Towards a simulation of ultrafast electron dynamics in correlated systems

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in collaboration with:
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Theory and Simulation of Photon-Matter Interaction
ELI-ALPS, Szeged, July 2018
Interaction of photons with correlated matter

### Modern light sources
*Photons on demand*

1. **Diagnostic tool**
   - Photon energy
   - Pulse shape
   - Synchronized pulses (Pump-probe)

2. **Excitation tool**
   - Laser amplitude
     ⇒ multiphoton processes
     ⇒ ionization
     ⇒ heating, compression

### Correlated Matter
*Properties determined by interactions*

1. **Correlated materials**
   - correlated electrons in solids
   - low-dimensional systems, e.g. *graphene nanoribbons*

2. **New states of matter**
   - highly excited solids, liquids
   - new electronic states, phases
   - dense plasmas (*warm dense matter*)

See "wd_uwe_summary.pdf"
Motivation

Our main interest: correlated charged particle systems in and out of equilibrium

Methods:

- Kinetic theory for plasmas (PIC-MCC), MD for surface processes
- *ab initio* thermodynamics for warm dense matter (quantum Monte Carlo, avoid sign problem, $f_{xc}^{\text{UEG}}$ with 0.3% accuracy)\(^1\), functional available in library *libxc*
- nonequilibrium Green functions (NEGF) approach to inhomogeneous systems

Recent nonequilibrium applications with NEGF:

- Time-resolved photoionization of few-electron atoms and molecules
- Dynamics of finite Hubbard clusters following a confinement quench
- Interaction of low-temperature plasmas with solids: ion stopping, electronic correlation effects, doublon formation
- Photoexcitation dynamics of graphene nanoribbons. Carrier multiplication

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\(^1\) Schoof et al. PRL 2015, Dornheim et al., PRL 2016, Groth et al., PRL 2017, Physics Reports 2018
Outline

1. Nonequilibrium Green functions (NEGF) - Theory
   - Applications to atoms and molecules
   - Hubbard model. Strong correlations
   - Problems of NEGF dynamics: myth and reality

2. Comparison of NEGF to exact DMRG solutions

3. Testing NEGF against 2D cold atom experiments

4. Optical excitation of graphene nanoribbons

5. Ion stopping in correlated materials
Time-dependent expectation values with NEGF

Wave function based approach (Schrödinger picture)

- time-dependent Schrödinger operator (e.g. laser field): \( \hat{O}_S(t), \hat{H}(t) \)
- time-dependent N-body state \( |\Psi(t)\rangle = U(t,t_0)|\Psi_0\rangle \), initial state \( |\Psi_0\rangle \)
- Expectation value: \( \langle \hat{O} \rangle(t) = \langle \Psi(t)|\hat{O}_S(t)|\Psi(t)\rangle \)

problem: TDCI prohibitively costly: "exponential wall", approximations: coupled clusters, MCTDHF, TD-RASCI\(^a\) etc.

\(^a\)Hochstuhl, Bonitz, JCP 2011, PRA 2012, EPJST 2014

Heisenberg-Keldysh picture (\( \Psi \) t-independent)

- N-particle density operator: \( \hat{\rho}_N = \sum_\alpha W_\alpha |\Psi^{(\alpha)}\rangle \langle \Psi^{(\alpha)}| \)
- \( \langle \hat{O} \rangle(t) = \langle \Psi_0|U(0,t)\hat{O}_S(t)U(t,0)|\Psi_0\rangle \), nasty expression (pure state)
- \( = \text{Tr} \hat{\rho}_0^N U(0,t)\hat{O}_S(t)U(t,0) \), mixed state–even more nasty
- \( = \sum_{kl} \hat{o}_{kl}(z) G_{lk}(z,z^+) \), 1-particle objects, pleasant
Failure of the Boltzmann/Balescu equation

\[
\left\{ \frac{\partial}{\partial t} + \mathbf{v}_1 \frac{\partial}{\partial \mathbf{r}_1} + \frac{1}{m} \mathbf{F}_1 \frac{\partial}{\partial \mathbf{v}_1} \right\} f(\mathbf{r}_1, \mathbf{p}_1, t) = I(\mathbf{r}_1, \mathbf{p}_1, t),
\]

\[I(\mathbf{r}_1, \mathbf{p}_1, t) = \int d^3p_2 \int d^3\bar{p}_1 \int d^3\bar{p}_2 \, P(\mathbf{p}_1, \mathbf{p}_2; \bar{\mathbf{p}}_1, \bar{\mathbf{p}}_2; t) \times \left\{ f(\mathbf{r}_1, \bar{\mathbf{p}}_1, t) f(\mathbf{r}_1, \bar{\mathbf{p}}_2, t) - f(\mathbf{r}_1, \mathbf{p}_1, t) f(\mathbf{r}_1, \mathbf{p}_2, t) \right\}, \tag{1}
\]

\[P(\mathbf{p}_1, \mathbf{p}_2; \bar{\mathbf{p}}_1, \bar{\mathbf{p}}_2; t) = \left| \frac{V(q)}{\epsilon(q, \omega; t)} \right|^2 \delta(p_{12} - \bar{p}_{12}) \delta(E_{12} - \bar{E}_{12})
\]

\[q = |\mathbf{p}_1 - \bar{\mathbf{p}}_1|, \quad \mathbf{p}_{12} = \mathbf{p}_1 + \mathbf{p}_2, \quad \hbar \omega = E_1 - \bar{E}_1, \quad \text{Pauli blocking factors}(1 \pm f)\text{omitted}
\]

- Equation (1): conserves quasi-particle energy, relaxes towards Fermi (Bose) function
- Equation (1): fails at short times, misses buildup of correlations, screening
  \( \Rightarrow \) unphysical fast relaxation dynamics \( \Rightarrow \) generalized quantum kinetic theory needed

\[1\text{M. Bonitz, } \textit{Quantum Kinetic theory}, \text{ Teubner 1998, 2nd ed.: Springer 2016}\]
2nd quantization

- Fock space $\mathcal{F} \ni |n_1, n_2 \ldots \rangle$, $\mathcal{F} = \bigoplus_{N_0 \in \mathbb{N}} \mathcal{F}^{N_0}$, $\mathcal{F}^{N_0} \subset \mathcal{H}^{N_0}$
- $\hat{c}_i, \hat{c}_i^\dagger$ creates/annihilates a particle in single-particle orbital $\phi_i$
- Spin accounted for by canonical (anti-)commutator relations
  \[
  \left[ \hat{c}_i^{(\dagger)}, \hat{c}_j^{(\dagger)} \right] = 0, \quad \left[ \hat{c}_i, \hat{c}_j^\dagger \right] = \delta_{i,j}
  \]
- Hamiltonian:
  \[
  \hat{H}(t) = \sum_{k,m} h_{km}^0 \hat{c}_k^\dagger \hat{c}_m + \frac{1}{2} \sum_{k,l,m,n} w_{klmn} \hat{c}_k^\dagger \hat{c}_l^\dagger \hat{c}_n \hat{c}_m + \hat{F}(t)
  \]
  \[
  \hat{H}_0 + \hat{W}
  \]

Particle interaction $w_{klmn}$
- Coulomb interaction
- electronic correlations

Time-dependent excitation $\hat{F}(t)$
- single-particle type
- em field, quench, particles
Keldysh Green functions (NEGF)

two times $z, z' \in \mathcal{C}$ ("Keldysh contour"), arbitrary one-particle basis $|\phi_i\rangle$

$$G_{ij}(z, z') = \frac{i}{\hbar} \left\langle \hat{T}_C \hat{c}_i(z) \hat{c}_j^\dagger(z') \right\rangle$$

average with $\rho^N$

Keldysh–Kadanoff–Baym equations (KBE) on $\mathcal{C}$ (2 × 2 matrix):

$$\sum_k \left\{ i\hbar \frac{\partial}{\partial z} \delta_{ik} - h_{ik}(z) \right\} G_{kj}(z, z') = \delta_{C}(z, z') \delta_{ij} - i\hbar \sum_{klm} \int_{\mathcal{C}} d\bar{z} \ w_{iklm}(z^+, \bar{z}) G^{(2)}_{lmjk}(z, \bar{z}; z', \bar{z}^+)$$

- $\int_{\mathcal{C}} wG^{(2)} \rightarrow \int_{\mathcal{C}} \Sigma G$, Selfenergy
- Nonequilibrium Diagram technique
- Example: Hartree–Fock + Second Born selfenergy

KBE: first equation of Martin–Schwinger hierarchy for $G, G^{(2)} \ldots G^{(n)}$
Real-time Keldysh-Kadanoff-Baym equations

- Contour Green function mapped to real-time matrix Green function

\[ G_{ij} = \begin{pmatrix} G_{ij}^R & G_{ij}^< \\ 0 & G_{ij}^A \end{pmatrix} \]

\[ G_{ij}^<(t_1, t_2) = \mp i \langle \hat{c}_j(t_2)\hat{c}_i(t_1) \rangle \]

\[ G_{ij}^>(t_1, t_2) = -i \langle \hat{c}_i(t_1)\hat{c}_j^+(t_2) \rangle \]

- Propagators (spectral properties)

\[ G^{R/A}(t_1, t_2) = \pm \theta [\pm (t_1 - t_2)] \{ G^>(t_1, t_2) - G^<(t_1, t_2) \} \]

- Correlation functions \( G^{\geq} \) (statistical properties) obey real-time KBE

\[
\left[i\partial_{t_1} - h_0(t_1)\right] G^<(t_1, t_2) = \int dt_3 \Sigma^R(t_1, t_3) G^<(t_3, t_2) + \int dt_3 \Sigma^<(t_1, t_3) G^A(t_3, t_2),
\]

\[
G^<(t_1, t_2) \left[-i\partial_{t_2} - h_0(t_2)\right] = \int dt_3 \Sigma^R(t_1, t_3) G^<(t_3, t_2) + \int dt_3 \Sigma^A(t_1, t_3) G^<(t_3, t_2).
\]
Information in the Nonequilibrium Green functions

Time-dependent single-particle operator expectation value

\[
\langle \hat{O} \rangle(t) = \mp i \int dx \left[ o(x't) G^<(xt, x't) \right]_{x=x'}
\]

- **Particle density**

\[
\langle \hat{n}(x, t) \rangle = n(1) = \mp i G^<(1, 1)
\]

- **Density matrix**

\[
\rho(x_1, x_1', t) = \mp i G^<(1, 1') \bigg|_{t_1=t_1'}
\]

- **Current density:**

\[
\langle \hat{j}(1) \rangle = \mp i \left[ \left( \frac{\nabla_1}{2i} - \frac{\nabla_1'}{2i} + A(1) \right) G^<(1, 1') \right]_{1'=1}
\]

**Interaction energy** (two-particle observable, [Baym/Kadanoff])

\[
\langle \hat{V}_{12} \rangle(t) = \pm i \frac{V}{4} \int \frac{d\vec{p}}{(2\pi\hbar)^3} \left\{ (i \partial_t - i \partial_{t'}) - \frac{p^2}{m} \right\} G^<(\vec{p}, t, t') \bigg|_{t=t'}
\]
Selfenergy approximations

Hartree–Fock (HF, mean field):
\[ \sim w^1 \]

Second Born (2B):
\[ \sim w^2 \]

GW: \[ \propto \] bubble summation, dynamical screening effects

particle-particle \(T\)-matrix (TPP):
\[ \propto \] ladder sum in pp channel

electron-hole \(T\)-matrix (TEH):
\[ \propto \] ladder sum in ph channel

FLEX (GW+TPP+TEH)

3rd order approx. (TOA):
\[ \sim w^3 \]

Choice depends on coupling strength, density (filling)

\[ ^2 \text{Conserving, nonequilibrium} \Sigma(t, t'), \text{ applies for ultra-short to long times} \]
Numerical solution of the KBE

**Full two-time solutions:** Danielewicz, Schäfer, Köhler/Kwong, Bonitz/Semkat/Balzer, Haug, Jahnke, van Leeuwen, Stefanucci, Verdozzi, Garny ...

1. Uncorrelated initial state \((t \to -\infty)\)
2. Adiabatically slow switch-on of interaction for \(t, t' \leq t_0\) [1-3]

\[ f_{AS}^{\tau, t_H}(t) = \exp \left( -\frac{A_{t_H}^\tau}{t / (2t_H)} \exp \left( \frac{B_{t_H}^\tau}{t / (2t_H) - 1} \right) \right) \]

\[ B_{t_H}^\tau := \frac{t_H}{\tau \ln(2)} - \frac{1}{2}, \quad A_{t_H}^\tau := \frac{\ln(2)}{2} e^{2B_{t_H}^\tau} \]

3. Solve KBE in \(t - t'\) plane for \(G(t, t')\)

Two-time simulations for macroscopic systems

1. perfect conservation of total energy
2. accurate **short-time** dynamics:
   - phase 1: correlation dynamics
   - 2: relaxation of $f(p)$, occupations
3. accurate **long-time** behavior: spectral functions $A(q, \omega)$, dyn. structure factor $S(q, \omega)$ from real-time KBE dynamics (via Fourier transform) [3]
4. extended to optical absorption, double excitations [4] etc.

Example: electrons in dense hydrogen, interaction quench [1], extended to e-h plasmas [2]

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Inhomogeneous systems: small molecules

- strong excitation and ionization of atoms and molecules [1]

- Example: XUV-pulse excitation of LiH (1d-model)

- Goals: correlated electron dynamics beyond Hartree-Fock, including Auger processes

[1] Balzer et al., PRA (2010); van Leeuwen, Stefanucci et al.
Numerical challenges of NEGF calculations

- Complicated structure of interaction $w_{klmn}$ and selfenergy $\Sigma$
- Collision integrals involve integrations over whole past
- CPU time $\sim N_t^3$, RAM $\sim N_t^2$

Typical computational parameters

- Spatial basis size: $N_b = 70$
- Time steps: $N_t = 10000$
- RAM consumption: 2 TB
- Number of CPUs used: 2048
- Total computation time: 2-3 days

Solutions

- Finite-Element Discrete Variable Representation [PRA 81, 022510 (2010)]
- Adiabatic switch-on of interaction [Phys. Scr. T151, 014036 ('12)]
- Parallelization [PRA 82, 033427 (2010)]

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strong excitation and ionization of atoms and molecules: need to resolve nucleus and large distances

Selfenergy in FEDVR largely diagonal

accurate 1D results

Alternative approaches: restricted active space and embedding methods

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4 Balzer et al., PRA 81, 022510 (2010)
Generalized Kadanoff-Baym-ansatz\(^5\) (GKBA)

- reduce computational effort: propagation along diagonal only (scaling \(T^3 \rightarrow T^2\))
- rigorous derivation from reduced density operators \([4]\)
- conserves total energy \([5]\)
- reduces artificial damping problems \([5]\)

- reconstruct off-diagonal NEGF from their values on time diagonal:

\[
G_{ss'}^{\geq}(t, t') = \pm \left[ G_{ss}^{\text{ret}}(t, t') \rho_{ss'}^{\geq}(t') - \rho_{ss}^{\geq}(t) G_{ss'}^{\text{adv}}(t, t') \right] \quad \text{with} \quad \rho_{ss'}^{\geq}(t) = \pm i \hbar G_{ss'}^{\geq}(t, t)
\]

- HF-GKBA: use Hartree-Fock-propagators for \(G_{ss'}^{\text{ret/adv}}\)

\[
G_{ss'}^{\text{ret/adv}}(t, t') = \mp i \Theta_C (\pm [t - t']) \exp \left( -\frac{i}{\hbar} \int_{t'}^{t} d\bar{t} \bar{h}_{\text{HF}}(\bar{t}) \right) \bigg|_{ss'}
\]


\([4]\) MB, Quantum Kinetic Theory, 2nd ed. Springer (2016)

\([5]\) Hermanns, Schlünzen, MB, PRB 2014.
The generalized Kadanoff-Baym ansatz: Conserving properties

- HF-GKBA: same conservation properties as two-time approximation
- damped propagators, local approximation violate total energy conservation
- Generalization of the energy conservation theorem of Baym and Kadanoff (relaxed conditions)

**Extensions**: Gauge invariant generalization of the GKBA to strong electro-magnetic fields, derivation of strong-field quantum kinetic equations containing inverse bremsstrahlung heating and multiphoton absorption and numerical solutions

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The Hubbard model. Correlated materials

\( \hat{H}(t) = J \sum_{ij,\alpha} h_{ij} \hat{c}_{i\alpha}^\dagger \hat{c}_{j\alpha} + U \sum_i \hat{c}_{i\uparrow}^\dagger \hat{c}_{i\uparrow} \hat{c}_{i\downarrow}^\dagger \hat{c}_{i\downarrow} + \sum_{ij,\alpha\beta} f_{ij,\alpha\beta}(t) \hat{c}_{i\alpha}^\dagger \hat{c}_{j\beta} \)

\( h_{ij} = -\delta_{\langle i, j \rangle} \) and \( \delta_{\langle i, j \rangle} = 1 \), if \( (i, j) \) nearest neighbors, \( \delta_{\langle i, j \rangle} = 0 \) otherwise; on-site repulsion \( (U > 0) \) or attraction \( (U < 0) \), \( U \) favors *doublons* (correlations)

- propagate NEGF in Hubbard basis, finite inhomogeneous system
- \( f \): arbitrary 1-particle hamiltonian: laser field, quench, particles etc.
- Selfenergies given by sparse matrices
Strong coupling: T-matrix selfenergy

- to access strong coupling: use T-matrix selfenergy (sum entire Born series)
- for Hubbard model simplification\(^\text{15}\)

\[
\Sigma_{ss',\uparrow(\downarrow)}^{\text{cor},\uparrow(\downarrow)}(z, z') = i\hbar T_{ss'}(z, z') G_{s's'}^{\downarrow(\uparrow)}(z', z),
\]

\[
T_{ss'}(z, z') = -i\hbar U^2 G_{s's'}^{\uparrow}(z, z') G_{s's'}^{\downarrow}(z, z')
\]

\[
+ i\hbar U \int_C \text{d}\bar{z} \, G_{s\bar{s}}^{\uparrow}(z, \bar{z}) \, G_{\bar{s}s}^{\downarrow}(z, \bar{z}) T_{\bar{s}s'}(\bar{z}, z').
\]

- T-matrix: well defined and conserving strong coupling approximation
- limitation: low density (binary collision approximation)
- numerical optimization: large systems, long propagation feasible\(^\text{16}\)
- no free parameters


Ground state results at half-filling

Dispersion of 40-site Hubbard chain (2B/SOA):

Band gap for the infinite 1D chain:

Band structure for the honeycomb lattice:

J.-P. Joost, N. Schlünzen, and M. Bonitz, to be published
Density in quasi-momentum space

1D:

- momentum distribution

\[ n_k(t) = \frac{1}{N_s} \sum_{ss'} e^{-i k (s - s')} n_{ss'}(t), \]

- positive \( U \): occupation of large energies
- negative \( U \): occupation of small energies

2D:
**Dispersion relation**

1D:

- spectral function

\[ A(\omega, k) = \frac{i\hbar}{N_s N_t} \sum_{s,s'} e^{-i k (s-s')} e^{-i \omega (t-t')} \left[ G_{ss'}^> (t, t') - G_{ss'}^< (t, t') \right] \]

- single-particle dispersion from peaks of \( A \)
- upper band: doublons
- doublon dispersion shifts up \( \sim U \)

2D:

- ...
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Properties of the selfconsistent KBE

Kadanoff-Baym dynamics of Hubbard clusters: Performance of many-body schemes, correlation-induced damping and multiple steady and quasi-steady states

Marc Puig von Friesen, C. Verdozzi, and C.-O. Almbladh

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small Hubbard clusters. Strong external excitation (Right Fig.: \( N_s = 6, n = 1/6, U = 2, w_0 = 5 \)) \( \Rightarrow \) artificial damping of many-body approximations. Best behavior: T-matrix

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Long-time behavior of two-time KBE and GKBA

Time-dependent excitation

Nonequilibrium initial state

- KBE with all many-body approximations show unphysical damping effects
- HF-GKBA: reduction or even removal of damping (small clusters)
Adrian Stan’s claims\textsuperscript{12}

1. Long propagation: homogeneous density (HDD) state is reached ("global attractor").

2. Unphysical damping occurs also for weak excitation (linear response regime).

3. Damping occurs also in uncorrelated systems (Hartree selfenergies), although without HDD (right fig.).

⇒ Previous studies “overlooked the physics” (too short)
⇒ KBE are practically useless (negligible range of validity)

\textsuperscript{12} A. Stan, Phys. Rev. B, Rapid Comm. 93, 041103 (2016) [Editors’ Choice]
Test of Stan’s claims (1)\textsuperscript{13}

Hubbard dimer in second Born approx.

Hartree(-Fock) dynamics

converged results (time step) show:

- no HDD state is reached, even for strong excitation
- no damping occurs in uncorrelated systems

A careful convergence analysis reveals:

- damping behavior and emergence of HDD state are artefact of
  - too large time step in collision integral
  - integration rule of too low order
- accompanied by dramatic violation of total energy conservation
- correlations in the system completely vanish, once the HHD is reached

\[ \implies \text{Unwarrented claims and generalizations (from Hubbard dimer).} \]
\[ \implies \text{All statements are wrong, numerical artefacts.} \]

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\[^{14}\text{N. Schlünzen, J.-Ph. Joost, and M. Bonitz, Phys. Rev. B 93, 041103 (2017)}\]
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Benchmarks of NEGF against DMRG (1D)\textsuperscript{1}

Expansion dynamics
large 1D system \((N_s = 65)\)

- confirm accurate asymptotic expansion velocities from NEGF T-matrix (within error bars)
- 2-time result (TMA) misses transient oscillations
- exact result bracketed by T-matrix and GKBA+T

\[ v_{\text{exp}}(t) = \frac{d}{dt}d(t) \]

\[ = \text{TMA} \]

\[ = \text{GKBA + TMA} \]

\[ U = 1 \]

\[ U = 2 \]

\[ U = 3 \]

\[ U = 5 \]

\[ \text{DMRG} \]

\textbf{artificial damping}\textsuperscript{2,3} in 2-time solution for strongly excited, finite systems

\textbf{removed by GKBA}

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\textsuperscript{3}N. Schlünzen, J.-P. Joost, and M. Bonitz, PRB 96, 117101 (2017)
Initial state:
charge density wave

- excellent agreement for densities, energies etc.
- sensitive observable: total double occupation
- very good quality transients of NEGF, up to $U \sim$ bandwidth
- accurate long-time behavior of GKBA+T-matrix (not shown)

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Complementarity of NEGF and DMRG\textsuperscript{16}

DMRG: advantageous for large coupling, simulation duration rapidly decreases with system size $L$

NEGF: advantageous at small to moderate coupling, good accuracy

NEGF have predictive capability:
- large systems
- long simulations
- any dimensionality

Summary: properties of the KBE

Advantages:

- perfect conservation of total energy\(^{17}\) and particle number
- time reversible (unitary) dynamics
- accurate description of dynamics far from equilibrium
- convenient and easy way to implement various many-body approximations

Problems and solutions for strongly excited small systems:

- full two-time KBE show unphysical damping dynamics\(^{18}\): (⇒ self-consistency leads to diagrams of infinite order that would cancel in exact case)
- get rid of damping by reducing the degree of self-consistency via HF-GKBA:
  - “reconstruction” of two-time Green functions eliminates infinite order iterations
  - Retains conserving behavior, additional class of conserving approximations\(^{19}\)
- large systems: two-time and one-time approximations of comparable accuracy

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\(^{17}\) “Conserving approximations” by Baym and Kadanoff
Recent computational breakthroughs

**Improved selfenergies:**
- p-p and p-h T-matrix, GW, third order

**Higher order numerical schemes:**
- Higher order integration of KBE
- Higher order adaptive integration of collision integrals

**Code optimization for graphics cards (GPU)**

**Result for lattice systems:**
- Increase of system size and propagation duration by 2...3 orders (finite systems with $N_s \sim 200$, $T \sim 200/J$, reach TD limit)
- work of Sebastian Hermanns, Niclas Schlünzen, Jan Philip Joost, Christopher Hinz
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Fermionic transport and out-of-equilibrium dynamics in a homogeneous Hubbard model with ultracold atoms

Ulrich Schneider\textsuperscript{1,2,*}, Lucia Hackermüller\textsuperscript{1,3}, Jens Philipp Ronzheimer\textsuperscript{1,2}, Sebastian Will\textsuperscript{1,2}, Simon Braun\textsuperscript{1,7}, Thorsten Best\textsuperscript{1}, Immanuel Bloch\textsuperscript{1,3,4}, Eugene Demler\textsuperscript{5}, Stephan Mandt\textsuperscript{6}, David Rasch\textsuperscript{6} and Achim Rosch\textsuperscript{9}
- 2D optical lattice, ca. 200 000 atoms
- atom-atom interaction strength tuned (via Feshbach resonance)
- \( t<0 \): confinement in trap center, doubly occupied lattice sites
- \( t=0 \): confinement rapidly removed ("quench"): system far from equilibrium \( \Rightarrow \) start of diffusion, equilibration

- at strong coupling: center ("core") does not expand due to **doublon** formation
Measured “Core expansion velocity”

- Measured HWHM of density distribution in Hubbard lattice

- Strongly correlated fermions. Core “shrinks” for Hubbard-$|U| \gtrsim 3$

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Semiclassical Boltzmann equation in relaxation time approximation:

\[ \partial_t f_q + v_q \nabla_r f_q + F(r) \nabla_q f_q = -\frac{1}{\tau(n)} (f_q - f_q^0(n)) \]

General problems of Boltzmann-type (Markovian) equations:
- incorrect asymptotic state, conservation laws
- isolated dynamics: expect reversibility

Additional limitations of RTA:
- local TD equilibrium assumption questionable (Heisenberg)
- no quantum dynamics effects
- linear response assumption questionable

⇒ cannot describe ultrafast quantum dynamics of correlated fermions

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A challenge for quantum many-body dynamics...

Quote from Schneider et al., (p. 216):

“Although the expansion can be modelled in 1D (...) using DMRG\textsuperscript{22} methods (...), so far no methods are available to calculate the dynamics quantum-mechanically in higher dimensions”

Similar claims in many experimental papers, for example:

“Quantengase unter dem Mikroskop”, M. Greiner, I. Bloch, Phys. Journal Okt. 2015:

“Ein anderes Gebiet, in dem Experimente schon heute leistungsfähiger als Computersimulationen sind, ist die Untersuchung von Nichtgleichgewichtsprozessen in Quanten-Vielteilchensystemen ... bisherige Algorithmen auf eindimensionale Systeme beschränkt sind und meistens nur die Dynamik für sehr kurze Zeiten berechnen können.”

Not exactly true...\textsuperscript{23}.

\textsuperscript{22}Density Matrix Renormalization Group

\textsuperscript{23}Nonequilibrium Green Functions (NEGF) exist for 50 years...
Fermion expansion and doublon decay

- $t = 0$: central array of doubly occupied sites.
- confinement quench initiates expansion.
- measured in cold atom experiments (Schneider et al.)
- expansion speed, dynamics time-dependent, depend on
  
  - dimensionality $D$, interaction strength $U$, particle number $N$
Time evolution of the expansion velocity

**Diffusion quantities**

- mean squared displacement
  \[ R^2(t) = \frac{1}{N} \sum_s n_s(t)[s - s_0]^2 \]
  \( s_0 \): center of the system
- rescaled cloud diameter
  \[ d(t) = \sqrt{R^2(t) - R^2(0)} \]
- expansion velocity
  \[ v_{\text{exp}}(t) = \frac{d}{dt}d(t) \]
- asymptotic expansion velocity
  \[ v_{\text{exp}}^\infty = \lim_{t \to \infty} v_{\text{exp}}(t) \]

**Example:**
- \( N = 58 \) doubly occupied sites in 2D
- Perform extrapolation with respect to \( N \)
- Similar procedure for “core expansion velocity” (\( \sim \) FWHM)

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NEGF result$^{25}$ vs. experiment and RTA$^{26}$

- agreement with measurements for the final stage of the dynamics
- in addition: NEGF predict early stages, correlation dynamics etc.


$^{26}$U. Schneider et al., Nature Physics 8, 213-218 (2012)
Site-resolved evolution of correlations

- double occupation $n_{s}^{↑↓}$
- local entanglement entropy $S_{s}$
- pair correlation function $\delta n_{s}^{↑↓} = n_{s}^{↑↓} - n_{s}^{↑}n_{s}^{↓}$

- insights into the early expansion phase
- measurable in quantum atom microscopes
Nonequilibrium Green functions (NEGF) - Theory
  - Applications to atoms and molecules
  - Hubbard model. Strong correlations
  - Problems of NEGF dynamics: myth and reality

Comparison of NEGF to exact DMRG solutions

Testing NEGF against 2D cold atom experiments

Optical excitation of graphene nanoribbons

Ion stopping in correlated materials
Graphene Nanoribbons (GNRs)

“In spite of this interest, the field of GNRs is still in its infancy and little is known about their photophysical properties, especially in the non-equilibrium regime.”
G. Soavi et al., Nature Communications 7, 2016

“Quasi-one-dimensional electron graphene nanoribbons with tuneable electron densities and band gaps should exhibit novel phenomena driven by strong many-body correlations.”

A. Kimouche et al., Nature Communications 6, 2015
interesting e-e correlations effects: Auger processes, carrier multiplication (CM) after pump

Number of conduction band electrons (red), energy per electron (blue)

Theoretical Description of GNRs

Theory has to describe:
- finite systems of up to 100 carbon atoms
- 2 dimensional geometry
- moderate electron correlations
- nonequilibrium long time dynamics

Existing theories fail:
- CI
- DMRG
- DMFT
- TDDFT

Our solution:
- map graphene onto an extended Hubbard model (small but accurate basis)
- use NEGF approach for field-matter coupling and correlation dynamics, dipole approximation: $H_L(t) = \sum_i -eE_L(t)r_i$
Time-resolved spectral properties

- **Local spectral function** at site \( s \) (\( G \) contains pump pulse information)

\[
A_{ss}(\omega) = i\hbar \int dt \, dt' \, e^{-i\omega(t-t')} \left[ G_{ss}^>(t,t') - G_{ss}^<(t,t') \right]
\]

- **Full energy dispersion**

\[
A(\omega, k) = \frac{i\hbar}{N_s} \sum_{ss'} e^{-ik(s-s')} \int dt \, dt' \, e^{-i\omega(t-t')} \left[ G_{ss'}^>(t,t') - G_{ss'}^<(t,t') \right]
\]

- **Time resolved photoemission spectrum**

\[
A^<(\omega, T) = -i\hbar \sum_{s} \int dt \, dt' \, S(t-T)S(t'-T)e^{-i\omega(t-t')} G_{ss}^<(t,t')
\]

\[
S(t) = \frac{1}{\sigma \sqrt{2\pi}} \exp \left( -\frac{t^2}{2\sigma^2} \right) \quad \text{← "probe pulse"}
\]


Extended Hubbard Model

- $\hat{H}_{\text{kin}} = J \sum_{ss', \alpha} t_{ss'} \hat{c}_{s\alpha} \hat{c}_{s'\alpha}$
- hopping up to 3rd nearest neighbor:
  \[ t_{ss'} = \begin{cases} 
  t_1 & \text{if } (s, s') \text{ is 1NN} \\
  t_2 & \text{if } (s, s') \text{ is 2NN} \\
  t_3 & \text{if } (s, s') \text{ is 3NN} \\
  0 & \text{else} \end{cases} \]
- orbital overlap included through overlap matrix $S$:
  \[ H \rightarrow U^\dagger H U \] with $U = S^{-1/2}$ (Löwdin)

<table>
<thead>
<tr>
<th>Structure</th>
<th>Set</th>
<th>$J$/eV</th>
<th>$t_1/J$</th>
<th>$t_2/J$</th>
<th>$t_3/J$</th>
<th>$s_1$</th>
<th>$s_2$</th>
<th>$s_3$</th>
</tr>
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<tr>
<td>2D Graphene</td>
<td>1NN</td>
<td>2.7</td>
<td>1</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
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<tr>
<td></td>
<td>3NN (Reich2002)</td>
<td>2.97</td>
<td>1</td>
<td>0.025</td>
<td>0.111</td>
<td>0.073</td>
<td>0.018</td>
<td>0.026</td>
</tr>
<tr>
<td>Graphene ribbons</td>
<td>3NN (Tran2017)</td>
<td>2.756</td>
<td>1</td>
<td>0.026</td>
<td>0.138</td>
<td>0.093</td>
<td>0.079</td>
<td>0.070</td>
</tr>
</tbody>
</table>
Ground State Results for Graphene

- discrete sampling of the first BZ due to finite system size

V.-T. Tran et al., AIP Advances, 7, 075212 (2017)

M. Bonitz (Kiel University)
Ground State Results for Graphene

- comparison between NEGF (colormap) and DFT / GW (lines)

\[ J = 2.756 \text{ eV} \]


- it is well known that GW shows larger gap than DFT
Ground State Results for Graphene

- comparison between NEGF (colormap) and DFT / GW (lines)

- gap opening can be reproduced with GWA and $U = 3.5J$
Carrier Multiplication during laser excitation

- scattering processes due to Coulomb interaction:
  - impact excitation (IE)
  - Auger recombination (AR)
- IE leads to carrier multiplication (CM) in the conduction band (CB)

Laser excitation

- dipole approximation
- \( U_{\text{pot}} = -\vec{E}_{\text{Laser}} \cdot \vec{x} \)
- \( E_{\text{Laser}} = E_0 \sin(\omega_0(t - t_0)) \cdot \exp\left(-\frac{(t-t_0)^2}{2\sigma^2}\right) \)
- \( \omega_0 = (1.55 - 1.85)J \)
- \( \sigma = 4.35J^{-1} \)
Carrier Multiplication - Setups

Polarization: Selfenergy: SOA

\[ N_s = 20 \]

\[ N_s = 24 \]

\[ N_s = 30 \]
Carrier Multiplication

SOA, \( U = 3.5J \), \( E_0 = 0.1 \)

- Conduction band density: \( N_{CB} = \int_{0}^{\infty} A^\omega(\omega) \, d\omega \), energy: \( E_{CB} = \int_{0}^{\infty} \omega A^\omega(\omega) \, d\omega \)
- CB occupancy and energy show IE-like behavior, for \( N_s = 20 \) and \( N_s = 30 \)
Carrier Multiplication

SOA, $U = 3.5 J$, $E_0 = 0.1$

- $\omega_0 > 2E_{\text{gap}}$, for $N_s = 20$ and $N_s = 30$
- $\omega_0 < 2E_{\text{gap}}$, for $N_s = 24$

SOA and GWA show same general trend (SOA: smaller gap $\rightarrow$ stronger excitation)

HF shows opposite effect (recombination instead of excitation), Joost, Schlünzen, and MB, to be published
Laser-induced band structure dynamics

- $N_s = 20$, $U = 3.5J$, $\omega_L = 3.2J$, $E_L = 0.2$
- **left**: band structure during and after pulse
- **red (blue)**: $e$ ($h$) density: CB (VB)
- **top r**: time resolved spectral function (top to bottom)
- **bottom r**: laser field
Outline

1. Nonequilibrium Green functions (NEGF) - Theory
   - Applications to atoms and molecules
   - Hubbard model. Strong correlations
   - Problems of NEGF dynamics: myth and reality

2. Comparison of NEGF to exact DMRG solutions

3. Testing NEGF against 2D cold atom experiments

4. Optical excitation of graphene nanoribbons

5. Ion stopping in correlated materials
Ion stopping in strongly correlated materials

- Example: finite graphene flake (use 2D honeycomb lattice of size $L$)

$$H_e = -J \sum_{\langle i,j \rangle, \sigma} c_{i\sigma}^\dagger c_{j\sigma} + U \sum_i (n_{i\uparrow} - \frac{1}{2}) (n_{i\downarrow} - \frac{1}{2})$$

$$+ \sum_{i, \sigma} W_i(t) c_{i\sigma}^\dagger c_{i\sigma} \quad \text{with} \quad W_i(t) = -\frac{e^2}{4\pi\varepsilon_0} \frac{Z_p}{|r_p(t) - R_i|}$$

- Simple projectile (proton, $\alpha$), treated classically [$Z_p$, $r_p(t)$, Ehrenfest dynamics]

- Parameters$^{27}$: $a_0 = 1.42 \, \text{Å}$, $J = 2.8 \, \text{eV}$, $r_p(t)/a_0 = \{-1/6, -\sqrt{3}/3, -z(t)\}$


Proton stopping. $U/T_0 = 4, \quad L = 54$

- **Top**: proton energy change. Uncorrelated (black) vs. correlated (red, blue)
- **Bottom**: electron density (4 sites adjacent to projectile)

(A)/(B) correspond to different initial states
Mean field approximation (black) not sufficient
NEGF description gives access to time-resolved photoemission spectra

\[ I_i(\omega, t_p) = -i \int dt \int dt' s(t - t_p)s(t' - t_p)e^{i\omega(t-t')} G^{<}_{ii\sigma}(t, t') \]

\[ s(t) = \frac{1}{\tau \sqrt{2\pi}} e^{-t^2/(2\tau^2)} \]

energy loss of ion causes occupation of upper Hubbard band
Relevance of correlation effects

Application to graphene

modified hopping amplitude to account for influence on the electron mobility:

\[ J_{\langle i,j \rangle}(t) = -J + \frac{\gamma}{2} (W_i(t) + W_j(t)) \]

parameters: \( a_0 = 1.42 \, \text{Å}, U/J = 1.6, J = 3.15 \, \text{eV}, \gamma = 0.55 \)
Doublon production due to ion stopping

- exact diagonalization
- parameters: 2D cluster, $N = 12$

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Doublon production: analytical model

- Dimer model. 
  t-dependent exact diagonalization, Gaussian model $W(t)$, width $\sigma \sim v$

- Doublon production probability (Landau-Zener model):
  \[
  P_{E_0 \rightarrow E_U} = 2p(1 - p)
  \]
  \[
  p = \exp \left( -\frac{2\pi V^2 \sqrt{e\sigma}}{W_0 E'} \right)
  \]
  \[
  E' = \frac{d(E_U - E_0)}{dW}
  \]

---

Doublon production due to multiple ions

- sequence of 20 equidistant kicks on site 1, $L = 8$.
- doublon distribution becomes homogeneous
- (c): Spectrum converges to symmetric form, $S(-E) = S(E)$, at half filling

---

\[ W(t)/J \]

\[ \frac{d}{L} \]

\[ \frac{E}{J} \]

\[ t/J^{-1} \]

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Conclusions

- 2D Graphene clusters, nanoribbons: promising electronic and optical properties due to correlations: ion stopping, carrier multiplication, photon sidebands
- GNR will be accessible with intense light sources (ARPES)
- NEGF well suited to describe nonequilibrium dynamics in correlated finite (inhomog.) systems, quantitatively reliable, predictive power
- Controlled choice of selfenergy: dictated by filling and interaction strength, presently accurate up to $U \simeq$ bandwidth
- 2 independent approximation schemes: 2-time and 1-time (GKBA). Exact result, typically, enclosed between both
- NEGF not restricted by geometry, dimensionality or ensemble. Approximately cubic scaling with $N_B, t$
- Needed for realistic materials: combination with DFT (e.g. Yambo code of Marini), hybrid schemes (e.g. DMFT)

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34 M. Bonitz, Quantum Kinetic Theory, 2nd ed. Springer 2016
K. Balzer, M. Bonitz, Nonequilibrium Green Functions Approach to Inhomogeneous systems, Springer 2013
www.itap.uni-kiel.de/theo-physik/bonitz
Beyond lattice models: *Ab initio NEGF*\(^{28}\)

- use Kohn-Sham basis as input for NEGF in collaboration with A. Marini, using Yambo

\[ n_i, n_e, f_{i,e}(\mathbf{r}, \mathbf{v}, t) \]

**Plasma description**

\[ G_{nk}^{\sigma}(t, t') \]

**NEGF (non-GPL part)**

\[ E^{LDA(+U)}, \varphi_{m}(\mathbf{r}) \]

**Abinit, PWscf**

\[ \text{new code interfaces for plasma processes} \]

\(^{1}\text{A. Marini, C. Hogan, M. Gruening, and D. Varsano, Comp. Phys. Comm. 180, 1392 (2009)}\]

\(^{28}\text{e.g. Pedro Miguel M. C. de Melo and Andrea Marini Phys. Rev. B 93, 155102 (2016)}\)
AGNRs can be divided into three families: \( N_a = 3p, N_a = 3p + 1 \) and \( N_a = 3p + 2 \), where \( N_a \) is their width (number of dimer lines) and \( p \) is an integer.

(a) tight-binding: large gap for \( N_a = 3p \) and \( N_a = 3p + 1 \), no gap for \( N_a = 3p + 2 \)

(b) LDA: \( N_a = 3p + 2 \) ribbons also have a small band gap

in general: band gap \( \sim N_a^{-1} \)

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Y.-W. Son et al., PRL 97, 216803 (2006)