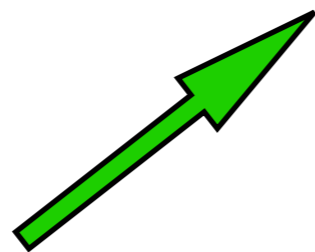on vibronic motion

By splitting the equation of motion in components, one obtains the set of Kadanoff-Baym equations. For example for the lesser component $G^<$:

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

The corresponding self-energy diagrams to 2nd order are :

$$\Sigma = $$ $+$ $+$ $+$

The interaction lines can represent Coulomb interactions or phonon propagators (also mixed diagrams)

If the equations of motion are solved self-consistently then we can guarantee satisfaction of conservation laws (electron particle number, energy, momentum)

Conserving many-body approximations

Hartree-Fock $\Sigma =$

2nd Born $\Sigma =$

GW $\Sigma =$

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 e-e interaction attains the form

$$v_{ijkl} = \int d\mathbf{x} \int d\mathbf{x}' \, \varphi_i^*(\mathbf{x}) \varphi_j^*(\mathbf{x}') v(\mathbf{r} - \mathbf{r}') \varphi_k(\mathbf{x}') \varphi_l(\mathbf{x})$$

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

The electronic self-energy for second Born is e.g. given by

$$\Sigma^{2B}(t,t') = \delta(t,t')\Sigma^{HF}(t) + \Sigma^{(2)}(t,t')$$

$$\Sigma_{ij}^{HF}(t) = -i\sum_{kl} G_{kl}(t,t^+)(2v_{ilkj} - v_{iljk})$$

$$\Sigma_{ij}^{(2)}(t,t') = \sum_{klmnpq} G_{kl}(t,t')G_{mn}(t,t')G_{pq}(t',t)\,v_{iqmk}(2v_{lnpj} - v_{nlpj})$$

(Nils Erik Dahlen, RvL,
Phys.Rev.Lett. 98, 153004 (2007))

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

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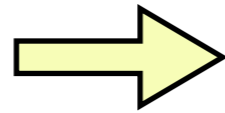\end{aligned}
$$

where all products are matrix products and the retarded and advanced functions are defined as
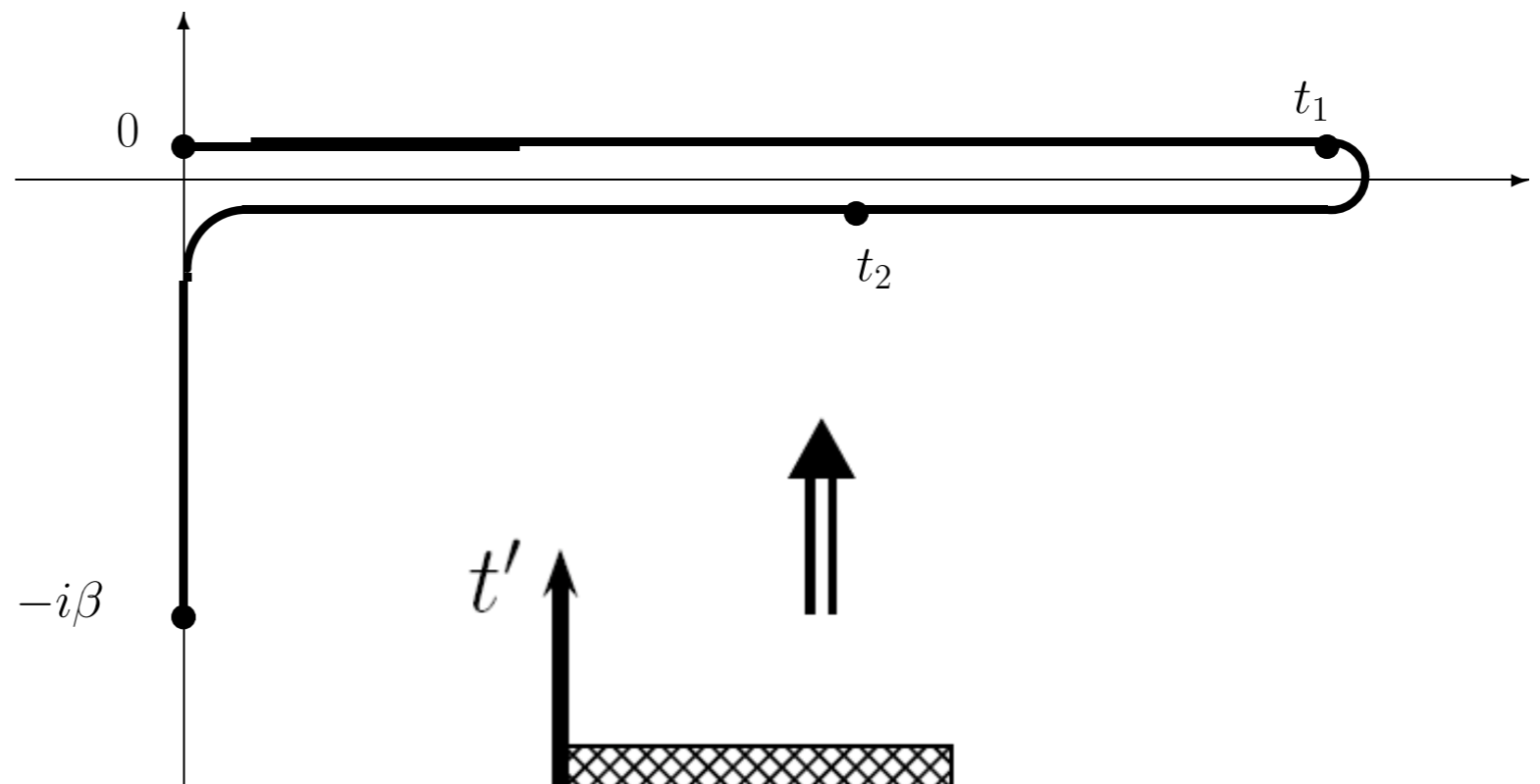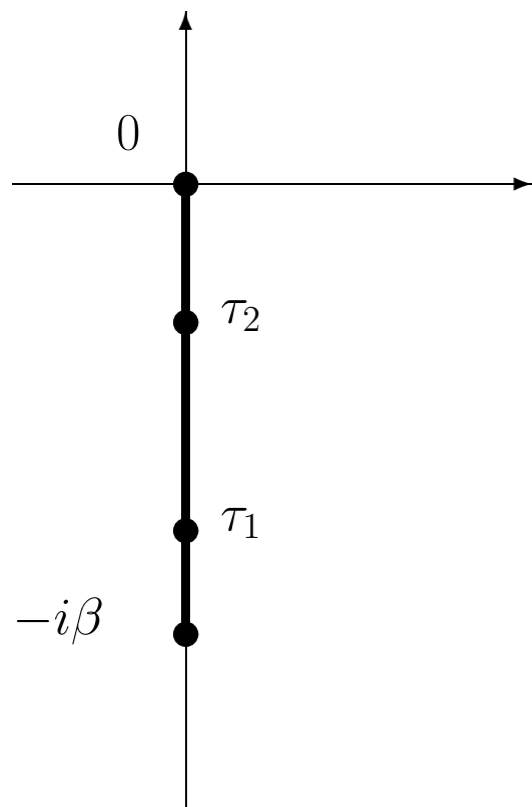
$$
k^R(t, t') = \theta(t - t')[k^>(t, t') - k^<(t, t')]
$$

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

Solve equilibrium case on the imaginary axis ⟹ Carry out time-stepping in the double-time plane (possibly with external field applied)
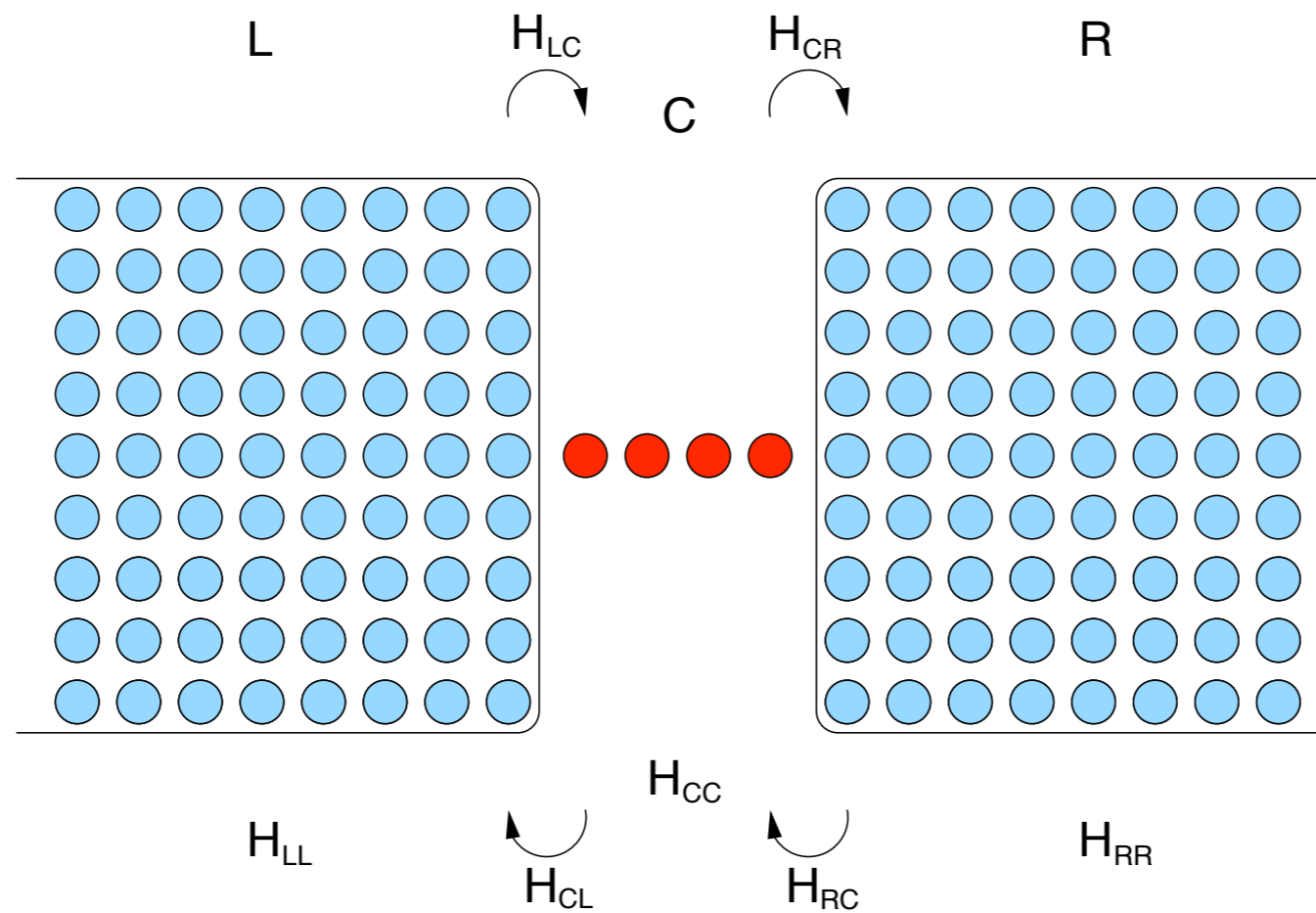

(Nils Erik Dahlen, RvL, Phys.Rev.Lett. 98, 153004 (2007), A.Stan, N.E.Dahlen, RvL, J.Chem.Phys.130, 224101 (2009))

The one-body part of the Hamiltonian is projected onto different regions

$$H = \begin{bmatrix} H_{LL} & H_{LC} & 0 \\ H_{CL} & H_{CC} & H_{CR} \\ 0 & H_{RC} & H_{RR} \end{bmatrix}$$

The Green function and the self-energy attain the form

$$
\boldsymbol{\mathcal{G}} = \begin{bmatrix} \boldsymbol{\mathcal{G}}_{\mathrm{LL}} & \boldsymbol{\mathcal{G}}_{\mathrm{LC}} & \boldsymbol{\mathcal{G}}_{\mathrm{LR}} \\ \boldsymbol{\mathcal{G}}_{\mathrm{CL}} & \boldsymbol{\mathcal{G}}_{\mathrm{CC}} & \boldsymbol{\mathcal{G}}_{\mathrm{RC}} \\ \boldsymbol{\mathcal{G}}_{\mathrm{RL}} & \boldsymbol{\mathcal{G}}_{\mathrm{CR}} & \boldsymbol{\mathcal{G}}_{\mathrm{RR}} \end{bmatrix} \qquad \boldsymbol{\Sigma}^{\mathrm{MB}} = \begin{bmatrix} 0 & 0 & 0 \\ 0 & \boldsymbol{\Sigma}^{\mathrm{MB}}_{\mathrm{CC}}[\boldsymbol{\mathcal{G}}_{\mathrm{CC}}] & 0 \\ 0 & 0 & 0 \end{bmatrix}
$$

with equations of motion for the complete system

$$
\begin{aligned}
i\partial_z \boldsymbol{\mathcal{G}}(z,z') &= \delta(z,z')\mathbf{1} + \mathbf{H}(z)\boldsymbol{\mathcal{G}}(z,z') \\
&\quad + \int d\bar{z}\, \boldsymbol{\Sigma}^{\mathrm{MB}}(z,\bar{z})\boldsymbol{\mathcal{G}}(\bar{z},z') \\
-i\partial_{z'} \boldsymbol{\mathcal{G}}(z,z') &= \delta(z,z')\mathbf{1} + \boldsymbol{\mathcal{G}}(z,z')\mathbf{H}(z') \\
&\quad + \int d\bar{z}\, \boldsymbol{\mathcal{G}}(z,\bar{z})\boldsymbol{\Sigma}^{\mathrm{MB}}(\bar{z},z)
\end{aligned}
$$

The equation of motion

The equation of motion projected on the central region has the form

$$\left\{ i\partial_z \mathbf{1} - \mathbf{H}_{\mathrm{CC}}(z) \right\} \boldsymbol{\mathcal{G}}_{\mathrm{CC}}(z, z')$$

$$= \delta(z, z')\mathbf{1} + \int d\bar{z} \left[\boldsymbol{\Sigma}_{\mathrm{CC}}^{\mathrm{MB}} + \boldsymbol{\Sigma}_{\mathrm{em}} \right](z, \bar{z}) \, \boldsymbol{\mathcal{G}}_{\mathrm{CC}}(\bar{z}, z').$$

where on top of the a many-body self-energy we also have
an effective embedding self-energy

$$\boldsymbol{\Sigma}_{\mathrm{em}}(z, z') = \sum_{\alpha} \boldsymbol{\Sigma}_{\mathrm{em},\alpha}(z, z') = \sum_{\alpha} \mathbf{H}_{\mathrm{C}\alpha} \, \mathbf{g}_{\alpha\alpha}(z, z')\mathbf{H}_{\alpha\mathrm{C}}$$

The total current flowing out of reservoir α is given by :

$$I_\alpha(t) = \frac{dN_\alpha(t)}{dt} = -2\,\mathrm{Re}\,\mathrm{Tr}_C[G^<_{C\alpha}(t,t)H_{\alpha C}]$$

This gives after some manipulations:

$$I_\alpha(t) = -2\mathrm{Re}\mathrm{Tr}_C \int_0^t dt' \left[G^<_{CC}(t,t')\Sigma^{\mathrm{A}}_{\mathrm{em},\alpha}(t',t) + G^{\mathrm{R}}_{CC}(t,t')\Sigma^<_{\mathrm{em},\alpha}(t,t') \right]$$

$$-2\mathrm{Re}\mathrm{Tr}_C \int_0^{-i\beta} dt' \left[G^{\rceil}_{CC}(t,t')\Sigma^{\lceil}_{\mathrm{em},\alpha}(t',t) \right]$$

Memory of initial correlations

Long time limit leads under some assumptions to Meir-Wingreen formula

The spectral function

The spectral function for a nonequilibrium system is defined as

$$A(t, t') = \mathrm{Tr}\mathbf{A}(t, t') \qquad \mathbf{A}_{ij}(t, t') = \langle \Psi_0 | \{ \hat{a}_{i,H}(t), \hat{a}_{j,H}^\dagger(t') \} | \Psi_0 \rangle$$

In equilibrium the spectral function only depends on the difference of the time coordinates and can be Fourier transformed to give

$$A_{ii}(\omega) = \sum_k |\langle \Psi_k^{N+1} | \hat{a}_i^\dagger | \Psi_0 \rangle|^2 \delta(\omega + E_0^N - E_k^{N+1})$$

$$+ \sum_k |\langle \Psi_k^{N-1} | \hat{a}_i | \Psi_0 \rangle|^2 \delta(\omega - E_0^N + E_k^{N-1})$$

It shows peaks at electron addition and removal energies

In the nonequilibrium case it is convenient to Fourier transform with respect to the relative times:

$$A(T,\omega) = \int \frac{d\omega}{2\pi} A(T + \frac{t}{2}, T - \frac{t}{2}) \, e^{i\omega t}$$

which can be calculated from the Green function as

$$A(T,\omega) = -\operatorname{Im}\operatorname{Tr}_{\mathrm{C}} \int \frac{dt}{2\pi} \, e^{i\omega t} [\boldsymbol{\mathcal{G}}_{\mathrm{CC}}^{>} - \boldsymbol{\mathcal{G}}_{\mathrm{CC}}^{<}](T + \frac{t}{2}, T - \frac{t}{2})$$

In the long time limit the spectral function becomes independent of T when a steady state is being reached

$$\lim_{T \to \infty} A(T,\omega) = A(\omega)$$

Simple example: e-e interactions

Interaction

$$v_{ijkl} = v_{ij}\delta_{il}\delta_{jk}$$

$$v_{ij} = \begin{cases} v_{ii} & i = j \\ \dfrac{v_{ii}}{2|i-j|} & i \neq j \end{cases}$$

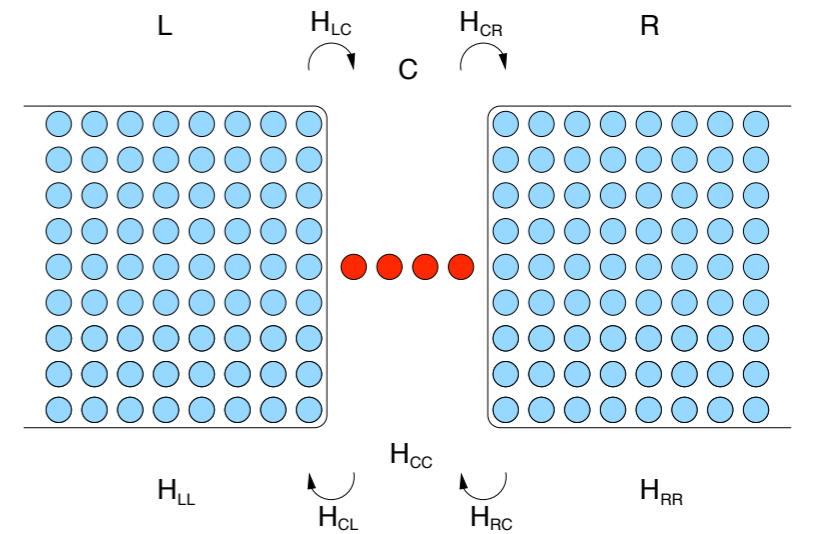$$v_{ii} = 1.5$$

Time-dependent bias

$$U_L(t) = -U_R(t) = U\,\theta(t - t_0)$$
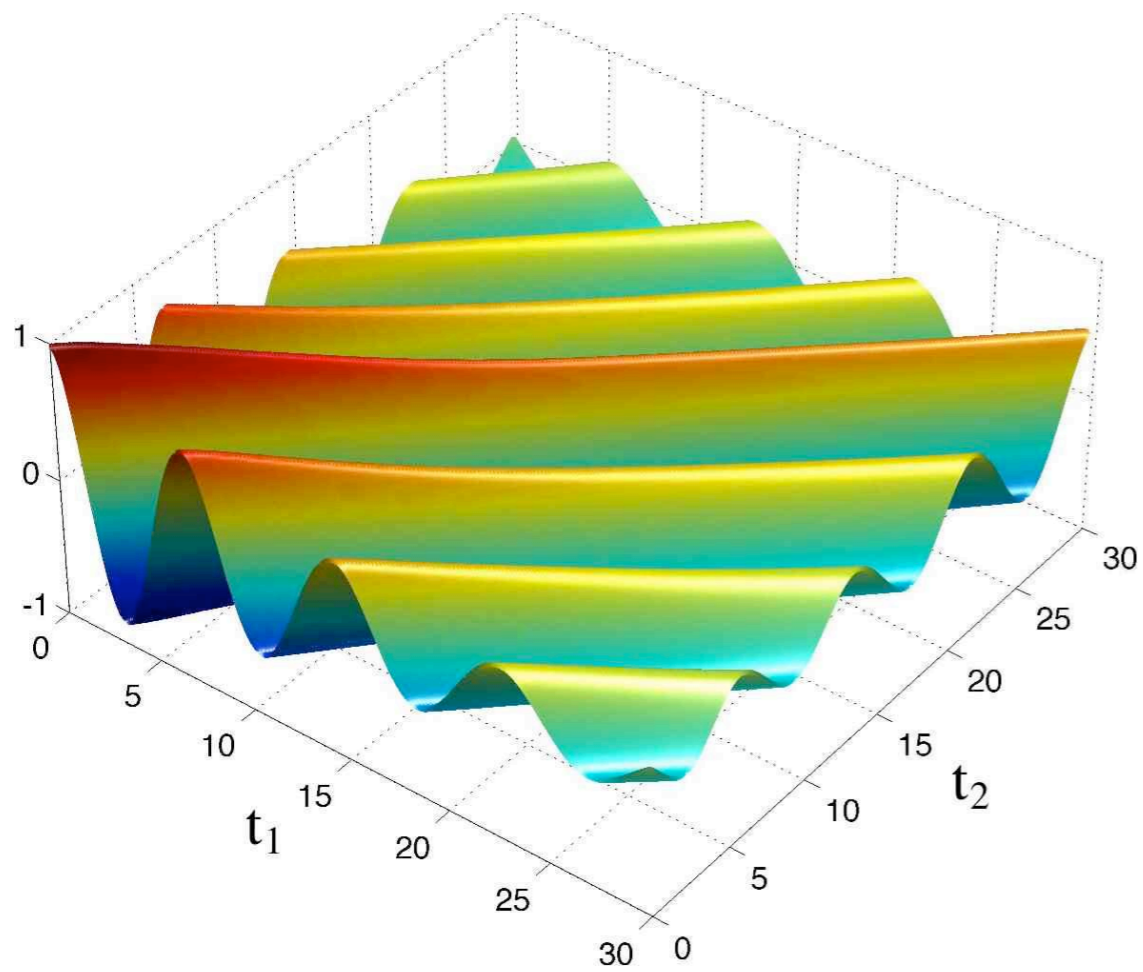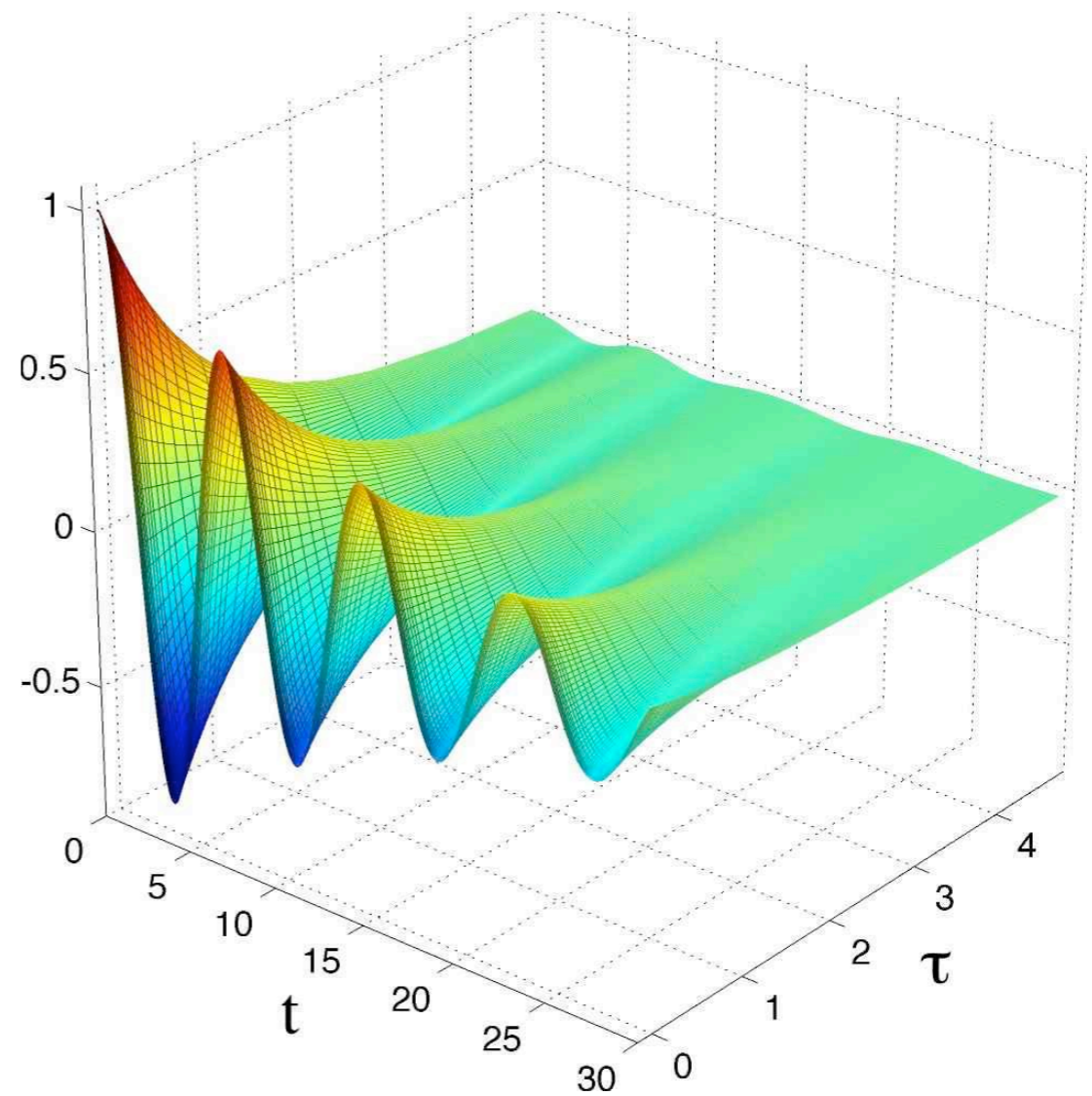
Hoppings:

$$t^{\alpha} = -2$$

$$t_C = -1$$

$$V_{1,5L} = V_{4,5R} = -0.5$$
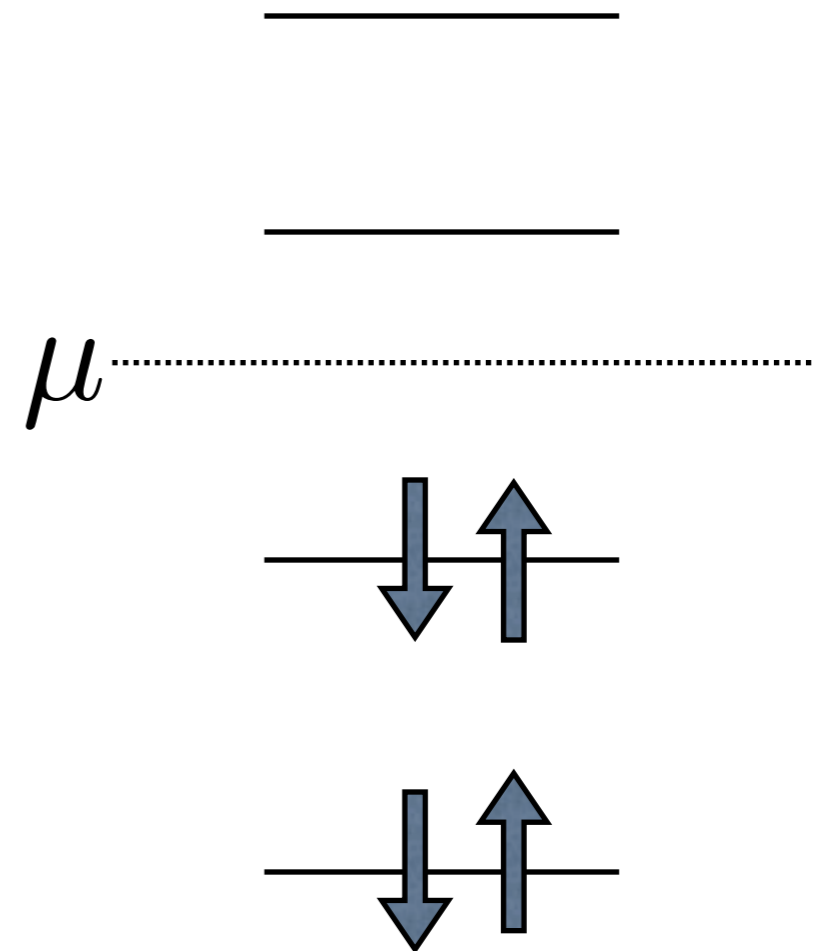
For the highest occupied molecular orbital the Green function matrix element has the following structure (imaginary part displayed)

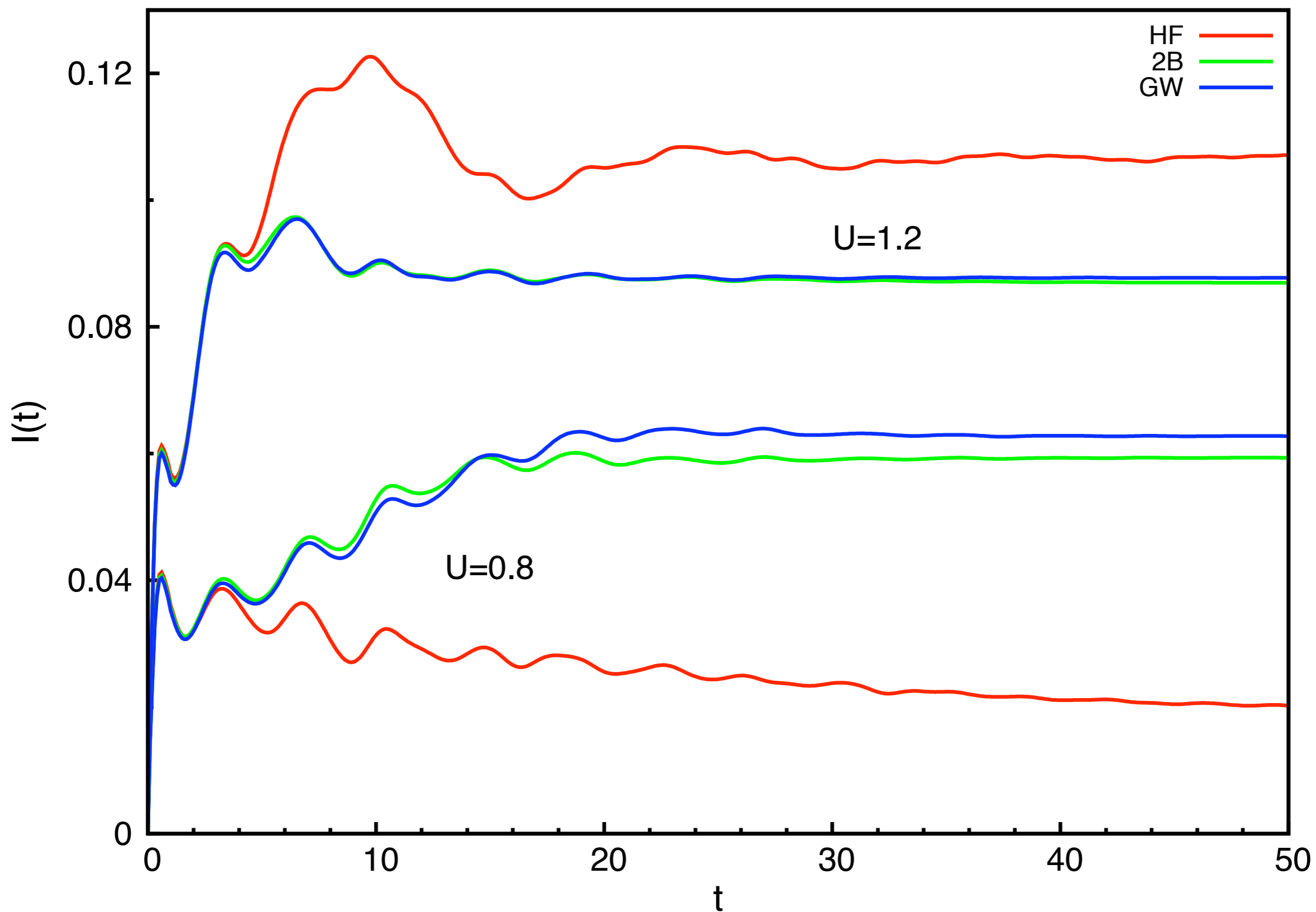$$\mathcal{G}^{<}_{\mathrm{CC},HH}(t_1, t_2)$$

$$\mathcal{G}^{\rceil}_{\mathrm{CC},HH}(t, \tau)$$

The transient currents

The spectral functions

Steady state regime

U=0.8 (solid line)   U=1.2 (dashed line)

HF

$\mu = 2.26$

2B

GW
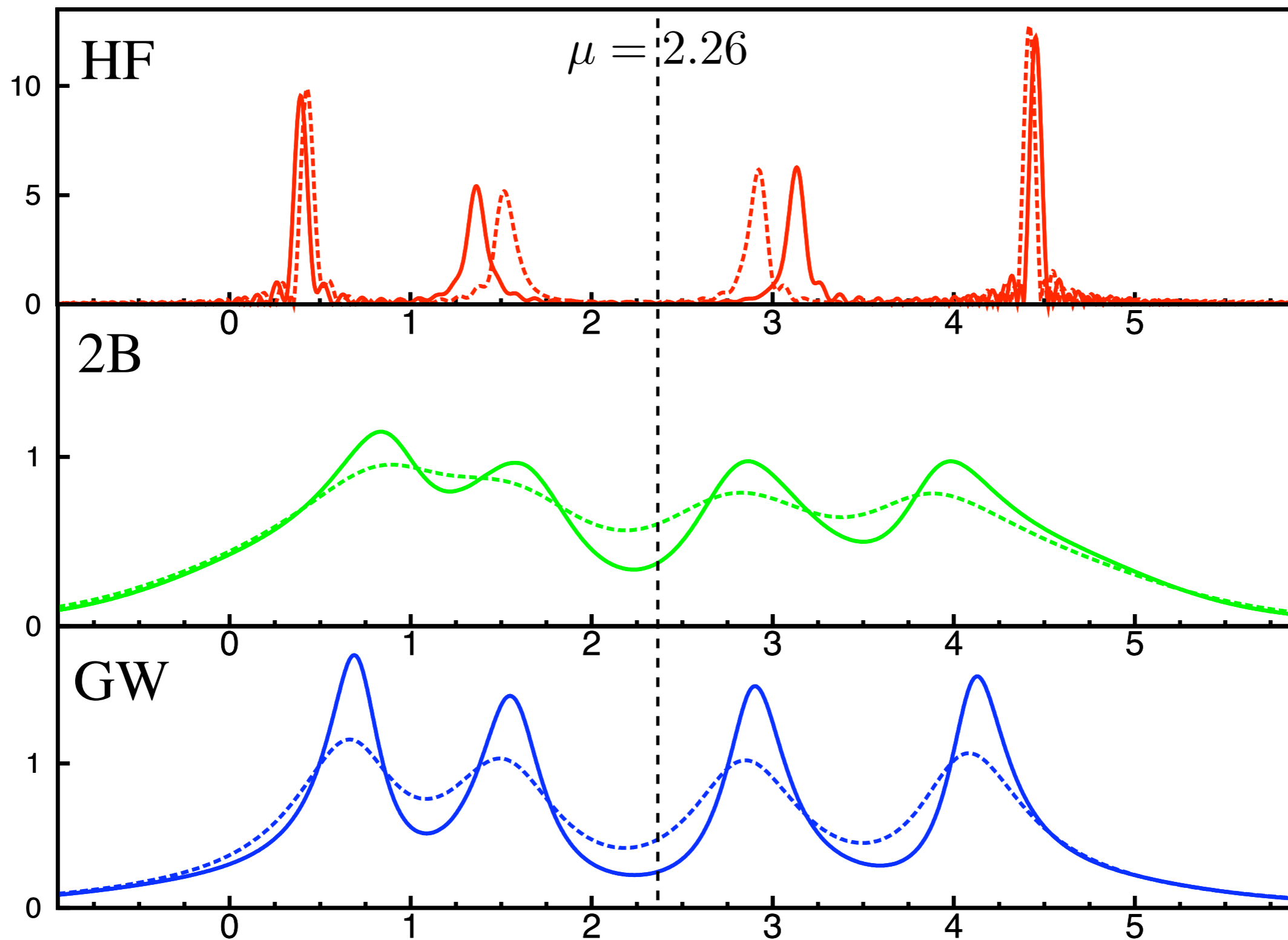
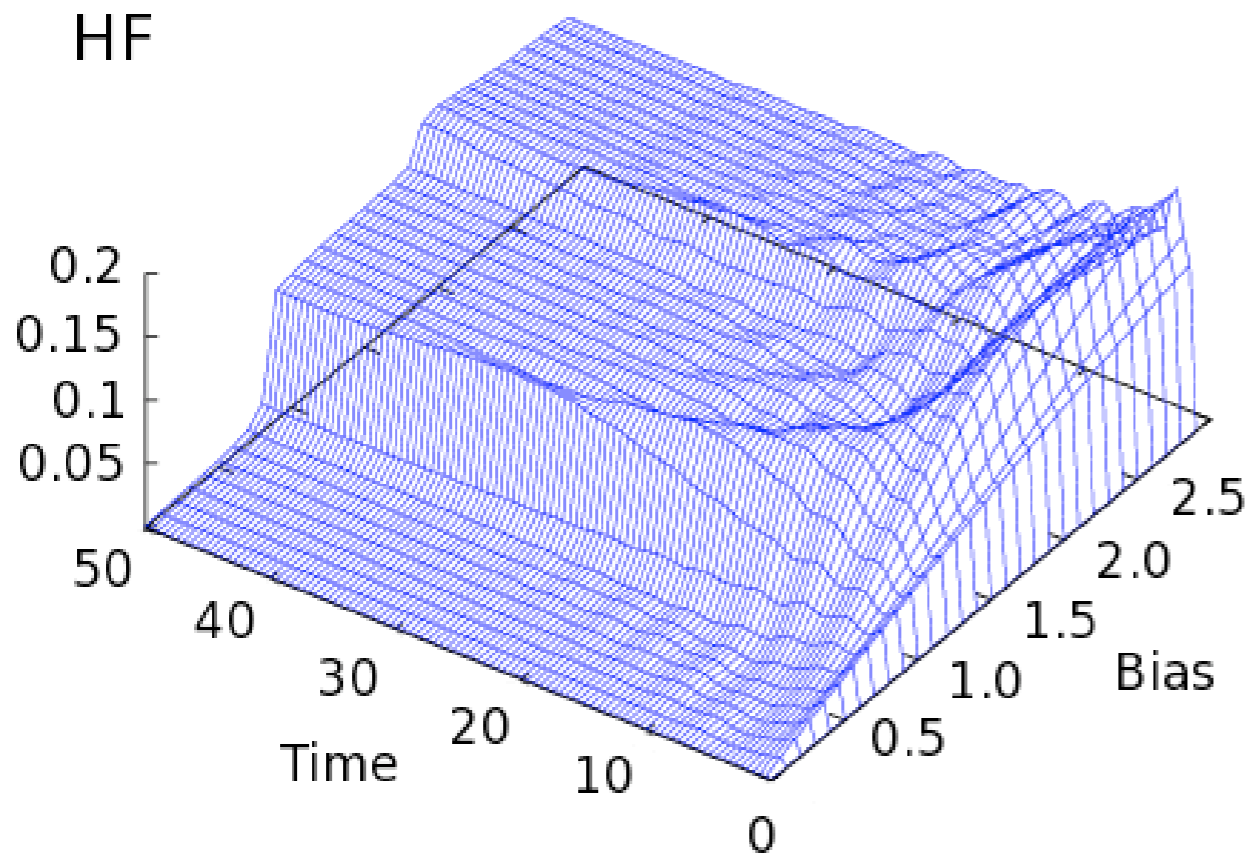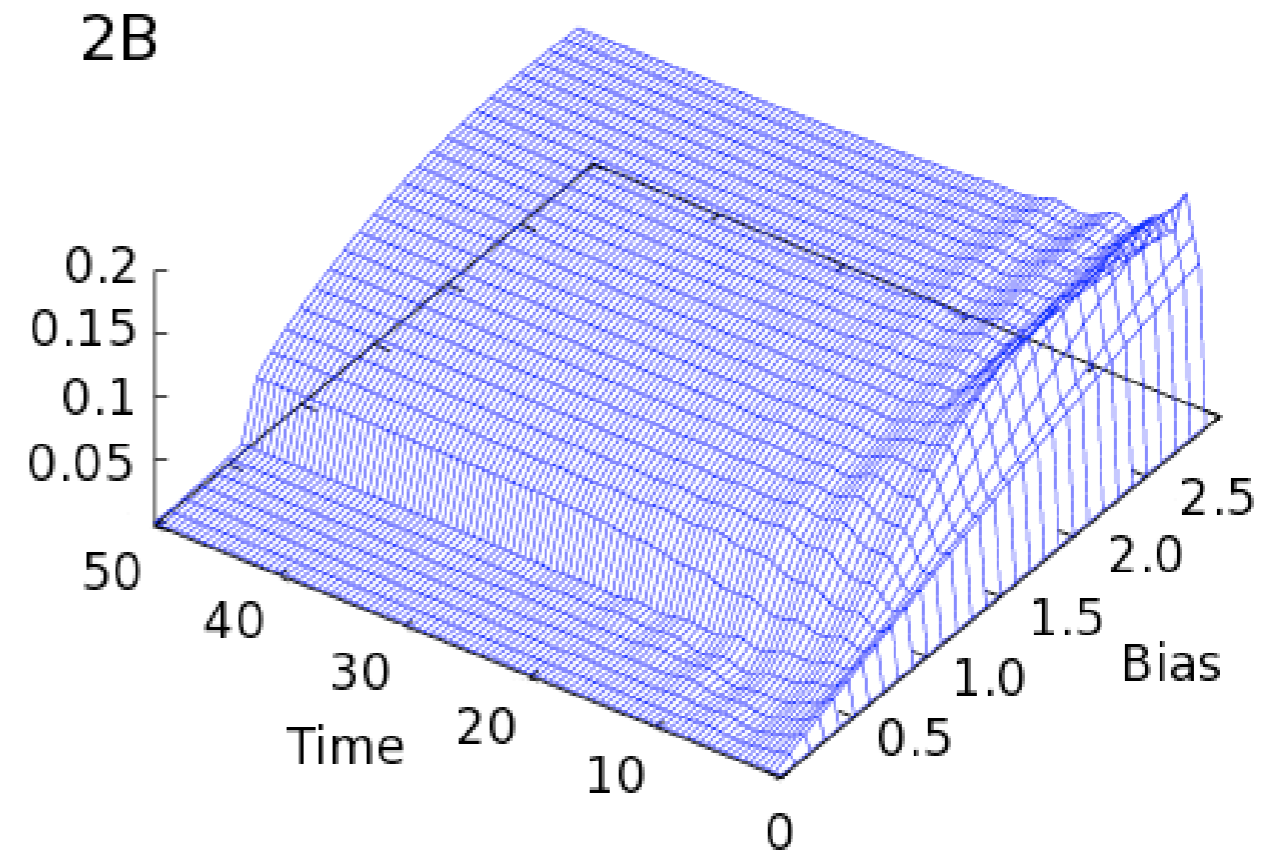# Time-dependent buildup of the I-V curves

Hartree-Fock   second Born

HF   2B

electron correlations beyond mean-field wash out I-V features
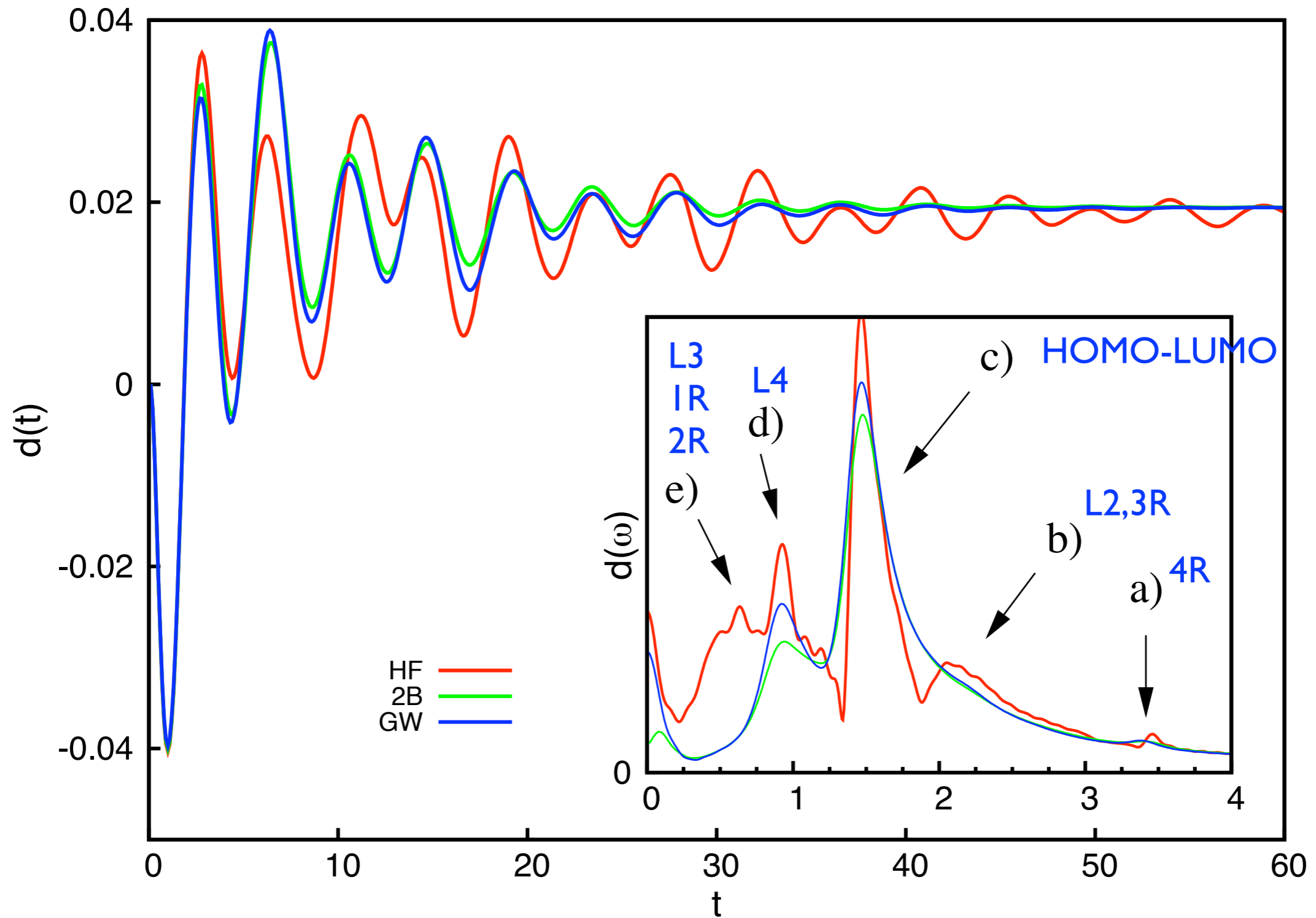
Electron-phonon interactions (test systems)

Holstein lattice system   (very preliminary results from Friday last week)

$$\hat{H} = \omega_0 \sum_i \hat{a}_i^\dagger \hat{a}_i - t \sum_{\langle i,j \rangle} \hat{c}_i^\dagger \hat{c}_j - \sum_i \hat{u}_i \hat{n}_i$$

$\hat{u}_i = \hat{a}_i^\dagger + \hat{a}_i$ displacement

$\hat{n}_i = \hat{c}_i^\dagger \hat{c}_i$ site density

Example 1 : Formation of a polaron after the switch-on of the electronic-vibrational interaction

$$\hat{H}(t) = \omega_0 \hat{a}^\dagger \hat{a} + \epsilon_0 \hat{c}^\dagger \hat{c} - g\theta(t)(\hat{a}^\dagger + \hat{a})\hat{c}^\dagger \hat{c}$$
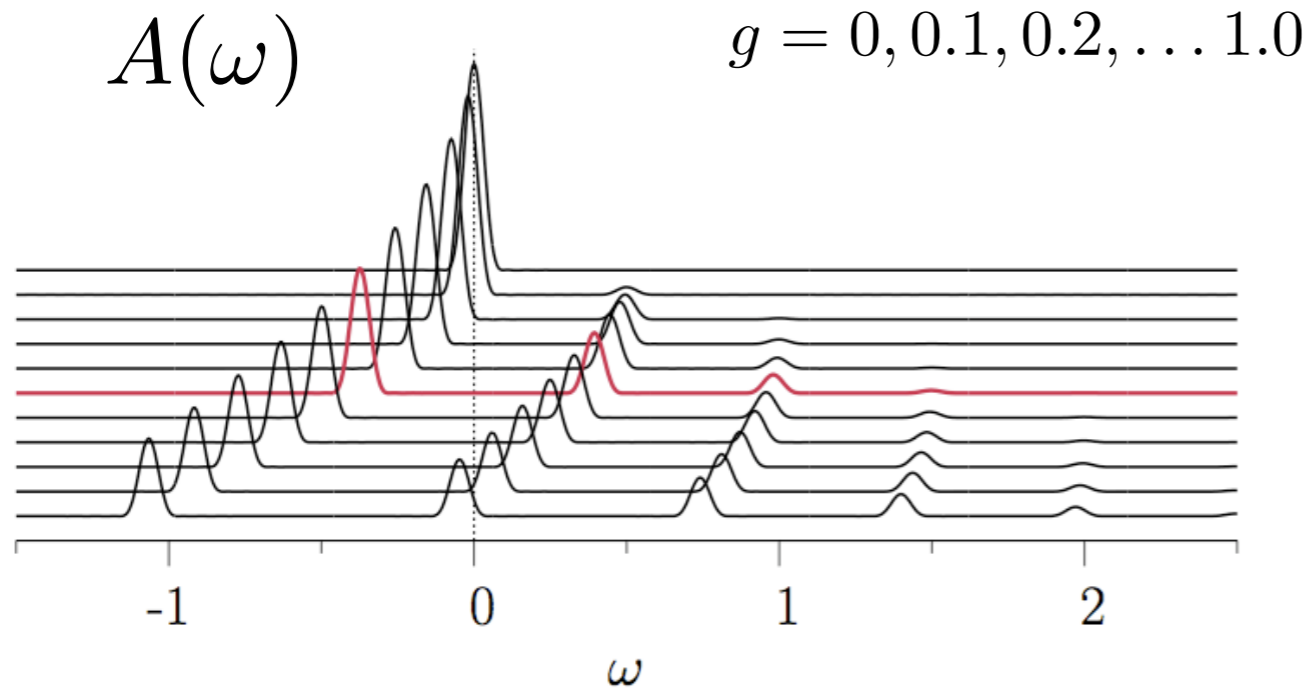
single mode

sudden switch-on of electron-phonon interaction

We use a self-energy in the self-consistent Born approximation

$$\Sigma_{\mathrm{SCBA}} = \quad + \quad$$

Spectral functions

$A(\omega)$

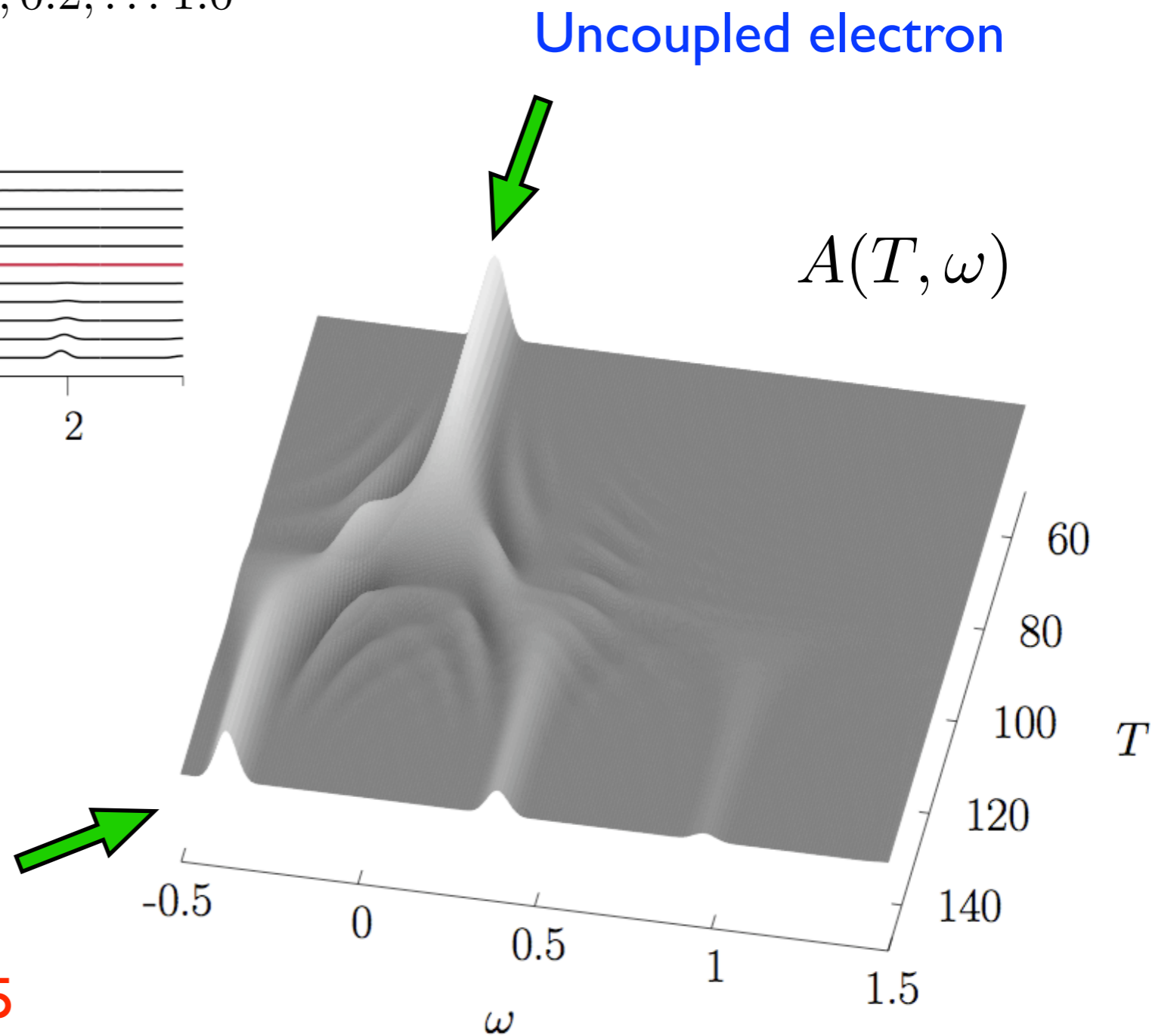$g = 0, 0.1, 0.2, \ldots 1.0$

Uncoupled electron

$A(T, \omega)$

Polaron shift and side bands

$\omega_0 = 0.5$
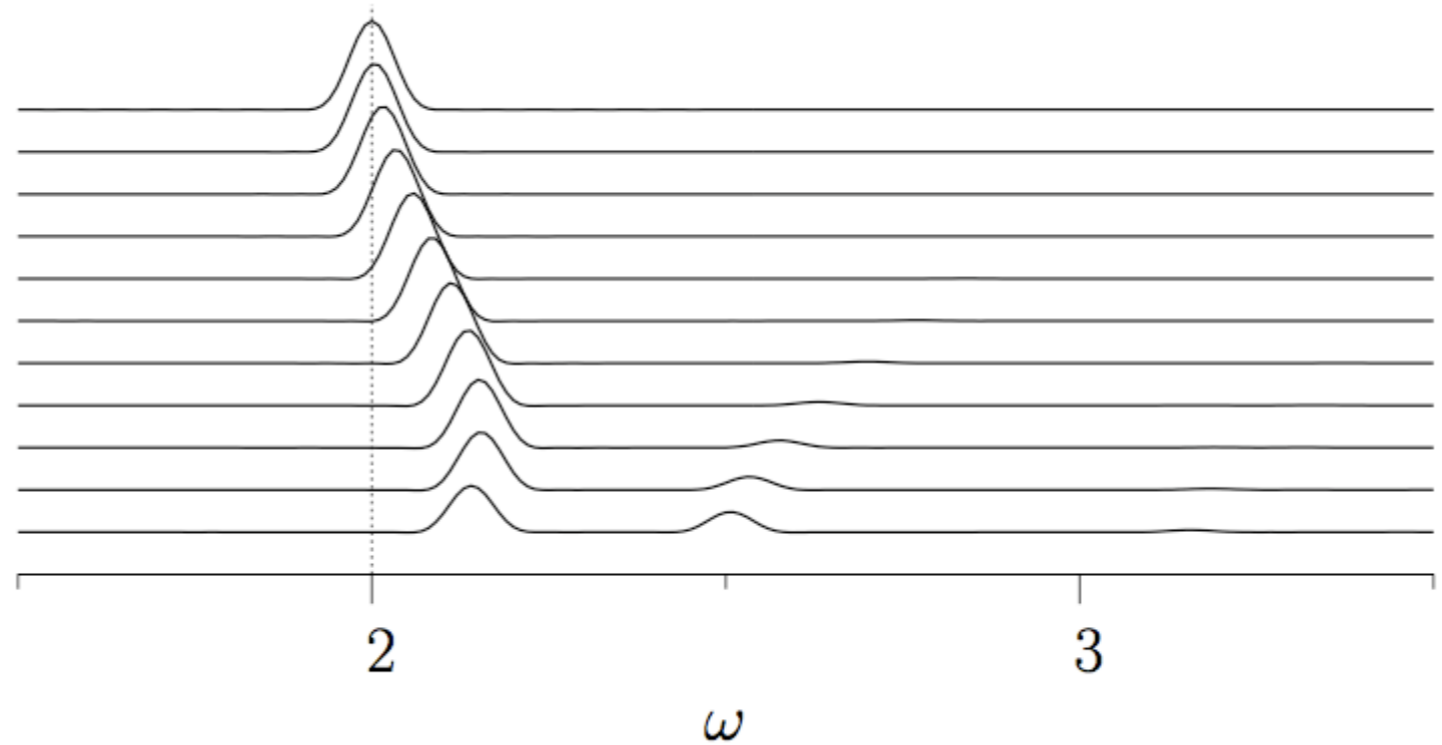
$\epsilon_0 = 0$

Polaron

g=0.5

Optical response of a Holstein dimer

$$\hat{H} = -(\hat{c}_1^\dagger \hat{c}_2 + \hat{c}_2^\dagger \hat{c}_1) + v\delta(t)\hat{n}_1 + \omega_0 \sum_{i=1}^{2} \hat{a}_i^\dagger \hat{a}_i - g \sum_{i=1}^{2} \hat{u}_i \hat{n}_i$$

$$\chi_{ij}(t) = \frac{\delta n_i(t)}{v_j}$$

This amounts to a solution of the Bethe-Salpeter eqn with phonon-dressed Green functions

$$\chi_{11}(\omega) = \int dt\, \chi_{11}(t) e^{i\omega t}$$

Outlook

- We will study transient phenomena in time-dependent transport involving both electron-electron and electron-phonon interactions (for example SSH + e-e interactions)

Open issues, to be studied:

- What is the combined effect for e-e and e-ph interactions?

    a) Structure of transients, I-V curves
    b) Bistability
    c) Gap closing/image charge effects with phonons
    d) What level of many-body perturbation theory do we need?
       (vertices beyong SCBA, mixed e-e / e-ph diagams)

- Towards realistic systems, can we cut memory depth to save computational cost without loosing accuracy?

Questions for the discussion

- The SCBA approximation is valid in the weak coupling limit.
  How to get beyond it?

  Or, in general, what is the importance of terms that are
  higher order in the electron-phonon interaction?
  (we also need to expand the Hamiltonian to higher order
   in the displacements which leads to new vertices)

- What is the interplay between e-e and e-ph interactions?
  (Bistability, gap closing, image charge effects, etc.)

- What is the importance of solving the Kadanoff-Baym
  equations for the phonon propagators as well?
  (heating effects)