

## On Some Dissipative Extensions of Quantum Mean-Field Theories

**L. Lacombe<sup>1</sup>, M. Vincendon<sup>1</sup>, P. M. Dinh<sup>1</sup>, P.-G. Reinhard<sup>2</sup>,  
E. Suraud<sup>1</sup>**

<sup>1</sup>Laboratoire de Physique Théorique, Université de Toulouse,  
CNRS, UPS, France

<sup>2</sup>Institut für Theoretische Physik, Universität Erlangen,  
D-91058 Erlangen, Germany

**Abstract.** We discuss a dissipative extension of Time Dependent Hartree Fock (TDHF), based on a stochastic extension of TDHF. We outline the method and present a few examples of applications in the context of electronic systems. The proposed framework is generic and can be applied to any system which can be described on the basis of a mean field theory as a good starting basis.

### 1 Introduction

The description of dissipative effects in finite quantum systems has a long history [1], which concerns several fields in physics and chemistry. The question was unfortunately never settled in a convenient manner and thus remains an open field of research. The interest in this question was recently renewed following studies on clusters and molecules excited by intense laser fields [2–4]. But the point is also considered for ballistic electron transport in nano systems [5], and in the case of trapped Fermi gases [6] as well. The molecular case has recently driven numerous studies [4, 7], because of the more and more detailed analysis of electronic emission (energy-, angular-resolved distributions...). The question was also deeply explored in nuclear physics in particular in nuclear fission and nuclear collisions [8]. In nuclear collisions, for example, the projectile kinetic energy is redistributed into thermal energy of the compound target+projectile system. This may possibly lead to the formation of truly “hot nuclei” subsequently deexciting via thermal emission and/or fragmentation. This case clearly points out the importance of “elementary collisional events” between system’s constituents. We will refer to these as “collisional correlations”, in relation to Fermi liquid theory [9] with incoherent reduction of two-body correlations to two-Fermion collisions.

Nuclear theory devoted major efforts since three decades to address the question of hot nuclei with a stronghold on semi-classical methods [8, 10, 11], somewhat similarly to the plasma physics strategy [12]. Molecular Dynamics approaches combining quantum features with a semi-classical treatment of dynamical correlations [13, 14] were also developed and have been heavily used

so far. But no complete practical quantum approach could be proposed in the field, in spite of numerous formal investigations [8, 15, 16]. The case of clusters and molecules was considered more recently, first, again, at semi classical level [17, 18], in a way very similar to the nuclear case. These approaches are, nevertheless, bound to simple metal clusters with soft binding, and even in this case, exhibit clear deficiencies because of the importance of resonance effects, only partly addressed at the semi classical level [19]. Furthermore (semi) classical approaches are primarily derived for high excitations such as in the case of very intense laser pulses [2]. In the case of moderate energy deposits quantum effects cannot be neglected. The system may be highly perturbed (far away from any equilibrium) system, but with moderate remaining excitation energy because a sizeable part of the excitation may have been released by ionization. This kind of (common) situation is far beyond the reach of semi-classical methods and thus requires a dedicated treatment.

There exist a few attempts, for example by treating dynamical correlations semi-classically on top of quantum mean field [20]. There are also fully quantum mechanical treatments in schematic model systems [21] as well as time-dependent configuration-interaction (TD-CI) calculations [22]. But these elaborate approaches are limited to low excitations and small systems. A robust quantum theory addressing the regime of moderate to high excitation energies is thus still missing. The present paper proposes a way to attack these questions by recurring to a stochastic extension of mean field theories. We will consider here applications to irradiated clusters and molecules as examples but the formal development underlying these applications can be applied to a wider variety of physical systems under non-linear excitations.

## **2 Outline of Theory**

### **2.1 Time dependent mean field, TDHF**

Time-Dependent Density Functional Theory (TDDFT) provides a robust and versatile access to the dynamics of irradiated clusters and molecules, especially at the effective mean field level of the widely used Time-Dependent Local-Density Approximation (TDLDA) [23]. But TDLDA misses by construction dissipative effects from electron-electron collisions, which limits its range of applicability to moderate excitations. In the electronic context Time Dependent Hartree Fock (TDHF) refers to a mean field theory in which exchange is treated exactly, at variance with TDLDA which corresponds to a Hartree theory with approximate (local) exchange. In the nuclear case TDHF usually refers to cases with effective density dependent hamiltonians and again approximate exchange, which is formally very similar to the electronic case. For the sake of simplicity we shall use the acronym TDHF to label the mean field theory on which we build up dynamical correlations.

## On Some Dissipative Extensions of Quantum Mean-Field Theories

For formal discussions it is worth re-expressing mean field dynamics in terms of the one-body density matrix  $\hat{\rho}$ , whose natural orbitals representation reads

$$\hat{\rho} = \sum_{\alpha=1}^{\infty} |\phi_{\alpha}\rangle W_{\alpha} \langle \phi_{\alpha}| \quad (1)$$

where the  $W_{\alpha}$  are the occupation numbers in this basis (eigenvalues of the density matrix). Mean field propagation can then be written as

$$i\partial_t \hat{\rho} = [\hat{h}[\varrho], \hat{\rho}] \quad (2)$$

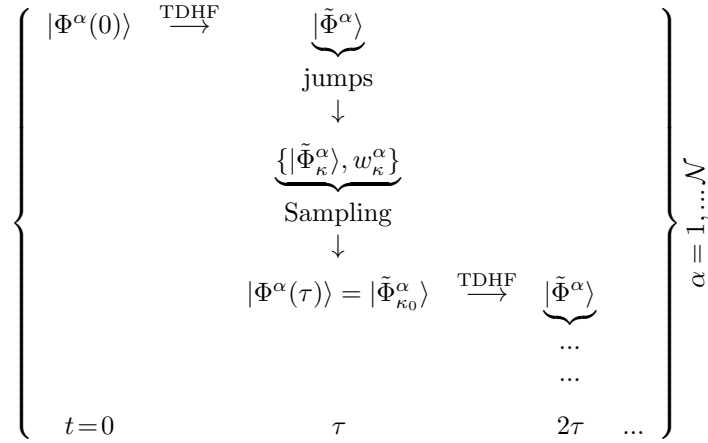
with the Hamiltonian  $\hat{h}[\varrho]$  computed from the diagonal part  $\varrho$  of the density matrix  $\hat{\rho}$ . The occupation numbers  $W_{\alpha}$  are time independent at mean field level.

### 2.2 Standard stochastic TDHF, STDHF

A natural evolution of TDHF towards the inclusion of dissipative effects is to complement it by a collision integral, following a hierarchy matrix strategy [24]. Still, the standard truncation schemes to attain a collision term miss fluctuations which are considered as corresponding to higher order effects. However according to the fluctuation-dissipation theorem, fluctuations scale with excitation energy so that they should be included in a concomitant way to dissipative features. While they can be overlooked at moderate excitation energy they should probably be accounted for at higher excitations. A possible solution is to consider more elaborate approaches including a Langevin treatment through a stochastic collision term [25, 26], which leads to stochastic kinetic equations which altogether leads to a Boltzmann equation complemented by a stochastic collision term [25, 26]. This originally classical approach can be extended to the quantum domain but leads to extremely involved equations, hardly solvable in practice. Some semi-classical approximations thereof were nevertheless used in nuclear dynamics [8, 27, 28].

An alternative quantum mechanical approach consists in directly extending TDHF in a stochastic manner [16]. The formalism can then be formally reduced to a quantum stochastic kinetic equation. The method, Stochastic Time-Dependent Hartree Fock (STDHF), nevertheless provides a formally simple framework for true quantum approaches. Dynamics is then represented by an ensemble of pure mean field states propagated in parallel, on top of which a perturbative (on the fly) account of collisional correlations is evaluated. Both the formalism and its realization are simple, except for computational cost mostly because of the necessary large size of the ensemble to reach statistically reliable estimates. Direct applications in realistic systems are thus not yet possible. Only model systems in 1D could be computed as proof of principle [29, 30]. The next step, which we discuss briefly here, is to simplify STDHF a bit in order to apply it to realistic 3D cases. Test cases will be presented here in 1D in order to comply with STDHF computations, though.

Let us first briefly remind the STDHF frame. The idea is to step from one mean field to an ensemble thereof which, in terms of associated Slater states  $|\Phi^\alpha\rangle$  amounts to step from one to a set of Slater states :  $|\Phi\rangle \rightarrow \{|\Phi^\alpha\rangle, \alpha = 1, \dots, \mathcal{N}\}$  where  $\mathcal{N}$  is the size of the stochastic ensemble. Each member of the ensemble is propagated according to its mean field during a time interval  $\tau$  long enough to allow a sufficient building up of correlations, but not too much, in order to allow a perturbative treatment. After  $\tau$ , correlations are evaluated perturbatively (Fermi Golden rule) for each member  $\alpha$  of the ensemble around the time evolved state  $|\Phi^\alpha\rangle$ . We practically restrict correlations to  $2p2h$  excitations around the mean field and assume loss of coherence between these various excitations. This practically delivers a correlated density matrix  $\hat{D}_\alpha = \sum_\kappa w_{\alpha\kappa} \hat{\rho}_\kappa^\alpha$  where the summation runs over all energy accessible (Fermi Golden rule preserves total energy)  $2p2h$  density matrices  $\hat{\rho}_\kappa$  built on top of  $\hat{\rho}^\alpha = |\Phi^\alpha\rangle\langle\Phi^\alpha|$ . Even for a single trajectory  $\alpha$  such a procedure rapidly diverges. The way out is to make a stochastic treatment and sample *one*  $\hat{\rho}_\kappa^\alpha$  out of the generated set according to the weights  $w_{\alpha\kappa}$ . This delivers a new Slater state (any  $2p2h$  excitation on the original Slater state delivers a Slater state) which is again propagated according to its mean field. The procedure is repeated for each member of the ensemble which thus evolve independently from each other, each of them developing its own mean field. The procedure can be cast in a pictorial form as follows:



With the thus constructed ensemble one can compute physical observables as statistical averages. For example one body observables can be accessed from the (correlated) one-body density matrix which reads

$$\rho(1; 1') = \frac{1}{\mathcal{N}} \sum_\alpha \rho^{(\alpha)}(1; 1') \tag{3}$$

### 2.3 From STDHF to average STDHF, ASTDHF

Stochastic TDHF is appealing. It integrates both dissipative effects (via collisional correlations) and associated fluctuations through the stochastic ensemble. It thus covers the expected dynamical behaviors in the dissipative regime. It can be furthermore shown that STDHF can be properly reduced to a stochastic kinetic equation [16]. Nevertheless, because of the involved computational effort it requires, it will mostly provide a benchmark for other, simpler, theories, after its validation in simple 1D model systems of covalent molecules [29, 30]. The major issue concerns the stochastic ensemble representation which requires hundreds of events for proper treatment. Each event carries its own mean field which at the end represents a major computational effort. As a consequence a mere STDHF calculation represents hundreds of times the cost of a TDHF one. Furthermore in the case of moderate excitation energies, transition probabilities become smaller, whence an increased effort to properly sample them. This is the regime, in turn, where fluctuations are expected to remain moderate. There is thus an interesting direction to explore here, which consists in considering a STDHF propagation with a common (averaged) mean field. We will label this simplification by the acronym Average STDHF, ASTDHF.

The new approach, ASTDHF, is intuitively simple to figure out, although it requires some caution in the implementation. We shall thus not enter technical detail here and remain at a simple level level of presentation providing a taste of how ASTDHF is constructed. For the sake of simplicity we present it in direct relation to STDHF in the following table:

STDHF	ASTDHF
Ensemble of pure states	One mixed state
Ensemble of mean fields	One mean field
$\{\hat{\rho}^\alpha, \hat{h}^\alpha[\hat{\rho}^\alpha]\}_{\alpha=1, \dots, \mathcal{N}}$	$\hat{\rho}, \hat{h}[\hat{\rho}]$
$\hat{\rho}_\alpha = \sum_{i=1}^{\mathcal{N}}  \varphi_i^\alpha\rangle\langle\varphi_i^\alpha $	$\hat{\rho} = \sum_{i=1}^{\infty} n_i  \varphi_i\rangle\langle\varphi_i $
Correlation in sampling $\{\hat{\rho}_\alpha, \alpha = 1, \dots, \mathcal{N}\}$	Correlations in occupation numbers $n_i$ $\{n_i, i = 1, \dots, \infty\}$

Here  $\mathcal{N}$  labels the number of particles in the system (number of occupied states, occupation 1). The single particle wave functions are labeled by  $\varphi$  with the index  $i$  indicating the label of the single particle level. In STDHF they are extra indexed by  $\alpha$  to label the member of the STDHF ensemble. In ASTDHF the latter index vanishes pointing out the fact that one deals with a single set of single particle wave functions, and accordingly a single mean field. The above picture is quite schematic and requires some technicalities to be worked out in detail. The key issue of course is the evaluation of the occupation numbers  $n_i$ . The way to increment the latter is the following. We propagate the mixed ASTDHF state over a time interval  $\tau$  similar to STDHF. The mixed state possesses fractional occupation numbers  $n_i$  which are preserved during this mean field propagation

over  $\tau$ . In order to use STDHF strategy we need to reconstitute, at time  $\tau$ , an ensemble of pure states, in the spirit of STDHF. This is achieved by sampling the distribution of fractional occupation numbers by an ensemble of pure states (occupation numbers 0 or 1), of course preserving the total energy in the process. For each member of this ensemble one now computes perturbations exactly the same way as in STDHF but, instead of sampling the obtained correlations, we add them up explicitly, for each member of the ensemble and pile up the contributions of each member. This produces a new one body density matrix whose eigenvalues are the new (updated by STDHF correlations) occupation numbers  $n_i$  associated to each natural orbital building up the one-body density matrix. Mean field propagation starts again with this new expression of the mixed state.

## 2.4 Extended TDHF, ETDHF

As mentioned above STDHF may be reduced to a stochastic kinetic equation. The simpler version thereof is the corresponding quantum kinetic equation (without stochastic collision term) which nevertheless contains as collision term  $\hat{I}[\hat{\rho}]$  a complicated operator which can hardly be solved in practice. ASTDHF provides an indirect way to resolve this problem and a clearcut derivation of the relation between ASTDHF and a quantum kinetic equation is still to be developed. In the mean time one can consider a simpler version of the collision term obtained by assuming that the one-body density matrix entering  $\hat{I}[\hat{\rho}]$  remains diagonal, of the form Eq. (1), with time-dependent weights  $W_\alpha$ . The effect of the collision integral can then be written as a rate equation for the  $W_\alpha$

$$\frac{dW_\alpha}{dt} \sim \sum_{\beta} \sum_{\gamma} \sum_{\delta} |V_{\alpha\beta\gamma\delta}|^2 [(1 - W_\alpha)(1 - W_\beta)W_\gamma W_\delta - W_\alpha W_\beta(1 - W_\gamma)(1 - W_\delta)] \delta(\varepsilon_\alpha + \varepsilon_\beta - \varepsilon_\gamma - \varepsilon_\delta) \quad (4)$$

where the  $\varepsilon_i$  label s.p. energies. The standard acronym for this approximation is Extended TDHF (ETDHF) and was in particular explored in nuclear physics [15]. It is thus also interesting to test this oversimplified picture and compare it to STDHF and ASTDHF.

## 3 Illustrative Results

As already indicated we shall perform tests in 1D in order to be able to use STDHF as benchmark. We thus consider a molecular 1D model system. The setup is similar to the one in [29, 30]. We mock up a 1D molecular/cluster system by a mean field Hamiltonian (in  $x$  representation, using  $\hbar = 1$ )

$$\hat{h}^\alpha = -\frac{\Delta}{2m} + V_{\text{ext}}(x) + \lambda \left( \varrho^{(\alpha)}(x) \right)^\sigma \quad (5)$$

The external potential  $V_{\text{ext}}(x)$  is a Woods-Saxon profile  $V_{\text{ext}}(x) = V_0/(1 + \exp((x - x_0)/a))$  with  $V_0 = -68$  eV,  $x_0 = 15$   $a_0$ ,  $a = 2$   $a_0$ . It is complemented by a density dependent self constant term mocking up an effective

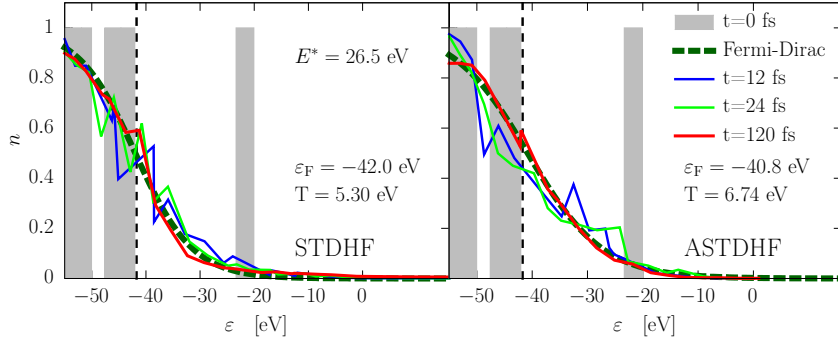


Figure 1. Comparison of time evolution of occupation numbers in STDHF (left panel) and ASTDHF (right panel) after a particle-hole excitation delivering an excitation energy of 26.5 eV. Ground state is full occupation below vertical dashed line. Initial excitation corresponds to grey shaded areas. Occupation numbers are shown at a few time steps.

interaction and taken as simple power of the local density, with  $\lambda = 68 \text{ Ry} \cdot a_0^2$  and  $\sigma = 2$ . The potential is complemented by a confining harmonic oscillator to ensure soft reflecting boundary conditions. This extra confining potential allows to fully eliminate ionization and focus the discussion on thermal effects. The residual interaction  $V_{\text{res}}$  used for computing correlations in the Fermi Golden rule is taken as a zero range term with intensity  $17.7 \text{ eV} \cdot a_0$ . The set of parameters has been tuned to reproduce a typical molecular setup with energies in the Ry range, see [29, 30] for details.

A first result is shown in Figure 1 displaying snapshots of occupation numbers and comparing STDHF to ASTDHF. In ASTDHF the occupation numbers are the  $n_i$  advocated above. In STDHF they are obtained by diagonalizing the ensemble one-body matrix Eq. (3). The initial excitation is delivered via a particle-hole excitation providing 26.5 eV excitation energy. This corresponds to drilling a hole deep in the sequence of occupied states as can be seen from the figure. We compare occupation distributions as a function of time and see that the initial hole is progressively filled while levels above Fermi energy are correlatively filled. Beyond about 100 fs both calculations have attained a Fermi-like shape of the occupation numbers. Furthermore, as far as one can estimate it from such a plot, STDHF and ASTDHF seem to behave in a very similar manner with relaxation taking place at a similar pace. This is a good indication that ASTDHF delivers a reasonable approximation to STDHF.

In order to quantify this way to thermal equilibrium we compute the one-body entropy

$$S = -k_B \sum_i [\nu_i \text{Log} \nu_i + (1 - \nu_i) \text{Log}(1 - \nu_i)] \quad (6)$$

where  $k_B$  is Boltzman constant. The notation  $\nu_i$  for the single particle occupation numbers covers various quantities, depending on the approximation. For

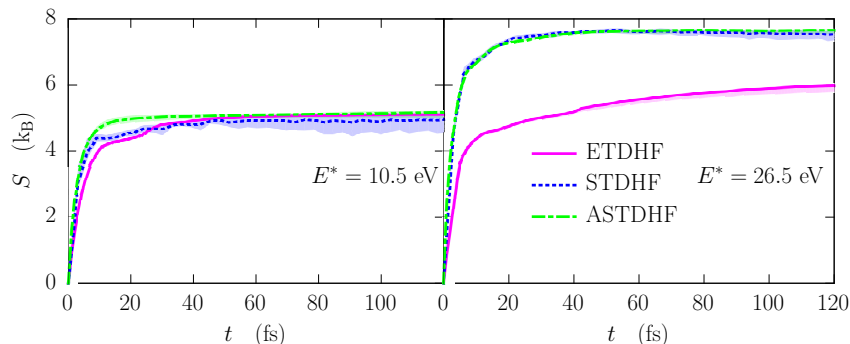


Figure 2. Comparison of time evolution of entropy  $S$  (in Boltzmann constant unit  $k_B$ ) computed with STDHF, ASTDHF and ETDHF approaches, for two excitation energies  $E^*$  as indicated. The shaded areas about the STDHF curves are the error bars from the fluctuations within the STDHF ensemble. For ASTDHF and ETDHF the shaded areas correspond to an estimate of the impact of numerical parameters used in the computations.

STDHF they label the eigenvalues of the ensemble one-body matrix Eq. (3); for ASTDHF they correspond to the values  $n_i$  discussed above and for ETDHF they correspond to the  $W_\alpha$ . The one-body entropy is plotted as function of time for two examples in Figure 2, comparing ASTDHF and ETDHF to STDHF. Initial excitation is again delivered by particle-hole excitations. At low excitation energy the three approaches deliver very similar results both in terms of asymptotic values and relaxation rate. The result is interesting as it shows that ETDHF, which is technically an order of magnitude simpler than ASTDHF (but only about a factor 2 quicker than ASTDHF computationally speaking, and typically 2 orders of magnitude cheaper than STDHF), performs in a similar manner in that case. The higher excitation case in turn delivers a different message. While again ASTDHF very nicely matches STDHF, ETDHF poorly fails even in terms of asymptotic value. This clearly shows the deficiency of ETDHF which can be attributed to the imposed diagonal approximation. The point can be cross checked by imposing, in the course of the ASTDHF step, a diagonal representation. In that case the result falls somewhat in between full ASTDHF and ETDHF, hinting again at the importance of off diagonal terms in the one-body density matrix.

#### 4 Conclusions and Perspectives

We have presented some extension of TDHF in order to address dissipative dynamics in finite fermion systems, taking as example small clusters and molecules. We have outlined the Stochastic TDHF method which provides a sound extension of TDHF accounting for both dissipation and fluctuations, but which is too involved for realistic computations. It can hence only serve as benchmark in



model cases. We thus have introduced two simplifications. The first one, coined ASTDHF, provides a direct simplification of STDHF by imposing a common mean field to all members of the stochastic ensemble of STDHF. ASTDHF provides a sound approximation to STDHF except for the account of fluctuations missing by construction. All average quantities computed do very well match with STDHF. The oversimplified ETDHF provides a very simple approximation allowing to directly evolve occupation numbers according to a rate equation. The method surprisingly works well at low excitations but fail at higher excitation. All in all, ASTDHF seems to provide the best compromise in accuracy and cost and should be further studied and applied to realistic 3D cases. Work along that line is in progress.

### **Acknowledgements**

We thank Institut Universitaire de France, European ITN network CORINF and French ANR contract MUSES 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).

### **References**

- [1] N. Bohr, *Nature* **137** (1936) 351.
- [2] U. Saalmann, C. Siedschlag and J.M. Rost, *J. Phys. B* **39** (2006) 1.
- [3] M. Kjellberg et al., *Phys. Rev. A* **81** (2010) 023202.
- [4] Th. Fennel et al., *Rev. Mod. Phys.* **82** (2010) 1793.
- [5] G. Chen, *Nanoscale Energy Transport and Conversion: A Parallel Treatment of Electrons, Molecules, Phonons, and Photons*, (Oxford University Press, New York, 2005).
- [6] J. Dalibard, Collisional dynamics of ultra-cold atomic gases, In: *Proceedings of the International School of Physics-Enrico Fermi, Course CXL*, Ed. M. Inguscio, S. Stringari and C. Wieman, (IOS Press, Amsterdam, 1999), 321.
- [7] P. Wopperer and P. M. Dinh and P.-G. Reinhard and E. Suraud, *Phys. Rep.* **562** (2015) 1.
- [8] Y. Abe, S. Ayik, P-G Reinhard and E. Suraud, *Phys. Rep.* **275** (1996) 49.
- [9] L.P. Kadanoff and G. Baym, *Quantum Statistical Mechanics: Green's Function Methods in Equilibrium and Nonequilibrium Problems*, *Frontiers in Physics* (Benjamin, New York, 1962).
- [10] A. Bonasera, F. Gulminelli and J. Molitoris, *Phys. Rep.*, **243** (1994) 1.
- [11] G.F. Bertsch and S. DasGupta, *Phys. Rep.* **160** (1988) 189.
- [12] J.W. Serene and D. Rainer, *Phys. Rep.* , **101** (1982) 221.
- [13] H. Feldmeier, *Nucl. Phys. A*, **515** (1990) 147.
- [14] A. Ono et al., *Phys. Rev. Lett.* **68** (1992) 2898.

- [15] K. Goeke and P.G. Reinhard, *TDHF and Beyond*, Lect. Notes in Physics, vol. 171 (Springer, Heidelberg, 1982).
- [16] P.G. Reinhard and E. Suraud, *Ann. Phys. (NY)* **216** (1992) 98.
- [17] A. Domsps et al., *Phys. Rev. Lett.* **81** (1998) 5524.
- [18] T. Fennel and G.F. Bertsch and K-H Meiwes-Broer, *Eur. Phys. J. D* **29** (2004) 367.
- [19] P.-G. Reinhard and E. Suraud, *Ann. Phys. (NY)* **354** (2015)183
- [20] A.K. Rajam and I. Raczkowska and N.T. Maitra, *Phys. Rev. Lett.* **105** (2010) 113002.
- [21] A. Dutta C. Trefzger and K. Sengupta, *Phys. Rev. B* **86** (2012) 085140.
- [22] P. Krause, T. Klamroth and P. Saalfrank, *J. Chem. Phys.*, **127** (2007) 034107.
- [23] M.A.L. Marques, N.T. Maitra, F.M.S. Nogueira, E.K.U. Gross and A. Rubio, *Fundamentals of Time-Dependent Density Functional Theory*, Lect. Notes in Phys. vol. 837 (Springer-Verlag, Berlin, 2012).
- [24] R. Balescu, *Equilibrium and non Equilibrium Statistical Mechanics*, (Wiley, New York, 1975).
- [25] M. Bixon and R. Zwanzig, *Phys. Rev.*, **187** (1969) 267.
- [26] R. Zwanzig, *J. Stat. Phys.*, **9** (1973) 215.
- [27] S. Ayik and C. Gregoire, *Phys. Lett. B* **212** (1988) 269.
- [28] P. Napolitani and M. Colonna, *Phys. Lett. B* **726** (2013) 382.
- [29] E. Suraud and P.-G. Reinhard, *New. J. Phys.* **16** (2014) 063066.
- [30] N. Slama, P.-G. Reinhard and E. Suraud, *Ann. Phys. (NY)* **355** (2015) 182.