Time-Dependent Density Functional Theory
from a Bohmian Perspective

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This article has been published as a chapter in “Chemical Reactivity Theory: A Density Functional View”, ed. P. K. Chattaraj (CRC Press, New York, 2009), ch. 8, p. 105. In it, an overview of the relationship between time-dependent DFT and quantum hydrodynamics is presented, showing the role that Bohmian mechanics can play within the ab-initio methodology as both a numerical and an interpretative tool.

I. INTRODUCTION

Since the early days of Quantum Mechanics, the wave-function theory has proven to be very successful in describing many different quantum processes and phenomena. However, in many problems of Quantum Chemistry and Solid State Physics, where the dimensionality of the systems studied is relatively high, \textit{ab initio} calculations of the structure of atoms, molecules, clusters and crystals, and their interactions are very often prohibitive. Hence, alternative formulations based on the direct use of the probability density, gathered under what is generally known as the density matrix theory \footnote{1}, were also developed since the very beginning of the new mechanics. The independent electron approximation or Thomas-Fermi model, and the Hartree and Hartree-Fock approaches are former statistical models developed in that direction \footnote{2}. These models can be considered direct predecessors of the more recent density functional theory (DFT) \footnote{3}, whose principles were established by Hohenberg, Kohn and Sham \footnote{4, 5} in the middle sixties. According to this theory, the fundamental physical
information about a many-body system is provided by single-particle densities in a three-dimensional space, which are obtained variationally within a time-independent framework. When compared with other previous formalisms, DFT presents two clear advantages: (i) it is able to treat many-body problems in a sufficiently accurate way and (ii) it is computationally simple. This explains why it is one of the most widely used theories to deal with electronic structure—the electronic ground-state energy as a function of the position of the atomic nuclei determines the structure of molecules and solids, providing at the same time the forces acting on the atomic nuclei when they are not at their equilibrium positions. At present, DFT is being used routinely to solve many problems in gas phase and condensed matter. Furthermore, it has made possible the development of accurate molecular dynamics schemes in which the forces are evaluated quantum-mechanically “on the fly”. Nonetheless, DFT is a fundamental tool provided the systems studied are relatively large; for small systems standard methods based on the use of the wave function render quite accurate results [6]. Moreover, it is also worth stressing that all practical applications of DFT rely on essentially uncontrolled approximations [7] (e.g., the local density approximation [4, 5], the local spin-density approximation or generalized gradient approximations [8]), and therefore the validity of DFT is conditioned to its ability to provide results sufficiently close to the experimental data.

As mentioned above, standard DFT is commonly applied to determine ground states in time-independent problems. Hence, reactive and non-reactive scatterings as well as atoms and molecules in laser fields have been out of the reach of the corresponding methodology. Nevertheless, though it is less known than the standard DFT, very interesting work in this direction can also be found in the literature [9, 10, 11, 12, 13, 14, 15], where DFT is combined with quantum hydrodynamics [or quantum-fluid dynamics (QFD)] (QFD-DFT) in order to obtain a quantum theory of many-electron systems. In this case, the many-electron wave function is replaced by single-particle charge and current densities. The formal grounds of QFD-DFT rely on a set of hydrodynamical equations [10, 11, 12]. It has the advantage of dealing with dynamical processes evolving in time in terms of single-particle time-dependent (TD) equations, as derived by different authors [14]. Apart from QFD-DFT, there are other TD-DFT approaches based on similar grounds, such as the Floquet DFT [16, 17] or the quantal DFT [18]. Furthermore, we would like to note that TD-DFT does not necessarily require to pass through a QFD or QFD-like formulation in order to be applied [19]. As
happens with standard DFT, TD-DFT can also be started directly from the many-body TD Schrödinger equation, the density being then determined from solving a set of TD Schrödinger equations for single, non-interacting particles [12].

Although trajectories are not computed in QFD-DFT, it is clear that there is a strong connection between this approach and the trajectory or hydrodynamical picture of quantum mechanics [20], independently developed by Madelung [21], de Broglie [22] and Bohm [23], and which is also known as Bohmian mechanics. From the same hydrodynamical equations, information not only about the system configuration (DFT calculations) but also about its dynamics (quantum trajectories) is possible to obtain. This fact is better understood when the so-called quantum potential is considered, since it allows us to associate the probability density (calculated from DFT) with the quantum trajectories. Note that this potential is determined by the curvature of the probability density and, at the same time, it governs the behavior displayed by the quantum trajectories. Because of the interplay between probability density and quantum potential, the latter conveys fundamental physical information: it transmits the nonseparability contained in the probability density (or, equivalently, the wave function) to the particle dynamics. This property, on the other hand, is connected with the inherent nonlocality of Quantum Mechanics [24], i.e., two distant parts of an entangled or nonfactorizable system will keep a strong correlation due to coherence exhibited by its quantum evolution.

The purpose of this chapter is to show and discuss the connection between TD-DFT and Bohmian mechanics, as well as the sources of lack of accuracy in DFT, in general, regarding the problem of correlations within the Bohmian framework or, in other words, of entanglement. In order to be self-contained, a brief account of how DFT tackles the many-body problem with spin is given in Sec. III. A short and simple introduction to TD-DFT and its quantum hydrodynamical version (QFD-DFT) is presented in Sec. III. The problem of the many-body wave function in Bohmian mechanics, as well as the fundamental grounds of this theory, are described and discussed in Sec. IV. This chapter is concluded with a short final discussion in Sec. V.
II. THE MANY-BODY PROBLEM IN STANDARD DFT

There are many different physical and chemical systems of interest which are characterized by a relatively large number of degrees of freedom. However, in most of cases, the many-body problem can be reduced to calculations related to a sort of inhomogeneous gas, i.e., a set of interacting point-like particles which evolve quantum-mechanically under the action of a certain effective potential field. This is the typical DFT scenario, with an ensemble of $N$ electrons in a nuclear or external potential representing the system of interest. DFT thus tries to provide an alternative approach to the exact, nonrelativistic $N$-electron wave function $\Psi(r_1 s_1, \ldots, r_N s_N)$, which satisfies the time-independent Schrödinger equation and where $r_N$ and $s_N$ are the space and spin coordinates, respectively. Because the methodology based on DFT is easy and computationally efficient in its implementation, this theory is still enjoying an ever-increasing popularity within the Physics and Chemistry communities involved in many-body calculations.

To understand the main idea behind DFT, consider the following. In the absence of magnetic fields, the many-electron Hamiltonian does not act on the electronic spin coordinates, and the antisymmetry and spin restrictions are directly imposed on the wave function $\Psi(r_1 s_1, \ldots, r_N s_N)$. Within the Born-Oppenheimer approximation, the energy of an $N$-electron system with a fixed $M$-nuclei geometry $R$ takes the following form in atomic units:

$$ E = -\frac{1}{2} \int_{r_1 = r'_1} \left[ \nabla \cdot \nabla^T \gamma_1(r_1; r'_1) \right] dr_1 + \int v_{\text{ext}}(R, r_1) \gamma_1(r_1) dr_1 + \int \frac{\gamma_2(r_1, r_2)}{r_{12}} dr_1 dr_2, \quad (1) $$

where $\gamma_1(r_1)$ and $\gamma_2(r_1, r_2)$ are the diagonal elements of $\gamma_1(r_1; r'_1)$ and $\gamma_2(r_1, r_2; r'_1, r'_2)$, respectively, which represent the one-electron (or one-particle) density and the electron-electron (or two-particle) correlation function, commonly used in DFT and electronic structure theory. In principle, it might seem that all the information about the system necessary to evaluate the energy is contained in $\gamma_1(r_1)$ and $\gamma_2(r_1, r_2)$, and therefore one could forget about manipulating the wave function. However, in order to avoid unphysical results in the evaluation of the energy, it is still necessary to compute the wave function $\Psi(r_1 s_1, \ldots, r_N s_N)$ that generates the correct $\gamma_1(r_1)$ and $\gamma_2(r_1; r_2)$ densities. Equation (1) is the starting point of DFT, which aims to replace both $\gamma_1(r_1; r'_1)$ and $\gamma_2(r_1, r_2)$ by $\rho(r)$. If we are only interested in the system ground state, the Hohenberg-Kohn theorems state that the exact ground-state
The total energy of any many-electron system is given by a universal, unknown functional of the one-electron density. However, only the second term of Eq. (1) is an explicit functional of $\rho(r)$. The first term corresponds to the kinetic energy, which is a functional of the complete one-electron density function $\gamma_1(r_1; r'_1)$. For $N$-electron systems the most important contribution to the electron-electron term comes from the classical electrostatic self-energy of the charge interaction, which is an explicit functional of the diagonal one-electron function. The remaining contribution to the electron-electron term is still unknown. These two terms are a functional of the one-electron density, namely the “exchange-correlation” functional. Thus, it is possible to define a universal functional which is derivable from the one-electron density itself and with no reference to the external potential $v_{\text{ext}}(R, r)$. According to McWeeny [25], we can reformulate the DFT by ensuring not only that a variational procedure leads to $\rho(r)$ —which is derivable from a wave-function $\Psi(r_1s_1, \ldots, r_Ns_N)$ (the so-called $N$-representability problem)—, but also the wave function belongs to the totally irreducible representation of the spin permutation group $A$. From a mathematical point of view, the above proposition can be expressed (in atomic units) as

$$
E = \min_{\rho \to \gamma_1 \text{ derived from } \Psi \in A} \left\{ -\frac{1}{2} \int_{r_1=r'_1} [\nabla \cdot \nabla^T \gamma_1(r_1; r'_1)] dr_1 + \int v_{\text{ext}}(R, r_1) \gamma_1(r_1) dr_1 + \frac{1}{2} \int \frac{\gamma_1(r_1) (I - \hat{P}_{12}) \gamma_1(r_2; r'_2)}{r_{12}} dr_1 dr_2 + \min_{\gamma_2 \text{ derived from } \Psi \in A} E_{\text{corr}}[\gamma_2(r_1, r_2)] \right\}.
$$

(2)

This equation shows the relationship between the one-electron function, $\gamma_1(r_1; r'_1)$, and the main part of the energy functional —the rest of the functional, which is the electron-electron repulsion, depends on $\gamma_2(r_1, r_2)$. The last term is also a functional of the one-electron density. In the new reformulation of DFT, the methodology is almost universally based on the Kohn-Sham approach and only differs in the particular way to model the unknown “exchange-correlation” term.

III. TIME-DEPENDENT DENSITY FUNCTIONAL THEORY

An extension of standard DFT is its TD version. This generalization is necessary when dealing with intrinsic TD phenomena. In addition, it preserves the appealing flavor of the classical approach to the theory of motion.
The rigorous foundation of the TD-DFT was started with the works by Bartolotti [10] and Deb and Ghosh [11]. However, the proofs of the fundamental theorems were provided by Runge and Gross [12]. One of those theorems corresponds to a Hohenberg-Kohn-like theorem for the TD Schrödinger equation. The starting point for the derivation of the TD Kohn-Sham (KS) equations is the variational principle for the quantum mechanical action (along this Section, atomic units are also used):

\[ S[\Psi] = \int_{t_0}^{t_1} \langle \Psi(t) | \left[ i \frac{\partial}{\partial t} - \hat{H}(t) \right] | \Psi(t) \rangle \, dt. \] (3)

This variational principle is not based on the total energy because in TD systems the total energy is not conserved. The so-called Runge-Gross theorem then states that there exists a one-to-one mapping between the external potential (in general, TD), \( v_{\text{ext}}(\textbf{r}, t) \), and the electronic density, \( \rho(\textbf{r}, t) \), for many-body systems evolving from a fixed initial state, \( \Psi(t_0) \). Runge and Gross thus open the possibility of rigorously deriving the TD version of the Kohn-Sham equations. This procedure yields the TD Schrödinger equation for the Kohn-Sham electrons described by the orbitals \( \phi_k(\textbf{r}, t) \),

\[ i \frac{\partial \phi_k(\textbf{r}, t)}{\partial t} = H_{\text{KS}}(\textbf{r}, t) \phi_k(\textbf{r}, t), \] (4)

where the KS Hamiltonian is

\[ H_{\text{KS}}(\textbf{r}, t) = -\frac{1}{2} \nabla^2 + v_{\text{KS}}[\rho(\textbf{r}, t)], \] (5)

with a TD-KS effective potential, usually given by the sum of three terms, which account for external, classical electrostatic and exchange interactions. The latter is the source of all non-trivial, non-local, strongly correlated many-body effects.

By construction, the exact TD density of the interacting system can then be calculated from a set of non-interacting, single-particle orbitals fulfilling the TD-KS equation (4) and reads

\[ \rho(\textbf{r}, t) = \sum_{k=1}^{N} |\phi_k(\textbf{r}, t)|^2. \] (6)

Further analysis from the minimum action principle shows that the exchange (xc) potential is then the functional derivative of that quantity in terms of the density,

\[ v_{\text{xc}}(\textbf{r}, t) = \frac{\delta S_{\text{xc}}}{\delta \rho(\textbf{r}, t)}, \] (7)
where \( S_{xc} \) includes all non-trivial many-body parts of the action. The above equations provide the starting ground for further derivations of the theory. Thus, in addition to the TD-KS scheme, other variants have been proposed across the years, which include the TD spin-DFT, the TD current-DFT, the TD linear response DFT and the basis-set DFT \cite{26}. Each method has its range of applicability, but discussing them is out of the scope of this chapter.

Here we focus on yet another implementation, the single-particle hydrodynamic approach or QFD-DFT, which it provides a natural link between DFT and Bohmian trajectories. The corresponding derivation is based on the realization that the density, \( \rho(r,t) \), and the current density, \( j(r,t) \) satisfy a coupled-set of “classical fluid”, Navier-Stokes equations:

\[
\frac{\partial \rho(r,t)}{\partial t} = -\nabla j(r,t), \tag{8}
\]

\[
\frac{\partial j(r,t)}{\partial t} = P[\rho](r,t), \tag{9}
\]

with

\[
P[\rho](r,t) = -i\langle \Psi[\rho](t)|[j(r),H(t)]|\Psi[\rho](t)\rangle, \tag{10}
\]

being a functional of the density and with initial conditions \( \rho(r,t_0) \) and \( j(r,t_0) \).

One can finally show that the above coupled equations translate into one single particle nonlinear differential equation for the hydrodynamical wave function \( \Phi(r,t) = \rho(r,t)^{1/2}e^{iS(r,t)} \) in terms of potential energy functionals:

\[
\left(-\frac{1}{2}\nabla^2 + v_{\text{eff}}[\rho]\right)\Phi(r,t) = i\frac{\partial \Phi(r,t)}{\partial t}, \tag{11}
\]

with \( v_{\text{eff}}[\rho] \) being given by

\[
v_{\text{eff}}[\rho] = \frac{\delta E_{\text{el-el}}}{\delta \rho} + \frac{\delta E_{\text{nu-el}}}{\delta \rho} + \frac{\delta E_{\text{xc}}}{\delta \rho} + \frac{\delta T_{\text{corr}}}{\delta \rho} + \frac{\delta E_{\text{ext}}}{\delta \rho} \tag{12}
\]

and where \( j(r,t) = \rho(r,t)v(r,t) \), with \( \nabla S(r,t) = v(r,t) \). For many particle systems, this is still an open problem (see next Section for a new discussion). In Eq. (12), each term corresponds, respectively, to the interelectronic repulsion energy, the Coulomb nuclear-electron attraction energy, the exchange and correlation energy, the nonclassical correction term to Weizsäcker’s kinetic energy, and the electron-external field interaction energy functionals. A judicious choice in the form of the above functionals yields surprisingly good results for selected applications.
As a simple mathematical approach to QFD-DFT, let us consider that the $N$-electron system is described by the TD orbitals $\phi_k(r,t)$ when there is an external periodic, TD potential, for which we want to obtain the (TD) density $\rho(r,t)$. These orbitals can be expressed in polar form,

$$\phi_k(r,t) = R_k(r,t) e^{iS_k(r,t)},$$  \hspace{1cm} (13)

where the amplitudes $R_k(r,t)$ and phases $S_k(r,t)$ are real functions of space and time, and the former are subject to the normalization condition

$$\int \int R_k(r,t) \overline{R_l(r,t)} dr = \delta_{kl},$$  \hspace{1cm} (14)

where $\int_t$ denotes the time-averaged integration over one period of time. The kinetic energy associated with this (noninteracting) $N$-electron system reads now [10] as

$$T_{\delta_0}(\{R_k, S_k\})_t = \frac{1}{2} \sum_{k=1}^{N} \int \int \left\{ R_k(r,t) [\nabla^2 R_k(r,t)] - R_k(r,t) [\nabla S_k(r,t)]^2 \right\} dr.$$  \hspace{1cm} (15)

Similarly to the time-independent case, here we also assume the constraint that the sum of the squares of the $R_k$ gives the exact density $\rho(r,t)$, i.e.,

$$\sum_{k=1}^{N} R_k^2(r,t) = \rho(r,t).$$  \hspace{1cm} (16)

Moreover, we introduce an additional constraint: the conservation of the number of particles,

$$\sum_{k=1}^{N} \frac{\partial R_k^2}{\partial t} \left( = \frac{\partial \rho}{\partial t} \right) = -\nabla \cdot \mathbf{j},$$  \hspace{1cm} (17)

where $\mathbf{j}$ is the single-particle quantum density current vector. After minimizing Eq. (15) with respect to the $R_k$ (which is subject to the previous constraints), we reach the Euler-Lagrange equation

$$-\frac{1}{2} \nabla^2 R_k + v_{\text{eff}} R_k = \epsilon_k R_k,$$  \hspace{1cm} (18)

where $v_{\text{eff}}(r,t)$ and $\epsilon_k(r,t)$ are the Lagrange multiplier associated with the constraint defined in Eq. (16) and the conservation of the number of particles given by Eqs. (14) and (17), respectively. Moreover, $\epsilon_k(r,t)$ can be split up as a sum of two terms

$$\epsilon_k(r,t) = \epsilon_k^{(0)} + \epsilon_k^{(1)}(r,t).$$  \hspace{1cm} (19)
The quantity $\epsilon_k^{(0)}$ is a result of the normalization constraint, while $\epsilon_k^{(1)}$ are the Lagrange multipliers associated with the charge-current conservation defined by Eq. (17). On the other hand, if Eq. (18) is divided by $R_k$ we can reexpress the corresponding equation as

$$Q_k(r, t) + v_{\text{eff}}(r, t) = \epsilon_k(r, t)$$  \hspace{1cm} (20)

where $Q_k$ is the so-called quantum potential associated with the state $\phi_k$,

$$Q_k(r, t) = -\frac{1}{2} \nabla^2 R_k.$$  \hspace{1cm} (21)

Next, we minimize $T_s[\{R_k, S_k\}]_t$ with respect to $S_k$ to be subject to the constraint

$$\frac{\partial S_k}{\partial t} = -\epsilon_k(r, t).$$  \hspace{1cm} (22)

The resulting Euler-Lagrange equation is given by

$$\frac{\partial R_k^2}{\partial t} + \nabla \cdot (R_k^2 \nabla S_k) = 0.$$  \hspace{1cm} (23)

The coupled equations, Eqs. (18) and (23), provide a means of determining the exact TD density of the system of interest. We note that, at the solution point, the current vector is given by

$$j(r, t) = \sum_{k=1}^{N} R_k^2(r, t) \nabla S_k(r, t).$$  \hspace{1cm} (24)

Note that, in the limit that the time-dependence is turned off, the TD-DFT approach correctly reduces to the usual time-independent DFT one, since $\nabla S_k$ vanishes, Eqs. (17), (22) and (23) are identically satisfied, and Eq. (15) will reduce to the time-independent kinetic energy of an $N$-electron system.

IV. BOHMIAN MECHANICS. A TRAJECTORY PICTURE OF QUANTUM MECHANICS

A. Single-particle trajectories

Apart from the operational, wave or action-based pictures of Quantum Mechanics provided by Heisenberg, Schrödinger or Feynman, respectively, there is an additional, fully trajectory-based picture: Bohmian mechanics [20, 23]. Within this picture, the standard
quantum formalism is understood in terms of trajectories defined by very specific motion rules. Although this formulation was independently formulated by Bohm, it gathers two former conceptual ideas: (1) the QFD picture proposed by Madelung, and (2) the pilot role assigned to the wave function, proposed by de Broglie. In this way, the time-evolution or dynamics of the system is described as an ideal quantum fluid with no viscosity; the evolution of this flow of identical particles is “guided” by the wave function.

The Bohmian formalism follows straightforwardly from the Schrödinger one in the position representation after considering a change of variables, from the complex wave function field \( (\Psi, \Psi^*) \) to the real fields \( (\rho, S) \) according to the transformation relation:

\[
\Psi(r, t) = R(r, t) e^{iS(r,t)/\hbar},
\]
with \( \rho = R^2 \). Substituting this relation into the TD Schrödinger equation for a single particle of mass \( m \),

\[
i\hbar \frac{\partial \Psi(r, t)}{\partial t} = \left[ -\frac{\hbar^2}{2m} \nabla^2 + V(r) \right] \Psi(r, t),
\]
and then separating the real and imaginary parts from the resulting expression, two real coupled equations are obtained:

\[
\frac{\partial \rho}{\partial t} + \nabla \cdot \left( \rho \frac{\nabla S}{m} \right) = 0,
\]
\[
\frac{\partial S}{\partial t} + \frac{(\nabla S)^2}{2m} + V_{\text{eff}} = 0,
\]
where

\[
V_{\text{eff}} = V + Q = V - \frac{\hbar^2}{2m} \frac{\nabla^2 R}{R} = V - \frac{\hbar^2}{4m} \left[ \frac{\nabla^2 \rho}{\rho} - \frac{1}{2} \left( \frac{\nabla \rho}{\rho} \right)^2 \right]
\]
is an effective potential resulting from the sum of the “classical” contribution, \( V \), and the so-called quantum potential, \( Q \), which depends on the quantum state via \( \rho \) —or, equivalently, on the instantaneous curvature of the wave function via \( R \). Note that in the case \( V = v_{\text{eff}} \) and \( \Psi \) given as in the previous Section, one gets \( V_{\text{eff}} = \epsilon_k \) or \( V_{\text{eff}} = \epsilon_k(r,t) \) depending on whether we are considering the time-independent or the TD case, respectively. The action of the whole ensemble through the wave function on the particle motion can be seen as a dynamical manifestation of quantum nonlocality. Equation (27a) is the continuity equation for the particle flow (or the probability density, from a conventional viewpoint) and (27b) is a generalized (quantum) Hamilton-Jacobi equation. As in classical mechanics,
the characteristics or solutions, $S$, of Eq. \((27)\) define the particle velocity field,

$$\mathbf{v} = \frac{\nabla S}{m}, \quad (29)$$

from which the quantum trajectories are known. Uncertainty arises from the unpredictability in determining the particle initial conditions—distributed according to $\rho(\mathbf{r}, t = 0)$—, but not from the impossibility to know the actual (quantum) trajectory pursued during its evolution.

An alternative way to obtain the quantum trajectories is by formulating Bohmian mechanics as a Newtonian-like theory. Then, Eq. \((29)\) gives rise to a generalized Newton’s second law,

$$m \frac{d\mathbf{v}}{dt} = -\nabla V_{\text{eff}}. \quad (30)$$

This formulation results very insightful; according to Eq. \((30)\), particles move under the action of an effective force, $-\nabla V_{\text{eff}}$, i.e., the nonlocal action of the quantum potential here is seen as the effect of a (nonlocal) quantum force. From a computational viewpoint, this formulation results very interesting in connection to quantum hydrodynamics \cite{21, 27}. Thus, Eqs. \((27)\) can be reexpressed in terms of a continuity equation and a generalized Euler equation. As happens with classical fluids, here also two important concepts come into play: the quantum pressure and the quantum vortices \cite{28} which occur at nodal regions where the velocity field is rotational.

Since TD-DFT is being applied to scattering problems in its QFD version, two important consequences of the nonlocal nature of the quantum potential worth stressing in this regard. First, relevant quantum effects can be observed in regions where the classical interaction potential $V$ becomes negligible and, more important, where $\rho(\mathbf{r}, t) \approx 0$. This happens because quantum particles respond to the “shape” of $\Psi$, but not to its “intensity”, $\rho(\mathbf{r}, t)$—notice that $Q$ is scale-invariant under the multiplication of $\rho(\mathbf{r}, t)$ by a real constant. Second, quantum-mechanically the concept of asymptotic or free motion only holds locally. Following the classical definition for this motional regime,

$$m \frac{d\mathbf{v}}{dt} \approx 0, \quad (31)$$

this means in Bohmian mechanics that $\nabla V_{\text{eff}} \approx 0$, i.e., the local curvature of the wave function has to be zero (apart from the classical-like requirement that $V \approx 0$). In scattering experiments this condition is satisfied along the directions specified by the diffraction
channels \(29\); in between, although \(V \approx 0\), particles are still subject to strong quantum forces.

**B. Bohmian trajectories describing many-body systems**

In the case of a many-body problem, the Bohmian mechanics for an \(N\)-body dynamics follows straightforwardly from the one for a single system, but replacing Eq. (25) by

\[
\Psi(r_1, r_2, \ldots, r_N; t) = R(r_1, r_2, \ldots, r_N; t) e^{iS(r_1, r_2, \ldots, r_N; t)/\hbar},
\]

with \(\rho(r_1, r_2, \ldots, r_N; t) = R^2(r_1, r_2, \ldots, r_N; t)\). If we are interested in the density of a single particle, we need to “trace” over the remaining \(N-1\) degrees of freedom in the corresponding density matrix (see Sec. IV C). On the other hand, in order to know the specific trajectory pursued by the particle associated with the \(k\)th degree of freedom, we have to integrate the equation of motion

\[
v_k = \frac{\nabla_k S}{m},
\]

where \(\nabla_k = \partial/\partial r_k\). The velocity field is irrotational in nature except at nodal regions. Obviously, there will be as many equations of motion as degrees of freedom. Note that since each degree of freedom represents a particle that is interacting with the remaining \(N-1\) particles in the ensemble, the corresponding trajectory will be strongly influenced by the evolution of those other \(N-1\) particles. This *entanglement* is patent through the quantum potential, which is given here as

\[
Q = -\frac{\hbar^2}{2m} \sum_{k=1}^{N} \frac{\nabla_k^2 R}{R},
\]

where \(Q = Q(r_1, r_2, \ldots, r_N; t)\) is nonseparable and, therefore, strongly nonlocal. Note that this nonlocality arises from correlation among different degrees of freedom, which is different from the nonlocality that appears when considering symmetry properties of the wave function, not described by the Schrödinger equation but by quantum statistics. In this sense, we can speak about two types of entanglement: symmetry and dynamics. The general \(N\)-body wave function is entangled in both aspects.

Now, if the many-body (electron) problem can be arranged in such a way that the many-body, nonseparable wave function is expressed in terms of a separable wave function which
depends on \( N \) single-particle wave functions (Hartree approximation), i.e.,

\[
\Psi(r_1, r_2, \ldots, r_N; t) = \Pi_{k=1}^{N} \psi_k(r_k; t) = \Pi_{k=1}^{N} R_k(r_k; t) e^{iS_k(r_k; t)/\hbar},
\]

(35)

then, in terms of trajectories, we find a set of uncoupled equations of motion,

\[
\bar{v}_k = \frac{\nabla_k S_k}{m},
\]

(36)

which will only depend implicitly (through \( v_{\text{eff}} \)) on the other particles. Note that the factorization of the wave function implies that the quantum potential becomes a separable function of the \( N \) particle coordinates and time,

\[
Q = -\frac{\hbar^2}{2m} \sum_{k=1}^{N} \nabla_k^2 R_k = \sum_{k=1}^{N} Q_k,
\]

(37)

where each \( Q_k \) measures the local curvature of the wave function associated with the \( i \)th orbital associated to the corresponding particle. Therefore, each degree of freedom can be studied separately from the rest (with the exception that we have to take into account the mean field created by the remaining \( N-1 \) particles). Factorizability implies physical independence, statistical independence or, in other words, that particles obey Maxwell-Boltzmann statistics (they are distinguishable) and the associate wave function is, therefore, not entangled.

In TD-DFT, the wave function is antisymmetrized and, therefore, nonfactorizable or entangled. However, as said above, it is not entangled from a dynamical point of view because the quantum forces originated from a nonseparable quantum potential like Eq. (34) are not taken into account.

C. The reduced quantum trajectory approach

In Sec. [IV.3] we have considered the problem of the reduced dynamics from a standard DFT approach, i.e., in terms of single-particle wave functions from which the (single-particle) probability density is obtained. However, one could also use an alternative description which arises from the field of decoherence. Here, in order to extract useful information about the system of interest, one usually computes its associated reduced density matrix by tracing the total density matrix, \( \hat{\rho}_t \) (the subscript \( t \) here indicates time-dependence), over the environment degrees of freedom. In the configuration representation and for an environment
constituted by $N$ particles, the system reduced density matrix is obtained after integrating

$$\tilde{\rho}(\mathbf{r}, \mathbf{r}'; t) = \int \langle\mathbf{r}, \mathbf{r}_1, \ldots, \mathbf{r}_N|\Psi(t)\rangle\langle\Psi(t)|\mathbf{r}', \mathbf{r}_1, \ldots, \mathbf{r}_N\rangle d\mathbf{r}_1 d\mathbf{r}_2 \cdots d\mathbf{r}_N. \quad (38)$$

The system (reduced) quantum density current can be derived from this expression, being

$$\tilde{j}(\mathbf{r}, t) \equiv \frac{\hbar}{m} \mathrm{Im}\left[\nabla_r \tilde{\rho}(\mathbf{r}, \mathbf{r}'; t)\right] \bigg|_{\mathbf{r}'=\mathbf{r}}, \quad (39)$$

which satisfies the continuity equation

$$\dot{\tilde{\rho}} + \nabla \tilde{j} = 0. \quad (40)$$

In Eq. (40), $\tilde{\rho}$ is the diagonal element (i.e., $\tilde{\rho} \equiv \tilde{\rho}(\mathbf{r}, \mathbf{r}; t)$) of the reduced density matrix. Taking into account Eqs. (39) and (40), now we define the velocity field, $\dot{\mathbf{r}}$, associated with the (reduced) system dynamics as

$$\tilde{j} = \tilde{\rho} \dot{\mathbf{r}}, \quad (41)$$

which is analogous to the Bohmian velocity field. Now, from Eq. (41), we define a new class of quantum trajectories as the solutions to the equation of motion

$$\dot{\mathbf{r}} \equiv \frac{\hbar}{m} \frac{\mathrm{Im}[\nabla_r \tilde{\rho}(\mathbf{r}, \mathbf{r}'; t)]}{\mathrm{Re}[\tilde{\rho}(\mathbf{r}, \mathbf{r}'; t)]} \bigg|_{\mathbf{r}'=\mathbf{r}}. \quad (42)$$

These new trajectories are the so-called reduced quantum trajectories [30], which are only explicitly related to the system reduced density matrix. The dynamics described by Eq. (42) leads to the correct intensity (whose time-evolution is described by Eq. (40)) when the statistics of a large number of particles is considered. Moreover, it is also straightforward to show that Eq. (42) reduces to the well-known expression for the velocity field in Bohmian mechanics when there is no interaction with the environment.

V. FINAL DISCUSSION AND CONCLUSIONS

Nowadays the success of DFT and TD-DFT is out of question in both the Physics and Chemistry communities. The numerical results obtained are most of cases in good agreement to those issued from experimental and other theoretical methods with a relative small computational effort. However, in this chapter, our goal has been to present the TD-DFT
from a Bohmian perspective and to analyze, from a conceptual level, some of the aspects which are deeply rooted in DFT.

Working with a system of fermions, where the total wave function has to be antisymmetrized with respect to two-particle interchanges, it gives rise to the appearance of new quantum forces from the quantum potential which are not described by the DFT Hamiltonian. The DFT wavefunction will be then nonfactorizable and, therefore, entangled from a symmetry point of view but not from a dynamical point of view. In this sense, as mentioned above, the effective potential $V_{\text{eff}}$ plays a fundamental role not only in the nonlocality of the theory, but in the so-called invertibility problem of the one-to-one mapping up to an additive time-dependent function between the density and $v_{\text{eff}}$. In our opinion, the central theorems of TD-DFT should be written in terms of $V_{\text{eff}}$ instead of $v_{\text{eff}}$, since the quantum potential is also state-dependent and a functional of the density. An infinite set of possible quantum potentials can be associated with the same physical situation and Schrödinger equation, and therefore the invertibility should be questioned. Moreover, for scattering problems, when $v_{\text{eff}}$ is negligible in the asymptotic region, the quantum potential can be still active and the time propagation should be extended much farther in order to obtain a good numerical convergence.

In Bohmian mechanics, the way how the full problem is tackled in order to obtain operational formulas can determine dramatically the final solution due to the context-dependence of this theory. More specifically, developing a Bohmian description within the many-body framework and then focusing on a particle is not equivalent to directly starting from the reduced density matrix or from the one-particle TD-DFT equation. Being well aware of the severe computational problems coming from the first and second approaches, we are still tempting to claim that those are the most natural ways to deal with a many-body problem in a Bohmian context.

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