

Ion Impact Induced Ultrafast Electron Dynamics in Finite Graphene-Type Hubbard Clusters

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Strongly correlated systems of fermions have an interesting phase diagram arising from the Hubbard gap. Excitation across the gap leads to the formation of doubly occupied lattice sites (doublons) which offers interesting electronic and optical properties. Moreover, when the system is driven out of equilibrium interesting collective dynamics may arise that are related to the spatial propagation of doublons. Here, a novel mechanism that was recently proposed by the authors [Balzer et al., *Phys. Rev. Lett.* 121, 267602 (2018)] is verified by exact diagonalization and nonequilibrium Green functions (NEGF) simulations – fermionic doublon creation by the impact of energetic ions. The formation of a nonequilibrium steady state with homogeneous doublon distribution is reported. The effect should be particularly important for correlated finite systems, such as graphene nanoribbons, and directly observable with fermionic atoms in optical lattices. It is demonstrated that doublon formation and propagation in correlated lattice systems can be accurately simulated with NEGF. In addition to two-time results, single-time results within the generalized Kadanoff–Baym ansatz (GKBA) with Hartree–Fock propagators (HF-GKBA) is presented. Finally systematic improvements of the GKBA that use correlated propagators (correlated GKBA) and a correlated initial state are discussed.

1. Introduction

The interaction of energetic charged particles with solid bodies is a phenomenon common to hot gases, plasmas, as well as astrophysical systems, including the solar wind and cosmic rays. When charged particles hit a solid surface, they deposit energy and momentum and may cause substantial surface modification the details of which strongly depend on the particle energy and the material properties. In low-

temperature plasma physics, this process is routinely used to clean surfaces from adsorbates or modify them via sputtering, for example ref. [1] or as a source of secondary electrons.^[2] On the other hand, ions impacting a solid can be used as a diagnostic tool of the electronic structure of the material by measuring the energy loss (or stopping power or stopping range) as a function of impact energy.^[3]

From the theory side, the interaction of ions with a solid surface has been studied with a variety of approaches including scattering theory^[4] or uniform electron gas models.^[5] More recently, ab initio simulations of ion stopping based on time-dependent density functional theory (TDDFT) became available for metals,^[6] semimetals,^[7] or boron nitride and graphene sheets^[8] and other materials. These simulations account primarily for valence electron excitation. Good results for the stopping power of high energy ions in matter are also provided by the SRIM code^[9] that uses the binary collision approximation in combination with an averaging over a large range of

experimental situations. Thus presently two main questions remain open: i) how does the stopping power change in correlated materials and what is the effect of the correlation strength? ii) How does the stopping power change when the system size is reduced or the geometry of the target is altered? And what is the role of electronic correlations in finite systems?

The motivation for these questions is fueled by the recent progress in nanostructured materials, clusters or finite nano-size systems. A particularly exciting example are finite honeycomb clusters or graphene nanoribbons (GNR). GNR hold the promise that they overcome the limitations of graphene arising from its semimetallic character. In contrast, GNR have been shown to have a finite bandgap $E_G(L)$ arising from the quantum confinement.^[10,11] Over a broad range of system widths L , the band gap increases nearly proportionally with L^{-1} .^[12] Typical values for the bandgap are found to be $E_G \leq 2.5\text{eV}$ according to tight-binding and DFT calculations.^[13] Taking into account quasiparticle corrections results in a significantly larger gap of $E_G \leq 5.5\text{eV}$.^[10] In electronic structure measurements for GNRs on substrates bandgaps

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of $E_G \sim 2.4 - 3.5\text{eV}$ were found.^[14–16] The finite band gap makes the material semiconducting which is crucial for applications in electronics and optics. Recent progress in synthetization methods of GNR,^[17–19] has drastically increased the number of exciting experiments over the past few years.^[20–23] Therefore, an accurate theoretical description of these systems in nonequilibrium and especially of their time-resolved correlation effects is needed.

However, finite graphene nanostructures, especially when driven out of equilibrium, are extremely complex, inhomogeneous systems that put high requirements on theory. The two-dimensional geometry of the graphene honeycomb lattice has to be modeled, and the correlated nonequilibrium dynamics of the system have to be accurately described for up to several femtoseconds within a reasonable amount of computing time. Due to the limitations of time-dependent density functional theory to weakly correlated systems and the difficulties of density matrix renormalization group (DMRG) approaches to treat two-dimensional systems, nonequilibrium Green functions (NEGF) have emerged as the first choice to provide such a description. This method has recently been shown to accurately describe the dynamics of finite strongly correlated lattice systems, for example, refs. [24–26] where both two-time simulations and single-time dynamics within the generalized Kadanoff–Baym ansatz (GKBA^[27]) were presented.^[28] Furthermore, in our recent work,^[29,30] we have shown that the NEGF approach is well capable to treat the correlated electron dynamics in lattice systems that is initiated by the impact of charged projectiles and, thus, is able to answer questions i) and ii) that were raised above.

The goal of this article is to present recent results on NEGF simulations of finite correlated lattice systems with a particular focus on doublon creation and propagation following the impact of one or several charged particles. We also discuss how to include the description of charge transfer processes between projectile and target that is observed at low impact velocities. Finally, we discuss theoretical issues that are related to the GKBA and to its extension to include correlated propagators.

The remainder of this article is organized as follows. In Section 2, we introduce the Hubbard model and the description of the interaction of the charged projectile with the electronic system. This is followed, in Section 3, by a brief introduction into the NEGF approach and the GKBA and a discussion of its further improvements. The main results are presented in Section 4 and include numerical data from two-time NEGF and GKBA simulations as well as analytical results for a representative two-site system, cf. Section 4.3. We conclude by presenting an embedding approach to treat the charge transfer between projectile and solid, in Section 5, and by an outlook, in Section 6.

2. Model

We consider a 1D or 2D system with moderate to strong electronic correlations that is modeled by a Hubbard hamiltonian (1) with hopping amplitude J [$\langle i, j \rangle$ denotes nearest neighbors] and onsite interaction strength U .



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$$H_c = -J \sum_{\langle i, j \rangle, \sigma} c_{i\sigma}^\dagger c_{j\sigma} + U \sum_i \left(n_{i\uparrow} - \frac{1}{2} \right) \left(n_{i\downarrow} - \frac{1}{2} \right) - \frac{Z_p e^2}{4\pi\epsilon_0} \sum_{i, \sigma} \frac{c_{i\sigma}^\dagger c_{i\sigma}}{|\mathbf{r}_p(t) - \mathbf{R}_i|} + \sum_{\langle i, j \rangle, \sigma} W_{ij}(t) c_{i\sigma}^\dagger c_{j\sigma} \quad (1)$$

The strength of correlations is measured by the ratio U/J . For finite graphene clusters (nanoribbons) a typical value is $U/J = 3.5$.^[31] For other 2D materials larger values are possible. Similarly, such finite clusters are straightforwardly realized from fermionic atoms in optical lattices where U/J can be very large. Here, we will mostly consider moderate values, $U/J = 4$ but also a few applications where $U/J = 10 \dots 15$. The latter cases are treated by exact diagonalization (CI) methods, for small systems, and the former with nonequilibrium Green functions, see Section 3.

The second line of Equation (1) contains the coupling of the lattice electrons located at coordinate \mathbf{R}_i with a positively charged projectile of charge Z_p that is treated classically (Ehrenfest dynamics) by solving Newton's equation for the trajectory $\mathbf{r}_p(t)$ under the influence of all Coulomb forces with the lattice electrons. The final term allows to improve the model by accounting for modification of the hopping rates due to the projectile according to $W_{ij}(t) = \gamma [W_{ii}(t) + W_{jj}(t)]/2$, where W_{ii} is the magnitude of the

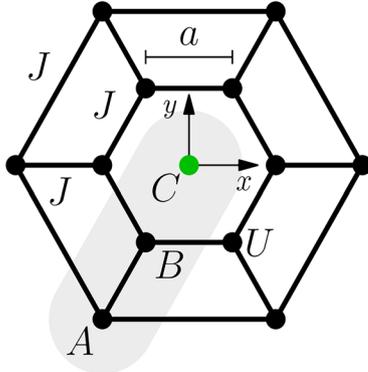


Figure 1. Sketch of a honeycomb cluster of $L=12$ sites and distance between sites a , showing the hopping and on-site interaction parameters in the hamiltonian (1). The dimer model of Section 4.3 consists of the representative sites A and B.

Coulomb potential of the projectile at lattice site “i,” and γ is a phenomenological parameter of the order unity.^[29]

Although the Hubbard model permits any geometry, here we will concentrate on single-layer honeycomb clusters, due to their relevance for graphene-type structures. A sketch of such a system is shown in **Figure 1**. For the special case of high symmetry, as in this figure, it is tempting to consider a reduced dimer model that consists only of sites A and B. This model can be solved analytically, even in the presence of a time-dependent external perturbation (such as a charged projectile^[30]), and this will be summarized in Section 4.3.

Of course, the Hubbard model (1) represents a strong simplification compared to graphene. Nevertheless, fairly accurate parameters can be obtained from DFT simulations. On the other hand, this model can be exactly realized with ultracold atoms in optical lattices. A first improvement to the model is achieved by using strongly reduced hopping rates at the cluster edge (due to the larger distances and to the termination with other atoms). We have tested this effect in ref. [30] and verified that this does not significantly change the response of the cluster to a projectile compared to the results that are presented below. A further improved description of graphene-type finite-size structures can be achieved via an *extended Hubbard model* where one includes also hopping beyond the nearest neighbor sites and non-vanishing orbital overlap, which is described in detail in ref. [31] but will not be used here.

3. Nonequilibrium Green Functions Formalism

The method of nonequilibrium (real-time) Green functions is a very powerful approach to quantum many-body systems out of equilibrium, cf. refs. [32,33]. The method successfully overcomes the limitations of the quantum Boltzmann equation, such as the restriction to times larger than the correlation time and fundamental problems such as failure for strongly correlated systems, incorrect conservation laws (e.g., conservation of kinetic energy instead of total energy) and relaxation toward an equilibrium state of an ideal gas (Fermi, Bose, or Maxwell distribution) instead of the one of an interacting system, for a detailed discussion, see refs. [34–38]. An extensive overview on

recent applications that span condensed matter physics, nuclear physics, laser plasmas, etc., can be found in the proceedings of the PNGF conferences.^[39–44]

3.1. Basic Concepts

The NEGF method is formulated in second quantization (for textbook or review discussions, see for example, refs. [24,33,45]), in terms of creation (annihilation) operators $c_{i\sigma}^\dagger$ ($c_{i\sigma}$) for electrons in a single-particle orbital $|i\rangle$ with spin projection σ that obey the standard fermionic anti-commutation relations. Below we will consider a spatially inhomogeneous lattice configuration where i labels the spatial coordinates of individual lattice points.

The central quantity that determines all time-dependent observables is the one-particle NEGF

$$G_{ij\sigma}(t, t') = -i\hbar \langle T_C c_{i\sigma}(t) c_{j\sigma}^\dagger(t') \rangle \quad (2)$$

where the expectation value is computed with the equilibrium density operator of the system, and times are running along the Keldysh contour C , with T_C denoting ordering of operators on C .^[32,46] The NEGF obeys the two-time Keldysh–Kadanoff–Baym equations (KBE)^[33]

$$\begin{aligned} \sum_k [i\hbar \partial_t \delta_{ik} - \bar{h}_{ik}(t)] G_{kj\sigma}(t, t') \\ = \delta_C(t - t') \delta_{ij} + \sum_k \int_C ds \Sigma_{ik\sigma}(t, s) G_{kj\sigma}(s, t') \end{aligned} \quad (3)$$

$$\begin{aligned} \sum_k G_{ik\sigma}(t, t') \left[-i\hbar \overleftarrow{\partial}_{t'} \delta_{kj} - \bar{h}_{kj\sigma}(t') \right] \\ = \delta_C(t - t') \delta_{ij} + \sum_k \int_C ds G_{kj\sigma}(t, s) \Sigma_{ik\sigma}(s, t') \end{aligned} \quad (4)$$

where we do not consider spin changes. The hamiltonian $\bar{h}(t)$ contains kinetic, potential, and mean field energy [including the projectile contributions in the second line of Equation (1)], whereas correlation effects are contained in the selfenergy Σ .

For numerical applications the Equation (3) for the Keldysh matrix Green function have to be rewritten for the correlation functions G^{\gtrless} :

$$\sum_l [i\hbar \partial_t \delta_{il} - \bar{h}_{il}(t)] G_{lj}^{\gtrless}(t, t') = I_{ij}^{(1)\gtrless}(t, t') \quad (5)$$

$$\sum_l G_{il}^{\gtrless}(t, t') \left[-i\hbar \overleftarrow{\partial}_{t'} \delta_{lj} - \bar{h}_{lj}(t') \right] = I_{ij}^{(2)\gtrless}(t, t') \quad (6)$$

with the collision integrals given by

$$\begin{aligned} I_{ij}^{(1)\gtrless}(t, t') = \\ \sum_l \int_{t_0}^{\infty} d\bar{t} \left\{ \Sigma_{il}^R(t, \bar{t}) G_{lj}^{\gtrless}(\bar{t}, t') + \Sigma_{il}^{\gtrless}(t, \bar{t}) G_{lj}^A(\bar{t}, t') \right\} \end{aligned} \quad (7)$$

$$I_{ij}^{(2)\gtrless}(t, t') = \sum_{t_s} \int_{t_s}^{\infty} d\bar{t} \left\{ G_{ij}^R(t, \bar{t}) \Sigma_{ij}^{\gtrless}(\bar{t}, t') + G_{ij}^{\gtrless}(t, \bar{t}) \Sigma_{ij}^A(\bar{t}, t') \right\} \quad (8)$$

where the retarded and advanced functions are given by

$$\begin{aligned} G_{ij}^{R/A}(t, t') &= \pm \Theta[\pm(t - t')] \left\{ G_{ij}^>(t, t') - G_{ij}^<(t, t') \right\} \\ \Sigma_{ij}^{R/A}(t, t') &= \pm \Theta[\pm(t - t')] \left\{ \Sigma_{ij}^>(t, t') - \Sigma_{ij}^<(t, t') \right\} \end{aligned} \quad (9)$$

Note that the correlation effects that are contained in the collision integrals $I^{1,2\gtrless}$ lead to memory effects, that is, time integrations over the past, starting from a start time t_s . In most of the simulations presented below, we will start at t_s with an uncorrelated system and slowly switch on the interaction (“adiabatic switching”^[28,47]) which produces, at time t_0 , a correlated ground state from which the excitation of the system starts. We return to the discussion of a correlated initial state in Section 3.4.

The system (3)–(9) is a closed set of equations for the dynamics of the NEGF once a selfenergy approximation $\Sigma[G]$ has been chosen. This issue is discussed in the following section.

3.2. Selfenergies

In this work we use the following selfenergy approximations to account for the electron–electron interaction. We consider Hartree-Fock (HF) contributions (i.e., mean field, note that, for Hubbard systems, the Fock terms are absent) and correlation effects. The latter are described on the level of the second Born (2B) and the T-matrix approximation (TM) where the former (latter) is adequate at weak (moderate) coupling.^[25,26] Moreover, we also consider the third-order approximation^[24,48] that includes all bubble and ladder-type diagrams to third order. The corresponding selfenergy diagrams are shown in **Figure 2**.

The KBE (3) are solved on the $t - t'$ -plane as described in refs. [24,49]. Due to the time integration involved in the collision integrals (memory) the numerical effort increases cubically with the simulation duration T_{tot} . The effort is particularly high for the GW and T-matrix approximations since for the effective interaction, an additional integral equation has to be solved, for example, ref. [24]. One way to reduce the computational effort is the restriction to the propagation along the time diagonal via the generalized Kadanoff–Baym ansatz (GKBA), proposed in ref. [27]. The GKBA reduces the computational effort of NEGF simulations with second order Born selfenergies from a scaling $\sim T_{\text{tot}}^3$ with the total simulation duration to $\sim T_{\text{tot}}^2$ as was confirmed in ref. [47]. The GKBA has the additional attractive feature that it reduces the degree of selfconsistency in the NEGF simulations^[28] and “cures” the artificial damping behavior of two-time simulations

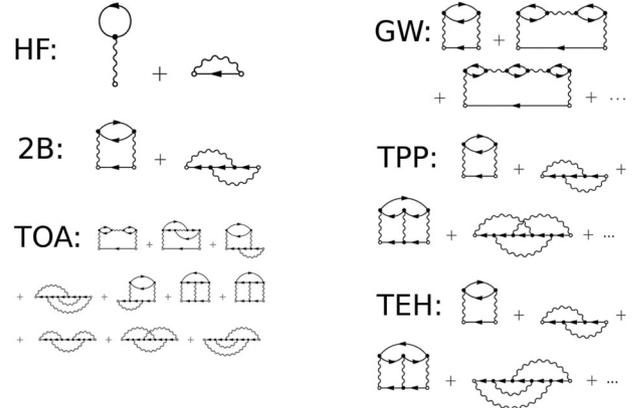


Figure 2. Feynman diagrams for the selfenergy approximations used in this work: Hartree–Fock (HF), Second order Born approximation (2B), particle–particle and particle–hole T-matrix (TPP, TEH), and third order approximation (TOA) which contains all diagrams with three interaction lines from GW, TPP, and TEH.

observed in small systems at very strong excitation,^[50] for computational aspects, see also ref. [51].

3.3. Generalized Kadanoff–Baym Ansatz: Extension to Correlated Propagators

Instead of propagating the Green functions in the two-time plane one can perform a propagation along the diagonal, $T = (t + t')/2$, only. The equation for $G^<$ is a commutator equation – the first equation of the BBGKY-hierarchy for the reduced density operators^[34]:

$$\begin{aligned} i\hbar \partial_T G_{ij}^<(T, T) &= [\bar{h}(T), G^<(T, T)]_{ij} + I_{ij}(T) \\ [A, B]_{ij} &= \sum_k (A_{ik} B_{kj} - B_{ik} A_{kj}) \end{aligned} \quad (10)$$

$$I_{ij}(T) = \sum_k \int_{t_0}^T d\bar{t} \left\{ \Sigma_{ik}^>(T, \bar{t}) G_{kj}^<(\bar{t}, T) - \Sigma_{ik}^<(T, \bar{t}) G_{kj}^>(\bar{t}, T) + \text{h.c.} \right\} \quad (11)$$

To compute the collision integral I , the Green functions $G^{\gtrless}(t, t')$ are required also away from the diagonal. In fact, due to the symmetry $G_{ij}^{\gtrless}(t, t') = -[G_{ji}^{\gtrless}(t', t)]^*$ values for $t \geq t'$ are sufficient. With the GKBA the following “reconstruction” approximation is made^[27]

$$G_{ij}^{\gtrless}(t, t') = i\hbar \sum_k G_{ik}^R(t, t') G_{kj}^{\gtrless}(t', t'), \quad t \geq t' \quad (12)$$

and with $G^{\gtrless}(t, t')$ also $\Sigma^{\gtrless}(t, t')$ are known. While the diagonal value $G_{kj}^{\gtrless}(t', t')$ is available from the solution of Equation (10), the retarded function has to be provided as an external input. Among the different approaches in macroscopic systems we mention the

use of ideal propagators (“Free GKBA” or FGKBA), and quasiparticle propagators, that are exponentially decaying as a function of $|t - t'|$ (QP-GKBA) which have been used extensively in semiconductor optics and transport, in particular, by the groups of Haug, Banyai, and Jahnke, for example, refs. [52–55] and references therein. For strong field physics in semiconductors and laser plasmas the gauge-invariant FGKBA has been introduced.^[53,56–58] The GKBA has also been used with propagators taken from a full two-time simulation (2t-GKBA) in ref. [59] which confirmed the good quality of the ansatz (12). A revival of the interest in the GKBA occurred with the NEGF study of finite systems about a decade ago, for example, ref. [45] and references therein. Here very good results were obtained with Hartree-Fock propagators (HF-GKBA).^[49,60–62]

Although earlier studies used the GKBA together with lowest order correlated selfenergies (second Born approximation) we recently demonstrated that the HF-GKBA can also be successfully used together with more advanced approximations such as the T-matrix, GW and third-order selfenergies, cf. Section 3.2. The most thorough test of the HF-GKBA (and of two-time NEGF simulations), so far, was performed in ref. [26] by benchmarks against quasi-exact DMRG simulations for 1D systems which are summarized in **Figure 3**. For weak and moderate coupling very good agreement with DMRG was obtained, if the HF-GKBA was combined with the adequate selfenergy: second order Born for $U/J \leq 1$ and T-matrix for $U/J \leq 4$ at weak (or high) filling. Around half filling the third order approximation showed the best behavior. This agreement is observed for all observables including densities and energies and even for very sensitive quantities such as the average double occupation, Equation (24), that is shown in Figure 3. While the NEGF simulations are more efficient than DMRG at

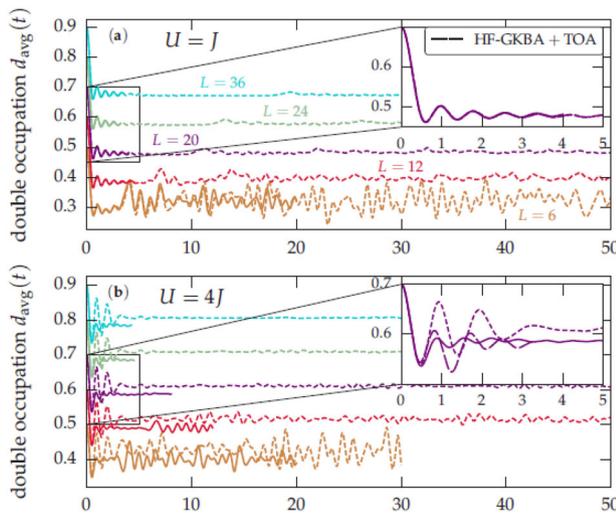


Figure 3. Benchmarks of the HF-GKBA against DMRG for a 1D charge density wave state of doublons (site occupations alternate 2, 0, 2 ...). System-size dependence and long-time evolution of the average double occupancy, Equation (24), for (a) $U = J$ and (b) $U = 4J$ and chain lengths $L = 6, 12, 20, 24, 36$. Full lines: DMRG, short dashes: HF-GKBA + TMA. The insets, in addition, show HF-GKBA + TOA results (long dashes). For better visibility, curves for different L are shifted vertically by 0.1. After ref. [26].

weak and moderate coupling (cf. the accessible simulation durations in Figure 3), for strong coupling, $U = 10$, in contrast to DMRG, no NEGF simulations were possible, indicating complementary applicability ranges of the two methods.^[26] In addition, NEGF have the remarkable advantage of being completely flexible in terms of system dimensionality and geometry which makes them an ideal approach to treat finite correlated systems such as GNR.

Despite the success of the HF-GKBA, it also has problems. While it removes most of the over-damping artifacts of two-time NEGF simulations (see above), it often underestimates the damping present in the exact dynamics and does not correctly reproduce the high-frequency features, cf. Figure 3. Also, due to the HF-propagators, the spectral function produced by the HF-GKBA is uncorrelated. There have been early attempts to modify the free propagators by an exponential damping, $G^R \sim e^{-\gamma|t-t'|}$ (cf. QP-GKBA above). However this choice of propagators violates energy conservation [as opposed to the FGKBA and HF-GKBA] due to a very slow ($1/\omega^2$) decay of the propagators in frequency space. This behavior was improved in ref. [63] by the use of non-Lorentzian damping factors, $G^R \sim 1/\cosh^a[\omega(t-t')]$, where ω is a characteristic frequency (phonon or plasmon frequency) and a is a positive fit parameter, but energy conservation is still violated. For a recent discussion of the reconstruction problem, see ref. [64].

Here we outline a systematic approach toward an improved version of the GKBA that goes beyond the HF-GKBA. The idea is to start from the equation of motion for the retarded propagators (Dyson equation)

$$G_{ij}^R(t, t') = G_{\text{HF},ij}^R(t, t') + \sum_k \int_{t'}^t \tilde{d}\tilde{t} G_{\text{HF},ik}^R(t, \tilde{t}) \tilde{I}_{kj}^R(\tilde{t}, t') \quad (13)$$

$$\tilde{I}_{ij}^R(t, t') = \sum_k \int_{t'}^t dt'' \tilde{\Sigma}_{ik}^R(t, t'') G_{kj}^R(t'', t')$$

where $\tilde{\Sigma}$ is a conserving selfenergy that may be different from the one used in I_{ij} .^[28] Since our main goal is to improve the single-time simulations beyond the HF-GKBA and to include damping effects, we may regard correlation effects in the GKBA as small corrections to $G_{\text{HF},ij}^R(t, t')$. While the HF-GKBA corresponds to the neglect of the integral in (13), an approximate treatment of the integral will be called *correlated GKBA* (C-GKBA). For this we propose several approximations that are listed in increasing order of accuracy, assuming that $\tilde{\Sigma}$ corresponds to weak correlations, that is, small \tilde{U}/J :

- replacement of all propagators in the integral (13) by ideal propagators, $G^R \rightarrow G_{\text{id}}^R$;
- replacement of all propagators in the integral (13) by HF propagators, $G^R \rightarrow G_{\text{HF}}^R$. The result $G_{\text{HF}}^{R,(1)}$ can be understood as first step of an iteration series that starts with $G_{\text{HF}}^{R,(0)} \equiv G_{\text{HF}}^R$;
- higher order iterations, $G_{\text{HF}}^{R,(l)}$, $l \geq 2$, that use $G_{\text{HF}}^{R,(l-1)}$ in the integral term;
- linearization of the collision integral in the correlated G^R . This means, products of retarded functions are replaced

according to $G_{ik}^R G_{kj}^R \rightarrow G_{HF,ik}^R G_{kj}^R + G_{ik}^R G_{HF,kj}^R$ and similarly, for more complex products;

- e) 2t-GKBA: exact solution of the Dyson equation for $G^R(t, t')$,^[59] see above.

Note that the Dyson Equation (13) for G^R is not closed since the selfenergy $\tilde{\Sigma}^R$, in general, also contains G^{\lessgtr} . However, in the spirit of perturbation theory, we can always reconstruct G^{\lessgtr} via $G^{R/A}$ applying again the GKBA (12).

This is a systematic scheme to incorporate correlations in the propagators. The drawback of the C-GKBA is, of course, that the evaluation of the integral term in Equation (13) is costly, scaling as T_{tot}^3 . However, this effort is warranted by the expected improved accuracy of the observables and spectral properties as compared to two-time NEGF simulations, on the one hand, and HF-GKBA results, on the other. The analytical and numerical properties of the C-GKBA are presently under investigation. Finally, we note that recently also improvements that take into account corrections beyond the GKBA have been studied for stationary transport problems by Kalvova et al.^[65] A modified reconstruction problem where the GKBA is applied also to the off-diagonal propagation (“extended GKBA”) was recently proposed by Hopjan et al.^[66,67] but the relation to the original reconstruction scheme of ref. [27] remains open.

3.4. Initial Correlations for NEGF and GKBA: Restart Capability

Until now we have only considered situations where, at the “initial” time where the evolution starts, the system is uncorrelated. This is, of course, a special case. In general, at this time, the system may be characterized by non-vanishing pair correlations c_{12} which may have a profound effect on the dynamics. The generalization of the KBE to include finite initial correlations goes back to Danielewicz^[68] who derived a collision integral I^{IC} that is due to c_{12} . Alternative derivations have been given by Kremp et al.^[56,69] who also derived initial correlation contributions to the selfenergy. In these articles also numerical results were given that demonstrate the effect of initial correlations. Text book discussions can be found in refs. [34,45,70]. Despite these early results and similar theoretical and numerical results for density operators, for example, ref. [34], numerical results for the GKBA have not been proposed so far. Only recently, two papers appeared that presented solutions for this problem.^[67,71]

Here we present an alternative approach that is based on ref. [72] that provides a complementary and more general view on this issue. In Equation (3) we introduced, on the right-hand side, the collision integral that involves the correlation selfenergy or, alternatively, the correlation part of the two-particle Green function $G^{(2)}$

$$\int d2V(1-2)G^{(2)}(12,1'2^+) = \int_C d\bar{1}\Sigma(1,\bar{1})G(\bar{1},1') \quad (14)$$

$$= I(1,1';-\infty) \equiv I(1,1';t_0) + I^{\text{IC}}(1,1') \quad (15)$$

Here $1 = (\mathbf{r}_1, s_1, t_1)$, V is a general interaction potential, and the third argument of I explicitly denotes the initial moment of the time evolution. When the evolution starts at $-\infty$, the system is assumed to be uncorrelated initially and, due to collisions, correlations are being build up until, at a finite time t_0 , they reach a value $c(t_0)$. This can be real dynamics driven by an external excitation. Alternatively, if one is interested in a correlated initial state, the evolution from $-\infty$ to t_0 can be generated “artificially” by adiabatically switching on the interaction, starting from an uncorrelated state, for example, ref. [28], or via including an imaginary track into the Keldysh contour, for example, refs. [45,49]. Even though the start of the dynamics is, in practice, set to a finite value, $-\infty \rightarrow t_-$ with $c(t_-) = 0$, both scenarios involve a time integration over the past in the r.h.s. of Equation (14) which is computationally costly, in particular for long propagation times.

This expensive time integration from t_- to t_0 can, in fact, be avoided in many cases^[56,71] as we show now. The r.h.s. of Equation (15) indicates that the collision integral can be identically rewritten as a scattering integral I , in which the evolution starts at t_0 , plus an additional collision integral I^{IC} that contains the initial correlations $c(t_0)$, for a detailed discussion, see ref. [72]. In that reference explicit results for a homogeneous system were given. Using the momentum representation (plane wave basis) the additional collision integral becomes, for second order Born selfenergy (the extension to the T-matrix approximation was presented in ref. [69]),

$$I_{p_1}^{\text{IC,2B}}(t, t') = -2i\hbar^5 V_0 \sum_{p_2 \bar{p}_1 \bar{p}_2} V_{p_1 - \bar{p}_1} \delta_{p_1 + p_2, \bar{p}_1 + \bar{p}_2} \times G_{\bar{p}_1}^R(t, t_0) G_{\bar{p}_2}^R(t, t_0) c_{\bar{p}_1, \bar{p}_2; p_1, p_2}(t_0) G_{\bar{p}_1}^A(t_0, t') G_{\bar{p}_2}^A(t_0, t') \quad (16)$$

where V_0 is the volume. This is the first crucial step and one realizes that Equation (16) does, indeed, not contain a time integral. The second important step is to derive the initial correlation function $c(t_0)$. This is done by going back to the connection between the two-particle Green function and the selfenergy, Equation (14), and to specialize this to the desired time moment, $t = t' \rightarrow t_0$. This leads to the following general relation

$$I_{p_1}^{\text{IC}}(t_0, t_0) = -2i\hbar V_0 \sum_{p_2 \bar{p}_1 \bar{p}_2} V_{p_1 - \bar{p}_1} \delta_{p_1 + p_2, \bar{p}_1 + \bar{p}_2} \times c_{\bar{p}_1, \bar{p}_2; p_1, p_2}(t_0) = \int_{t_-}^{t_0} d\bar{t} \left\{ \Sigma_{p_1}^>(t_0, \bar{t}) G_{p_1}^<(\bar{t}, t_0) - \Sigma_{p_1}^<(t_0, \bar{t}) G_{p_1}^>(\bar{t}, t_0) \right\} \quad (17)$$

which constitutes an equation for the matrix $c(t_0)$ in terms of the selfenergy and the correlation functions built up from the uncorrelated state at t_- . An explicit result for $c(t_0)$ can be obtained for direct second order Born selfenergies (first 2B diagram in Figure 2), for $\bar{p}_1 + \bar{p}_2 = p_1 + p_2$ (the other matrix elements are equal to zero),

$$c_{\bar{p}_1, \bar{p}_2; p_1, p_2}^{\text{2B}}(t_0) = \frac{i\hbar}{V_0} \int_{t_-}^{t_0} d\bar{t} V_{p_1 - \bar{p}_1} \times \left\{ G_{\bar{p}_1}^>(t_0, \bar{t}) G_{\bar{p}_2}^>(t_0, \bar{t}) G_{\bar{p}_1}^<(\bar{t}, t_0) G_{\bar{p}_2}^<(\bar{t}, t_0) - (>\leftrightarrow<) \right\} \quad (18)$$

which was presented in ref. [72] for the general case of NEGF propagation in the two-time plane.

Expression (18) is immediately rewritten for the case of propagation along the time diagonal within the GKBA scheme, cf. Section 3.3, by replacing the functions G^{\lessgtr} via (12),

$$c_{\bar{p}_1, \bar{p}_2, p_1, p_2}^{2B, GKBA}(t_0) = \frac{i\hbar}{V_0} \int_{t_-}^{t_0} d\bar{t} V_{p_1 - \bar{p}_1} \times G_{\bar{p}_1}^R(t_0, \bar{t}) G_{\bar{p}_2}^R(t_0, \bar{t}) G_{p_1}^A(\bar{t}, t_0) G_{p_2}^A(\bar{t}, t_0) \times \left\{ f_{p_1}^>(t_0) f_{p_2}^>(t_0) f_{p_1}^<(t_0) f_{p_2}^<(t_0) - \langle \leftrightarrow \rangle \right\} \quad (19)$$

where $f^>(t_0)$ is the Wigner function of the initial state, and $f^< = 1 \pm f^>$. If HF propagators are chosen this agrees with the result of ref. [71], but improved propagators can also be used, as was discussed in Section 3.3. Since the distribution functions are taken at a fixed time, the time integral in Equation (19) involves only the propagators. For HF propagators it can be done analytically whereas for more complicated propagators numerical integration remains to be done, but only once, prior to the start of the time propagation.

Another approach is to derive $c(t)$, Equation (18), from the Bethe-Salpeter equation for $G^{(2)}$. For any choice of the selfenergy $\Sigma(G)$ it is, in principle, possible to find the functional $G^{(2)}[G]$, as was explicitly demonstrated for the Born approximation in ref. [73]. With the GKBA this also provides the result for $c^{GKBA}(t_0)$, Equation (19). In fact, the result for $c^{GKBA}(t_0)$ with HF propagators does not require NEGF input at all. It follows directly from density operator theory within the single-time BBGKY-hierarchy where it has been computed for a variety of many-particle approximations including second order Born, T-matrix^[38,69] or GW approximation.^[34]

Finally we note that this approach of computing the quantum dynamics within the two-time NEGF or single-time GKBA scheme by starting from a correlated state at a finite time t_0 has another important application. Indeed, the pair correlation $c(t_0)$ is not necessarily that of the ground state or the equilibrium state, but it is arbitrary, as long as it fulfills condition (17) as was shown in ref. [72]. For example, it can be the correlations that have been built up during a previous real dynamics, for $t \leq t_0$, and which can be used to restart (continue) the evolution, for $t \geq t_0$, cf. ref. [72]. This is possible in cases when a unique solution of Equation (17) for the entire matrix of c exists.

3.5. NEGF-Ehrenfest Approach to Ion Stopping

Let us now come back to the problem of ion stopping and the associated electronic correlation effects in finite graphene-type clusters that we discussed above in Sections 1 and 2. For the numerical analysis, we use the Kadanoff–Baym Equations (3) with the electronic hamiltonian (1). The impacting ion acts as a time-dependent external attractive potential for all electrons. This potential is sharply peaked as a function of time, reaching its maximum (negative) value when the projectile traverses the honeycomb layer. The energy loss of the ion is treated classically via solution of Newton's equation (Ehrenfest dynamics). Processes of charge transfer between target and projectile which

are important at low impact velocities will be considered separately, in Section 5.

From the NEGF all time-dependent single-particle observables can be computed according to

$$\langle \hat{A} \rangle(t) = -i\hbar \sum_{ij} A_{ij} G_{ji}^<(t, t) \quad (20)$$

including the single-particle energy and the site-resolved density, $n_{i\sigma} = \langle \hat{n}_{i\sigma}(t) \rangle$. Another important quantity is the time-resolved photoemission spectrum^[74]

$$A^<(\omega, T) = -i\hbar \sum_i \int dt dt' S_{\kappa}(t - T) S_{\kappa}(t' - T) \times e^{-i\omega(t-t')} G_{ii}^<(t, t') \quad (21)$$

which measures the occupied states of the system. It allows for a direct comparison with time-resolved (pump-probe) photoemission experiments where S_{κ} mimicks a Gaussian probe pulse of width κ ,

$$S_{\kappa}(t) = \frac{1}{\kappa\sqrt{2\pi}} \exp\left(-\frac{t^2}{2\kappa^2}\right)$$

The energy exchange between projectile and the cluster can be computed from the increase of the total energy of the electrons or, equivalently, from the energy loss of the projectile,

$$S_e = m_p \frac{\dot{r}_p^2(t \rightarrow +\infty)}{2} - m_p \frac{\dot{r}_p^2(t \rightarrow -\infty)}{2} \quad (22)$$

which is just the difference of kinetic energies far away from the target before and after the impact. With this we assume that the interaction between different projectiles or with a surrounding plasma medium is negligible. Further, we do not resolve internal degrees of freedom of the projectile. Also two-particle expectation values such as the correlation energy and the double occupation d_i are accessible in the NEGF approach taking advantage of the two-time information in G and Σ . Thus we compute the expectation value of the site-resolve doublon number, its cluster-average and the long-time limit of the latter, after passing of the projectile, according to

$$d_i(t) = \langle \hat{n}_{i\uparrow}(t) \hat{n}_{i\downarrow}(t) \rangle = -\frac{i\hbar}{U} \sum_k \int_C ds \Sigma_{ik}(t, s) G_{ki}(s, t) \quad (23)$$

$$d_{av}(t) = \frac{1}{L} \sum_{i=1}^L d_i(t), \quad d_{av}^{\infty} = \lim_{t \rightarrow \infty} \frac{1}{\Delta t} \int_t^{t+\Delta t} d\bar{t} d_{av}(\bar{t}) \quad (24)$$

4. Results

We now turn to the results for the time-resolved coupled electron-projectile dynamics. A detailed investigation has been

presented in refs. [30,75] some results of which are briefly summarized here and complemented with additional data. For small clusters, $L \leq 12$, we have performed exact diagonalization calculations whereas for larger systems we solved the Keldysh–Kadanoff–Baym Equation (3) for the NEGF. In the latter case the accuracy of the results is determined by the choice of the selfenergy Σ . In this article, we present simulations within the second order Born approximation using the HF-GKBA, cf. Section 3.3 and selected data with more advanced selfenergies that were introduced in Section 3.2. Prior to the NEGF simulations we have performed detailed numerical convergence tests that include particle number and energy conservation^[51] and time reversibility.^[76,77] In addition, for small systems we have performed tests against exact diagonalization calculations. Further tests of the present code (T-matrix selfenergy) include comparisons with cold atom experiments^[25] where excellent agreement was found. Finally we mention extensive benchmarks against density matrix renormalization group (DMRG) calculations,^[26] a typical example – for the GKBA – was shown above in Figure 3. An important outcome of the benchmarks of ref. [26] was that the exact result is often enclosed between the two-time simulations and the HF-GKBA. From this we can conclude that the present NEGF stopping simulations are reliable and have predictive power.

4.1. Energy Loss of the Projectile

Let us start with the total energy loss of the projectile, Equation (22), as a function of impact energy which is shown in **Figure 4**, for the case of a proton. The overall behavior is well-known: the energy loss vanishes, both, for very low and very high impact energies. An optimum projectile-target interaction is observed at intermediate impact energies, in the range of several keV per mass unit u . The decrease at large energies is due to the reduced interaction duration and is consistent with the standard non-relativistic Bethe formula, for example, ref. [3], and with linear response treatments (based on the density–density correlations and dynamic structure factor). Not surprisingly, here correlations in the material have very little influence which can be seen in the convergence of the curves for different U . In the opposite limit, the energy available for transfer to the target is small. At the same time, in the range left of the maximum the influence of the target properties on the energy loss is significant: here the curves for different coupling strength U differ significantly.

This overall trend of the energy loss (stopping power) is well reproduced with our NEGF simulations, and the results agree well with other approaches, such as TDDFT and the SRIM code, at high energies. On the other hand, in the low energy range the situation is less clear. One reason is that, previously, most attention focused on high-energy particle beams or hot plasmas. Only more recently low projectile energies in the range of several hundred or tens of eV attracted interest because this is the typical energy range in low-temperature plasmas and surface physics, for example, ref. [2]. In this range, correlation effects in the target (the value of U/J in our model) play a crucial role, and also size and geometry effects are expected to be relevant. The influence of system size is clearly seen in our simulations, compare parts (a)

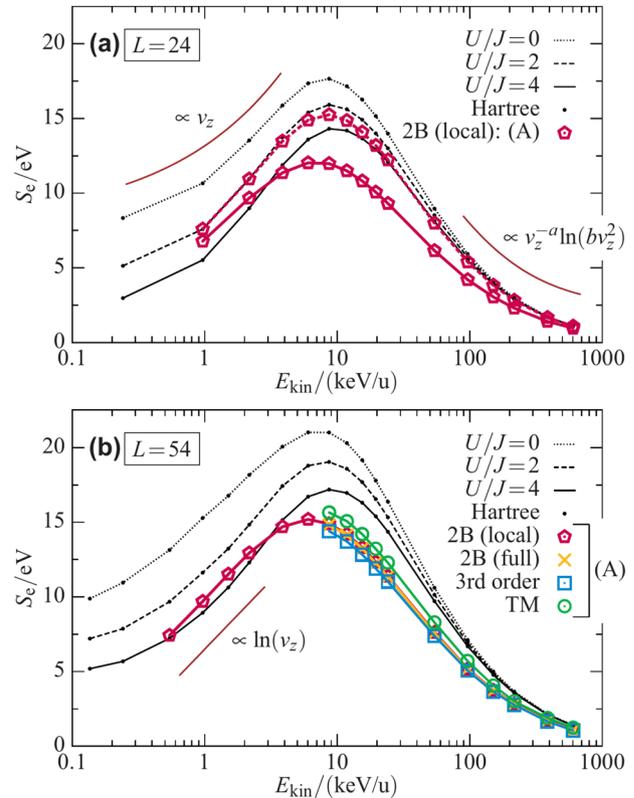


Figure 4. Energy loss of a proton with initial energy E_{kin} during passage through a honeycomb cluster [cf. Figure 1] of size $L = 24$ (top) and $L = 54$ (bottom). Local 2B denotes the local approximation for the second Born selfenergy ($\Sigma_{ij} = \delta_{ij}\Sigma_i$). Reproduced with permission.^[29] Copyright 2016, American Physical Society.

and (b) of Figure 4: with increasing size of the cluster more electrons are excited by the projectile and, hence, the energy deposition, S_e , grows.

With the increasing role of correlations, also the requirements for theory increase. For NEGF simulations, this means that the proper choice of the selfenergy becomes important, whereas, at high impact energy, the difference between different selfenergy approximations is rather small, cf. Figure 4(b). At the same time, reducing the impact energy increases the interaction time and, thus, also the simulation duration in our nonequilibrium approach grows rapidly. For this reason, in the range of $1\text{keV}/u$ and below, so far, mostly local second order Born simulations (assuming $\Sigma_{ij} \sim \Sigma_i\delta_{ij}$) were performed. A comparison to mean field (Hartree) simulations clearly signals the importance of correlations for the stopping for strongly correlated materials, cf. curves for $U/J = 4$ in Figure 4(a).

4.2. Ion Impact Induced Doublon Excitation

A particularly interesting observation is that the deviation of the correlated simulations from the mean field result changes sign. While for high energy, correlations seem to lower the energy deposition, at impact energies below approximately $3\text{keV}/u$, correlation effects enhance the stopping power. This is a

surprising effect, and one may speculate that this is due to an increase of the correlation energy. To verify this hypothesis we analyze, in the following, the doublon number, Equation (23), that is induced by the projectile. In fact, the total number of doublons or its cluster average, d_{av} , Equation (24), minus the mean field result,

$$d_i^H = \langle \hat{n}_{i\uparrow}(t) \rangle \langle \hat{n}_{i\downarrow}(t) \rangle = n_{i\uparrow}(t)n_{i\downarrow}(t) \quad (25)$$

is proportional to the correlation energy in the system.

The numerical analysis for the system in Figure 1 confirms, indeed, that a charged projectile with an impact energy in the range of a few hundred electron volts may create a significant number of doublons.^[30] Details of this analysis are shown in **Figure 5** for the case of strong correlations ($U/J = 10$). In part (a), we show the electron densities at two lattice sites B and A adjacent to the impact point. During the impact of the projectile ($t = t_0$) electrons from the second nearest site (A) are attracted toward the nearest site B whereas the mean density remains constant. After the projectile has left, both densities, with some retardation, return to their initial values. Consider now the associated dynamics of the mean double occupations at sites A and B. While here, too, doublons are transferred from site A to B, the mean value, d_{av} increases significantly. Most importantly, after the projectile has left, d_{av} does not return to its initial value but remains at a significantly larger value. We conclude that the projectile has deposited correlation energy in the system that remains stored there. This is also confirmed by comparison with the uncorrelated average doublon number, Equation (25), which follows the average density and, hence, remains almost constant. In a quantum-mechanical language, under the action of the projectile, the electron system undergoes a transition to an excited state that is associated with a higher double occupation.^[30] This explanation is directly confirmed by a representative dimer model that is discussed in Section 4.3.

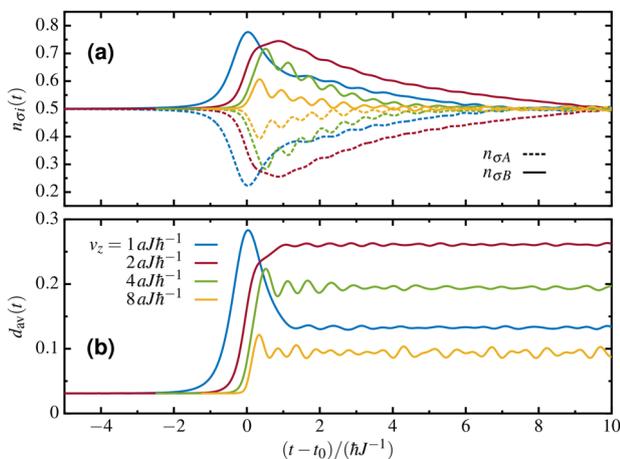


Figure 5. Time-dependent response of a strongly correlated finite honeycomb cluster of Figure 1 for $U/J = 10$ to a charged projectile with charge $Z = 2$ penetrating through the center (point C in Figure 1). a) The densities on sites A (dashed line) and B (full) closest to the projectile. b) Site-averaged double occupation, Equation (24). Exact diagonalization results, after ref. [30].

4.3. Analytical Dimer Model

For a qualitative examination of the doublon generation in the system of Figure 1, the simplest possible setup is a dimer consisting of only the two sites, A and B, being driven by a pulsed attractive external potential. Since we expect that the excitation of doublons is governed only by the potential difference on sites A and B, it is sufficient to consider the excitation only on one site (B). The time dependence of the excitation is chosen as

$$W(t) = -W_0 \exp^{-(t-t_0)^2/2\tau^2} \quad (26)$$

which closely resembles a positively charged projectile passing close to one site, where the two parameters W_0 and τ have clear implication as the amplitude (proportional to the charge of the ion) and the interaction duration (proportional to one over the velocity), respectively. For sufficiently large U this can lead to a significant and lasting increase of the mean double occupation d_{av}^∞ , Equation (24). However d_{av}^∞ strongly depends on W_0 and τ , as is confirmed by exact diagonalization results that are shown in **Figure 6**. For an excitation amplitude W_0 smaller than U , the Hubbard-gap prevents the creation of doublons. For $W_0 > U$ doublon production is possible, and for larger W_0 , oscillations caused by transient Bloch oscillations are observed,^[30] the frequency of which grows with W_0 . Interestingly, the envelopes of these curves are very similar to the stopping-power curves, cf. Figure 4. There the total energy gain of the electrons was plotted versus kinetic energy of the projectile which here corresponds to the inverse of τ^2 . The results of Figure 6 reflect the fraction of the projectile energy that is transferred into an increase of the double occupation in the target, and a detailed analysis of the different energy contributions remains to be performed in future work. The most notable result is, that for an optimal choice of τ and W_0 a permanent increase of the double occupation of up to 0.5 per site can be achieved.

We have shown in ref. [30] that the dimer model captures the excitation physics not only qualitatively correctly. Using a Landau-Zener^[78,79] approach the probability for doublon excitation of our model agrees even semi-quantitatively with

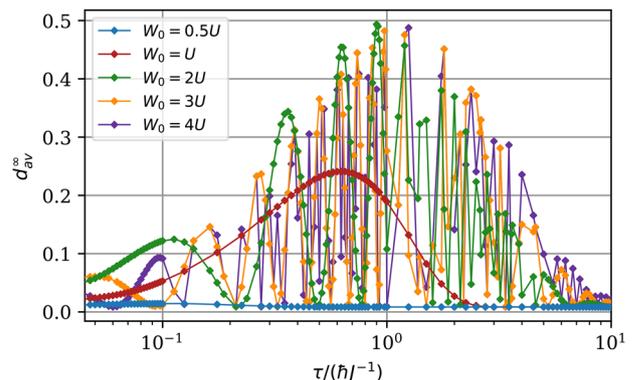


Figure 6. Asymptotic value of the average double occupation, Equation (24), of the dimer versus τ (proportional to the inverse projectile velocity) for $U = 15$ and different excitation amplitudes, W_0 . When W_0 exceeds U , doublons are excited and remain in the system.

the simulation results for the $L=12$ cluster of Figure 1 and shows the correct trends also for other systems, including the optimal coupling strength and projectile velocity that maximize the induced doublon number.

4.4. Doublon Dynamics Excited by Multiple Ion Impacts

The average doublon number in the system can be further increased by repeating the impact once or even more often. The analysis presented in ref. [30] showed that this allows to achieve an asymptotic average doublon number of $d_{av}^{\infty} = 0.25$ and even larger. A representative example is shown in Figure 7. At each impact the projectile rapidly increases d_i at the impact point, at the expense of the doublon number at the two nearest neighbor sites. This is followed by a spreading of $d_i(t)$ along the chain (notice the wave fronts). At the same time, with each successive impact, the average doublon number can be systematically increased which can be seen from the increasing doublon level in the foreground. In that figure the excitation is intentionally kept localized at the same central site [keeping only a single term in the sum over “ i ” in Equation (1)] in order to monitor the propagation of the doublon occupation along the cluster. Note that, when one restores the long-range ion–electron interaction (all terms in the sum over “ i ”), this gives rise to even larger values of d_{av}^{∞} .^[30]

The ion induced nonequilibrium dynamics of the electron system can also be tracked in the spectral function which can be directly measured in photoemission experiments. In Figure 8 we plot the photoemission spectrum, Equation (21), that gives information about the occupied energies. The projectiles induce transitions of electrons into the upper Hubbard band corresponding to $\omega > 0$. With each successive impact the spectral weight (corresponding to the fraction of electrons) in the upper Hubbard band grows, cf. the shaded areas.

As in the case of a single impact, Figure 5, also after multiple impacts, the many-electron system remains in the excited state characterized by a significantly increased average doublon occupation d_{av}^{∞} , after all projectiles have left. This stationary nonequilibrium state will be stable until additional dissipation

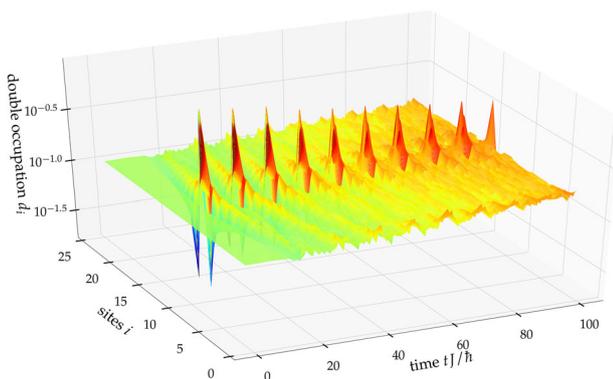


Figure 7. Time evolution of the site-resolved doublon number, $d_i(t)$, Equation (23), for a 1D cluster with $L = 24$ sites (periodic boundary conditions) and $U/J = 4$. The cluster is excited by ten ion impacts in the center (at site 12) using the Gaussian model (26). The increase of $d_{av}^{\infty}(t)$ can be seen from the slope of the surface. Note the logarithmic scale.

channels (e.g., to phononic degrees of freedom) set in and is another example of a pre-thermalized state, for example, refs. [80,81]. In contrast to previous spatially homogeneous doublon excitation scenarios that used time-dependent electric fields or a modulation of the lattice depth, for example, ref. [82], here a local excitation is used that has much more degrees of freedom, including timing and locations of the impacts, and a potential to achieve higher doublon numbers and an increased stopping power.

5. Embedding Scheme to Capture Charge Transfer Dynamics Between Projectile and Target

So far we have considered only the case of high projectile velocities where the feedback from the surface to the ion is small and restricted to a reduction of its velocity whereas quantum effects are neglected. On the other hand, when the impact velocity is reduced, the interaction duration of the projectile with the lattice increases and electron transfer between both systems may occur.

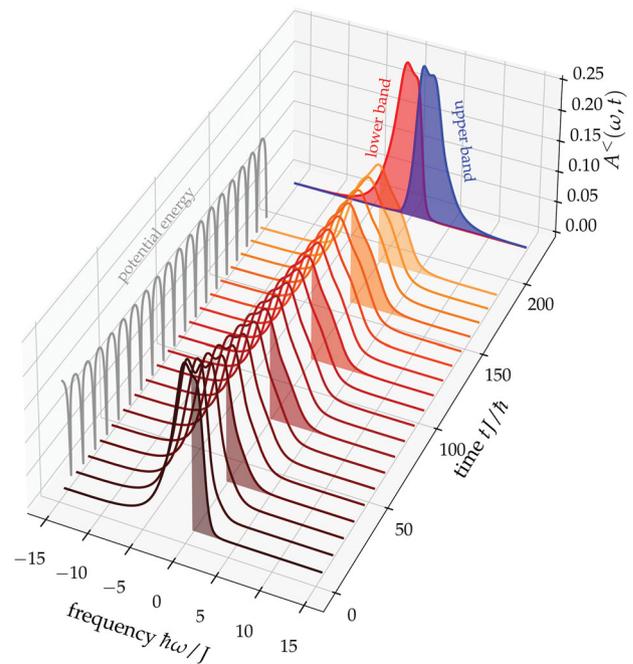


Figure 8. Time evolution of the spectral function of the occupied states, $A^<$ (photoemission spectrum), for the honeycomb cluster with $L = 12$ sites, Figure 1, and $U/J = 4$, from a two-time NEGF simulation with second order Born selfenergies. The cluster is excited by 20 equidistant ion impacts (at times 10, 20, ... 200) in the center using a Coulomb potential for the electron–projectile interaction, cf. Equation (1) and the grey line on the left. The projectiles lead to an increased occupation of the upper Hubbard band corresponding to $\omega > 0$, cf. the shaded areas. The spectra are shown at times 5, 15, ... 195 with a width of the probe pulse [cf. Equation (21)] of $\kappa = 2.5\hbar/J$ which causes a spectral broadening. For comparison, we also present the results of an unexcited cluster, where only the lower Hubbard band is occupied, depicted by the red filled area corresponding to $A^<$, whereas the unoccupied upper Hubbard band ($A^>$) is shown by the blue area.

Quantum transitions inside the projectile and charge transfer have been studied approximately with quantum kinetic models (Newns-Anderson model) where the projectile was treated as a few level system.^[83] Furthermore, there have been a number of TDDFT studies of ions impinging onto correlated materials such as graphene or boron nitride (BN)^[7,8] and on finite systems such as metal clusters,^[84,85] carbon nanostructures,^[86] or graphene fragments^[87] (for more references see ref. [2]), where quantum transitions inside the projectile are taken into account. However, the uncertainties in the quality of the adiabatic LDA and the model parameters in the Newns-Anderson model, respectively, as well as the neglect of correlation effects in the material^[2] make it desirable to develop an independent many-body approach to this problem.

Here, we present a nonequilibrium Green functions approach for the electron transfer dynamics between projectile and a strongly correlated solid. We start from the second-quantized many-body Hamiltonian for the electrons in the plasma–solid interface and separate the system into a plasma (p) and solid surface part (s) [we denote $\Omega = \{p, s\}$ and do not write the spin index explicitly],

$$H_{\text{interface}} = \sum_{a\beta \in \Omega} \sum_{ij} H_{ij}^{a\beta}(t) c_i^{a\dagger} c_j^\beta + \frac{1}{2} \sum_{a\beta\gamma\delta \in \Omega} \sum_{ijkl} W_{ijkl}^{a\beta\gamma\delta} c_i^{a\dagger} c_j^{\beta\dagger} c_k^\gamma c_l^\delta \quad (27)$$

Here, the operator $c_i^{a\dagger}$ (c_i^a) creates (annihilates) an electron in the state i of part a . The one-particle Hamiltonian $H(t)$ contains the kinetic and the time-dependent potential energy of electrons, and W accounts for all possible electron–electron Coulomb interactions within and between the two parts.

Considering individual energetic plasma ions, which penetrate into the solid, undergo scattering and stopping in the surface layers or are reflected, we describe the system (27) by a one-particle nonequilibrium Green function (2), $G_{ij}^{a\beta}(t, t')$, which now has an additional 2×2 matrix structure ($\alpha, \beta = \{p, s\}$),

$$G_{ij}^{a\beta}(t, t') = -i\hbar \langle T_C c_i^a(t) c_j^{\beta\dagger}(t') \rangle \quad (28)$$

$$\rho_{ij}^{a\beta}(t) = -i\hbar G_{ji}^{\beta a}(t, t^+) \quad (29)$$

for example, refs. [45,88], and the time-diagonal elements provide the density matrix (29). The diagonal elements, ρ_{ij}^{pp} [ρ_{ij}^{ss}], refer to the plasma part, describing the dynamics of free electrons and electrons bound in the ion [to the solid part, describing electrons in bound states of the solid surface]. Moreover, the density matrix component ρ_{ij}^{ps} is related to charge transfer processes between plasma and solid and will be of special interest in the following.

The equations of motion for the NEGF are the generalization of Equation (3) to the plasma–solid interface,

$$i\hbar \partial_t G_{ij}^{a\beta}(t, t') - \sum_{\delta \in \Omega, k} H_{ik}^{a\delta}(t) G_{kj}^{\delta\beta}(t, t') = \delta_{ij}^{a\beta} \delta_C(t, t') + \sum_{\delta \in \Omega, k} \int_C d\bar{t} \Sigma_{ik}^{a\delta}[W, G](t, \bar{t}) G_{kj}^{\delta\beta}(\bar{t}, t') \quad (30)$$

where the self-energy $\Sigma^{a\beta}(t, t')$ describes the interaction between the electrons and with phonons. Even though a complete solution of the KBE (30) for real materials and with a full quantum treatment of the plasma electrons is out of reach, these equations provide the rigorous starting point for the development of consistent approximations. In the following, we show how it is possible to include the electronic states of the ion via an embedding self-energy approach that was previously applied to quantum transport and photoionization problems, for example, refs. [89,90], for a text book discussion, see ref. [45]. Here the embedding approach allows us to study resonant (neutralization and ionization) processes at the plasma–solid interface. While this embedding approach is based on a formal decoupling of the surface and plasma parts of the KBE, it retains one-electron charge transfer in the Hamiltonian H^{sp} , cf. Equation (33), see below. A closed description of the solid can be maintained if correlations in the plasma part and the feedback of the solid on the plasma can be neglected, that is, for $\Sigma^{sp} \approx \Sigma^{pp} \approx 0$. This is usually well fulfilled in plasmas, except for plasmas at or beyond atmospheric pressure or in warm dense matter^[91] where small correlation corrections should be taken into account. Then, the KBE (3) for the plasma part simplifies to

$$\sum_k \{i\hbar \partial_t \delta_{ik} - H_{ik}^{pp}(t)\} g_{kj}^{pp}(t, t') = \delta_{ij} \delta_C(t, t') \quad (31)$$

where the solution $g^{pp}(t, t')$ denotes the NEGF of the electrons inside the plasma ions [here we do not consider processes involving free electrons in the plasma phase because they do not contribute to charge transfer except for heavy particle induced secondary electron emission], whereas the time dependence of $H^{pp}(t)$ accounts for possible parametric changes of the energy levels (e.g., as function of the distance of the ion from the surface).

The main result of the embedding procedure is a closed equation for $G^{ss}(t, t')$:

$$\sum_k \{i\hbar \partial_t \delta_{ik} - H_{ik}^{ss}(t)\} G_{kj}^{ss}(t, t') = \delta_{ij} \delta_C(t, t') + \sum_k \int_C d\bar{t} \{ \Sigma_{ik}^{ct}(t, \bar{t}) + \Sigma_{ik}^{ss}[G^{ss}](t, \bar{t}) \} G_{kj}^{ss}(\bar{t}, t') \quad (32)$$

to be complemented with the adjoint equation, with the charge transfer (or embedding) self-energy that involves the charge transfer hamiltonian

$$\Sigma_{ij}^{ct}(t, t') = \sum_{kl} H_{ik}^{sp}(t) g_{kl}^{pp}(t, t') H_{lj}^{ps}(t') \quad (33)$$

$$H_{ij}^{sp}(t) = \int d^3r \phi_i^s(\mathbf{r}) (\hat{T} + \hat{V}) \phi_j^p(\mathbf{r}; t) \quad (34)$$

Equation (32) shows how the many-body description of an isolated (but correlated) solid is altered by the presence of the electronic states of a plasma ion (or neutral), with the latter giving rise to an additional self-energy $\Sigma^{ct}(t, t')$. While, for $\Sigma^{ct} = 0$, the KBE (32) conserve the particle number and total energy [for a conserving approximation of the self-energy Σ^{ss} ,

such as the ones discussed in Section 3.2], the inclusion of the embedding self-energy explicitly allows for time-dependent changes of the particle number (and energy) in the solid and, thus, accounts for ion charging and neutralization effects. For the practical solution of Equation (32), the charge transfer Hamiltonian $H^{sp}(t)$ has to be computed by selecting the relevant electronic transitions between solid and plasma and computing the matrix elements of the kinetic and potential energy operators \hat{T} and \hat{V} , with the electronic single-particle wave functions ϕ^s (ϕ^p) in the solid (ion).

A first test of this embedding scheme is shown in **Figure 9**, where a correlated Hubbard chain (for simplicity only the last site is correlated) is coupled to a single active energy level $\epsilon_p = J$ of an approaching ion *via* the charge transfer hamiltonian $H_i^{sp}(t) = \delta_{iL}\Gamma(t)$, cf. the sketch on top of Figure 9. The time dependence of H_i^{sp} is approximated by $\Gamma(t) = \Gamma_0 e^{-(t-t_0)^2/(2\tau^2)}$,

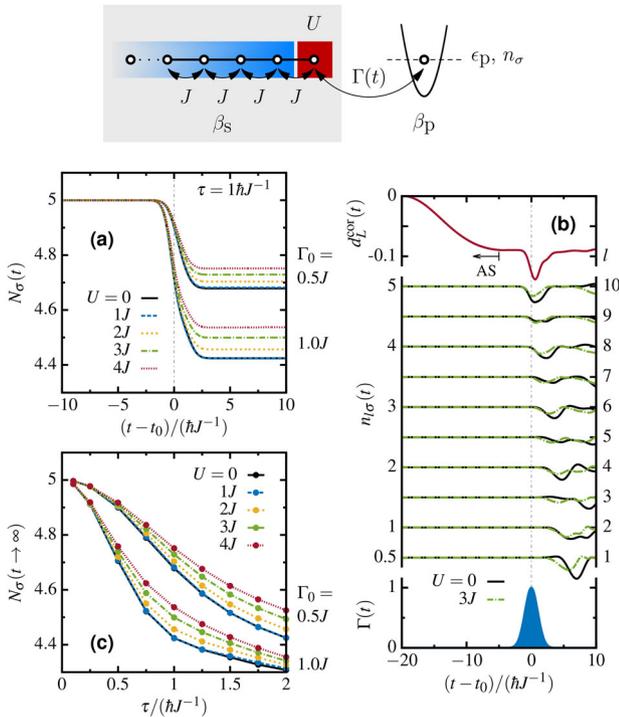


Figure 9. Numerical illustration of the embedding scheme. An initially half-filled tight-binding chain ($L = 10$ sites, nearest-neighbor hopping J , Hubbard interaction strength U on the last site, and inverse temperature $\beta_s = 100J^{-1}$) is interacting with an external energy level $\epsilon_p = J$ via a time-dependent coupling $\Gamma(t) = \Gamma_0 e^{-(t-t_0)^2/(2\tau^2)}$, cf. bottom of part (b), giving rise to the transfer of charge. The initial occupation of the energy level is given by $n_\sigma = 0.269$ (corresponding to a Fermi distribution with an inverse temperature $\beta_p = 1J^{-1}$). a) Time evolution of the total particle number $N_\sigma(t)$ for different U and Γ_0 , computed from Equation (32) with a local second Born self-energy ($\Sigma_{ij} = \delta_{ij}\Sigma_i$); $\tau = 1\hbar J^{-1}$. b) Local electron densities $n_{\sigma l}(t)$ and correlation part of the double occupation $d_L^{cor}(t) = d_L(t) - d_L^H(t)$ on the last site $l = L = 10$ for $U = 3, \Gamma_0 = 1J$ and $\tau = 1\hbar J^{-1}$; for times $t - t_0 \lesssim -5$ the time evolution of $d_L^{cor}(t)$ corresponds to the ground state preparation by adiabatic switching (AS). c) Final values of the particle number $N_\sigma(t \rightarrow \infty)$ as function of the interaction time τ for different U and Γ_0 .

and the initial occupation of the energy level ϵ_p is set to $n_\sigma = 0.269$.

The charge transfer from the chain to the ion, seen in the reduction of the total electron number in the chain, $N_\sigma(t) = \sum_i n_{i\sigma}(t)$, is shown as a function of time in Figure 9 (a). The reduction of N_σ is found to be nearly proportional to the ion charge (amplitude Γ_0) up to the resonance condition $\Gamma_0 = J$. Thus, as expected, a highly charged ion will be more strongly neutralized. For $\Gamma_0 > J$, away from resonance, the net transfer of charge will decrease again. The neutralization time is given by the interaction duration τ which is inversely proportional to the projectile velocity. The dependence of the magnitude of the charge transfer on τ is analyzed in Figure 9(c) and again confirms the expected trend: the charge transfer increases with τ , i.e., is larger for slower projectiles, whereas for $\tau \lesssim 0.1\hbar/J$ it is negligible. Figure 9(b) shows the spatial propagation of the removed charge (hole) along the chain as a function of time (the distortion of the dip is due to reflections from the edge of the chain). Again one sees that, in the presence of correlations, the propagation speed is reduced, in agreement with simulations of fermion propagation in optical lattices.^[24,25]

Finally, we can analyze the effect of correlations in the target on the charge transfer. As can be seen in Figure 9(a) and (c), an increase of electron–electron correlations reduces the charge transfer, which is a consequence of the reduced mobility of the electrons in the chain. An increase of the interaction strength from zero to $U = 4/J$, which is a realistic range for graphene nanoribbons, reduces the charge transfer by about 20%, in the present setup.

In conclusion, we have demonstrated a NEGF approach to charge transfer between a plasma ion and a strongly correlated finite electron system. The next task is to derive improved data for the energy levels and occupations of the projectile. Further, the resonant charge transfer, studied in this section, and the energy deposition and electronic excitation of the target that were discussed in Section 4, should be integrated into a single model to take into account the mutual influences of both processes.

6. Summary and Discussion

In this article, we studied correlated inhomogeneous finite graphene-type Hubbard clusters. Our results are expected to be relevant for ultracold fermionic atoms in optical lattices as well as for electrons in graphene clusters and nanoribbons. We considered the electronic response to a spatially and temporally localized excitation by a charged particle. Using a nonequilibrium Green functions approach we computed, via an Ehrenfest approach, the time-dependent interaction of the projectile with the many-electron system and the dependence of the energy transfer on the impact energy.^[29] An interesting observation was that, at low projectile energies, correlation effects lead to an enhanced energy transfer. Our analysis revealed that the ion impact causes a transition of the system across the Hubbard gap leading to the formation of doubly occupied lattice sites (doublons).^[30] We investigated the spatial propagation of the doublon number across the cluster. Eventually a homogeneous nonequilibrium steady state is reached that is long lived and may

have interesting electronic and optical properties. A physically intuitive picture was given in terms of an analytical model for a two-site system where the doublon formation is explained in terms of a twofold passage of an avoided crossing (Landau-Zener picture^[30]). The effect should be of relevance for graphene nanoribbons and be particularly important for strongly correlated finite systems. For an experimental observation the best candidates are fermionic atoms in optical lattices. There the projectile impact can be easily mimicked by a proper time-dependent modulation of the lattice potentials nearest to the “impact” point.

We demonstrated that doublon formation and propagation in correlated finite lattice systems can be accurately simulated with NEGF. In addition to two-time results we presented single-time results within the generalized Kadanoff–Baym ansatz (GKBA) with Hartree–Fock propagators (HF-GKBA). To further improve the accuracy of GKBA calculations in the future, we introduced the correlated GKBA (C-GKBA) that allows to systematically incorporate correlation effects in the propagators $G^{R/A}$. Moreover, we discussed how to systematically take into account initial correlations in the GKBA and presented an idea that is complementary to recent results for equilibrium correlations.^[67,71]

Aside from an accurate treatment of correlation effects, quantitatively reliable NEGF results also require to improve the underlying model. One way to go beyond the present one-band Hubbard model is to use an extended Hubbard model as demonstrated in ref. [31], or to perform ab initio NEGF simulations using a Kohn–Sham basis, for example, on the basis of the Yambo code.^[92]

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Conflict of Interest

The authors declare no conflict of interest.

Keywords

correlated dynamics, doublon dynamics, graphene nanoribbons, Hubbard model, ion stopping, nonequilibrium Green function

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