

## An average stochastic approach to two-body dissipation in finite fermion systems

Lionel Lacombe, Eric Suraud, Paul-Gerhard Reinhard, Phuong Mai Dinh

### ► To cite this version:

Lionel Lacombe, Eric Suraud, Paul-Gerhard Reinhard, Phuong Mai Dinh. An average stochastic approach to two-body dissipation in finite fermion systems. Annals of Physics, 2019, 406, pp.233-256. 10.1016/j.aop.2018.10.009 . hal-02290929

## HAL Id: hal-02290929 https://hal.science/hal-02290929

Submitted on 25 Oct 2021

**HAL** is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers. L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.



Distributed under a Creative Commons Attribution - NonCommercial 4.0 International License

## An average stochastic approach to two-body dissipation in finite fermion systems

L. Lacombe

Laboratoire de Physique Théorique, Université de Toulouse, CNRS, UPS, France Hunter College, CUNY, New York, NY 10065 USA

E. Suraud

Laboratoire de Physique Théorique, Université de Toulouse, CNRS, UPS, France

P.-G. Reinhard

Institut für Theoretische Physik, Universität Erlangen, Staudtstraße 7, D-91058 Erlangen, Germany

P. M.  $Dinh^1$ 

Laboratoire de Physique Théorique, Université de Toulouse, CNRS, UPS, France

#### Abstract

We present average stochastic time-dependent Hartree-Fock (ASTDHF) as a theory for efficient handling of incoherent dynamical correlations in finite fermion systems at fully quantum-mechanical level. The basic time evolution is given by time-dependent mean-field theory. The two-body collisions beyond mean-field propagation are evaluated stochastically in an incoherent ensemble of mean-field states as was done in the previously developed STDHF. The new, and time saving, feature in ASTDHF is that it employs one common mean field throughout the whole ensemble. A detailed presentation of ASTDHF is given and extensive comparison with STDHF and other approaches to dissipation are discussed. ASTDHF is found to be a very efficient approach for well bound systems where mean-field fluctuations remain small.

Keywords:

Preprint submitted to Annals of physics

July 20, 2019

<sup>&</sup>lt;sup>1</sup>corresponding author : dinh@irsamc.ups-tlse.fr

#### 1. Introduction

The topic of this paper is the theoretical description of dynamical correlations associated with dissipation in finite fermion systems in the dynamical regime of moderate excitation. The natural starting point for simulation of dynamical evolution are time-dependent mean-field models using effective energy-density functionals which are widely used in various areas, called Time-Dependent Hartree-Fock (TDHF) in nuclear physics [1, 2, 3] or Time-Dependent Local-Density Approximation (TDLDA) in electronic systems [4, 5]. These methods are well suited up to moderate system sizes and low excitation energies [6, 7, 8]. Such approaches do not include dissipative features which come into play at higher excitation and/or long simulation times. But dissipative effects can become important. They were observed, e.g., in excitation of clusters and molecules by intense laser fields [9, 10, 11, 12, 13], in the ballistic electron transport in nano-systems [14], but also in trapped Fermi gases in terms of thermalization pattern [15].

The theoretical description of dissipative features in many-body systems is a long standing question, even a field of research on its own, namely nonequilibrium statistical physics [16]. Well established strategies exist for bulk fermion systems [17, 18]. The case of finite fermion systems is much more demanding. Correspondingly, there do not yet exist fully convincing approaches treating dissipative features in finite fermion systems, especially when quantum features remain noticeable. There exists a couple of manageable schemes for simulating dynamical correlations which rely on semi-classical methods. They have been developed over the years and applied to various systems close to fermion liquids such as nuclei [19, 20, 21] and the electron cloud of metal clusters [22, 23]. However, such approaches are bound to sufficiently high excitation energies for which quantum shell effects become unimportant. At even higher energies, classical molecular dynamics [9] or rate equations [24] become applicable.

The truly challenging regime comes with lower excitation energies where quantum shell effects cannot be ignored. Meanwhile, there exist a few quantum mechanical approaches: dynamical correlations still semi-classically but on top of quantum mean field [25], the Time-Dependent Density Matrix approach [26, 27, 28], Multi Configurational Time-Dependent Hartree-Fock (MC-TDHF) [29], the time-dependent configuration-interaction method [30], and tests of the full many-body Schrödinger equation descriptions in schematic model systems [31]. All of these near exact methods are considerably expensive and not suited for large scale applications in realistic systems. More approximate, but manageable schemes have come up more recently. For example, dissipation has been effectively included in a relaxation time approximation [32, 33]. It employs relaxation rates optimized in bulk systems [23] and is applicable to systems with only moderate density variations (metal clusters, nuclei). In case of strong perturbation, the most versatile approach is Stochastic TDHF (STDHF) which describes a correlated many-body state as an incoherent ensemble of mean-field states (Slater states) [34, 21, 35]. The ensemble description gives access not only to dissipation but also to the fluctuations intimately related to dissipation [16]. The first practical implementations of STDHF came up only recently [36, 37] and proved that STDHF provides a reliable description of dissipation and fluctuations.

However, STDHF becomes increasingly expensive at lower excitation energies because the then lower collision rates require huge stochastic ensembles to attain statistically reliable predictions. On the other hand, this energy domain corresponds to a regime where mean field fluctuations remain small and can thus be safely ignored. This allows to reduce the ensemble of STDHF mean-fields hamiltonians to one average hamiltonian which reduces enormously the expense of propagation. This approximation is coined Average Stochastic TDHF (ASTDHF) and its first realization was presented briefly in [38]. The aim of the present paper is to provide a more detailed and comprehensive description of ASTDHF together with extensive comparisons between STDHF and ASTDHF, using again the 1D schematic model of a cluster/molecule along the line presented in [36, 37, 38]. We will see that ASTDHF has a strong connection to the old proposal of Extended TDHF (ETDHF) where the dynamical correlations are simply accounted for via a rate equation for occupation numbers added to mean-field propagation [39, 40]. Thus we will also compare ASTDHF with ETDHF and show that ASTDHF has a broader range of applicability.

The paper is organized as follows. Section 2 describes formal aspects and provides a detailed description of the ASTDHF approach to dynamical correlations. The reference theory is here STDHF which is briefly summarized. Section 2.6 provides technical details related to the numerical realization of ASTDHF. In section 3, we discuss ASTDHF in terms of a couple of illustrative examples. Comparisons between various levels of the theory are also shown, with STDHF as reference, ASTDHF as a basic approximation and ETDHF as the simplest version of a quantum-mechanical theory of dissipation in finite systems.

#### 2. The formal side of ASTDHF

#### 2.1. The idea behind ASTDHF

The acronym ASTDHF, standing for Average Stochastic Time-Dependent Hartree-Fock, carries information on the composition of this approach. TDHF stands for the underlying dynamical mean-field model which is, in practice, an effective mean-field model at the level of time-dependent density functional theory which is coined TDLDA (time-dependent local-density approximation) in electronic systems [41] but TDHF in nuclear context [1]. We use here TDHF for simplicity. STDHF goes beyond mean field as it aims to unfold progressively through a sequence of two-particle collisions a correlated many-body state in terms of an ensemble of Slater states. This ensemble is very general and can cover large fluctuations of the mean field. The full capabilities of STDHF thus require considerable computational expense and turn out to be overkilled in situations where mean-field fluctuations remain small. This is where ASTDHF comes into play which deals with a propagation along an average mean field which is obtained from averaging in each step the ensemble of (slightly) different fields produced by the two-body collisions generated by STDHF.

The two schemes, STDHF and ASTDHF, are sketched in Fig. 2.1. The meaning of each scheme will become fully clear only later on, when the figure is taken up again (see sections 2.5 and Appendix B.3). At the present stage, we concentrate on a general impression. Time propagates from the top to the bottom. The left side illustrates the propagation of the STDHF ensemble, each column labeled by an index  $\alpha$  and representing one member of this ensemble. The broad vertical lines stand for propagation of a mean-field state over a time interval  $\tau$ . At each mutiple of  $\tau$ , say  $t_j$  (see horizontal dashed line), the two-body correlations which have been accumulated during the propagation interval are sampled into a sub-ensemble of mean-field states (fascicles emerging out of broad line). One of these mean field states is picked stochastically (at next horizontal dashed line symbolizing the end of the time step  $t_j$  at which correlations are evaluated) and propagation continues from there on using this specific mean field (full line fascicle). This is done for a sufficiently large ensemble of  $\mathcal{N}$  members in parallel. It is evident that



Figure 1: Schematic view of the time propagation of STDHF (left part) and ASTDHF (right part). See text for more detailed explanations.

independent evolutions along different branches of the fascicles can thus build up in the course of time leading to potentially to large fluctuations.

The right part of Fig. 2.1 illustrates in the same manner propagation according to ASTDHF. Initialization by a mean-field state, subsequent propagation for a certain time interval  $\tau$ , mapping correlations into a sub-ensemble of mean-field states are similar to STDHF (although sampling covers here two steps, to be explained later). The difference is that then all members of the sub-ensemble together are used to compose a common one-body state and according mean field. This one-body state is not a Slater state any more, but a mixed state where single-particle wave functions are occupied with probabilities between zero and one.

The above explanation views ASTDHF as an efficient approximation to dynamical correlations in the regime of small amplitude fluctuations. An important, complementing aspect is that ASTDHF constitutes an approximate solution of the quantum Boltzmann equation (QBE) :

$$i\hbar\partial_t\hat{\rho} - \left[\hat{h},\hat{\rho}\right] = \hat{K}$$
 (1)

The left-hand-side represents TDHF propagation of the one-body density operator  $\hat{\rho}(t)$  under the mean field Hamiltonian  $\hat{h}$ , while  $\hat{K}$  at the righthand-side stands for the collision term, for details see Appendix C. A direct solution of the QBE is hardly possible due to prohibitively large summations. This led formerly to extended TDHF (ETDHF) as a dramatic approximation in which all ingredients in  $\hat{K}$  were reduced to diagonal elements of  $\hat{\rho}$  only, see section 2.7. ETDHF has its range of validity in close vicinity to equilibrium. By virtue of exploiting the elaborate collision strategy (called jumps later on) of STDHF, ASTDHF is able to account for a large part of the off-diagonal terms in the collision operator  $\hat{K}$  and is thus a much better approximation to QBE.

After all, we dispose of a hierarchy of schemes for handling dynamical correlations. At the lowest level stays ETDHF as a diagonal approximation to QBE. Above that comes the QBE which is approximately solved by AST-DHF. At this level, we describe dissipation (relaxation) caused by dynamical correlations but ignore largely the fluctuations which come along with dissipation. Typical applications are dynamical processes where a system is stirred up by an external field, but stays basically intact (e.g. molecule under moderate laser pulses, thermalization of an excited nucleus in the regime of giant resonances). Finally, STDHF is designed to account for (large) fluctuations as well. The corollary at the side of the QBE is the quantum version of the Boltzmann-Langevin equation [21], where a stochastic term  $\delta K$  complements the QBE. Such theories are capable to deal with reactions covering very different exit channels (e.g. electron transfer in molecules, nuclear fragmentation). All theories mentioned so far describe dynamical correlations in Markovian approximation (no memory). This requires that collision times are significantly shorter than time scales for mean-field changes. One must keep in mind that this is not always granted in which case one has to watch out for ways to treat memory effects. But this goes far beyond the scope of this paper.

#### 2.2. Mean field states and propagation

In the following, we will deal with a great variety of many-body states. Basis of the description are single-particle (s.p.) states  $\varphi$  which we can use in different representations, in coordinate space as  $\varphi(\mathbf{r})$  or in configuration space as  $|\varphi\rangle$ . Practically, we deal with a finite set

$$\{\varphi_{\nu}, \nu = 1, \dots, \Omega\} \tag{2}$$

where the available size  $\Omega$  of s.p. space is much larger than the actual electron number N to create sufficient supply of mean-field configurations for covering the needed many-body correlations.

A mean-field state, also called Slater state, is a determinant of N occupied s.p. states out of the  $\Omega$  available s.p. states. We can characterize it by the occupation numbers  $n_{\nu}$  of each s.p. state  $\varphi_{\nu}$ , summarized in an occupation vector **n** as

$$\mathbf{n} = (n_1, \dots, n_{\Omega})$$
 ,  $n_{\nu} \in \{0, 1\}$  ,  $\sum_{\nu=1}^{\Omega} n_{\nu} = N$  . (3a)

This corresponds to a Slater state

$$|\Phi_{\mathbf{n}}\rangle = \prod_{\nu=1}^{\Omega} (\hat{a}_{\nu}^{\dagger})^{n_{\nu}} |\text{vac}\rangle$$
(3b)

where the  $\hat{a}^{\dagger}_{\nu}$  are Fermion creating operators. This reads in coordinate space representation

$$\Phi_{\mathbf{n}}(\mathbf{r}_1,...,\mathbf{r}_N) = \mathcal{A}\{\prod_{k=1}^N \varphi_{h_k}(\mathbf{r}_k)\} \quad , \tag{3c}$$

$$(h_1, \dots, h_N) \quad \leftrightarrow \quad n_{h_k} = 1 \quad , \tag{3d}$$

where  $\mathcal{A}$  stands for anti-symmetrization, and the  $h_k$  are the indexes of the occupied (hole) states out of the available states. The complementing unoccupied (particle) states are labeled by  $p_k$  with  $1 \leq k \leq \Omega - N$  and  $n_{p_k} = 0$ . These index sequences are constructed from the occupation vector  $\mathbf{n}$ . In other words, the Slater state can be equivalently dealt with through the mean-field state  $|\Phi_{\mathbf{n}}\rangle$  or the occupation vector  $\mathbf{n}$ .

The many-body density operator for this mean field state  $|\Phi_{\mathbf{n}}\rangle$  is

$$D_{\mathbf{n}} = |\Phi_{\mathbf{n}}\rangle\langle\Phi_{\mathbf{n}}| \quad . \tag{4}$$

This is by construction a pure state. The computation of the mean-field and all one-body observables relies on the one-body density which is thus another central object in (A)STDHF. The one-body density operator derived from the many-body state  $D_{\mathbf{n}}$  is simply

$$\hat{\rho} = \sum_{\nu=1}^{\Omega} |\varphi_{\nu}\rangle n_{\nu} \langle \varphi_{\nu}| = \sum_{k=1}^{N} |\varphi_{h_{k}}\rangle \langle \varphi_{h_{k}}| \quad ,$$
(5a)

or in coordinate-space representation:

$$\rho(\mathbf{r},\mathbf{r}') = \sum_{\nu=1}^{\Omega} \varphi_{\nu}(\mathbf{r}) \, n_{\nu} \, \varphi_{\nu}^{*}(\mathbf{r}') = \sum_{k=1}^{N} \varphi_{h_{k}}(\mathbf{r}) \varphi_{h_{k}}^{*}(\mathbf{r}') \quad . \tag{5b}$$

The local density which determines the local mean field and other local observables is deduced from the one-body density matrix as  $\rho(\mathbf{r}) = \rho(\mathbf{r}, \mathbf{r})$ .

A key operation in (A)STDHF are jumps  $\mathbf{n} \longrightarrow \mathbf{m}$  between mean-field states within a given mean-field basis. As these jumps are driven by the residual two-body interaction, they consist only in two-particle-two-hole (2*ph*) transitions

$$\mathbf{n} \longrightarrow \mathbf{m} \in \mathcal{J}_{2ph}(\mathbf{n}) \quad , \quad \mathcal{J}_{2ph}(\mathbf{n}) = \left\{ \mathbf{m} \middle/ \sum_{\nu=1}^{\Omega} |n_{\nu} - m_{\nu}| = 4 \right\}$$
(6)

where the symbol  $\mathcal{J}_{2ph}(\mathbf{n})$  summarizes the space of 2ph transitions about  $\mathbf{n}$ . To give an example, we show here a couple of transitions for  $\Omega = 10$ , highlighted by numbers in a larger font:

$$\begin{array}{cccc} \mathcal{J}_{0}(\mathbf{n}) & \mathbf{m} \in \mathcal{J}_{1ph}(\mathbf{n}) & \mathbf{m} \in \mathcal{J}_{2ph}(\mathbf{n}) & \mathbf{m} \in \mathcal{J}_{3ph}(\mathbf{n}) \\ \mathbf{n} & (1111001100) & (1111001100) & (1111001100) & (1111001100) \\ & \downarrow & \downarrow & \downarrow & \downarrow \\ \mathbf{m} & (1111001100) & (11110001110) & (1110100101) & (00011101111) \end{array}$$

The 1*ph* space  $\mathcal{J}_{1ph}$  plays no role because it is incorporated in the TDHF propagation. The  $\mathcal{J}_{3ph}$  cannot be reached by one step with a two-body interaction. What remains are the 2*ph* space,  $\mathcal{J}_{2ph}$ , and the non-jump space,  $\mathcal{J}_0$ . These together form the active space  $\mathcal{J} = \mathcal{J}_0 \cup \mathcal{J}_{2ph}$  for the stochastic jumps in ASTDHF. In terms of Slater states, the transitions  $\mathbf{n} \longrightarrow \mathbf{m}$  actually mean

$$|\Phi_{\mathbf{n}}\rangle \longrightarrow |\Phi_{\mathbf{m}}\rangle \quad , \quad D_{\mathbf{n}} \longrightarrow D_{\mathbf{m}} \quad ,$$
 (7)

where both notations describe, of course, the same action.

In the mere mean-field propagation, the time-evolution of the s.p. states is given by the TDHF, or TDLDA, equation  $i\partial_t \varphi = \hat{h}\varphi$  where  $\hat{h}$  is the mean field Hamiltonian, depending on the actual density  $\varrho$ . In formal compact manner, the propagation can be expressed through the time-evolution operator  $\mathcal{U}$  as

$$\varphi_{\nu}(t) = \mathcal{U}(t, t')\varphi_{\nu}(t')$$
 (8a)

$$\mathcal{U}(t_2, t_1) = \mathcal{T} \exp\left[-\frac{\mathrm{i}}{\hbar} \int_{t_1}^{t_2} \mathrm{d}t \, \hat{h}(t)\right]$$
(8b)

where  $\mathcal{T}$  is the time ordering operator.

#### 2.3. Brief review of STDHF

This section gives a brief summary of STDHF, for details see Appendix B or [36, 37]. STDHF describes a correlated N-body state as an incoherent superposition

$$\mathcal{D}(t) = \frac{1}{\mathcal{N}} \sum_{\alpha=1}^{\mathcal{N}} D^{(\alpha)}(t)$$
(9)

where the  $D^{(\alpha)} = |\Phi^{(\alpha)}\rangle \langle \Phi^{(\alpha)}|$  are pure Slater states and  $\mathcal{N}$  stands for the size of the ensemble. The correlated state  $\mathcal{D}$  is distinguished by calligraphic notation. It is important to note that each  $D^{(\alpha)}$  in the ensemble is allowed to generate its own mean-field  $\hat{h}^{(\alpha)}$ , hence the upper script  $\alpha$ . The STDHF ensemble is thus capable of covering situation with large fluctuations of the mean field as it occurs, e.g., in electron transfer or fragmentation processes.

The advantage of the incoherent superposition is that each entry  $D^{(\alpha)}(t)$  can be propagated independently (parallel ensemble strategy). While mean field dynamics is followed on a fine time grid  $\delta t$ , dissipative dynamics, represented by STDHF steps, is considered only on a coarse time grid characterized by a time step  $\tau$  ( $\tau \gg \delta t$ ) chosen long enough to allow correlations to build up in an incoherent manner, still not too long to justify a dominant mean field propagation [34]. STDHF jumps thus occur at sampling times  $t_j = j\tau$  and we consider in detail one coarse step from  $t_{j-1} \longrightarrow t_j = t_{j-1} + \tau$ :

- 1. We start from Slater state  $D^{(\alpha)}(t_{j-1}) \equiv D^{(\alpha)}_{\mathbf{n}_0}(t_{j-1})$  and extend for the moment the notation to protocol the initial configuration  $\mathbf{n}_0$ . Mind that  $\mathbf{n}_0$  does depend on  $\alpha$ . We however omit this upper script for the sake of clarity. We allow correlations to develop for a while at the level of time-dependent perturbation theory. This yields at time  $t_j$  a coherently correlated state  $\mathcal{D}^{(\alpha)}(t_j) = \sum_{\mathbf{nn}'} |\Phi^{(\alpha)}_{\mathbf{n}}(t_j)\rangle c^{(\alpha)*}_{\mathbf{n}'}(t_j) \langle \Phi^{(\alpha)}_{\mathbf{n}'}(t_j)|$  where  $\mathbf{n}, \mathbf{n}'$  run over the various configurations in the mean field basis of  $\hat{h}^{(\alpha)}$ .
- 2. The key step is to reduce the still coherent  $\mathcal{D}^{(\alpha)}(t_j)$  to an incoherent sum  $\mathcal{D}^{(\alpha)}(t_j) \approx \sum_{\mathbf{n}} |\Phi_{\mathbf{n}}^{(\alpha)}(t_j)\rangle \left| c_{\mathbf{n}}^{(\alpha)}(t_j) \right|^2 \langle \Phi_{\mathbf{n}}^{(\alpha)}(t_j) | = \sum_{\mathbf{n}} P_{\mathbf{n}_0 \to \mathbf{n}}^{(\alpha)} D_{\mathbf{n}}^{(\alpha)}(t_j)$ . The occupation probability  $P_{\mathbf{n}_0 \to \mathbf{n}}^{(\alpha)} = \left| c_{\mathbf{n}}^{(\alpha)}(t_j) \right|^2$  amounts eventually to Fermi's golden rule for transition  $\mathbf{n}_0 \to \mathbf{n}$ . As explained in Sec. 2.2, these transitions cover only 0ph and 2ph states. These are, furthermore, restricted to 2ph states of the same energy as the initial 0ph state, see Eq. (B.4).

- 3. To avoid uncontrollable expansion of the ensemble, we randomly choose one new  $D^{(\alpha)}(t)$  out of the many given  $D_{\mathbf{n}}^{(\alpha)}(t)$  according to probability  $P_{\mathbf{n}_0 \to \mathbf{n}}^{(\alpha)}$ .
- 4. Finally, we collect all  $D^{(\alpha)}(t)$  to the new correlated ensemble  $\mathcal{D}(t)$ , see Eq. (9), and are ready for the next step.

This STDHF scheme has been applied successfully and is found to describe well the dynamics of energetic processes [36, 37].

#### 2.4. ASTDHF: use of a common mean-field

STDHF becomes inefficient for low and moderate excitation. Phase space for jumps as well as jump probabilities shrink and one needs ever larger ensembles to collect a sufficient amount of relevant events. On the other hand, these are just the situations where the fluctuations of the mean field are small. This allows us to replace the many different mean fields  $\hat{h}^{(\alpha)}$  by one common mean field Hamiltonian  $h_{\text{aver}} = h[\varrho]$  which is a functional of the (average) density  $\rho$  of the full ensemble. In the following, we drop the index "aver" and use simply h. In accordance with using the average mean-field, we call the modified scheme Averaged STHDF (ASTDHF). The mean field Hamiltonian h generates one common basis (2) of s.p. states for all Slater states  $D_{\mathbf{n}}$  in the ensemble. This reduces dramatically the numerical expense at the side of mean-field propagation because only one set of s.p. states has to be handled. The handling of the ensemble is also simplified because everything can be evaluated on the same s.p. basis which, in turn, allows us to implement a much more detailed collection of statistics, a necessary feature in the regime of low excitation.

As now only the configurations  $\mathbf{n}$  vary, it will rather often happen that a jump  $D_{\mathbf{n}} \longrightarrow D_{\mathbf{m}}$  ends up in an already active state  $D_{\mathbf{m}}$ . The jump merely enhances its weight. Rather than handling multiple identical copies of a state  $D_{\mathbf{n}}$ , it is now possible, and more efficient, to associate to each state  $D_{\mathbf{n}}$  an occupation weight  $W_{\mathbf{n}}$ . We thus consider a weighted ensemble  $\{D_{\mathbf{n}}, W_{\mathbf{n}}\}$  and the correlated state of ASTDHF becomes

$$\mathcal{D} = \sum_{\mathbf{n}=1}^{\aleph} W_{\mathbf{n}} D_{\mathbf{n}} \tag{10}$$

which is the equivalent of the STDHF state (9). The summation over  $\mathbf{n}$  deserves a comment. It runs, in principle, over all conceivable  $\mathbf{n}$ . But the overwhelming majority of them has negligible weight  $W_{\mathbf{n}}$  and is irrelevant.

Thus we work in practice with a much smaller (still large, though) selection  $\aleph$  of states **n** which have sufficient weight for our purposes. This selection can be readjusted in the course of the propagation if new configurations acquire more weight or old ones lose importance. This is a technical detail which will be explained in connection with the practical procedure, see sections 2.5 and Appendix A.

The common mean field can be characterized most compactly and unambiguously in terms of the one-body density operator. Each pure state  $D_{\mathbf{n}}$ leads to a pure one-body density  $\hat{\rho}_{\mathbf{n}}$  according to Eq. (5). The one-body density corresponding to the ASTDHF state (10) is then accumulated as

$$\hat{\rho} = \sum_{\mathbf{n}} W_{\mathbf{n}} \sum_{\nu} |\varphi_{\nu}\rangle n_{\nu} \langle \varphi_{\nu}| = \sum_{\nu} |\varphi_{\nu}\rangle \underbrace{\left(\sum_{\mathbf{n}} W_{\mathbf{n}} n_{\nu}\right)}_{w_{\nu}} \langle \varphi_{\nu}|$$

leading to its representation in natural orbitals as:

$$\hat{\rho} = \sum_{\nu} |\varphi_{\nu}\rangle w_{\nu} \langle \varphi_{\nu}| \quad , \tag{11}$$

with fractional occupation numbers  $0 \leq w_{\nu} \leq 1$  (at variance with the integer occupation numbers  $n_{\nu}$ ). This actually describes the straightforward mapping  $\mathcal{D} = \sum_{\mathbf{n}} W_{\mathbf{n}} D_{\mathbf{n}} \Rightarrow \hat{\rho} = \sum_{\nu} |\varphi_{\nu}\rangle w_{\nu} \langle \varphi_{\nu}|$ . The reverse mapping  $\hat{\rho} \Rightarrow \mathcal{D} = \sum_{\mathbf{n}} W_{\mathbf{n}} D_{\mathbf{n}}$  is more involved. It will be briefly discussed in the next section and detailed in Appendix A.

#### 2.5. ASTDHF: the propagation scheme

The central object in ASTDHF containing all wanted information is thus the one-body density (11). The aim is to propagate the one-body density  $\hat{\rho}(t)$  which means to determine the time evolution of  $\varphi_{\nu}(t)$  together with their  $w_{\nu}(t)$ . This is done in combination of mean-field propagation (8a) of the set  $\{\varphi_{\nu}(t)\}$  over a coarse time interval  $\tau$  and STDHF jumps at sampling times  $t_j = j\tau$  which effectively determines the propagation of the  $w_{\nu}(t)$ . Time stepping of the  $w_{\nu}$  is thus done on a coarse time step  $\tau$  as in STDHF. We consider in detail one coarse step from  $t_{j-1} \longrightarrow t_j = t_{j-1} + \tau$ :

1. At time  $t_{j-1}$ , we are given the one-body density operator  $\hat{\rho}(t_{j-1})$ . We propagate each s.p. state according to the mean field  $\hat{h}$  as  $\tilde{\varphi}_{\nu}(t_j) = \mathcal{U}(t_j, t_{j-1})\varphi_{\nu}(t_{j-1})$ while keeping the occupation numbers fixed during mean-field propagation, i.e.  $w_{\nu}(t) = w_{\nu}(t_{j-1})$  for  $t_{j-1} \leq t \leq t_j$ . The tilde used here serves to denote states which have not undergo any transition yet.

As a result, we have at time  $t_j$  the one-body density operator  $\tilde{\rho}(t_j)$  and the time-evolved pure states  $\tilde{D}_{\mathbf{n}}(t_j)$  as:

$$\widetilde{\rho}(t_j) = \sum_{\nu} |\widetilde{\varphi}_{\nu}(t_j)\rangle w_{\nu}(t_{j-1})\langle \widetilde{\varphi}_{\nu}(t_j)| ,$$
  
$$\widetilde{D}_{\mathbf{n}}(t_j) = \mathcal{U}(t_j, t_{j-1}) D_{\mathbf{n}}(t_{j-1}) \mathcal{U}(t_{j-1}, t_j)$$

2. In preparation for evaluating the STDHF jumps, we map the one-body density operator back to an equivalent ensemble of Slater states, i.e. we search by a minimization procedure the selection of relevant occupation vectors **n** and their corresponding weight  $\widetilde{W}_{\mathbf{n}}$  from the knowledge of the  $w_{\nu}$ :

$$\widetilde{\rho}(t_j) \implies \widetilde{\mathcal{D}} = \sum_{\mathbf{n}=1}^{\aleph} \widetilde{W}_{\mathbf{n}}(t_j) \widetilde{D}_{\mathbf{n}}(t_j) \quad .$$
(12)

In this reverse mapping, that we will call in the following "Slater ensemble mapping", we insist here upon the fact that we search for occupation vectors **n** only. This implicitly means that we work on the unique single particle basis generated by the  $\varphi_{\nu}$  when constructing the set of  $D_{\mathbf{n}}$ . Note that the weights  $\widetilde{W}_{\mathbf{n}}(t_j)$  do not correspond yet to the final weights in the ASTDHF ensemble  $\{D_{\mathbf{n}}, W_{\mathbf{n}}\}$  at time  $t_j$ .

A key issue in the Slater ensemble mapping is to preserve energy, namely to generate Slater states, each of them with an energy matching the energy of the system, within some uncertainty. This subtle aspect and the associated involved procedure (12) is outlined in Appendix A. A crucial part is here to pre-select states with nearly appropriate energy in order to confine the sample entering the tedious computation of jump rates (step 3 below).

3. The actual evaluation of jumps is the most elaborate step in ASTDHF. Here we have to deviate for a while from the concept of a common mean field because the involved  $D_{\mathbf{n}}$  have each their own mean field  $\hat{h}^{(\mathbf{n})}$  associated to their specific occupation vector  $\mathbf{n}$ . Each active  $D_{\mathbf{n}}(t_{j-1})$  is considered as a separate source of correlations unfolding on the way from  $t_{j-1}$  to  $t_j$  and reduced to jumps at  $t_j$ . The detailed reasoning is given in connection with STDHF in Appendix B.2. We repeat here the essential sub-steps exemplified for one specific  $\widetilde{D}_{\mathbf{n}}(t_j)$ . (a) We then evaluate the particular mean field  $\hat{h}^{(\mathbf{n})}$  specific to  $\widetilde{D}_{\mathbf{n}}(t_j)$ . This is needed for proper treatment of time-dependent perturbation theory about  $\widetilde{D}_{\mathbf{n}}(t_j)$ . We then determine a new, intermediate s.p. basis  $\{\varphi'_{\nu}^{(\mathbf{n})}\}_{\nu=1...\Omega}$ . It is obtained from the actual common set  $\{\widetilde{\varphi}_{\nu}(t_j)\}$  by diagonalizing the actual mean field  $\hat{h}^{(\mathbf{n})}$  (we drop the upper index **n** for simplicity):

$$\varphi'_{h_k}(t_j) = \sum_{k'=1}^{N} u_{h_k h_{k'}} \widetilde{\varphi}_{h_{k'}}(t_j) \quad , \quad \varphi'_{p_l}(t_j) = \sum_{l'=1}^{\Omega-N} u_{p_l p_{l'}} \widetilde{\varphi}_{p_{l'}}(t_j) \quad , \tag{13}$$

where  $h_k$  stands for occupied states and  $p_k$  for unoccupied ones. The u matrix above composes unitary matrices which diagonalize the mean-field hamiltonian in occupied and unoccupied subspaces of vector  $\mathbf{n}$ . This operation minimizes the energy uncertainty of the s.p. states and so prepares ground for applying Fermi's golden rule in the next sub-step.

(b) Correlations unfold  $\widetilde{D}_{\mathbf{n}}(t_j)$  to a superposition over all configurations  $\mathbf{m}$  in the mean field  $\hat{h}^{(\mathbf{n})}$  which we denote as  $D_{\mathbf{m}}^{(\mathbf{n})}$  (mind that  $D_{\mathbf{n}}^{(\mathbf{n})} = \widetilde{D}_{\mathbf{n}}$  and that the  $D_{\mathbf{m}}^{(\mathbf{n})}$  are evaluated at time  $t_j$ ). With the standard steps of time-dependent perturbation theory, we derive a Fermi's golden rule [42, 34] for the jump probabilities:

$$P_{\mathbf{n}\to\mathbf{m}} = \frac{2\pi\tau}{\hbar} \left| \langle \Phi_{\mathbf{m}}^{(\mathbf{n})} | \widehat{V}_{\text{res}} | \Phi_{\mathbf{n}} \rangle \right|^2 \delta \left( E_{\mathbf{m}}^{(\mathbf{n})} - E_{\mathbf{n}} \right) \Theta \left( \mathbf{m} \in \mathcal{J}_{2ph}(\mathbf{n}) \right)$$
(14a)

$$P_{\mathbf{n}\to\mathbf{n}} = 1 - \sum_{\mathbf{m}\in\mathcal{J}_{2ph}(\mathbf{n})} P_{\mathbf{n}\to\mathbf{m}}$$
 (14b)

We remind that  $\tau = t_j - t_{j-1}$ .  $\hat{V}_{res}$  stands for the residual interaction. The  $\Theta$  function limits the jumps to 2ph configurations with respect to  $\mathbf{n}$  and the  $\delta$  function further select jumps at constant energy. In practice, this  $\delta$  has a finite width  $\Gamma$  to allow an energy matching for a discrete density of states as we have in a finite system.

This produces from  $\widetilde{D}_{\mathbf{n}}(t_i)$  the incoherently correlated state:

$$\mathcal{D}_{\mathbf{n}}(t_j) = \sum_{\mathbf{m}} P_{\mathbf{n} \to \mathbf{m}}(t_j) D_{\mathbf{m}}^{(\mathbf{n})} \quad .$$
(15)

4. Having evaluated in the previous step the correlations in  $\mathcal{D}_{\mathbf{n}}(t_j)$  for each **n** separately, we now collect to the result for the whole system. This reads

for the *N*-body state  $\mathcal{D}(t_j) = \sum_{\mathbf{n}} W_{\mathbf{n}}(t_{j-1})\mathcal{D}_{\mathbf{n}}(t_j)$ . The practical collection is actually done at the level of the one-body density operator. To this end, for each  $\mathbf{n}$ , we evaluate  $\hat{\rho}_{\mathbf{n}}(t_j)$ , corresponding to  $\mathcal{D}_{\mathbf{n}}(t_j)$ , as  $\hat{\rho}_{\mathbf{n}}(t_j) = \sum_{\mathbf{m}} \sum_{\nu} |\varphi'_{\nu}\rangle m_{\nu} P_{\mathbf{n} \to \mathbf{m}} \langle \varphi'_{\nu} |$  (we have dropped the  $t_j$  dependence in the r.h.s. for the sake of compactness). We use again the common basis set  $\{\widetilde{\varphi}_{\nu}(t_j)\}$  to express the matrix elements of  $\hat{\rho}_{\mathbf{n}}(t_j)$ :

$$\hat{\rho}_{\mathbf{n}}(t_j) = \sum_{\mu\mu'} |\widetilde{\varphi}_{\mu}\rangle(\rho_{\mathbf{n}})_{\mu\mu'}\langle\widetilde{\varphi}_{\mu'}| \quad , \tag{16}$$

$$(\rho_{\mathbf{n}})_{\mu\mu'} = \sum_{\mathbf{m}} \sum_{\nu} \langle \widetilde{\varphi}_{\mu} | \varphi'_{\nu} \rangle m_{\nu} P_{\mathbf{n} \to \mathbf{m}} \langle \varphi'_{\nu} | \widetilde{\varphi}_{\mu'} \rangle \quad .$$
(17)

This allows the superposition of the various one-body density operators stemming from each  $\mathbf{n}$  to compose the one-body density operator of the whole system as:

$$\hat{\rho}(t_j) = \sum_{\mathbf{n}} W_{\mathbf{n}}(t_{j-1}) \hat{\rho}_{\mathbf{n}}(t_j) = \sum_{\mu\mu'} |\widetilde{\varphi}_{\mu}\rangle \sum_{\mathbf{n}} W_{\mathbf{n}}(t_{j-1}) (\rho_{\mathbf{n}})_{\mu\mu'} \langle \widetilde{\varphi}_{\mu'}| \quad .$$
(18)

5. Finally, we diagonalize the new one-body density operator (18), thus restoring the natural orbital representation:

$$\hat{\rho}(t_j) = \sum_{\nu} \left| \varphi_{\nu}(t_j) \right\rangle w_{\nu}(t_j) \left\langle \varphi_{\nu}(t_j) \right| \quad .$$
(19)

This completes one full ASTDHF step delivering eventually a new common mean-field basis set  $\{\varphi_{\nu}(t_i)\}$  with new occupation numbers  $w_{\nu}(t_i)$ .

Figure 2 illustrates the above outlined propagation scheme. Note that all procedures from  $t_j$  to  $t_j^+$  take place at one instant of time. They are expanded graphically for a better visualization.

# 2.6. Efficient implementation of ASTDHF: stepping parameters and energy considerations

Similar as in STDHF, the ASTDHF procedure implies three parameters: (i) the size of the coarse time step  $\tau$ , (ii) the width  $\Gamma$  of the energy-matching  $\delta$  function in Eq. (14a), and (iii) the selection of the active phase space  $\aleph$ . The time step  $\tau$  has to be large enough to allow the reduction to Fermi's golden rule, but still small enough to track global changes of the mean field.



Figure 2: Schematic view of the time propagation of the ASTDHF scheme. See text for the definition of the various quantities indicated in the figure.

The width  $\Gamma$  has to be large enough to catch all jumps occurring within the time interval  $\tau$ , but sufficiently small to deliver satisfying energy conservation along the evolution with ASTDHF. The situation for these two parameters is thus exactly the same as it was in STDHF. It was studied extensively in this context and good working compromises had been found [36, 37]. These are taken over for the present application in ASTDHF.

The third point, the selection of active space  $\aleph$  of configurations **n**, is naturally specific to ASTDHF. One important new aspect is here that the total energy  $E_{\text{tot}} = E[\hat{\rho}] \equiv E$  is computed from the common one-body density operator  $\hat{\rho}$ . There is also the energy  $E_{\mathbf{n}}$  of state  $|\Phi_{\mathbf{n}}\rangle$  for each member of the ensemble which enters sensitively the jump probability (14). This  $E_{\mathbf{n}}(t)$  is not strictly conserved under propagation in the common ASTDHF mean field  $\hat{h}$ , thus  $E_{\mathbf{n}}(t_j) \neq E_{\mathbf{n}}(t_{j-1})$ . This raises no principle problem because what counts is to conserve the total energy  $E[\hat{\rho}]$ . However, a proper focusing  $E_{\mathbf{n}} \approx E[\hat{\rho}]$  is necessary to keep the energy variance in the ensemble low and such a focusing is also beneficial as it limits the size of the active ensemble  $\aleph$ . This is achieved by selecting in the Slater ensemble mapping  $\hat{\rho} \Rightarrow \mathcal{D} = \sum_{\mathbf{n}} W_{\mathbf{n}} D_{\mathbf{n}}$  (see step 2 and Appendix A) only samples  $D_{\mathbf{n}}$  whose energy remains in a certain window:

$$|E_{\text{tot}} - E_{\mathbf{n}}| \le \Gamma_{\text{map}} \quad , \quad \Gamma_{\text{map}} \gtrsim \Gamma \quad .$$
 (20)

The choice of the value of  $\Gamma_{\text{map}}$  very much depends on the system under study, in particular on its density of states (see Sec. 3 for the numerical values used in the reported results). A practical challenge is that the selection of the  $\aleph$  Slater states has to be adapted dynamically along the evolution. Energy  $E_{\mathbf{n}}(t)$  is not strictly conserved and thus some of the  $\mathbf{n} \in \aleph$  leave the allowance band (20). In return, new configurations will enter and these have to be found efficiently. Starting from one sample  $D_{\mathbf{n}}$ , the most likely energetically close configurations are the 2ph states  $\mathbf{m}$  with respect to configuration  $\mathbf{n}$ . It occasionally happens that this selection of configurations is still too small to allow a sufficient precise mapping  $\hat{\rho} \Rightarrow \mathcal{D}$ . In that case, we extend the search to 2ph states built on the already determined energetically compatible 2ph states and proceed in same fashion. Understandably, this dynamical readjustment of the active configurations is the most expensive part in the ASTDHF scheme.

#### 2.7. Extended TDHF

The build-up and propagation of incoherent correlations is traditionally handled in terms of a Quantum Boltzmann Equation (QBE) which we explain for completeness in Appendix C. ASTDHF can be considered as an approximate solution to the QBE, still rather formidable. An even simpler route to render the QBE manageable was proposed long ago [40], often used under the name Extended TDHF (ETDHF). We keep the acronym ETDHF although we use it here on the basis of TDLDA. The awful six-fold summation in the collision term of the QBE is reduced in ETDHF to just affordable three-fold summation by simply ignoring the off-diagonal elements of the one-body density matrices. This yields the diagonal collision term

$$K_{\nu\nu\nu'} = 2\pi \delta_{\nu\nu'} \sum_{\beta\gamma\delta} \delta\left(\varepsilon_{\nu} + \varepsilon_{\beta} - \varepsilon_{\gamma} - \varepsilon_{\delta}\right) \\ \left|v_{\gamma\delta\nu\beta}\right|^{2} \left[n_{\nu}n_{\beta}(1-n_{\gamma})(1-n_{\delta}) - (1-n_{\nu})(1-n_{\beta})n_{\gamma}n_{\delta}\right] (21)$$

where the single particle energies  $\varepsilon_{\nu}$  are the eigenenergies of the natural orbitals  $(\hat{h}\varphi_{\nu} = \varepsilon_{\nu}\varphi_{\nu})$  and  $v_{\gamma\delta\nu\beta}$  are the matrix elements for the two-body

residual interaction. This collision term is easy to implement and rather inexpensive to use. It underestimates, however, the relaxation of the offdiagonal terms of  $\hat{\rho}$ . In the tests below, we will also compare (A)STDHF with ETDHF to explore the range of validity for this latter approach.

#### 2.8. Diagonal ASTDHF

By construction, ETDHF is much simpler than ASTDHF as it reduces to a rate equation on occupation numbers only, thus neglecting any impact from off-diagonal elements of the one-body density matrix. We recall that ASTDHF manages to account for a great deal of these off-diagonal effects by the unitary transformation (13) to a *ph*-diagonal basis, see step 3a in Sec. 2.5. Off-diagonal contributions may still be small for low excitations energies which was one argument in favor of ETDHF. If that reasoning applies, we can also simplify ASTDHF by just omitting this transformation step 3a, an approximation which we call here "diagonal ASTDHF" and which should deliver a theory closer to ETDHF. This schemes works in natural-orbital basis throughout. The omission of diagonalization and transformation for each sample separately saves considerable computing expense. It is thus worth checking and so we will complement the subsequent comparisons also by diagonal ASTDHF.

#### 3. Results

ASTDHF is an efficient approach to dynamical correlations which will allow large-scale applications in realistic systems. However, in the following applications, we aim at comparisons with STDHF which is the more demanding theory. This sets the limits and so we employ here the 1D model mimicking a molecular system, as already used in [36, 37, 38].

#### 3.1. The 1D model

The 1D molecular/cluster model is described by the following mean field Hamiltonian (in x representation, using  $\hbar = 1$ ):

$$\hat{h} = -\frac{\Delta}{2m} + V_{\text{ext}}(x) + \lambda \varrho(x)^{\sigma}$$
(22)

in which  $\rho(x) = \sum_{\nu} w_{\nu} |\varphi_{\nu}(x)|^2$  is the local density. This mean-field Hamiltonian can be derived from the following energy functional

$$E = \sum_{\nu} \left\langle \varphi_{\nu} \right| - \frac{\Delta}{2m} + V_{\text{ext}}(x) \left| \varphi_{\nu} \right\rangle + \lambda \int \mathrm{d}x \ \frac{\varrho(x)^{\sigma+1}}{\sigma+1}$$

where V(x) stands for the external potential from nuclear/ionic field and the term  $\propto \lambda$  models a density functional for exchange and correlations. We use  $\lambda = 68 \text{ eV } a_0^2$  and  $\sigma = 2 a_0$  in the results presented below [38]. The external potential  $V_{\text{ext}}$  has been chosen as a Woods-Saxon profile,  $V_{\text{ext}}(x) =$  $v_0/[1 + \exp((x - x_0)/a)]$ , where  $v_0 = -68$  eV,  $x_0 = 15$  a<sub>0</sub>, a = 2 a<sub>0</sub> in most cases [38]. We add to this potential an extra confining harmonic oscillator (not explicitly written here) to install soft reflecting boundary conditions. The aim of this work is to focus on thermalization effects, and these reflecting boundary conditions suppress the competition with ionization. As a consequence, absolute values of energies are somewhat arbitrary. However, we took care to keep the structure of s.p. spectrum "realistic". We have also explored other sets of parameters leading to different single particle spectra. The results obtained with these other potentials were qualitatively similar to those we present here, even if they may differ quantitatively. One case will be discussed in Fig. 9 for completeness. There remains the residual interaction  $\hat{V}_{res}$  entering the jump probabilities Eq. (B.4a) for STDHF and Eq. (14a) for ASTDHF. It has been chosen as a simple zero-range interaction  $V_{\rm res}(x, x') = V_1 \delta(x - x')$  with  $V_1 = 18.4$  eV [38].

The considered test system has N = 9 physical particles. Without loss of generality, we do not take into account spin effects here. Our working space is thus composed of 9 hole levels and an arbitrary number of empty levels, taken here as 14. The total size  $\Omega$  of s.p. space (holes and particles) is thus 23. We have checked that our results are stable when using larger values of  $\Omega$  and we will use variation of  $\Omega$  as one means to estimate error bars on the results, see Secs. 3.5 and 3.6. With the given model parameters, the lowest orbital has an energy of -58.8 eV, the HOMO is at -43.0 eV and the HOMO-LUMO gap is equal to 2.4 eV. It represents the lowest value of the excitation energy accessible by a one-particle-one-hole (1ph) transition. A sketch of the model system is shown in Fig. 3.

Finally, the initial excitation  $E^*$  of the system is achieved by performing at t = 0 a 1ph transition chosen from the ground state s.p. spectrum, as in [36, 37, 38]. The various choices of the 1ph transitions deliver all the different values of excitation energy  $E^*$  in this survey (we have also checked delivering excitation energy  $E^*$  via 2ph excitations and they make no significant difference for the present purposes).



Figure 3: External potential  $V_{\text{ext}}$  (red dashes), local electronic density (green thin curve), and total potential  $V_{\text{ext}} + \lambda(\varrho)^{\sigma}$  (blue thick curve) entering the mean-field Hamiltonian (22) of the 1D model. The horizontal lines indicate the single-particle spectrum and the black dots the 9 physical particles in the ground state.

#### 3.2. Computational parameters

The coarse time step  $\tau$  for evaluation of stochastic jumps has been varied between 0.1 fs and 2 fs with no sizable effects. The default value used in the following is  $\tau = 0.242$  fs, which is typical of cluster and molecular time scales. The overall propagation time is typically 120 fs, more than enough to reach asymptotic states in the energy range under consideration.

The size of the STDHF ensemble  $\mathcal{N}$  is at least equal to 100, to ensure valuable statistics in the target energy range at a computationally acceptable cost. Larger and larger values of  $\mathcal{N}$  become compulsory when decreasing the excitation energy. We have tested different values up to  $\mathcal{N} = 500$  for the results presented in Secs. 3.5 and 3.6, and use this variation also to estimate error bars on the STDHF results. Increasing  $\mathcal{N}$  is problematic in STDHF because a sizable fraction of computation time is eaten up in pure mean field propagation. This is precisely the point where ASTDHF gains significant computation time because it has to propagate only one common mean field. The expense for evaluating the stochastic jumps depends on the size  $\aleph$  of the instantaneous ensemble of Slater states in ASTDHF. In practice, we use  $\aleph = 100$ . Mind that this does not mean that, from one coarse time step to the other, the same  $\aleph$  Slater states are used in the ASTDHF scheme. Instead,

in step 2 of Sec. 2.5, we update the Slater states for the Slater ensemble mapping  $\hat{\rho} \Rightarrow \mathcal{D}$  while keeping a total number of  $\aleph$  states. The details of this procedure is presented in Appendix A. For dynamics at short times in which the freshly excited system is far from equilibrium, there are many replacements of Slater states from one coarse time step to the other. At later times, when thermalization has set in, small update, or even no update at all, occurs and one can keep almost the same ensemble from one time step to the next.

As compared to a mere mean field propagation, the cost of ASTDHF mostly lies in the Slater ensemble mapping, plus a marginal contribution from the evaluation of correlations via STDHF instantaneous steps. This strongly differs from pure STDHF propagation in which most computation time is spent in the mean field evolution of each member of the ensemble. We performed systematic studies of the actual cost of ASTDHF and found that, all in all, we reach computations times 5–10 more expensive than pure mean field propagation. This has to be compared with a STDHF dynamics costing at least  $\mathcal{N}$  times a mean field propagation. This means that ASTDHF is at least one order of magnitude faster than STDHF.

As already discussed in Sec. 2.6, there are two model parameters related to energy conservation, or energy uncertainty respectively. The first one is the width  $\Gamma$  in the energy-conserving  $\delta$  function in the jump probability, see Eqs. (14a) or (B.4a). A finite width  $\Gamma$  is required to capture all level crossings occurring in a discrete spectrum within the coarse time step  $\tau$ . Too large  $\Gamma$ , however, spoils energy conservation. A good compromise is  $\Gamma = 1.63$  eV and has been used in all computations. It delivers energy conservation within 0.3 % both in STDHF and ASTDHF.

The second energy parameter is  $\Gamma_{\text{map}}$  used in ASTDHF to confine the preselection of Slater states in the ensemble for the Slater ensemble mapping (see Sec. 2.6 and Appendix A). We have varied it in the range 1.4 to 12.2 eV. This is one more ingredient to the error bars on the ASTDHF computations shown in Secs. 3.5 and 3.6. Too large  $\Gamma_{\text{map}}$  allows us to easily attain conveniently large ensembles for the Slater ensemble mapping from the one-body density matrix  $\hat{\rho}$  to the N-body density matrix  $\mathcal{D}$ , however at the price of large energy violation. In turn, too small values can degrade the mapping. A good working compromise was found with  $\Gamma_{\text{map}} \simeq 5\Gamma = 8.2$  eV. Mind that  $\Gamma_{\text{map}}$ only addresses the pre-selection of the ensemble from which 2ph transitions are built. It does not affect the total energy conservation which is enforced at any dissipative step by  $\Gamma$  to pick energetically allowed 2ph transitions, whence the global 0.3% energy conservation mentioned above.

#### 3.3. Two-body densities

By construction, STDHF and ASTDHF deliver correlated density matrices. This point was discussed at length in the case of STDHF in [37] and we shall only recall the salient features here, including also the new case of ASTDHF.

Let us start with STDHF. It provides an ensemble description of manybody density matrices, see Eq. (9). The nice feature here is that any reduced density matrix can be immediately evaluated because the correlated N-body density is an incoherent sum of N-body densities of Slater states which are explicitly known and easy to handle. Correlations emerge from the ensemble average. We focus here on (correlated) one-body  $\hat{\rho}$  and two-body  $\hat{\rho}_2$  density matrices which can be immediately written as

$$\hat{\rho} = \frac{1}{\mathcal{N}} \sum_{\alpha=1}^{\mathcal{N}} \rho^{(\alpha)}$$
(23)

$$\hat{\rho}_2 = \frac{1}{\mathcal{N}} \sum_{\alpha=1}^{\mathcal{N}} \rho_2^{(\alpha)} \tag{24}$$

where the one-body density matrix  $\hat{\rho}^{(\alpha)}$  of the Slater state  $D^{(\alpha)}$  is given as in Eq. (5), and where  $\rho_2^{(\alpha)}$  for a Slater state simply reads, in coordinate space representation:

$$\rho_2^{(\alpha)}(\mathbf{r}_1, \mathbf{r}_2; \mathbf{r}_1', \mathbf{r}_2') = \rho^{(\alpha)}(\mathbf{r}_1, \mathbf{r}_1')\rho^{(\alpha)}(\mathbf{r}_2, \mathbf{r}_2') - \rho^{(\alpha)}(\mathbf{r}_2, \mathbf{r}_1)\rho^{(\alpha)}(\mathbf{r}_1, \mathbf{r}_2') .$$
(25)

Note that we could as well compute higher order density matrices, again on the basis of this simple Slater state construction. But we shall remain at the second order here.

The situation in ASTDHF, although formally slightly different, is similar. The N-body density (10) is, again, an incoherent sum of Slater states, however in different book-keeping and weighted by probabilities  $W_n$ . The strategy to construct reduced density matrices is thus exactly the same as in STDHF. For example, the two-body matrix reads:

$$\hat{\rho}_2 = \frac{1}{\aleph} \sum_{\mathbf{n}=1}^{\aleph} W_{\mathbf{n}} \,\hat{\rho}_{2,\mathbf{n}} \tag{26}$$

with  $\hat{\rho}_{2,\mathbf{n}}$  expressed in Eq. (25) as a function of the "Slater" one-body density matrices  $\hat{\rho}_{\mathbf{n}}$  associated to each  $D_{\mathbf{n}}$ , see Eq. (17).

A comparison between STDHF and ASTDHF two-body density matrices is shown in Fig. 4. The two-body density depends on four coordinates



Figure 4: Snapshots of the two-body density matrix  $\rho_2(x, y; x, y)$  after initial excitation by a 1ph transition delivering an excitation energy  $E^* = 20.7$  eV. Upper left panel: color-map plot of full  $\rho_2(x, y; x, y)$  at initial time (same for all approaches). Other panels : cut of  $\rho_2$ along y = R - x (see white line in upper left panel) for TDHF, STDHF, ASTDHF and initial  $\rho_2$ .

which is hard to represent. We consider only the part  $\rho_2(x, y; x, y)$  which is presented in full for initial time in the upper left panel. Even with such a simplification, it is hard to visualize  $\rho_2(x, y; x, y)$  as a function of time while comparing various approaches. We thus restrict the representation to the second diagonal  $\rho_2(x, R - x; x, R - x)$ , R being the box radius, as indicated by the white dotted line on the left upper panel, and show in the other panels snapshots of this quantity at three different instants. We observe in all three snapshots that ASTDHF and STDHF remain very close to each other, showing a smoothing of the initial pattern as expected from dissipative mechanisms. Quite in contrast, pure mean field (TDHF) propagation maintains the large fluctuations given initially due to lack of dissipation. The most important point here is the remarkable similarity between STDHF and ASTDHF. The fact that highly detailed quantities such as  $\hat{\rho}_2$  are comparable in both theories allows us to infer that any observable derived thereof (typically through integration) will match even better because of the extra average brought by a further integration of the quantities. We shall, nevertheless, present in the following a few such one-body observables in different cuts to complement this picture.

#### 3.4. Distribution of occupations and one-body entropy

The most compact description of the one-boy density operator  $\hat{\rho}$  is given by the natural orbital representation (11) (it is, in fact, a central object in ASTDHF). Key quantities therein are the single particle occupation numbers  $w_{\nu}$  because they carry the signature of thermalization. Dissipation should drive them in the course of time evolution towards a Fermi-Dirac distribution, characterizing thermal equilibrium at a finite temperature corresponding to excitation energy. The left panel of Fig. 5 shows snapshots of the distribution of  $w_{\nu}$  along the time evolution following an initial 1ph initial excitation at  $E^* = 29.8$  eV. The initial distribution (gray shaded boxes) shows the flat occupations up to Fermi energy with a hole cut in between and this particle moved up to some higher lying s.p. state. The further snapshots show the initial non-equilibrium sharp edged distribution which is progressively smoothed and finally approaches equilibrium in form of a Fermi-Dirac distribution (thick dashed curve) as it should. The final distribution fits to a Fermi energy  $\varepsilon_{\rm F} = -40.8$  eV and a temperature of T = 7.6 eV, that is 18.6% of  $\varepsilon_{\rm F}$ , confirming the thermalization of the system.

The way to equilibrium can be quantified by one number deduced from the distribution of  $w_{\nu}$ , the one-body entropy

$$S = -k_B \sum_{\nu} [w_{\nu} \log(w_{\nu}) + (1 - w_{\nu}) \log(1 - w_{\nu})] \quad .$$
 (27)

The right panel of Fig. 5 shows the time evolution of S. Initially, it starts from S = 0 which is obvious for a distribution with  $w_{\nu} = 0$  or 1. It increases



Figure 5: Left: Snapshots of the distribution of occupation numbers  $w_{\nu}$  as function of s.p. energy propagated with ASTDHF after an initial 1ph excitation delivering an excitation energy  $E^* = 29.8$  eV. The initial distribution is indicated as gray shaded boxes. The four instants at which  $w_{\nu}$  are shown are indicated by vertical dashed lines in the right panel. The thick dashed curve corresponds to a fit of the final occupation number distribution by a Fermi-Dirac distribution. Right: One-body entropy S(t) deduced from the distribution of occupation with Eq. (27) for the same case (ASTDHF, excitation  $E^* = 29.8$  eV) as shown in the left panel.

quickly and monotonously towards its maximum which is reached more or less above  $\simeq 40$  fs. Maximum entropy corresponds to thermal equilibrium and so the present plot of S(t) demonstrates the thermalization and provides an idea of the corresponding relaxation time which is of order 5 fs for the given excitation energy, or temperature respectively.

#### 3.5. Dependence of thermalization with excitation energy

The above results for one given excitation energy  $E^*$  indicate that AST-DHF is very close to STDHF. To check this further, we now consider different initial 1ph transition thus varying  $E^*$ . We compare the time evolution of the one-body entropy S defined in Eq. (27) since it constitutes a compact indicator of relaxation and thermalization. Figure 6 compares the ASTDHF entropy for four different  $E^*$  with that computed from STDHF. The latter is computed from the eigenvalues of the STDHF one-body density (23) injected into Eq. (27) in place of the  $\omega_{\nu}$  [36]. It is gratifying to see that ASTDHF remains in all cases very close to STDHF. Not only the asymptotic values are extremely close, thus corresponding to similar temperatures, but also the whole evolution and with it the relaxation times associated to the path



Figure 6: Time evolution of the one-body entropy S after excitation by an initial 1ph transition, computed with ETDHF (dots), STDHF (dashes) and ASTDHF (full curves), at four different excitation energies  $E^*$  as indicated. The STDHF and ASTDHF results are shown with error bands deduce from variation of algorithmic parameters  $\Omega$ ,  $\tau$ ,  $\mathcal{N}$ , and  $\Gamma_{\text{map}}$ .

towards equilibrium. This is an important result showing that ASTDHF, although simplified, remains a highly accurate method even at high  $E^*$  for which one my have expected that the fluctuations of the mean-field, neglected in ASTDHF, might affect average properties. This has to be put into perspective in connection with the present model which simulates systems with a deep binding potential well. The result then holds for all such singly connected, well bound electron clouds. However, one should remain aware that there exist other situations prone to larger fluctuations as, e.g., multi-centered molecules or fragmentation dynamics in which one should reach the limits of ASTDHF.

The ASTDHF results in Fig. 6 are shown with error bars, indicated as shaded areas. These are deduced from variation of numerical parameters within reasonable ranges (see Sec. 3.2): the number  $\Omega$  of states in the s.p. basis, the coarse time step  $\tau$ , and the pre-sampling width  $\Gamma_{\text{map}}$  for ASTDHF or ensemble size  $\mathcal{N}$  for STDHF and Slater ensemble size  $\aleph$  for the reverse mapping. We note that, at the vertical scale chosen here, the error bars on S(t) for ASTDHF are almost invisible, reflecting the high stability of this scheme against the involved numerical parameters. STDHF produces visible, still small, error bands. These are predominantly uncertainties from limited sampling. The width of the error bands could be reduced by going to higher  $\mathcal{N}$  which, however, grows quickly very expensive.

Last, but not least, it is interesting to notice that, in general, the STDHF entropy lies slightly below that of ASTDHF. We attribute this effect not to a defect of ASTDHF but rather to a defect of STDHF to the extent that STDHF by construction suffers from sampling accuracy, which is not the case of ASTDHF. This defect is also reflected in the fact that the ASTDHF curves are smoother than the STDHF ones.

As a next step, we extend the comparison of STDHF and ASTDHF to ETDHF and diagonal ASTDHF (see Secs. 2.7 and 2.8). We remind that ET-DHF, by construction, gets rid of the off-diagonal elements of the one-body density matrix, while diagonal ASTDHF exclusively works in the natural orbital basis, rendering the final diagonalization of the ASTDHF one-body density matrix (see step 5) useless. Figure 7 compares the four schemes for two different excitation energies. At low  $E^*$  (left panel), all four approaches



Figure 7: Comparison of the time evolution of the one-body entropy S computed by four different methods, STDHF (blue dashes), ASTDHF (red full curves), ETDHF (green dots) and diagonal ASTDHF (magenta dotted dashes), after an initial excitation by a 1ph transition, at two different excitation energies  $E^*$  as indicated.

compare very well. This is plausible because the smaller excitation energy produces smaller off-diagonal elements of the one-body density. The situation changes at higher  $E^*$  (right panel) where one observes sizable differences between ETDHF and ASTDHF/STDHF, which reflects the importance of treating off-diagonal terms of the one-body density matrix properly. The degraded version of ASTDHF, diagonal ASTDHF, interestingly enough lies in between full ASTDHF and ETDHF. This again points out the key importance of off-diagonal effects neglected in ETDHF. An interesting side product of this comparison, nevertheless, lies in the fact that ETDHF looks acceptable at low excitation energy. However, a drawback remains: one does not have access to an internal quality assessment of ETDHF. In other words, by computing only at ETDHF level, it is hard to be sure that calculations are correct.

#### 3.6. Asymptotic entropy

In order to show trends with  $E^*$  systematically, we look at the asymptotic entropy  $S_{\infty}$  as a function of the excitation energy  $E^*$  as an even more compact way to compare the various approaches. In a Fermi gas at finite (small) temperature T, it is well known that entropy and excitation energy scale with temperature as  $E^* \propto T^2$ ,  $S_{\infty} \propto T$ , thus  $S_{\infty}^2 \propto E^*$  [18]. In previous works, we have already checked that both STDHF [37] and ASTDHF [38] reproduce this scaling. We now extend the comparison to ETDHF and diagonal ASTDHF.

Results are shown in Fig. 8, including error bands as in Figs. 6 and 7. They confirm a close to perfect proportionality between  $S^2$  and  $E^*$  in the case of STDHF and ASTDHF. In addition, both stay very close to each other over the whole range of excitation energy explored here. ETDHF and diagonal ASTDHF also start with good reproduction of the trend at low energies, but soon deviate and continue with fluctuations, not even a monotonous trend. The reasons for these fluctuations in  $S^2_{\infty}(E^*)$  are not clear and it would require further inspection to find them out. At the moment, we can safely conclude that there is a range of validity for ETDHF, although a rather limited one.

To end this discussion, we consider slight variations of the model concerning energetics and spectral density. To do so, we modify the parameters of the external potential  $V_{\text{ext}}$  to  $v_0 = 54.4 \text{ eV}$ ,  $x_0 = 25 a_0$  and  $a = 10 a_0$ . This set delivers a denser spectrum: while the average energy separation in potential 1 is about 2 eV, in potential 2, it shrinks to 1 eV (see inset of Fig. 9 where "potential 1" corresponds to the set of parameters used throughout this paper and "potential 2" to the here modified set). Figure 9 shows  $S^2_{\infty}(E^*)$  for this potential. The calculations with the modified potential were done with



Figure 8: Square of the asymptotic value of the one-body entropy,  $S_{\infty}^2$ , as a function of the excitation energy  $E^*$  (generated by instantaneous 1*ph* excitation) for ETDHF, STDHF, ASTDHF and diagonal ASTDHF.



Figure 9: Same as in Fig. 8 but for a modified potential, coined "potential 2" (see inset), see text for details.

one choice of numerical parameters such that we do not dispose here of error bands. We expect them to be similar to the standard case shown in Fig. 8. The results in Fig. 9 also reproduce nicely the trend  $S_{\infty}^2 \propto E^*$ . Here, we even see that ETDHF stays valid to higher energies than in the previous case. This shows that validity of the approaches depends not only on excitation energy, but also on other circumstances as, e.g., spectral density. It is advisable to check validity in new applications anew.

One may be disquieted by the difference between STDHF and ASTDHF for energy 10–15 eV. It is probably a statistical fluctuation and stays in the range of error bands seen in Fig. 8. For the same reasons on error bands, the fact that ASTDHF is below or above STDHF has no sufficient significance.

#### 4. Conclusions and perspectives

We have presented in this paper a new approach for describing dissipative dynamics in finite fermion systems as encountered in a manifold of experimental situations. The discussion was focused on finite electronic systems for which many experiments are presently performed. Our approach is based on an extension of mean-field theory by a stochastic treatment of two-body collisions, coined Stochastic Time-Dependent Hartree-Fock (STDHF). While STDHF provides a powerful description at high excitation energies, it is limited at lower excitations by the increasing cost when sampling rare events. To overcome this sampling problem, we confine the stochastic propagation to one common mean field for all samples. This reduces the cost of meanfield propagation dramatically and so allows, together with the now simpler book-keeping, to deal with much larger ensembles. The dynamical correlations are still evaluated by stochastic scan through two-body collisions. But this is done at larger time steps than mean-field propagation. Together, this typically saves between 1 and 2 orders of magnitude computation times as compared to STDHF and costs in the present application example only a factor 2-3 more than pure mean field propagation. The common mean field is formally obtained by averaging. Thus the new approach is coined Average STDHF (ASTDHF).

A large part of the present paper was devoted to a detailed presentation of ASTDHF from a formal side. The other aim was a comparison with the predecessor theory STDHF and the still simpler extended TDHF (ETDHF) approach which accounts only for collisional effects on the occupation numbers (eigenvalues of the one-body density matrix assumed diagonal). As an intermediate approach, we also look at ASTDHF without off-diagonal terms, denoted as diagonal ASTDHF. To allow extensive comparisons, we have worked here with a 1D test system modeling a well bound cluster/molecule. Remarkable agreement between ASTDHF and STDHF has been found up to large excitation energies, at least twice the ionization potential. The simpler ETDHF can also deliver good results, however with its range of validity severely limited to lower energies. The diagonal ASTDHF is also found to be limited to lower energies, although reaching a bit farther up than ETDHF.

In conclusion, the newly introduced ASTDHF approach represents a big step forward in the description of dissipative dynamics in finite fermion systems. It promises affordable calculations for realistic, three dimensional systems in electronic and nuclear physics in situations where fluctuations of the mean field can be expected to remain small. The next step to be explored are open systems where dissipation and ionization are competing. Work along that line is in progress.

#### Acknowledgments

We thank Institut Universitaire de France, and the CNRS and the Midi-Pyrénées region (doctoral allocation number 13050239) for support during the realization of this work. It was also granted access to the HPC resources of CalMiP (Calcul en Midi-Pyrénées) under the allocation P1238, and of RRZE (Regionales Rechenzentrum Erlangen).

#### Appendix A. Mapping a one-body density operator to an AST-DHF ensemble

The mapping from the many-body density  $\mathcal{D}$  to the one-body density operator  $\hat{\rho}$  is straightforward, as discussed at the end of Sec. 2.4. The reverse mapping, called the Slater ensemble mapping,  $\hat{\rho} \Rightarrow \mathcal{D}$  performed in Step 2 of Sec. 2.5 amounts to satisfy a relation between given s.p. occupations  $w_{\nu}$ and appropriate  $W_{\mathbf{n}}$  in the representation (10), that is,  $w_{\nu} = \sum_{\mathbf{n}} W_{\mathbf{n}} n_{\nu}$ . This mapping is not unique and has only approximate solutions. This is performed by a least squares fit minimizing

$$\chi^{2} = \sum_{\nu} \left( w_{\nu} - \sum_{\mathbf{n}=1}^{\aleph} n_{\nu} W_{\mathbf{n}} \right)^{2} + \eta \sum_{\mathbf{n}} W_{\mathbf{n}}^{2} , \qquad (A.1)$$

where  $\eta$  is some small positive numerical parameter. The minimization is done with the constraint  $0 \leq W_n \leq 1$ . The second term weighted by  $\eta$  serves to prefer the solution with the most evenly distributed coefficients  $W_n$ . In practice, one starts by picking  $\aleph$  Slater states from the reservoir to build  $\chi^2$ . One then replaces one Slater state in the sums appearing in Eq. (A.1) by another Slater state from the reservoir and tests if this produces a smaller  $\chi^2$ . If yes, the replacement is validated and one keeps on testing new Slater states from the reservoir until a threshold on  $\chi^2$  (taken equal to  $10^{-6}$  in our calculations) is achieved. At the same time, in the course of this minimization procedure on  $\chi^2$ , one starts with  $\eta = 1$  and, at each step, reduces it by a factor 16 down to  $\eta \ll 10^{-12}$ .

A word is in place here concerning energy conservation. A key issue in the Slater ensemble mapping is to preserve energy. The best working point we have found up to now is not to include it via a Lagrange multiplier in a variational principle in Eq. (A.1) but rather to directly work with a set of Slater states which already have the right energy (again up to some accuracy). This is what covers the notion of reservoir we have just mentioned. Now, the question is how to constitute this reservoir of energy matching states. There is no unique recipe to do so. We presently progressively build it by constructing 2p2h transitions first on top of the initial state of the system and then progressively from the reservoir of states themselves. This procedure has the advantage of using the well established and energy preserving 2ph scheme used to perform STDHF steps. In case of failure, namely if the procedure fails to reach a reservoir of states large enough, it can be iterated (2ph states built on top of 2ph states). Experience has shown that it is usually more than enough.

Finding  $W_{\mathbf{n}}$  corresponds to solving the non-negative least square (NNLS) problem. There are many algorithms available to do that. We have modified the sequential coordinate-wise algorithm from [43] for the NNLS problem to include the term  $\propto \eta$ . This algorithm has been chosen because it is easy to modify and to implement. It is also expected to be efficient when the number of  $W_{\mathbf{n}}$  is a much larger than the number of  $w_{\nu}$  which is precisely the case we are facing. Since this algorithm is gradient-descent-based, it allows us to use a previous calculation as a starting point. This property is used in our calculations and this is why we store the  $W_{\mathbf{n}}$  from the previous ASTDHF step, see Steps 2 and 4 of the ASTDHF scheme discussed in Sec. 2.5.

#### Appendix B. Formal summary of STDHF

The STDHF scheme is explained briefly in Sec. 2.3. We complement here more details, referring to steps in the enumerated list in this section.

#### Appendix B.1. Evolution of correlations

Step 1 deals with the built-up of correlations. For a given pure Slater state  $D^{(\alpha)}(t_0)$ , we evaluate two-body correlations on top of the TDHF evolution over a finite time span  $\tau = t - t_0$  long enough to gather a sufficient amount of correlations and short enough to keep mean field as leading component (thus allowing a perturbative treatment). The correlations are expanded in the various configurations **n** of single particle (s.p.) states to  $\hat{h}^{(\alpha)}$ , i.e.

$$|\Psi^{(\alpha)}(t)\rangle = \sum_{\mathbf{n}} |\Phi_{\mathbf{n}}^{(\alpha)}(t)\rangle c_{\mathbf{n}}^{(\alpha)}(t) \quad , \quad |\Phi_{\mathbf{n}}^{(\alpha)}(t)\rangle = \mathcal{U}^{(\alpha)}(t,t_0)|\Phi_{\mathbf{n}}^{(\alpha)}(t_0)\rangle \quad (B.1)$$

where the Slater states are propagated by the mean field evolution operator  $\mathcal{U}^{(\alpha)}$  while the  $c_{\mathbf{n}}^{(\alpha)}(t)$  account for effects beyond mean field. Note that **n** does also depend on  $\alpha$  but for the sake of compactness, we omit the upper script  $\alpha$  for **n** in the following. This yields the correlated N-body density:

$$\mathcal{D}^{(\alpha)}(t) = \sum_{\mathbf{n},\mathbf{n}'} |\Phi_{\mathbf{n}}^{(\alpha)}(t)\rangle \ c_{\mathbf{n}}^{(\alpha)}(t) \ c_{\mathbf{n}'}^{(\alpha)*}(t) \ \langle \Phi_{\mathbf{n}'}^{(\alpha)}(t)| \quad . \tag{B.2}$$

Appendix B.2. Reduction to an incoherent superposition

In step 2, Eq. (B.2) is reduced to an incoherent superposition of Slater states as:

$$\mathcal{D}^{(\alpha)}(t) \approx \sum_{\mathbf{n}} P_{\mathbf{n}_0 \to \mathbf{n}}^{(\alpha)} D_{\mathbf{n}}^{(\alpha)}(t) \quad , \quad P_{\mathbf{n}_0 \to \mathbf{n}}^{(\alpha)} = \left| c_{\mathbf{n}}^{(\alpha)}(t) \right|^2 \quad , \qquad (B.3)$$

by assuming that off-diagonal elements are wiped out by their fast phase oscillations [16].

The coefficients  $c_{\mathbf{n}}^{(\alpha)}(t)$  are propagated by first order time-dependent perturbation theory, which means that  $c_{\mathbf{n}}^{(\alpha)}(t)$  is of order of  $\langle \Phi_{\mathbf{n}}^{(\alpha)} | \hat{V}_{\text{res}}^{(\alpha)} | \Phi_{\mathbf{n}_0}^{(\alpha)} \rangle$ . The residual interaction  $\hat{V}_{\text{res}}^{(\alpha)}$  depends on  $\alpha$  to comply with the splitting of the total Hamiltonian into the mean field  $\hat{h}^{(\alpha)}$  and its associated residual interaction. This two-body interaction can thus only couple configurations  $\mathbf{n}$ which are 2ph excitations with respect to the initial  $\mathbf{n}_0$ , i.e.  $\mathbf{n} \in \mathcal{J}_{2ph}(\mathbf{n})$  in the notation of Sec. 2.2. Integrating out the  $|c_{\mathbf{n}}(t)|^2$  finally yields an explicit expression for the transition probabilities in terms of a Fermi's golden rule [34]:

$$P_{\mathbf{n}_{0}\to\mathbf{n}}^{(\alpha)} = \frac{2\pi\tau}{\hbar} \left| \langle \Phi_{\mathbf{n}}^{(\alpha)} | \widehat{V}_{\mathrm{res}}^{(\alpha)} | \Phi_{\mathbf{n}_{0}}^{(\alpha)} \rangle \right|^{2} \delta(E_{\mathbf{n}}^{(\alpha)} - E_{\mathbf{n}_{0}}^{(\alpha)}) \Theta(\mathbf{n} \in \mathcal{J}_{2ph}(\mathbf{n}_{0})) \quad (B.4a)$$

$$P_{\mathbf{n}_{0}\to\mathbf{n}_{0}}^{(\alpha)} = 1 - \sum_{\mathbf{n}\in\mathcal{J}_{2ph}(\mathbf{n}_{0})} P_{\mathbf{n}_{0}\to\mathbf{n}}^{(\alpha)}$$
(B.4b)

where  $\Theta(\mathbf{n} \in \mathcal{J}_{2ph}(\mathbf{n}_0))$  limits the jumps to 2ph configurations about  $\mathbf{n}_0$ . In the usual case of weak residual interaction, the energy difference can be approximated by the s.p. energies of the transition states

$$\delta(E_{\mathbf{n}}^{(\alpha)} - E_{\mathbf{n}_0}^{(\alpha)}) \approx \delta(\varepsilon_{p_1} + \varepsilon_{p_2} - \varepsilon_{h_1} - \varepsilon_{h_2})$$
(B.4c)

where  $p_i$  are the two states which are occupied after the jump and the  $h_i$  those which are depleted. We actually use this approximate form only as a filter to preselect potentially energy conserving transitions. The energies of the thus preselected transitions are then explicitly computed. The  $\delta$  function on energies has in practice a finite width  $\Gamma$  due to a finite sampling time  $\tau$ . At the same time, a finite width is necessary to allow application of Eq. (B.4) in connection with a discrete energy spectrum. The actual choice of  $\Gamma$  is a compromise: it has to be large enough to smooth sampling of jumps and sufficiently small to maintain satisfying energy conservation. In fact, this means energy conservation in the average because  $E_{\mathbf{n}}^{(\alpha)}$  and  $E_{\mathbf{n}_0}^{(\alpha)}$  are the expectation values for their corresponding states which, being mean-field states, carry some energy uncertainty. For the results presented in Sec. 3, we have used  $\Gamma = 1.63$  eV.

The transition probability (B.4a), often with approximation (B.4c), is more involved than it looks at first glance: it is not fully defined. The initial Slater state  $D_{\mathbf{n}_0}$  is invariant against unitary transformations among the occupied s.p. states, i.e. among all  $\nu$  with  $n_{\nu} = 1$ . There is also the freedom of unitary transformations among the unoccupied states, all  $\nu$  with  $n_{\nu} = 0$ . The standard derivations of Fermi's golden rule rely on a stationary mean field and the  $\varepsilon_{\nu}$  are naturally the eigenstates of the static Hamiltonian [42]. We here develop the perturbation theory about a time-dependent mean field where the occupied states are not fully compatible with the eigenstates of the actual mean-field Hamiltonian. All s.p. states acquire unavoidably some energy variance. What we still can do is to ask for s.p. states closest to eigenstates. And these are the s.p. states which have minimal energy variance. This is now the place where we must exploit the freedom of unitary transformations (within occupied space and unoccupied space separately) to achieve minimal energy variance of the s.p. states. We thus perform a basis transformation:

$$\varphi_{h_k}^{(\alpha)}(t) = \sum_{k'=1}^{N} u_{h_k h_{k'}}^{(\alpha)} \widetilde{\varphi}_{h_{k'}}^{(\alpha)}(t) \quad , \quad \varphi_{p_l}^{(\alpha)}(t) = \sum_{l'=1}^{\Omega-N} u_{p_l p_{l'}}^{(\alpha)} \widetilde{\varphi}_{p_{l'}}^{(\alpha)}(t) \tag{B.5}$$

 $h_k$  stands for occupied states and  $p_k$  for unoccupied ones, the  $\tilde{\varphi}_{\nu}^{(\alpha)}$  are the s.p. basis before and the  $\varphi_{\nu}^{(\alpha)}$  the basis after the transformation, and the  $u^{(\alpha)}$  matrix composes unitary matrices which diagonalize the mean-field Hamiltonian  $\hat{h}^{(\alpha)}$  in occupied and unoccupied subspaces, thus minimizing energy uncertainty for the new s.p. states. Only having done this, we can go ahead and evaluate the jumps which is also a tedious process. After all, this step 2 turns out to be the most involved one in the STDHF scheme.

#### Appendix B.3. Sketch of the procedure

Thus far, we have explained one STDHF step. The full propagation consists in connecting a great set of such steps which are, in fact, coarse time steps  $t_{j-1} \longrightarrow t_j = t_{j-1} + \tau$ . The mean-field propagation involves much higher virtual frequencies and has to be determined with much higher resolution. The coarse step  $\tau$  covers typically 50–100 TDHF time steps summarized in the time-evolution operator  $\mathcal{U}^{(\alpha)}$  in Eq. (B.1). The STDHF scheme is sketched in Fig. B.10.

Each column corresponds to one sample  $\alpha$  with  $\alpha \in [1, \mathcal{N}]$ . The thick vertical lines indicate pure mean-field time propagation between STDHF jumps. Starting from Slater state  $D^{(\alpha)}(t_{j-1})$ , we denote by  $\widetilde{D}^{(\alpha)}(t_j)$  the corresponding time-propagated state from  $t_{j-1}$  to  $t_j$ . The horizontal dashes indicate the coarse time steps at which the STDHF jumps are evaluated. To better visualize the unfolding of correlations, we have expanded the infinitesimal interval  $[t_j, t_j^+]$ . The dashed green lines in this span indicate the sub-samples generated by second order perturbation theory (steps 1 and 2 described in Appendix B.1 and Appendix B.2). One of these is drawn as a full red line. This is the sample which is finally selected for further propagation in step 3. This illustrates the key features of STDHF: constant size of ensembles, temporary unfolding of sub-ensembles covering new correlations, stochastic selection of one sample in each sub-ensemble for further propagation. The procedure converges to the exact incoherent propagation in case of an arbitrarily large ensemble.



Figure B.10: Schematic illustration of the STDHF procedure. For explanations, see text.

#### Appendix C. The quantum-Boltzmann collision term

The traditional prototype kinetic equation is the Boltzmann equation which is used for classical bulk systems [44]. The pure mean-field dynamics for finite fermion systems is described by the much celebrated Vlasov equation [45]. It is extended to a kinetic equation by adding a Boltzmann collision term modified to respect the Pauli principle during collisions, yielding the Vlasov-Uehling-Uhlenbeck (VUU) equation [46]. The VUU equation deals with a common mean field as the Vlasov equation does. Extensions which incorporate fluctuations of the mean field are summarized under the label Boltzmann-Langevin equation (BLE), see e.g. [21]. An approximate quantum-mechanical realization of the latter is achieved by STDHF as shown in [34]. What remains is a quantum Boltzmann equation (QBE) as quantum extension of VUU. This QBE is then the kinetic equation which should correlate with ASTDHF similar as the BLE correlates with STDHF. In this appendix, we will summarize briefly the QBE.

Pure mean-field propagation is solution of the one-body Liouville equa-

tion, already outlined in Eq. (1),

$$\mathrm{i}\hbar\partial_t\hat{\rho} = \left[\hat{h},\hat{\rho}
ight]$$

where  $\hat{h}[\hat{\rho}]$  is the mean-field according to  $\hat{\rho}$ . The occupation numbers are frozen during mean-field propagation (as in Step 1 of Sec. 2.5). The onebody Liouville equation is extended to a quantum kinetic equation by adding a two-body collision term  $\hat{K}$  [47, 48]:

$$\begin{split} \mathrm{i}\hbar\partial_{t}\hat{\rho} &= \left[\hat{h},\hat{\rho}\right] + \hat{K} , \qquad (\mathrm{C.1a}) \\ K_{\nu\nu'} &= \pi \sum_{\alpha\beta\ldots\gamma'\delta'} \delta\left(\varepsilon_{\alpha} + \varepsilon_{\beta} - \varepsilon_{\gamma} - \varepsilon_{\delta}\right) \left\{\delta_{\gamma\nu'}v_{\nu\delta\alpha\beta}\widetilde{\rho_{\alpha\alpha'}\rho_{\beta\beta'}}v_{\alpha'\beta'\gamma'\delta'}\widetilde{\rho_{\gamma'\gamma}\rho_{\delta'\delta}}\right. \\ &\left. -\delta_{\gamma\nu'}v_{\nu\delta\alpha\beta}\widetilde{\rho_{\alpha\alpha'}\rho_{\beta\beta'}}v_{\alpha'\beta'\gamma'\delta'}\widetilde{\rho_{\gamma'\gamma}\rho_{\delta'\delta}}\right. \\ &\left. -\delta_{\alpha\nu}v_{\gamma\delta\nu'\beta}\widetilde{\rho_{\alpha\alpha'}\rho_{\beta\beta'}}v_{\alpha'\beta'\gamma'\delta'}\widetilde{\rho_{\gamma'\gamma}\rho_{\delta'\delta}}\right. \\ &\left. +\delta_{\alpha\nu}v_{\gamma\delta\nu'\beta}\widetilde{\rho_{\alpha\alpha'}\rho_{\beta\beta'}}v_{\alpha'\beta'\gamma'\delta'}\widetilde{\rho_{\gamma'\gamma}\rho_{\delta'\delta}}\right\} \qquad (\mathrm{C.1b}) \\ &\hat{h}\varphi_{\nu} = \varepsilon_{\nu}\varphi_{\nu} , \qquad (\mathrm{C.1c}) \end{split}$$

$$\widetilde{\rho_{\alpha\alpha'}\rho_{\beta\beta'}} = \rho_{\alpha\alpha'}\rho_{\beta\beta'} - \rho_{\alpha\beta'}\rho_{\beta\alpha'} , \ \overline{\rho}_{\alpha\alpha'} = \delta_{\alpha\alpha'} - \rho_{\alpha\alpha'} .$$

The interaction in the collision term is the residual interaction which is just that part of the two-body interaction not accounted for in the mean field. This means that it can only connect true 2ph transitions. Furthermore, it is important to note that this collision term is formulated in the *h*-diagonal basis of s.p. states which obey Eq. (C.1c). This is required to formulate the energy conserving  $\delta$  function in the expression and it implies that the one-body density has non-vanishing off-diagonal elements in a typical offequilibrium situation.

Although this QBE looks formally straightforward, it is extremely cumbersome to evaluate because it involves a sixfold summation over the whole space of s.p. states. To the best of our knowledge, it has not been applied so far in realistic finite fermionic systems. What exists are applications in bulk systems where translation symmetry helps to reduce the complexity [17, 18]. In this case, translation symmetry also serves to establish momentum conservation in the course of collisions. Instead, finite systems are localized in space, and this spoils momentum conservation in collisions. There remains only energy conservation and, also important to mention, conservation of particle number which is guaranteed by the compensation of gain and loss terms.

The question remains to what extent ASTDHF simulates the QBE (C.1). Without a solid proof, we sketch at least the idea here. In ASTDHF, the one-body density is represented by an ensemble  $\hat{\rho} = \sum_{\mathbf{n}} W_{\mathbf{n}} \hat{\rho}_{\mathbf{n}}$  which is the one-body equivalent of Eq. (10). Each sample  $\hat{\rho}_{\mathbf{n}}$  in the ensemble represents a pure one-body state and all states  $\hat{\rho}_{\mathbf{n}}$  are defined with respect to the same ortho-normal s.p. basis. The ensemble representation is inserted into the QBE. The residual interaction in the collision term (C.1b) selects automatically the 2ph transitions which reduces the terms to a collection close to ASTDHF. One crucial approximation is now that ASTDHF does not proceed to the exactly h-diagonal basis (C.1c), but restricts diagonalization to the two sub-spaces of occupied and un-occupied states separately, see Sec. 2.5, Step 3a in the ASTDHF scheme. This approximation renders ASTDHF well manageable at the price of leaving some energy uncertainty in the 2ph transitions as compared to the exact quantum collision term (C.1b). The same approximation was already used in STDHF and tested successfully in an exactly solvable model [49]. It turned out to well perform. We assume that the same holds even more so in the moderate excitation regime typically treated with ASTDHF.

#### References

- [1] J. W. Negele, Rev. Mod. Phys. **54** (1982) 913.
- [2] C. Simenel, Eur. Phys. J. A 48 (2012) 152.
- [3] J. A. Maruhn, P.-G. Reinhard, P. D. Stevenson, A. S. Umar, Comp. Phys. Comm. 185 (2014) 2195.
- [4] R. M. Dreizler, E. K. U. Gross, Density Functional Theory: An Approach to the Quantum Many-Body Problem, Springer-Verlag, Berlin, 1990.
- [5] P.-G. Reinhard, E. Suraud, Introduction to Cluster Dynamics, Wiley, New York, 2003.
- [6] F. Calvayrac, P.-G. Reinhard, E. Suraud, C. A. Ullrich, Phys. Rep. 337 (2000) 493.

- [7] M. A. L. Marques, N. T. Maitra, F. M. S. Nogueira, E. K. U. Gross, A. Rubio, Fundamentals of Time-Dependent Density Functional Theory, Lect. Notes in Phys. vol 837, Springer-Verlag, Berlin, 2012.
- [8] P. Wopperer, P. M. Dinh, P.-G. Reinhard, E. Suraud, Phys. Rep. 562 (2015) 1.
- [9] U. Saalmann, C. Siedschlag, J. M. Rost, J. Phys. B **39** (2006) R39.
- [10] T. Fennel, K.-H. Meiwes-Broer, J. Tiggesbäumker, P.-G. Reinhard, P. M. Dinh, E. Suraud, Rev. Mod. Phys. 82 (2010) 1793.
- [11] M. Kjellberg, O. Johansson, F. Jonsson, A. V. Bulgakov, C. Bordas, E. E. B. Campbell, K. Hansen, Phys. Rev. A 81 (2010) 023202.
- [12] K. Hansen, Statistical physics of nanoparticles in the gas phase, Springer Netherlands, Amsterdam, 2013.
- [13] J. O. Johansson, G. G. Henderson, E. E. B. Campbell, J. Phys. Chem. A 118 (2014) 8067.
- [14] G. Chen, Nanoscale Energy Transport and Conversion: A Parallel Treatment of Electrons, Molecules, Phonons, and Photons, Oxford University Press, New York, 2005.
- [15] J. Dalibard, Collisional dynamics of ultra-cold atomic gases, in: M. Inguscio, S. Stringari, C. Wieman (Eds.), Proceedings of the International School of Physics-Enrico Fermi, Course CXL, IOS Press, Amsterdam, 1999, p. 321.
- [16] R. Balescu, Equilibrium and non equilibrium statistical mechanics, Wiley, New York, 1975.
- [17] L. P. Kadanoff, G. Baym, Quantum Statistical Mechanics: Green's Function Methods in Equilibrium and Nonequilibrium Problems, Frontiers in physics, Benjamin, New York, 1962.
- [18] D. Pines, P. Nozières, The Theory of Quantum Liquids, W A Benjamin, New York, 1966.
- [19] G. F. Bertsch, S. Das Gupta, Phys. Rep. **160** (1988) 190.

- [20] A. Bonasera, F. Gulminelli, J. Molitoris, Phys. Rep. **243** (1994) 1.
- [21] Y. Abe, S. Ayik, P.-G. Reinhard, E. Suraud, Phys. Rep. **275** (1996) 49.
- [22] A. Domps, P.-G. Reinhard, E. Suraud, Phys. Rev. Lett. 81 (1998) 5524.
- [23] T. Fennel, G. F. Bertsch, K.-H. Meiwes-Broer, Eur. Phys. J. D 29 (2004) 367.
- [24] T. Ditmire, T. Donnelly, A. M. Rubenchik, R. W. Falcone, M. D. Perry, Phys. Rev. A 53 (1996) 3379.
- [25] A. K. Rajam, I. Raczkowska, N. T. Maitra, Phys. Rev. Lett. 105 (2010) 113002.
- [26] R. Requist, O. Pankratov, Phys. Rev. A 81 (2010) 042519.
- [27] F. Lackner, I. Brezinova, T. Sato, K. L. Ishikawa, J. Burgdörfer, Phys. Rev. A 91 (2015) 023412.
- [28] F. Lackner, I. Brezinova, T. Sato, K. L. Ishikawa, J. Burgdörfer, 2rdm2, Phys. Rev. A 95 (2017) 033414.
- [29] J. Zhangellini, M. Kitzler, T. Brabec, A. Scrinzi, J. Phys. B 37 (2004) 763.
- [30] P. Krause, T. Klamroth, P. Saalfrank, J. Chem. Phys. 127 (2007) 034107.
- [31] A. Dutta, C. Trefzger, K. Sengupta, Phys. Rev. B 86 (2012) 085140.
- [32] P.-G. Reinhard, E. Suraud, Ann. Phys. (N.Y.) **354** (2015) 183.
- [33] M. Vincendon, E. Suraud, P.-G. Reinhard, Eur. Phys. J D. 71 (2017) 179
- [34] P.-G. Reinhard, E. Suraud, Ann. Phys. (NY) **216** (1992) 98.
- [35] D. Lacroix, S. Ayik, Eur. Phys. J. A **50**(2014) 95.
- [36] E. Suraud, P.-G. Reinhard, New J. Phys. **16** (2014) 063066.
- [37] N. Slama, P.-G. Reinhard, E. Suraud, Ann. Phys. (N.Y.) 355 (2015) 182.

- [38] L. Lacombe, P. M. Dinh, P.-G. Reinhard, E. Suraud, J. Phys. B 49 (2016) 245101.
- [39] K. Goeke, P.-G. Reinhard, Time-Dependent Hartree-Fock and Beyond, Lecture Notes in Physics, vol. 171, Springer, Heidelberg, 1982.
- [40] C. Y. Wong, K. T. R. Davies, Phys. Rev. C 28 (1983) 240.
- [41] M.A.L. Marques, E.K.U. Gross, Annual Rev. Phys. Chem. 55 (2004) 427.
- [42] C. Cohen-Tanoudji, B. Diu, F. Laloe, Quantum Mechanics, Wiley, New York, 2006.
- [43] V. Franc, V. Hlaváč, M. Navara, in: A. Gagalowicz, W. Philips (Eds.), CAIP'05 Proceedings of the 11th international conference on Computer Analysis of Images and Patterns, Springer-Verlag Berlin, Heidelberg, 2005, p. 407.
- [44] C. Cercignani, The Boltzmann equation and its applications, Applied Mathematical Sciences 67, Springer, New York, 1988.
- [45] A. A. Vlasov, Many Particle Theory and Its Applications to Plasma, Gordon & Breach, New York, 1950.
- [46] E.-A. Uehling, G.-E. Uhlenbeck, Phys. Rev. 43 (1933) 552.
- [47] H. Reinhardt, P.-G. Reinhard, K. Goeke, Phys. Lett. B 151 (1985) 177.
- [48] K. Goeke, P.-G. Reinhard, H. Reinhardt, Ann. Phys. **166** (1986) 257.
- [49] L. Lacombe, P.-G. Reinhard, E. Suraud, P. M. Dinh, Ann. Phys. (NY) 373 (2016) 216.