Green functions simulation of the energy and charge transfer between highly charged ions and 2D materials

Michael Bonitz, Karsten Balzer, Hannes Ohldag, Jan-Philip Joost

Institute for Theoretical Physics and Astrophysics, Kiel University
in collaboration with Anna Niggas and Richard Arthur Wilhelm, TU Vienna

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pdf at http://www.theo-physik.uni-kiel.de/bonitz/talks.html

Ultrafast, strong and local excitation of quantum materials[1]

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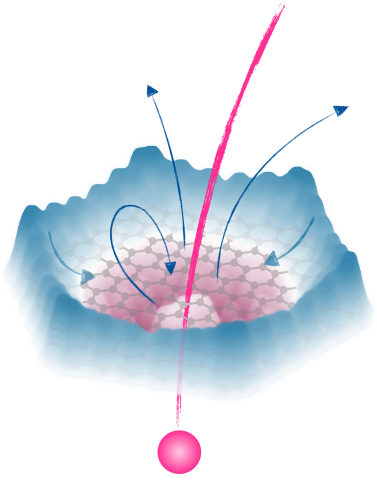
- Experiments with highly charged ions at TU Vienna (R. Wilhelm)
- Xe^{40+} ion penetrates monolayers of graphene and MoS_2
- ultrafast emission of slow electrons into vacuum: ca. 80 per ion, 6 times more electrons released from graphene $\Rightarrow$ sensitive local probe of electronic properties
- theoretical explanation?
  suitable approaches?



[1] A. Niggas *et al.*, Phys. Rev. Lett. **129**, 086802 (2022), Editors' Choice

Time-dependent Schrödinger equation. Scaling bottleneck

- time-dependent many-electron Hamiltonian

$$H(t) = \underbrace{\sum_{i=1}^{N} h(\boldsymbol{r}_i, t)}_{\text{one-body operators}} + \underbrace{\frac{1}{2}\sum_{i\neq j}^{N} W(\boldsymbol{r}_i, \boldsymbol{r}_j)}_{\textbf{pair-wise} \text{ interactions}}$$

- time-dependent Schrödinger equation (TDSE)

$$i\partial_t \Psi(\boldsymbol{r}_i, \ldots, \boldsymbol{r}_N; t) = H(t)\Psi(\boldsymbol{r}_i, \ldots, \boldsymbol{r}_N; t) \quad \overset{\text{direct solution}}{\not\Longrightarrow} \quad \Psi(\boldsymbol{r}_i, \ldots, \boldsymbol{r}_N; t)$$

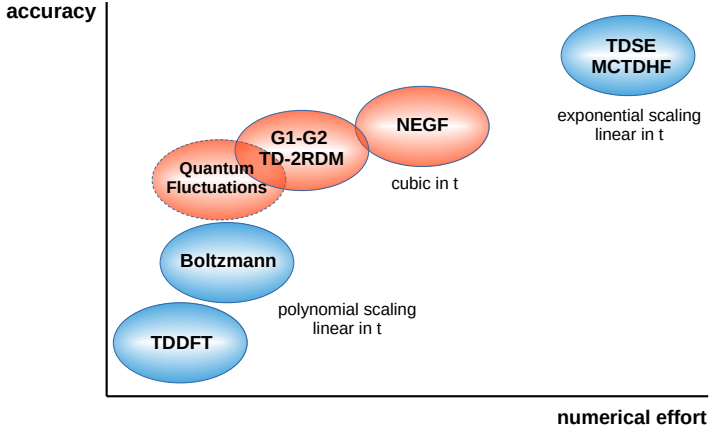
exponential scaling of numerical effort

- **solutions to overcome exponential scaling:**
  1. approximations to TDSE: TD-RASCI, TD-CASSCF, truncated CC, TD-R-matrix etc. D. Hochstuhl and M. Bonitz, PRA (2012) and EJP-ST (2014), embedding techniques
  2. propagation of simpler observables: density (TDDFT), distribution function (Kinetic theory), correlation functions etc.

Scaling of selected quantum many-body methods

NEGF: systematically captures electronic correlations, scattering, on all time scales
but: computationally expansive. Complementary to TDDFT

G1–G2 scheme: acceleration of NEGF, time-linear scaling



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2nd quantization

- Fock space $\mathcal{F} \ni |n_1, n_2 \ldots\rangle$, $\quad \mathcal{F} = \bigoplus_{N_0 \in \mathbb{N}} \mathcal{F}^{N_0}$, $\quad \mathcal{F}^{N_0} \subset \mathcal{H}^{N_0}$
- $\hat{c}_i$,$\hat{c}_i^\dagger$ creates/annihilates a particle in single-particle orbital ϕ_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

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

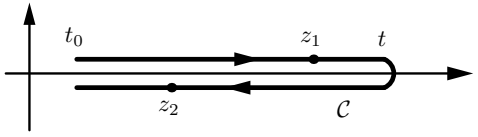
$$\boxed{G_{ij}(z,z') = \tfrac{\mathrm{i}}{\hbar}\left\langle \hat{T}_{\mathcal{C}} \hat{c}_i(z) \hat{c}_j^\dagger(z') \right\rangle}$$

average with $\hat{\rho}_N$

pure or mixed state

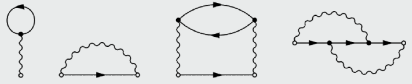
Keldysh–Kadanoff–Baym equations (KBE) on $\mathcal{C}$ (2×2 matrix):

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



KBE: first equation of Martin–Schwinger hierarchy for $G, G^{(2)} \ldots G^{(n)}$

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



Real-Time Keldysh–Kadanoff–Baym Equations (KBE)

- Correlation functions $G^{\gtrless}$ obey real-time KBE

$$\sum_l \left[\mathrm{i}\hbar\frac{\mathrm{d}}{\mathrm{d}t}\delta_{i,l} - h^{\mathsf{eff}}_{il}(t)\right] G^{>}_{lj}(t,t') = I^{(1),>}_{ij}(t,t')\,,$$

$$\sum_l G^{<}_{il}(t,t')\left[-\mathrm{i}\hbar\frac{\overleftarrow{\mathrm{d}}}{\mathrm{d}t'}\delta_{l,j} - h^{\mathsf{eff}}_{lj}(t')\right] = I^{(2),<}_{ij}(t,t')\,,$$

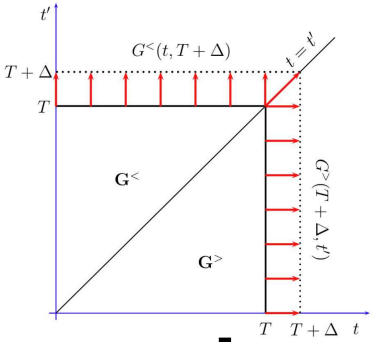
with the effective single-particle **Hartree–Fock Hamiltonian**

$$h^{\mathsf{eff}}_{ij}(t) = h^{0}_{ij} \pm \mathrm{i}\hbar\sum_{kl} w^{\pm}_{ikjl} G^{<}_{lk}(t)$$

and the collision integrals

$$I^{(1),>}_{ij}(t,t') \coloneqq \sum_l \int_{t_\mathsf{s}}^{\infty} \mathrm{d}\bar{t}\left\{\Sigma^{\mathsf{R}}_{il}(t,\bar{t})G^{>}_{lj}(\bar{t},t') + \Sigma^{>}_{il}(t,\bar{t})G^{\mathsf{A}}_{lj}(\bar{t},t')\right\},$$

$$I^{(2),<}_{ij}(t,t') \coloneqq \sum_l \int_{t_\mathsf{s}}^{\infty} \mathrm{d}\bar{t}\left\{G^{\mathsf{R}}_{il}(t,\bar{t})\Sigma^{<}_{lj}(\bar{t},t') + G^{<}_{il}(t,\bar{t})\Sigma^{\mathsf{A}}_{lj}(\bar{t},t')\right\}.$$



$$\mathcal{O}(N_\mathsf{t}^3)$$

- two-time structure contains spectral information
- numerically demanding due to cubic scaling with number of time steps N_t

Selfenergy Approximations[2]

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

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

GW: ∞ bubble summation, dynamical screening effects

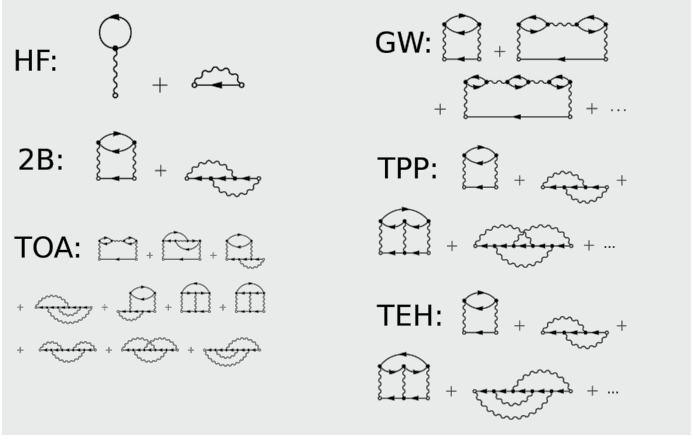
particle-particle T-matrix (TPP): ∞ ladder sum in pp channel

particle-hole T-matrix (TPH/TEH): ∞ ladder sum in ph channel

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

dynamically screened ladder (DSL)*: $\sim \mathrm{2B} + GW + \mathrm{TPP} + \mathrm{TPH}$

Choice depends on coupling strength, density (filling)

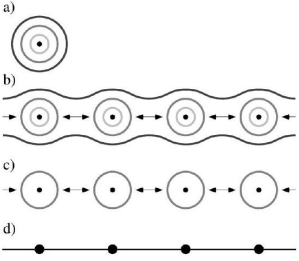


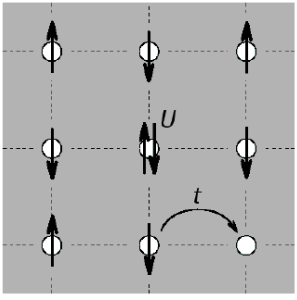
[2]Conserving approximations, nonequilibrium $\Sigma(t, t')$, applies for ultra-short to long times

Review: Schlünzen *et al.*, J. Phys. Cond. Matt. **32**, 103001 (2020); *Joost *et al.*, PRB (2022)

Testing various selfenergies: the Hubbard model

- Simple, but versatile model for strongly correlated solid state systems, 2D materials
- Suitable for single band, small bandwidth; atoms in optical lattices





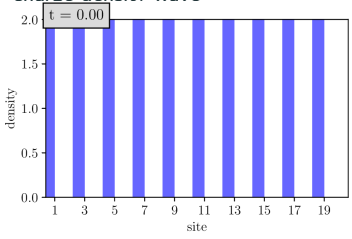
$$\hat{H}(t) = J \sum_{ij,\,\alpha} h_{ij}\, \hat{c}^{\dagger}_{i\alpha} \hat{c}_{j\alpha} + U \sum_i \hat{c}^{\dagger}_{i\uparrow} \hat{c}_{i\uparrow} \hat{c}^{\dagger}_{i\downarrow} \hat{c}_{i\downarrow} + \sum_{ij,\alpha\beta} f_{ij,\alpha\beta}(t)\, \hat{c}^{\dagger}_{i\alpha} \hat{c}_{j\beta}$$

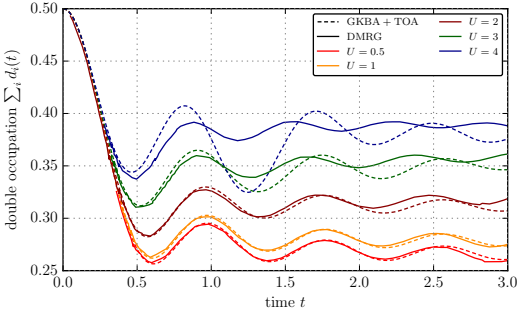
$h_{ij} = -\delta_{\langle i,\,j\rangle}$ nearest neighbor hopping, on-site repulsion ($U > 0$) or attraction ($U < 0$),

- f : external single-particle potential: e.g. potential quench, laser field, ion impact
- parameters from electronic structure calculations (DFT) or experiment
- can be systematically improved: extended Hubbard and PPP model, multiple bands

Benchmarks of NEGF against DMRG (1D)[4]

Initial state:
charge density wave





- sensitive observable: total double occupation
- good quality transients NEGF up to $U \simeq$ bandwidth
- accurate long-time behavior of GKBA+T-matrix (not shown)
- performance of different selfenergies vs. coupling and filling[3]

[3] N. Schlünzen, S. Hermanns, M. Scharnke, and M. Bonitz, J. Phys.: Cond. Matt. 32 (10), 103001 (2020)

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

Local density of states of graphene nanoribbons: Bulk vs. End

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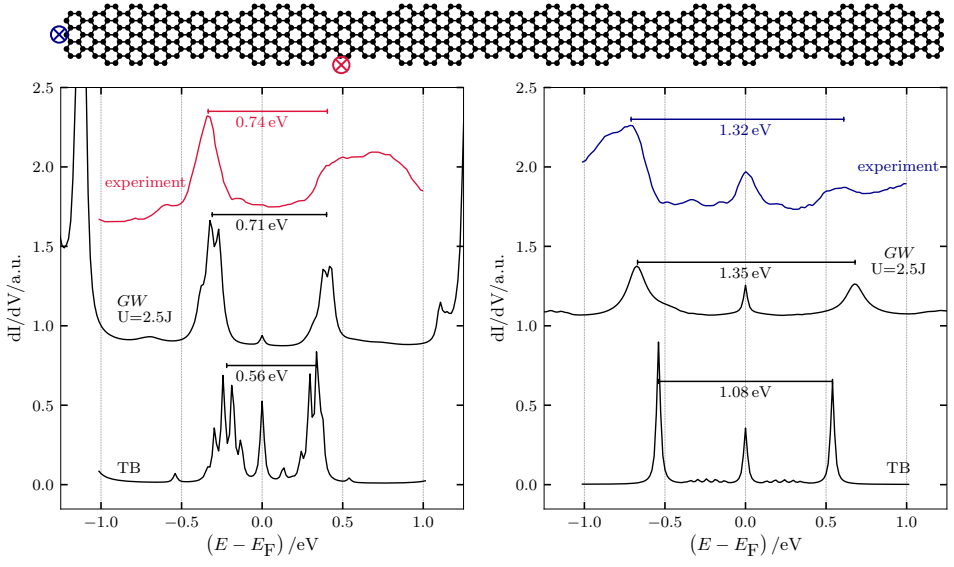


Failure of tight binding and Hartree-Fock. Excellent agreement of NEGF-GW: electronic correlations crucial

Experiments: Rizzo et al. Nature, **560**, 204 (2018), NEGF simulations: Joost et al. Nano Lett. **19**, 9045 (2019)

Acceleration: Generalized Kadanoff–Baym Ansatz (GKBA)[5]

- full propagation on the time diagonal ($I \coloneqq I^{(1),<}$):

$$\mathrm{i}\hbar\frac{\mathrm{d}}{\mathrm{d}t}G^<_{ij}(t) = \left[h^{\mathrm{HF}}, G^<\right]_{ij}(t) + \left[I + I^\dagger\right]_{ij}(t)$$

- reconstruct off-diagonal NEGF from time diagonal:

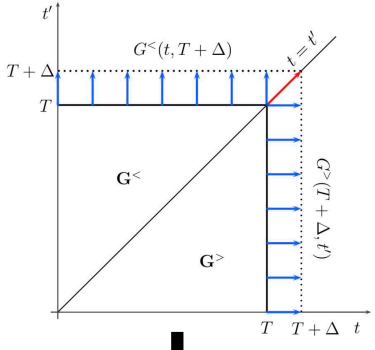
$$G^{\gtrless}_{ij}(t,t') = \pm\left[G^{\mathrm{R}}_{ik}(t,t')\rho^{\gtrless}_{kj}(t') - \rho^{\gtrless}_{ik}(t)G^{\mathrm{A}}_{kj}(t,t')\right]$$

with $\quad \rho^{\gtrless}_{ij}(t) = \pm\mathrm{i}\hbar G^{\gtrless}_{ij}(t,t)$

- HF-GKBA: use Hartree–Fock propagators for $G^{\mathrm{R/A}}_{ij}$

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

- conserves total energy



$$\mathcal{O}\left(N_{\mathsf{t}}^2\right)$$

[6] P. Lipavský, V. Špička, and B. Velický, Phys. Rev. B **34**, 6933 (1986);
K. Balzer and M. Bonitz, Lecture Notes in Physics **867** (2013)

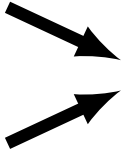
Time-linear NEGF simulations: the G1–G2 Scheme[6]

- full propagation on the time diagonal as for ordinary HF-GKBA:

$$\mathrm{i}\hbar\frac{\mathrm{d}}{\mathrm{d}t}G^<_{ij}(t) = \left[h^{\mathrm{HF}}, G^<\right]_{ij}(t) + \left[I + I^\dagger\right]_{ij}(t)$$

- but collision integral defined by correlated two-particle Green function

$$I_{ij}(t) = \pm\mathrm{i}\hbar\sum_{klp} w_{iklp}(t)\mathcal{G}_{lpjk}(t)$$



$$\mathcal{O}(N_\mathrm{t}^1)$$

- which obeys an ordinary differential equation

$$\mathrm{i}\hbar\frac{\mathrm{d}}{\mathrm{d}t}\mathcal{G}_{ijkl}(t) = \left[h^{(2),\mathsf{HF}}, \mathcal{G}\right]_{ijkl}(t) + \Psi^\pm_{ijkl}(t)$$

- the initial values

$$G^{0,<}_{ij} = \pm\frac{1}{\mathrm{i}\hbar}n_{ij}(t_0) =: \pm\frac{1}{\mathrm{i}\hbar}n^0_{ij}\,,$$
$$\mathcal{G}^0_{ijkl} = \frac{1}{(\mathrm{i}\hbar)^2}\left\{n^0_{ijkl} - n^0_{ik}n^0_{jl} \mp n^0_{il}n^0_{jk}\right\}\,,$$

determine the density and the pair correlations existing in the system at the initial time $t = t_0$

[6] N. Schlünzen, J.-P. Joost, and M. Bonitz, Phys. Rev. Lett. **124**, 076601 (2020)

The G1–G2 Scheme: beyond 2nd Born selfenergy

- other selfenergy approximations can be reformulated in the G1–G2 scheme in similar fashion:[7]

$$\mathrm{i}\hbar\frac{\mathrm{d}}{\mathrm{d}t}\mathcal{G}_{ijkl}(t) = \Big[h^{(2),\mathsf{HF}}(t),\mathcal{G}(t)\Big]_{ijkl} + \Psi^{\pm}_{ijkl}(t) + \underbrace{L_{ijkl}(t)}_{\text{TPP}} + \underbrace{P_{ijkl}(t)}_{GW} \pm \underbrace{P_{jikl}(t)}_{\text{TPH}}$$

$$L_{ijkl} \coloneqq \sum_{pq}\left\{\mathfrak{h}^{L}_{ijpq}\mathcal{G}_{pqkl} - \mathcal{G}_{ijpq}\Big[\mathfrak{h}^{L}_{klpq}\Big]^{*}\right\}, \qquad \mathfrak{h}^{L}_{ijkl} \coloneqq (\mathrm{i}\hbar)^2\sum_{pq}\left[\mathcal{G}^{\mathsf{H},>}_{ijpq} - \mathcal{G}^{\mathsf{H},<}_{ijpq}\right] w_{pqkl}\,,$$

$$P_{ijkl} \coloneqq \sum_{pq}\left\{\mathfrak{h}^{\Pi}_{qjpl}\mathcal{G}_{piqk} - \mathcal{G}_{qjpl}\Big[\mathfrak{h}^{\Pi}_{qkpi}\Big]^{*}\right\}, \qquad \mathfrak{h}^{\Pi}_{ijkl} \coloneqq \pm(\mathrm{i}\hbar)^2\sum_{pq} w^{\pm}_{qipk}\left[\mathcal{G}^{\mathsf{F},>}_{jplq} - \mathcal{G}^{\mathsf{F},<}_{jplq}\right]$$

and the Hartree/Fock (H/F) two-particle Green functions

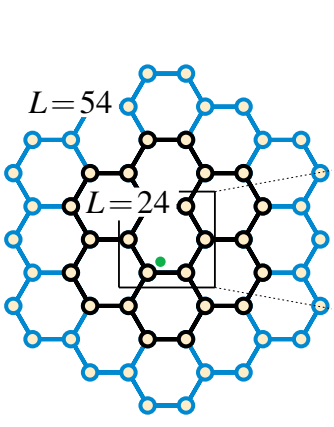
$$\mathcal{G}^{\mathsf{H},\gtrless}_{ijkl}(t) \coloneqq G^{\gtrless}_{ik}(t,t)G^{\gtrless}_{jl}(t,t)\,, \qquad \mathcal{G}^{\mathsf{F},\gtrless}_{ijkl}(t) \coloneqq G^{\gtrless}_{il}(t,t)G^{\lessgtr}_{jk}(t,t)$$

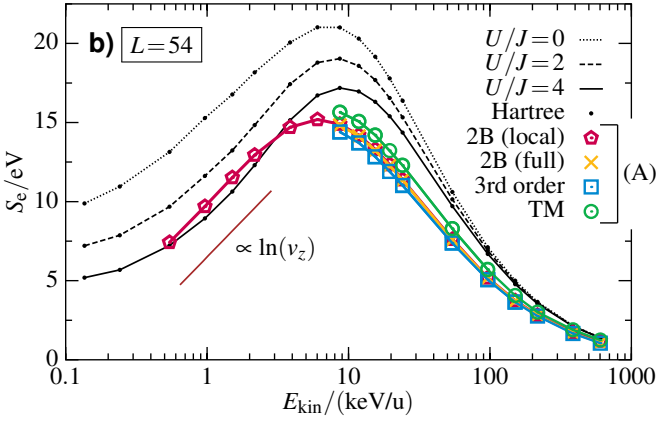
- include TPP, GW and TPH terms simultaneously: dynamically-screened-ladder (DSL) approximation. Conserving, applicable to short times. No explicit selfenergy known.[8]
- nonequilibrium generalization of ground state result (Bethe-Salpeter equation)

[7] J.-P. Joost, N. Schlünzen, and M. Bonitz, PRB **101**, 245101 (2020), Joost et al., PRB **105**, 165155 (2022);

[8] J.-P. Joost, PhD thesis, Kiel University 2023

NEGF-Ehrenfest simulations of ion stopping: ion energy loss

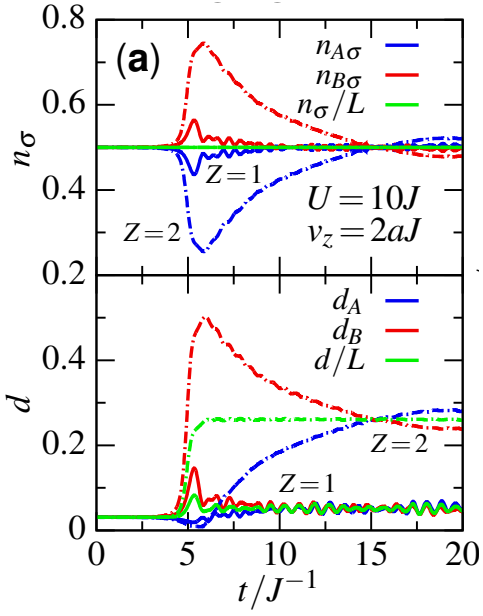




Left: finite honeycomb cluster and impact point of ion (green). Right: Ion energy loss S_e vs. impact energy. Black lines: Hartree approximation for e-e interaction. Colors: different approximations for the correlation selfenergy. Electron correlations generally reduce stopping, except for low impact energy.

From: K. Balzer, N. Schlünzen, and M. Bonitz PRB **94**, 245118 (2016)

Space resolved density and doublon dynamics during ion impact



Central impact of proton (full lines) or α-particle (at $t = 6J$) in honeycomb cluster of 12 sites.
B: inner ring, A: outer ring, mean

Top: electron density dynamics. Mean density constant, only redistribution (green)

Bottom: doublon number. Ion causes increase of doublon number (electronic excitation), remains in cluster after impact (before dissipation to lattice). Spreads uniformly across cluster.

From: Balzer *et al.* PRL **121**, 267602 (2018)

NEGF-approach to open systems: embedding scheme

Physical system (s) embedded in ("large") environment (e) that is treated in simplified manner

$$\Omega = \{s, e\}: \qquad H_{\text{total}} = \sum_{\alpha\beta\in\Omega}\sum_{ij} h_{ij}^{\alpha\beta}(t) c_i^{\alpha\dagger} c_j^{\beta} + \frac{1}{2}\sum_{\alpha\beta\gamma\delta\in\Omega}\sum_{ijkl} w_{ijkl}^{\alpha\beta\gamma\delta} c_i^{\alpha\dagger} c_j^{\beta\dagger} c_k^{\gamma} c_l^{\delta}\,.$$

$$\text{NEGF, density matrix}: \quad G_{ij}^{\alpha\beta}(t,t') = -\mathrm{i}\langle T_C c_i^{\alpha}(t) c_j^{\beta\dagger}(t')\rangle\,, \qquad \rho_{ij}^{\alpha\beta}(t) = -\mathrm{i}G_{ji}^{\beta\alpha}(t,t^+)\,,$$

Keldysh-Kadanoff-Baym equations of total system including coupling (se) terms:

$$\left\{\mathrm{i}\partial_t\delta_{ik} - h_{ik}^{\mathrm{HF,s}}(t)\right\} G_{kj}^{\mathsf{s}}(t,t') = h_{i\underline{k}}^{\mathrm{HF,se}}(t) G_{\underline{k}j}^{\mathsf{es}}(t,t') + \delta_{ij}\delta_C(t,t') + \int_C \mathrm{d}\bar{t}\,\Sigma_{ik}^{\mathsf{s}}(t,\bar{t}) G_{kj}^{\mathsf{s}}(\bar{t},t')\,.$$

$$\left\{\mathrm{i}\partial_t\delta_{\underline{ik}} - h_{\underline{ik}}^{\mathrm{HF,e}}(t)\right\} G_{\underline{k}j}^{\mathsf{es}}(t,t') = h_{\underline{i}k}^{\mathrm{HF,es}}(t) G_{kj}^{\mathsf{s}}(t,t')\,,$$

$$\left\{\mathrm{i}\partial_t\delta_{\underline{ik}} - h_{\underline{ik}}^{\mathrm{HF,e}}(t)\right\} G_{\underline{kj}}^{\mathsf{e}}(t,t') = \delta_{\underline{ij}}\delta_C(t,t')\,.$$

Effect of environment can be rewritten as additional selfenergy to retain closed equation for G^s:

$$\Sigma_{ij}^{\mathrm{emb}}(t,t') = \sum_{\underline{kl}} h_{i\,\underline{k}}^{\mathrm{HF,se}}(t) G_{\underline{k}\,\underline{l}}^{\mathsf{e}}(t,t') h_{\underline{l}\,j}^{\mathrm{HF,es}}(t')\,, \qquad h_{i\underline{j}}^{\mathsf{se}}(t) = \int \mathrm{d}^3 r\,\phi_i^{\mathsf{s}*}(\vec{r})(T+V)\chi_{\underline{j}}^{\mathsf{e}}(\vec{r};t)\,.$$

Appl. to resonant charge transfer: Bonitz *et al.*, Front. Chem. Sciences Engin. **13**, 201-237 (2019)

NEGF-embedding scheme for charge transfer from graphene nanoflake to impacting high-Z ion

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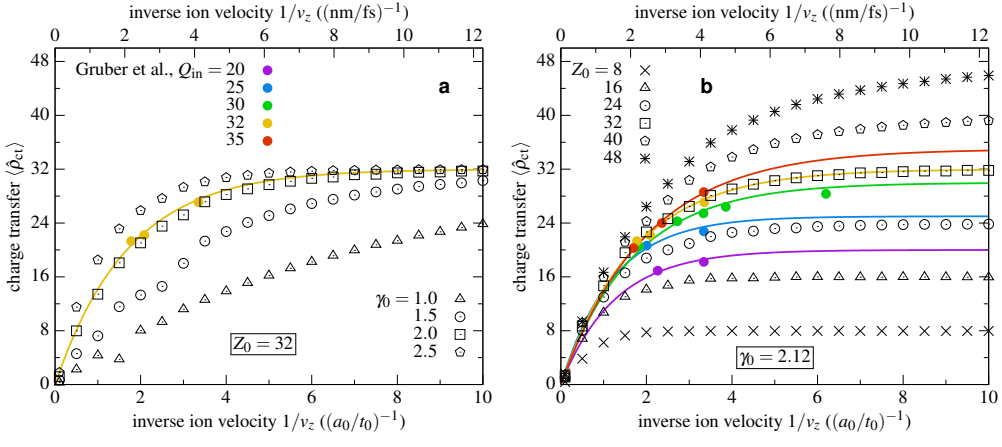
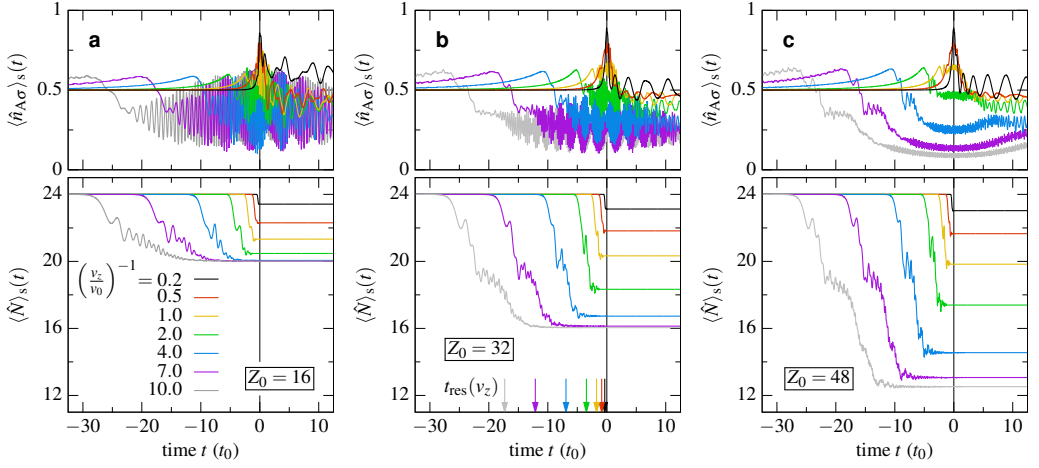


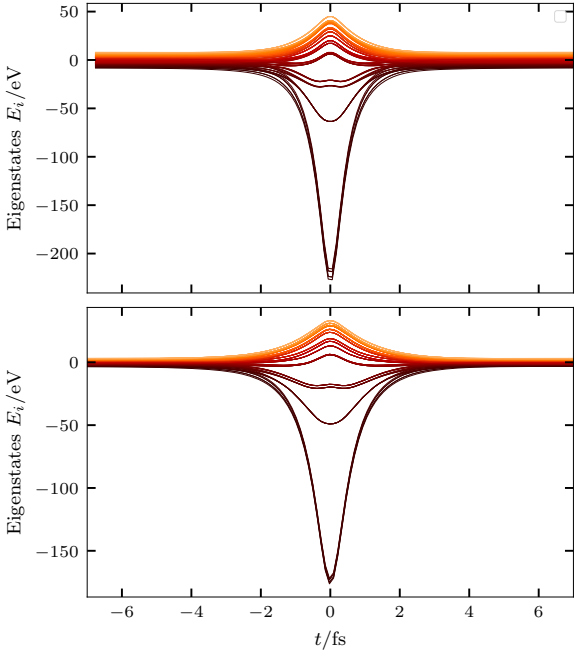
NEGF-embedding selfenergy scheme for resonant charge transfer, $L = 24$. Exp. data from Gruber et al. Nat. Commun. 2016, **7**(1), 13948. Single adjustable parameter γ_0 works for all charges. Figure from Balzer and Bonitz, Contrib. Plasma Phys. **62** (2) e202100041 (2022)

Charge transfer from graphene nanoflake to impacting high-Z ion

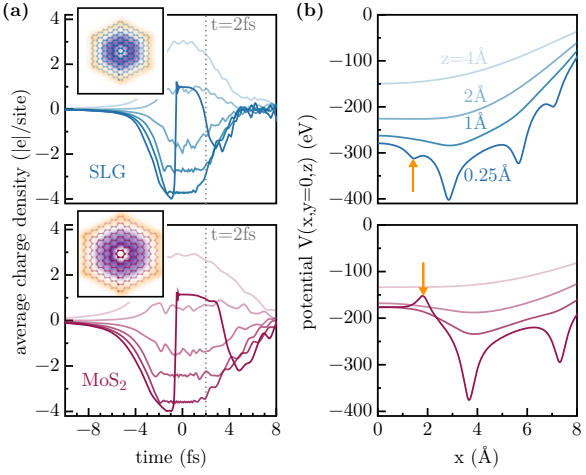


Bottom: total particle number (in one band) and Top: occupation of innermost honeycomb (graphene, $L = 24$ sites) during ion impact. Colors: NEGF results for different ion velocities. Arrows: moment when ion passes through the resonance point $z_{\mathrm{res}} = \sqrt{3}a_0$, in front of the plane.
From Balzer and Bonitz, Contrib. Plasma Phys. **62** (2) e202100041 (2022).

Energy eigenvalues during ion impact (top: SLG, bottom: MoS_2)



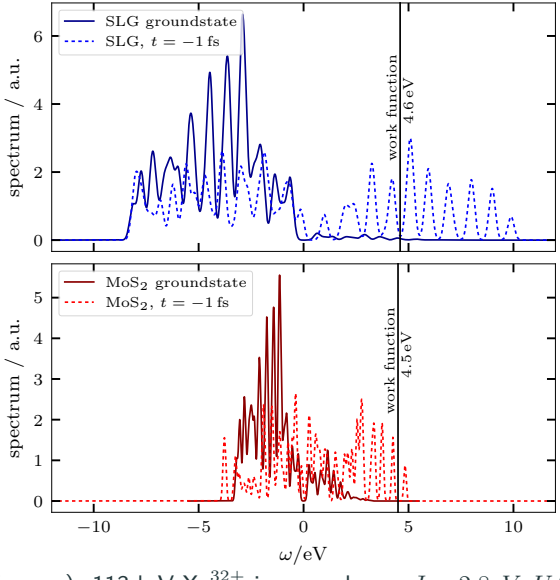
Local density dynamics (a) and electrostatic potential after ion impact



(a) time resolved radial electron density. (b) Induced electrostatic potential, $V(\mathbf{r}, t)$ at $t = 2$ fs, versus radial coordinate x, at four distances z from the monolayer. The arrows indicate the position of the innermost honeycomb from which electron emission is expected to occur primarily. 113 keV Xe^{32+} ions passing through the center of a 216-site cluster. Niggas. *et al.*, Phys. Rev. Lett. **129**, 086802 (2022)

Energy spectrum without ion and directly before impact

Christian-Albrechts-Universität zu Kiel
Mathematisch-Naturwissenschaftliche Fakultät



G1-G2 scheme (SOA selfenergy): 113 keV Xe^{32+} ion, graphene: $J = 2.8eV$, $U/J = 1.6$, $a_L = 1.42$Å
MoS_2: $J = 1.1eV$, $U/J = 4.0$, $a_L = 1.83$Å, Niggas. et al., Phys. Rev. Lett. **129**, 086802 (2022)

Summary and Outlook

- Exciting novel experiments with highly charged ions and graphene/TMDC monolayers
- NEGF simulations well suited to follow dynamics of electronic correlations with single-site resolution on (sub-)fs time scale
- advanced selfenergies capture key electronic excitation processes; require electronic structure theory (DFT) input for accurate lattice model or proper basis sets.
- Neutralization via resonant charge transfer modeled using a NEGF embedding selfenergy approach.
- G1–G2 calculations allow for long and efficient simulations (linear in time)[9]
- Outlook: - combine embedding concept with G1–G2 scheme: arXiv:2211.09615 (PRB 2023)
  - improved description of ion
  - embedding approach to Auger processes and ICD

[9] N. Schlünzen, J.-P. Joost and M. Bonitz, Phys. Rev. Lett. **124**, 076601 (2020)

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J.-P. Joost, N. Schlünzen, H. Ohldag, M. Bonitz, F. Lackner, and I. Brezinova, Phys. Rev. B **105**, 165155 (2022)