# Towards a simulation of ultrafast electron dynamics in correlated systems

Michael Bonitz[1]

in collaboration with:
Niclas Schlünzen[1], Jan-Philip Joost[1], Maximilian Rasmussen[1], and Karsten Balzer[2]

[1]Institut für Theoretische Physik und Astrophysik
Christian-Albrechts-Universität zu Kiel, Germany

[2]Rechenzentrum, Christian-Albrechts-Universität zu Kiel, Germany

*Theory and Simulation of Photon-Matter Interaction*
ELI-ALPS, Szeged, July 2018

Christian-Albrechts-Universität zu Kiel
Mathematisch-Naturwissenschaftliche Fakultät

## Modern light sources

*Photons on demand*

1. **Diagnostic tool**
   - Photon energy
   - Pulse shape
   - Synchronized pulses (Pump-probe)
2. **Excitation tool**
   - Laser amplitude
     $\Rightarrow$ multiphoton processes
     $\Rightarrow$ ionization
     $\Rightarrow$ 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_ueg_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, $f_{xc}^{\mathrm{UEG}}$ 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

[1] Schoof *et al.* PRL 2015, Dornheim *et al.*, PRL 2016, Groth *et al.*, PRL 2017, Physics Reports 2018 -> w_d_uegs_sum_rule

# 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

Christian-Albrechts-Universität zu Kiel
Mathematisch-Naturwissenschaftliche Fakultät

## 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: $\boxed{\langle\hat{O}\rangle(t) = \langle\Psi(t)|\hat{O}_S(t)|\Psi(t)\rangle}$
  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)

$$= \mathrm{Tr}\,\hat{\rho}_0^N U(0,t)\hat{O}_S(t)U(t,0),$$ mixed state–even more nasty

$$= \boxed{\sum_{kl}\hat{o}_{kl}(z)G_{lk}(z,z^+)}$$ 1-particle objects, pleasant

# Failure of the Boltzmann/Balescu equation[1]

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

$$I(\mathbf{r}_1,\mathbf{p}_1,t) = \int d^3p_2 \int d^3\bar{p}_1 \int d^3\bar{p}_2\; P(\mathbf{p}_1,\mathbf{p}_2;\bar{\mathbf{p}}_1,\bar{\mathbf{p}}_2;t)$$

$$\times\left\{f(\mathbf{r}_1,\bar{\mathbf{p}}_1,t)f(\mathbf{r}_1,\bar{\mathbf{p}}_2,t) - f(\mathbf{r}_1,\mathbf{p}_1,t)f(\mathbf{r}_1,\mathbf{p}_2,t)\right\}, \qquad (1)$$

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

$q = |\mathbf{p}_1-\bar{\mathbf{p}}_1|, \quad \mathbf{p}_{12} = \mathbf{p}_1+\mathbf{p}_2, \quad \hbar\omega = E_1-\bar{E}_1,$ Pauli blocking factors $(1\pm f)$ 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] M. Bonitz, *Quantum Kinetic theory*, Teubner 1998, 2nd ed.: Springer 2016

C|A|U
Christian-Albrechts-Universität zu Kiel
Mathematisch-Naturwissenschaftliche Fakultät

## 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
  $\left[\hat{c}_i^{(\dagger)}, \hat{c}_j^{(\dagger)}\right]_\mp = 0, \quad \left[\hat{c}_i, \hat{c}_j^\dagger\right]_\mp = \delta_{i,j}$
- Hamiltonian: $\hat{H}(t) = \underbrace{\sum_{k,m} h^0_{km} \hat{c}_k^\dagger \hat{c}_m}_{\hat{H}_0} + \underbrace{\frac{1}{2} \sum_{k,l,m,n} w_{klmn}\, \hat{c}_k^\dagger \hat{c}_l^\dagger \hat{c}_n \hat{c}_m}_{\hat{W}} + \hat{F}(t)$

## Particle interaction $w_{klmn}$

- Coulomb interaction
- electronic correlations

## Time-dependent excitation $\hat{F}(t)$

- single-particle type
- em field, quench, particles

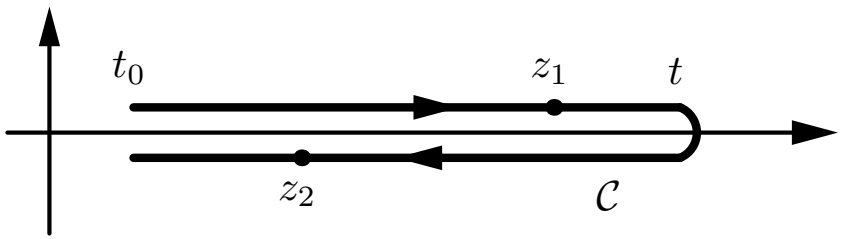
Christian-Albrechts-Universität zu Kiel
Mathematisch-Naturwissenschaftliche Fakultät

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

$$\boxed{G_{ij}(z,z') = \frac{\mathrm{i}}{\hbar}\left\langle \hat{T}_{\mathcal{C}} \hat{c}_i(z) \hat{c}_j^\dagger(z') \right\rangle} \qquad \text{average with } \rho^N$$

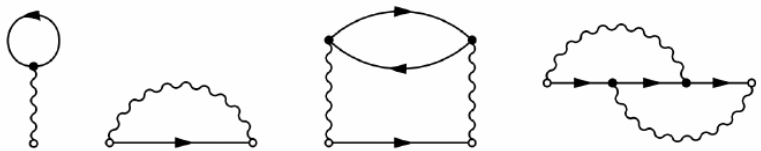
Keldysh–Kadanoff–Baym equations (KBE) on $\mathcal{C}$ ($2 \times 2$ matrix):

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




- $\int_{\mathcal{C}} wG^{(2)} \to \int_{\mathcal{C}} \Sigma G$, 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

$$\mathbf{G}_{ij} = \begin{pmatrix} G^{\mathsf{R}}_{ij} & G^{<}_{ij} \\ 0 & G^{\mathsf{A}}_{ij} \end{pmatrix}$$

$$G^{<}_{ij}(t_1,t_2) = \mp \mathrm{i} \left\langle \hat{c}^{\dagger}_j(t_2)\hat{c}_i(t_1) \right\rangle$$

$$G^{>}_{ij}(t_1,t_2) = -\mathrm{i} \left\langle \hat{c}_i(t_1)\hat{c}^{\dagger}_j(t_2) \right\rangle$$

- Propagators (spectral properties)

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

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

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

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

C | A | U
Christian-Albrechts-Universität zu Kiel
Mathematisch-Naturwissenschaftliche Fakultät

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

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

- 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])

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

# Selfenergy approximations[2]

Christian-Albrechts-Universität zu Kiel
Mathematisch-Naturwissenschaftliche Fakultät

Choice depends on coupling strength, density (filling)

**Hartree–Fock (HF, mean field)**: $\sim w^1$

**Second Born (2B)**: $\sim w^2$

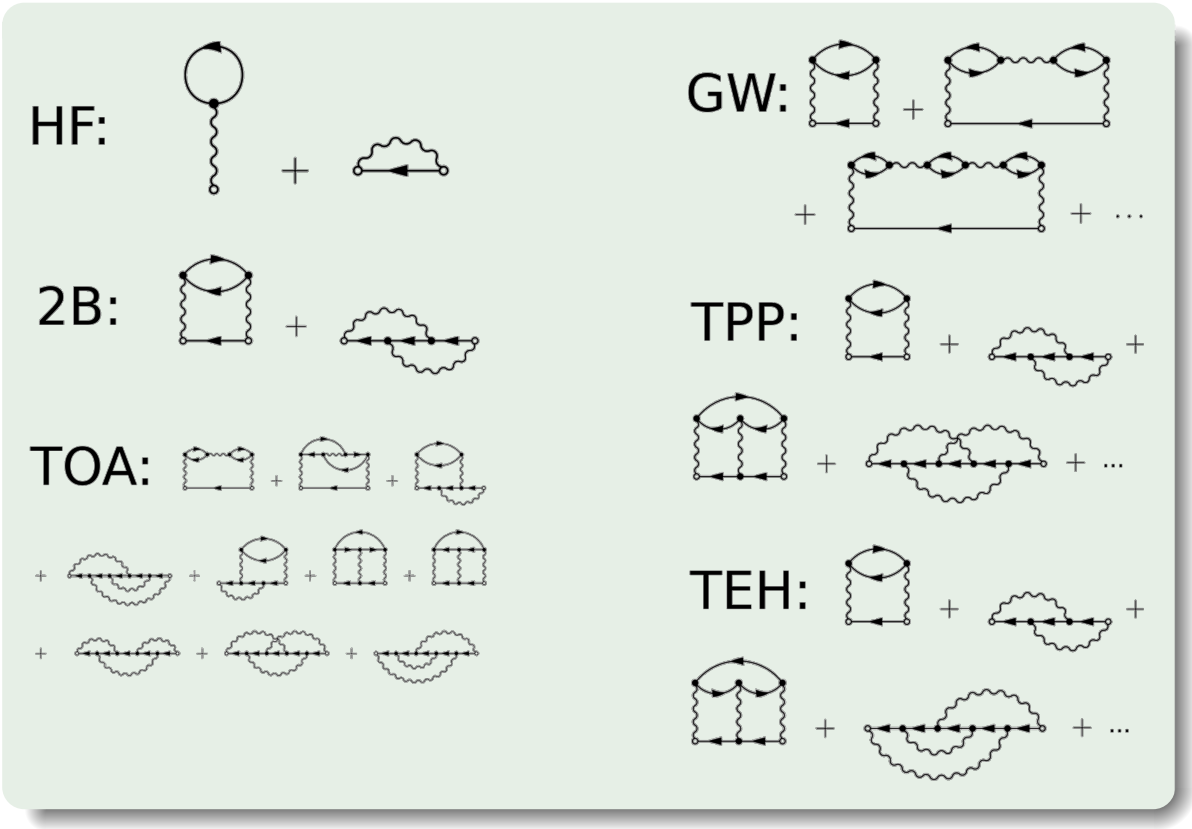
**GW**: $\infty$ bubble summation, dynamical screening effects

**particle-particle $T$-matrix (TPP)**: $\infty$ ladder sum in pp channel

**electron-hole $T$-matrix (TEH)**: $\infty$ ladder sum in ph channel

**FLEX** (GW+TPP+TEH)

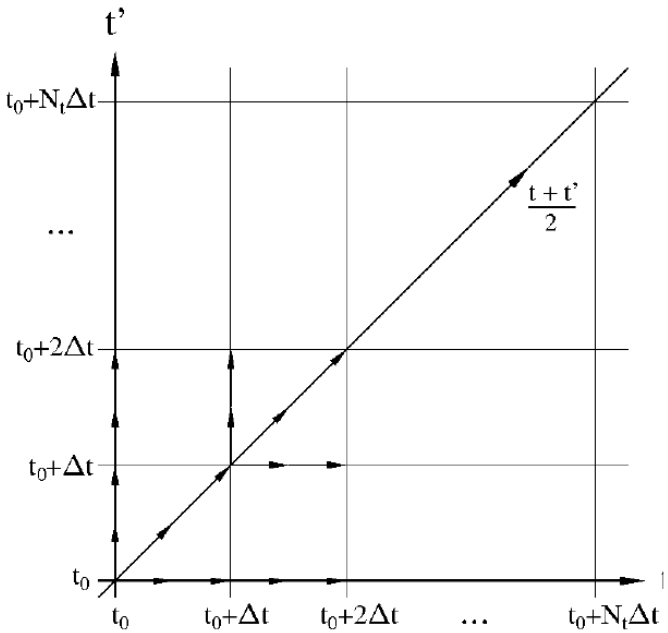
**3rd order approx. (TOA)**: $\sim w^3$

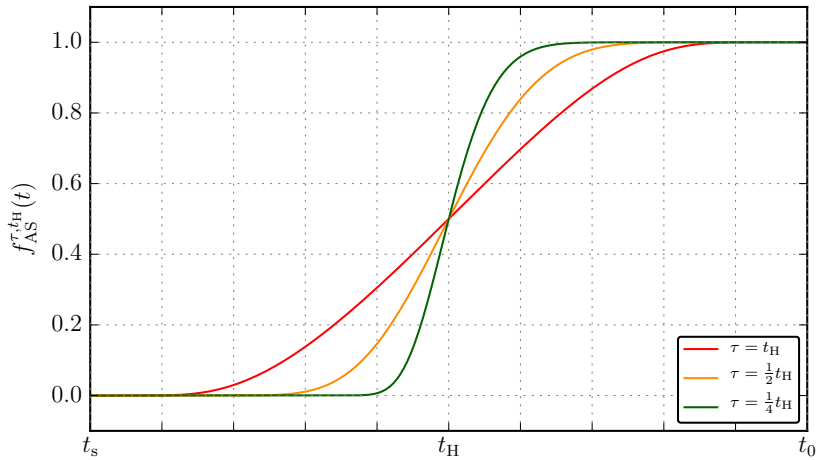



[2] Conserving, nonequilibrium $\Sigma(t,t')$, applies for ultra-short to long times

Christian-Albrechts-Universität zu Kiel
Mathematisch-Naturwissenschaftliche Fakultät

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




$$f_{\rm AS}^{\tau,t_{\rm H}}(t) = \exp\left(-\frac{A^{\tau}_{t_{\rm H}}}{t/(2t_{\rm H})}\exp\left(\frac{B^{\tau}_{t_{\rm H}}}{t/(2t_{\rm H})-1}\right)^{t}\right)$$

$$B^{\tau}_{t_{\rm H}} := \frac{t_{\rm H}}{\tau\ln(2)} - \frac{1}{2}\,, \quad A^{\tau}_{t_{\rm H}} := \frac{\ln(2)}{2}\mathrm{e}^{2B^{\tau}_{t_{\rm H}}}$$

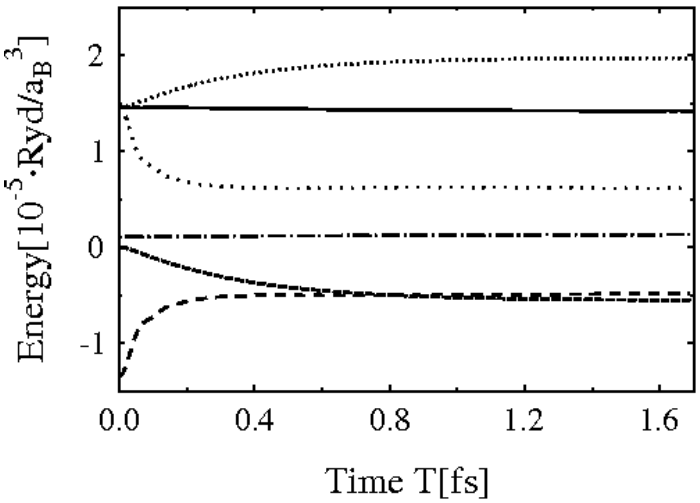
1. Uncorrelated initial state ($t \to -\infty$)
2. adiabatically slow switch-on of interaction for $t, t' \leq t_0$ [1-3]
3. solve KBE in $t - t'$ plane for $G^{\gtrless}(t, t')$

[1] A. Rios et al., Ann. Phys. **326**, 1274 (2011), [2] S. Hermanns et al., Phys. Scr. **T151**, 014036 (2012)
[3] M. Watanabe and W. P. Reinhardt, Phys. Rev. Lett. **65**, 3301 (1990)

# Two-time simulations for macroscopic systems

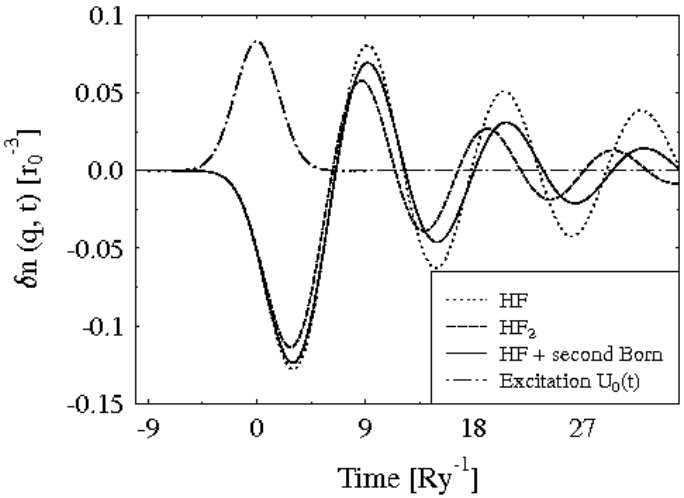
Christian-Albrechts-Universität zu Kiel
Mathematisch-Naturwissenschaftliche Fakultät

1. perfect conservation of total energy
2. accurate **short-time** dynamics:
   phase 1: correlation dynamics
   2: relaxation of $f(p)$, occupations




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

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.

[1] MB and D. Semkat, PRE 1997, 1999, MB, *Quantum Kinetic Theory*, 2nd ed. Springer 2016

[3] N. Kwong and MB, PRL **84**, 1768 (2000), [4] K. Balzer, S. Hermanns, MB, EPL **98**, 67002 (2012)

# Outline

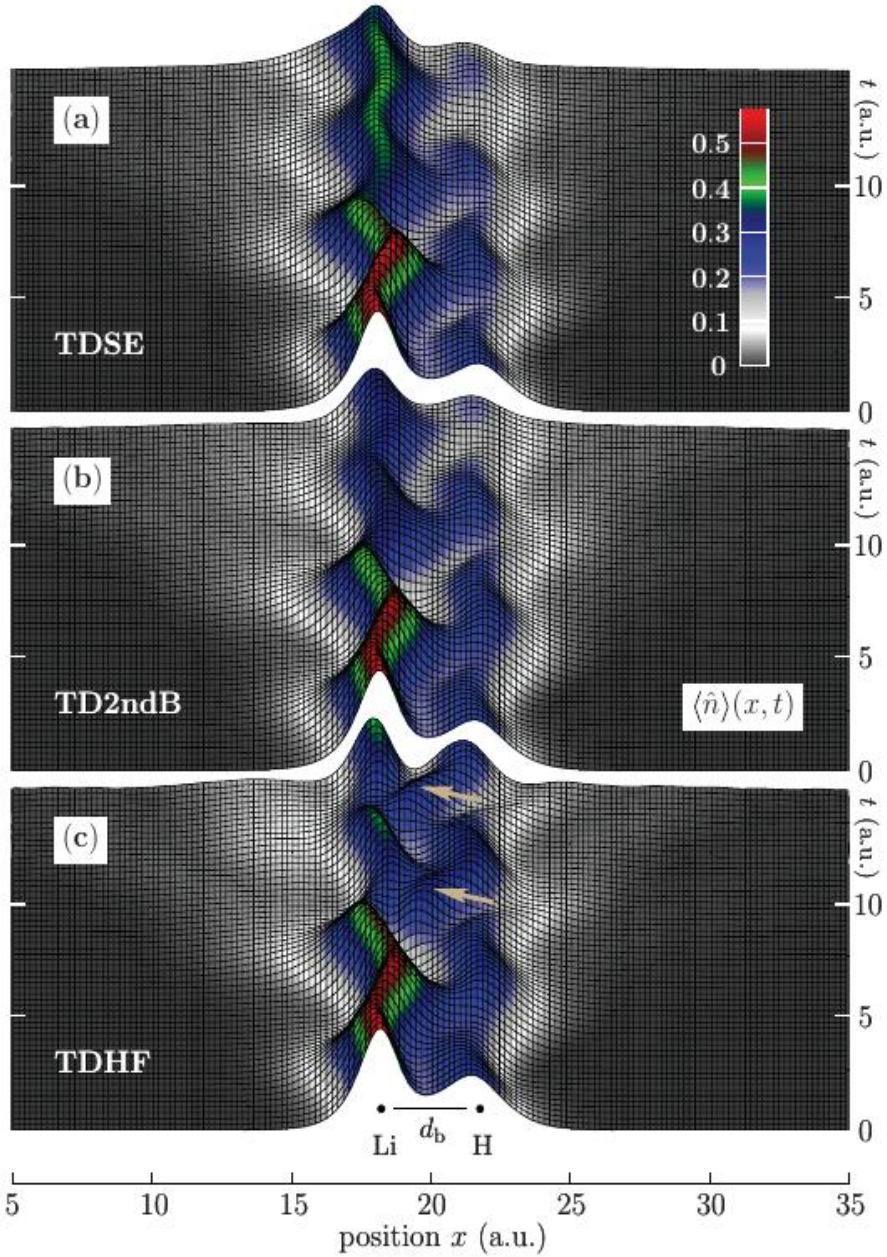


1. Nonequilibrium Green functions (NEGF) - Theory
   - Applications to atoms and molecules
   - Hubbard model. Strong correlations
   - Problems of NEGF dynamics: myth and reality
2. Comparison of NEGF to exact DMRG solutions
3. Testing NEGF against 2D cold atom experiments
4. Optical excitation of graphene nanoribbons
5. Ion stopping in correlated materials

# Inhomogeneous systems: small molecules

Christian-Albrechts-Universität zu Kiel
Mathematisch-Naturwissenschaftliche Fakultät

- 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

Christian-Albrechts-Universität zu Kiel
Mathematisch-Naturwissenschaftliche Fakultät

- Complicated structure of interaction $w_{klmn}$ and selfenergy $\Sigma$
- Collision intergrals 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[3]

- Finite-Element Discrete Variable Representation [PRA **81**, 022510 (2010)]
- Generalized Kadanoff–Baym ansatz [Phys. Scr. **T151**, 014036 ('12), JPCS **427**, 012006 ('13)]
- Adiabatic switch-on of interaction [Phys. Scr. **T151**, 014036 ('12)]
- Parallelization [PRA **82**, 033427 (2010)]

[3] K. Balzer, M. Bonitz, Lecture Notes in Phys. vol. 867 (2013)

# FEDV-Representation[4]



- 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

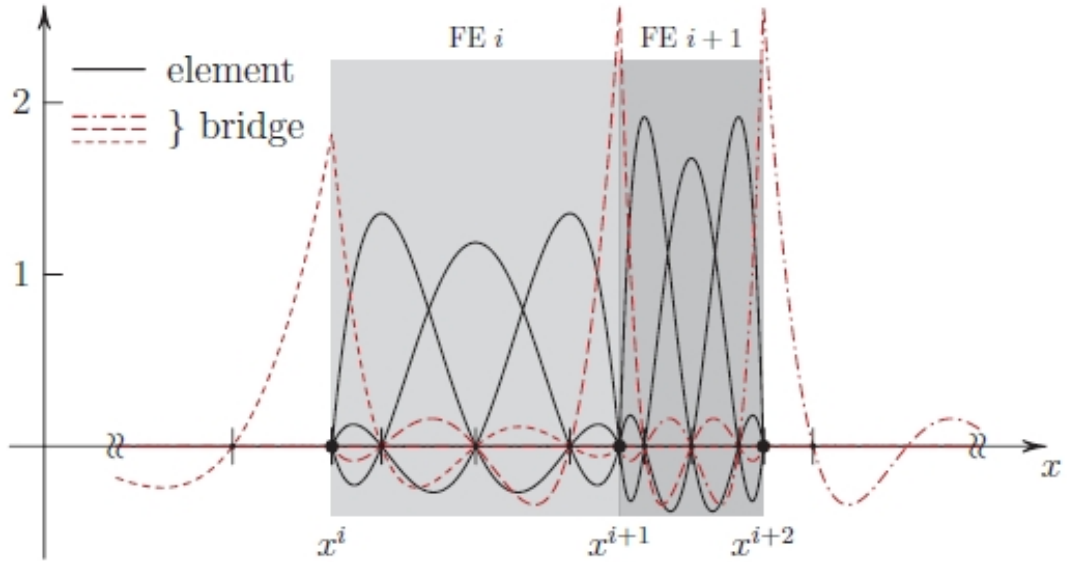


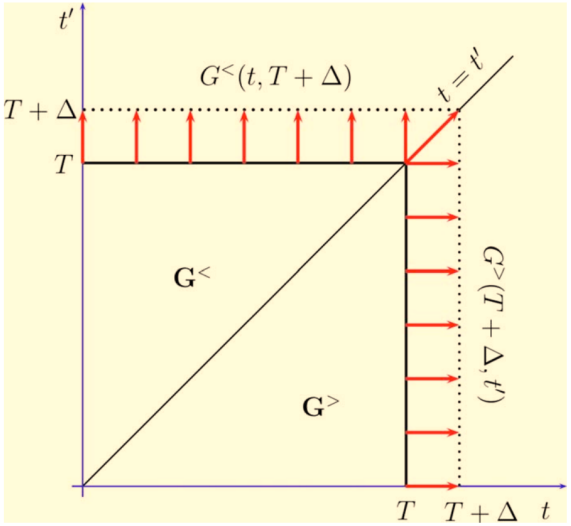

FIG. 2. (Color online) Structure of a FE-DVR basis $\{\chi_m^i(x)\}$ with $n_g = 4$ (i.e., five local DVR basis functions in each element). While the element functions (solid) are defined in a single FE, the bridge functions (dashed and dashed-dotted lines) link two adjacent FEs.

[4] Balzer *et al.*, PRA **81**, 022510 (2010)

# Generalized Kadanoff-Baym-ansatz[5] (GKBA)

Christian-Albrechts-Universität zu Kiel
Mathematisch-Naturwissenschaftliche Fakultät

- reduce computational effort: propagation along diagonal only (scaling $T^3 \longrightarrow T^2$)
- 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:

$$G^{\gtrless}_{ss'}(t,t') = \pm\left[G^{\text{ret}}_{s\bar{s}}(t,t')\rho^{\gtrless}_{\bar{s}s'}(t') - \rho^{\gtrless}_{s\bar{s}}(t)G^{\text{adv}}_{\bar{s}s'}(t,t')\right] \quad \text{with} \quad \rho^{\gtrless}_{ss'}(t) = \pm \mathrm{i}\hbar G^{\gtrless}_{ss'}(t,t)$$

- HF-GKBA: use Hartree-Fock-propagators for $G^{\text{ret/adv}}_{ss'}$

$$G^{\text{ret/adv}}_{ss'}(t,t') = \mp \mathrm{i}\Theta_{\mathcal{C}}\left(\pm[t-t']\right) \exp\left(-\frac{\mathrm{i}}{\hbar}\int_{t'}^{t} \mathrm{d}\bar{t}\, h_{\text{HF}}(\bar{t})\right)\Big|_{ss'}$$

[5] P. Lipavský, V. Špička, and B. Velický, Phys. Rev. B **34**, 6933 (1986),
[4] MB, *Quantum Kinetic Theory*, 2nd ed. Springer (2016)
[5] Hermanns, Schlünzen, MB, PRB 2014.

# The generalized Kadanoff-Baym ansatz: Conserving properties

Christian-Albrechts-Universität zu Kiel
Mathematisch-Naturwissenschaftliche Fakultät

- HF-GKBA: same conservation properties as two-time approximation[6]
- damped propagators, local approximation violate total energy conservation[7]
- Generalization of the energy conservation theorem of Baym and Kadanoff (relaxed conditions)[8]

**Extensions**: Gauge invariant generalization of the GKBA to strong electro-magnetic fields, derivation of strong-field quantum kinetic equations containing inverse bremsstrahlung heating and multipohoton absorption[9] and numerical solutions[10]

[6] G. Baym and L.P. Kadanoff, Phys. Rev. **124**, 287 (1961)

[7] M. Bonitz, D. Semkat, H. Haug, Eur. Phys. J. B (1999)

[8] S. Hermanns, N. Schlünzen, and M. Bonitz, Phys. Rev. B (2014)

[9] D. Kremp, Th. Bornath, M. Bonitz, and M. Schlanges, Phys. Rev. E (1999)

[10] H. Haberland, M. Bonitz, and D. Kremp, Phys. Rev. E (2001)

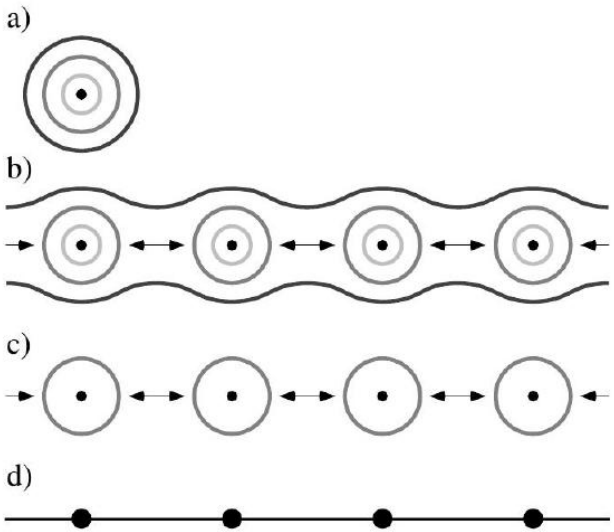
# Outline

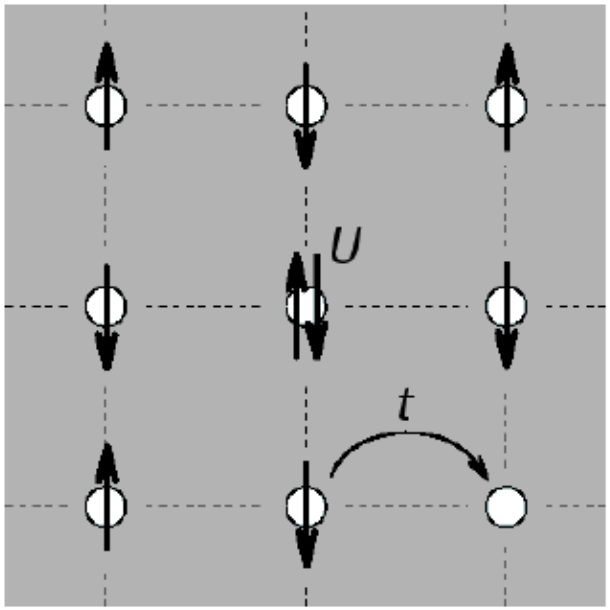


1. Nonequilibrium Green functions (NEGF) - Theory
   - Applications to atoms and molecules
   - Hubbard model. Strong correlations
   - Problems of NEGF dynamics: myth and reality
2. Comparison of NEGF to exact DMRG solutions
3. Testing NEGF against 2D cold atom experiments
4. Optical excitation of graphene nanoribbons
5. Ion stopping in correlated materials

# The Hubbard model. Correlated materials

Christian-Albrechts-Universität zu Kiel
Mathematisch-Naturwissenschaftliche Fakultät




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

$h_{ij} = -\delta_{\langle i,\,j\rangle}$ 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)

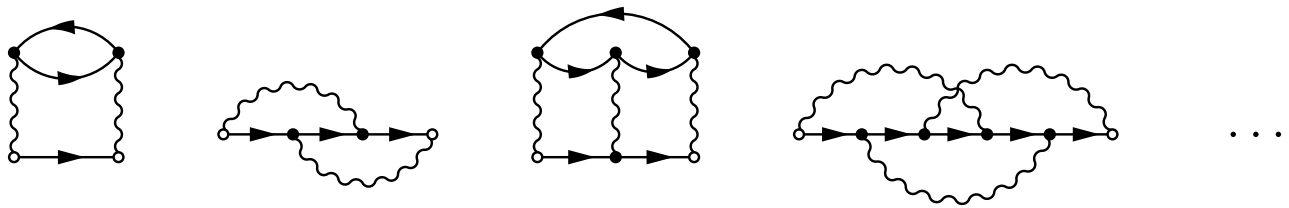
- propagate NEGF in Hubbard basis, finite inhomogeneous system
- $f$: arbitrary 1-particle hamiltonian: laser field, quench, particles etc.
- Selfenergies given by sparse matrices

# Strong coupling: T-matrix selfenergy

- to access strong coupling: use T-matrix selfenergy (sum entire Born series)
- for Hubbard model simplification[15]

$$\Sigma^{\mathrm{cor},\uparrow(\downarrow)}_{\boldsymbol{s}\boldsymbol{s}'}(z,z') = \mathrm{i}\hbar\, T_{\boldsymbol{s}\boldsymbol{s}'}(z,z')\, G^{\downarrow(\uparrow)}_{\boldsymbol{s}'\boldsymbol{s}}(z',z)\,,$$

$$T_{\boldsymbol{s}\boldsymbol{s}'}(z,z') = -\mathrm{i}\hbar\, U^2\, G^{\uparrow}_{\boldsymbol{s}\boldsymbol{s}'}(z,z')\, G^{\downarrow}_{\boldsymbol{s}\boldsymbol{s}'}(z,z') + \mathrm{i}\hbar\, U \int_{\mathcal{C}} \mathrm{d}\bar{z}\, G^{\uparrow}_{\boldsymbol{s}\bar{\boldsymbol{s}}}(z,\bar{z})\, G^{\downarrow}_{\boldsymbol{s}\bar{\boldsymbol{s}}}(z,\bar{z}) T_{\bar{\boldsymbol{s}}\boldsymbol{s}'}(\bar{z},z')\,.$$



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

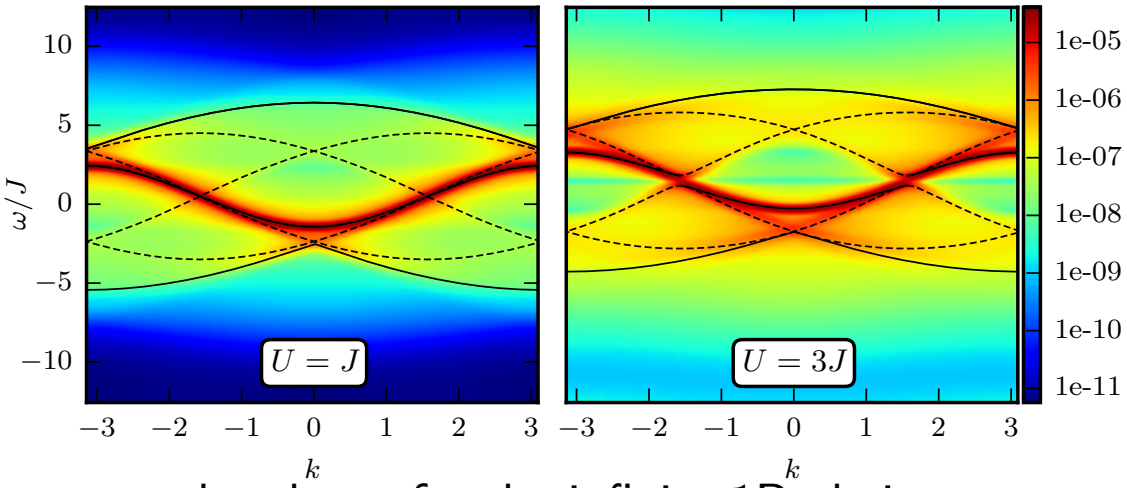
[15] P. von Friesen, C. Verdozzi, and C.O. Almbladh, Phys. Rev. B **82**, 155108 (2010)

[16] M. Bonitz, N. Schlünzen, and S. Hermanns, Contrib. Plasma Phys. **55**, 152 (2015)

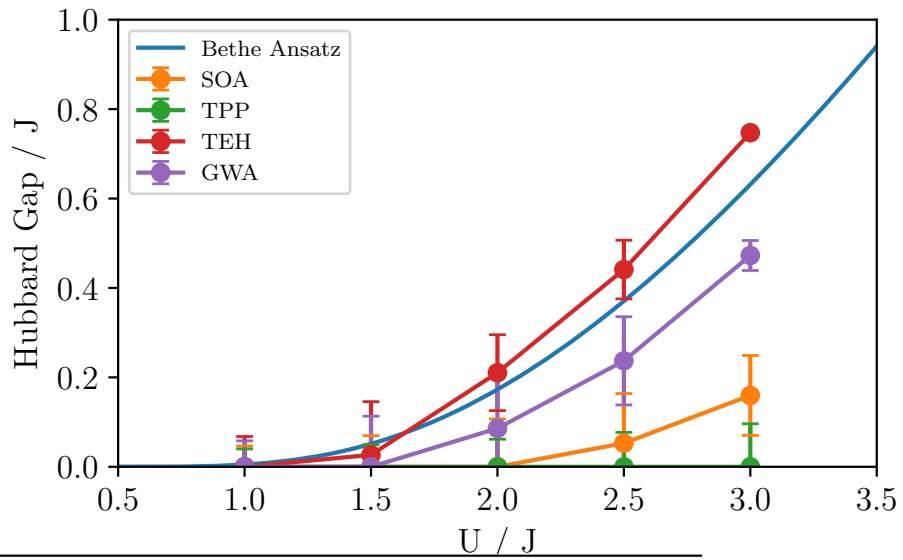
# Ground state results at half-filling

Christian-Albrechts-Universität zu Kiel
Mathematisch-Naturwissenschaftliche Fakultät

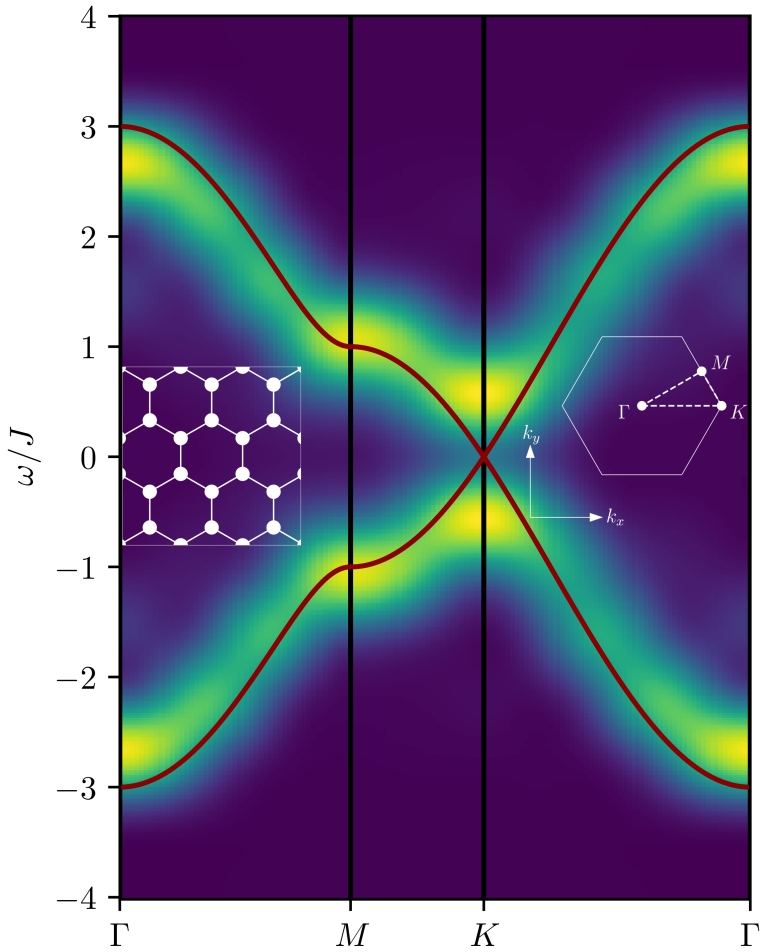
dispersion of 40-site Hubbard chain (2B/SOA):




band gap for the infinite 1D chain:




band structure for the honeycomb lattice:

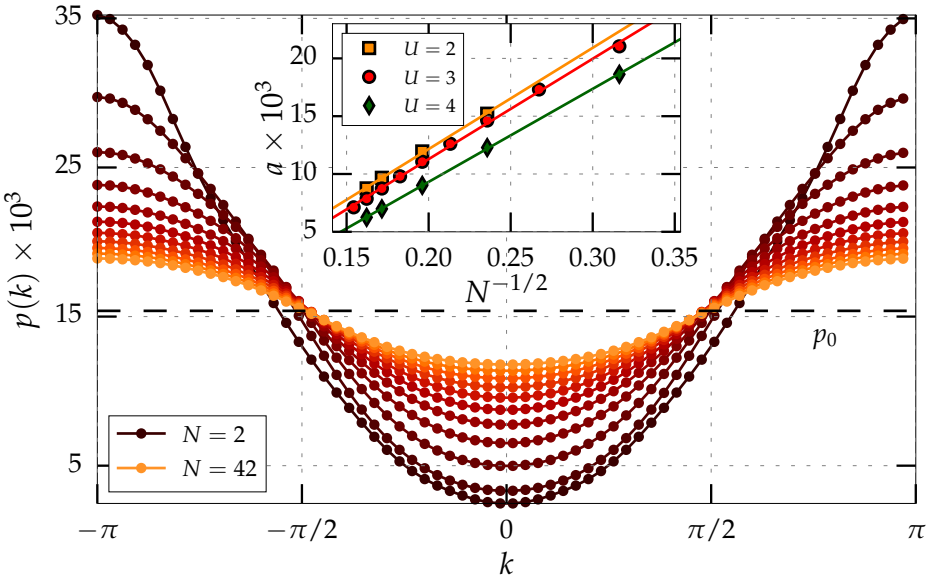



J.-P. Joost, N. Schlünzen, and M. Bonitz, *to be published*

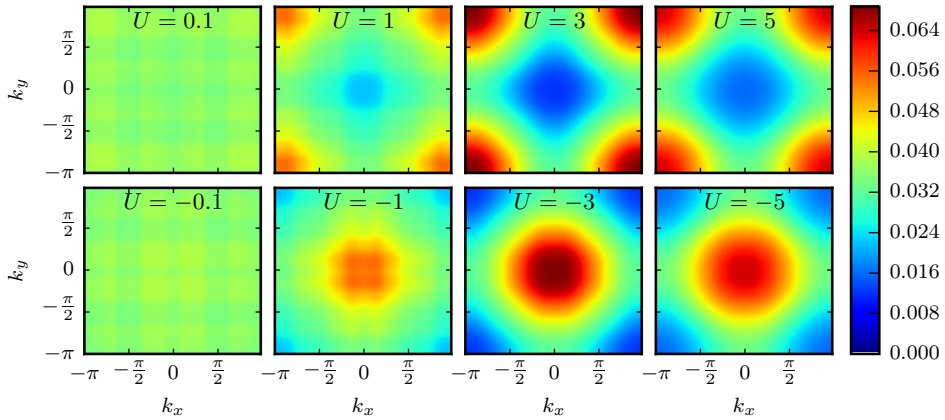
# Density in quasi-momentum space

Christian-Albrechts-Universität zu Kiel
Mathematisch-Naturwissenschaftliche Fakultät

**1D:**




**2D:**




- momentum distribution

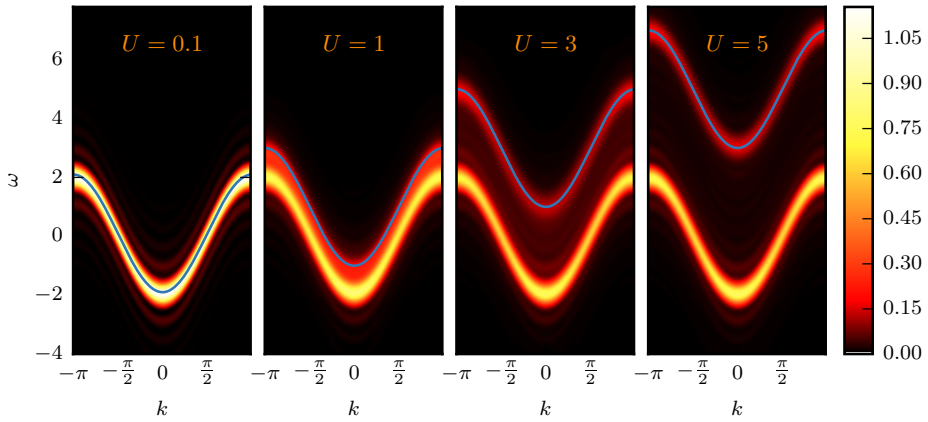
$$n_{\boldsymbol{k}}(t) \quad = \quad \frac{1}{N_s} \sum_{\boldsymbol{ss'}} \mathrm{e}^{-\mathrm{i}\boldsymbol{k}(\boldsymbol{s}-\boldsymbol{s'})} n_{\boldsymbol{ss'}}(t),$$

- positive $U$: occupation of large energies
- negative $U$: occupation of small energies

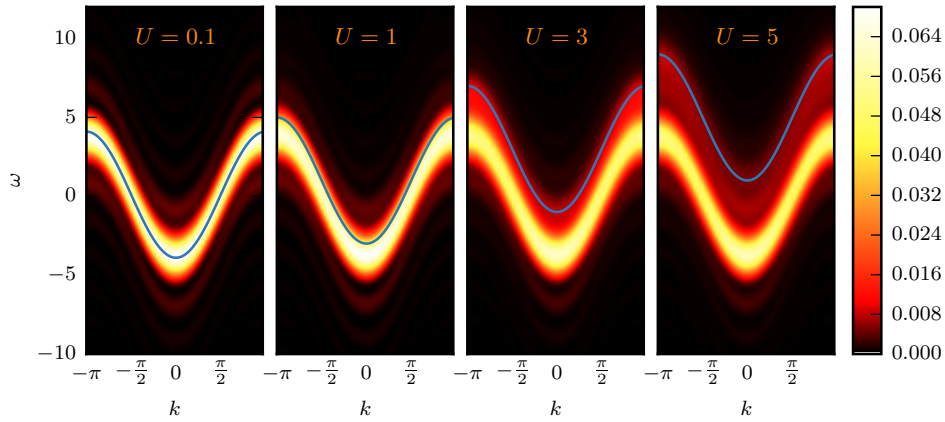
# Dispersion relation

Christian-Albrechts-Universität zu Kiel
Mathematisch-Naturwissenschaftliche Fakultät

**1D:**




**2D:**




- spectral function

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

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

# 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

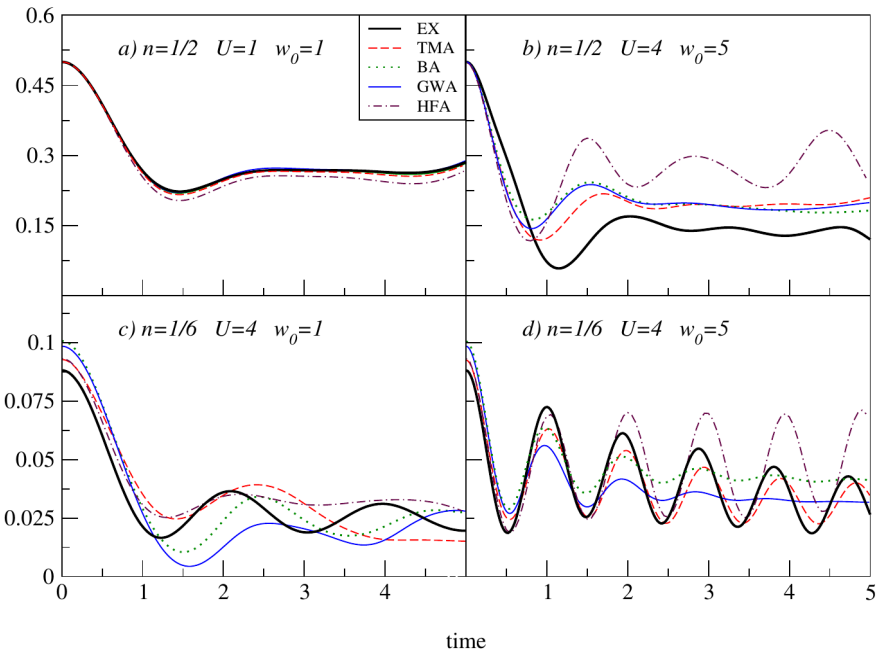
# Properties of the selfconsistent KBE[11]

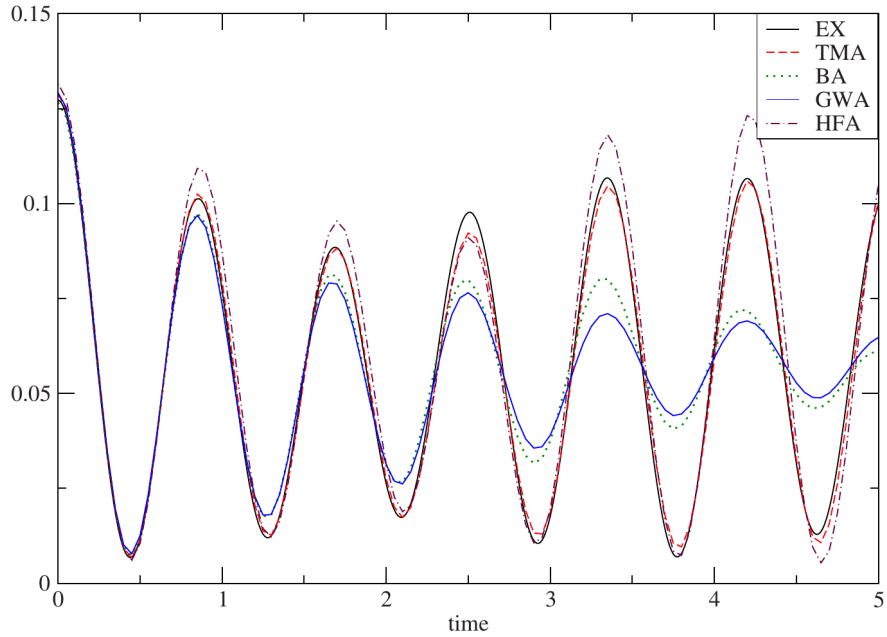


PHYSICAL REVIEW B **82**, 155108 (2010)

**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
*Mathematical Physics and European Theoretical Spectroscopy Facility (ETSF), Lund University, 22100 Lund, Sweden*



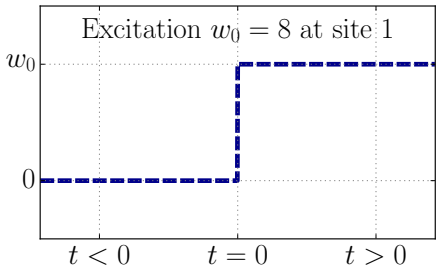

*small* Hubbard clusters. Strong external excitation (Right Fig.: $N_s = 6, n = 1/6, U = 2, w_0 = 5$)
$\Rightarrow$ artificial damping of *many-body* approximations. Best behavior: T-matrix

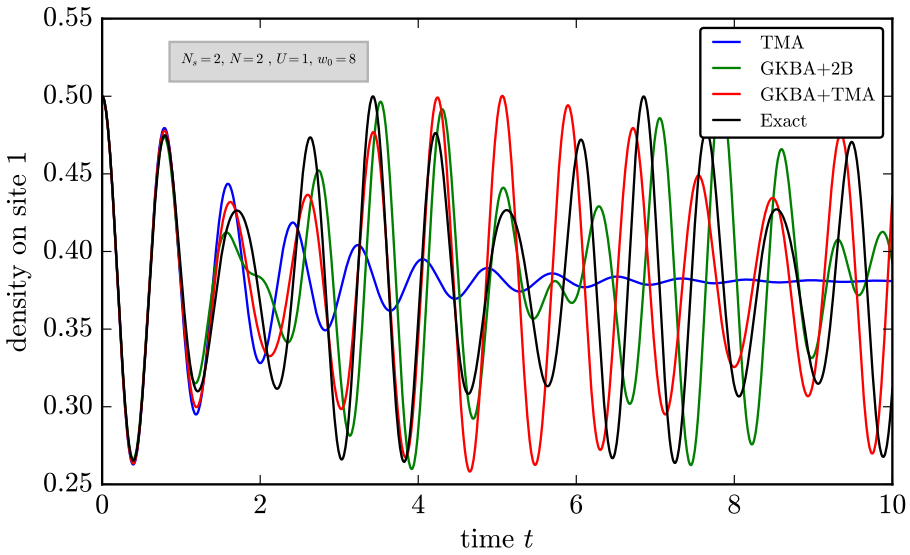
[11] see also: M. P. von Friesen, C. Verdozzi, and C.-O. Almbladh, Phys. Rev. Lett. **103**, 176404 (2009)

# Long-time behavior of two-time KBE and GKBA

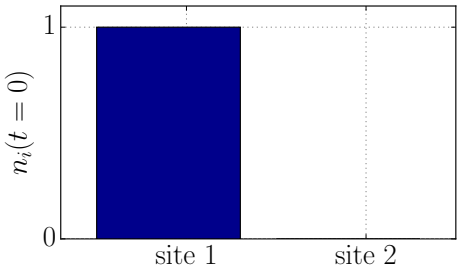
Christian-Albrechts-Universität zu Kiel
Mathematisch-Naturwissenschaftliche Fakultät

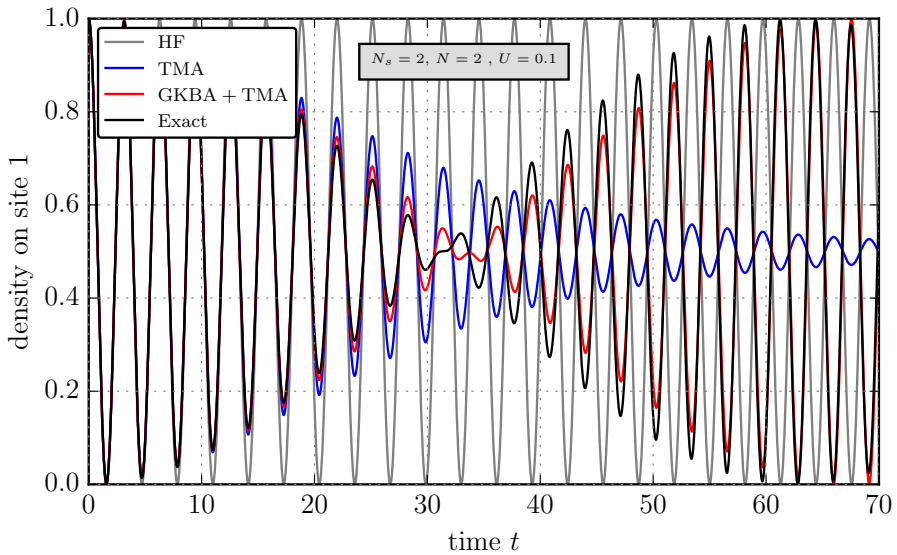
## Time-dependent excitation




## Nonequilibrium initial state



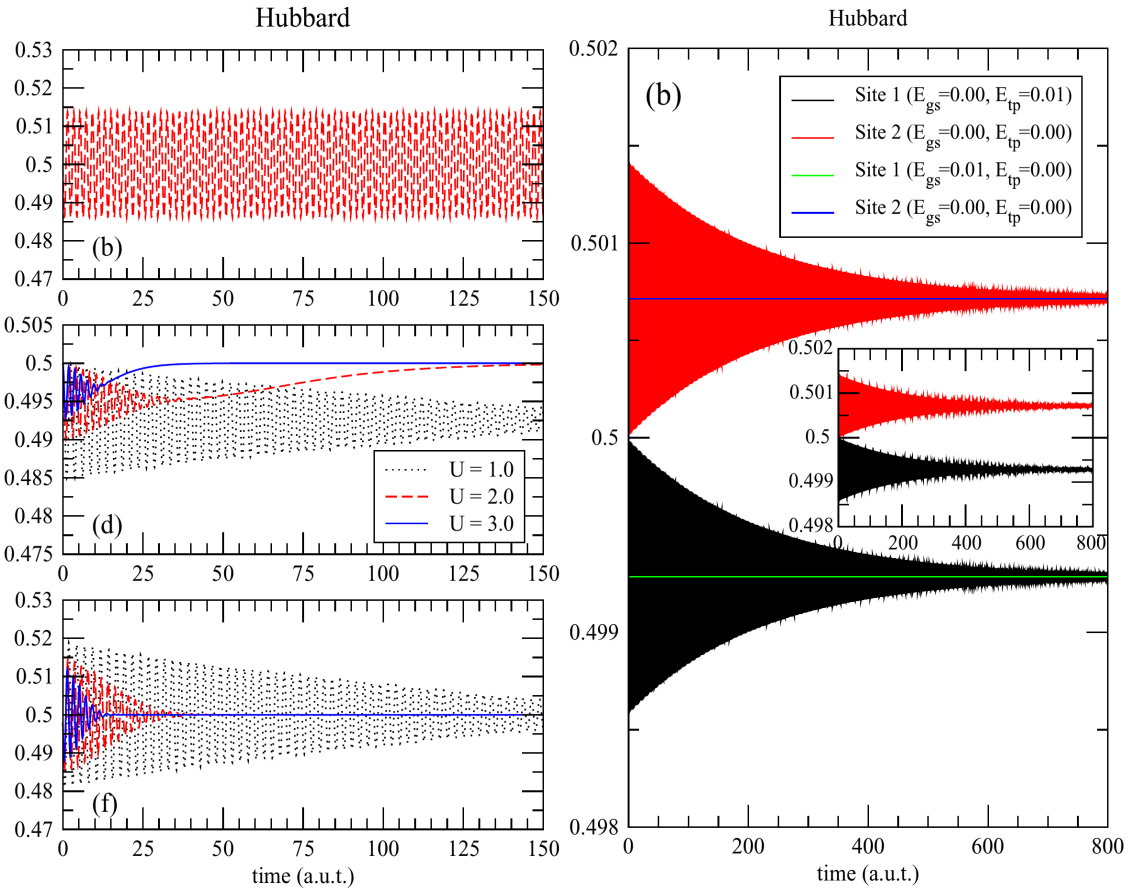




- KBE with all many-body approximations show unphysical damping effects
- HF-GKBA: reduction or even removal of damping (*small clusters*)

# Adrian Stan's claims[12]

Christian-Albrechts-Universität zu Kiel
Mathematisch-Naturwissenschaftliche Fakultät

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.).



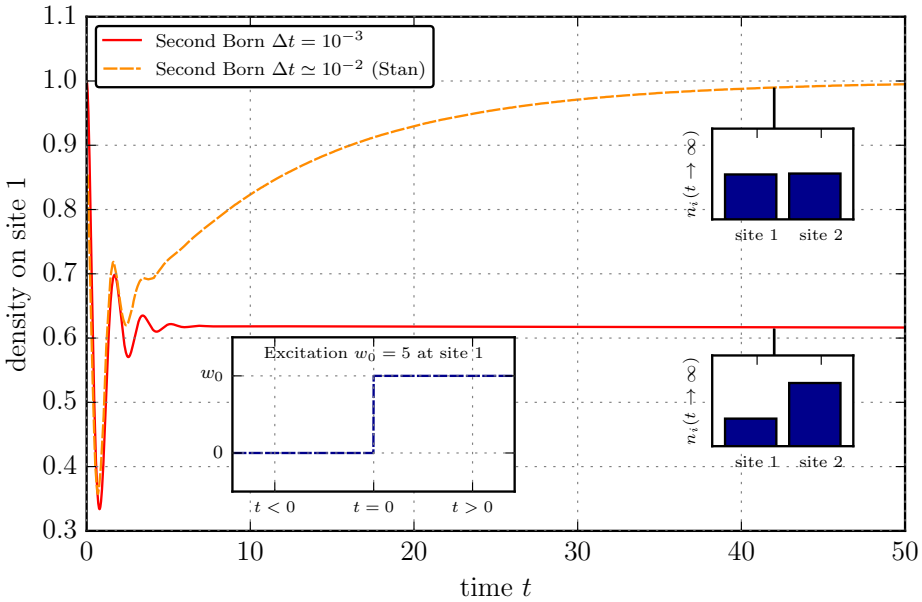

⇒ **Previous studies "overlooked the physics"** (too short)
⇒ **KBE are practically useless** (negligible range of validity)

[12] A. Stan, Phys. Rev. B, Rapid Comm. **93**, 041103 (2016) [Editors' Choice]

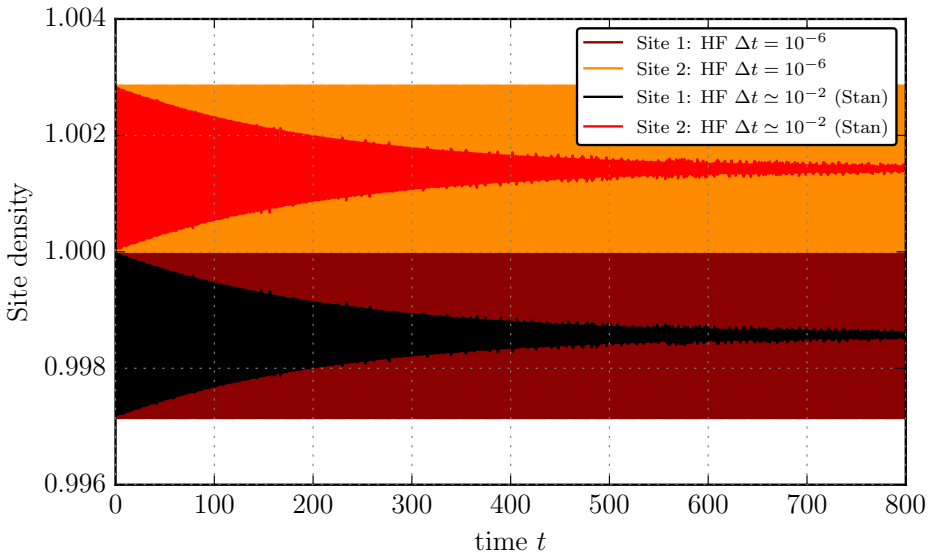
# Test of Stan's claims (1)[13]

Christian-Albrechts-Universität zu Kiel
Mathematisch-Naturwissenschaftliche Fakultät

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

[13] N. Schlünzen, J.-Ph. Joost, and M. Bonitz, Phys. Rev. B **93**, 041103 (2017)

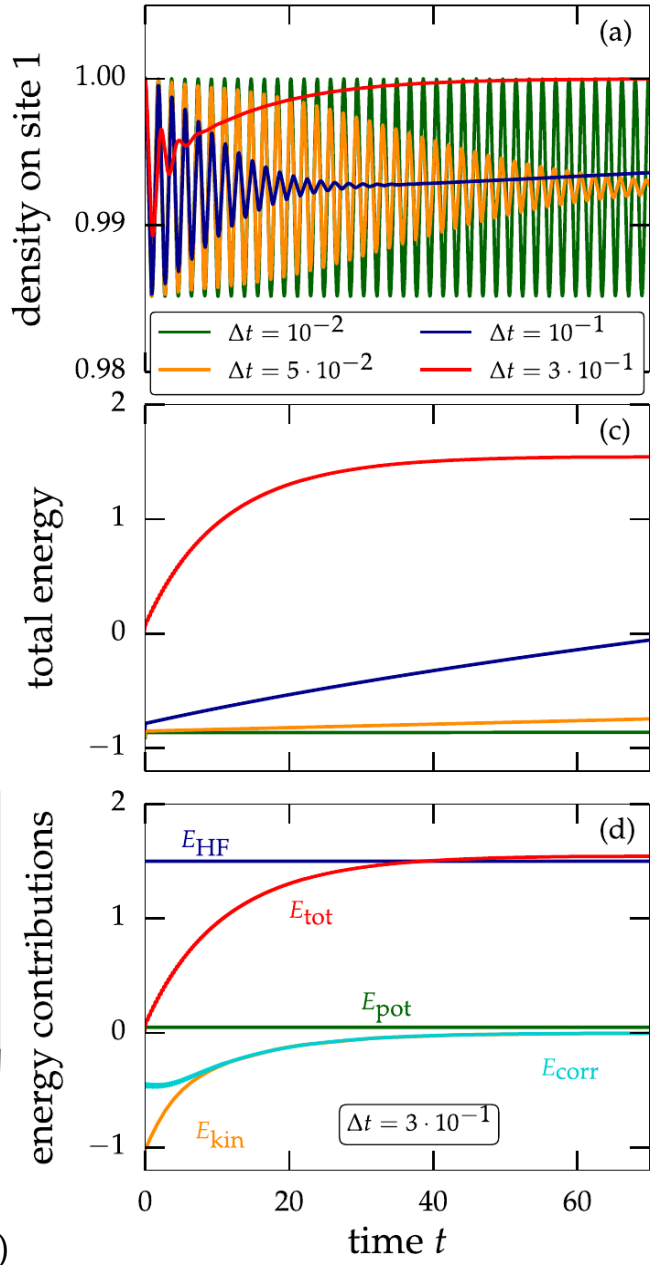
# Test of Stan's claims (2)[14]

Christian-Albrechts-Universität zu Kiel
Mathematisch-Naturwissenschaftliche Fakultät

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

⇒ Unwarrented claims and generalizations (from Hubbard dimer).
⇒ All statements are wrong, numerical artefacts.




[14] N. Schlünzen, J.-Ph. Joost, and M. Bonitz, Phys. Rev. B **93**, 041103 (2017)

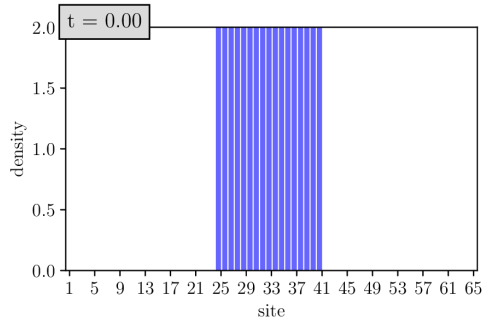
# Outline

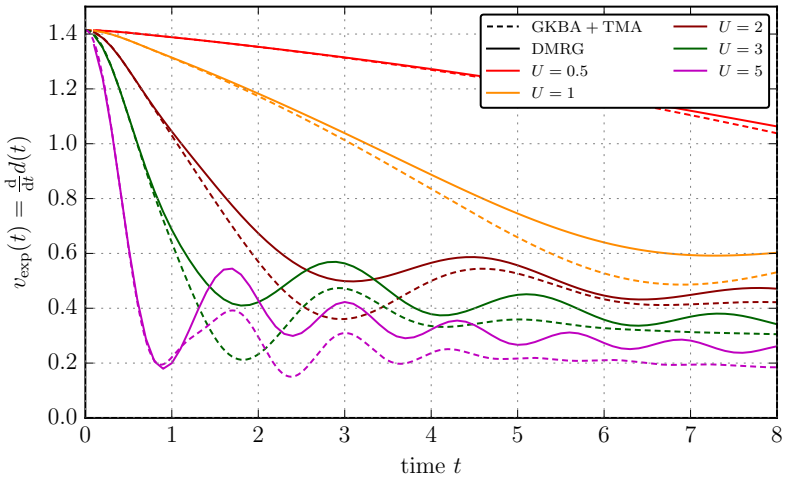
# Benchmarks of NEGF against DMRG (1D)[1]

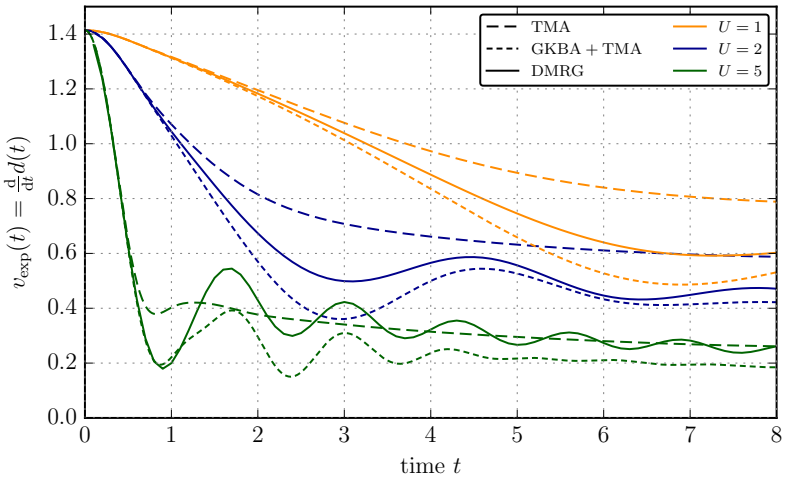
Christian-Albrechts-Universität zu Kiel
Mathematisch-Naturwissenschaftliche Fakultät

## 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

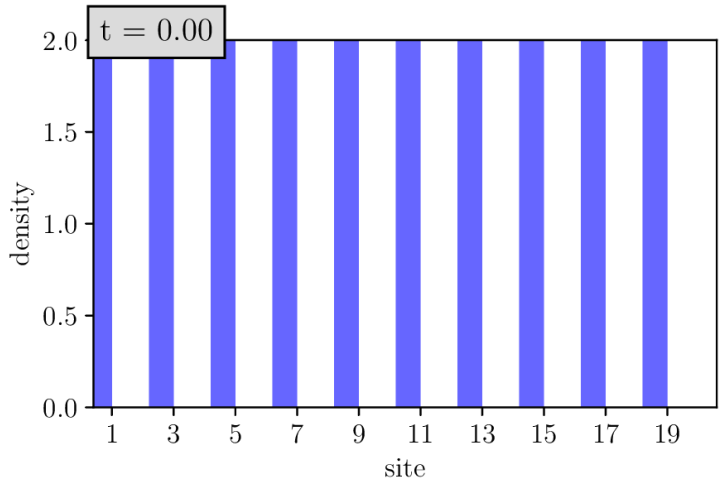
- artificial damping[2,3] in 2-time solution for strongly excited, finite systems
- removed by GKBA

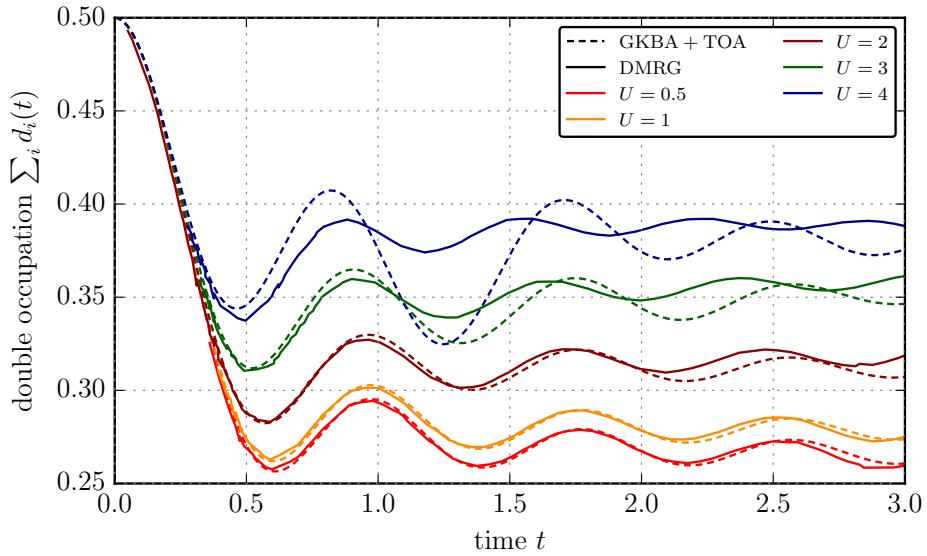
[1] N. Schlünzen, J.-P. Joost, F. Heidrich-Meisner, and M. Bonitz, Phys. Rev. B **95**, 165139 (2017)
[2] M. P. von Friesen, C. Verdozzi, and C.-O. Almbladh, Phys. Rev. Lett. **103**, 176404 (2009)
[3] N. Schlünzen, J.-P. Joost, and M. Bonitz, PRB **96**, 117101 (2017)

# Benchmarks of NEGF against DMRG (1D)[15]

Christian-Albrechts-Universität zu Kiel
Mathematisch-Naturwissenschaftliche Fakultät

Initial state:
charge density wave



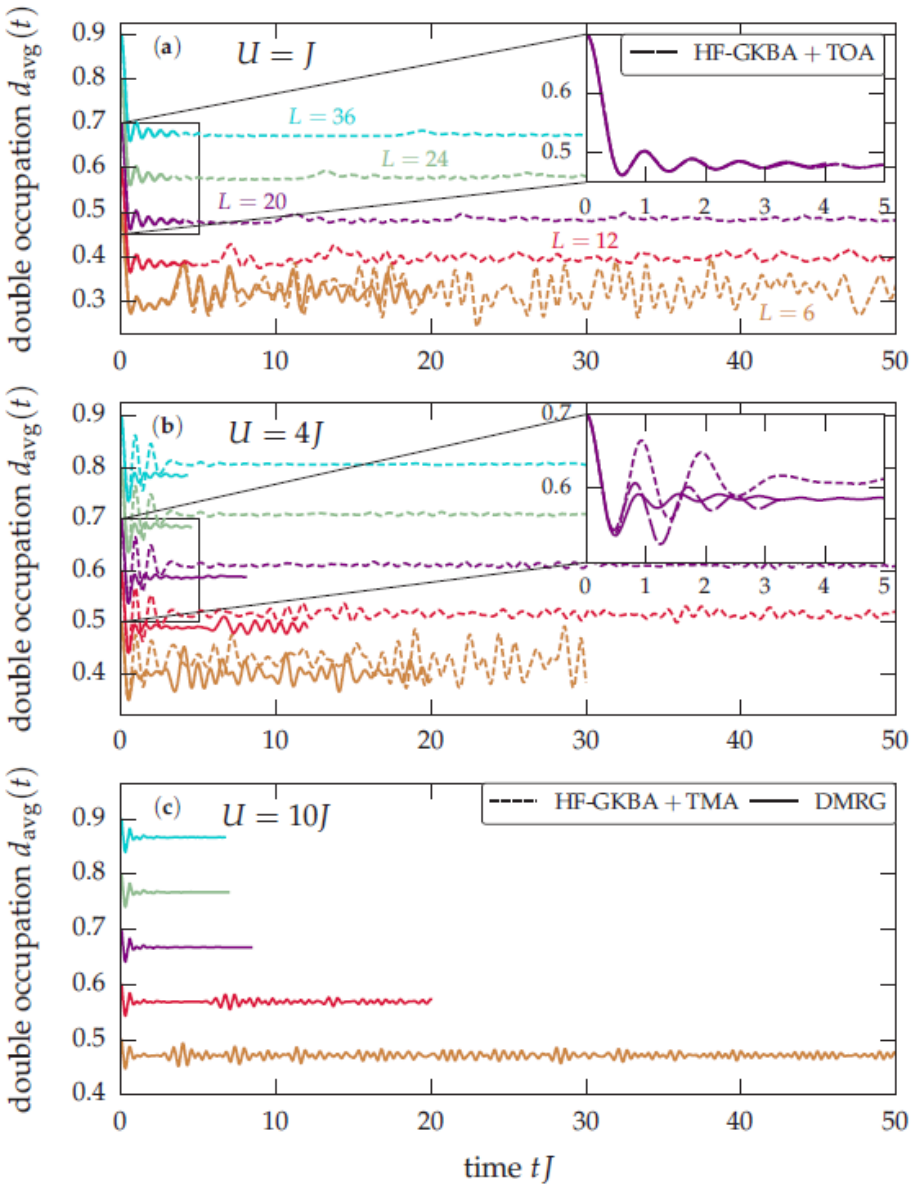




- excellent agreement for densities, energies etc.
- sensitive observable: total double occupation
- very good quality transients of NEGF, up to $U \simeq$ bandwidth
- accurate long-time behavior of GKBA+T-matrix (not shown)

[15] N. Schlünzen, J.-P. Joost, F. Heidrich-Meisner, and M. Bonitz, Phys. Rev. B **95**, 165139 (2017)

# Complementarity of NEGF and DMRG[16]

Christian-Albrechts-Universität zu Kiel
Mathematisch-Naturwissenschaftliche Fakultät




- 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

[16] N. Schlünzen, J.-P. Joost, F. Heidrich-Meisner, and M. Bonitz, Phys. Rev. B **95**, 165139 (2017)

# 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]:
  ($\Rightarrow$ 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

[17] "Conserving approximations" by Baym and Kadanoff

[18] M. P. von Friesen, C. Verdozzi, and C.-O. Almbladh, Phys. Rev. B **82**, 155108 (2010)

[19] S. Hermanns, N. Schlünzen, and M. Bonitz, Phys. Rev. B **90**, 125111 (2014)

# 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

# Outline

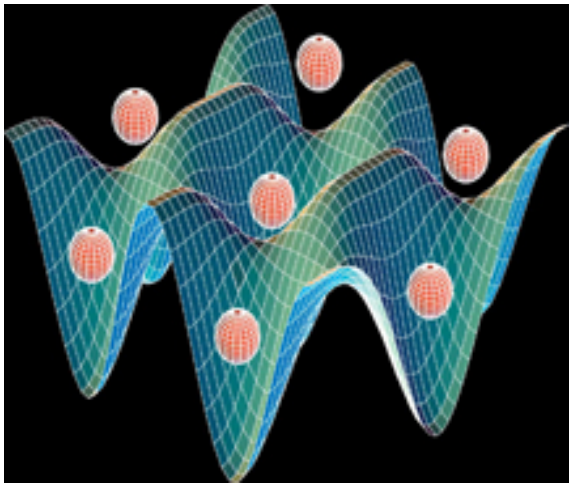
# Time-resolved expansion of fermionic atoms

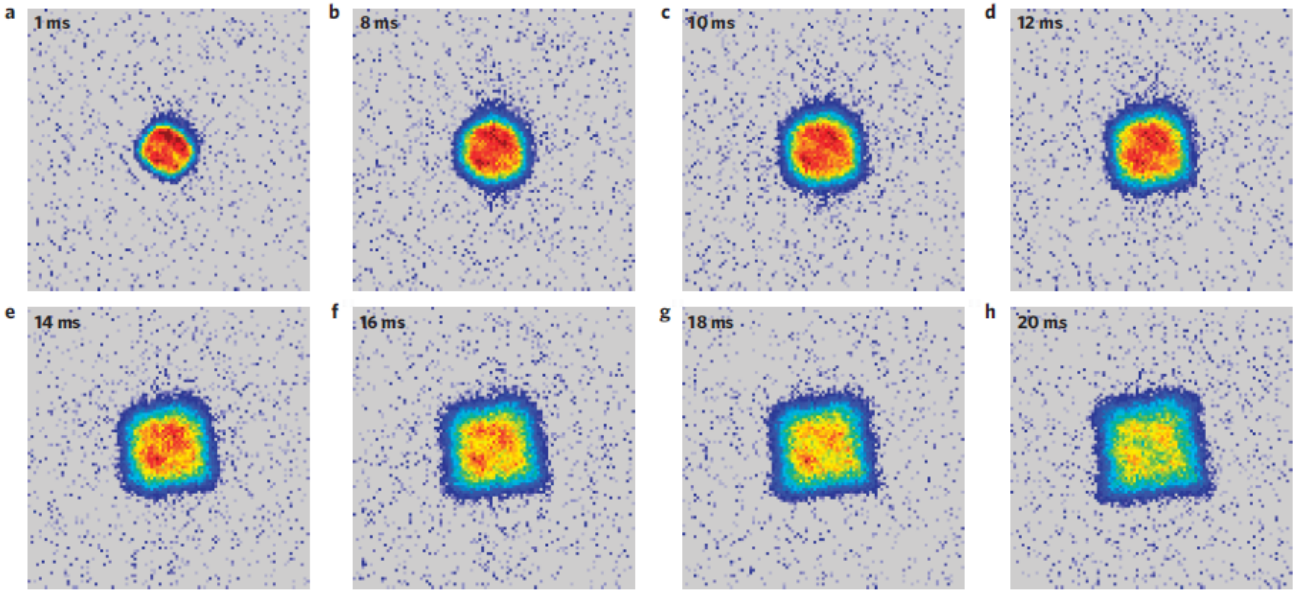


nature physics
ARTICLES
PUBLISHED ONLINE: 15 JANUARY 2012 | DOI: 10.1038/NPHYS2205

**Fermionic transport and out-of-equilibrium dynamics in a homogeneous Hubbard model with ultracold atoms**

Ulrich Schneider[1,2]*, Lucia Hackermüller[1,3], Jens Philipp Ronzheimer[1,2], Sebastian Will[1,2], Simon Braun[1,2], Thorsten Best[1], Immanuel Bloch[1,2,4], Eugene Demler[5], Stephan Mandt[6], David Rasch[6] and Achim Rosch[6]

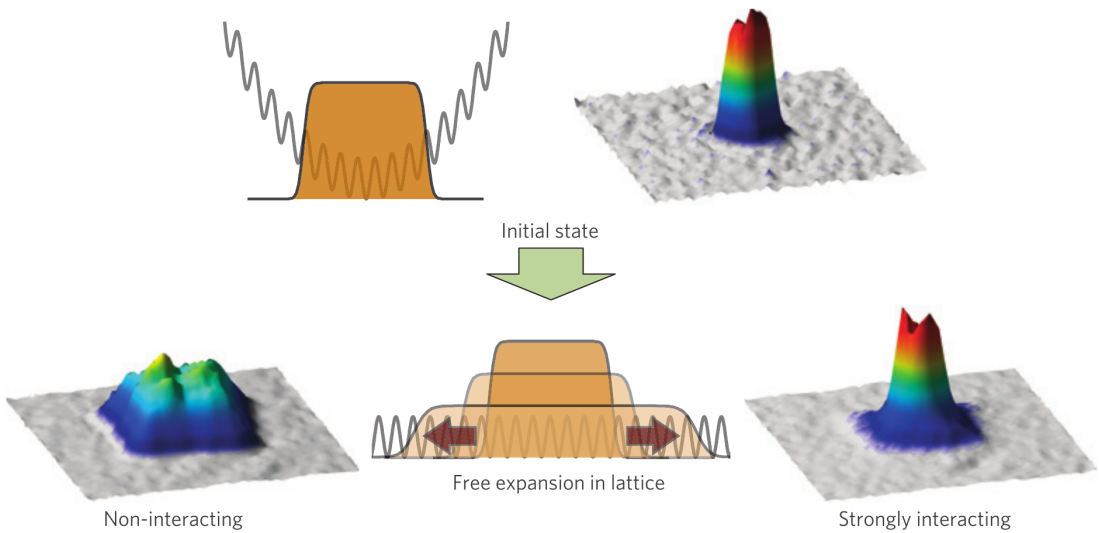




# Time-resolved expansion of fermionic atoms (cont.)

Christian-Albrechts-Universität zu Kiel
Mathematisch-Naturwissenschaftliche Fakultät

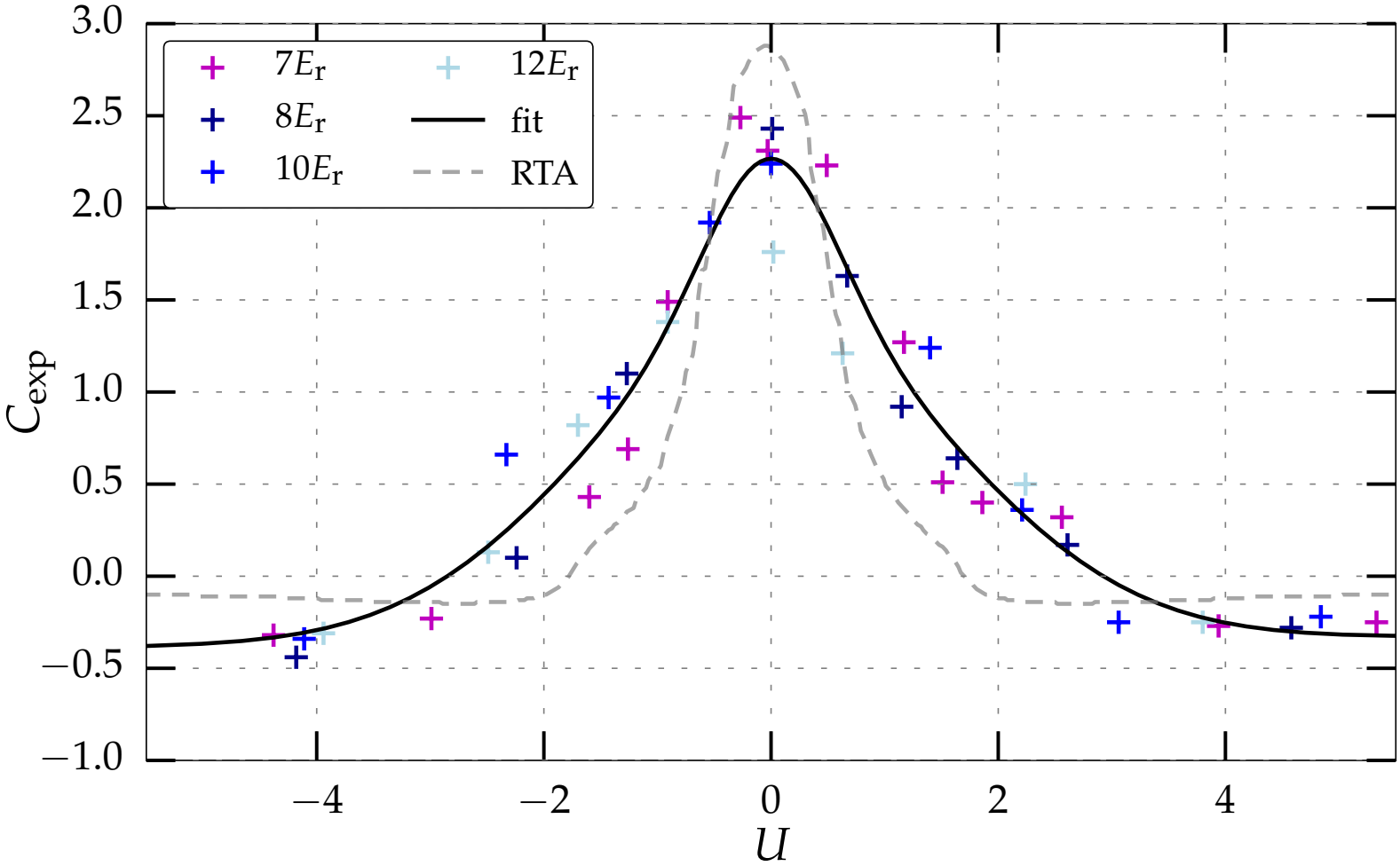
- 2D optical lattice, ca. 200 000 atoms
- atom-atom interaction strength tuned (via Feshbach resonance)
- $t<0$: confinement in trap center, doubly occupied lattice sites
- $t=0$: confinement rapidly removed ("quench"):
  system far from equilibrium $\Rightarrow$ start of diffusion, equilibration




- at strong coupling: center ("core") does not expand due to **doublon** formation

# Measured "Core expansion velocity"

- Measured HWHM of density distribution in Hubbard lattice[20]
- Strongly correlated fermions. Core "shrinks" for Hubbard-$|U| \gtrsim 3$




[20] U. Schneider *et al.*, Nature Physics **8**, 213-218 (2012)

# Theoretical model used by Schneider et al.[21]

Christian-Albrechts-Universität zu Kiel
Mathematisch-Naturwissenschaftliche Fakultät

**Semiclassical Boltzmann equation in relaxation time approximation**:

$$\partial_t f_{\mathbf{q}} + \mathbf{v}_{\mathbf{q}} \nabla_{\mathbf{r}} f_{\mathbf{q}} + \mathbf{F}(\mathbf{r}) \nabla_{\mathbf{q}} f_{\mathbf{q}} = -\frac{1}{\tau(\mathbf{n})} \left( f_{\mathbf{q}} - f^0_{\mathbf{q}}(\mathbf{n}) \right)$$

**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

$\Rightarrow$ **cannot describe ultrafast quantum dynamics of correlated fermions**

[21] U. Schneider *et al.*, Nature Physics **8**, 213-218 (2012)

# A challenge for quantum many-body dynamics...

Christian-Albrechts-Universität zu Kiel
Mathematisch-Naturwissenschaftliche Fakultät

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

*"Although the expansion can be modelled in 1D (...) using DMRG*[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.*"

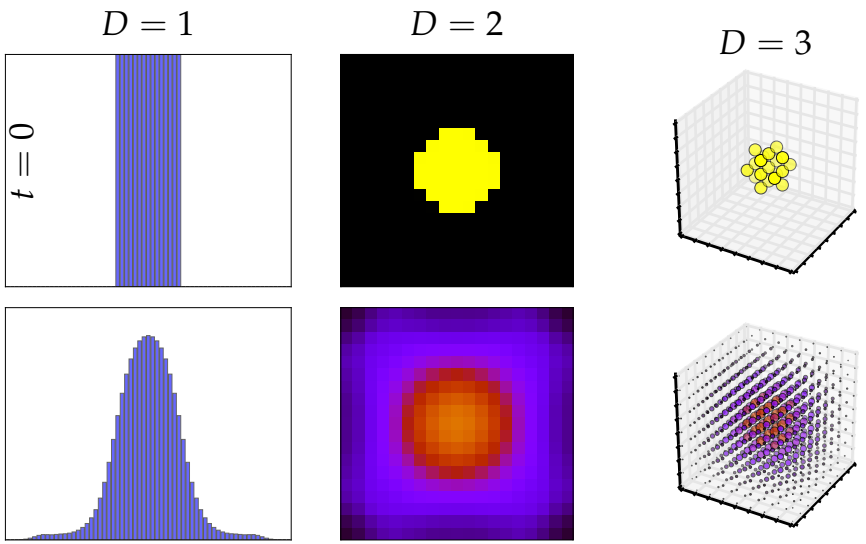
**Not exactly true...**[23].

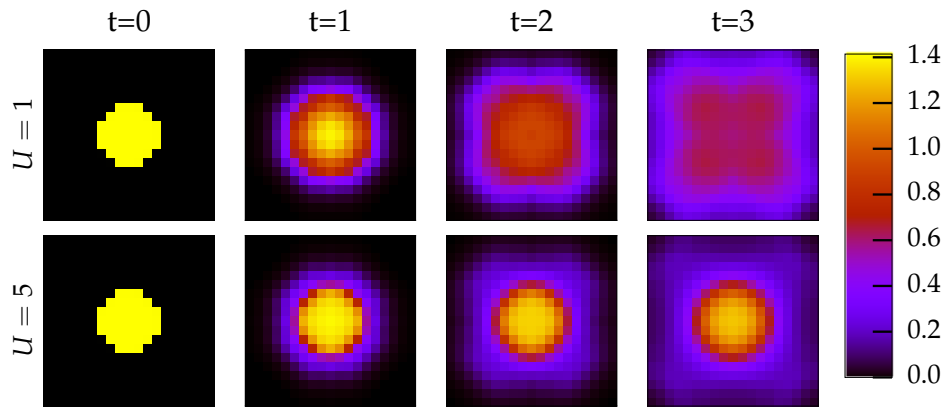
[22] Density Matrix Renormalization Group

[23] Nonequilibrium Green Functions (NEGF) exist for 50 years...

# Fermion expansion and doublon decay

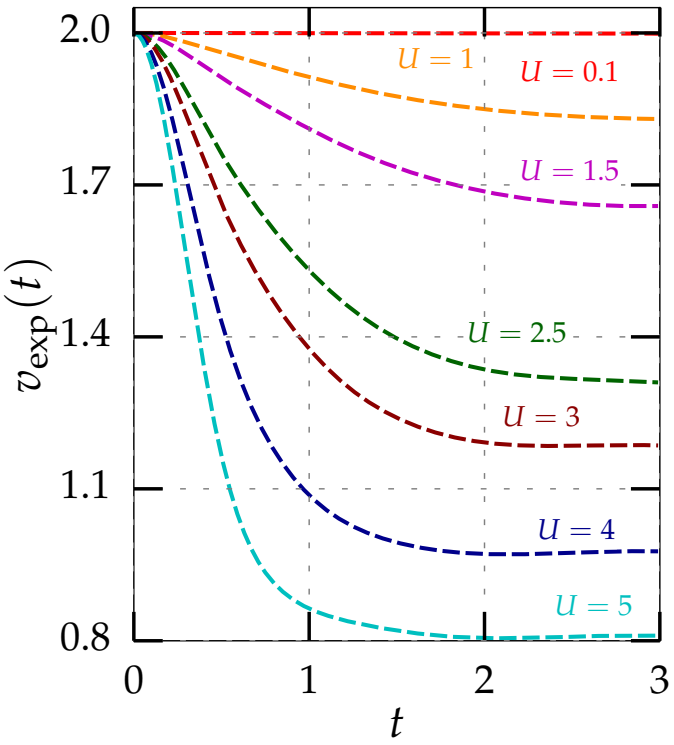
- $t = 0$: central array of doubly occupied sites.
- confinement quench initiates expansion.
- measured in cold atom experiments (Schneider *et al.*)
- expansion speed, dynamics time-dependent, depend on
  - dimensionality $D$, interaction strength $U$, particle number $N$



# Time evolution of the expansion velocity[24]

Christian-Albrechts-Universität zu Kiel
Mathematisch-Naturwissenschaftliche Fakultät




## Diffusion quantities

- **mean squared displacement**

$$R^2(t) = \frac{1}{N} \sum_{\boldsymbol{s}} n_{\boldsymbol{s}}(t) [\boldsymbol{s} - \boldsymbol{s}_0]^2$$

  $\boldsymbol{s}_0$: center of the system

- rescaled cloud **diameter**
  $d(t) = \sqrt{R^2(t) - R^2(0)}$
- **expansion velocity** $v_{\mathrm{exp}}(t) = \frac{\mathrm{d}}{\mathrm{d}t} d(t)$
- **asymptotic expansion velocity**

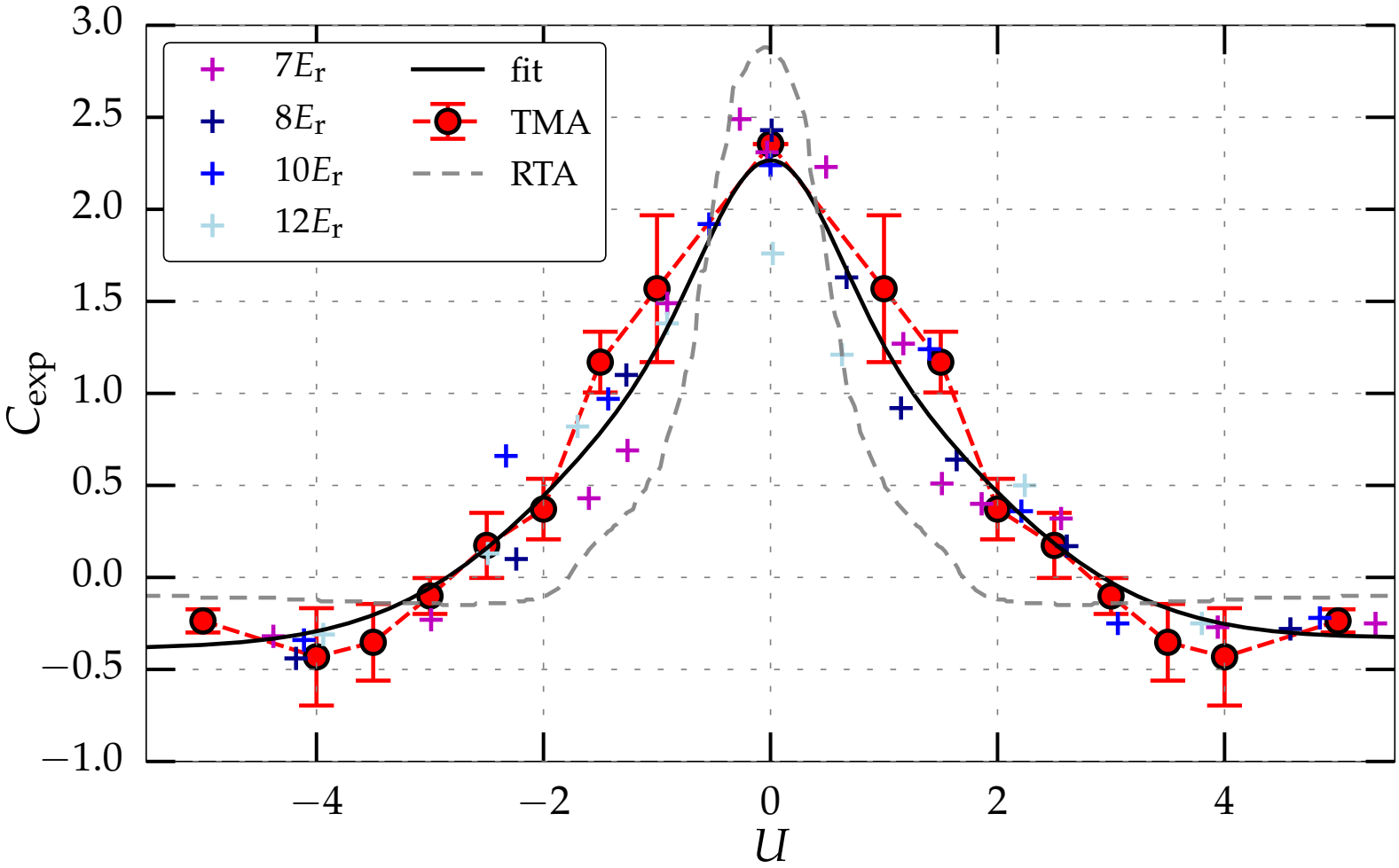
$$v_{\mathrm{exp}}^{\infty} = \lim_{t \to \infty} v_{\mathrm{exp}}(t)$$

- example: $N = 58$ doubly occupied sites in 2D
- perform extrapolation with respect to $N$
- similar procedure for "core expansion velocity" ($\sim$ FWHM)

[24] N. Schlünzen, S. Hermanns, M. Bonitz, and C. Verdozzi, Phys. Rev. B **93**, 035107 (2016)

# NEGF result[25] vs. experiment and RTA[26]

Christian-Albrechts-Universität zu Kiel
Mathematisch-Naturwissenschaftliche Fakultät




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

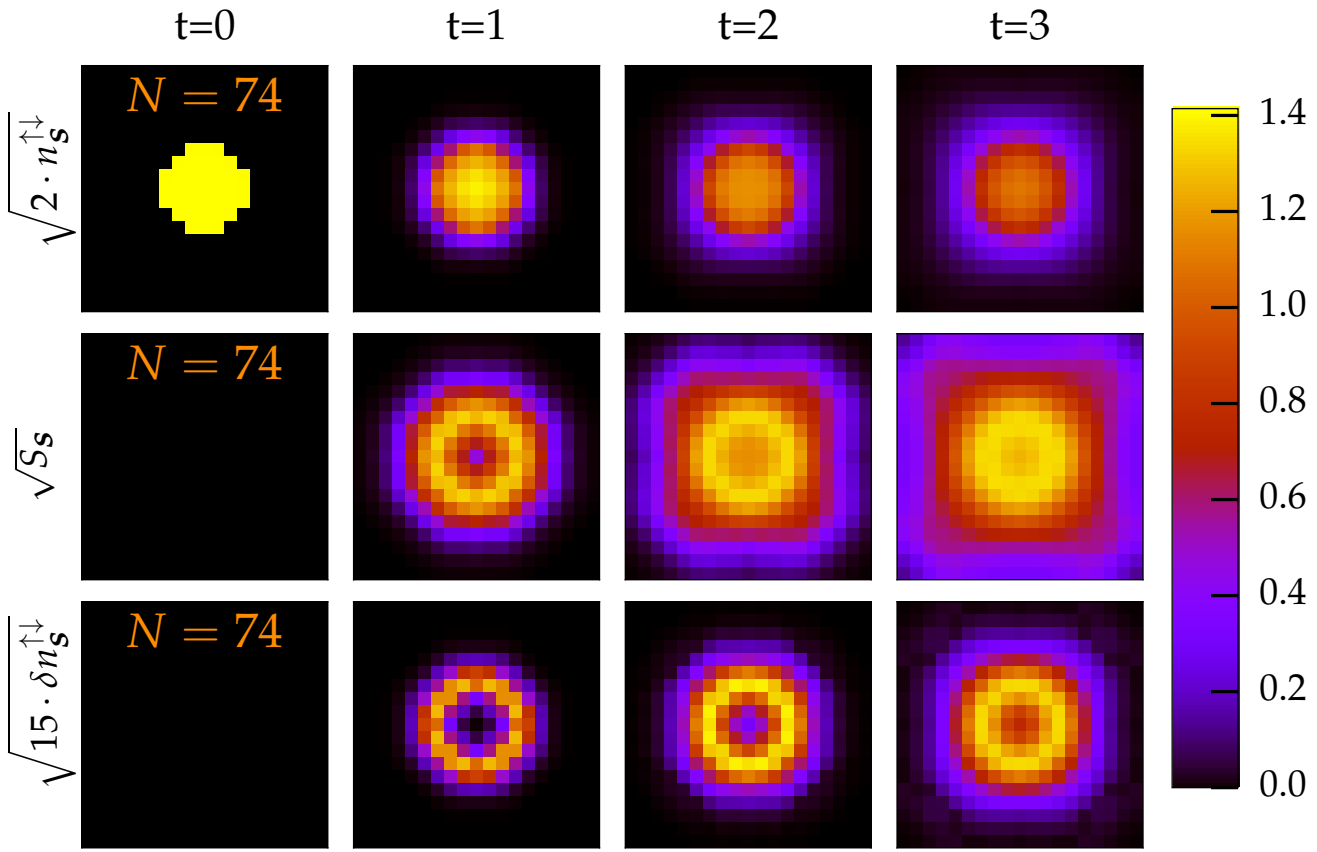
[25] 2-time T-matrix, N. Schlünzen, S. Hermanns, M. Bonitz, and C. Verdozzi, Phys. Rev. B **93**, 035107 (2016)

[26] U. Schneider *et al.*, Nature Physics **8**, 213-218 (2012)

# Site-resolved evolution of correlations

Christian-Albrechts-Universität zu Kiel
Mathematisch-Naturwissenschaftliche Fakultät

- double occupation $n_s^{\uparrow\downarrow}$
- local entanglement entropy $S_s$
- pair correlation function $\delta n_s^{\uparrow\downarrow} = n_s^{\uparrow\downarrow} - n_s^{\uparrow} n_s^{\downarrow}$




- insights into the early expansion phase
- measurable in quantum atom microscopes

# Outline

# Graphene Nanoribbons (GNRs)

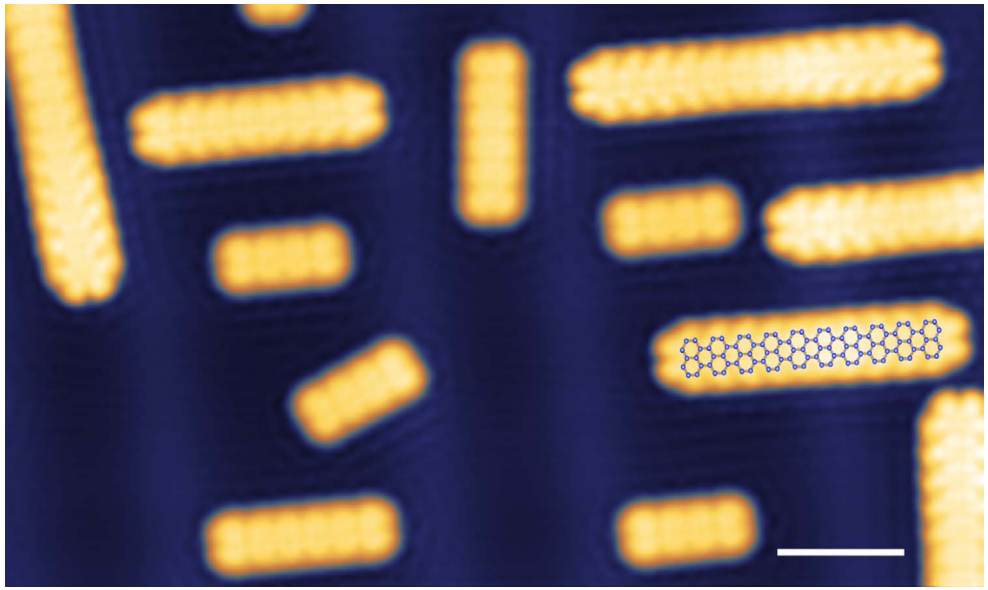
Christian-Albrechts-Universität zu Kiel
Mathematisch-Naturwissenschaftliche Fakultät

"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."

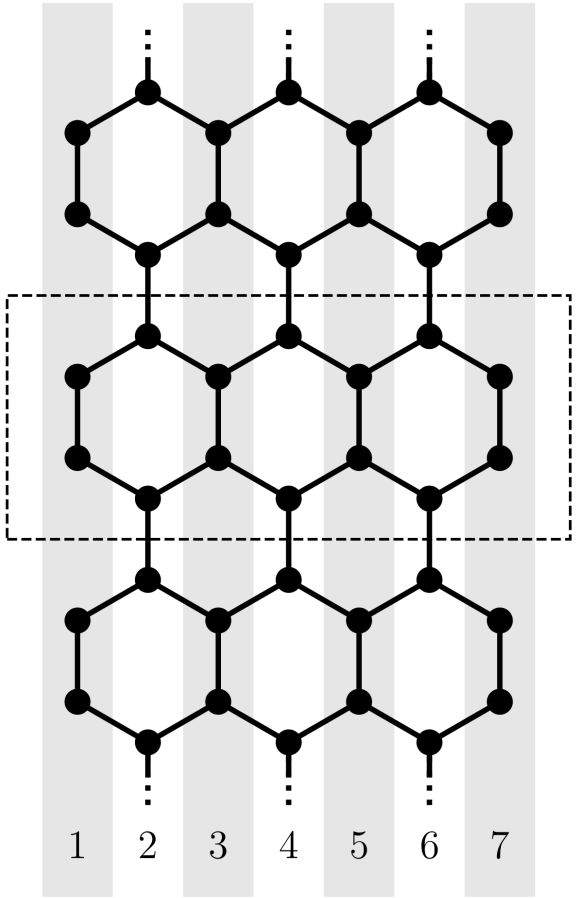
G. Soavi *et al.*, Nature Communications **7**, 2016

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

D. Neilson *et al.*, Journal of Physics: Conf. Series **702**, 2016

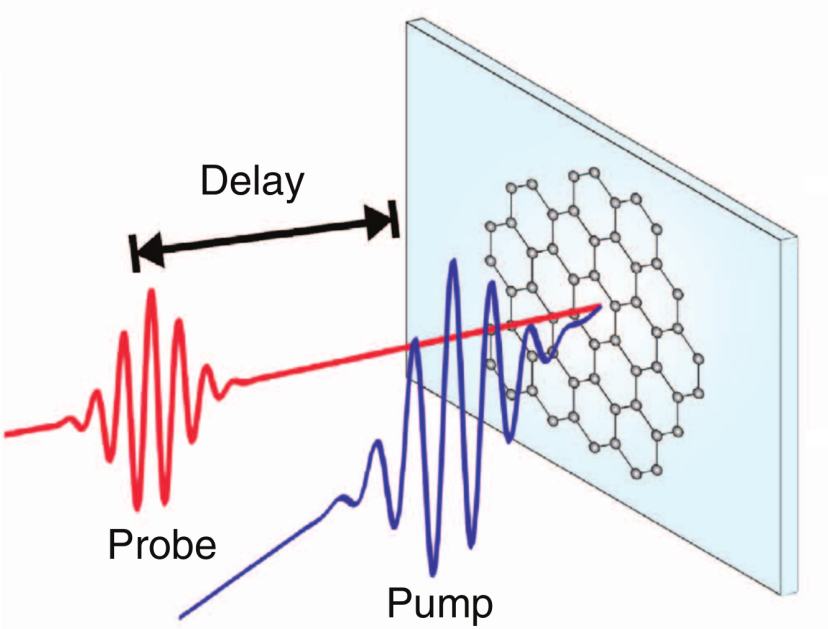


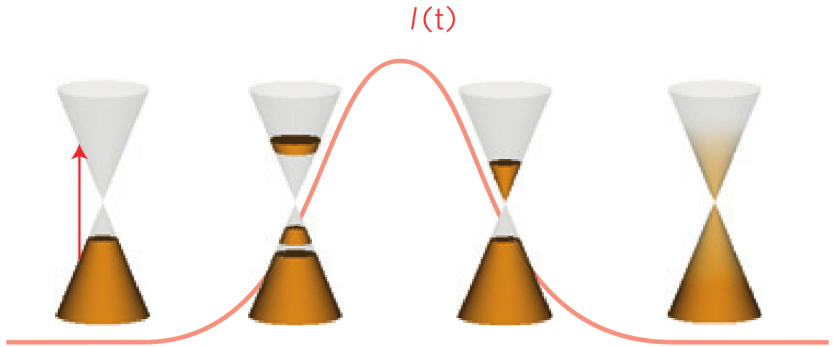
A. Kimouche *et al.*, Nature Communications **6**, 2015

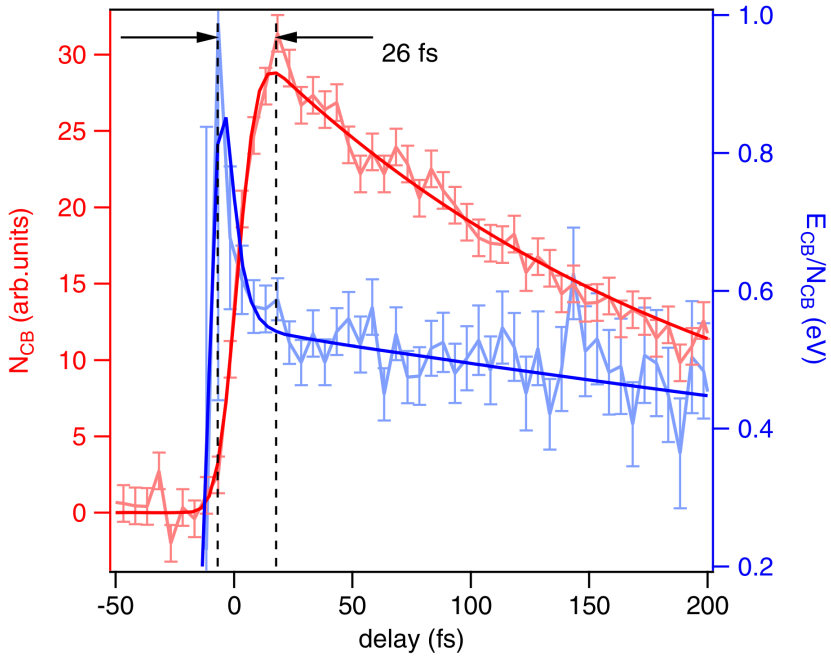


# Laser Excitation and Carrier Multiplication

Christian-Albrechts-Universität zu Kiel
Mathematisch-Naturwissenschaftliche Fakultät




- interesting e-e correlations effects: Auger processes, carrier multiplication (CM) *after pump*
- Number of conduction band electrons (red), energy per electron (blue)

I. Gierz, A. Cavalleri *et al.*, PRL **115**, 086803 (2015)

# 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: $H_L(t) = \sum_i -e\mathbf{E}_L(t)\mathbf{r}_i$

Christian-Albrechts-Universität zu Kiel
Mathematisch-Naturwissenschaftliche Fakultät

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

$$A_{\boldsymbol{ss}}(\omega) \quad = \quad \mathrm{i}\hbar \int \mathrm{d}t\, \mathrm{d}t'\, \mathrm{e}^{-\mathrm{i}\omega(t-t')} \left[G^{>}_{\boldsymbol{ss}}(t,t') - G^{<}_{\boldsymbol{ss}}(t,t')\right]$$

- Full **energy dispersion**

$$A(\omega, \boldsymbol{k}) \quad = \quad \frac{\mathrm{i}\hbar}{N_s} \sum_{\boldsymbol{ss'}} \mathrm{e}^{-\mathrm{i}\boldsymbol{k}(\boldsymbol{s}-\boldsymbol{s'})} \int \mathrm{d}t\, \mathrm{d}t'\, \mathrm{e}^{-\mathrm{i}\omega(t-t')} \left[G^{>}_{\boldsymbol{ss'}}(t,t') - G^{<}_{\boldsymbol{ss'}}(t,t')\right]$$

- Time resolved **photoemission spectrum**

$$A^{<}(\omega, T) \quad = \quad -\mathrm{i}\hbar \sum_{\boldsymbol{s}} \int \mathrm{d}t\, \mathrm{d}t'\, \mathcal{S}(t-T)\mathcal{S}(t'-T)\mathrm{e}^{-\mathrm{i}\omega(t-t')} G^{<}_{\boldsymbol{ss}}(t,t')$$

$$\mathcal{S}(t) \quad = \quad \frac{1}{\sigma\sqrt{2\pi}} \exp\left(-\frac{t^2}{2\sigma^2}\right) \qquad \longleftarrow \qquad \text{“probe pulse”}$$

M. Eckstein and M. Kollar, Phys. Rev. B **78**, 245113 (2008)
G. Stefanucci and R. v. Leeuwen, *Nonequilibrium many-body theory of quantum systems: a modern introduction*, Cambridge University Press, Cambridge, 2013

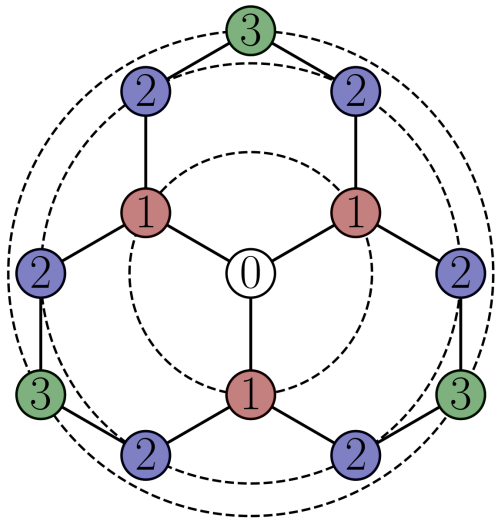
# Extended Hubbard Model

Christian-Albrechts-Universität zu Kiel
Mathematisch-Naturwissenschaftliche Fakultät

- $\hat{H}_{\text{kin}} = J \sum_{ss',\alpha} t_{ss'}\, \hat{c}^{\dagger}_{s\alpha} \hat{c}_{s'\alpha}$
- hopping up to 3rd nearest neighbor:

$$t_{ss'} = \begin{cases} t_1 \text{ if } (s,s') \text{ is 1NN} \\ t_2 \text{ if } (s,s') \text{ is 2NN} \\ t_3 \text{ if } (s,s') \text{ is 3NN} \\ 0 \text{ else} \end{cases}$$

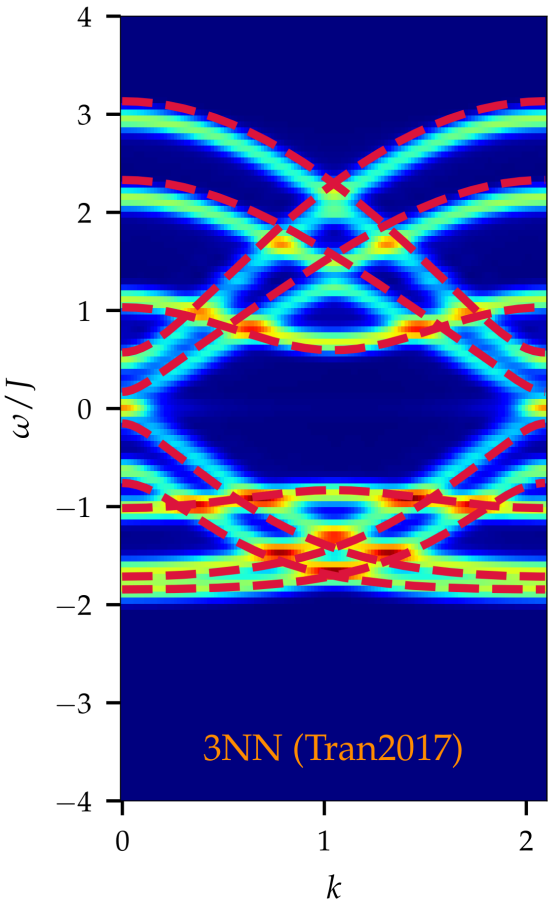
- orbital overlap included through overlap matrix $S$ : $H \to U^{\dagger} H U$ with $U = S^{-1/2}$ (Löwdin)

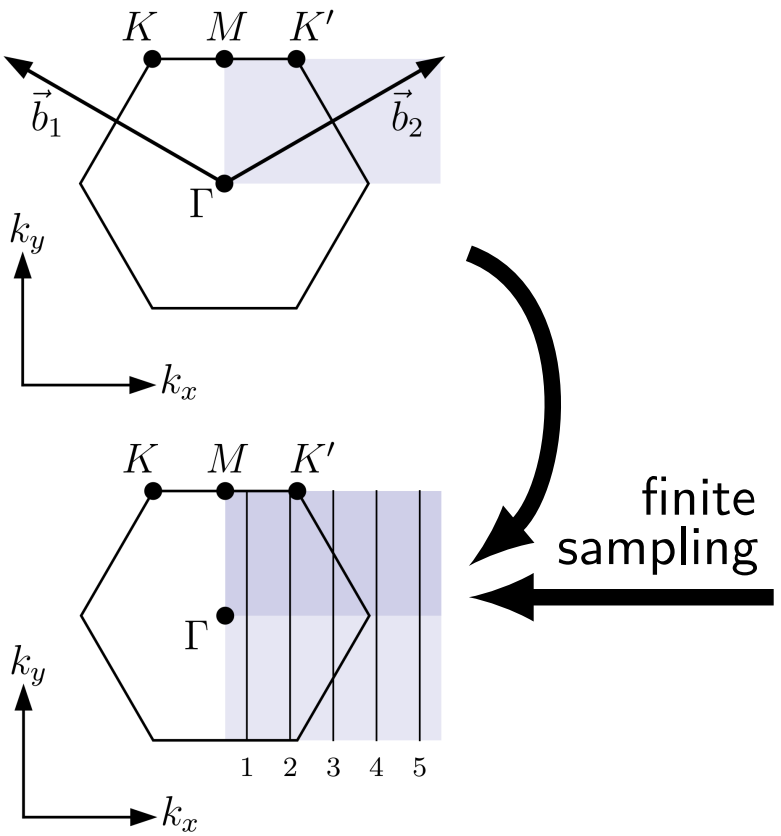


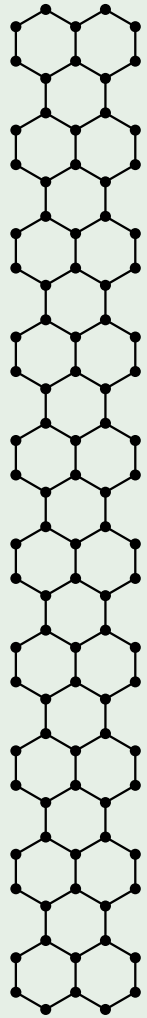

| Structure | Set | $J$/eV | $t_1/J$ | $t_2/J$ | $t_3/J$ | $s_1$ | $s_2$ | $s_3$ |
|---|---|---|---|---|---|---|---|---|
| 2D Graphene | 1NN | 2.7 | 1 | - | - | - | - | - |
| | 3NN (Reich2002) | 2.97 | 1 | 0.025 | 0.111 | 0.073 | 0.018 | 0.026 |
| Graphene ribbons | 3NN (Tran2017) | 2.756 | 1 | 0.026 | 0.138 | 0.093 | 0.079 | 0.070 |

# Ground State Results for Graphene

Christian-Albrechts-Universität zu Kiel
Mathematisch-Naturwissenschaftliche Fakultät



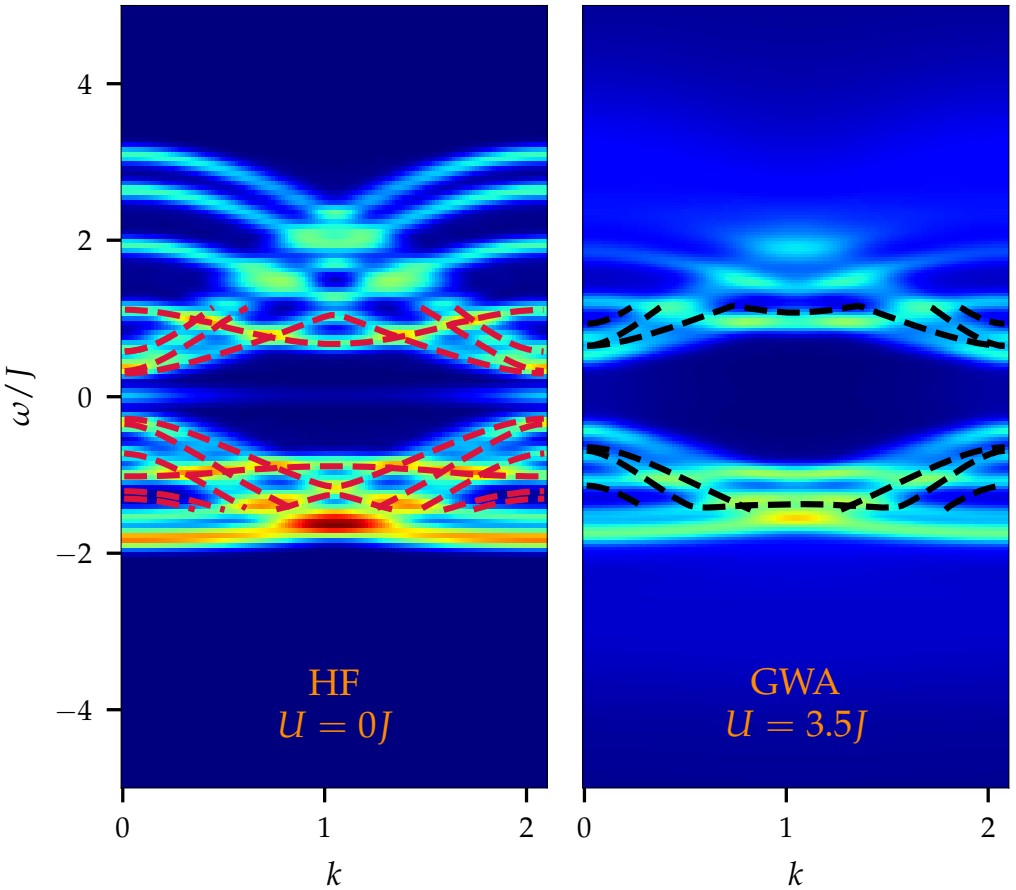
$N_s = 100$

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

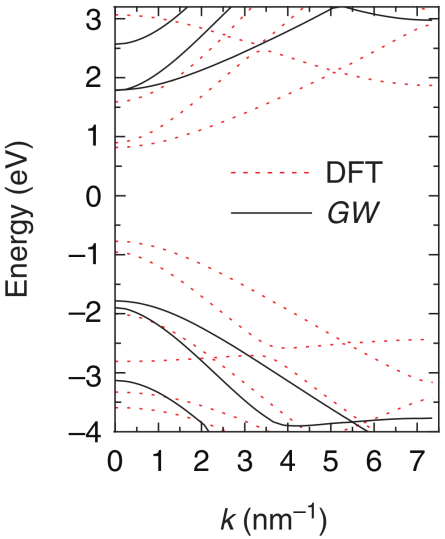
V.-T. Tran *et al.*, AIP Advances, **7**, 075212 (2017)

# Ground State Results for Graphene

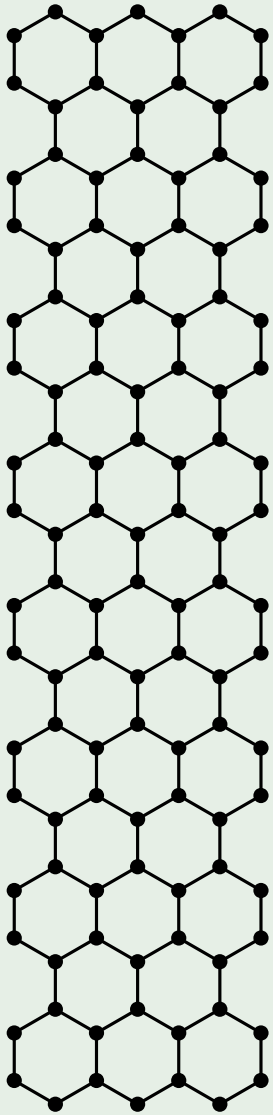
- comparison between NEGF (colormap) and DFT / GW (lines)




$J = 2.756\,\mathrm{eV}$




S. Wang *et al.*, Nat. Commun. **7**, 2016



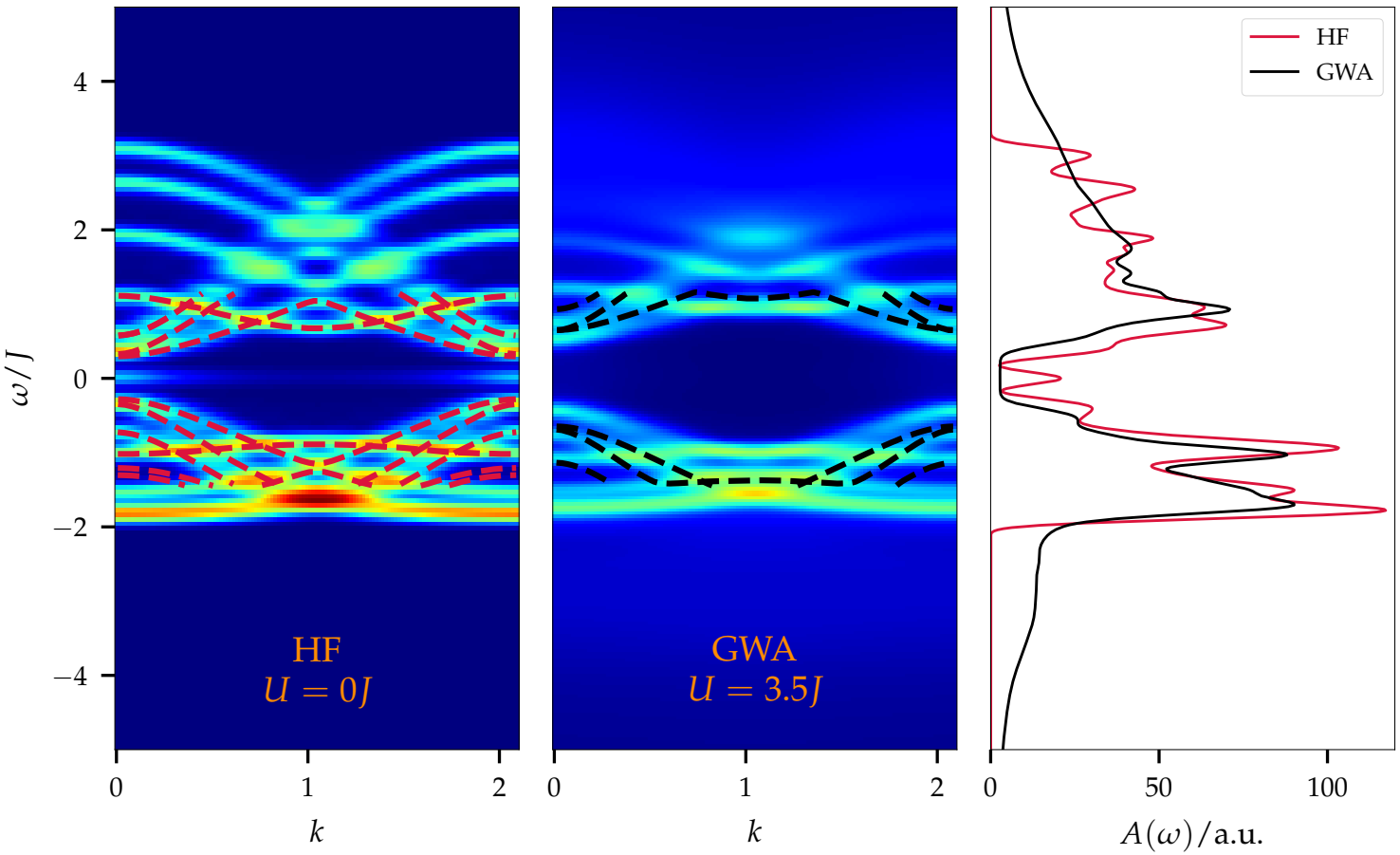
$N_s = 112$

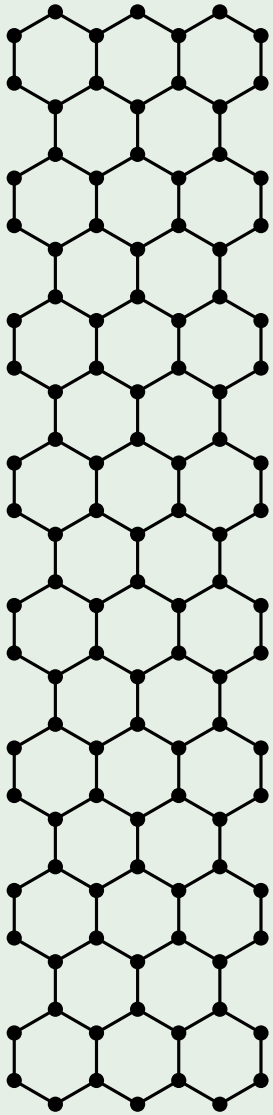
- it is well known that GW shows larger gap than DFT

# Ground State Results for Graphene

Christian-Albrechts-Universität zu Kiel
Mathematisch-Naturwissenschaftliche Fakultät

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

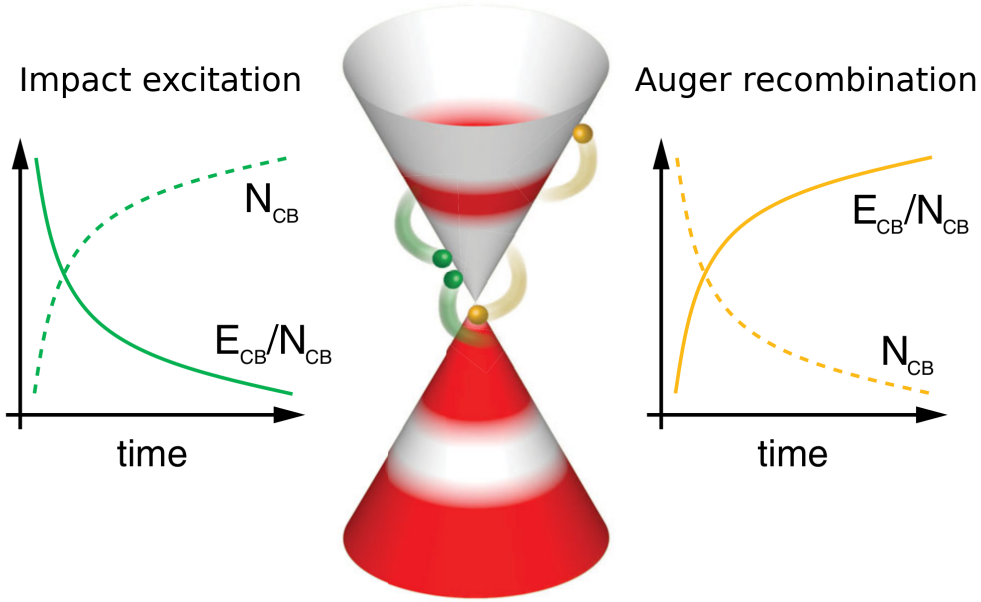



- gap opening can be reproduced with GWA and $U = 3.5J$

# Carrier Multiplication during laser excitation

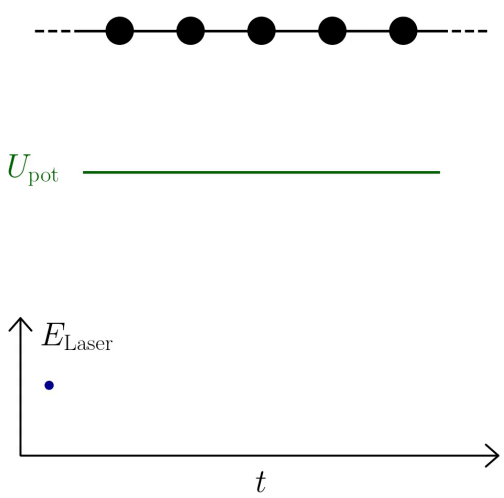
Christian-Albrechts-Universität zu Kiel
Mathematisch-Naturwissenschaftliche Fakultät




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

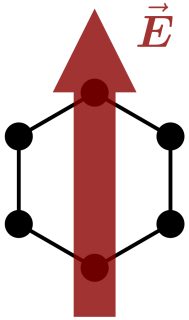
## Laser excitation

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

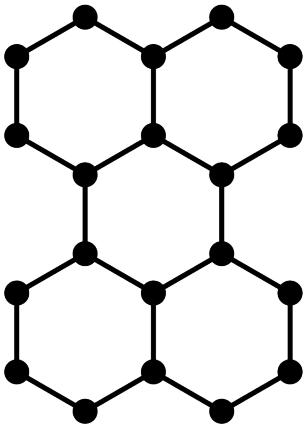


Christian-Albrechts-Universität zu Kiel
Mathematisch-Naturwissenschaftliche Fakultät

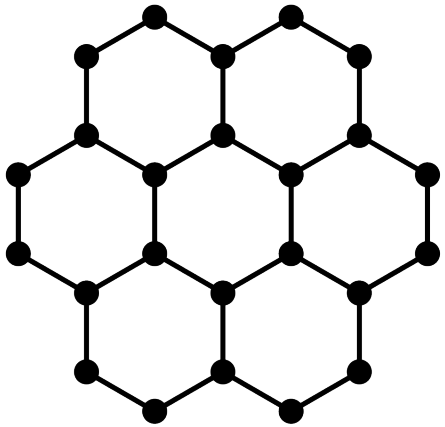
Polarization:



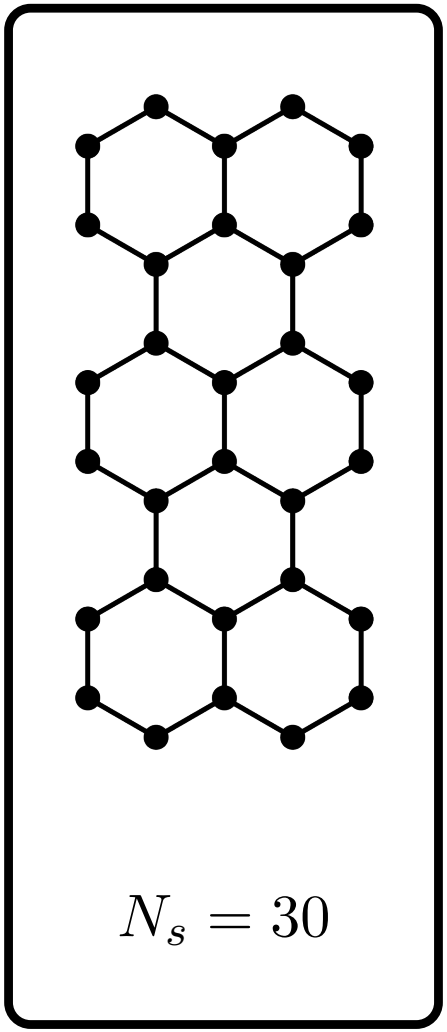

Selfenergy: SOA



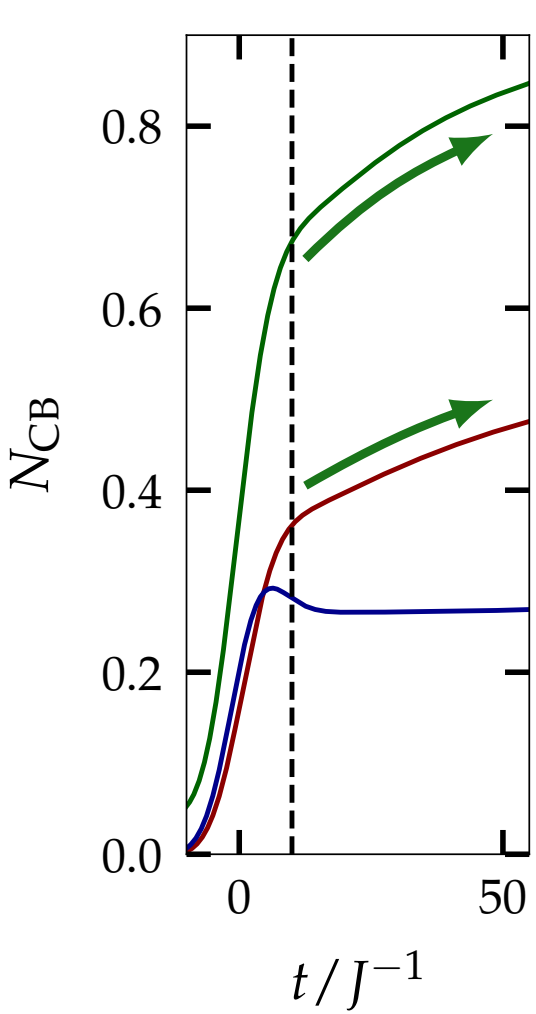
$N_s = 20$

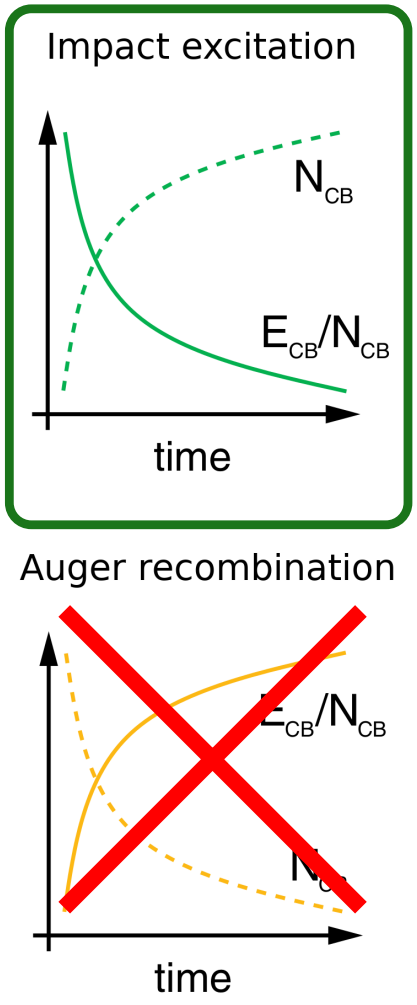


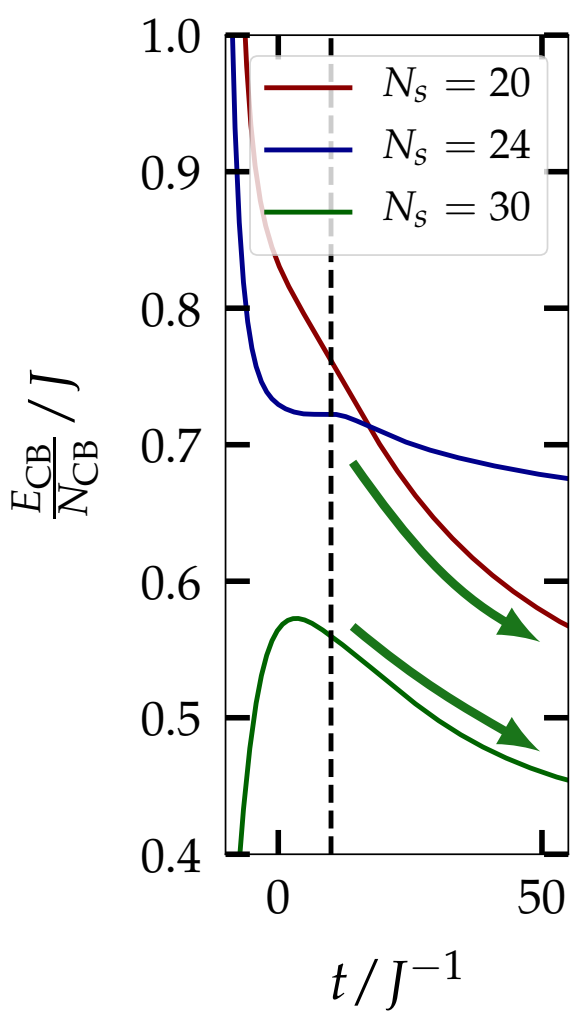
$N_s = 24$



$N_s = 30$

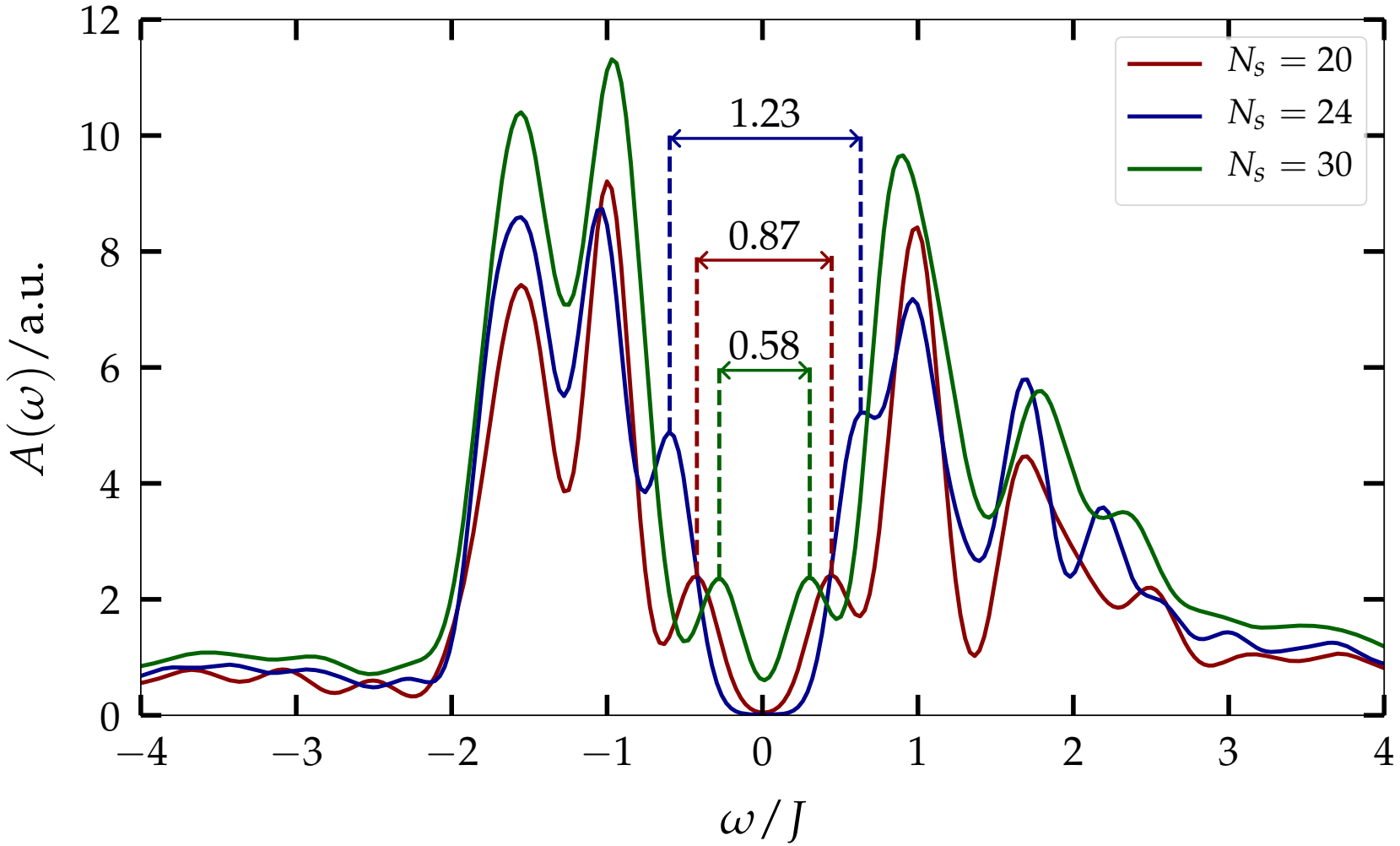



- conduction band density: $N_{\mathrm{CB}} = \int_0^\infty A^<(\omega)\,\mathrm{d}\omega$, energy: $E_{\mathrm{CB}} = \int_0^\infty \omega A^<(\omega)\,\mathrm{d}\omega$
- CB occupancy and energy show IE-like behavior, for $N_s = 20$ and $N_s = 30$

Christian-Albrechts-Universität zu Kiel
Mathematisch-Naturwissenschaftliche Fakultät

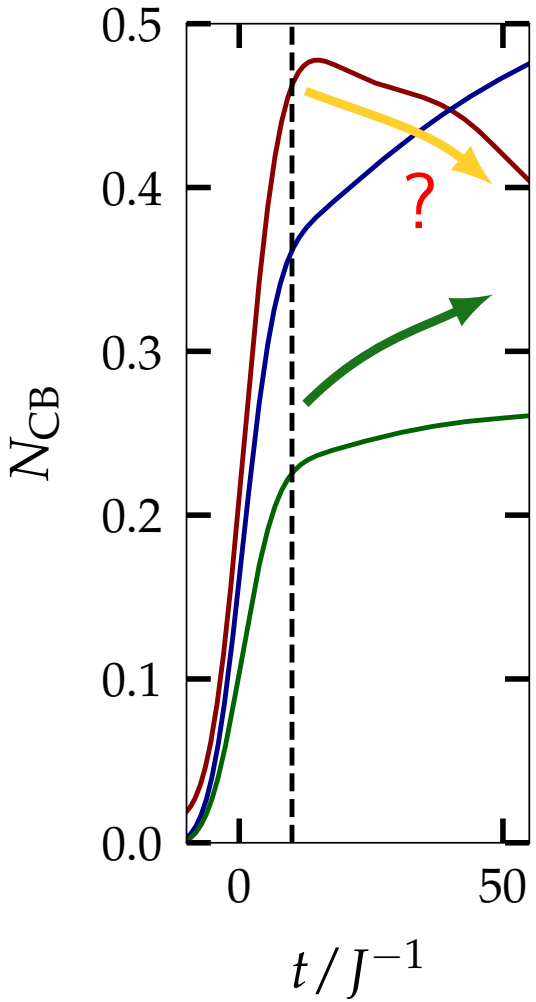


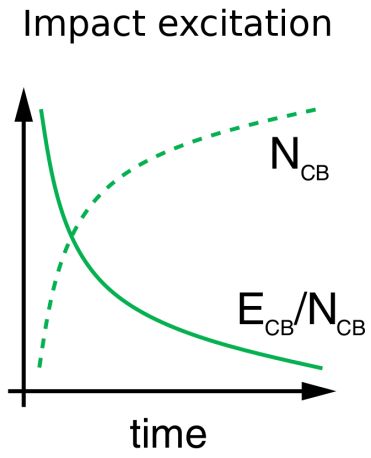

- $\omega_0 > 2E_{\text{gap}}$, for $N_s = 20$ and $N_s = 30$
- $\omega_0 < 2E_{\text{gap}}$, for $N_s = 24$

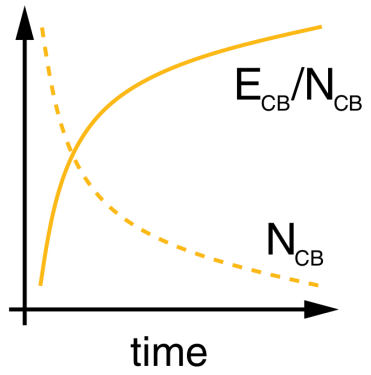
$\omega_0 = 1.85J$

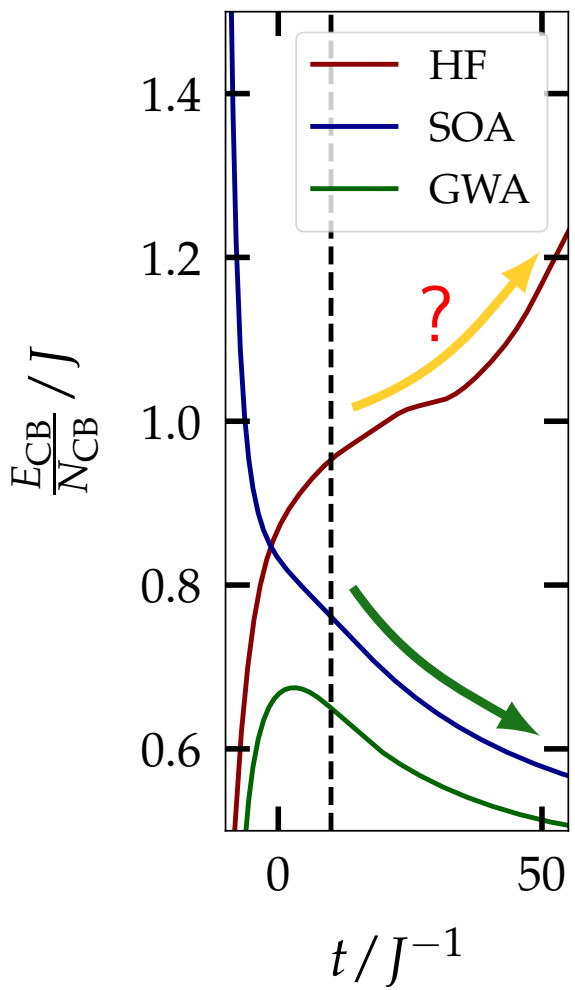
M.Gabor, Acc. Chem. Res., **46**, 1348–1357 (2013)

Christian-Albrechts-Universität zu Kiel
Mathematisch-Naturwissenschaftliche Fakultät



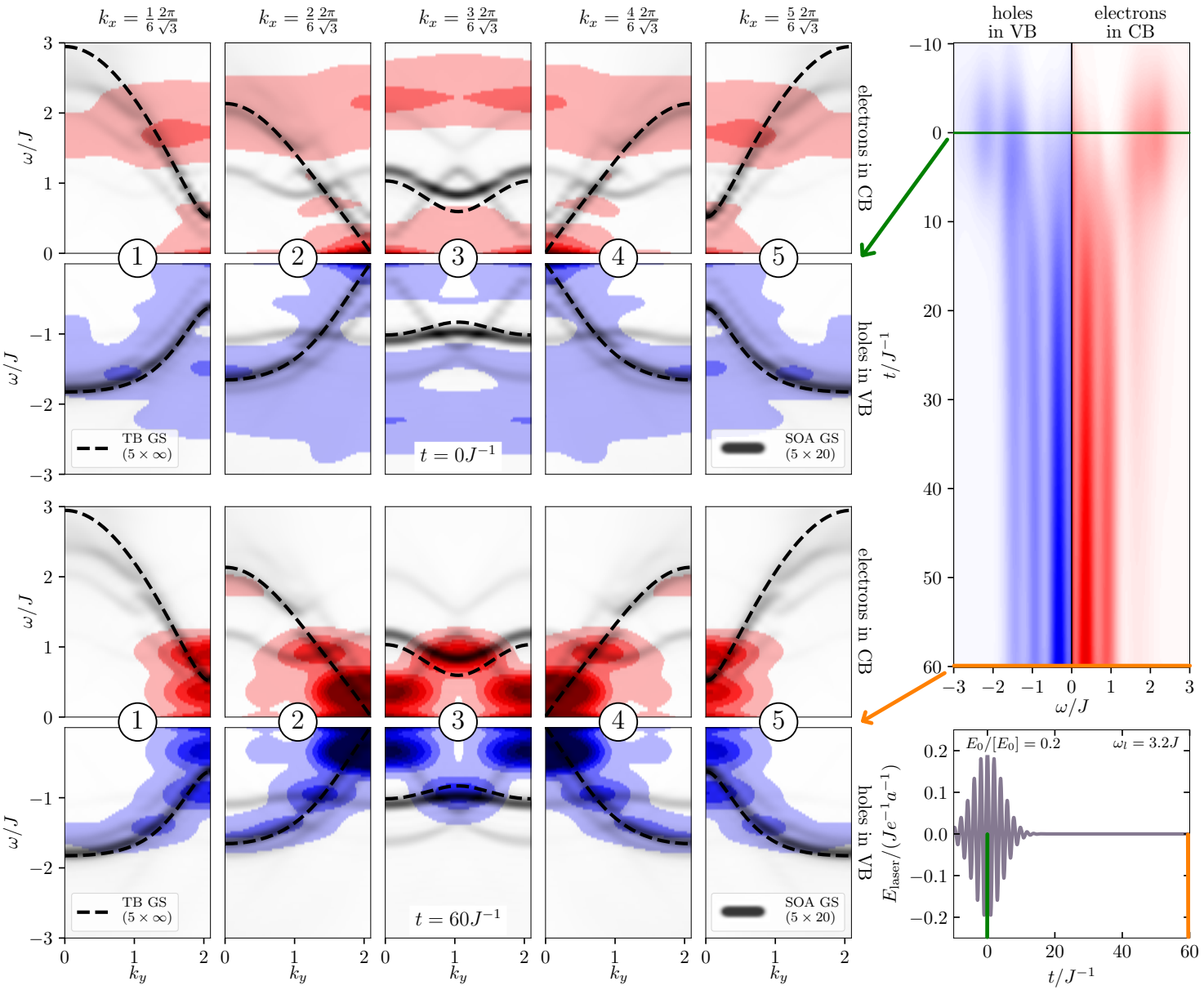




- SOA and GWA show same general trend (SOA: smaller gap $\rightarrow$ stronger excitation)
- HF shows opposite effect (recombination instead of excitation), Joost, Schlünzen, and MB, to be published

# 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

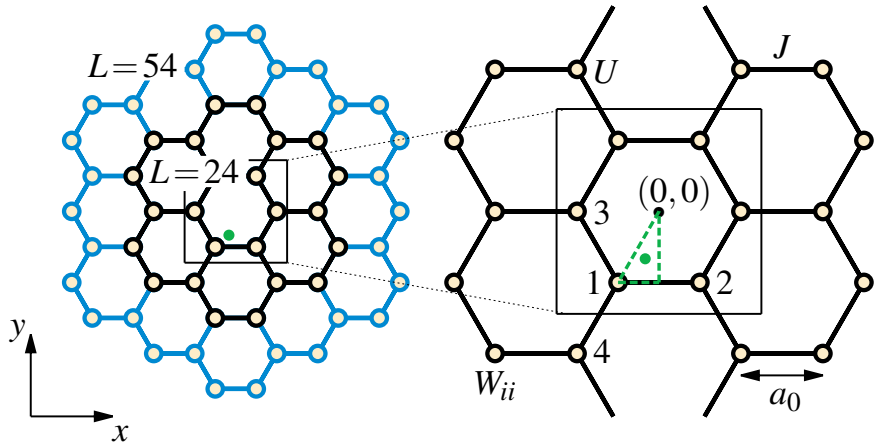


1. Nonequilibrium Green functions (NEGF) - Theory
   - Applications to atoms and molecules
   - Hubbard model. Strong correlations
   - Problems of NEGF dynamics: myth and reality
2. Comparison of NEGF to exact DMRG solutions
3. Testing NEGF against 2D cold atom experiments
4. Optical excitation of graphene nanoribbons
5. Ion stopping in correlated materials

# Ion stopping in strongly correlated materials[28]

Christian-Albrechts-Universität zu Kiel
Mathematisch-Naturwissenschaftliche Fakultät

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




$$H_{\mathrm{e}} = -J \sum_{\langle i,j\rangle,\sigma} c^\dagger_{i\sigma} c_{j\sigma} + U \sum_i (n_{i\uparrow} - \tfrac{1}{2})(n_{i\downarrow} - \tfrac{1}{2})$$
$$+ \sum_{i,\sigma} W_i(t) c^\dagger_{i\sigma} c_{i\sigma} \qquad \text{with} \qquad W_i(t) = -\frac{e^2}{4\pi\epsilon_0} \frac{Z_{\mathrm{p}}}{|\boldsymbol{r}_{\mathrm{p}}(t) - \boldsymbol{R}_i|}$$

- simple projectile (proton, $\alpha$), treated classically [$Z_p, \boldsymbol{r}_{\mathrm{p}}(t)$, Ehrenfest dynamics]
- parameters[27]: $a_0 = 1.42\,\text{Å}$, $J = 2.8\,\text{eV}$, $\boldsymbol{r}_{\mathrm{p}}(t)/a_0 = \{-1/6, -\sqrt{3}/3, -z(t)\}$

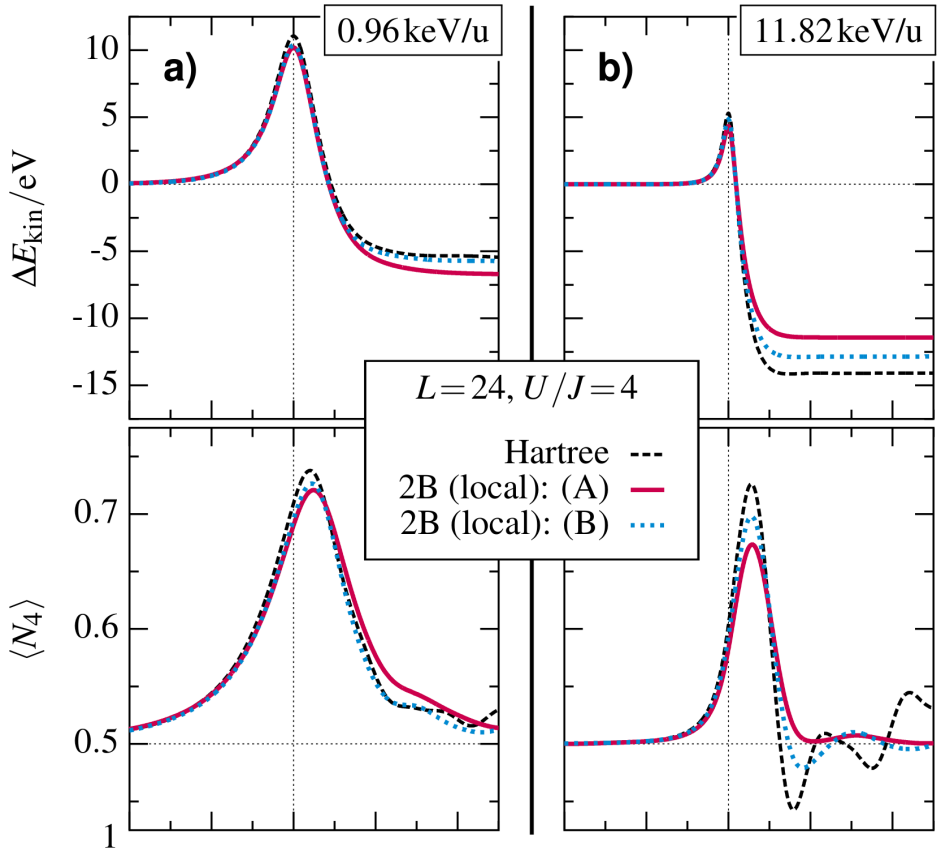
[27] TDDFT: Zhao *et al.*, J. Phys.: Cond.Matt. **27**, 025401 (2015)

[28] K. Balzer, N. Schlünzen, and M. Bonitz, Phys. Rev. B **94**, 245118 (2016)

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

Christian-Albrechts-Universität zu Kiel
Mathematisch-Naturwissenschaftliche Fakultät

- **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

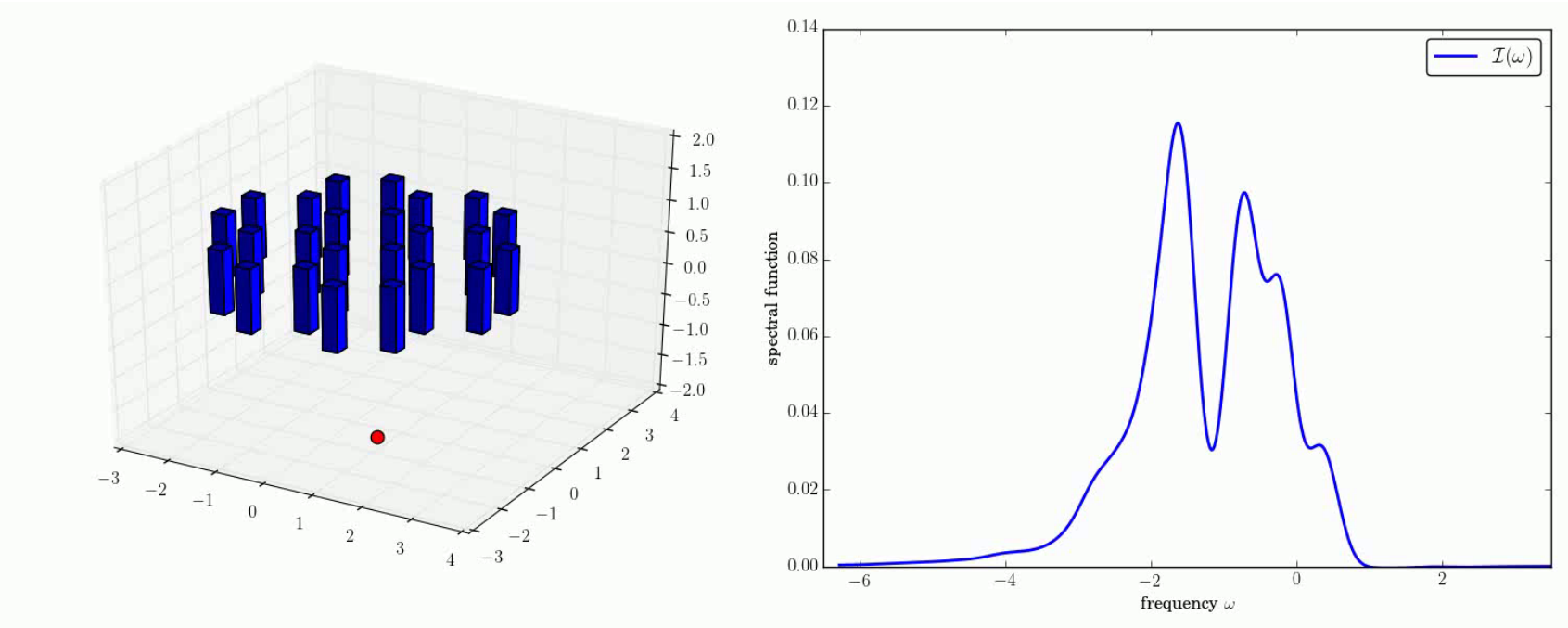
# Ion stopping: Photoemission spectrum

- NEGF description gives access to time-resolved photoemission spectra

$$\mathcal{I}_i(\omega, t_\mathsf{p}) = -\mathrm{i} \int \mathrm{d}t \int \mathrm{d}t'\, s(t - t_\mathsf{p}) s(t' - t_\mathsf{p}) e^{\mathrm{i}\omega(t-t')} G^<_{ii\sigma}(t, t')$$

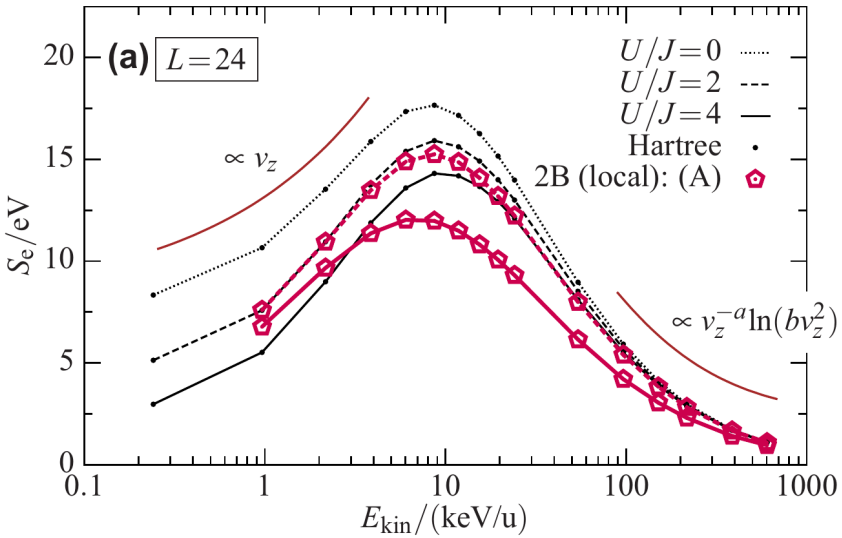
$$s(t) = \frac{1}{\tau\sqrt{2\pi}} e^{-t^2/(2\tau^2)}$$

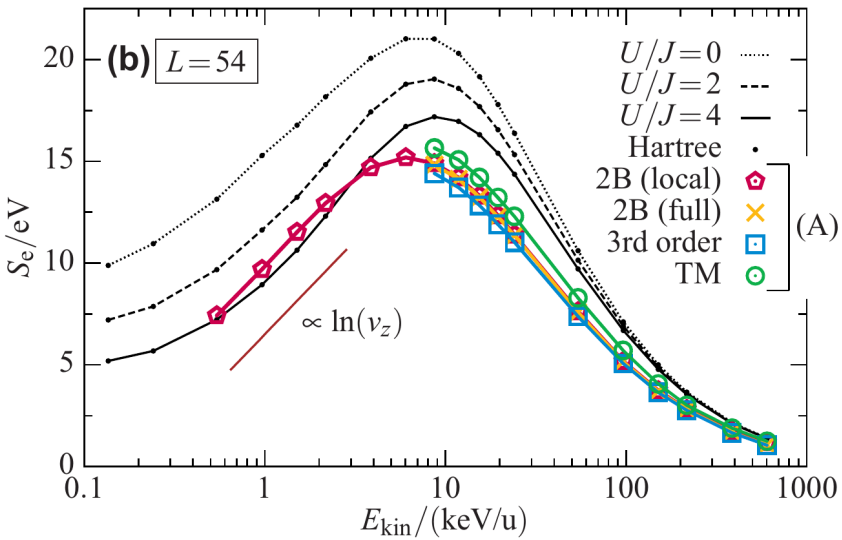
- energy loss of ion causes occupation of upper Hubbard band



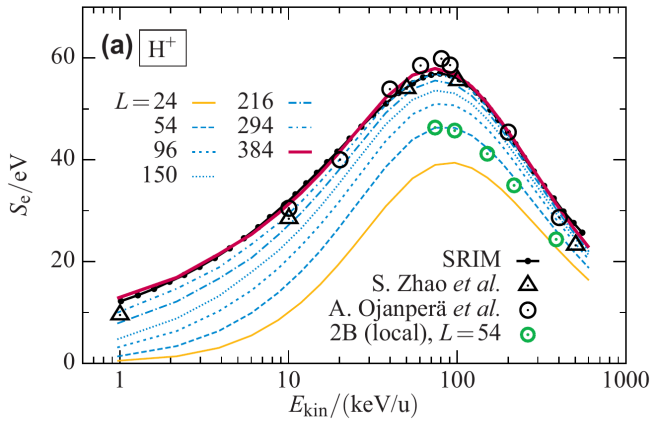
# Ion energy loss: performance of NEGF[29]

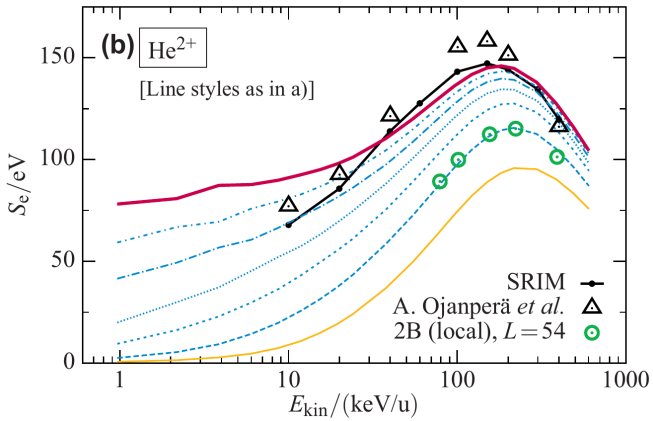
- Relevance of correlation effects




- Application to graphene



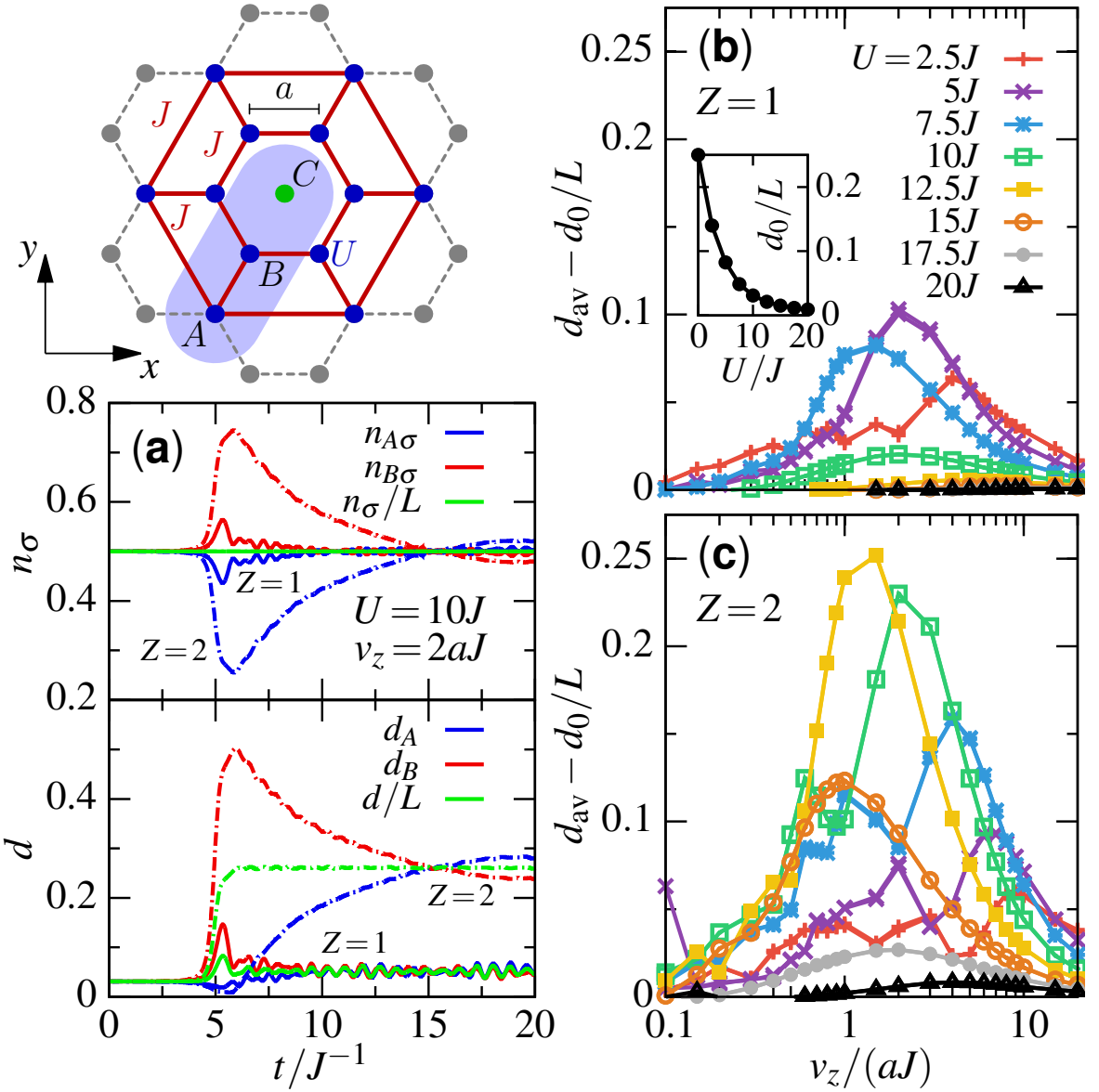

- modified hopping amplitude to account for influence on the electron mobility:
  $J_{\langle i,j\rangle}(t) = -J + \frac{\gamma}{2}\left(W_i(t) + W_j(t)\right)$
- parameters: $a_0 = 1.42\,\text{Å}$, $U/J = 1.6$, $J = 3.15\,\text{eV}$, $\gamma = 0.55$

[29] K. Balzer, N. Schlünzen, and M. Bonitz, Phys. Rev. B **94**, 245118 (2016)

# Doublon production due to ion stopping[30]

Christian-Albrechts-Universität zu Kiel
Mathematisch-Naturwissenschaftliche Fakultät

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




[30] K. Balzer, M. Rasmussen, N. Schlünzen, and M. Bonitz, submitted (2018), arXiv:1801.05267

# Doublon production: analytical model[31]

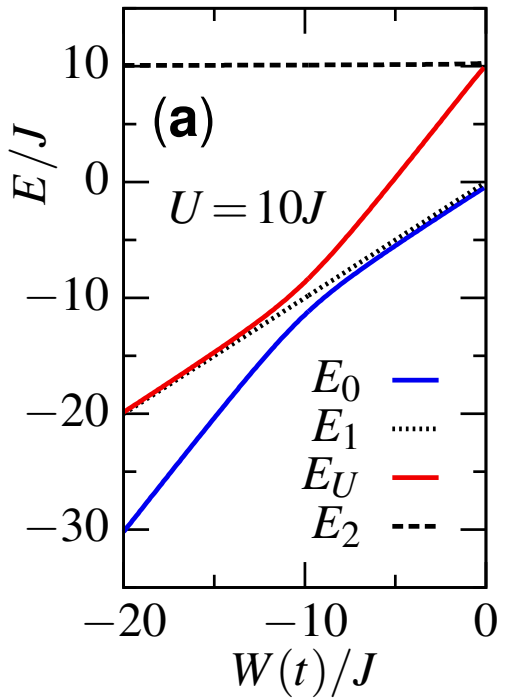
Christian-Albrechts-Universität zu Kiel
Mathematisch-Naturwissenschaftliche Fakultät

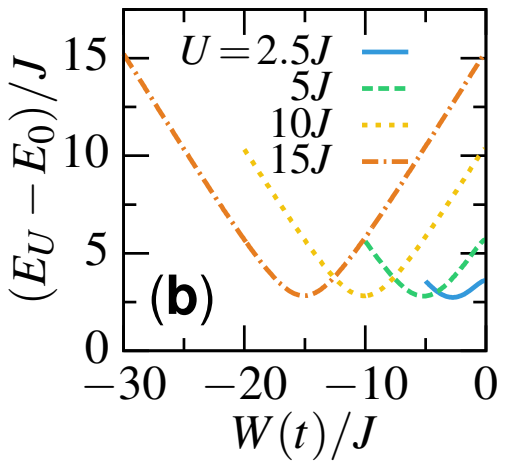
- Dimer model. t-dependent exact diagonalization, Gaussian model $W(t)$, width $\sigma \sim v$
- Doublon production probability (Landau-Zener model):

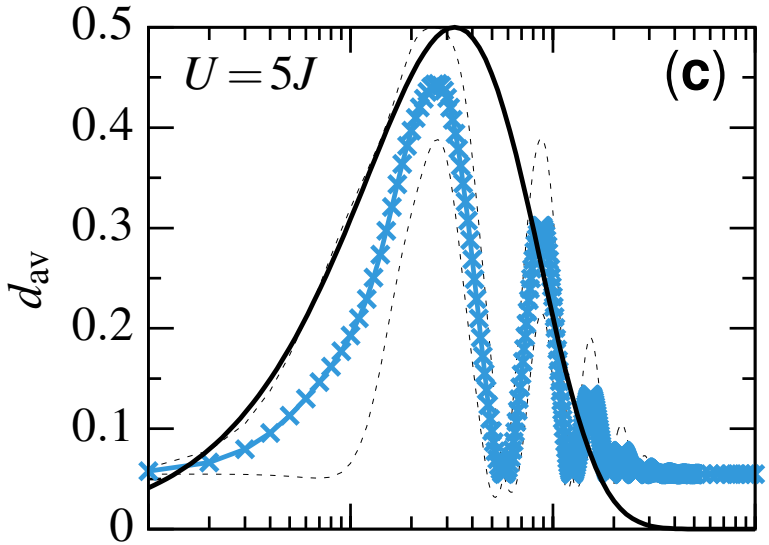
$$P_{E_0 \to E_U} = 2p(1-p)$$

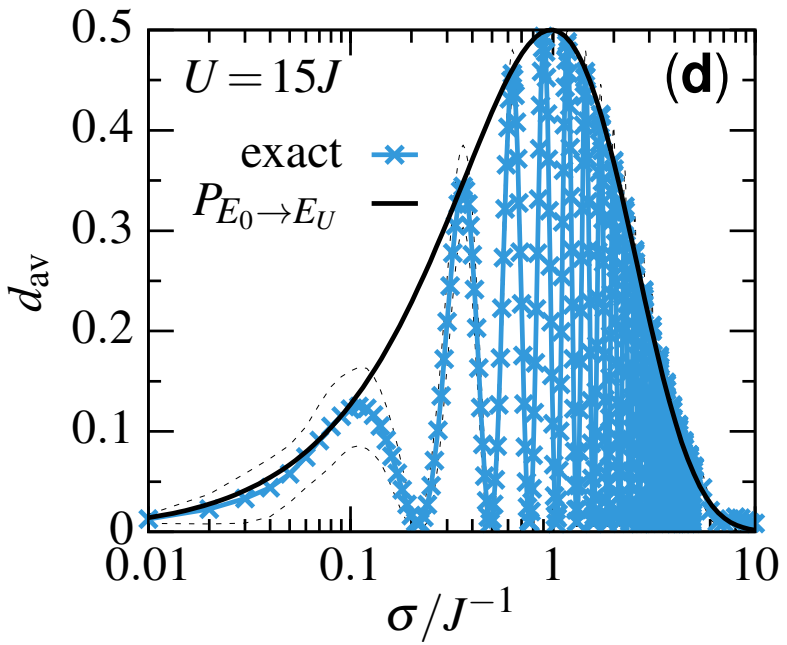
$$p = \exp\left(-\frac{2\pi V^2 \sqrt{e}\sigma}{W_0 E'}\right)$$

$$E' = \frac{d(E_U - E_0)}{dW}$$



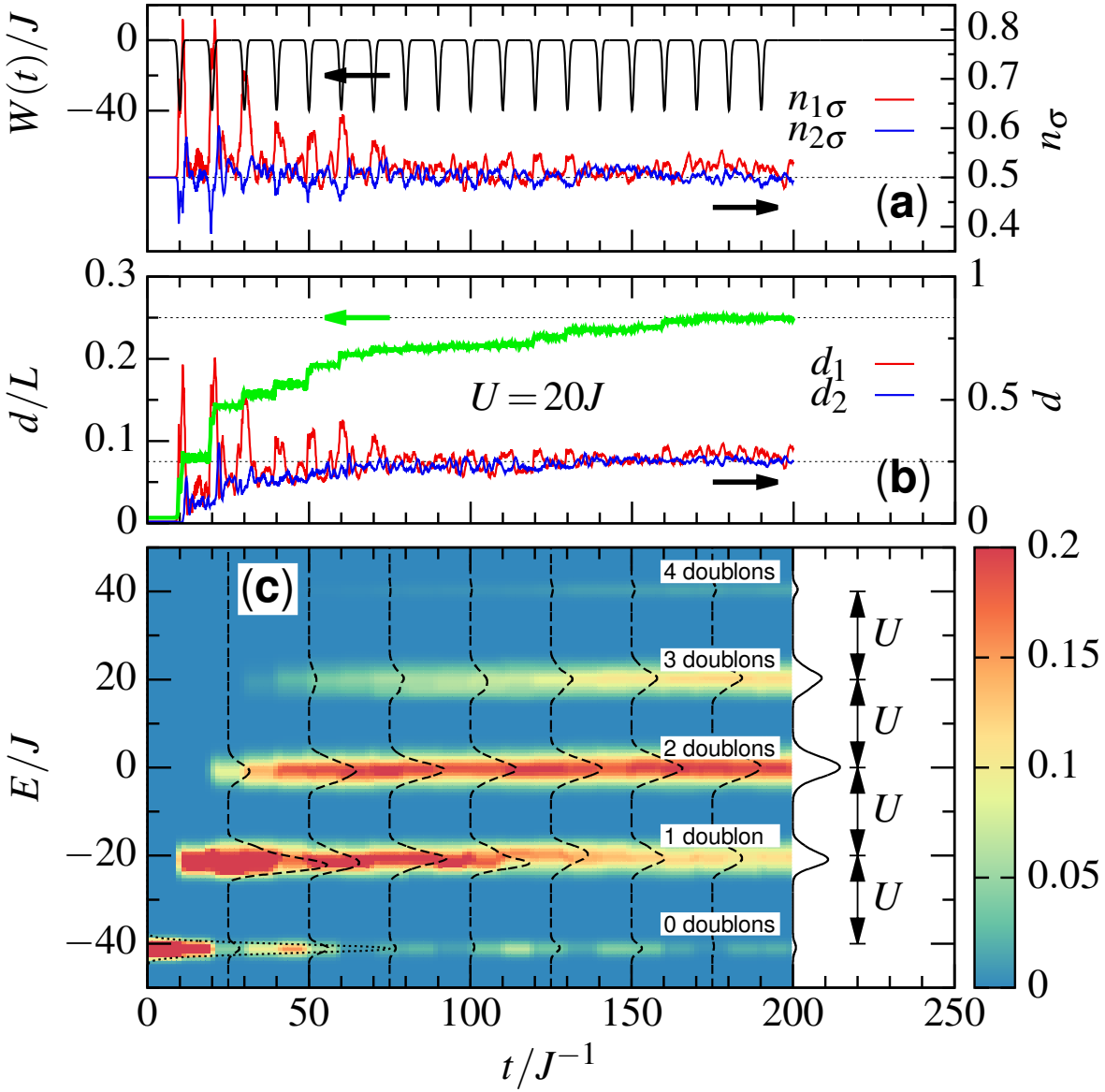




[31] K. Balzer, M. Rasmussen, N. Schlünzen, and M. Bonitz, submitted (2018), arXiv:1801.05267

# Doublon production due to multiple ions [32]

Christian-Albrechts-Universität zu Kiel
Mathematisch-Naturwissenschaftliche Fakultät

- 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




[32] K. Balzer, M. Rasmussen, N. Schlünzen, and M. Bonitz, submitted (2018), arXiv:1801.05267

# Conclusions[34]

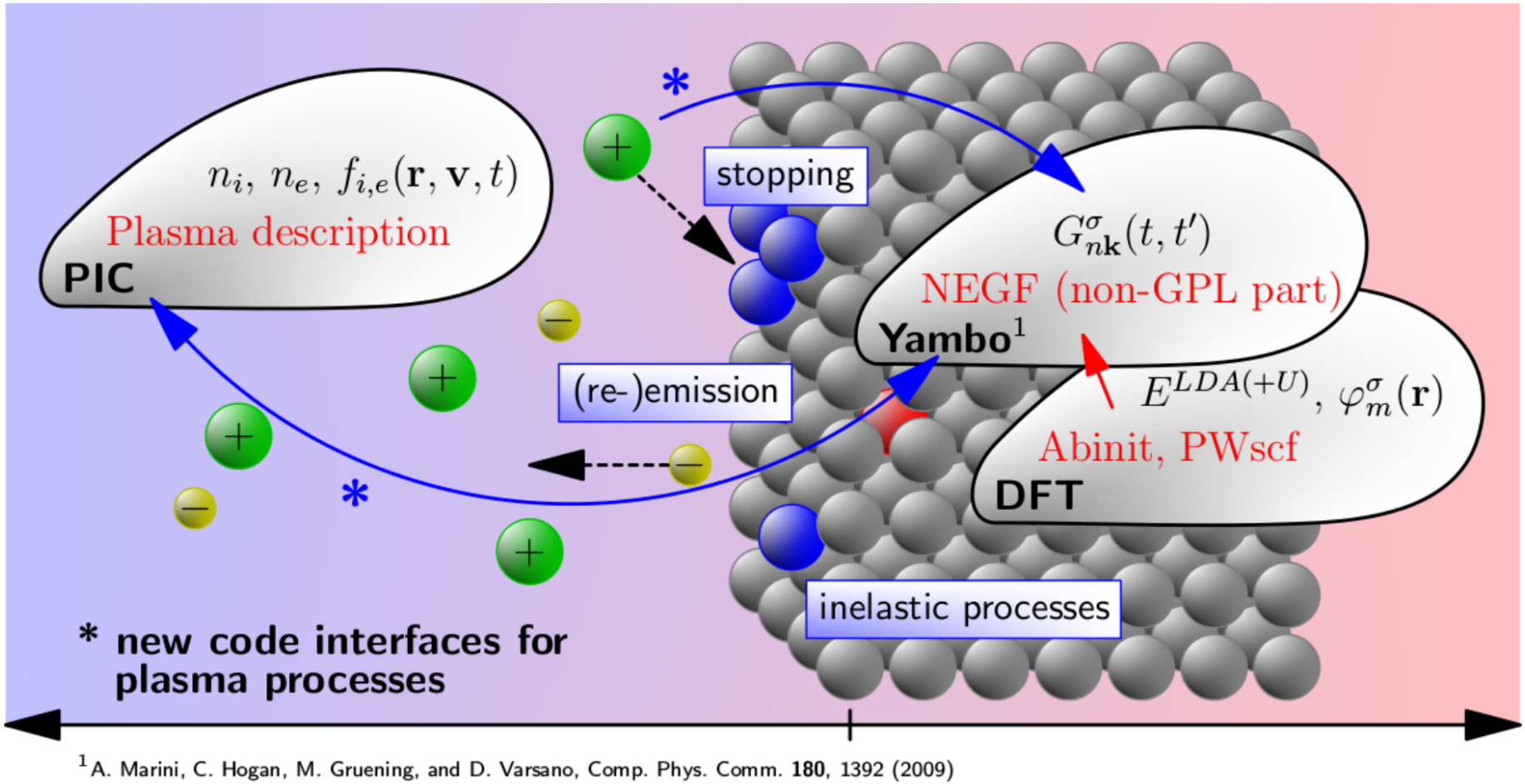


- **2D Graphene clusters, nanoribbons**: promising electronic and optical properties due to correlations: ion stopping, carrier multiplication, photon sidebands
- GNR will be accessible with intense light sources (ARPES)
- **NEGF** well suited to describe **nonequilibrium dynamics in correlated finite (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)

[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

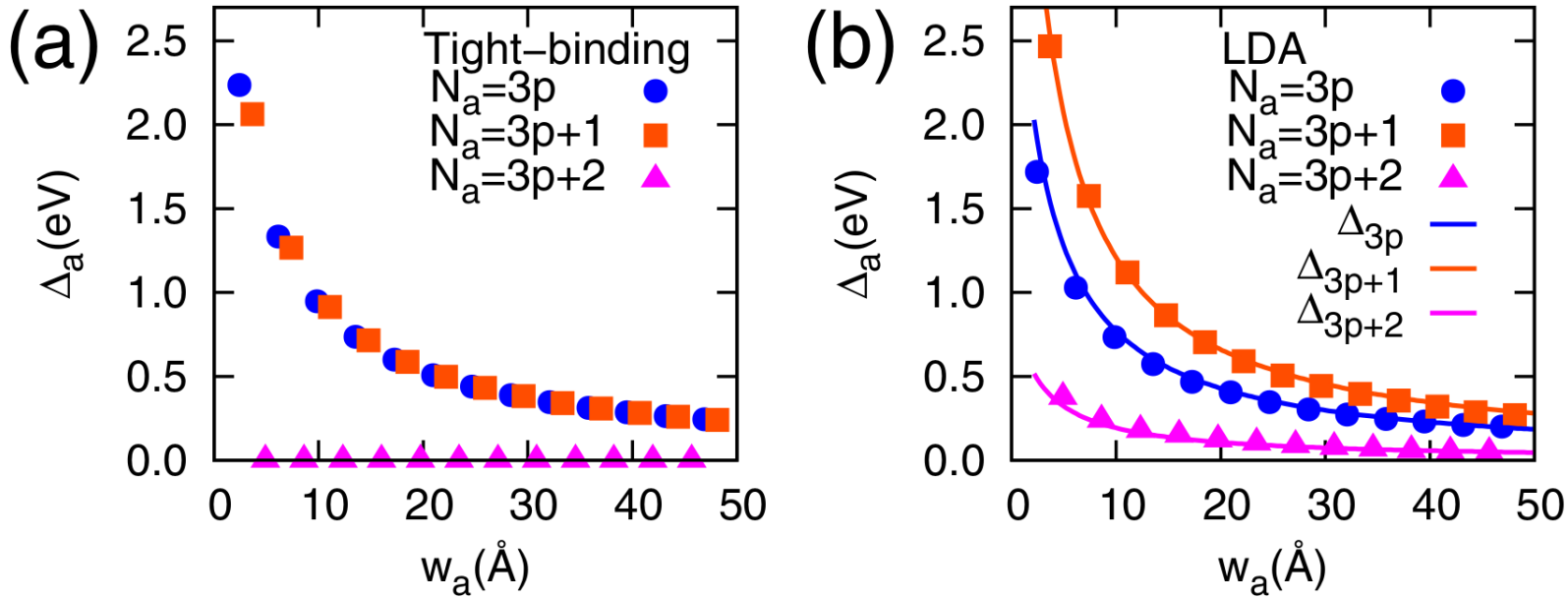



[1] A. Marini, C. Hogan, M. Gruening, and D. Varsano, Comp. Phys. Comm. **180**, 1392 (2009)

[28] e.g. Pedro Miguel M. C. de Melo and Andrea Marini Phys. Rev. B **93**, 155102 (2016)

# Band gap vs. width of AGNRs

Christian-Albrechts-Universität zu Kiel
Mathematisch-Naturwissenschaftliche Fakultät




- 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 $\sim N_a^{-1}$

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