PHASE SPACE EXPLORATIONS IN TIME DEPENDENT DENSITY FUNCTIONAL THEORY

by

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Abstract

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Time dependent density functional theory (TDDFT) is one of the useful tools for the study of the dynamic behavior of correlated electronic systems under the influence of external potentials. The success of this formally exact theory practically relies on approximations for the exchange-correlation potential which is a complicated functional of the co-ordinate density, non-local in space and time. Adiabatic approximations (such as ALDA), which are local in time, are most commonly used in the increasing applications of the field. Going beyond ALDA, has been proved difficult leading to mathematical inconsistencies. We explore the regions where the theory faces challenges, and try to answer some of them via the insights from two electron model systems.

In this thesis work we propose a phase-space extension of the TDDFT. We want to answer the challenges the theory is facing currently by exploring the one-body phase-space. We give a general introduction to this theory

and its mathematical background in the first chapter. In second chapter, we carryout a detailed study of instantaneous phase-space densities and argue that the functionals of distributions can be a better alternative to the non-locality issue of the exchange-correlation potentials. For this we study in detail the interacting and the non-interacting phase-space distributions for Hookes atom model.

The applicability of ALDA-based TDDFT for the dynamics in strong-fields can become severely problematic due to the failure of single-Slater determinant picture.. In the third chapter, we analyze how the phase-space distributions can shine some light into this problem. We do a comparative study of Kohn-Sham and interacting phase-space and momentum distributions for single ionization and double ionization systems. Using a simple model of two-electron systems, we have showed that the momentum distribution computed directly from the exact KS system contains spurious oscillations: a non-classical description of the essentially classical two-electron dynamics.

In Time dependent density matrix functional theory (TDDMFT), the evolution scheme of the 1RDM (first order reduced density matrix) contains second-order reduced density matrix (2RDM), which has to be expressed in terms of 1RDMs. Any non-correlated approximations (Hartree-Fock) for 2RDM would fail to capture the natural occupations of the system. In our fourth chapter, we show that by applying the quasi-classical and semi-classical approximations one can capture the natural occupations of the excited systems.We study a time-dependent Moshinsky atom model for this.

The fifth chapter contains a comparative work on the existing non-local exchange-correlation kernels that are based on *current density* response frame work and the *co-moving* frame work. We show that the two approaches though coinciding with each other in linear response regime, actually turn out to be different in non-linear regime.

Dedicated to my parents

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Chapter 1

General Introduction

1.1 Density Functional Theory(DFT)

Density functional theory(DFT) is one of the most successful fundamental quantum mechanical approaches to matter. For the past few decades it has become one of the most widely used methods for calculating the properties of complex electronic systems: molecules, solids, polymers and even biomolecules. DFT was introduced in the 1960s (Hohenberg and Kohn (1964), Kohn and Sham(1965)), to describe the system in terms of one-body electronic density(and possibly additional densities such as the spin density, the current density, etc.)with out explicit reference to the many body wave function. At first sight, it seems impossible. How can the subtle correlations encoded in an N-electron wave function be adequately represented by a simple collective 3-variable entity, such as density? But Hohenberg and

Kohn(HK)[19], were able to show that the ground state energy of a quantum system can be determined by minimizing the energy as a functional of the density (a 3 variable entity), in much the same way as, in traditional quantum mechanics, one can determine the energy by minimizing the expectation value of the hamiltonian with respect to the wave function(includes 3N variables).In fact they proved that all properties of the static system are functionals of the one-body density alone.

The implementation of HK mimimum principle leads to mean-field-like equations, known as the Kohn-Sham (KS) equations.The key advantage of the whole of this approach is the KS equations [20] can be solved on a computer in a time that grows as a power of N where as an exact solution of the N-electron Schrodinger equation requires a time that grows exponentially with N!. Computationally the method scales more favorably that the Hartree-Fock (HF) method, yet it captures the correlation. It took less than seven hours to calculate the ground state energy of crambin ($C_{203}H_{317}N_{55}O_{64}S_{66}$) which has 2528 electrons on a 1.5GHz HP workstation [46]

Within the Born-Oppenheimer approximation,the many-particle Schrodinger equation is given by:

$$\left[\sum_{i}^{N}\left(-\frac{\nabla_i^2}{2}+v(\mathbf{r}_i)\right)+\sum_{i<j}U(\mathbf{r}_i,\mathbf{r}_j)\right]\Psi(r_1,r_2,...,r_N)=E\Psi(r_1,r_2,...,r_N) \tag{1.1}$$

where N is the number of electrons and $U(\mathbf{r}_i,\mathbf{r}_j)$ is the electron-electron interaction. $v(\mathbf{r})$ is the external local potential. Through out this proposal atomic units : $e^2=1,\hbar=1,m=1$ are used.

In traditional quantum mechanics, given that $v(r)$ is known, one solves the system by putting it in Schrodinger‘s equation and solves for the wave function Ψ and then calculates the observables.

$$v(\mathbf{r})\Rightarrow\Psi\Rightarrow\quad Observables \tag{1.2}$$

One among the observables that are calculated in this way is the one-body particle density

$$n(\mathbf{r})=N\int d^3\mathbf{r}_2...\int d^3\mathbf{r}_N|\Psi(\mathbf{r},\mathbf{r}_2,....,\mathbf{r}_N)|^2 \tag{1.3}$$

Many powerful methods for solving Schrodinger equation have been developed during decades of struggling with the many-body problem. In physics, for example, one has diagrammatic perturbation theory (based on Feynmann diagrams and Green function), while in chemistry one often uses CI (configuration interaction) methods, which are based on systematic expansion in Slater determinants. A host of more special techniques also exists. The problem with these methods is is the great demand they place on one‘s computational resources.

It is here where DFT is a viable alternative, and provides a way to a systematically map the many body problem with U, onto a single body problem without U. This is done by promoting the particle density n(r) from just one among many observables to the status of key variable, on which the calculation of all other observables can be based.

1.2 Proof of HK Theorem

The HK theorem proves that the nondegenerate ground-state wave function is a unique functional of ground state density

$$\Psi_0 = \Psi[n] \tag{1.4}$$

Given surjective mappings (f_1 and f_2) from the external potential to the interacting groundstate and from the interacting ground state to the ground state density

$$f_1 : v_{ext} \longrightarrow \Psi_0 \tag{1.5}$$

$$f_2 : \Psi_0 \longrightarrow n \tag{1.6}$$

Hohenberg and Kohn were able to prove in their first paper [19] that f_1 and f_2 are injective and thus both of these mappings could be inverted. This means there exist a one to one mapping between the external potential and the ground state density.

$$v_{ext} \longleftrightarrow n \tag{1.7}$$

The HK theorem first proves that the density $n(\mathbf{r})$ uniquely determines the the external potential $v(\mathbf{r})$ (up to an arbitrary constant) to which the many-particle system is subjected. The proof of this statement is given by *reductio ad absurdum*. It assumes that two potentials $v(\mathbf{r})$ and $v'(\mathbf{r})$ with ground states Ψ_0 and Ψ'_0 give rise to the same density such that:

$$\hat{v} \neq \hat{v}' + constant \tag{1.8}$$

The Schrodinger equations for these two potentials are:

$$(\hat{T} + \hat{v} + \hat{U})\Psi_0 = E_0\Psi_0 \tag{1.9}$$

$$(\hat{T} + \hat{v}' + \hat{U})\Psi'_0 = E'_0\Psi'_0 \tag{1.10}$$

If Ψ_0 and Ψ'_0 were to be same, then by subtracting the above two equations one gets

$$(\hat{v} - \hat{v}')\Psi_0 = (E_0 - E'_0)\Psi_0 \tag{1.11}$$

Since $\hat{v}$ and $\hat{v}'$ are multiplicative operators, the above equation leads to

$$\hat{v} - \hat{v}' = E_0 - E_0' \tag{1.12}$$

which contradicts our initial assumption. It then follows from the Rayleigh-Ritz variational principle that the inequality

$$E = \langle\Psi_0|\hat{H}|\Psi_0\rangle \quad < \quad \langle\Psi_0'|\hat{H}|\Psi_0'\rangle \tag{1.13}$$

$$= \langle\Psi_0'|\hat{H} + \hat{v} - \hat{v}'|\Psi_0'\rangle \tag{1.14}$$

$$= E_0' + \int \left[v(\mathbf{r}) - v'(\mathbf{r})\right] n(\mathbf{r}) d\mathbf{r} \tag{1.15}$$

is strictly specified. Interchanging the primed and unprimed variables we also obtain

$$E_0' < E_0 + \int \left[v'(\mathbf{r}) - v(\mathbf{r})\right] n(\mathbf{r}) d\mathbf{r} \tag{1.16}$$

Thus we arrive at the contradiction

$$E_0 + E_0' < E_0' + E_0 \tag{1.17}$$

which proves the falsehood of the initial assumption. Thus the theorem is proved.

An elegant constructive proof was later found by Levy [55],[56] which does not require the assumption of the non-degenerate ground state. The HK theorem was originally proved only for densities that were ground-state density of some interacting electronic problem. The constrained search scheme extended this to any densities extracted from a single wave function and this domain has been further extended to the densities which result from the ensemble of wave functions.

1.3 Kohn-Sham Description

The idea behind the establishment of the Kohn-Sham (KS) scheme is: For any interacting system, there exists a local single particle potential $v_s(r)$ such that the exact ground state density $n(r)$ of the interacting system equals the equals the ground state density of the auxiliary (non-interacting or fictitious) system with the Hamiltonian

$$\hat{H}_s = \hat{T} + V_s \tag{1.18}$$

so that

$$n(r) = n_s(r) \tag{1.19}$$

If the ground state of $\hat{H}_s$ is non-degenerate, the ground state density $n_s(r)$ (equal to $n(r)$) possesses a unique representation

$$n(\mathbf{r}) = \sum_{i=1}^{N} |\phi_i(\mathbf{r})|^2 \tag{1.20}$$

in terms of the N single particle orbitals (know as KS orbitals) obtained from

Schrodinger equation

$$\left[-\frac{1}{2}\nabla^2 + v_s(\mathbf{r})\right]\phi_i(\mathbf{r}) = \epsilon_i\phi_i(\mathbf{r}) \tag{1.21}$$

Since the $v_s(\mathbf{r})$ generates the density $n(\mathbf{r})$, from the HK theorem it is unique. Thus the single-particle orbitals in the above equation are unique functionals of the density $n(\mathbf{r})$.

$$\phi_i(\mathbf{r}) = \phi_i([n];\mathbf{r}) \tag{1.22}$$

Neither KS orbitals ϕ_i nor the KS eigen values ϵ_i have a compelling physical significance. In particular, "Kohn-Sham wave function", that is, the Slater determinant constructed from the N-lowest lying KS orbitals, is by no means a good approximation to the ground-state wave function. Similarly the KS eigen values do not correspond, in general, to physical excitation energies of the system.

However, in finite systems, it can be proved [55] that the negative of the highest occupied KS eigen value ϵ_N equals to the exact ionization potential when the KS potential vanishes at infinity.

The non-interacting kinetic energy

$$T_s[n] = -\sum_{i=1}^{N}\int \phi_i^*(\mathbf{r})\left[\frac{1}{2}\nabla^2\right]\phi(\mathbf{r})d^3r \tag{1.23}$$

is a unique implicit functional of $n(\mathbf{r})$ as well.This is why one works with the KS-system orbitals rather than the density directly. Although the latter can be done in principle, with the Euler-Legrange equation coming from minimizing energy as a functional of the density, it is very hard to come up with accurate approximations for the various energy functionals. Most difficult is the kinetic energy but in Kohn-Sham scheme, a large part of the kinetic energy is (T_s) is treated exactly as orbital functional.

Now we write the ground state energy functional of the interacting system in terms of non-interacting kinetic energy ,the external potential energy, the Hartree energy and the remainder exchange-correlation energy

$$E[n] = V_{ext}[n] + T_s[n] + V_H[n] + E_{xc}[n] \tag{1.24}$$

The Hartree energy V_H is given by

$$V_H[n] = \frac{1}{2}\int d\mathbf{r}\int d\mathbf{r}'\frac{n(\mathbf{r})n(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} \tag{1.25}$$

From the variation principle for the density, One can write the variation of the energy functional $E_{var}[n]$ due to an infinitesimal variation in the density as

$$E = \min_{n(\mathbf{r})}\left[F[n] + \int V_{ext}n(\mathbf{r})d(\mathbf{r})\right] \tag{1.26}$$

where

$$F[n] = \min_{\Psi\rightarrow n}\left\langle \Psi\middle|\hat{T}+\hat{U}\middle|\Psi\right\rangle \tag{1.27}$$

Assuming the functional derivative of $F[n]$ exists, One can write the variation of the energy functional $E_{var}[n]$ due to an infinitesimal variation in the density as

$$E_{var}[n + \eta\delta n] - E_{var}[n] = \eta \int \left[\frac{\delta[n]}{\delta n(\mathbf{r})} + V_{ext}(\mathbf{r}) \right] + O(\eta^2) \tag{1.28}$$

which leads to

$$\frac{\delta F[n]}{\delta n(\mathbf{r})} = -V_{ext}(\mathbf{r}) \tag{1.29}$$

The above equation ofter referred to as the stationary condition. Therefore for the KS case we can obtain

$$\frac{\delta T_s[n]}{\delta n(\mathbf{r})} + \frac{\delta V_H[n]}{\delta n(\mathbf{r})} + \frac{\delta Exc[n]}{\delta n(\mathbf{r})} = -V_{ext}(\mathbf{r}) \tag{1.30}$$

Thus the KS-potential $v_s(\mathbf{r})$ has the form

$$v_s(\mathbf{r}) = v_{ext}(\mathbf{r}) + \int d^3r \frac{n(\mathbf{r})}{|\mathbf{r} - \mathbf{r}'|} + v_{xc}[n](\mathbf{r}) \tag{1.31}$$

where the exchange correlation potential v_{xc} is defined as

$$v_{xc} = \frac{\delta E_{xc}}{\delta n(\mathbf{r})} \tag{1.32}$$

and the middle term is known as the hartree potential $v_H(\mathbf{r})$

For systems of a large number of particles, the KS single particle equations are much simpler to solve than the coupled Schrodinger equation. However, although the HK theorem guarantees that E_{xc} is a density functional, we dont know the exact form of it. So in practice, E_{xc} must be approximated.

1.4 Exchange-Correlation

Lets look at the energy-equivalence in both the interacting and KS-schemes,

$$T[n] + U[n] + v_{ext}[n] = T_s[n] + V_H[n] + E_{XC}[n] + v_{ext}[n] \tag{1.33}$$

By definition E_{xc} contains basically two different differences $T - T_s$ and $U - V_H$. Since we know the explicitly the non-interacting T_s in terms of KS orbitals (which are unique functional of density), $T - T_s$ contributes only to the correlation (T_c) part of E_{xc}. The Pauli exchange is in-built in the KS orbitals (ie., single slater determinant of KS orbitals). In density functional theory, one defines the exchange energy as

$$E_x[n] = \left\langle \phi[n] | \hat{U} | \phi[n] \right\rangle - V_H[n] \tag{1.34}$$

The remaining unknown and most crucial piece of the energy E_c is defined as

$$E_c[n] = F[n] - T_s[n] - V_H[n] - E_x[n] \tag{1.35}$$

where

$$F[n] = \min_{\Psi \to n} \left\langle \Psi \middle| \hat{T} + \hat{U} \middle| \Psi \right\rangle \tag{1.36}$$

1.5 Various Approximations in DFT

1.5.1 Local Density Approximation (LDA)

The Local Density Approximation (LDA) is historically a most significant approximation and for many years a workhorse of solid state physics. The full kinetic energy in LDA-DFT is approximated as

$$T_s^{LDA} = \int d^3r t_s^{hom}(n(r)) = const. \int d^3r n(r)^{5/3} \tag{1.37}$$

where $t_s^{hom}(n(r))$ is the non-interacting kinetic energy if one assumes the system to be homogeneous and computes it at $n = n(r)$. But because there is an exact treatment for T_s in terms of KS-orbitals (Eq. 1.24) this local approximation for kinetic energy is never used in modern DFT calculations. The LDA turned out to be higly useful for another component of the total energy, the exchange-correlation energy $E_{xc}[n]$. The LDA procedure is very simple for $E_x[n]$ since exact exchange is known for homogeneous case. ie.,

$$E_x^{LDA} = -const. \int d^3r n(r)^{4/3} \tag{1.38}$$

For the correlation energy $E_c[n]$, LDA is not so easy as the $e_c^{hom}(n)$ is not known analytically. So one needs a parametrization approximation for LDA in this case. Perdew and Wang [41] proposed a simple analytic representation of the correlation energy as a function of two parameters: r_s and relative spin polarization ξ. There are several parametrization approximations exist in the literature. Eg., Green‘s function Monte Carlo type parametrization by Ceperley-Alder[67], Vosko-Wilk-Nussair, and by Perdew-Zunger [68]. However, independent of parameterization, the LDA for E_{xc} formally consists

$$E_{xc}^{LDA} = \ d^3 r e_{xc}^{hom}|_{n=n(r)} = \int d^3 r e_{xc}^{hom}(n(r)) \tag{1.39}$$

where $e_{xc}^{hom} = e_x^{hom} + e_c^{hom}$. And the corresponding xc potential is simply

$$v_{xc}[n](r) = \left. \frac{\partial e_{xc}^{hom}(n)}{\partial n} \right|_{n=n(r)} \tag{1.40}$$

A partial explanation for LDA to be successful is that it has a systematic error cancellation. It underestimates E_c but overestimates E_x, resulting in good values for E_{xc}. The typical erros in LDA for atomization energies, cohesive energies are good to within about 1.3 eV (over bound) while HF has errors of more like 3.1 eV (under bound). Bond-lengths/geometries are remarkably good, to within 1 percent error. The success of LDA is because it is based on a physical system (the uniform electron gas) which satisfy many fundamental exact conditions the real physical systems satisfy, such as the sum-rule on the exchange-correlation hole:

$$\int d^3 r' n_{xc}^{LDA}(r, r') = -1 \tag{1.41}$$

1.5.2 GEA and GGA

LDA is based on the assumption that the system is highly homogeneous and this approximation is infact exact a homogeneous system. In this approximation one looks at the density at point r. However any real system is spatially inhomogeneous. ie., the system has spatially varying density. So this variation of density with position should be added as a correction to LDA. This kind of approximation is known as GEA, Gradient-Expansion Approximation. A typical lowest order gradient correction to the LDA for $E_x$has the form

$$E_x^{GEA}[n] = E_x^{LDA}[n] - const. \int d^3r \frac{|\nabla n(r)|^2}{n(r)^{4/3}} \tag{1.42}$$

This kind of lower order(2)corrections did not improve the LDA much and in some cases made the results worse. The root of this problem was the breakdown of exact conditions that LDA satisfies but GEA does not. One could try to include higher order corrections (> 2) which are very difficult to calculate. During the eighties it was realized that instead of higher order systematic gradient expansion, one could experiment with a general type of function of both $n(r)$ and $\nabla n(r)$. This kind of approximation is called Generalized Gradient Approximation (GGA). E_{xc} in such an approximation has a general form of

$$E_{xc}^{GGA}[n] = \int d^3r f(n(r), \nabla n(r)) \tag{1.43}$$

Different GGA differ in the choice of the function $f(n, \nabla n)$. This approximation is most successful in present day DFT calculations. The most popular GGAs are PBE (proposed by Perdew, Burke and Ernzerof) and BLYP (Becke (exchange) and Lee, Yang, Parr (correlation)) [18].Among these two, PBE is non-empirical while BLYP was developed in parallel in the chemistry community and is empirical [27], [28], [29].

1.5.3 Hybrid Approximations-Jacob‘s Ladder

The quest for beyond GGA functionals goes on. J.P.Perdew suggested a “Jacob’s Ladder” analogy to view the accuracy and computational cost. Increase in each rung of the ladder from the bottom increases the accuracy and the computational cost. The lowest rung is the local approximation, LSD where input is just the density, second rung is GGA (where input is density and gradient), 3rd rung is meta-GGA where one includes additionally local kinetic energy density, 4th rung is hyper-GGA that includes exact exchange, and 5th rung is RPA-like functionals that involve all orbitals (even unoccupied), and numerically expensive. Meta-GGAs,OEP (Orbital Effective Potential), SIC(self interaction correction),B3LYP are some of the well-known functionals. Most popular hybrid functional is B3LYP, where one treats exchange with Becke‘s 3-parameter functional and LYP‘s correlation functional. In Meta-GGAs one includes the Kohn-Sham kinetic energy density in addition to n and ∇n.

1.6 Successes and Challenges for DFT

Ground state DFT has become quite reliable work horse for calculating electronic structure and other properties of molecules and solids [53] over the past few decades.(Ref. [10] - [13]). The PKZB(Perdew,Kurth,Zupan and Blaha) meta-GGA(one parameter) achieves very accurate atomization energies of molecules, surface energies of metals, and lattice constants of solids [14], [15]. On the other hand, meta-GGA's with many empirical parameters, give less accurate surface energies and lattice constants than the those of non-empirical GGA's or even LSD [15]. The PKZB functional predicts bond lengths for molecules which are typically longer and less accurate than those of GGA [16]. So all these various approximation schemes have their own areas of successes over each other depending up on the problem of interest [53]. However all the approximations (LDA,GGA,Some Hybrids) suffer from some common failures. The correlation energy of one electron systems is zero: But these approximations fail to satisfy this property. None of these approximations capture the derivative discontinuity: The potential do not show any jump as the particle number passes through an integer. All these approximations fail to capture proper behavior at distances far from the nuclei as they rapidly decay at the tail ends.(Orbital dependent functionals can capture these effects to some extent) .Both the LDA and the GGA fail badly to describe the van der Walls interactions. In most of the band structure calculations, Chemical accuracy (a max error of 0.04 ev) has not yet completely

been attained even by GGA
DFT remains the most popular and reliable electronic structure method today, as was recognized by the Nobel Prize in Chemistry in 1998 half of which went to the physicist Walter Kohn for his development of DFT, and half to for implementation of methods like DFT in quantum chemical codes [3].

1.7 Time Dependent Density Functional Theory (TDDFT)

The success of static (or ground-state) DFT prompted people to extend it to the time dependent systems. This extension is known as Time Dependent Density Functional Theory(TDDFT). Nowadays the use of TDDFT is continuously growing in all areas where interactions are important, but direct solution of the Schrodinger is too demanding (up till today, at most two electrons in the strong fields can be calculated exactly quantum mechanically [43]). Like the ground state DFT, the idea of TDDFT is to describe the time evolution of electronic quantum many particle system in terms of time-dependent particle density. TDDFT was formulated in 1984 by Runge and Gross (RG). RG theorem(Time dependent analogue of HK theorem) [1] states that, there is a one-to-one correspondence between time-dependent one-particle densities and time-dependent one particle external potentials for a given initial state. Presently, the most popular application of TDDFT is the extraction of electronic excited state properties, especially transition frequencies. By applying TDDFT after the ground-state of a molecule has been found, one can explore and understand the complexity of its spectrum, thus providing more information about the species. TDDFT has a especially strong impact in the photochemistry of biological molecules, where the molecules are too large to be handled by traditional time-dependent quantum mechanical methods. The theory has wide applications in high-intensity laser interactions, non-equilibrium phenomena, non-adiabatic excited-state dynamics, and low-energy electron scattering. The available approximations in each application, work well for some properties, but occasionally fail for others.

1.8 Proof of Runge-Gross Theorems

The proof for the Runge-Gross (RG) theorem is based on some preliminary requirement the potential must be Taylor expandable around the initial time $t = t_0$. This proof shows that the densities $n(\mathbf{r}, t)$ and $n'(\mathbf{r}, t)$ evolving from a common initial state $\psi_0 = \psi(t = t_0)$ under the influence of two potentials $v(\mathbf{r}, t)$ and $v'(\mathbf{r}, t)$ which are Taylor expandable about t_0, are always different provided that the potentials differ by more than a purely time-dependent(r-independent) function. We will now outline this proof.

Consider two potentials that differ more than just a time-dependent constant.

$$v(\mathbf{r}, t) \neq v'(\mathbf{r}, t) + c(t) \tag{1.44}$$

Now

$$v(\mathbf{r},t) = \sum_{k=0}^{\infty} \frac{1}{k!} v_k(\mathbf{r})(t-t_0)^k \tag{1.45}$$

$$v'(\mathbf{r},t) = \sum_{k=0}^{\infty} \frac{1}{k!} v'_k(\mathbf{r})(t-t_0)^k \tag{1.46}$$

Equation (1.44) implies that there exists a smallest integer k ≥ 0 such that

$$w_k(\mathbf{r}) = v_k(\mathbf{r}) - v'_k(\mathbf{r}) = \frac{\partial^k}{\partial t^k}(v(\mathbf{r},t) - v'(\mathbf{r},t))|_{t=t_0} \neq const \tag{1.47}$$

We first consider that the current densities

$$\mathbf{j}(\mathbf{r},\mathbf{t}) = \left\langle \mathbf{\Psi}(\mathbf{t}) | \hat{\mathbf{j}}_{\mathbf{p}}(\mathbf{r}) | \mathbf{\Psi}(\mathbf{t}) \right\rangle \tag{1.48}$$

and

$$\mathbf{j}'(\mathbf{r},\mathbf{t}) = \left\langle \mathbf{\Psi}'(\mathbf{t}) | \hat{\mathbf{j}}_{\mathbf{p}}(\mathbf{r}) | \mathbf{\Psi}'(\mathbf{t}) \right\rangle \tag{1.49}$$

are different for different potentials v and v'. Here

$$\hat{\mathbf{j}}_p(\mathbf{r}) = \frac{1}{2i} \sum_{j=1}^{N} \{\nabla_{r_j}, \delta(r - r_j)\}_+ \tag{1.50}$$

is the paramagnetic current density operator.

The quantum mechanical equation of motion for the difference between the two current densities:

$$\frac{\partial}{\partial t}(\mathbf{j}(\mathbf{r},t)-\mathbf{j}'(\mathbf{r},t))|_{t=t_0} = -i\left\langle \Psi_0 \left| \left[\hat{\mathbf{j}}_p(\mathbf{r}), \hat{\mathbf{H}}(t_0) - \hat{\mathbf{H}}'(t_0)\right] \right| \Psi \right\rangle \tag{1.51}$$

$$= -n_0(\mathbf{r})\nabla(v(r,t_0) - v'(r,t_0)) \tag{1.52}$$

where $n_0(\mathbf{r}) = n(\mathbf{r}, t_0)$

If the condition (1.47) is satisfied for k=0 the RHS of the above equation cannot vanish identically and $\mathbf{j}$ and $\mathbf{j}'$ will become different infinitesimally later than t_0. If not, one can repeatedly ($(k+1)$ times) use the equation of motion to arrive at

$$\left.\frac{\partial^{k+1}}{\partial t^{k+1}}(\mathbf{j}(\mathbf{r},t)-\mathbf{j}'(\mathbf{r},t))\right|_{t=t_0} = -n_0(\mathbf{r})\nabla w_k(\mathbf{r}) \tag{1.53}$$

with

$$w_k(\mathbf{r}) = \left.\left(\frac{\partial}{\partial t}\right)^k (v(\mathbf{r},t) - v'(r,t))\right|_{t=t_0} \tag{1.54}$$

From Eq (1.44) that there is a k such that $w_k \neq 0$; therefore the $(k+1)$ th time derivatives of the current derivatives differ.

We can conclude then that the two current-densities will differ later than t_0. To prove the corresponding statement for densities we use the continuity equation

$$\frac{\partial n}{\partial t} = -\nabla.\mathbf{j}(\mathbf{r},t) \tag{1.55}$$

which, after differentiating $k+1$ times, gives for the density difference at t_0

$$\frac{\partial^{k+2}}{\partial t^{k+2}}(n(\mathbf{r},t)-n'(\mathbf{r}',t))\bigg|_{t=t_0} = \nabla.(n_0(\mathbf{r})\nabla w_k(\mathbf{r})) \tag{1.56}$$

The RHS of this expression can not vanish for the following arguments. We note that

$$\int n_0(\mathbf{r})\left|\nabla w_k(\mathbf{r})\right|^2 d^3\mathbf{r} = \oint n_0(\mathbf{r})w_k(\mathbf{r})\nabla w_k(\mathbf{r})d\mathbf{s} - \int w_k(\mathbf{r})\nabla.(n_0(\mathbf{r})\nabla w_k(\mathbf{r}))d^3\mathbf{r} \tag{1.57}$$

where we have applied Gauss‘s theorem. For finite systems the surface integral will vanish, since any realistic potential (i.e., potentials due to normalizable external charge densities) falls off at least as fast as $1/r$ as $r \to \infty$, while the density will decay exponentially.

Thus $\nabla.(n_0(\mathbf{r})\nabla w_k(\mathbf{r}))$ can not vanish everywhere otherwise the LHS of the above equation would be zero. This in turn would imply that $|\nabla w_k(\mathbf{r})|^2 = 0$, which is in contradiction to the assumption that $w_k(\mathbf{r})$ is not a constant. This completes the proof of the theorem for finite systems.

1.9 Kohn-Sham TDDFT

The Runge-Gross theorem shows that for any arbitrary particle-particle interaction, the one-to-one correspondence between time-dependent potentials and time-dependent densities holds for a given initial state. So as in the ground state KS-DFT, it is proved (by van Leeuwen) [36] that the time-dependent density $n(\mathbf{r}, t)$ obtained from a many-particle system with Hamiltonian $\hat{H}(t)$ and initial state Ψ_0 can be reproduced exactly in a different system evolving from a different initial state Ψ_0' , under a different Hamiltonian $\hat{H}'(t)$ (ie., with a different two particle interaction and external potential), provided that the initial density and initial first derivative of the density are the same in both systems. Likewise in ground state DFT, it follows that one introduce a fictitious system of non-interacting electrons, which satisfies the time-dependent Kohn-Sham equations

$$i\frac{\partial \phi_j(\mathbf{r}, t)}{\partial t} = \left[-\frac{\nabla^2}{2} + v_S[n; \phi_0](\mathbf{r}, t)\right] \tag{1.58}$$

reproducing the density of the interacting system, via

$$n(\mathbf{r}, t) = \sum_{j=1}^{N} |\phi_j(\mathbf{r}, t)|^2 \tag{1.59}$$

which is exactly that of the interacting system. The auxiliary potential $v_s(r, t)$ is a combination of 3 (external, Hartree and exchange-correlation) potentials and is uniquely determined up to a purely time-dependent function:

$$v_s(\mathbf{r}, t) = v_{ext}(\mathbf{r}, t) + \int d^3\mathbf{r}' \frac{n(\mathbf{r}', t)}{|\mathbf{r} - \mathbf{r}'|} + v_{xc}(\mathbf{r}, t) \tag{1.60}$$

The external potential contains contains both nuclear attraction as well as the external time dependence such as from the laser field.
Out of all these three potentials the crucial one is the time-dependent exchange correlation $v_{xc}(\mathbf{r}, t)$ potential. The exact form of this potential as a functional is unknown. However approximations for this term can be done based on exact constraints that $v_{xc}(\mathbf{r}, t)$ must satisfy [151].

1.10 Linear Response and ALDA

Perturbative techniques are traditionally simplest ways to get the excitations of a system. Within a given approximation for xc potential, TDKS equations can be used to extract the electronic excitations of the system. To perform such calculations, one needs to know about the linear-density-response of the system. In this linear response formalism, one considers a small time dependent perturbation $v_1(\mathbf{r}, t)$ and assumes that the system is its ground state at $t_0 < t$. And the corresponding density is $n_0(r)$. i.e.,

$$v_{ext}(\mathbf{r}, t) = v_0(\mathbf{r}) + v_1(\mathbf{r}, t) \tag{1.61}$$

We know that $n(r, t) = n[v_{ext}](r, t)$ From the Runge-Gross 1-1 correspondence, we can invert the above equations as

$$v_{ext}(\mathbf{r}, t) = v_{ext}[n](\mathbf{r}, t) \tag{1.62}$$

If we expand $n[v_{ext}]$ into a Taylor series with respect to the perturbation $v_1(\mathbf{r}, t)$, we get

$$n(\mathbf{r}, t) = n_0(\mathbf{r}, t) + n_1(\mathbf{r}, t) + n_2(\mathbf{r}, t) + n_3(\mathbf{r}, t) + ... \tag{1.63}$$

where the lower indices denote the orders in v_1. The first order density response is given by

$$n_1(\mathbf{r}, t) = \int dt' \int d^3r' \chi[n_0](\mathbf{r}, t, \mathbf{r}', t')v_1(\mathbf{r}', t') \tag{1.64}$$

with the density response function

$$\chi[n_0](\mathbf{r}, t, \mathbf{r}', t') = \left.\frac{\delta n[v_{ext}](\mathbf{r}, t)}{\delta v_{ext}(\mathbf{r}', t')}\right|_{v0} \tag{1.65}$$

For the non-interacting particles moving in the KS potential $v_s(\mathbf{r}, t)$, the above analysis holds good as well. Therefore

$$n(\mathbf{r}, t) = n[v_s](\mathbf{r}, t) \tag{1.66}$$

can be inverted

$$v_s(\mathbf{r}, t) = v_s[n](\mathbf{r}, t) \tag{1.67}$$

The corresponding non-interacting density response function is given by

$$\chi_s(\mathbf{r}, t, \mathbf{r}', t') = \left.\frac{\delta n[v_s](\mathbf{r}, t)}{\delta v_s(\mathbf{r}', t')}\right|_{v_{s0}} \tag{1.68}$$

If we apply the chain rule, the functional derivative of v_s with respect to v_{ext}

$$\chi(\mathbf{r},t,\mathbf{r}',t') = \int d^3x \int dT \, \frac{\delta n(r,t)}{\delta v_s(X,T)} \frac{\delta v_s(X,T)}{\delta v_{ext}(r',t')}\bigg|_{n_0} \tag{1.69}$$

By following the chain rule once again for the right side term in the above integrand, one can show a Dyson like equation relating χ and χ_s

$$\begin{aligned}\chi(\mathbf{r},t,\mathbf{r}',t') = \chi_s(\mathbf{r},t,\mathbf{r}',t') + \int d^3x \int dT \int d^3x' \int d^3T' \chi_s(\mathbf{r},t,\mathbf{X},T) \\ \times \left(\frac{\delta(T-T')}{|X-X'|} + f_{xc}[n_0]\chi(\mathbf{X}',T',\mathbf{r}',t') \right)\end{aligned} \tag{1.70}$$

where the time-dependent xc kernel is given by

$$f_{xc}[n_0](\mathbf{r},t,\mathbf{r}',t') = \frac{\delta v_{xc}[n](\mathbf{r},t)}{\delta n(\mathbf{r}',t')}\bigg|_{n_0} \tag{1.71}$$

The simplest approximation to the exchange-correlation potential is the adiabatic local density approximation (ALDA), which is similar to the LDA in the static DFT. This approximation basically evaluates the LDA expression for the ground-state exchange correlation potential at the time-dependent local density,

$$v_{xc}(\mathbf{r},t) = v_{xc}^{hom}(n(\mathbf{r},t)) = \frac{d}{dn}(n e_{xc}^{hom}(n))|_{n(\mathbf{r},t)} \tag{1.72}$$

where $e_{xc}^{hom}(n)$ is the exchange-correlation energy per particle of the homogeneous electron gas with density n. The essential feature of ALDA is it is local in time as well as space. In principle, ALDA should be valid in nearly homogeneous systems where the densities vary very slowly in time; in practice however, it works quite well beyond this domain of applicability. The exchange-correlation kernel in ALDA within the linear response regime has the form

$$f_{xc}^{ALDA}(\mathbf{r},\mathbf{r}',t,t') = \delta(t-t')\delta(\mathbf{r}-\mathbf{r}')\frac{d^2}{dn^2}(ne_{xc}^{hom}(n))|_{n_0(\mathbf{r})} \tag{1.73}$$

This kernel is local in space and time. When Fourier-transformed, the locality in time implies that f_{xc}^{ALDA} is frequency independent, ie., the adiabatic approximation gives rise to frequency independent kernels. In quantum chemistry Eq (5.10) has been recast into matrix form. These matrix type equations are often called Casida‘s [42] equation.

1.11 Memory Dependence

In TDDFT, the term memory is used in the sense that it refers to dependence of the observables on earlier times. This memory is basically of two types: one is due to the initial state dependence and the other one is due to the history dependence of the density. One cause for the memory is the fact that, in TDDFT, the one-to-one mapping between the density and external potential is constrained by a a given initial-state. This implies that the potentials generally are functionals of the initial state of the system, as well as of the density; and, not just of the instantaneous density but of its entire history. In KS-TDDFT, the quantity which depends on initial state and history of density is the exchange-correlation potential $v_{xc}(\mathbf{r}, t)$. The Hartree potential does not have this memory dependence as the classical Coulomb interaction depends on the instantaneous density only. In Adiabatic LDA for v_{xc} (Equation (5.15)), this memory effect is completely neglected as one takes the instantaneous density into account. A precise review article on the initial state dependence and the history dependence can be found in Ref. [73]. Maitra and Burke clearly demonstrated the initial state dependence of two non-interacting electrons system in a parabolic potential [6]. In 2002, Maitra et al [147] clrealy explained the intimate relation between the history dependence and initial dependence.

1.12 v-Representability

RG-theorem states that for a given initial state the time dependent density $n(\mathbf{r}, t)$ is a unique functional of the external potential $v(\mathbf{r}, t)$. Now one can ask whether the same time-dependent density can be reproduced by an external potential $v'(\mathbf{r}, t)$ in a system with a different given initial state and with a different particle interaction(v'_{ee})? and if so, whether this potential is unique? Now, the KS system is a special case for this question as it doesn't have particle interaction but it does have a different initial state ie., slater determinant of the KS orbitals. The above question is called the problem of v-representabilty in TDDFT. Is a density belonging to an interacting system also non-interacting v-representable? Robert van Leeuwen in 1999 and in 2001 [36], [31] answered these questions affirmatively with some conditions on the initial states and potentials. The conditions are

Condition-1: The initial state ψ'_0 of the other system should yield the same initial density $n(r, t_0)$ as well as same initial time derivative of the density $\dot{n}(r, t_0)$
Condition-2: The external potential $v'(\mathbf{r}, t)$ should be Taylor expandable and satisfy $v' \rightarrow 0$ as $\mathbf{r} \rightarrow \infty$

For the KS case, If we put $v'_{ee} = 0$, It implies that there exists a unique potential $v_s(\mathbf{r}, t)$ that produces the exactly same density at all times.

1.13 Practical TDDFT and Self-consistency

In both the static and time dependent cases, the KS potential must be calculated self consistently with the density. In the static case, v_s determines, via KS orbitals, a ground state density which is used to recalculate v_s until self consistency is achieved. In time-dependent theory, the initial density determines the initial potential which is then used to recalculate the density at an infinitesimally later time, and so on. In other words, the numerical solution of the time dependent KS equation by incremental steps in time plays the same role as the self consistency loop of the static theory.

1.14 TDDMFT and TDCDFT

Similar to DFT, Density Matrix Functional Theory(DMFT) is an approach where the basic variable is the one-body density matrix (1DM) instead of the density . Very recently there has been a renewed interest in the theory [75] and the preliminary results proved to be successful over the regular DFT for strongly correlated systems. In DMFT, the functionals are approximated in terms of reduced 1-body density matrixρ_1. From a many body (ground state)wave function ψ, the reduced ρ_1 is defined by

$$\rho_1(r,r') = N\int dr_2..dr_N\psi(r,r_2,..,r_N)\psi(r',r_2,..,r_N) \tag{1.74}$$

Gilbert‘s theorem [24] (*For systems with non-degenerate ground states and a Hamiltonian with fixed interaction and a possibly non-local external potential, the ground-state wavefunction is uniquely determined by the reduced one-body matrix*) guarantees that ψ is uniquely determined from ρ_1

$$\rho_1 \quad \rightarrow \quad \psi_1 \tag{1.75}$$

The exact exchange energy as a function of ρ_1 is given by,

$$E_x[\rho_1] = -\frac{1}{2}\int\int\frac{\rho_1(r,r)\rho_1(r',r')}{|r-r'|}drdr' \tag{1.76}$$

But the exact expression for correlation energy as a functional of ρ_1 or its natural orbitals is unknown.

Natural orbitals are eigen-functions of the ρ_1 with occupation numbers (eigenvalues) f_j;

$$\int \rho_1(r, r')\phi_j(r') = f_j\phi_j(r') \tag{1.77}$$

In DMFT, there is no kinetic correlation as one defines the kinetic energy as an exact functional in terms of natural orbitals. Due to the success of static DMFT in areas where the traditional DFT is facing limitations, it seems desirable to consider the density matricies in time-dependent context. Such an extension is called Time-Dependent Density Matrix Functional Theory (TDDMFT). Similar to the static case, the fundamental entity in TDDMFT is the reduced time dependent 1-body density matrix $\rho_1(r, r', t)$.

$$\rho_1(r, r', t) = \sum_j f_j\phi_j(r, t)\phi_j^*(r', t) \tag{1.78}$$

This theory is still in its budding stage. The extension of Gilbert‘s theorem in case of time-dependent systems is still an open question. The equations of motion for the time-dependent reduced density matrices follow a set of chained equations, called the BBGKY (Bogoliubov, Born, , Green, Kirkwood and Yvon) heirarchy. BBGKY heirarchy couples the reduced density matrices of order n to the respective matrix of the next higher order. There are different approaches to truncate this heirarchy depending on the correlations of the system in which one is interested. Some more details on this theory are given in the fourth chapter of this thesis.

In 1996, Vignale and Kohn formulated Time-dependent current density functional theory (TDCDFT) [2],[4]. As the name, in TDCDFT, the basic variable is the time-dependent current density $\mathbf{j}(\mathbf{r}, t)$. The relevant generalization of RG theorem was actually proved by Ghosh and Dhara in late 1980s [83]. It states that for a given initial state, the time-dependent current current density determines the vector potential up to a guage transformation. Vignale-Kohn particularly showed that the xc vector potential A_{xc} admits a local approximation in terms of the current density $\mathbf{j}$: therefore, the nonlocality problem that plagues the time-dependent DFT, does not occur in current-density functional theory. The essence of this theory is that the nonlocality of v_{xc} as a functional of n can be entirely absorbed into the nonlocal relations between A_{xc} and v_{xc} and n and $\mathbf{j}$.

1.15 Successes and Challenges in TDDFT

Most of the applications of TDDFT are in the linear response regime. Various organic structures(Fullerenes)have been studied using [84]-[88] TDDFT. The optical response of many transition metal complexes have been calculated [89]-[97]. In photobiology, the potential curves for the trans-cis isomerization of protonated Schiff base [98] of retinal have been calculated. In Photochemistry, properties of chromophores and dyes have been computed ([128]-[136]).An other major area of applications is in metallic (and covelent) clusters ([99]-[106]) of small and big sizes. In all these fields, there is a growing interest in second and higher order response regimes.In particular the field of non-linear optics (two photon absorption) has been investigated [106]-[119]. In all these successful applications, standard available approximations are used both for the groundstate and the excitations. However there are areas where these adiabatic approximations found to fail. The failures in the adiabatic approximations, are due to the locality in time. This is known as Memory effect as we discussed in the previous section, which demands the XC kernel to be frequency dependent. These approaches are noticed to perform poorly for the calculations of higher excitations (double excitations). When applying to extended systems, such as polymers or solids, one needs a long-ranged XC kernel as the Coulomb interaction is long-ranged. However the local approximations yields short-ranged XC kernel. Different approaches currently exist to go around the failures of the standard approximations ([72], [40]). Vignale-Kohn (VK) develpoed a formalism by considering the current density as a basic variable $j(r,t)$ which is known as TDCDFT (we will discuss this in detail in our next chapters). An other approach is to construct the orbital dependent functionals that have explicit frequency dependence(OEP). This approach is more complex and expensive for computational point of view than the simple Kohn-Sham (KS) equations.

Chapter 2

TDDFT in Phase-Space

2.1 Introduction

For TDDFT to be successful as its ground state counterpart, there is a need for more accurate time-dependent functionals, especially beyond the linear response theory. Recent works by Maitra and Burke [6], [71], [7] and [147] emphasized on memory effects, from frequency-dependence of exchange-correlation kernel in the linear response regime, to full history and initial-state-dependence in the general case. The basic aim of this study is to develop a new approach based on time-dependent one body density matrix $\rho_1(\mathbf{r}, \mathbf{r}', t)$ and phase-space distribution $w(\mathbf{r}, \mathbf{p}, t)$. The idea behind this approach is that functionals made out of these distributions are more simpler than those made out of usual co-ordinate distributions ($n(\mathbf{r}, t)$). We name this approach as One-body Phase-Space Density functional theory (PSDFT).

This theory is formally equivalent to the recently developed time-dependent one-body density matrix functional theory (1DMFT). Similar to the 1DMFT, the phase-space distribution of a interacting system can not be reproduced by the non-interacting(KS) system (the one-body reduced density matrix for a non-interacting system is idempotent while it is non-idempotent for an interacting system).

There are few phase space distributions available in the literature [33], [34], [35]. Because of the Heisenberg‘s uncertainty, these distribution do not fall under the definition of exact probability distributions, but often called as quasi-probability distributions. Wigner distribution and Husimi distributions are the important ones. Husimi function can describe the quantum uncertainty more than wigner. Though it is positive everywhere unlike the Wigner distribution, in a sense is more Heisenberg friendly, it is mathematically complicated than the Wigner. Husimi distribution $h(r, p)$ is interpreted as a Gaussian convolution of Wigner $w(r, p)$ in both the position and momentum space.

$$h(\mathbf{r}, \mathbf{p}) = \int e^{-K(\mathbf{r}-\mathbf{r}')^2} e^{-(\mathbf{p}-\mathbf{p}')^2/K} w(\mathbf{r}', \mathbf{p}') d\mathbf{r}' d\mathbf{p}' \tag{2.1}$$

Here the uncertainty parameter K is defined to tune the uncertainties in position $\mathbf{r}$ and in momentum $\mathbf{p}$. It is the selection of values for this adjustable parameter that is very crucial and is not clear how to choose proper values for

K. Our formalism focuses on the Wigner distribution due to its simpler form. Later, in practical applications, we may transform to Husimi representation due its smoother properties. At first, this distribution was proposed by Wigner in 1932 [33], to represent a system in a state defined by the first order density matrix:

$$w(q,p) = \frac{1}{\pi} \int dy \, \langle q - y | \hat{\rho} | q + y \rangle \, e^{2ipy} \tag{2.2}$$

In case of a pure state ψ it is defined as

$$w(q,p) = \frac{1}{\pi} \int dy \psi^*(q+y)\psi(q-y)e^{2ipy} \tag{2.3}$$

One can also generalize it to the n-body system with the time dependent Hamiltonian as

$$\begin{aligned} w(q_1, q_2, .., q_n, t) = \pi^{-n} \int ... \int dy_1 ... dy_n \psi^*(q_1 + y_n, ..., q_n + y_n, t) \\ \times \psi(q_1 - y_1, ..., q_n - y_n, t) exp[2i(p_1 y_1 + ... + p_1 y_1] \end{aligned} \tag{2.4}$$

There has been a remarkable amount of research carried out on the phase space (reduced density matrix) and momentum space approaches for the static DFT. However for the TDDFT, the research in the lines of phase-space, momentum space as well as in the reduced density matrix approach is still in budding stage. In 1973, Lam and Platzmann [63] derived an exact expression for the ground state momentum distribution from the exact exchange-correlation energy functional. Zhao-Parr [64] developed a novel method to obtain KS orbitals for a given coordinate density using Levy's constrained search approach [81]. In a recent work, Ragot [74] studied the HF and KS momentum distributions for two-fermion systems and the comparisons were studied in detail. Wigner phase space approach within HF approximation for the closed shell atoms was studied by Springborg and Dahl [76]. They derived an approximated expression for the first-order wigner function in terms of the natural orbitals. For the static case, Buijse and Baerends [75] derived an approximate xc-hole density expression in terms of the natural orbitals. They approximated the Fermi and Coulomb holes (hole amplitudes) in terms of natural orbitals by employing the local values of the natural orbitals and the density. In a recent paper, Harbola et al [66] showed a scheme to describe the approximated ground-state momentum profile directly from the ground-state coordinate density, via Zhao-Parr search. Gross et al [69] looked at the double-ionization problem within the HF using center of mass motion in wigner phase space. A different theory known as Intracule functional theory (IFT) was developed by Gill [80] to explain the correlation. In IFT, one condenses the second order phase space distribution $w_2(\mathbf{r_1}, \mathbf{p_1}, \mathbf{r_2}, \mathbf{p_2})$ into a different distribution called omega intracule which is a function of relative displacement and relative momentum $\Omega(|\mathbf{r_1} - \mathbf{r_2}|, |\mathbf{p_1} - \mathbf{p_2}|, \omega)$ where the ω is the angle between the relative displacement and the relative momentum. The physics properties and the inequalities satisfied by this n-body wigner distribution are extensively discussed in a review article by Hillery et al [65].

Although initially introduced to treat many-particle dynamics, the majority of the applications of the Wigner actually involve one-particle systems, especially for making quantum-classical correspondence. It has been argued that Wigner function is a particularly suitable approach to studying transport due to its setting within asemiclassical picture while yet being rigorously quantum mechanical.

One can get the regular position co-ordinate density $n(\mathbf{r})$ from $w_1(\mathbf{r}, \mathbf{p}, t)$ from the following equation:

$$n(\mathbf{r}, t) = \int d\mathbf{p} w_1(\mathbf{r}, \mathbf{p}, t) \tag{2.5}$$

where w_1 is one-body wigner distribution.

Runge-Gross(RG) proof for PSDFT can be argued from the following steps. We have the unique mapping

$$w_1(\mathbf{r}, \mathbf{p}, t) \rightarrow n(\mathbf{r}, t) \tag{2.6}$$

Also from the RG theorem of TDDFT, we have an other unique mapping:

$$(n(\mathbf{r}, t), \Psi_0) \rightarrow \Psi(t) \tag{2.7}$$

Therefore for a given initial state(Ψ_0), there is a 1-1 mapping between the one-body Wigner function ($w_1(\mathbf{r}, \mathbf{p}, t)$) and the many-body wavefunction ($\Psi(t)$). This 1-1 mapping holds for time-dependent local external potentials. Although a generalized proof for the time-dependent non-local potentials is yet to be found, the mapping may be generalized to vector potentials $\mathbf{A}(\mathbf{r}, t)$

The time-dependent current density is defined from $w_1(\mathbf{r}, \mathbf{p}, t)$ as

$$\mathbf{j}(\mathbf{r}, t) = \int \mathbf{p} w_1(\mathbf{r}, \mathbf{p}, t) d\mathbf{p} \tag{2.8}$$

Therefore we can write

$$w_1(\mathbf{r}, \mathbf{p}, t) \rightarrow \mathbf{j}(\mathbf{r}, t) \tag{2.9}$$

Ghosh-Dhara [83] proved a 1-1 mapping between currents and vector-potentials.

$$(\mathbf{j}(\mathbf{r}, t), \Psi_0) \rightarrow \Psi(t) \tag{2.10}$$

That is, any observable of any time-dependent interacting electronic system evolving under an external vector potential, is a functional of its initial state Ψ_0 and and the time dependent one-body phase-space density.

2.2 BBGKY Hierarchy

The one-particle density matrix of an N-particle system under a time-dependent external potential is given by

$$\rho_1(\mathbf{r'},\mathbf{r},t) = N\int \Psi^*(\mathbf{r'},\mathbf{r_2},...,\mathbf{r_n},t)\Psi(\mathbf{r},\mathbf{r_2},...,\mathbf{r_n},t)d^3\mathbf{r_2}...d^3\mathbf{r_n} \qquad (2.11)$$

If we solve the equation of motion for ρ_1, we get

$$\begin{aligned} i\dot{\rho_1}(\mathbf{r'},\mathbf{r},t) = &\left[-\nabla^2/2+\nabla'^2/2+v_{ext}(\mathbf{r}t)-v_{ext}(\mathbf{r'}t)\right]\rho_1(\mathbf{r},\mathbf{r'},t)+\\ &\int d\mathbf{r}_2\left[\frac{1}{|\mathbf{r}-\mathbf{r_2}|}-\frac{1}{|\mathbf{r'}-\mathbf{r_2}|}\right]\rho_2(\mathbf{r'},\mathbf{r},\mathbf{r_2},\mathbf{r_2},t) \quad (2.12)\end{aligned}$$

where

$$\begin{aligned}\rho_2(\mathbf{r'},\mathbf{r},\mathbf{r'_2},\mathbf{r_2},t) = N(N-1)\int &d\mathbf{r_3}d\mathbf{r_4}...d\mathbf{r_N}\Psi^*(\mathbf{r'},\mathbf{r'_2},\mathbf{r_3},...,\mathbf{r_N},t)\\ &\times\Psi(\mathbf{r},\mathbf{r_2},\mathbf{r_3},...,\mathbf{r_N},t) \quad (2.13)\end{aligned}$$

is known as the second order density matrix. The time evolution of 1DM (first-order density matrix) involves the higher order(second) matrix and so on. ie., In general the evolution of mth order distribution contains distributions up to the (m+1)th order. This kind of chain of equations are called BBGKY equations. One has to truncate this chain at some order. Our goal is to approximate ρ_2 in terms of ρ_1. The truncation of such hierarchy is often crucial in dealing with highly correlated systems. We also looked at Boltzmann type of truncation for our study. Boltzmann type of truncation often works very well only if the system can respect the binary interaction between the particles. The quantum Boltzmann type of truncation works well only for the systems of short range inter-particle interaction. The binary collision method is based on the "*stosszahlansatz*" assumption made by Boltzmann. It assumes that the correlation between the electrons has no history dependence.

However the systems we are looking at are strongly correlated and the interaction force is the Coulomb force

Time-dependent phase-space density functional theory (TD-PSDFT) involves solving the equation of motion for the Wigner function:

$$\begin{aligned}
\dot{w_1}(\mathbf{r},\mathbf{p},t) &= -\mathbf{p}\cdot\nabla w_1(\mathbf{r},\mathbf{p},t) \\
&\quad -i\int d^3p'\int d^3y e^{-i(\mathbf{p}-\mathbf{p'})\cdot\mathbf{y}} \\
&\quad \times\left[v_{ext}(\mathbf{r}+\frac{\mathbf{y}}{\mathbf{2}},t)-v_{ext}(\mathbf{r}-\frac{\mathbf{y}}{\mathbf{2}},t)\right]w_1(\mathbf{r},\mathbf{p},t) \\
&\quad -i\int d^3y d^3p_1 d^3p_2 d^3r_2 e^{i(\mathbf{p}-\mathbf{p_1})\cdot\mathbf{y}} \\
&\quad \times\left(\frac{1}{|\mathbf{r}-\mathbf{r_2}+\frac{\mathbf{y}}{2}|}-\frac{1}{|\mathbf{r}-\mathbf{r}_2-\frac{y}{2}|}\right)w_2(\mathbf{r},\mathbf{r}_2,\mathbf{p}_1,\mathbf{p}_2,t)
\end{aligned} \tag{2.14}$$

The accuracy of TD-PSDFT depends on approximating functionals for the term involving the second order wigner distribution w_2 in terms of the first order wigner distribution w_1. In Chapter-4, We will present an approximation scheme for w_2 (ρ_2) using quasi-classical methods

2.3 Non-locality in Correlation - Hooke's Atom

In Ref.[71] it is demonstrated from an exactly (numerically) solvable example (Hooke's atom), that the correlation potential depends on the density ultra-non-locally in time. The origin for this is due to the "memory-dependence" that we have discussed in Chapter.1. We will revisit this example, with a view to asking whether one-body phase-space distributions when used as basic variable can capture the memory-dependence.

Hooke's atom is a model system, where two electrons interact coulombically in a harmonic well potential $(1/2)kr^2$. Lately Hooke's atom model has become an important model in DFT community. These models are used in describing the confining potentials for quantum dots. However this model can not give any physical description for ionization as it does not ionize. In its time dependent version, we include the time-dependence in the force constant $k(t) = \overline{k} - \epsilon\cos(\omega t)$. The values of the force constant k oscillate around the average value $\overline{k}$. One can cover a more general evolution of the system with this kind of time dependence.

Also one might think of an external potential of type $-\mathbf{F}.\mathbf{r}cos(\omega t)$. But this type of potential satisfies the Harmonic Potential Theorem(HPT) [82] from which one can state that

$$n(\mathbf{r}, t) = n_0(\mathbf{r} - \mathbf{R}(t)) \tag{2.15}$$

where $\mathbf{R}(t)$ is the position of the origin of the moving frame with respect to rest frame. HPT basically states that *the center of mass of a system confined in a parabolic well and subjected to a uniform time dependent electric field should evolve in time in exactly the same way a single electron would.* So with this type of perturbation potetials only a limited time dependent behavior can be observed as it couples to the center of mass Hamiltonian.

The Hamiltonian for the Hookian atom can be written as

$$\hat{H}(\mathbf{r_1}, \mathbf{r_2}, t) = -\frac{1}{2}\nabla_{r1}^2 - \nabla_{r2}^2 + \frac{1}{2}k(t)(r_1^2 + r_2^2) + \frac{1}{|\mathbf{r_2} - \mathbf{r_2}|} \tag{2.16}$$

If we go to the center of mass and relative co-ordinates,

$$\mathbf{R} = \frac{1}{2}\mathbf{r_1} + \frac{1}{2}\mathbf{r_2} \tag{2.17}$$

$$\mathbf{u} = \mathbf{r_2} - \mathbf{r_1} \tag{2.18}$$

then the total Hamiltonian splits into

$$\hat{H} = \hat{H}_R + \hat{H}_u \tag{2.19}$$

$$\hat{H}_R = -\frac{1}{4}\nabla_R^2 + k(t)R^2 \tag{2.20}$$

$$\hat{H}_u = -\nabla_u^2 + \frac{1}{4}k(t)u^2 + \frac{1}{u} \tag{2.21}$$

Therefore

$$\Psi(\mathbf{r_1}, \mathbf{r_2}, t) = \chi(\mathbf{R}, t)\xi(\mathbf{u}, t) \tag{2.22}$$

From these exact wave functions one can solve the density $n(\mathbf{r})$. The knowledge of the exact density allows us the possibility to calculate the correlation energy $E_c(t)$ for the system.

In the Kohn-Sham description, we have a doubly occupied spatial orbital(spin-singlet) defined as

$$\phi(\mathbf{r}, t) = A(\mathbf{r}, t)e^{i\alpha(\mathbf{r},t)} \tag{2.23}$$

$$n(\mathbf{r}, t) = 2\left|\phi(\mathbf{r}, t)\right|^2 \tag{2.24}$$

Now if we invert the time-dependent KS equation

$$\left[\nabla_r^2 + v_s(r, t)\right]\phi(\mathbf{r}, t) = i\frac{\partial}{\partial t}\phi(\mathbf{r}, t) \tag{2.25}$$

to obtain the potential v_s.

With the knowledge of v_s one can construct v_{xc} using

$$v_{xc}(\mathbf{r}, t) = v_s(\mathbf{r}, t) - v_{ext}(\mathbf{r}, t) - \int d\mathbf{r}'\frac{n(\mathbf{r}', t)}{\mathbf{r} - \mathbf{r}'} \tag{2.26}$$

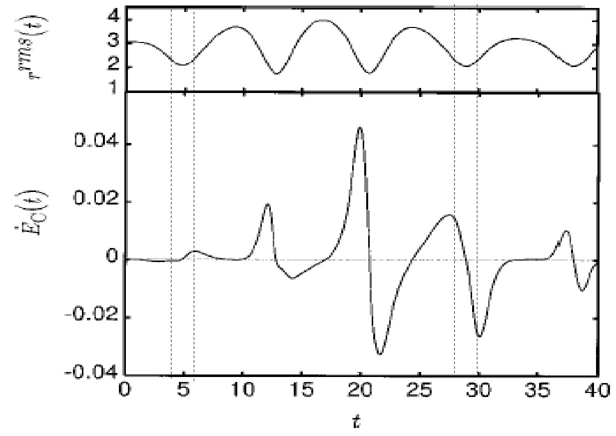

Figure 2.1: Nonlocality of the correlation potential in time: $\int v_c(r,t)\dot{n}(r,t)d^3r$ (lower panel) and $r_{rms}(t)$ (top panel). In the two time slices indicated, the density is almost identical locally in time, whereas the density-weighted correlation potential in the lower panel is quite distinct.

In Ref. [71], the dynamics of density are reflected in the spread parameter $< r^{rms}(t) >$ which is root-mean-square (rms) variance. It is observed that at times where the density profile behaves exactly the same, the correlation component of the system $\dot{E}_c$ behaves entirely different. Therefore $v_c(\mathbf{r},t)$ can not be an instantaneous functional of the density and rather depends on its history. The ALDA completely neglects this fact. The correlation component $\dot{E}_c$ is defined by

$$\dot{E}_c = \int d^3r\dot{n}(\mathbf{r},t)v_c(\mathbf{r},t) \qquad (2.27)$$

The spread in the density is defined as

$$\langle r^2\rangle(t) = \frac{1}{2}\int 4\pi r^4 n(r,t)dr \qquad (2.28)$$

For the physical wave functions and Kohn-Sham orbitals defined and solved numerically by the Crank-Nicholson method, We defined the Phase space (wigner) distributions w and w_s. One important thing here to note is that, though the KS orbitals and the true wave functions look different, they generate the same position co-ordinate density $n(\mathbf{r})$. However the phase space distributions (w and w_s) look entirely different at each point of time. We also showed that the momentum distributions (phase-space distributions as well) are also different.

From the exact two-electron wave function $\Psi(\mathbf{r_1}, \mathbf{r_2}, t)$ one defines the phase space distribution(wigner) as

$$w(\mathbf{r}, \mathbf{p}, t) = \frac{2}{\pi^3} \int \int e^{-2i\mathbf{p}.\mathbf{y}} \Psi^*(\mathbf{r} + \mathbf{y}, \mathbf{r_2}, t)\Psi(\mathbf{r} - \mathbf{y}, \mathbf{r_2}, t) d^3y d^3r_2 \tag{2.29}$$

Similarly

$$\Psi(\mathbf{r} - \mathbf{y}, \mathbf{r_2}) = \chi(\frac{1}{2}|\mathbf{r} - \mathbf{y} + \mathbf{r_2}|)\xi(|\mathbf{r} - \mathbf{y} - \mathbf{r_2}|) \tag{2.30}$$

From the CM and relative coordinates, We write the wave function as

$$\Psi^*(\mathbf{r} + \mathbf{y}, \mathbf{r_2}, t) = \chi^*(\frac{1}{2}|\mathbf{r} + \mathbf{y} + \mathbf{r_2}|, t)\xi^*(|\mathbf{r} + \mathbf{y} - \mathbf{r_2}|, t) \tag{2.31}$$

We define $\mathbf{x} = \mathbf{r_2} - \mathbf{y}$ and θ as the angle between $\mathbf{r}$ and $\mathbf{x}$. We chose the method of tranformation of proper co-ordinate system and arrived at,

$$w(\mathbf{r},\mathbf{p},\alpha,t) = \Bigg| \int_0^\infty x^2 dx \int_{-1}^{+1} e^{-ipx\cos\alpha\cos\theta}$$
$$\times\, J_0(px\sin\alpha\sqrt{1-\cos^2\theta})\chi^*(\frac{1}{2}\sqrt{r_+},t)\xi(\sqrt{r_-},t)d(\cos\theta)\Bigg|^2 \tag{2.32}$$

where $r_+ = r^2 + x^2 + 2rx\cos\theta$ and $r_- = r^2 + x^2 - 2rx\cos\theta$

For the Kohn-Sham case, the the doubly occupied KS orbital $\phi(\mathbf{r},t)$ is defined as

$$\phi(\mathbf{r},t) = \sqrt{n(\mathbf{r},t)/2}e^{i\alpha(\mathbf{r},t)} \tag{2.33}$$

Knowing the KS orbital ϕ, the KS-wigner distribution w_s is obtained as

$$w_s(\mathbf{r},\mathbf{p},\alpha,t) = \int_0^\infty x^2 dx \int_{-1}^{+1} e^{-ipx\cos\alpha\cos\theta}$$
$$\times J_0(2px\sin\alpha\sqrt{1-\cos^2\theta})\phi^*(\frac{1}{2}\sqrt{r_+},t)\phi(\sqrt{r_-},t)d(\cos\theta) \tag{2.34}$$

here α is the angle between $\mathbf{r}$ and $\mathbf{p}$ and r=$|\mathbf{r}|$ and J_0 is the Bessel function of zeroth order

Both the distributions w and w_s depend on the angle explicitly. We have considered the angle averaged distributions for simplicity.

The angle-averaged wigner phase space distribution is defined by

$$w(\mathbf{r},\mathbf{p},t) = \int_0^\pi w(\mathbf{r},\mathbf{p},\alpha,t)\sin^2\alpha d\alpha \tag{2.35}$$

We have numerically solved both the wigner functions and the coordinate density profiles and momentum density profiles. We obtained momentum densities by the expression

$$\tilde{n}(\mathbf{p}, t) = \int w(\mathbf{r}, \mathbf{p}, t) d\mathbf{p} \tag{2.36}$$

Similarly for the KS case,

$$\tilde{n_s}(\mathbf{p}, t) = \int w_s(\mathbf{r}, \mathbf{p}, t) d\mathbf{p} \tag{2.37}$$

We define the correlation component of the phase space density as

$$w_c(\mathbf{r}, \mathbf{p}, t) = w(\mathbf{r}, \mathbf{p}, t) - w_s(\mathbf{r}, \mathbf{p}, t) \tag{2.38}$$

Similarly we define momentum space correlation component as

$$\tilde{n_c}(\mathbf{p}, t) = \tilde{n}(\mathbf{p}, t) - \tilde{n}_s(\mathbf{p}, t) \tag{2.39}$$

We focused on time intervals where the v_c is significantly varying (indicating the memory dependence) the spread in the position density (r^{rms}) is the

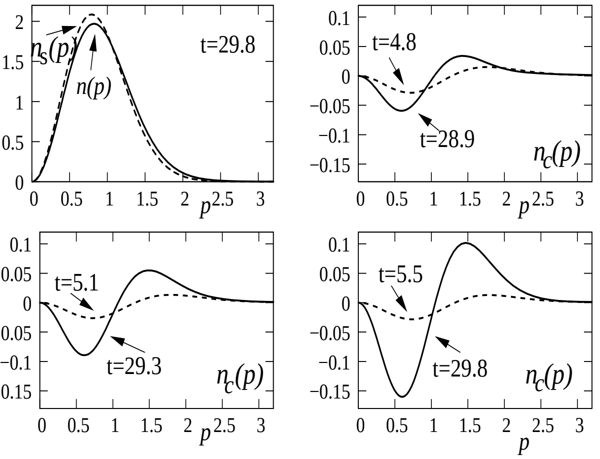

Figure 2.2: Top left panel: the true (solid) and KS (dashed) momentum densities, at $t = 29.8$. Top right and lower two panels: correlation components of the momentum distributions $n_c(p)$ at three different time-pairs indicated. In each time-pair, the coordinate density, $n(r,t)$, is identical, while the momentum-density is not, with the difference in its correlation component $n_c(p)$ growing as the difference in the density-weighted correlation potential $\dot{E}c$ at those times.

same (Fig. 2.1). This indicates that position density $n(\mathbf{r}, t)$ can not recognize the memory effect with time. Thus any functional approximation based on instantaneous $n(\mathbf{r}, t)$ would more likely completely neglect this non-locality of correlation. We then asked, whether, if the momentum-distribution information was included in the basic variable, the correlation potential would be just as non-local in time as a functional of phase-space density, or whether the phase-space density could distinguish the state of the system at these times. In fig. 2.2, The top left panel shows the true and momentum-distributions at t=29.8, which has one of the larger values for the density-weighted correlation potential. Although the differences in phase-space (for simplicity here the momentum distributions) distributions are not identical, the differences are relatively small. We now study their difference $n_c(p)$. The other three panels show $n_c(p)$ at pairs of times at which the position-density are particularly identical (i.e. essentially distinguishable to the eye on scale of plots similar to the top panel). The first time-pair, (4.8, 29.8), is chosen near the minimum of the r^{rms} at each of the two time slices indicated in Fig. 2.1; here the difference in $\dot{E}_c$ is relatively small (0.0005 au), while it bigger (0.011 au) in the second pair (5.1,29.3), and bigger still (0.0264) at the third pair (5.5, 29.3). In contrast to the coordinate(position)-density, the momentum-densities are not identical at these pairs of time. Moreover, their differences increase with the difference in the value of the density-weighted correlation potential as those times. Therefore these result suggest that having momentum information in the basic variable may reduce their memory-dependence.

This in turn suggests that functionals of the phase-space density may be less non-local in time.

2.4 Numerical Scheme:Crank Nicholson Method

In this section explain the numerical method that was used in this study. The FORTRAN code was built on the program initially written by Paul Hessler in Ref. [71]. First to solve for the exact wave function, we solved both the Schrodinger equations in CM and relative coordinates. The CN method uses the fact that the time evolution operator has to be unitary. This gives us great stability. The basic scheme for CN method is given by

$$\left[1 - \frac{i}{2}\hat{H}\right] |\Psi(t) >= \left[1 + \frac{i}{2}\hat{H}\right] |\Psi(t + dt) > \tag{2.40}$$

For the descretization we employ a variable transformation for the position r (0 to ∞) to a uniform grid y (1 to 0)

$$y = \frac{1}{1 + \frac{r}{r_0}} \tag{2.41}$$

$$r = r_0 \left[\frac{1}{y} - 1\right] \tag{2.42}$$

So the prominent region of the wave function(as r tends to 0) is sampled with more grid points and the grid gets sparse for r tending to ∞.

The run started from calculating the ground states for both the R and u

systems. During the entire run we checked the norm of the density which is supposed to stay fixed if the size of the time step is small enough. The phase space distributions are computed from the CM and relative co-ordinate wave functions (for the true case ie., w) and from the KS-orbital (for KS case ie., w_s). We chose $\overline{k}$ value as 0.25 and the magnitude of the oscillator ϵ as 0.1 and ω as 0.75 throughout our generic run.

2.5 Conclusion

In conclusion, we argue that our approach based on instantaneous phase-space distributions, can be an alternative way to go for where the adiabatic approximations based on instantaneous coordinates densities fail. This work proposes the need of developing phase-space functionals in order to capture the memory effects in strongly correlated systems. This approach also suggests applying phase-space methods to existing standard approximations in TDDMFT.

Chapter 3

Momentum Distributions: An Observable Problem

3.1 Introduction

The accuracy of TDDFT depends on the approximation used for the xc potential $v_{xc}(\mathbf{r}, t)$. This is generally known to have "memory-dependence"-that is $v_{xc}(r, t)$ depends on the history $n(r, t'), t' < t$ and the initial states. Almost all the approximations used today, neglect this, and bootstrap a ground sate functional: that is, the instantaneous density is input into an approximate ground state functional $v_{xc}^{gs}[n(r, t)]$. These adiabatic approximation schemes have been very successful in the linear response regime.The time-dependent response of the electronic systems to super-intense laser fields $(I = 10^{14} - 10^{16}W)$ has been an active area of research for a long time. The electronic systems under the influence of the super-intense laser fields can give rise to several phenomena such as double-ionization, auto-ionization and di-electronic recombination. To explain these phenomena with in TDDFT one has to understand the time-dependent electronic correlation of the system. So far the role of electron correlation in these super-intense laser fields is not fully understood and explained. Among these ionization processes, the non-sequential double ionization(NSDI) serves as the major challenge for the available TDDFT techniques(approximations). NSDI is phenomenologically a result of significant increase in the double-ionization yield caused by the electron correlations in the lower intensity regimes. Therefore one can see a "shoulder" or a widely discussed "knee" structure in the double-ionization spectrum. There have been two mechanisms that try to explain this ionization process. Fittingoff et al [107] proposed a "shake-off" mechanism in which the inner electron undergoes a rapid change in it's potetial due to the escape of the outer electron. A widely accepted mechanism ("rescattering") is proposed by Corkum [108] in which the outer electron is driven back to the inner core with some probability by the oscillating laser fields and it will then ionize the inner electron. Until very recently all the known TDDFT approximations failed to reproduce the "knee" structure in the double-ionization yields. The two known reasons for this failure are (i) the approximation of the xc potential $v_{xc}(\mathbf{r}, t)$ (ii) the functional approximation in the calculation of the double-ionization probabilities. The second reason of "observable functionals" is again a fundamental problem: that is, the any observable of interest must be expressed in terms of the KS wave function. However the double ionization probabilities require an interacting pair density as function of the density or the (KS orbitals) which is highly non-trivial. Therefore this type of observables can not be directly easily expressed in terms of the density although the Runge-Gross (RG) theorem guarantees that all observables of interest can be obtained from the KS orbitals which are implicit density functionals. Recently there have been very few formalisms that reproduced the "knee" structure in the double ionization calculations using TDDFT. Lein and Kummel[109] addressed the reason(i) and showed that one can retrieve the knee structure in the double ionization probability by including the derivative discontinuity(at integer number of bound electrons)in the correlation potential. The second reason is addressed by Wilken and Bauer [110] by defining the double-ionization probability in terms of a correlation integral function as well as the intensity of the laser field.

Wilken and Bauer [111]in their comparative work,defined the double-ionization yields in terms of the momentum pair densities and showed that the momentum pair densities, derived from the KS(Kohn-Sham or ks)-orbitals poorly fail to capture the non-sequential double ionization.

Here we study two model ionization systems in the momentum as well as in the phase-space. We argue that (i) in ionization processes, extreme caution must be used when interpreting momentum distributions computed from KS orbitals. We will give examples of model systems demonstrating ionization that we are able to solve exactly and show that even the exact KS momentum distributions are typically poor approximations to the true momentum distributions even for single ionization. (ii) however momentum densities defined from the KS formalism can be a good choice to explain the double ionization under certain constraints on the ionization area (or the overlap area) and the direction of escaping electrons.

3.2 1D Single Ionization Model

Even a simple model consisting of two electrons in one-dimension illustrates the discrepancy between the KS and true momentum-densities in ionization or scattering problems. With an exactly solvable model, one can pinpoint the origin of the differences between the momentum distributions of the true and KS systems.In this particular example, we will see it is due to the single-Slater determinant description being a poor description of a state in which two electrons are doing completely different things. One electron is at rest (modelling a bound electron), while the other is moving away from it (modelling a scattered or ionizedelectron), and we consider that enough time has elapsed that the true wavefunction describes independent electrons:

$$\Psi(x,x',t) = \frac{1}{\sqrt{2}}\left(\psi_0(x)\psi_p(x',t) + \psi_0(x')\psi_p(x,t)\right) \tag{3.1}$$

where the inner electron assumes a gaussian state

$$\psi_0(x) = \frac{1}{\pi^{\frac{1}{4}}} e^{-x^2/2} \tag{3.2}$$

and the moving(outer) electron assumes a dispersed gaussian state

$$\psi_p(x,t) = \frac{1}{\pi^{\frac{1}{4}}} \sqrt{\frac{\Delta}{(1+it\Delta^2)}} e^{\left(\frac{ip_0x-\Delta^2x^2/2-ip_0^2t/2}{1+i\Delta^2t}\right)} \tag{3.3}$$

. We can think of this outer electron as(if) it was ejected by a laser field(and turned off later) whose average momentum is p_0 and the spread in the position is $1/\Delta$ Now the interacting position density is given by

$$n(x,t) = 2\int \Psi^*(x,x',t)\Psi(x,x',t)dx' \tag{3.4}$$

By Fourier transforming the interacting wave function into the momentum space, one can define the interacting momentum density as

$$\tilde{n}(p,t) = 2\int \Psi^*(p,p',t)\Psi(p,p',t)dp' \tag{3.5}$$

In KS formalism we describe both the inner and outer electrons with the same initial orbital $(\phi_0(x)\phi_0(x'))$. Therefore both the electrons are described by the same doubly occupied single orbital $\phi(x,t)$which is given by

$$\phi(x,t) = \sqrt{\frac{n(x,t)}{2}} \exp\left(i\int^x dx' \frac{J(x',t)}{n(x',t)}\right) \tag{3.6}$$

where $J(x,t)$ is the time dependent current density which is defined by

$$\begin{aligned} J(x,t) &= \Im\left(\psi_p(x,t)\nabla\psi_p(x,t)\right) \\ &= \left\{\frac{p_0 + \Delta^4 tx}{1+\Delta^4 t^2}\right\}\psi_p^*(x,t)\psi_p(x,t) \end{aligned} \tag{3.7}$$

Therefore one can write the ks-position density as well as the the ks-momentum densities in the following form

$$n_s(x,t) = 2\left|\phi(x,t)\right|^2 \tag{3.8}$$

$$\tilde{n_s}(p,t) = 2\left|\phi(p,t)\right|^2 \tag{3.9}$$

where $\phi(p,t) = \frac{1}{2\pi}\int e^{ipx}\phi(x,t)dx$.

We define the instantaneous phase space density $w(x,p,t)$ for the interacting(true) case as

$$\begin{aligned} w(x,p,t) &= \frac{1}{2\pi}\int dy e^{ipy}\psi_0^*(x+y/2)\psi_0(x-y/2) \\ &+ \frac{1}{2\pi}\int dy e^{ipy}\psi_p^*(x+y/2,t)\psi_p(x-y/2,t) \end{aligned} \tag{3.10}$$

. Substituting the expressions for ψ_0 and ψ_p we can derive an analytic ex-

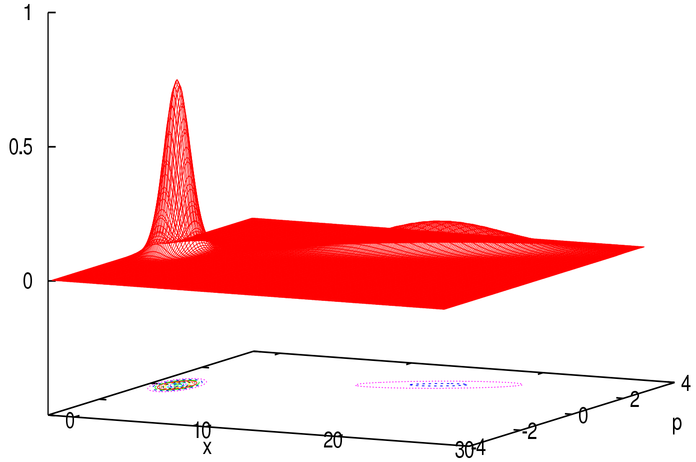

Figure 3.1: 'True' Wigner distribution for the single ionization model

pression for the "true" phase-space density(wigner distribution) as

$$\begin{aligned} w(x,p,t) &= \frac{1}{\pi}e^{-x^2-p^2} \\ &+ \frac{1}{\pi}e^{\left\{\frac{2p_0\Delta^2xt-p_0^2*\Delta^2t^2-\Delta^2x^2}{1+\Delta^4t^2}\right\}}e^{\left\{\frac{-(p-p_0+\Delta^4pt^2-\Delta^4tx)^2}{\Delta^2(1+\Delta^4t^2)}\right\}} \end{aligned} \tag{3.11}$$

Similarly from the doubly occupied KS-orbital, we define the instantaneous KS-phase space density as

$$w_s(x,p,t) = \frac{1}{2\pi}\int dye^{ipy}\phi^*(x+y/2,t)\phi(x-y/2,t) \tag{3.12}$$

For $\Delta = 0.8$ and $p_0 = 0.8$ we plotted the instantaneous phase-space profiles at time $t = 8$. From the following figures (Fig. 3.1,Fig. 3.2) of the true and KS-phase densities, it is obvious that the KS-orbitals do not reproduce the true phase-space density. The reason behind this is the KS orbital is

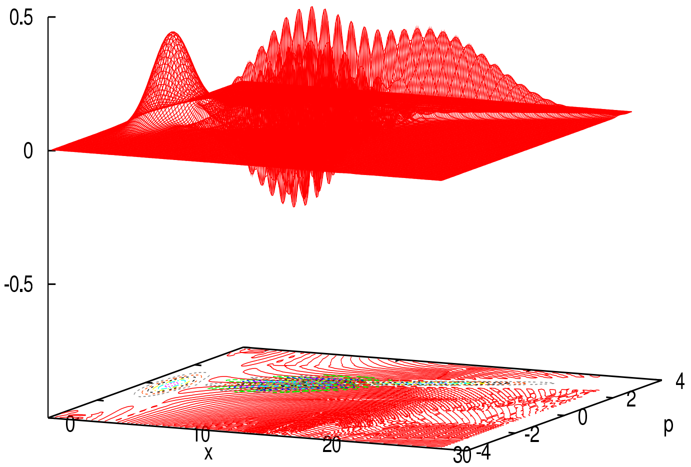

Figure 3.2: KS-Wigner distribution for the single ionization model

originally different from the true (interacting) wave function. By describing two electrons in a delocalized doubly occupied orbital is fundamentally not the same as the true (interacting) anti-symmetric wave function. The true and KS phase-space densities look entirely different from each other in shape. From the Fig. 3.1, We understand that the true phase-space density shows the classical nature: the two gaussian wave packets are localized in different phase space co-ordinates independently. One can also see that for this particular case, the true phase-space density does not have any non-positive regions. On the contrary, the KS phase-space density (Fig. 3.2) shows prominent oscillations which is a clear indication of the non-classical behavior: that is, the KS orbital describes an electron spatially delocalized in two regions. Therefore the oscillations are due to the coherence between the two separated parts of the wavepacket. Integrating over the momentum washes out the oscillations and yields as sum of two Gaussians as shown in the co-ordinate density profile.

Also for the same parametrization of Δ, p_0, and t, we plot the position(co-ordinate) and the momentum density profiles in the Fig. 3.2. As expected the KS- orbital reproduces the same coordinate(position) density as the true (interacting) wavefunction. However the KS-momentum density $\tilde{n_s}(p)$ does not exactly resemble the true momentum density$\tilde{n}(p)$. Both the momentum densities have a common overlap regions in the momentum space. The KS momentum profile shows distinct wiggles which is due to the coherence between the two Gaussians that represent the two electrons independently. Therefore any quantity that is proposed as a functional of the KS momentum density to study the single ionization process would fail to capture the physics fully. Now one ask what if we adjust the parametrization of the system such that there will not be any overlap regions. We will discuss this case in detail in our next section on 1D double ionization model.

3.3 1D Double Ionization Model

Here we describe the system as the doubly ionized state where the two electron are moving from each other with momenta (p_{01} and p_{02}). This doubly ionized system is described by the interacting(true) wave function as

$$\Psi(x, x', t) = \frac{1}{\sqrt{2}} \left(\psi_1(x,t)\psi_2(x',t) + \psi_1(x',t)\psi_2(x,t)\right) \tag{3.13}$$

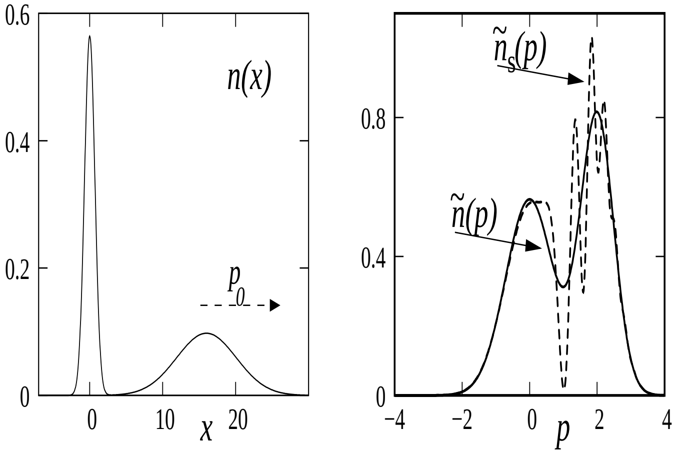

Figure 3.3: 'True' and KS-position(left) and momentum(right) distributions for the single ionization model

We assume the first electron in the state

$$\psi_1(x,t) = \frac{1}{\pi^{\frac{1}{4}}}\sqrt{\frac{\Delta}{(1+it\Delta^2)}}e^{\left(\frac{ip_{01}x-\Delta^2x^2/2-ip_{01}^2t/2}{1+i\Delta^2t}\right)} \tag{3.14}$$

and the second electron in the state

$$\psi_2(x,t) = \frac{1}{\pi^{\frac{1}{4}}}\sqrt{\frac{\Delta}{(1+it\Delta^2)}}e^{\left(\frac{ip_{02}x-\Delta^2x^2/2-ip_{02}^2t/2}{1+i\Delta^2t}\right)} \tag{3.15}$$

Therefore the interacting position density is defined as

$$n(x,t) = 2\int \Psi^*(x,x',t)\Psi(x,x',t)dx' \tag{3.16}$$

As desrcibed in the previous model, we still stick to the single doubly occupied description of KS orbital in this case as well.

$$\phi(x,t) = \sqrt{\frac{n(x,t)}{2}} \exp\left(i \int^{x} dx' \frac{J(x',t)}{n(x',t)}\right) \tag{3.17}$$

where the current density is basically due the two escaping electrons.

$$\begin{aligned} J(x,t) &= J_1(x,t) + J_2(x,t) \\ &= \Im(\psi_1^*(x,t)\nabla\psi_1(x,t) + \psi_2^*(x,t)\nabla\psi_2(x,t)) \\ &= \left\{\frac{p_{01} + \Delta^4 tx}{1 + \Delta^4 t^2}\right\} n_1(x,t) + \left\{\frac{p_{02} + \Delta^4 tx}{1 + \Delta^4 t^2}\right\} n_2(x,t) \end{aligned} \tag{3.18}$$

One can also define the KS-position density as

$$n_s(x,t) = 2\left|\phi(x,t)\right|^2 \tag{3.19}$$

Also the interacting momentum density can be defined as

$$\tilde{n}(p,t) = \left|\psi_1(p,t)\right|^2 + \left|\psi_2(p,t)\right|^2 \tag{3.20}$$

where $\psi_1(p,t) = \frac{1}{2\pi}\int e^{ipx}\psi_1(x,t)dx$ and $\psi_2(p,t) = \frac{1}{2\pi}\int e^{ipx}\psi_1(x,t)dx$. Similarly the KS-momentum density is given by

$$\tilde{n_s}(p,t) = \left|\phi(p,t)\right|^2 \tag{3.21}$$

where $\phi(p,t) = \frac{1}{2\pi}\int e^{ipy}\phi(x,t)dx$ is the KS-doubly occupied momentum orbital.

We choose p_{01}=-$p_{02} = -2a.u$ and $\Delta = 0.7$ .ie, We assume that the electrons are moving from each other in opposite directions with the same average momentum. For these values, we plot the instantaneous (t=8) true and KS position densities as well as the momentum densities. As show in the Fig. 3.4, the KS and the true momentum distributions match to the eye with each other unlike in the single ionization model. The reason behind this is the lack of overlap region in the momentum density profile. Regardless of the fact that the two highly delocalized electrons are described by a single KS orbital, it still reproduces the true momentum density profile. Thus for this particular case, we argue that the KS momentum profiles can be reliable to study the double-ionization process.

Now we explore the behavior of the phase-space distributions for this particular case. We define the interacting phase-space density as

$$\begin{aligned} w(x,p,t) &= \frac{1}{2\pi}\int dy e^{ipy}\psi_1^*(x+y/2,t)\psi_1(x-y/2,t) \\ &\quad +\frac{1}{2\pi}\int dy e^{ipy}\psi_2^*(x+y/2,t)\psi_2(x-y/2,t) \end{aligned} \tag{3.22}$$

After substituting the expressions for the interacting(true) wavefunction,we

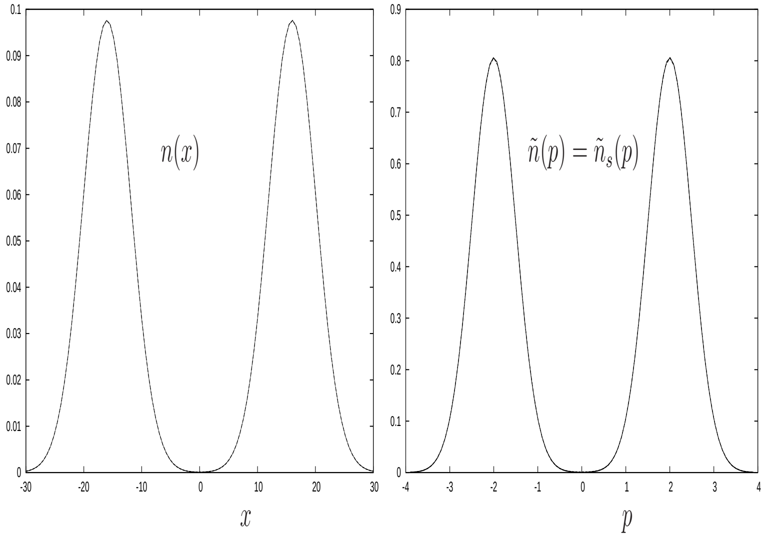

Figure 3.4: 'True' and KS-position(left) and momentum(right) distributions for the double-ionization model

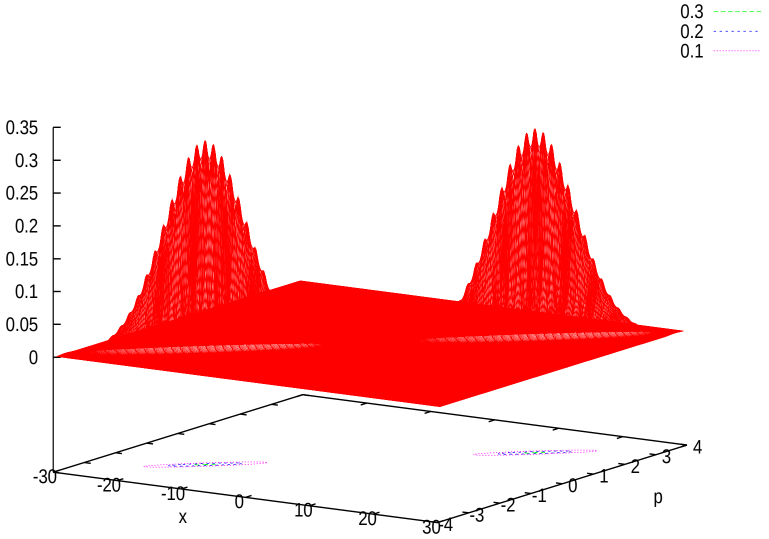

Figure 3.5: 'True' Wigner distribution for the double-ionization model

get

$$\begin{aligned} w(x,p,t) &= \frac{1}{\pi} e^{\left\{\frac{2p_{01}\Delta^2 xt - p_{01}^2 * \Delta^2 t^2 - \Delta^2 x^2}{1+\Delta^4 t^2}\right\}} e^{\left\{\frac{-(p-p_{01}+\Delta^4 pt^2 - \Delta^4 tx)^2}{\Delta^2(1+\Delta^4 t^2)}\right\}} \\ &+ \frac{1}{\pi} e^{\left\{\frac{2p_{02}\Delta^2 xt - p_{02}^2 * \Delta^2 t^2 - \Delta^2 x^2}{1+\Delta^4 t^2}\right\}} e^{\left\{\frac{-(p-p_{02}+\Delta^4 pt^2 - \Delta^4 tx)^2}{\Delta^2(1+\Delta^4 t^2)}\right\}} \end{aligned} \quad (3.23)$$

Similarly the KS phase space density for the double ionization system is defined as

$$w_s(x,p,t) = \frac{1}{2\pi} \int dy e^{ipy} \phi^*(x+y/2,t)\phi(x-y/2,t) \quad (3.24)$$

.

For the same values of parameters, we plot the instantaneous phase-space densities for both true and KS cases.

Similar to our previous single ionization model, the true and KS phase-space densities do not resemble each other. The KS phase space profile(Fig. 3.3) still shows the oscillations in the negative regions indicating the non-classical nature. The true phase-space density profile(Fig. 3.3) shows the classical nature as described in the single ionization case.

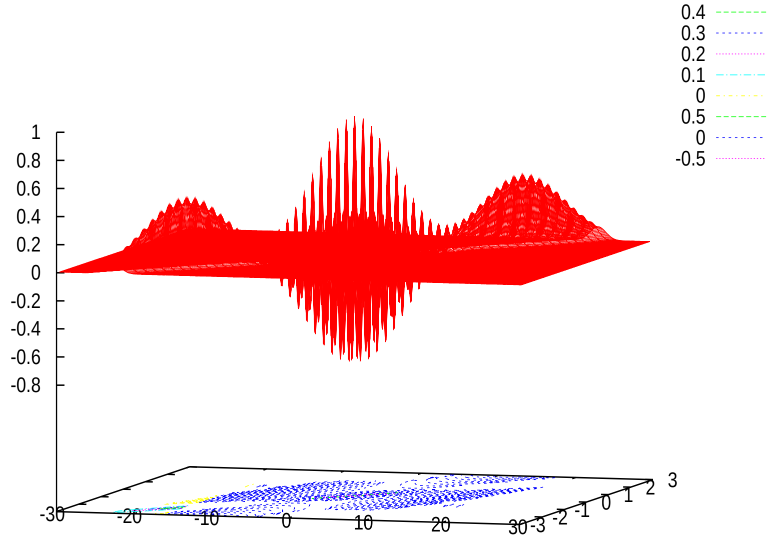

Figure 3.6: KS-Wigner distribution for the double-ionization model

3.4 Conclusion

We conclude that the KS phase space densities can not be always chosen to explain any ionization phenomenon. The oscillations will be smeared out if a Husimi function was taken, depending on the size of the Gaussian taken in defining the Husimi distribution $h(\mathbf{r}, \mathbf{p}, t)$. A non-interacting system can never be found for which the phase-space density exactly reproduce the phase-space density of the interacting system due to the non-idempotency of the underlying density matrix. However the KS momentum distributions can be a good choice for certain ionization schemes with certain parametrization. We have shown that the KS (non-interacting) momentum (or phase-space) distributions are in general different from the interacting distributions.

Chapter 4

Quasi-Classical Approach to TDDFT

4.1 Introduction:

In time-dependent Reduced Density Matrix Functional Theory(TD-RDMFT), the basic variable is the one-body reduced density matrix$\rho_1(\mathbf{r}, \mathbf{r'}, \mathbf{t})$. This is defined uniquely from the many-body wave function as

$$\rho_1(\mathbf{r}, \mathbf{r}', t) = N \int \psi(\mathbf{r}, \mathbf{r_2}, \mathbf{r_3}, ..., \mathbf{r_n}, \mathbf{t}) \psi^*(\mathbf{r}', \mathbf{r_2}, \mathbf{r_3}, ..., \mathbf{r_n}, \mathbf{t}) d\mathbf{r_2} d\mathbf{r3} ... d\mathbf{r_n} \tag{4.1}$$

The eigen vectors of this matrix are generally known as "time dependent natural orbitals"($\phi_j(\mathbf{r}, t)$) and the eigen values as "time dependent occupation numbers"$(\eta_j(t))$.

$$\rho_1(\mathbf{r},\mathbf{r}',t) = \sum_j \eta_j(t)\phi_j(\mathbf{r},t)\phi_j^*(\mathbf{r}',t) \tag{4.2}$$

From this one can derive the time evolution of the time dependent occupation numbers as

$$\dot{\eta}_i(t) = \int\int d\mathbf{r}' d\mathbf{r} \dot{\rho}_1(\mathbf{r},\mathbf{r}',t)\phi_i^*(\mathbf{r},t)\phi_i(\mathbf{r}',t) \tag{4.3}$$

Substituting the expression for $\dot{\rho}_1$ from the equation of motion Eq.(2.12) for ρ_1, We get

$$\begin{aligned} \dot{\eta}_i(t) &= \frac{1}{i}\int\int\int d\mathbf{r}d\mathbf{r}'d\mathbf{r}_2 v_{ee}(\mathbf{r},\mathbf{r}_2)\rho_2(\mathbf{r},\mathbf{r}_2,\mathbf{r}',\mathbf{r}_2,t)\phi_i^*(\mathbf{r},t)\phi_i(\mathbf{r}',t) \\ &\quad - C.C. \end{aligned} \tag{4.4}$$

The right hand side of the above equation is non-zero if the contractions of ρ_2 on to the natural orbitals $\phi_i^*(\mathbf{r},t)\rho_2(\mathbf{r}',\mathbf{r}_2,\mathbf{r}',\mathbf{r}_2,t)\phi_i(\mathbf{r}',t)$ is imaginary. Therefore any un-correlated product expansion of ρ_2 (eg., TDHF) will leave the occupation numbers unchanged. It was also shown that any adiabatic extension ([126],[127]) of known static RDMFT functionals will make the occupation numbers unchanged. Therefore if the temporal change of the system is not negligible, these approximations fail poorly. One alternative to tackle this problem could be truncating the BBGKY hierarchy at the next order (ρ_3) and expression it as an un-correlated product. However it has been shown that this violates the fundamental trace relations between the density matrices of different order. Capturing the change of occupation numbers via KS-TDDFT remains as a challenge for quantum control effects..In ref ([147]), is clearly shown that using two different KS potentials v_s one can reach the same target state. The authors showed that the density of two single orbitals of an excited state in a harmonic KS potential, can be exactly reproduced by a doubly occupied orbital (singlet) of a plucked harmonic KS potential. Therefore a proper control of occupations can not be possible using the KS approach. The problem of expressing ρ_2 appropriately in terms of ρ_1 which could capture the the temporal change in the occupation numbers while retaining the fundamental properties is an important area of research.

We propose a novel approach to this problem based on quasiclassical (or semiclassical) dynamics. In the next section we review what these methods are for one-particle problems. We then present how we shall apply these methods to N-electron dynamics, and in particular, address the challenge of changing occupation numbers.

4.2 Semiclassical Methods

Rigorous quantum mechanical treatment of the dynamics of complex systems is often not feasible numerically. Now a days MD (Molecular Dynamics) simulations are applied to a large chemical or bio-chemical systems. However such classical treatments are not accurate especially when the process under consideration exhibits quantum effects. Typical examples are the processes that involve motion of electrons, observables that require phase information (interference,tunneling process etc). With this as a starting point, the development of methods that employ classical trajectories yet recover quantum effects, has been taken place.This kind of method is usually called as a "Semiclassical Method". Semiclassical method can be chosen as an alternative to a an expensive- rigorous quantum mechanical method and also to an easy-inadequate classical method. As these methods employ classical trajectories, they overcome the exponential scaling with the number of particles (degrees of freedom) as in a straight forward quantum mechanical calculation.

There are different types of semiclassical methods exist in the literature. A simplest one could be the one which involves the quantum mechanical calculations using a simplified path integral formalism, with a focus on classical motion of the particle. In the path integral formalism of Feynman, a probability amplitude is associated with an entire motion of particle as a function of time, rather than simply with a position of the particle at a particular time. In quantum mechanics, all paths, classical (the one along which the Hamilton's principle function is extremum) and non-classical, that connect the initial and final points are considered. The total amplitude is an appropriate superposition of the amplitudes of all these paths.However in the semiclassical approximation, the probability amplitude is approximated only by its contribution from its classical path. A simple explanation is to recall the propagator (often called as Green Function) for a free particle: (In this chapter we be will using the regular physics units)

$$G_0(x,x',t) = \sqrt{\frac{1}{2\pi i\hbar}}\sqrt{\frac{m}{t}}e^{\frac{im}{\hbar 2t}(x-x')^2} \tag{4.5}$$

One can notice that the prefactor $\frac{m}{t}$ is nothing but $det(-\frac{\partial^2 S_0}{\partial x \partial x'})$ and the exponent is exactly equal to the Hamilton's principal function $S_0(x,x',t)$. Therefore we can express the above quantum mechanical propagator as

$$G_0(x,x',t) = \sqrt{\frac{1}{2\pi i\hbar}}\sqrt{det(-\frac{\partial^2 S_0}{\partial x \partial x'})}e^{\frac{i}{\hbar}S_0(x,x',t)} \tag{4.6}$$

Basing on this Van Vleck([137]) proposed a (semi)classical description for a particle under the influence of any potential as

$$G_V^{SC}(\mathbf{r},\mathbf{r}',t) = (2\pi i\hbar)^{-D/2}\sqrt{detC}e^{\frac{i}{\hbar}S(\mathbf{r},\mathbf{r}',t)} \tag{4.7}$$

where $C_{ij} = -\frac{\partial^2 S}{\partial r_i \partial r'_j}$ and D are the dimensions. Using the Stationary Phase method, Gutzwiller re-derived the semiclassical propagator from the path-integral method and made an important modification to the result of Van Vleck propagator by adding a phase term that made it consistent at the conjugate (or turning) points of the classical motion also by including all the classical paths.If n is the number of conjugate points from ($\mathbf{r}$',0) to ($\mathbf{r}$,t) and if there exist few classical paths between them (direct and reflected), The Van Vleck-Gutzwiller semiclassical propagator is given by

$$G^{SC}_{VG}(\mathbf{r},\mathbf{r'},t)=\sum_{class.paths}(2\pi i\hbar)^{-D/2}\sqrt{detC}e^{\frac{i}{\hbar}S(\mathbf{r},\mathbf{r'},t)}e^{-in\pi/2} \tag{4.8}$$

In the Feynman path integral method,

$$G_F(\mathbf{r},\mathbf{r'},t)=\sum_{allpaths}e^{\frac{i}{\hbar}S(\mathbf{r},\mathbf{r'},t)} \tag{4.9}$$

the exponential $e^{\frac{i}{\hbar}S(\mathbf{r},\mathbf{r'},t)}$ oscillates violently if $\hbar$ is too small compared to S. In fact this is the case when $\hbar = 0$ (classical limit). Thus the contribution from the most of the paths (non-classical) will be canceled in the Feynman path sum. Therefore the only paths that prominently contribute are the ones which satisfy the Hamilton‘s variational principle. The assumption that $\hbar <<< R$ is known as the stationary phase method.

From the Van Vleck-Gutzwiller semiclassical ([139],[138]) propagator G^{SC}_{VG}, one can define the conjugate points as the points where the determinant $detC$ goes to zero (or infinity). The action is usually “minimum” everywhere except at these turning points where the action is treated as “maximum”.When the caustic condition is met, ie., $det(C^{-1})$=0, this approximation breaks down. The VVG propagator is exact for harmonic potentials. Gutzwiller further developed this semiclassical method by using number of conjugate points along a closed orbit with a fixed energy E and derived a trace-formula called Gutzwiller trace formula. This was quite successful approach for isolated periodic orbits.However for the systems with high symmetries such as Harmonic oscillator and Coulomb potentials, where the periodic orbits become degenerate, this method has some limitations. Moreover in higher dimensions, solving the boundary value problem is numerically hard as the trajectories are determined by initial and final points . Also as the time increases the numerical search for the "sum over the classical paths" becomes difficult as it is not unique. In addition to these limitations, the problem at caustics still exists in Gutzwiller development.

In an attempt to address the challenges in VG (Vanvleck-Gutzwiller) semiclassical approach, Miller proposed an initial value representation of the semiclassical propagator.The root-search problem in VG approach is circumvented by expressing the semiclassical propagator into an integration over initial conditions[142].

4.3 Heller-Herman-Kulk-Kay Method

An alternative approach of semiclassical calculations which is derived from more intuitive physical picture, was proposed by Eric Heller in 1976. This method basically starts with expanding the initial wave function (state) as combination of random Gaussians (this expansion is over complete and non-unique) and deriving (approximting) the final state as a combination of

Frozen Gaussians(FG) [140].

$$
\begin{aligned}
\psi(x,t) \approx \psi^{FG}(x,t) = \sum_n c_n G_n^{FG}(x,t) \\
G_n^{FG}(x,t) = e^{\frac{i}{\hbar}\gamma_{tn}} g_n(x,t)
\end{aligned}
\tag{4.10}
$$

where

$$
g_n(x,t) = (\frac{\omega}{\pi\hbar})^{1/4} e^{\frac{\omega}{2\hbar}(x-x_{tn})^2 + ip_{tn}(x-x_{tn})/\hbar}
\tag{4.11}
$$

Here γ_{tn} is a modified classical action.And ω is fixed for all the time making the Gaussian frozen. Therefore this is an (Semiclassical) Initial Value Representation (SC-IVR) scheme where one decomposes the initial wavefunction superposition of Gaussian wave packets (coherent states), representing the classical phase-space points, propagates them classically, and then reassembles the wave-packet at a later time t. Which means the constraint in this technique is that the average position and average momenta of each Frozen Gaussian(shape held fixed) is to execute a classical trajectory. Heller and coworkers applied this technique to construction of vibrational states of coupled nonlinear oscillators and to inelastic scattering problems. An improved version of Frozen Gaussian technique was proposed by Herman and Kulk by using a Van Vleck type prefactor C in addition to the usual classical action integral[141].They show this in an integral form:

$$\psi(x,t) = \frac{1}{h}\int\int dr_i dp_i < x|r_t, p_t > C(r_i, p_i, t)e^{\frac{i}{\hbar}S(r_i,p_i,t)} < r_i, p_i|\psi_0 >$$

$$< x|r, p >= (\omega')^{1/4}e^{\omega'(x-r)^2+ip(x-r)/\hbar}$$

$$< x|\psi_0 >= \psi(x, 0)(4.12)$$

Where the Van-Vleck type pre-factor $C(r_i, p_i, t)$ is given by

$$C(r_i, p_i, t) = \left|\frac{\partial p_t}{\partial p_i} + \frac{\partial r_t}{\partial r_i} - 2\omega' i\hbar\frac{\partial r_t}{\partial p_i} + \frac{i}{2\omega'\hbar}\frac{\partial p_t}{\partial r_i}\right|^{1/2} \tag{4.13}$$

Here ω' is the width of the Gaussian. This method has been very reliable in studying the molecular dynamics when compared to the Boundary value Semiclassical methods(Van Vleck type). Due to the evolution of the prefactor C, the numerical effort per trajectory scales as N^3; methods which neglect this scale more favourably as N but at the cost of losing accuracy and semi-classical rigor.

4.4 Quasiclassical Approach

A rigorous semi-classical approach is computationally expensive. A more simplified method is the one which neglects the prefactor and the phase yielding a quasi-classical Wigner method [144]. The quantum evaluation of a Phase-space distribution $w(q, p, t)$ is given by

$$\begin{aligned}\frac{\partial w}{\partial t} \;=\; & -\frac{\partial H}{\partial p}\frac{\partial w}{\partial q} + \frac{\partial H}{\partial q}\frac{\partial w}{\partial p} \\ & -\frac{\hbar^2}{24}\frac{\partial^3 H}{\partial q^3}\frac{\partial^3 w}{\partial p^3} + \frac{\hbar^4}{1920}\frac{\partial^5 H}{\partial q^5}\frac{\partial^5 w}{\partial p^5} + O(\hbar^6) + ... \end{aligned} \tag{4.14}$$

Note: $q = \{q\}$=$\{q_1, q_2, ..., q_n\}$ and similarly p=$\{p\}$=$\{p_1, p_2, ...p_n\}$. The first two terms in the above equation are the classical Lioville equation of motion for a phase-space distribution. Therefore one can assume the Quantum Liovillian L_Q as

$$L_Q = L_{Cl} + O(\hbar^2) + O(\hbar^4) + ... \tag{4.15}$$

In a typical quasi-classical approach one replaces $L_Q w$ with $L_{Cl} w$. By doing this one escapes from the non-causal nature of the Quantum Liovillian L_Q unlike the Classical Liovillian L_{Cl} which remains causal.ie., If we start with an initial distribution from a point (q_0, p_0) at an instant of time t_0 in phase-space as $w(q, p, t_0) = \delta(q - q_0)\delta(p - p_0)$, at a later time t it still remains as $w(q, p, t) = \delta(q - q_t)\delta(p - p_t)$. Therefore the dynamics of the problem can be captured using the Hamilton's equations of motion:

$$\begin{aligned}\dot{q}_t &= \frac{\partial H}{\partial p} \\ \dot{p}_t &= -\frac{\partial H}{\partial q}\end{aligned} \tag{4.16}$$

This approach (quasi-classical) coincides with the exact calculations if the Hamiltonian is quadratic in nature (as the higher order terms ($\frac{\partial^3 H}{\partial q^3}$) become zero). The quasi-classical method is numerically much simpler than the semi-classical methods in which the oscillations come from the action exponent. The semi-classical approaches can in principle capture interference, zero-point energy, and, to some extent, tunneling mechanisms. However, in quasi-classical approaches, the quantum mechanics enters only via the initial state, and, the interference effects can not be captured.

4.5 The Scheme

In this section we are going to explore the approximations for ρ_2 (or w_2) in quasi classical approximations. The equation of motion for the one-particle wigner distribution $w_1(r, p.t)$ is given by,

$$
\begin{aligned}
\dot{w_1}(\mathbf{r},\mathbf{p},t) &= -\mathbf{p}\cdot\nabla w_1(\mathbf{r},\mathbf{p},t) \\
&\quad -i\int d^3p'\int d^3y e^{-i(\mathbf{p}-\mathbf{p}')\cdot\mathbf{y}} \\
&\quad \times\left[v_{ext}(\mathbf{r}+\frac{\mathbf{y}}{\mathbf{2}},t)-v_{ext}(\mathbf{r}-\frac{\mathbf{y}}{\mathbf{2}},t)\right]w_1(\mathbf{r},\mathbf{p},t) \\
&\quad -i\int d^3yd^3p_1d^3p_2d^3r_2e^{i(\mathbf{p}-\mathbf{p_1})\cdot\mathbf{y}} \\
&\quad \times\left(\frac{1}{|\mathbf{r}-\mathbf{r_2}+\frac{\mathbf{y}}{2}|}-\frac{1}{|\mathbf{r}-\mathbf{r}_2-\frac{y}{2}|}\right)w_2(\mathbf{r},\mathbf{r}_2,\mathbf{p}_1,\mathbf{p}_2,t)
\end{aligned}
\tag{4.17}
$$

The idea of TDPSDFT (Time-Dependent Phase Space Density Functional Theory) is to approximate the second-order phase-space distribution w_2 in terms of w_1. We can first extract out the independent particle term in the following way:

$$w_2(\mathbf{r}_1, \mathbf{p}_1, \mathbf{r}_2, \mathbf{p}_2, t) = w_1(\mathbf{r}_1, \mathbf{p}_1, t) w_1(\mathbf{r}_2, \mathbf{p}_2, t) + w_{2XC}(\mathbf{r}_1, \mathbf{r}_2, \mathbf{p}_1, \mathbf{p}_2, t) \tag{4.18}$$

where w_{2XC} is the exchange-correlation part. From the above expression, one can see its similarity with the second order density matrix ρ_2 in terms of the one-particle density matrix ρ_1 as:

$$\begin{aligned} \rho_2(\mathbf{r}_1, \mathbf{r}_2; \mathbf{r}'_1, \mathbf{r}'_2, t) &= \rho_1(\mathbf{r}_1, \mathbf{r}'_1, t)\rho_1(\mathbf{r}_2, \mathbf{r}'_2, t) - \rho_1(\mathbf{r}_1, \mathbf{r}'_2, t)\rho_1(\mathbf{r}_2, \mathbf{r}'_1, t) \\ &\quad + \rho_{2C}(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}'_1; \mathbf{r}'_2, t) \end{aligned} \tag{4.19}$$

where ρ_{2C} is the second order correlation matrix.The second term is basically due to the exchange part.It is not possible to extract out the exchange effect dealing directly with the wigner function [26].As a first investigation, we simply employ Eq.(4.18), treating both exchange and correlation together.

In this scheme, we intend to approximate the second-order (xc-part) time dependent density matrix ρ_{2XC} quasi-classically (QC). Since the phase-space distributions are nothing but the Fourier transform of the the density matricies, we infact approximate the w_{2XC}. Later we Fourier transform in into

ρ_{2XC} and solve the equation of motion for ρ_1.

$$w_{2XC}(\mathbf{r}_1, \mathbf{p}_1, \mathbf{r}_2, \mathbf{p}_2, t) \approx w_{2XC}^{QC}(\mathbf{r}_1, \mathbf{p}_1, \mathbf{r}_2, \mathbf{p}_2, t) \tag{4.20}$$

This quasi-classical "exchange correlation" part of the wigner distribution can again be written in terms of second and first order (quasi-classical) wigner distributions as:

$$w_{2XC}^{QC}(\mathbf{r}_1, \mathbf{p}_1, \mathbf{r}_2, \mathbf{p}_2, t) = w_2^{QC}(\mathbf{r}_1, \mathbf{p}_1, \mathbf{r}_2, \mathbf{p}_2, t) - w_1^{QC}(\mathbf{r}_1, \mathbf{p}_1, t) w_1^{QC}(\mathbf{r}_2, \mathbf{p}_2, t) \tag{4.21}$$

We write the evolution of w^{QC} to a time t as a sum of weighted delta functions

$$w^{QC}(\{\mathbf{r}\}, \{\mathbf{p}\}, t) = \sum_j \omega_j \delta(\{\mathbf{r}\} - \{\mathbf{r}_j(t)\}) \delta(\{\mathbf{p}\} - \{\mathbf{p}_j(t)\}) \tag{4.22}$$

where $\dot{\mathbf{r}}_j(t) = \frac{\partial H}{\partial p_j}$ and $\dot{\mathbf{p}}_j(t) = -\frac{\partial H}{\partial q - j}$ are the classical equations of motion. Here we used the notation: $\{\mathbf{r}\} = \mathbf{r}_1, \mathbf{r}_2, ..., \mathbf{r}_N$. For eg. the quasiclassical representation of second order phase-space distribution w_2 is given by

$$w_2^{QC}(r_1, p_1, r_2, p_2, t) = \sum_j \omega_j \delta(r_1 - r_{1j}(t)) \delta(r_2 - r_{2j}(t)) \delta(p_1 - p_{1j}(t)) \delta(p_2 - p_{2j}(t)) \tag{4.23}$$

Fourier transforming the above expression one can derive ρ_2^{QC} (and ρ_1^{QC}). By also including the symmetry properties of ρ_2 ($\rho_2(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}'_1, \mathbf{r}'_2, t) = \rho_2^*(\mathbf{r}'_1, \mathbf{r}'_2, \mathbf{r}_1, \mathbf{r}_2, t)$

and $\rho_2(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}'_1, \mathbf{r}'_2, t) = \rho_2(\mathbf{r}_2, \mathbf{r}_1, \mathbf{r}'_1, \mathbf{r}'_2, t))$ we arrive at,

$$\begin{aligned}\rho_2^{QC}(r_1, r_2; r'_1, r'_2, t) &= \frac{1}{2}\sum_j \omega_j e^{-i(p_{1j}(t)(r_1-r'_1)+p_{2j}(r_2-r'_2))} \\ &\quad \times\delta(\frac{r_1+r'_1}{2} - r_{1j}(t))\delta(\frac{r_2+r'_2}{2} - r_{2j}(t)) \\ &\quad +\frac{1}{2}\sum_j \omega_j e^{-i(p_{1j}(t)(r_2-r'_1)+p_{2j}(r_1-r'_2))} \\ &\quad \times\delta(\frac{r_2+r'_1}{2} - r_{1j}(t))\delta(\frac{r_1+r'_2}{2} - r_{2j}(t)) \quad (4.24)\end{aligned}$$

Also, Since the nature of the phase-space distributions are assumed to be unchanged with evolution in time, the quasi-classical evolution of w^{QC} may be written as:

$$w^{QC}(\{r\}, \{p\}, t) = w^{QC}_{initial}(\{r_j(-t)\}, \{p_j(-t)\}, 0) \tag{4.25}$$

We want to calculate w^{QC} from a general initial phase space distribution $w^{QC}_{initial}$. For this we start with a proper quantum mechanical N-particle initial state and calculate the N-particle phase space distribution. Using the classical evolutions backward in time, We calculate the evolved N-particle wigner distribution and from there we get second order wigner distribution w_2. We plan to employ the Leapfrog-Verlet numerical methods to get the evolutions.

4.6 TD-Moshinsky Atom

Exactly solvable systems are needed in order to study and test their properties and applications.There have been very few works where the exact reduced density matrices were calculated. L. Cohen and C. Lee, in 1985, derived expressions for the exact reduced density matrices for a system (time-independent) of harmonically interacting N-bosons, each one coupled harmonically to a nucleus [120]. The TD(time-dependent)-Moshinsky atom is a model-system of two electrons repelling harmonically while trapped harmonically $k(t)$ about a nucleus. The gs-Moshinsky atom was extensively studied by N.H.March et al [123],[124]. Here we solve for the time-dependent first order density matrix $\rho_1(\mathbf{r_1}, \mathbf{r'_1}, t)$ to this model system. The Hamiltonian for the time-dependent Moshinsky atom is given by,

$$H(\mathbf{r_1}, \mathbf{r_2}, t) = \frac{-\nabla^2_{r_1}}{2} - \frac{\nabla^2_{r_2}}{2} + \frac{k(t)}{2}(r_1^2 + r_2^2) + \frac{\lambda}{4}\left|\mathbf{r_1} - \mathbf{r_2}\right|^2 \tag{4.26}$$

This system can be exactly solved. Lets define new co-ordinates as

$$\mathbf{R} = \frac{\mathbf{r_1} + \mathbf{r_2}}{2} \tag{4.27}$$

$$\mathbf{u} = \mathbf{r_1} - \mathbf{r_2} \tag{4.28}$$

The Hamiltonian in the new co-ordinate system becomes

$$H(\mathbf{R},\mathbf{u},t) = -\nabla_{\mathbf{u}}^2 - \frac{1}{4}\nabla_{\mathbf{R}}^2 + \frac{1}{4}k(t)(4R^2+u^2) + \frac{\lambda}{4}u^2 \tag{4.29}$$

Therefore

$$\Psi(\mathbf{r_1},\mathbf{r_2},t) = \Psi(\mathbf{R},\mathbf{u},t) = \phi(\mathbf{R},t)\zeta(\mathbf{u},t) \tag{4.30}$$

where

$$\left[-\frac{\nabla_{\mathbf{R}}^2}{4} + k(t)R^2\right]\phi(\mathbf{R},t) = i\frac{\partial\phi(\mathbf{R},t)}{\partial t} \tag{4.31}$$

$$\left[-\nabla_{\mathbf{u}}^2 + \frac{1}{4}(k(t)+\lambda)u^2\right]\zeta(\mathbf{u},t) = i\frac{\partial\zeta(\mathbf{u},t)}{\partial t} \tag{4.32}$$

For n=0,l=0, m=0 case, If we adopt the solution from [121] and [122]

$$\boxed{\phi(\mathbf{R},t) = \sqrt{\frac{4(2)^{3/2}}{\sqrt{\pi}}(\dot{\alpha}(t))^{\frac{3}{4}}e^{-i\frac{3}{2}[\alpha(t)-\alpha(0)]}e^{-\left[\dot{\alpha}(t)-i\frac{d\ln X(t)}{dt}\right]R^2}}\sqrt{\frac{1}{4\pi}}} \tag{4.33}$$

where $\ddot{X}(t) = -k(t)X(t)$, $X(t) = |X(t)|e^{i\alpha(t)}$ and $\dot{\alpha}(t) > 0$, $X(0) = \frac{1}{\sqrt{\sqrt{k(0)}}}$ and $\dot{X}(0) = i\sqrt{\sqrt{k(0)}}$.

Similarly

$$\boxed{\zeta(\mathbf{u},t) = \sqrt{\frac{4(\frac{1}{2})^{3/2}}{\sqrt{\pi}}(\dot{\beta}(t))^{\frac{3}{4}}e^{-i\frac{3}{2}[\beta(t)-\beta(0)]}e^{-\frac{1}{4}\left[\dot{\beta}(t)-i\frac{d\ln Y(t)}{dt}\right]u^2}}\sqrt{\frac{1}{4\pi}}} \tag{4.34}$$

where $\ddot{Y}(t) = -(k(t)+\lambda)Y(t)$, $Y(t) = |Y(t)|e^{i\beta(t)}$ and $\dot{\beta}(t) > 0$, $Y(0) = \frac{1}{\sqrt{\sqrt{k(0)+\lambda}}}$ and $\dot{Y}(0) = i\sqrt{\sqrt{k(0)+\lambda}}$ Therefore,

$$\boxed{\Psi(\mathbf{R},\mathbf{u},t) = A(t)e^{-D(t)R^2}e^{-F(t)u^2}} \tag{4.35}$$

where $D(t) = \dot{\alpha}(t) - i\frac{d\ln X(t)}{dt}$, $F(t) = \frac{1}{4}\left[\dot{\beta}(t) - i\frac{d\ln Y(t)}{dt}\right]$ and

$$A(t) = \sqrt{\frac{4(2)^{3/2}}{\sqrt{\pi}}}\sqrt{\frac{4(1/2)^{3/2}}{\sqrt{\pi}}}(\dot{\alpha}(t))^{\frac{3}{4}}e^{-i\frac{3}{2}[\alpha(t)-\alpha(0)]} \times (\dot{\beta}(t))^{\frac{3}{4}}e^{-i\frac{3}{2}[\beta(t)-\beta(0)]}\frac{1}{4\pi} \tag{4.36}$$

If we replace $R^2 = (r_1^2 + r_2^2)/2 - u^2/4$ and $u^2 = |\mathbf{r_1} - \mathbf{r_2}|^2$ in the above equation, we get

$$\boxed{\Psi(\mathbf{r_1},\mathbf{r_2},t) = A(t)e^{-D(t)/2(r_1^2+r_2^2)}e^{-(F(t)-D(t)/4)|\mathbf{r_1}-\mathbf{r_2}|^2}} \tag{4.37}$$

The first order td-density matrix is given by

$$\rho_1(\mathbf{r_1},\mathbf{r_1'},t) = 2 \times \int d^3\mathbf{r_2}\Psi(\mathbf{r_1},\mathbf{r_2},t)\Psi^*(\mathbf{r_1'},\mathbf{r_2},t) \tag{4.38}$$

i.e.

$$\begin{aligned}\rho_1(\mathbf{r_1},\mathbf{r_1'},t) &= B(t)e^{-Dr_1^2/2}e^{-D^*r_1'^2/2}e^{-(F-D/4)r_1^2}e^{-(F^*-D^*/4)r_1'^2} \\ &\times \int d^3\mathbf{r_2}e^{-[D/2+D^*/2+F-D/4+F^*-D^*/4]r_2^2}e^{\left[2(F-D/4)\mathbf{r_1}+2(F^*-D^*/4)\mathbf{r_1'}\right].\mathbf{r_2}}\end{aligned} \tag{4.39}$$

where $B(t) = A^*(t)A(t)$

After some steps of simplification, it becomes,

$$\begin{aligned}
\rho_1(\mathbf{r_1}, \mathbf{r'_1}, t) &= B(t)e^{-Dr_1^2/2}e^{-D^*r_1'^2/2}e^{-(F-D/4)r_1^2}e^{-(F^*-D^*/4)r_1'^2}\int d^3\mathbf{r_2}e^{-\gamma r_2^2}e^{\mathbf{S}.\mathbf{r_2}} \\
&= B(t)e^{-(F+D/4)r_1^2}e^{-(F^*+D^*/4)r_1'^2}2\pi\int dr_2 r_2^2 e^{-\gamma r_2^2}\int_{-1}^{+1} d(\cos\theta)e^{Sr_2\cos\theta} \\
&= B(t)e^{-(F+D/4)r_1^2}e^{-(F^*+D^*/4)r_1'^2}2\pi\frac{1}{S}\int_0^\infty dr_2 r_2\left[e^{-\gamma r_2^2+Sr_2} - e^{-\gamma r_2^2-Sr_2}\right] \\
&= B(t)e^{-(F+D/4)r_1^2}e^{-(F^*+D^*/4)r_1'^2}2\pi\frac{1}{S}\frac{\sqrt{\pi}\sqrt{\gamma}Se^{S^2/(4\gamma)}}{2\gamma^2}
\end{aligned}$$

where $\gamma = F + D/4 + F^* + D^*/4$ and $\mathbf{S} = 2(F - D/4)\mathbf{r_1} + 2(F^* - D^*/4)\mathbf{r'_1}$. Therefore We have,

$$\rho_1(\mathbf{r_1}, \mathbf{r'_1}, t) = \frac{2}{\pi\sqrt{\pi}} \times (\dot{\alpha}(t))^{6/4}(\dot{\beta}(t))^{6/4}e^{-(F+D/4)r_1^2}e^{-(F^*+D^*/4)r_1'^2}(\gamma)^{-3/2}e^{S^2/(4\gamma)} \tag{4.40}$$

Substituting the expressions for γ and S, We get

$$\begin{aligned}
\rho_1(\mathbf{r_1}, \mathbf{r'_1}, t) = \frac{2}{\pi\sqrt{\pi}} &\times (\dot{\alpha}(t))^{3/2}(\dot{\beta}(t))^{3/2} \times (F(t) + D(t)/4 + F^*(t) + D^*(t)/4)^{-3/2} \\
&\times e^{-(F(t)+D(t)/4)r_1^2}e^{-(F^*(t)+D^*(t)/4)r_1'^2} \\
&\times e^{|2(F(t)-D(t)/4)\mathbf{r_1}+2(F^*(t)-D^*(t)/4)\mathbf{r'_1}|^2/[4(F(t)+D(t)/4+F^*(t)+D^*(t)/4)]}
\end{aligned} \tag{4.41}$$

The above can be explicitly expressed in terms of the angle (Γ) between the vectors $\mathbf{r}$ and $\mathbf{r}'$ as

$$\boxed{\begin{gathered}\rho_1(\mathbf{r_1},\mathbf{r'_1},\Gamma,t) = \frac{2}{\pi\sqrt{\pi}} \times \left(\frac{\dot{\alpha}(t)\dot{\beta}(t)}{F(t)+D(t)/4+F^*(t)+D^*(t)/4}\right)^{3/2} \\ \times e^{-(F(t)+D(t)/4-M^2(t))r_1^2} e^{-(F^*(t)+D^*(t)/4-M^{*2}(t))r_1'^2} \\ \times e^{2M(t)M^*(t)r_1 r_1' \cos\Gamma}\end{gathered}} \tag{4.42}$$

where

$$M(t) = \frac{2(F(t)-D(t)/4)}{\sqrt{4(F(t)+D(t)/4+F^*(t)+D^*(t)/4)}}$$

For our purpose it is however enough to explore the 1D case. The 1D time dependent density matrix for the Moshinsky atom can be shown as

$$\boxed{\begin{gathered}\rho_1(x_1,x_1',t) = \frac{2}{\sqrt{\pi}} \times \left(\frac{\dot{\alpha}(t)\dot{\beta}(t)}{F(t)+D(t)/4+F^*(t)+D^*(t)/4}\right)^{1/2} \\ \times e^{-(F(t)+D(t)/4-M^2(t))x_1^2} e^{-(F^*(t)+D^*(t)/4-M^{*2}(t))x_1'^2} \\ \times e^{2M(t)M^*(t)x_1 x_1'}\end{gathered}} \tag{4.43}$$

This is the expression(exact) for the first order density matrix for the time dependent Moshinsky atom. The position density of this model atom

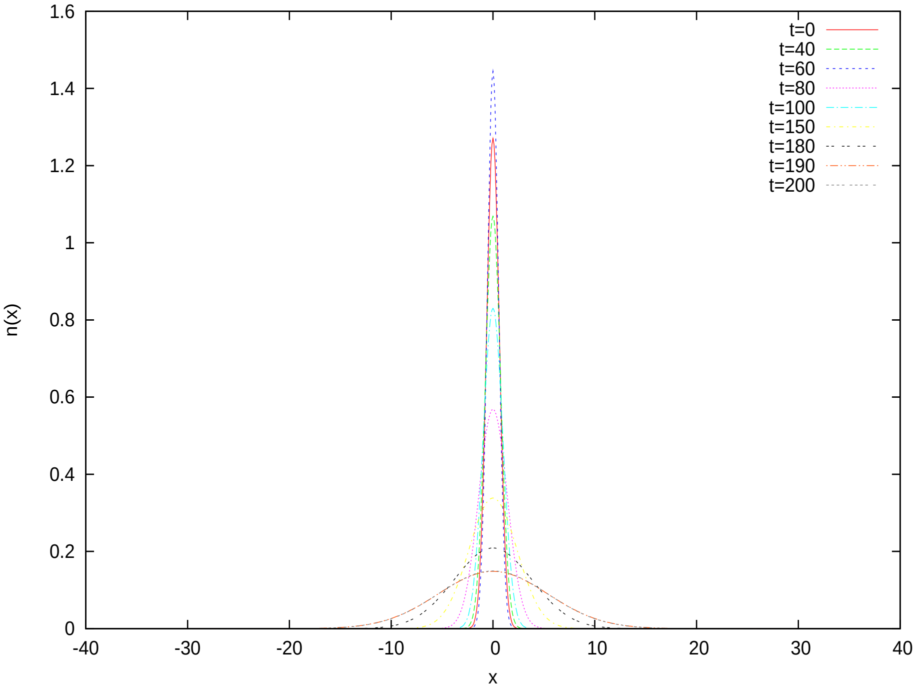

Figure 4.1: The density profile of the Moshinsky atom as a function of t for $k(t) = 1 - 0.05\sin(2t)$: A Breathing Pattern

is calculated ($n(x,t) = \rho_1(x,x,t)$) and plotted for various times. It shows a breathing pattern as function of time (See Fig. 4.6). This is due to the double harmonium nature in the Hamiltonian. We dont see the "sloshing" pattern in the density that supports HPT (Harmonic Potential Theorem): as the external pulse is not a regular laser pulse which is linear in x but harmonic in x ($k(t)x^2$).

We diagonalize this matrix to get the time dependent occupations (eigen values) and study how the occupations change with the time. We have explored both the adiabatic and non-adiabatic cases for this. For any adiabatic run (where the system remains in ground state), the occupation numbers would not change noticeably with time resulting in no pumping in the system. We chose the frequency of (non-adiabatic) the external pulse (ω) as 2 which corresponds to a transition frequency of the ground state Moshinsky atom (ie., singlet state to excited state). For the non-interacting case, we can see that

$$E = (n_{CM} + \frac{1}{2})\omega_{CM} + (n_{RM} + \frac{1}{2})\omega_{RM} \tag{4.44}$$

where ω_{CM} For the transition frequency we have:

$$\begin{aligned} \omega &= E_{20} - E_{00} \\ &= \frac{5}{2}\omega_{CM} + \frac{1}{2}\omega_{RM} - \{\frac{1}{2}\omega_{CM} + \frac{1}{2}\omega_{RM}\} \\ &= 2\omega_{CM} = 2\sqrt{k(0)} = 2 \end{aligned} \tag{4.45}$$

Though we are not optimally controlling the excitations in this system, We see, by decomposing the non-interacting ($\lambda = 0$)case wavefunction as the product of two individual harmonic oscillator wavefunctions, that (2,0)(n_{CM}, n_{RM}) to (0,0) corresponds to the first accessible excitation in the system. A rigorous optimally controlled potential will of course accurately capture the excitations properly. But in the interest of our current work, we only require to study the change in occupation numbers as function of time.

4.7 Numerical Scheme: LAPACK and Mathematica

The time dependent Moshinsky atom is solved numerically for $k(t) = k_0 + \epsilon \sin(\omega t)$. For a small random ϵ (=0.05) value and a maximum coupling value ($k_0 = 1$), we chose the frequency of oscillation as ω =2.0. $\alpha(t)$,$\beta(t)$, $D(t)$, $F(t)$ (See Eq.(**??**))are numerically solved for this particular quadratic pulse on Mathematica 7.0. Also the interaction strength λ is chosen to be 2. The time-dependent density shows a breathing-modes with time. We used LAPACK (Linear Algebra Package) sub-routines to numerically diagonalize the expression for $\rho_1(x_1, x_1', t)$ to get the time dependent eigen values (occupation numbers)(Fig. 4.7). At a We chose a step-size in x and x' as 0.01 which gives an accuracy till 8 decimals in the norm. The diagonalization is performed for each 1RDM for step size in time as 0.1. We have chosen the spatial range in x and x' from -30 to 30 atomic units to capture a wide spread of the

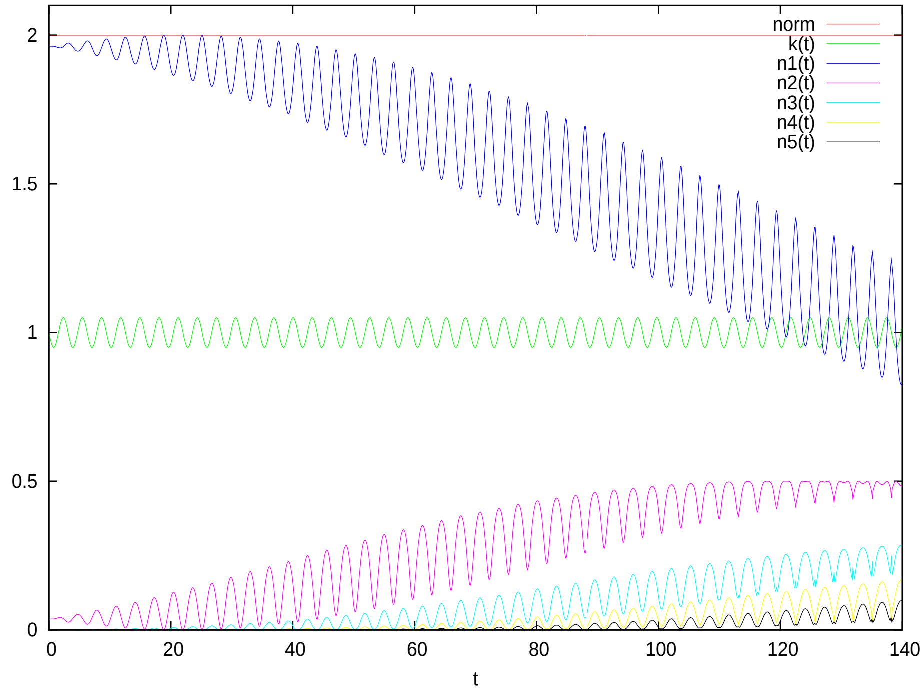

Figure 4.2: The natural (fractional) occupation numbers $\eta_i(t)$(colours), norm(red), and $k(t)$(green) of the 1D-Moshinsky Atom

distributions.

4.8 Conclusion

This is the first real-time self contained approach that can change the occupation number significantly. We solved for the time-dependent natural occupation numbers(η_i) by diagonalizing the 1RDM (first order reduced density matrixρ_1) of the time dependent Moshinsky model system(Fig. 4.7). The above mentioned quasi classical treatment becomes exact for the systems with quadratic potentials. As the Moshinsky atom is exactly solvable, We argue that our approach is equivalent to the method that incorporates quasiclassical 1RDM (ρ_{1xc}^{QC} or w_{1xc}^{QC}) in the equation of motion for $\dot{\rho}_1$ and then diagonalizing the ρ_1. We are in the process of extending the rigorous quasi classical method to the non-quadratic(real) systems such as soft-Coulomb potential. Since we start with a quantum mechanical initial state in our quasiclassical approach, the initial state dependence (which usual adiabatic approximations ignore) comes naturally in this frame work. The quasiclassical representation of the xc part of the second order density matrices proved to be successful in capturing the change in occupation numbers (Fig: 4.7) of the natural orbitals. Though we take the classical correlation into account, it is shown to capture the pumping in the system. Moreover this quasiclassical approach scales as equivalent to classical schemes.

Chapter 5

TDDFT - Beyond Linear Response

5.1 Introduction

Perturbative techniques are traditionally simplest ways to get the excitations of a system. Within a given approximation for xc potential, TDKS equations can be used to extract the electronic excitations of the system. To perform such calculations, one needs to know about the linear-density-response of the system. In this linear response formalism, one considers a small time dependent perturbation $v_1(\mathbf{r}, t)$ and assumes that the system is its ground state at $t_0 < t$. And the corresponding density is $n_0(r)$. i.e.,

$$v_{ext}(\mathbf{r}, t) = v_0(\mathbf{r}) + v_1(\mathbf{r}, t) \tag{5.1}$$

We know that $n(r,t) = n[v_{ext}](r,t)$ From the Runge-Gross 1-1 correspondence, we can invert the above equations as

$$v_{ext}(\mathbf{r},t) = v_{ext}[n](\mathbf{r},t) \tag{5.2}$$

If we expand $n[v_{ext}]$ into a Taylor series with respect to the perturbation $v_1(\mathbf{r},t)$, we get

$$n(\mathbf{r},t) = n_0(\mathbf{r},t) + n_1(\mathbf{r},t) + n_2(\mathbf{r},t) + n_3(\mathbf{r},t) + ... \tag{5.3}$$

where the lower indices denote the orders in v_1. The first order density response is given by

$$n_1(\mathbf{r},t) = \int dt' \int d^3r' \chi[n_0](\mathbf{r},t,\mathbf{r}',t') v_1(\mathbf{r}',t') \tag{5.4}$$

with the density response function

$$\chi[n_0](\mathbf{r},t,\mathbf{r}',t') = \left.\frac{\delta n[v_{ext}](\mathbf{r},t)}{\delta v_{ext}(\mathbf{r}',t')}\right|_{v_0} \tag{5.5}$$

For the non-interacting particles moving in the KS potential $v_s(\mathbf{r},t)$, the above analysis holds good as well. Therefore

$$n(\mathbf{r},t) = n[v_s](\mathbf{r},t) \tag{5.6}$$

can be inverted

$$v_s(\mathbf{r},t) = v_s[n](\mathbf{r},t) \tag{5.7}$$

The corresponding non-interacting density response function is given by

$$\chi_s(\mathbf{r},t,\mathbf{r}',t') = \left.\frac{\delta n[v_s](\mathbf{r},t)}{\delta v_s(\mathbf{r}',t')}\right|_{v_{s0}} \tag{5.8}$$

If we apply the chain rule, the functional derivative of v_s with respect to v_{ext}

$$\chi(\mathbf{r},t,\mathbf{r}',t') = \int d^3x \int dT \left.\frac{\delta n(\mathbf{r},t)}{\delta v_s(\mathbf{x},T)} \frac{\delta v_s(\mathbf{x},T)}{\delta v_{ext}(r',t')}\right|_{n_0} \tag{5.9}$$

By following the chain rule once again for the right side term in the above integrand, one can show a Dyson like equation relating χ and χ_s

$$\begin{aligned}\chi(\mathbf{r},t,\mathbf{r}',t') = \chi_s(\mathbf{r},t,\mathbf{r}',t') + \int d^3x \int dT \int d^3x' \int d^3T' \chi_s(\mathbf{r},t,\mathbf{x},T) \\ \times \left(\frac{\delta(T-T')}{|\mathbf{x}-\mathbf{x}'|} + f_{xc}[n_0](\mathbf{r},t,\mathbf{r}',t')\right) \chi(\mathbf{x}',T',\mathbf{r}',t')\end{aligned} \tag{5.10}$$

where the time-dependent xc kernel is given by

$$f_{xc}[n_0](\mathbf{r},t,\mathbf{r}',t') = \left.\frac{\delta v_{xc}[n](\mathbf{r},t)}{\delta n(\mathbf{r}',t')}\right|_{n_0} \tag{5.11}$$

Eq. (5.10) can be written in the frquency domain as

$$\begin{aligned}\chi(\mathbf{r},\mathbf{r}',\omega) &= \chi_s(\mathbf{r},\mathbf{r}',\omega)+\int d^3xd^3x'\chi_s(\mathbf{r},\mathbf{x},\omega)\Bigg\{\frac{1}{|\mathbf{x}-\mathbf{x}'|}+\\ &\quad +f_{xc}(\mathbf{x},\mathbf{x}',\omega))\chi(\mathbf{x}',\mathbf{r}',\omega)\Bigg\} \qquad (5.12)\end{aligned}$$

This can also be written as

$$\chi^{-1}(\mathbf{r},\mathbf{r}',\omega)=\chi_s^{-1}(\mathbf{r},\mathbf{r}',\omega)-\frac{1}{|\mathbf{r}-\mathbf{r}'|}-f_{xc}(\mathbf{r},\mathbf{r}',\omega) \qquad (5.13)$$

The excitation energies are finally obtained from the poles of the above inverse interacting density-density response function. Therefore the calculation of the exact excitations within TDDFT framework, basically depends on finding the frequency dependent xc kernel f_{xc}. The simplest approximation to the exchange-correlation potential is the adiabatic local density approximation (ALDA), which is similar to the LDA in the static DFT. This approximation basically evaluates the LDA expression for the ground-state exchange correlation potential at the time-dependent local density,

$$v_{xc}(\mathbf{r},t)=v_{xc}^{hom}(n(\mathbf{r},t))=\frac{d}{dn}(n\epsilon_{xc}(n))\bigg|_{n(\mathbf{r},t)} \qquad (5.14)$$

where $\epsilon_{xc}(n)$ is the exchange-correlation energy per particle of the homogeneous electron gas with density n. The essential feature of ALDA is it is local in time as well as space. In principle, ALDA should be valid in nearly homogeneous systems where the densities vary very slowly in time; in practice however, it works quite well beyond this domain of applicability. The exchange-correlation kernel in ALDA within the linear response regime has the form

$$f_{xc}^{ALDA}(\mathbf{r}, \mathbf{r}', t, t') = \delta(t - t')\delta(\mathbf{r} - \mathbf{r}')\frac{d^2}{dn^2}(n\epsilon_{xc}(n))|_{n_0(\mathbf{r})} \tag{5.15}$$

This kernel is local in space and time. When Fourier-transformed, the locality in time implies that f_{xc}^{ALDA} is frequency independent, ie., the adiabatic approximation gives rise to frequency independent kernels. Though ALDA is a remarkably successful approach in dealing with the excitations of many body systems that have a direct counterpart in KS system, such as atomic and molecular single particle excitations, it fails to explain the phenomena like double excitations or the long range charge transfer. The reason for this is the exact functional dependence of $v_{xc}[n](r, t)$ is non-local in space and in time. However the adiabatic approximations are widely used approximation for the cases where the densities vary very slowly in time as well as in space. There are several attempts to go beyond ALDA and to device a frequency dependent kernel and so that to include the memory dependence in the xc=potential.

5.2 Gross-Kohn(GK) Formalism

In 1985, Gross and Kohn [145] proposed the first freqency-dependent(ie., retatded in time)approximation to the xc potential. This approximation reads

$$
\begin{aligned}
f_{XC}(\mathbf{r},\mathbf{r}',\omega) &\sim f^h_{XC}(|\mathbf{r}-\mathbf{r}'|,\omega) \\
v_{xc1}(\mathbf{r},\omega) &= f^h_{xc}(q=0,\omega)n_1(\mathbf{r},\omega)
\end{aligned}
\tag{5.16}
$$

where $v_{xc1}(\mathbf{r},\omega)$ and $n_1(\mathbf{r},\omega)$ are the Fourier transforms of $v_{xc}(r,t)-v_{xc}(r)$ and $n(r,t)-n_0(r)$ respectively and $f^h_{xc}(q,\omega)$ (Fourier transforms of $f^h_{XC}(|\mathbf{r}-\mathbf{r}'|,\omega)$) is the so called xc kernel of a homogeneous electron liquid evaluated at the local ground state density $n_0(\mathbf{r})$ One can write it as the density-density response function of the homogeneous electron gas χ^h and the Lindhard function χ_0.

$$
f^h_{xc}(q,\omega) = 1/\chi_0(q,\omega) - 1/\chi^h(q,\omega) - 1/q^2 \tag{5.17}
$$

Using certain frequency sum rules as well as the well-known features of χ^h and χ_0, Gross-Kohn and Iwamato-Gross [146] derived the two limiting cases for f^h_{xc}.

$$
\lim_{q\to 0} f^h_{XC}(q,0,n) = \frac{d^2}{dn^2}[n\epsilon(n)] = f^h_{XC}(0) \tag{5.18}
$$

and

$$
\lim_{q\to 0} f^h_{XC}(q,\infty,n) = -\frac{4}{5}n^{2/3}\frac{d}{dn}\left\{\frac{\epsilon(n)}{n^{2/3}}\right\} + 6n^{1/3}\frac{d}{dn}\left\{\frac{\epsilon(n)}{n^{2/3}}\right\} = f^h_{XC}(\infty) \tag{5.19}
$$

This approximation however has some problems and failres. The limit expressed in Eq. (5.18) is not quite correct because the terms $\lim_{q\to 0}\lim_{w\to 0} f^h_{xc}(q,\omega)$ and $\lim_{w\to 0}\lim_{q\to 0} f^h_{xc}(q,\omega)$ are not the same. On a more fundamental level, it was pointed out by Dobson [82] that GK approximation also failes to satisy the Harmonic potential theorem (HPT). These failures again trace back to the fact as the local approximations to $v_{xc}(\mathbf{r},t)$ do not exist.

5.3 Vignale-Kohn (VK) Formalism

Vignale and Kohn (VK) showed [149] that the non-locality problem could be solved by working with the current density rather than the density as a basic variable. They derived an expression for the linearized xc vector potential $\mathbf{a}(\mathbf{r},t)$ for a system of slowly varying density, subject to a spatially varying external vector potential at a finite frequency ω.It turns out that xc vector potential does admit a local approximation in terms of the current density $j(\mathbf{r},t)$. By considering the linear current response $j_1(\mathbf{r},\omega)e^{-i\omega t}$ of interacting electrons in their ground state to a time-dependent vector potential $a_1(\mathbf{r},\omega)$, they showed xc potential in terms of a tensor xc (homogeneous) kenel $\mathbf{f}$

$$a_{1xc}(\mathbf{r},\omega) = \int \mathbf{f}_{xc}(\mathbf{r},\mathbf{r}',\omega)\cdot j_1(\mathbf{r}',\omega)d\mathbf{r}' \tag{5.20}$$

where,

$$\mathbf{f}^h_{xc,ij}(\mathbf{k},\omega) = \frac{1}{\omega^2}[f^h_{XCL}(\omega)k_ik_j + f^h_{XCT}(\omega)(k^2\delta_{ij} - k_ik_j)] \tag{5.21}$$

In the linear response limit they derived an expression for the xc vector potential $a_{1xc}(\mathbf{r},\omega)$ in generl inhomogeneity case. In case of one-dimensional inhomogeneity it becomes,

$$\begin{aligned} a_{1xc}(x,\omega) &= -\frac{1}{\omega^2}\Big\{\frac{d}{dx}[f^h_{XCL}\frac{dj_1(x,\omega)}{dx} - \delta f^h_{XCL}\frac{n'_0(x)}{n_0(x)}j_1(x,\omega)] \\ &\quad +\delta f^h_{XCL}n'_0(x)\frac{d}{dx}(\frac{j_1(x,\omega)}{n_0(x)})\Big\} \end{aligned} \tag{5.22}$$

This approximation satisfies all the inconsistencies that Gross-Kohn (GK) approximation failed to. VK satisies the so called Harmonic potential theorem, Zero force theorem, Onsagar identity etc [156]. This approximation becomes exact in the limit $k << \omega/v_F, k_F$ and $q << \omega/v_F$. Here v_F (k_F) is the Fermi velocity(momentum) and k^{-1} and q^{-1} are the characteristic length scales for variation of the external potential and equilibrium density respectively. This formalism proved to be a much improvement over ALDA in calculating the axial polarizabilities in molecular chains [150].

5.4 Nonlinear Response-VUC Formalism

Although in the VK formalism the local approximation to the vector xc potential is possible, it comes with a price that it is computationally more expensive to work with the vector quantities than the ALDA and GK formalisms. Furthermore, VK formalism is restricted to the linear response regime. To give more physical meaning to the above VK formalism and to extend the VK approach to the nonlinear response regime, Vignale, Ullirich and Conti(VUC) recast [152] the VK formalism in terms of hydrodynamic visco elastic stress tensor. They treated the velocity $\mathbf{u} = \mathbf{j}/n$ is more natural variable than the current. They started with an assumption that the gradients of the density and the velocity fields be small. They incorporated the memory dependence of the system in the form of the fluid elment $\mathbf{R}(t'|\mathbf{r}, t)$. The stress tensor $\sigma_{xc,ij}$ is local in $n(\mathbf{R}, t')$and $j(\mathbf{R}, t)$. Here $\mathbf{R}(t'|\mathbf{r}, t)$ is the position at a time t' og the fluid element which evolves into $\mathbf{r}$ at a time t. Upto a validity in the second order in the spatial derivatives, they set up an equation for $a_{xc}(\mathbf{r}, t)$:

$$\frac{e}{c}\frac{\partial a_{xc,i}(\mathbf{r}, t)}{\partial t} = -\nabla_i v_{xc}^{ALDA}(\mathbf{r}, t) + \frac{1}{n(\mathbf{r}, t)} \sum_j \frac{\partial \sigma_{xc,ij}(\mathbf{r}, t)}{\partial r_j} \tag{5.23}$$

where the stress tensor $\sigma_{xc,ij}$ in terms of velocity field $\vec{u}$ and the viscosity coefficients $\tilde{\eta}$ and $\tilde{\zeta}$is given by

$$\begin{aligned} \sigma_{xc,ij}(\mathbf{r}, t) &= \int_{-\infty}^{t} \left\{ \tilde{\eta}(n(\mathbf{r}, t), t - t') \left[\frac{\partial u_i(\mathbf{r}, t')}{\partial r_j} + \frac{\partial u_j(\mathbf{r}, t')}{\partial r_i} \right.\right. \\ &\left.\left. -\frac{2}{3}\vec{\nabla} \cdot \vec{u}(\mathbf{r}, t')\delta_{ij} \right] + \tilde{\zeta}(n(\mathbf{r}, t), t - t')\vec{\nabla} \cdot \vec{u}(\mathbf{r}, t')\delta_{ij} \right\} dt' \end{aligned} \tag{5.24}$$

The viscosity coefficients are given in terms of the homogeneous electron gas functions $f^h_{XCL}(\omega, n)$ and $f^h_{XCT}(\omega, n)$ (L for longitudinal, T for transverse).

$$\tilde{\zeta}(n, \omega) = -\frac{n^2}{i\omega}\left(f^h_{XCL} - \frac{4}{3} f^h_{XCT} - \frac{d^2\epsilon_{xc}(n)}{dn^2} \right) \tag{5.25}$$

and

$$\tilde{\eta}(n,\omega) = \frac{n^2}{i\omega} f^h_{XCT} \tag{5.26}$$

One can achieve a better improvement of this approximation if $\vec{u}(\mathbf{r},t')$ is replaced with $\vec{u}(\mathbf{R}(t'|\mathbf{r},t')$. This approximation in the linear response regime exactly coincides with the VK formalism. Recently it was observed that this approximation suffers from a problem called "dissipation" of energy in the finite systems [158], [157], [159]. Thus there is a need for not only including the memory term in the xc-potential but also to design a formalism which captures the multi excitations more accurately.

5.5 Dobson-Bunner-Grosss (DBG) Formalism

Dobson, Bunner and Gross (DBG) in 1997 [148] introduced an ansatz for the xc force per particle using the same idea of fluid element method in which the memory resides not with each fixed point $\mathbf{r}$ in space, but rather with each separate fluid element. Thus the element which arrives at location $\mathbf{r}$ at time t "remembers" what happened to it at earlier times t' when it was locations $\mathbf{R}' = \mathbf{R}(t'|\mathbf{r})$ different from its present location $\mathbf{r}$.

$$F_{xc}(r,t) = -\frac{1}{n(\mathbf{r},t)}\nabla \int_{-\infty}^{\infty} \Pi_{xc}(n(\mathbf{R}',t'),t-t')dt' \tag{5.27}$$

where $\mathbf{R}' = \mathbf{R}(t'|\mathbf{r},t)$ and $\Pi_{xc}(n,\tau)$ is a pressure like scalar memory function. The above expression is a modified local-density assumption, in that for a fixed $\mathbf{r}, t$, and t', v_{xc} depends only on the density at one place $\mathbf{R}'$. Therefore the "locality" is defined relative to a fluid element rather than to a fixed position $\mathbf{r}$. We notice that

$$u(\mathbf{R}, t') = \frac{\partial}{\partial t'}(\mathbf{R}, t') = \frac{j(\mathbf{R}, t')}{n(\mathbf{R}, t')} \tag{5.28}$$

One can write Π_{xc} as

$$\Pi_{xc}(n, \omega) = \int_0^n \rho f^h_{XCL}(\rho, \omega) \tag{5.29}$$

In linear regime this approach give rise to the first order perturbation to to the xc force

$$\begin{aligned} F_{xc1}(\mathbf{r}, \omega) \quad &= \quad -\frac{\nabla n_0(\mathbf{r}, w)}{n_0(\mathbf{r}} \left\{ n1(\mathbf{r}, \omega) + \nabla n_0(\mathbf{r} \cdot \mathbf{x}(\mathbf{r}, \omega) \right\} \delta f \\ & \quad\quad -\nabla \left\{ \nabla n_0(\mathbf{r}) \cdot \mathbf{x}(\mathbf{r}, \omega) \delta f + n_1(\mathbf{r}, t') f \right\}, \end{aligned} \tag{5.30}$$

where $f = f^h_{XCL}(n_0(\mathbf{r}), \omega)$ and

$$\delta f = f^h_{XCL}(\omega) - f^h_{XCL}(0) \tag{5.31}$$

If we use the lineaized relations $\mathbf{j}/n_0 = -i\omega\mathbf{x}$ and $n1 = -n_0 \nabla \cdot \mathbf{x} - \mathbf{x} \cdot \nabla n_0$ the above expression coincides with the $a^{VK}_{xc1}(\mathbf{r}, \omega)$ (Eq.(5.22)) when the inhomogenity is in 1D.

5.6 Comparison of VUC and DBG

Though both the VUC and DBG non-linear formalisms coincide with the VK approach in the linear regime. It would be interesting to compare both the non-linear expressions for the scaler xc potentials $v_{xc}^{VUC}(r,t)$ and $v_{xc}^{DBG}(r,t)$

$$v_{xc}^{DBG}(\mathbf{r},t) = -\int^{r} F_{xc}(\mathbf{r}',t)d\mathbf{r}' \tag{5.32}$$

By substituting Eq.(5.27) in the above equation we get,

$$v_{xc}^{DBG}(\mathbf{r},t) = \int^{\mathbf{r}} dr' \frac{1}{n(r',t)} \nabla \int_{-\infty}^{\infty} \Pi_{xc}(n(R',t'),t-t')dt' \tag{5.33}$$

Using the definition of the pressure like kernel in DBG formalism(Eq.(5.29)), We get,

$$v_{xc}^{DBG}(\mathbf{r},t) = \int^{\mathbf{r}} dr' \frac{1}{n(r',t)} \frac{d}{dr'} \int_{-\infty}^{\infty} dt' \int d\omega e^{i\omega(t-t')} \int_{0}^{n(\mathbf{R}',t')} \rho f_{XCL}^{h}(\rho,\omega)d\rho \tag{5.34}$$

By substituing Eq.(5.31)in the above expression, we get,

$$\begin{aligned}
v_{xc}^{DBG}(\mathbf{r},t) &= \int^{\mathbf{r}} dr' \frac{1}{n(r',t)} \frac{d}{dr'} \int_{-\infty}^{\infty} dt' \int d\omega e^{i\omega(t-t')} \\
&\times \int_0^{n(\mathbf{R}',t')} \rho f_{XCL}^h(0) d\rho \\
&+ \int^{\mathbf{r}} dr' \frac{1}{n(r',t)} \frac{d}{dr'} \int_{-\infty}^{\infty} dt' \int d\omega e^{i\omega(t-t')} \\
&\times \int_0^{n(\mathbf{R}',t')} \rho \delta f_{XCL}^h(\omega) d\rho \qquad (5.35)
\end{aligned}$$

After further simplification it becomes,

$$\begin{aligned}
v_{xc}^{DBG}(\mathbf{r},t) &= \int^{\mathbf{r}} r dr' \frac{1}{n(r',t)} \frac{d}{dr'} \int_{-\infty}^{\infty} dt' \delta(t-t') \\
&\times \int_0^{n(\mathbf{R}',t')} \rho f_{XCL}^h(0) d\rho \\
&+ \int^{\mathbf{r}} dr' \frac{1}{n(r',t)} \frac{d}{dr'} \int_{-\infty}^{\infty} dt' \int d\omega e^{i\omega(t-t')} \\
&\times \int_0^{n(\mathbf{R}',t')} \rho \delta f_{XCL}^h(\omega) d\rho \qquad (5.36)
\end{aligned}$$

Therefore at $t = t'$ the position of the fluid element becomes $r' = R'$ and so $n(\mathbf{R}',t)$ should be replaces by $n(\mathbf{r}',t')$ in the first term. After simplification we get,

$$\begin{aligned} v_{xc}^{DBG}(\mathbf{r},t) &= \int^{\mathbf{r}} \frac{d}{dr'}\left(\frac{d\epsilon_{xc}}{dn}\right) \\ &+ \int^{\mathbf{r}} dr' \frac{1}{n(r',t)} \frac{d}{dr'} \int_{-\infty}^{\infty} dt' \\ &\times \int d\omega e^{i\omega(t-t')} \int_0^{n(\mathbf{R}',t')} \rho \delta f_{XCL}^h(\omega) d\rho \end{aligned} \tag{5.37}$$

Therefore the dynamic xc-potential in the non-linear regime is given by

$$\begin{aligned} v_{xc}^{DBG}(\mathbf{r},t) &= v_{xc}^{ALDA}(\mathbf{r},t) \\ &+ \int^{\mathbf{r}} dr' \frac{1}{n(r',t)} \frac{d}{dr'} \int_{-\infty}^{\infty} dt' \\ &\times \int d\omega e^{i\omega(t-t')} \int_0^{n(\mathbf{R}',t)} \rho \delta f_{XCL}^h(\omega) d\rho \end{aligned} \tag{5.38}$$

In case of 1D-inhomogenity, $a_{xc}(\mathbf{r},t)$ of VUC that is expressed in the Eq.(5.23) together with Eq.(5.25) and Eq.(5.26), we can show that the dynamic scalar xc potential can be expressed as

$$\begin{aligned} v_{xc}^{VUC}(r,t) &= v_{xc}^{ALDA}(r,t) \\ &+ \int^{r} dr' \frac{1}{n(r',t)} \frac{d}{dr'} \int_{-\infty}^{t} dt' \\ &\times \int d\omega e^{i\omega(t-t')} \frac{n^2(r',t)}{i\omega} \delta f_{XCL}^h(\omega) \frac{du(r',t')}{dr'} \end{aligned} \tag{5.39}$$

The above VUC expression for the xc potential appears similar to the xc potential in the DBG formalism $v_{xc}^{DBG}(\mathbf{r},t)$(See Eq.(5.38)). But these two are not exactly the same(except the ALDA term). We carried out further more simplification of both v_{xc}^{DBG} and v_{xc}^{VUC} expressions to map the similar terms if there are any. Our intension is to explore the physical meaning of the the terms that are different in both the formalisms.

For this we re-write the time-dependent xc potential in the DBG formalism as

$$\begin{aligned} v_{xc}^{DBG}(\mathbf{r},t) &= v_{xc}^{ALDA}(\mathbf{r},t) + \int^{r} dr' \frac{1}{n(r',t)} \int dt' \int d\omega e^{i\omega(t-t')} \\ &\quad \times \frac{dn(R',t')}{dR'} \frac{dR'}{dr'} n(R',t') \delta f_{XCL}^{h}(n(R',t'),\omega) \end{aligned} \tag{5.40}$$

After simplification the above expression comes into the following form

$$\begin{aligned} \Delta v_{xc}^{DBG}(r,t) &= \int_{\infty}^{\infty} dt' \int^{r} dr' \frac{1}{n(r',t)} \delta f_{XCL}^{h}(n(R',t'),t-t') \\ &\quad \times \frac{dn(R',t')}{dR'} \frac{dR'}{dr'} n(R',t') \end{aligned} \tag{5.41}$$

One can also re-write the time-dependent xc potential in VUC formalism as

$$\begin{aligned} \Delta v_{xc}^{VUC}(\mathbf{r},t) &= \int^{r} dr' \frac{1}{n(r',t)} \frac{d}{dr'} \Big\{ n^2(r',t) \int_{\infty}^{t} dt' \frac{du(r',t')}{dr'} \\ &\quad \times \int d\omega \frac{e^{i\omega(t-t')}}{i\omega} \delta f_{xc}^{h}(n,\omega) \Big\} \end{aligned} \tag{5.42}$$

$$\begin{aligned}\Delta v_{xc}^{VUC}(\mathbf{r},t) &= \int_{-\infty}^{t} dt' \int^{r} dr' \frac{1}{n(r',t)} \frac{d}{dr'} \Big\{ n^2(r',t) \frac{du(r',t')}{dr'} \\ &\qquad \times \int_{-\infty}^{(t-t')} d(t-t') \delta f_{XCL}^{h}(n,t-t') \Big\} \qquad (5.43)\end{aligned}$$

which becomes after simplification,

$$\begin{aligned}\Delta v_{xc}^{VUC}(\mathbf{r},t) &= \int_{-\infty}^{t} dt' \int^{r} dr' \frac{dn(r',t)}{dr'} \frac{du(r',t')}{dr'} \int_{-\infty}^{\tau} d\tau \delta f_{XCL}^{h}(n(r',t),\tau) \\ &+ \int_{-\infty}^{t} dt' n(r,t) \frac{du(r,t')}{dr'} \int_{-\infty}^{\tau} d\tau \delta f_{XCL}^{h}(n(r,t),\tau) \qquad (5.44)\end{aligned}$$

Here $\tau = t - t'$. We know that $u(r',t') = \frac{j(r',t')}{n(r',t')} = \frac{dr'}{dt'}$. If we substitute $\frac{du(r',t')}{dr'} = \frac{d}{dr'} \frac{dR'}{dt'} \frac{dr'}{dR'} = \left[\frac{d}{dt'}\left(\frac{dR'}{dr'}\right)\right] \frac{dr'}{dR'}$ in Eq. (5.43),We get

$$\begin{aligned}\Delta v_{xc}^{VUC}(r,t) &= \int_{-\infty}^{t} dt' \int^{r} dr' \frac{dn(r',t)}{dr} \delta f_{XCL}^{h}(n(r',t),t-t') d\tau \\ &- \int^{t} dt' \int^{r} dr' \frac{dn(r',t)}{dr} \frac{d^2 r'}{dR' dt'} \int^{\tau} \delta f_{XCL}^{h}(n(r',t),\tau) d\tau \\ &+ \int^{t} dt' n(r,t) \frac{du(r.t')}{dr'} \int^{\tau} \delta f_{XCL}^{h}(n(r,t'),\tau) d\tau \qquad (5.45)\end{aligned}$$

The first term in the above expression exactly coincides with the DBG expression Eq.(5.41) if we replace r' with R'. So with in the limit $r' = R'$ the difference between the VUC xc potential and the DBG xc potential is given by

$$\begin{aligned} v_{xc}^{VUC}(r,t) - v_{xc}^{DBG}(r,t) &= -\int_{-\infty}^{t} dt' \int^{r} dr' \frac{dn(r',t)}{dr'} \left.\frac{d^2 r'}{dR' dt'}\right|_{R'=r'} \\ &\times \int^{\tau} d\tau \delta f_{XCL}^{h}(n(r',t),\tau) \\ &+ \int^{t} dt' n(r,t) \frac{du(r,t')}{dr} \\ &\times \int^{\tau} d\tau \delta f_{XCL}^{h}(n(r,t'),\tau) \qquad (5.46) \end{aligned}$$

Thus we have arrived at an expression that shows even in the limit $r' = R'$ the two approaches (VUC and DBG) are different. The above equation is the main part of our work. We would like explore these differences further more in terms of an other but more general approach given by Tokatly and Pankratov.

A more general (local) nonadiabatic and nonlinear approximation for the xc potential is given by Tokatly and Pankratov (TP) [154]. The xc potential is expressed in terms of a stress tensor, which is a local nonlinear functional of two basic variables: the displacement vector and and a second rank tensor. In this formalism they considered the system under the Lengrangian frame of reference.Legrangian frame is local reference frame that moves with the system. Therefore the memory or initial state dependence of the dynamic xc potential is absent in the Legrangian frame. In this formalism the exact vector xc potential is defined by

$$-\frac{\partial a_{xc,i}}{\partial t} = \frac{c}{n}\nabla_j P_{xc,ij} - v_j[\nabla_i a_{xc,j} - \nabla_j a_{xc,i}] \tag{5.47}$$

where $P_{xc,ij} = P_{ij} - T_{ij}^{KS}$ is the difference of the full stress tensor of the interacting system, P_{ij} and the kinetic stress tensor of the KS system, T_{ij}^{KS} .

Using a nonlinear transformation of coordinates one moves the formulation can be tranfomed into the comoving Langarangian frame

$$\mathbf{r} = \mathbf{r}(\xi, t) \tag{5.48}$$

where $\mathbf{r}(\xi, t)$ is the trajectory of the fluid element whose inital coordinates are $(\xi, 0)$. In the comoving Legrangian frame the basic varible becomes the Green‘s deformation tensor, g_{ij}

$$g_{ij}(\xi, t) = \frac{\partial r_k(\xi, t)}{\partial \xi_i}\frac{\partial r_k(\xi, t)}{\partial \xi_j} \tag{5.49}$$

By substituting $P_{xc,ij}[\bar{g}_{ij}(\mathbf{r}, t)]$ in Eq.(5.47) yields a_{xc} , where $\bar{g}_{ij}$ is known as Cauchy‘s deformation tensor or the inverse deformation tensor. Using the determinant of this tensor, $\bar{g}(\mathbf{r}, t)$ one can write,

$$n(\mathbf{r}, t) = \sqrt{\bar{g}(\mathbf{r}, t)}n_0(\xi(\mathbf{r}, t)) \tag{5.50}$$

Specifically for 1D motion, the non-linear elastic approximation for the xc-potential is given by,

$$v_{xc}(r,t) = v_{xc}^{ALDA}(r,t) + \int_{-\infty}^{r} \frac{dr'}{dn(r',t)} \frac{\partial}{\partial r'} P_{xc,rr}(n(r',t), \bar{g}(r',t)) \tag{5.51}$$

where the xc stress tensor in 1D motion $P_{xc,rr}$ is given by

$$P_{xc,xx}(n,\bar{g}) = \frac{2}{3}\bar{g}^{3/2}\epsilon_{kin}(\frac{n}{\sqrt{\bar{g}}}) + \left\{\frac{\bar{g}}{\bar{g}-1}(\frac{\sqrt{\bar{g}-1} - tan^{-1}\sqrt{\bar{g}-1}}{\sqrt{\bar{g}-1}})\right\}\epsilon_{pot}(\frac{n}{\sqrt{\bar{g}}}) \tag{5.52}$$

Here ϵ_{kin} and ϵ_{pot} are the xc kinetic and potential energy per unit volume of a homogeneous electron gas. This TP formalism exactly coincides with the VUC formalism under the small deformation limit[155],

$$\begin{aligned} \bar{g}_{ij}(\mathbf{r},t) &= \delta_{ij} + \delta\bar{g}_{ij}(\mathbf{r},t), and \\ P_{xc,ij}(\mathbf{r},t) &= P_{xc}^{ALDA}(n(\mathbf{r},t))\delta_{ij} + \delta P_{ij}(\mathbf{r},t) \end{aligned} \tag{5.53}$$

We now compare the TP formalism in the small deformation limit to the DBG formalism. We re-write the Eq.(5.41) in the following form to quantitatively compare to the TP formalism,

$$\begin{aligned} \Delta v_{xc}^{DBG}(r,t) &= \int^{r} dr' \frac{1}{n(r',t)} \int_{-\infty}^{\infty} dt' \int d\omega e^{i\omega(t-t')} \\ &\quad \frac{dn(R',t')}{dr'} n(R',t') \delta f_{XCL}^{h}(n(R',t'),\omega) \end{aligned} \tag{5.54}$$

ie.,

$$\begin{aligned}\Delta v_{xc}^{DBG}(r,t) &= \int^{r} dr' \frac{1}{n(r',t)} \int_{-\infty}^{\infty} dt' \\ &\quad \frac{dn(R',t')}{dr'} n(R',t') \delta f_{XCL}^{h}(n(R',t'), t-t') \qquad (5.55)\end{aligned}$$

Here we used $\frac{d}{dr'} = \frac{dn(R',t')}{dr'} \frac{d}{dn(R',t')}$. Now we identify that

$$\frac{\bar{g}(r',t)}{\bar{g}(R',t')} = \left\{ \frac{dR'}{dr'} \right\}^{2} \qquad (5.56)$$

If we assume that the system evolves from $(\xi, 0)$ and reaches (R', t') via an intermidiate location (r', t). Therefore we can write,

$$\begin{aligned} n(r',t) &= \sqrt{\bar{g}(r',t)} n_0(\xi) \\ n(R',t') &= \sqrt{\bar{g}(R',t')} n_0(\xi) \qquad (5.57)\end{aligned}$$

With this the expression for v_{xc}^{DBG} becomes,

$$\begin{aligned}\Delta v_{xc}^{DBG}(r,t) &= \int^{r} dr' \frac{1}{\sqrt{\bar{g}(r',t)} n_0(\xi)} \int_{infty}^{\infty} dt' \frac{\sqrt{\bar{g}(r',t)}}{\sqrt{\bar{g}(R',t')}} \\ &\quad \frac{d}{dR'} (\sqrt{\bar{g}(R',t')} n_0(\xi)) \sqrt{\bar{g}(r',t)} n_0(\xi) \\ &\quad \delta f_{XCL}^{h}(n(R',t'), t-t') \qquad (5.58)\end{aligned}$$

where, $\frac{dn(R',t')}{dr'}$ as $\frac{dR'}{dr'} \frac{dn(R',t')}{dR'}$. Thus we arrive at

$$\Delta v_{xc}^{DBG}(r,t) = \int^{r} dr' \int_{-\infty}^{\infty} dt' n_0(\xi) \frac{d}{dR'}(\sqrt{\bar{g}(R',t')})\delta f_{XCL}^{h}(n(R',t'),t-t') \tag{5.59}$$

5.7 Conclusion

In this chapter, we have carried out a detailed comparative study of the two existing non-linear and non-adiabatic approaches. We showed that: though in linear response regime, these two (VUC and DBG) coincide with each other, they are formally different in non-linear response regimes. The two approaches are based on similar grounds but not the same. We would extend our study in future for different model systems and examine what can the difference between these two approaches in the non-linear response regime can suggest in terms of applicability.

Chapter 6

Conclusions

Due to its favourable system size scaling, TDDFT has achieved an unprecedented balance between accuracy and efficiency for the calculation of excitation spectra and response, as described in Chapters 1 and 2. However there are regimes in which the theory performs poorly, and challenges for functional approximations lie particularly in strong-field regime. A dominant challenge is memory-dependence (both history and initial-state), that is known to be a property of the exact functional but due to difficulties in modelling it, almost all calculations today use approximations where this is ignored. A second important ingredient in the strong-field regime are observable functionals – how to extract the quantity of interest from the fictitious KS system.

To address the first challenge, In our 2nd Chapter, we studied a model system (Hooke's atom) and showed that phase-space distributions can recognize the temporal non-locality in the correlation potential which the position densities fail to. Hence we suggest the functionals based on phase-space densities (or in turn the momentum densities) are less-non-local in time and can capture the memory effect.

The second challenge is of observable functionals. As demonstrated in Chapter-3, this problem typically wreaks havoc for momentum distributions in strong-field phenomena such as ionization. We show that for the description of ionization processes, KS- momentum densities are not always the best optionals as they may not in principle yield the momentum densities of the interacting system. We studied a single-ionizations model system and a double-ionization model system to support our conclusion.

A more generalization of TDDFT to phase-space densities is explored , via a quasi or semi-classical approach to correlation which appears to partially solve both the problems of memory-dependence and of observable functionals. In this approach the memory is carried along naturally with the classical trajectories. Moreover, the method allows for time-evolving occupation numbers, an important feature of applications such as ionization and quantum control. We studied time-dependent Moshisky atom as an example. As the future work, we plan to explore the approach in more realistic systems, and to extend to semi classical approaches which are able to capture the interference.

The non-locality in time is intimately connected to non-locality in space. We studied in detail two non-local and nonlinear methods (VUC and DBG) for the xc-kernal (f_{xc}) and showed a connection between them.

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