Bohmian Pathways into Chemistry: A Brief Overview

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Perhaps because of the popularity that trajectory-based methodologies have always had in Chemistry and the important role they have played, Bohmian mechanics has been increasingly accepted within this community, particularly in those areas of the theoretical chemistry based on quantum mechanics, e.g., quantum chemistry, chemical physics, or physical chemistry. From a historical perspective, this evolution is remarkably interesting, particularly when the scarce applications of Madelung’s former hydrodynamical formulation, dating back to the late 1960s and the 1970s, are compared with the many different applications available at present. As also happens with classical methodologies, Bohmian trajectories are essentially used to described and analyze the evolution of chemical systems, to design and implement new computational propagation techniques, or a combination of both. In the first case, Bohmian trajectories have the advantage that they avoid invoking typical quantum-classical correspondence to interpret the corresponding phenomenon or process, while in the second case quantum-mechanical effects appear by themselves, without the necessity to include artificially quantization conditions. Rather than providing an exhaustive revision and analysis of all these applications (excellent monographs on the issue are available in the literature for the interested reader, which can be consulted in the bibliography here supplied), this Chapter has been prepared in a way that it may serve the reader to acquire a general view (or impression) on how Bohmian mechanics has permeated the different traditional levels or pathways to approach molecular systems in Chemistry: electronic structure, molecular dynamics and statistical mechanics. This is done with the aid of some illustrative examples — theoretical developments in some cases and numerical simulations in other cases.

1.1. Introduction

Quantum mechanics has acquired a prominent role over the years in different areas of the theoretical chemistry, including the quantum chemistry, the physical chemistry or the chemical physics, as well as other areas at the borderline between Chemistry and Physics. It is not surprising that the idea of analyzing and understanding quantum-mechanically chemical systems by means of a hydrodynamic language, which dates back to the late 1960s and early 1970s [1–6], has also permeated all these areas. Bohmian mechanics [7–17], the widespread denomination that is now used for the hydrodynamic picture or reformulation of the Schrödinger equation [18] — formerly suggested by Madelung in 1926 [19] —, has thus made its own pathways throughout Chemistry [15, 17, 20, 21]. This is not a minor issue
taking into account that Chemistry is at present a sort of crossroad for a number of overlapping disciplines, such as atomic and molecular physics, optics and quantum optics, solid state physics, condensed matter physics, chemical physics, nanotechnology, biochemistry or molecular chemistry, and more recently also different branches associated with the so-called quantum technologies [22], such as quantum information and computation [23, 24], chemicals and materials quantum design [25–29] or quantum biology [30–33].

A question that naturally arises is why Bohmian mechanics now receives more attention than about half a century ago, when it was hardly considered a worthless hidden-variable theory almost relegated to oblivion — a source of much controversy within the quantum foundations community (something that unfortunately has survived to date without a truly deep physical justification). Perhaps a suitable answer can be given taking on a pragmatic view on what Bohmian mechanics is and what Bohmian mechanics is not in simple terms, that is, at a very basic (that is, pragmatic) level, without entering a lengthy discussion on the issue. In this sense, on the one hand, we find a hydrodynamic model that describes the evolution (actually, diffusion) of a quantum system in time throughout the corresponding configuration space — just in the same way classical hydrodynamic systems behave —, in compliance with Madelung’s view [19]. The particularity of the quantum system versus a classical hydrodynamic one is that, a priori, if no further specifications are made, quantum pure states evolve as ideal, inviscid fluids [34]. This does not introduce any new interpretation for the quantum mechanics based on the presence or not of external observers, since the mathematics of the Schrödinger equation are just the mathematics of the diffusion equation with a pure imaginary diffusion constant, as noticed by Fürth [35] or Comisar [36]. Actually, the idea of devising quantum systems as quantum fluids has also been a viewpoint shared by others apart from Madelung, as Landau [37] or London [38], and is of common use in solid state physics and condensed matter physics (actually, in many cases, Madelung is not even credited for it).

On the other hand, we have de Broglie’s pilot wave theory [39–41], which after the 5th Solvay Conference and further (rather tough) discussions has reached us as the (oversimplified) concept of de Broglie’s hypothesis: electrons (and any kind of material system, in general, from tiny electrons or neutrons to large, complex organic molecular compounds) display both particle-like and wave-like properties in the same way that light is also characterized by both properties (after Einstein’s 1905 explanation for the photoelectric effect). However, the idea formerly supported by de Broglie in 1924 (and taken as a basis by Schrödinger in the derivation of his famous equation) is that quantum systems consist of two subjects: a carrier (pilot) wave field and a carried singularity (point-like) representing the electron. Unlike Madelung’s proposal, de Broglie’s one already implies a certain way to understand or “interpret” quantum systems, and therefore it found too much opposition at the Solvay Conference, eventually being rejected in its former version. However, from the hydrodynamic perspective mentioned above, there is nothing wrong with it, since de Broglie’s approach is, in the end, only a way to describe with a quantum language the evolution of, saying it in simple terms, a leaf re-
leased on the surface of a stream: the leaf conveys information about the evolution of the stream, but tells nothing about the evolution of the elementary compounds of such a stream, which is still in compliance with the Copenhagen (Bohr’s) view. These streamlines thus allow a visualization of the evolution of the quantum fluid just as the path pursued by a (classical) tracer particle [42, 43] (e.g., charcoal dust) is used to follow the flow of a classical fluid [44, 45]. Since 2005, experiments with bouncing droplets in vibrating fluids, independently performed by the groups of Yves Couder and Emmanuel Fort in Paris [46–52] and John Bush in Boston [53–55], have become nice illustrations of a classical analog de Broglie’s proposal.

Madelung and de Broglie devised their approaches during the early days of quantum mechanics, when the theory was still being developed. About a quarter of a century afterwards, Bohm proposed another analogous model to challenge the formal and conceptual grounds of quantum mechanics, which was already a widely accepted theory. It is interesting to note, though, that Bohm’s approach, formerly suggested as a counterproof to von Neumann’s theorem on the impossibility of (local) hidden-variable theories compatible with quantum mechanics [7], gathers the flavors of both Madelung’s hydrodynamic formulation and the insight of de Broglie’s pilot-wave theory. The most remarkable aspect of Bohm’s suggestion is the fact that it emphasizes very clearly that quantum mechanics is intrinsically nonlocal, thus introducing a cutting-edge view of this theory that transcends the understanding of physical systems according to the principle of locality. This was the main reason for its rejection by the mid-1950s, until Bell decided to analyze such implications and formalize them about a decade later, producing his brilliant proof on the nonlocal nature of quantum mechanics in terms of an inequality. Some applications of Bohm’s started appearing by the late 1970s and during the 1980s and 1990s, where different physical problems typical of the quantum mechanics were translated into Bohm’s trajectory-based model. Nonetheless, the model was strongly attached to interpretational (metaphysical-like) connotations related to the measurement problem in quantum mechanics [56], and therefore it was often neglected or not taken too seriously by the community. The landscape started changing by the late 1990s, when it underwent a remarkable boost through its applications and potential interests in Chemistry, not only to describe and explain the dynamics exhibited by quantum systems, but also as a source of new computational tools, where the key element is precisely the Bohmian trajectory. Also the negative metaphysical (“surrealistic” [57]) connotations associated with Bohm’s trajectories started changing, since, in the end, they are properly defined from a formal viewpoint. For those familiarized with the treatment and solution of partial differential equations, such trajectories are just the curves arising from the method of characteristics, well-known in mathematical physics to solve finite-order partial differential equations [58]. In quantum mechanics, the method of quantum characteristics is applied, by analogy to its classical counterpart, to the flows in the configuration space defined by the Weyl-Wigner transform [59, 60], which eventually gives rise to the appearance of an infinite-order, with respect to the classical case, through the Moyal product [61] (in the classical limit, the bracket that defines this product becomes the Poisson bracket, which implies an order re-
duction due to the disappearance of nonlocal correlations). Alternatively, by virtue of a suitable decoupling between the phase and the amplitude of the wave function, Schrödinger’s equation can be recast in the form of a differential equation susceptible to also be solved by the method of characteristics, either in terms of real-valued trajectories [15, 62–64] or complex-valued ones [65–72].

From a historical perspective, it is remarkable the fact that Bohmian mechanics entered Chemistry from Madelung’s approach instead of Bohm’s one, more closely connected, perhaps, to Physics due to its deep metaphysical (interpretational) connotations discussed above, which are absent in Madelung’s one. Madelung’s approach, moreover, is in compliance with the tradition in Chemistry of appealing to pictorial representations of the systems under study (the pictorial view enabled by Bohmian mechanics was also a positive feature remarked by Bell [73]). Setting as our “coordinate origin” the two categories pointed out by Wyatt [15], namely analytic and synthetic, this acceptance and future development is even more understandable. Within the analytic approach [16, 17], first the wave function is propagated and then the Bohmian trajectories are obtained “on the fly” from its evolution. The goal of this approach is essentially interpretational, in a sense that it is used to understand what is going on with the system along its evolution in time. This kind of information complements the information obtained by means of other standard quantum techniques, thus providing a wider understanding of the underlying phenomenology. The synthetic approach [15], on the other hand, is aimed at computing quantum-mechanical quantities “on the fly” by directly synthesizing the Bohmian trajectories, that is, acting the other way around, without any need for pre-determining the wave function. In this case, the equations of motion for the trajectories are integrated alongside the quantum Hamilton-Jacobi equation (which rules the trajectory dynamics) and the continuity equation (which rules the “ensemble” dynamics).

The applications revisited in this Chapter constitute a brief account on both approaches, analytic and synthetic, within Chemistry. Due to the many problems where it has been applied and their different nature, the discussion will be limited to some illustrative examples that cover a series of aspects that are discussed with more detail in monographs on the issue [15, 17, 20, 21] as well as in the bibliography here provided. With this in mind, the Chapter has been organized as follows. An overview on the different levels at which molecular systems are traditionally studied is presented in Sec. 1.2, starting from the Born-Oppenheimer approximation [74] and then revisiting (in general terms) the methodologies available to deal with both electronic configuration [75–81] and dynamics, distinguishing in this latter case between molecular dynamics for a few degree-of-freedom systems [82, 83] and statistical mechanics (many-body problems) [84–89]. Analogously, a discussion on some fundamental aspects of Bohmian mechanics is introduced in Sec. 1.3. Some specific illustrations of the application of Bohmian mechanics to problems typical of the levels mentioned before are described in Sec. 1.4. Finally, a general, summarizing reflection on the matter in Sec. 1.5 concludes this Chapter.
1.2. Approaching molecular systems at different levels

Molecular systems typically include a rather large number of degrees of freedom, which makes unaffordable their direct study. Different approximations and/or approaches have thus been considered to cope with this inconvenience. Usually, given the different time-scales involved in the dynamics of the different components, namely nuclei and electrons, the first important approximation is the so-called Born-Oppenheimer approximation [74], which allows us to simplify the study of any molecular system (this notion is taken here in a broad sense, thus including simple molecules, solid surfaces, polymeric chains, clusters, crystalline structures, etc.) by splitting it into its nuclear and electronic parts. This division has led to three levels or types of methodologies in Chemistry to study and explain molecular systems: electronic structure [75–81], dynamics [82, 83] and statistics [84–89].

Electronic structure methods (e.g., valence bond theory, \textit{ab initio} methods, density functional theory, etc.) are aimed at obtaining properties associated with the electronic configuration, such as the chemical bonding and intermolecular forces [81]. Basically all these methods are based on quantum mechanics and are included under what is known as quantum chemistry. Molecular dynamics and statistical mechanics methods are based either in classical mechanics or in quantum mechanics, and essentially constitute the scope of the chemical physics and physical chemistry. Molecular dynamics methods, e.g., wave-packet propagation methods, are used to describe the properties associated with the nuclear motion (dynamics), necessary to understand chemical reaction processes, for example. In this case, the role of electrons manifests through effective potential functions, namely potential energy surfaces, generated from their bonding to the nuclei. At this point, it is worth highlighting that, for practical purposes, a division has been considered between a few degree-of-freedom treatments, which are henceforth denoted as molecular dynamics methods, and those to deal with many-body problems, which will be referred to as statistical mechanics methods. This convenient classification allows us to distinguish between methods and problems where the full system dynamics is relevant, from those where we are more interested in statistical properties or we only need to focus our attention on a part of the total system (neglecting the remaining “environmental” degrees of freedom). Bearing this in mind, when the number of nuclei involved is relatively large, we shall talk of statistical methods (e.g., molecular dynamics, Monte Carlo, path integrals, etc.), which include methodologies and theories developed to tackle open quantum systems, complex systems, systems far from equilibrium, etc., all of them approximate.

Of course, sometimes the Born-Oppenheimer approximation cannot be used and the above division can no longer be considered. In such cases, one needs to consider a full treatment of the molecular system (electronic plus nuclear parts) using “on the fly” methods that take into account the interaction between electrons and nuclei at the same time in a sort of two-step feedback process: electrons accommodate to a certain nuclei configuration, which is then used to evolve the nuclei and, from the latter new rearrangement, a new electron configuration is determined, and so on, until the full dynamical-configurational simulation is completed. Dealing with this kind of systems is often complicated and highly com-
putationally demanding, although different methods have been developed to deal with them [90–92], but this is a topic that goes beyond the scope of this Chapter.

1.2.1. The Born-Oppenheimer approximation

Molecular systems are usually characterized by a large number of degrees of freedom, which makes complicated and even computationally prohibitive their study. To circumvent this inconvenience we can take advantage of the remarkable mass difference between nuclei and electrons ($m_n \gg m_e$), which physically translates into very different time scales ruling their respective dynamics (electrons are faster than nuclei) as well as very different kinetic energies ($\langle p_n^2 \rangle / 2m_n \ll \langle p_e^2 \rangle / 2m_e$). Accordingly, at a first level of approximation, it is reasonable to assume that nuclei are almost at rest, while electrons move under the action of the effective potential field generated by point-like particles (the nuclei) that occupy definite positions. This is the basic idea behind the Born-Oppenheimer approximation, which we can also find in other contexts where there is an important asymmetry between time scales and that serves us to simplify the dynamical study of different sets of degrees of freedom. For example, in molecular dynamics it can be used to describe some degrees of freedom according to Newton’s equation (classical trajectories) under the action of some effective generalized potential functions, while other degrees of freedom evolve quantum-mechanically (Bohmian trajectories). A simple illustrative example of this splitting will be seen with more detail in Sec. 1.4.5. The same idea can also be found in the context of the theory of open quantum systems [86–89], where large systems can be split up into two subsystems, each ruled by its own dynamical time scales (see Sec. 1.2.4). Depending on the difference between these scales and the coupling strength between the two subsystems, more or less complex treatment can be devised to tackle the corresponding problem.

More specifically, the Born-Oppenheimer approximation arises in Chemistry as a need for solving one of its major problems: finding solutions of the non-relativistic, time-independent Schrödinger equation that describes a molecular system,

$$\hat{H} \Phi_\ell(\vec{R}_1, \vec{R}_2, \ldots, \vec{R}_M, q_1, q_2, \ldots, q_N) = E_\ell \Phi_\ell(\vec{R}_1, \vec{R}_2, \ldots, \vec{R}_M, q_1, q_2, \ldots, q_N).$$

(1.1)

The energy eigenvalues that we extract from this equation serve us to determine the electronic configuration of the system and, therefore, chemical and physical properties, such as bonding, electric, magnetic, phase transitions and states of matter, geometry, etc. In Eq. (1.1), $\Phi_\ell$ stands for the wave function of the $\ell$th state of the molecular system, which depends on the $3N$ space coordinates $\{\vec{r}_i\}_{i=1}^N$ and the $N$ spin coordinates $\{s_i\}_{i=1}^N$ of its electrons, collectively denoted as $\{q_i\}_{i=1}^N$, and the $3M$ space coordinates of its nuclei $\{\vec{R}_A\}_{A=1}^M$; $E_\ell$ is the eigenenergy associated with the state $\Phi_\ell$; and $\hat{H}$ is the Hamiltonian describing the $M$ nuclei and $N$ electrons as well as their interactions. In the absence of external fields (e.g., gravitational, electromagnetic, etc.), $\hat{H}$ reads (in atomic units) as

$$\hat{H} = -\frac{1}{2N} \sum_{i=1}^N \nabla_{\vec{r}_i}^2 + \frac{1}{2} \sum_{i=1}^N \sum_{j>i}^N \frac{1}{r_{ij}} - \frac{1}{2} \sum_{A=1}^M \frac{\nabla^2 \vec{R}_A}{M_A} + \sum_{A=1}^M \sum_{B>A}^M \frac{Z_A Z_B}{R_{AB}} - \sum_{i=1}^N \sum_{A=1}^M \frac{Z_A}{r_{iA}},$$

(1.2)
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where \( r_{ij} = |\vec{r}_i - \vec{r}_j| \) is the distance between the \( i \)th and \( j \)th electrons (the same holds for \( r_{iA} \) and \( R_{AB} \) for the electron-nucleus and nucleus-nucleus distances, respectively). The first two terms in Eq. (1.2) are the total electron kinetic energy and the electron-electron repulsive potential interaction, respectively, and represent the (full) electronic contribution to the Hamiltonian, which we generically denote as \( \hat{h}_e \). Similarly, the third and fourth terms describe the total nuclear kinetic energy and the nucleus-nucleus repulsive potential interaction, respectively, which we gather under the label \( \hat{H}_n \). Finally, the fifth term gives the attractive electron-nucleus electrostatic interaction, which will be labeled as \( \hat{V}_{en} \), since it couples the electronic and nuclear motions. Accordingly, Eq. (1.2) can be expressed in a more compact form as

\[
\hat{H} = \hat{H}_n + \hat{h}_e + \hat{V}_{en},
\]

(1.3)

which has the same form of the generic potentials in the theory of open quantum systems [86–89],

\[
\hat{H} = \hat{H}_S + \hat{H}_E + \hat{V}_{\text{int}},
\]

(1.4)

where the full system is partitioned into two subsystems: the system of interest (\( S \)) and a surrounding environment or bath (\( E \)), with their interaction being described by the term \( \hat{V}_{\text{int}} (= \hat{V}_{en}) \).

At this level of approximation (it is here where the Born-Oppenheimer approximation comes into play), the nuclei are assumed to have zero motion. Therefore, for a certain fixed position of all the involved nuclei, i.e., what we call a nuclear configuration, only the second and third terms in (1.3) are relevant, i.e.,

\[
\hat{H}_e = \hat{h}_e + \hat{V}_{en}.
\]

(1.5)

The description of the molecular system thus only depends on the distribution of the electrons (electronic cloud) around the nuclei, which play the role of a fixed environment that acts upon the electrons through \( \hat{V}_{en} \), but that do not feel any back-action from the electrons. The total wave function of the system can then be factorized and represented as the product of two separate wave functions, one accounting for the electronic cloud and the other for the ensemble of nuclei. That is, we have

\[
\Phi_\ell(\vec{R}_1, \vec{R}_2, \ldots, \vec{R}_M, q_1, q_2, \ldots, q_N) \\
\approx \varphi^{(\ell)}_{n,M}(\vec{R}_1, \vec{R}_2, \ldots, \vec{R}_M) \otimes \phi^{(\ell)}_{e,N}(q_1, q_2, \ldots, q_N),
\]

(1.6)

where \( \varphi^{(\ell)}_{n,M} \) and \( \phi^{(\ell)}_{e,N} \) denote \( M \)- and \( N \)-particle wave functions, respectively. Notice that each electronic coordinate depends parametrically on all the nuclear ones, i.e., \( q_i = q_i(\vec{R}_1, \vec{R}_2, \ldots, \vec{R}_M) \), for \( i = 1, 2, \ldots, N \), but not vice versa. After this factorization, the total energy of the system, obtained from the partitioned Hamiltonian (1.2), reads as

\[
E_{\text{tot}} = E_n + E_e,
\]

(1.7)

which, as can be seen, consists of the sum of two separate terms. The first term,

\[
E_n = \sum_{A=1}^{M} \sum_{B>A}^{M} \frac{Z_A Z_B}{R_{AB}},
\]

(1.8)
is a constant associated with the nucleus-nucleus Coulomb-type repulsive interaction, which can be determined either classically or quantum-mechanically, depending on the degree of sophistication of the method considered (and the accuracy requested). It is a constant, because it only depends on the position of the nuclei, which is assumed to be, by hypothesis, fixed. The second term,

$$E^{(f)}_e = \langle \phi^{(f)}_e | \hat{H}_e | \phi^{(f)}_e \rangle,$$

(1.9)

corresponds to the expectation value of the Hamiltonian (1.5) in the electronic state $\phi^{(f)}_e$. Unlike the nuclear term, the electronic one changes each time the nuclear configuration changes; all values generated in this way provide us with the potential energy surface associated with the molecular system under study, from which we eventually determine dynamical properties (e.g., ionization and photoionization, isomerization, reaction and scattering rates, electron transfer properties, diffraction, etc.).

### 1.2.2. Electronic configuration

As seen above, once the nuclear and electronic parts of the full molecular Hamiltonian are specified and split up by virtue of the Born-Oppenheimer approximation, the next step consists in solving the Schrödinger equation for the electronic Hamiltonian (1.5). The main goal of electronic structure methods is to obtain “exact” quantum energy states by further factorizing the problem, recasting the total poly-electronic wave function $\phi^{(f)}_{e,N}$ as a product of uncorrelated, single-electron wave functions, $\phi^{(f)}_{e,j}$:

$$\phi^{(f)}_{e,N}(q_1, q_2, \ldots, q_N) \rightarrow \prod^{N}_{j=1} \phi^{(f)}_{e,j}(q_j),$$

(1.10)

where the products combine in the form of Slater determinants in order to preserve the corresponding electron antisymmetry properties. These wave functions are plugged into their corresponding reduced Schrödinger equations, characterized by a single-particle Hamiltonian, $\hat{h}_{e,j}$, which is a function of an effective potential where the interaction with the other $N-1$ electrons is accounted for as a sort of average or mean effective field — in this sense, the $N$ electrons are commonly regarded as noninteracting. Then, after a variational process in which the energy, assumed to be a functional of the single-particle probability density, is required to be an extremum, both the “correct” wave function (1.10) and energy (1.7) are found.

After proceeding in that way, the electronic structure of the molecular system is determined, which is the same to say how electrons distribute throughout the system. With this information we can obtain the system chemical properties, such as chemical bonding, intermolecular interactions, electronic charge distributions, dipole and multipole moments or vibrational/rotational frequencies, for instance. Now, only in the case of the hydrogen atom, the corresponding Schrödinger equation can be exactly solved; for any other atomic or molecular system, involving three or more particles, different approximate approaches have been proposed in the literature [76–80] to tackle the problem of determining their electronic configurations. These approaches or methodologies arise basically from two models [93]: the wave model and the density matrix model.
In the wave model each atom is assumed to be a point-like, positively charged nucleus surrounded by an electronic cloud, which is associated with a certain orbital and represents the electron probability distribution in configuration space. The two types of theories arisen from this model are the valence bond theories and the molecular orbital theories. Valence bond theories [94] are based on the assumption that orbitals primarily localize on each nuclei (atomic orbitals), thus they essentially focus on pairwise interactions, and therefore establish a direct link with the classical chemical models based on the drawings of bonds typical of Lewis structures. Though not very common nowadays, the concepts such as resonance [95] (chemical aromaticity) and orbital hybridization [96] arise from this theory.

Molecular orbital theories [76–78], on the contrary, consider delocalized orbitals covering the whole molecule (molecular orbitals). Thus, the molecular orbital wave function is expressed as a linear combination of atomic orbitals (Slater determinants). These atomic orbitals can be hydrogen-like or Gaussian functions. The basic method within the molecular orbital approach is the Hartree-Fock (HF) method, an \emph{ab initio} approach based on assuming that $\phi^{(f)}_{e,N}$ is given by a Slater determinant, which leads to a set of $N$ coupled mono-electronic Schrödinger equations. In these equations, the electron-electron repulsion interactions involved in $\hat{h}_e$ are accounted for by a mean field interaction (i.e., the averaged action of the $N-1$ remaining electrons), thus neglecting electron correlation. In those cases where large molecules are considered and the HF method becomes inoperative, one can apply the so-called semiempirical molecular quantum-mechanical methods (e.g., the Hückel and extended Hückel methods or the Pariser-Parr-Pople method), where a simple Hamiltonian plus a set of fitting parameters are used to adjust the experimental data. On the other hand, within the \emph{ab initio} stream, there are different routes to tackle the problem of the electron correlation, and therefore to improve the HF results, such as the post-Hartree-Fock methods (e.g., configuration interaction, coupled cluster or Møller-Plesset), the multi-configurational self-consistent field or the multireference configuration interaction.

Regarding the density matrix model [79, 97], the interest in developing this type of methodology arises as a need from the very high computational demand involved in the study of large molecular systems by means of \emph{ab initio} methodologies. Thus, although the latter are more accurate physically, this accuracy is sacrificed in order to get computational advantages. The first attempt in this direction is the Thomas-Fermi model [98, 99], where the electron kinetic energy of an atom is expressed as a functional of the atom electronic distribution. This model is the precursor of the modern density functional theory [79] (DFT), where the fundamental physical information about the molecular system is obtained from a single-particle density in a three-dimensional space, derived variationally either within a time-independent framework [79] (ground state) or a time-dependent one [100, 101] (excited states). Nowadays, DFT is a very popular calculation method in quantum chemistry, as well as in solid state physics, due to its computational simplicity combined with its (numerical) accuracy. Also within the density matrix model it is worth stressing the role of those approaches which are aimed at including the electronic correlation, utilizing for such a purpose a reduced density matrix formal-
ism [102–116].

By changing the positions of the nuclei, one obtains different values of the electronic energy, thus describing a multidimensional energy surface parameterized in terms of the nuclei positions, \( \{ \vec{R}_A \}_{A=1}^M \). This is the so-called *potential energy surface* or Born-Oppenheimer surface, which reflects the configuration of the molecular system and determines its dynamical behavior (i.e., its physical/chemical properties). An alternative approach to obtain the potential energy surface of a molecular system is by using *molecular mechanics* or *force field methods*. Unlike the previously described methods, molecular mechanics is not based on quantum mechanics, but on a classical treatment of systems. In this case, the system is modeled by a collection of atoms (by “atom” it is assumed a single unity rather than a true physical atom) held together by spring-like force functions (force fields) and a corresponding set of fitting parameters. Each atom is characterized by a radius (usually, the van der Waals one), a charge and polarizability, and the potential energy surface is obtained by minimizing some energy functional at different nuclei positions using some optimization method (e.g., the Metropolis algorithm or the Monte Carlo method). Strictly speaking, these methods cannot be considered electronic structure ones, since electrons are not explicitly taken into account. However, they are assumed to be in an optimal distribution around the fixed nuclei positions, and therefore are implicitly responsible for the nuclear structural arrangement. Furthermore, in order to improve the performance of these methods, hybrid quantum mechanical molecular mechanics approaches are considered [117], which combine “on the fly” molecular mechanics with forces evaluated quantum-mechanically from either *ab initio* or DFT calculations.

Finally, it is also worth mentioning the availability of schemes based on topology, devised to analyze the structures (potential energy surfaces) obtained and determine, for example, eventual *reaction paths* or *minimum energy paths*, i.e., the paths connecting reactants with products following steepest descent curves [118] (curves with the fastest descent from a potential hill to a valley). These paths are used to understand and interpret chemical reactions as well as to determine kinetic constants, and therefore reaction rates without involving any dynamical simulation. This is part of what is known as mathematical chemistry.

1.2.3. *Dynamics of “small” molecular systems*

Once the electronic structure — or, equivalently, the effective interaction among nuclei due to the combination of the electromagnetic interaction and the quantum nature of the electrons — is determined and characterized by a potential energy surface, the next step consists in obtaining properties associated with the motion of the nuclei, which occurs at slower timescales — actually, many times it happens that the motion refers to some associated effective degrees of freedom, e.g., vibrational or rotational modes, rather than the nuclei themselves, which allows to further simplify the study of the full system. This procedure not only provides dynamical information about the system, but also allows us to test the accuracy of the potential energy surfaces, previously obtained by means of the electronic structure methods described in previous section, by comparing the corresponding
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Simulations with the experimental data recorded (e.g., the potential energy surface characterizing a certain metal surface can be compared with the real surface by computing the associated Bragg peaks and then comparing this result with the experimental diffraction pattern). And, through this procedure, we also test the accuracy and suitability of the electronic configurations computed.

To tackle the problem of the quantum dynamics, there are basically two approaches [119, 120]: time-independent and time-dependent. Due to the complexity involved in solving the time-dependent Schrödinger equation, historically the time-independent approach was first developed. By the 1960s, different time-dependent classical and quantum-mechanical numerical schemes started to developed, this also being the starting point of computational chemistry. This is the reason why former calculations and numerical schemes in electronic structure as well as in dynamics, with the obtention of spectral lines or collision cross sections, were mostly developed within the first 25 years of quantum mechanics. However, in the case of the dynamics, it is worth stressing that part of the work was already done: the time-independent Schrödinger equation is analogous to the Helmholtz equation that appears in classical wave theory and electromagnetism, so many solutions were already known since the XIXth century [121]. In the case of hard-wall like potential models, one deals with standard boundary condition problems, either in bound systems to find spectral lines, or in the continuum to determine scattering cross sections.

For space-dependent potentials, such as those describing bound systems or tunneling problems [122, 123], also electromagnetism provided a well-known methodology: the JWKB method [124–128]. More recently, different numerical methods have been developed in the literature to solve directly the time-independent Schrödinger equation and determine the bound levels associated with (bound) potentials [129, 130], which are based either in the so-called “shooting and matching” strategies or in variational techniques. In either case one can discretize the space or consider some basis functions (e.g., Gaussians, sinc-functions) and express the solution as a linear combination of these functions. Also, as an analytical tool, classical trajectories have been employed, taking into account the correspondence between eigenstates (bound states) and classical periodic orbits [131, 132].

In the case of processes and phenomena in the continuum, soon after the establishment of quantum mechanics, a quantum scattering theory was developed [133, 134]. Essentially, in this theory an incoming particle is represented by a coherent plane wave, $e^{ik \cdot r}$, at some initial time at $t \to -\infty$. At $t = 0$, the particle collides with a target and gets diffracted, which translates into an outgoing wave function consisting of a superposition of scattering states (also coherent plane waves) at $t \to +\infty$. Apart from the analytical partial waves approach, there is also a number of numerical methods which have been developed in the literature [119, 120], such as the close-coupling method, which basically consists of splitting the time-independent Schrödinger equation into a set of coupled one-dimensional Schrödinger equations accounting for each of the eventual diffraction channels. Also, as in the case of bound systems, classical trajectories have
been used to determine, for example, diffraction probabilities [135, 136]; although
diffraction is a quantum concept, in principle it is possible to obtain good estimates
in scattering [137–139] and pre-ionization [140–142].

Regarding the time-dependent domain, the strategies developed [83, 120, 143,
144] are aimed at solving the time-dependent Schrödinger equation directly, which
allow to monitor the system evolution along time from the initial to the final
asymptotic state, instead of passing directly from the former to the latter. Usually,
wave-packet propagation methods are the most commonly used to to carry out
these studies, although other approximate techniques have also been developed
in order to find a balance between accuracy and computational demand. These
approaches result interesting, for example, to monitor the passage from reactants
to products in a chemical reaction (e.g., in proton transfer reactions, isomerization
reactions or coherent-control schemes), and are usually accompanied and comple-
mented by classical, trajectory-based studies (quantum-classical correspondence
schemes).

1.2.4. Statistical approach to large (complex) molecular systems

Typically, the dynamical studies mentioned above are related to systems which
are considered as isolated from a surrounding medium or environment. However,
real physical and chemical systems interact, exchanging energy, with their sur-
roundings and deviations from their isolated behavior are observed. A very re-
markable effect, in this regard, is the broadening undergone by atomic and molec-
ular spectral lines, for example, which is a signature of the life-time associated
with the corresponding quasi-bound (stationary) states. But we also find such
situations when measures involving bulk properties (e.g., the viscosity of liquid
water or its crystallization) are involved, and a connection between the micro-
scopic description and the macroscopic observations has to be established. Ob-
viously, a full quantum-mechanical calculation involving the system of interest
plus its environment results unaffordable computationally. Thus, different ap-
proximated statistical approaches have been developed in the literature, based
on the theory of open quantum systems, with the main analysis tool being the
correlation function, which allows to extract the most relevant properties associ-
ated with the system. The correct way to tackle a statistical problem in quantum
mechanics is through the Liouville-von Neumann equation, which is the equiva-
 lent of Schrödinger’s equation, but for the density matrix operator or, simply, den-
sity matrix, \( \hat{\rho}(t) = \sum_\alpha |\Psi_\alpha(t)\rangle\langle\Psi_\alpha(t)| \), instead of the wave function, \( |\Psi(t)\rangle \). How-
ever, full many degree-of-freedom, quantum-mechanical dynamical problems re-
sult prohibitive computationally and different strategies have been developed in
the literature to deal with them. Within the different methodologies commonly
employed, there are basically three schemes, which correspond to the three lev-
els at which a quantum statistical problem can be solved: quantum-mechanical,
mixed/hybrid quantum-classical and fully classical. Nevertheless, independently
of the level of accuracy of our statistical description, there is always a very clear
distinction between system and environment, this being the starting point in any
of these approaches. In this regard, it is worth mentioning that this is also the par-
1.2. Approaching molecular systems at different levels

Partitioning philosophy used in some recent ab initio approaches: instead of studying in detail a full macro-molecular structure, the total system is partitioned into the reactive (or more active) part and the surrounding, which is described in terms of an effective, embedding potential.

It is also worth mentioning that, depending on the properties of the environment, we can refer to it in different ways [87]. For example, usually, when it consists of a few degrees of freedom, it is commonly referred as environment, while the term reservoir is used when there is a large number of degrees of freedom. If it is in thermal equilibrium, i.e., its properties remain stationary with time (except for small fluctuations) — in other words, this is the limit where the environment “forgets” information about its initial state and stays in equilibrium at a certain temperature —, then we employ the term thermal bath. For example, a harmonic oscillator coupled to another harmonic oscillator acts as an environment with respect to the latter because there is an energy and coherence transfer from the latter to the former. If instead of one harmonic oscillator, we couple an infinite number of oscillators, the environment becomes a reservoir and, if such collection of oscillators is at thermal equilibrium, as in the so-called Caldeira-Leggett model [145–147], we will have a thermal bath acting on the system oscillator.

Within the first level, the quantum-mechanical one, one starts from the Liouville-von Neumann equation. Proceeding algebraically according to some assumptions on the timescales associated with system and environment, one can reformulate the problem in terms of a master equation describing only the system evolution, and where the effects of the environment appear in terms of some dissipative operators or dissipators after assuming the Markovian approximation (i.e., the detailed dynamics of the environment becomes irrelevant, and only its effects are important regarding the system dynamics). This is achieved by partially tracing over the environment states, which leads to the so-called reduced density matrix, \( \hat{\rho}_S \), describing the system (or subsystem) of interest or reduced system. Note that this splitting between system and environment as a function of their corresponding timescales (i.e., \( \hat{\rho} = \hat{\rho}_S \otimes \hat{\rho}_E \)) is not other than the Born-Oppenheimer approximation considered in ab initio methods to separate the electronic motion from the nuclear one (see Sec. 1.2.1). This procedure thus gives rise to very well known master equations for the system reduced density matrix, such as the Lindblad equation or its version in the Markovian weak-coupling limit, namely the so-called Redfield equation [148–151]. But, also, one can obtain master equations to describe the evolution of system expectation values starting from the Heisenberg representation, such as the quantum Langevin equation [84, 152, 153], which is the Heisenberg equation of motion for the coordinate of a Brownian particle coupled to a thermal bath. At this stage, apart from analytical derivations, there are basically two methods to solve these equations quantum-mechanically: the path integral method [154–157] and the quantum state diffusion theory [89]. In the first case, one directly attacks the problem of the density matrix, while in the latter one solves a stochastic Schrödinger equation, obtained from the transformation \( \hat{\rho}_S = (1/N) \sum_{k=1}^{N} |\Psi_k\rangle \langle \Psi_k| \), where the \( \Psi_k \) are (stochastic) solutions of such an equation [158].

Whenever the environment dynamics is relevant, the Markov approximation
cannot be applied. Then, we are in the next level, that of the mixed or hybrid quantum-classical methods, where usually the system dynamics is accounted for quantum-mechanically, while the environment dynamics is described by means of classical mechanics, this splitting also being based in the Born-Oppenheimer approximation, as mentioned above. Different methods and techniques have been developed in the literature to tackle this problem, such as mean-field theories [159], surface-hopping methods [160] or semiclassical initial value representations [161–171], which allow to describe both the effects of the environment over the system and vice-versa in spite of their different (classical or quantum) mechanical evolution. In this regard, it is worth stressing that, depending on whether interatomic interactions can be described by a potential energy surface or not, we may have adiabatic or non-adiabatic dynamics. In the latter case, the interaction between different coupled potential energy surfaces (corresponding to different electronic molecular states) has to be included into the corresponding dynamical description [172], thus not satisfying the Born-Oppenheimer approximation, which implies finding good descriptors of the coupling between the electronic and nuclear parts of the Hamiltonian. Now, for certain cases, one can further proceed and represent the system also classically, thus leading to the third level, which is constituted by purely classical methodologies (i.e., based on Newton’s equations), such as simple molecular dynamics simulations, or refinements of them, such as the classical Wigner method or the linearized initial value representation, where a particular choice of the initial conditions is considered (though the propagation is fully classical). Sometimes, molecular dynamics calculations are combined with DFT in order to obtain “on the fly” the potential energy surfaces governing the nuclear motion, as happens in the Car-Parrinello method [173, 174].

1.3. Bohmian Mechanics

1.3.1. Fundamentals

For simplicity, but without loss of generality, we are going to start with the Schrödinger equation associated with a non-relativistic particle (system) of mass $m$. The general solutions to this equation are given in the form of time-dependent complex-valued fields, which we generally call wave functions and represent the state of the system (quantum states) at a given time throughout the full accessible configuration space associated with the physical system studied. From these solutions we extract all relevant physical information about the quantum system, that is, intensities and coherence-based properties (interference effects). Without entering here a discussion on the well-known debate about the completeness of the wave function (actually, not necessary at all), but taking into account that such information is encoded in the probability density (i.e., the square of the amplitude of the wave function) and the phase of the wave function, we can recast the latter in terms of two real-valued fields. This is actually a closer approach to Schrödinger’s derivation of his equation from Hamilton’s formulation of classical mechanics and de Broglie’s novel idea of associating a wave to nonzero mass systems (the so-called Hamiltonian analogy [118]).
From a formal viewpoint, in principle, if we consider time-independent, eigenvalue problems, Schrödinger’s equation acquires the form of a general wave equation (Helmholtz equation), which has exactly the same solutions as the homologous equations we find in electromagnetism or classical wave mechanics [58, 121]. However, in the time-dependent case this analogy is not direct. If the Helmholtz equation is rewritten in paraxial form, it is true that it resembles Schrödinger’s equation, although with one of the coordinates playing the role of the evolution parameter (time). However, in general, what we really observe is a closer resemblance to the heat equation, since it is also a parabolic partial differential equation, as diffusion equations are, although with the particularity that the diffusion coefficient is a pure imaginary constant. This fact was already stressed by Fürth [35] shortly after the equation appeared and later on by Comisar [36]. Nelson also introduced [175] a Markovian approach from which Schrödinger’s equation arose as a result of diffusion process in a subquantum medium.

Taking into account the previous discussion, let us consider the nonlinear transformation

$$\Psi(\vec{r}, t) = R(\vec{r}, t) \, e^{iS(\vec{r}, t)/\hbar},$$

which allows us to recast the complex-valued field $\Psi$ in terms of two real-valued fields, one accounting for the amplitude of such a complex field, and the other one for the phase that any complex quantity introduces. The same transformation is also considered for the conjugate complex (we go from two field variables to another two field variables), with the only difference being that the phase acquires a minus sign. The equations of motion for the amplitude ($R$) and phase ($S$) fields arise after substitution of the wave fields ($\Psi$ and $\Psi^*$) into the time-dependent Schrödinger equation and its complex form, respectively. After a brief rearrangement of terms, adding and subtracting these equations, we obtain their imaginary and real parts, which read, respectively, as

$$\frac{\partial \rho}{\partial t} + \vec{\nabla} \cdot \left( \rho \, \frac{\vec{\nabla} S}{m} \right) = 0.$$  \hspace{1cm} (1.12)

$$\frac{\partial S}{\partial t} + \frac{(\vec{\nabla} S)^2}{2m} + V_{\text{eff}} = 0.$$  \hspace{1cm} (1.13)

In Eq. (1.13), the third term on the left-hand side,

$$V_{\text{eff}} = V + Q = V - \frac{\hbar^2}{2m} \nabla^2 R$$

$$= V - \frac{\hbar^2}{4m} \left[ \nabla^2 \rho - \frac{1}{2} \left( \frac{\vec{\nabla} \rho}{\rho} \right)^2 \right],$$

is an effective potential resulting from the sum of the external potential function $V$ (particle-particle interactions in electronic structure problems and potential energy surfaces in dynamics ones; other external contributions, such as the application of external laser fields or gravity, are also included), and the quantum potential, $Q$. The latter is responsible for transferring the nonlocality property of quantum mechanics [176, 177] (which manifests through the phenomenon of quantum entanglement [178,
179]) to the particle’s motion due to its dependence on the quantum state (through the probability density $\rho$).

As it can be noticed, Eq. (1.12) is the well-known probability conservation equation, which states that for a pure state the probability must preserve along time, but also that if we specify a certain region of the configuration space, the probability contained in it must also remain constant along time if its boundaries vary in time in a prescribed way [180]. In classical mechanics [83], this variation takes place according to the evolution in phase space of (Newtonian) trajectories with initial conditions selected on the boundary; the evolution of the trajectories generates tubes in phase space where the probability is confined all the way through. Quantum-mechanically the same also holds [180] if we choose as the confining trajectories the ones that arise from the equation of motion

$$\vec{v} = \frac{\vec{J}}{\rho} = \frac{\vec{\nabla} S}{m},$$

(1.15)

although the preservation of the probability takes places in the system configuration space instead of a generalized phase space. This transport equation arises naturally in the standard formulations of quantum mechanics if we divide the quantum flux or probability current [181, 182],

$$\vec{J} = \frac{\hbar}{2mi} (\Psi^* \nabla \Psi - \Psi \nabla \Psi^*),$$

(1.16)

by the probability density. In other words, physically it means that the transport or diffusion of probability through the system configuration space can be described as a velocity vector field multiplying the probability density, in compliance with usual diffusion (transport) equations. Nonetheless, the way how Bohm introduced that quantity in 1952 was postulating it once the quantum or generalized Hamilton-Jacobi equation (1.13) was settled [7]. That is, he established a direct analogy with classical mechanics, where an analogous equation arises within the Hamilton-Jacobi formulation, namely the Jacobi momentum law. In the classical case, $S$ denotes the classical (mechanical) action, which is a hypersurface in configuration space associated with the evolution of the system directly linked to the geometric phase in the *eikonal approximation* [118]; in quantum mechanics, the phase field $S$ is a direct analog of the classical action, although it is specified in the configuration space of the system. It is by virtue of this constraint (i.e., to restrict the motion to the configuration space instead of a phase space with coordinates and momenta independent of each other) that nonlocality arises (or manifests) in quantum mechanics.

Notice that the trajectories that one obtains by integration (in time) of Eq. (1.15) describe the flow of the probability throughout the corresponding configuration space. That is, such trajectories are just probability streamlines, analogous to those that we find in classical hydrodynamics (this is precisely the point emphasized by Madelung in 1926). However, one can also be tempted to identify such trajectories with the actual motion of real particles in order to establish a (alternative) quantum theory without observers. Although this has been a major issue of debate over years and, actually, one of the main reasons why Bohmian mechanics has been generally rejected, there is nothing in the theory, not even current experiments,
supporting such a link. The only accessible information to date in an experiment is the quantum flux, as it has been recently shown [183], which is in compliance with the usual theory [184].

Equation (1.15) together with the time-dependent Schrödinger equation are the two basic equations within the analytic approach discussed above [15], for they allow us to obtain the evolution of the wave function $\Psi$ as well as the associated Bohmian trajectories, necessary to interpret the flow of the probability or, equivalently, the motion of a swarm of non-interacting quantum particles [16, 17, 144, 185].

On the other hand, from a computational viewpoint, schemes aimed at integrating partial equations are always affected by numerical instabilities, as happens with Eqs. (1.12) and (1.13). Hydrodynamically speaking [186, 187], these equations are expressed within an Eulerian framework, i.e., from a fixed space point we will observe the quantum fluid passing by. So, an easier way to proceed consists in taking advantage of Eq. (1.15) to define the Lagrange time derivative,

$$\frac{d}{dt} = \frac{\partial}{\partial t} + \vec{v} \cdot \vec{\nabla}.$$ (1.17)

Recasting Eqs. (1.12), (1.13) and (1.15) in terms of this operator, which renders the set of coupled equations of motion

$$\frac{d\rho}{dt} = -\rho \vec{\nabla} \cdot \vec{v},$$ (1.18)

$$\frac{d\vec{v}}{dt} = -\frac{\vec{\nabla} V_{\text{eff}}}{m},$$ (1.19)

$$\frac{dS}{dt} = \frac{1}{2} mv^2 - V_{\text{eff}},$$ (1.20)

or, equivalently,

$$\frac{d\rho}{dt} = -\rho \vec{\nabla} \cdot \vec{v},$$ (1.21)

$$\frac{dS}{dt} = \frac{1}{2} mv^2 - V_{\text{eff}},$$ (1.22)

$$\frac{d\vec{r}}{dt} = \vec{v} = \frac{\vec{\nabla} S}{m}.$$ (1.23)

This set of equations constitutes the core of the so-called (Bohmian) quantum trajectory method [15], an algorithm based on Bohmian mechanics to obtain quantum-mechanical results. It was firstly proposed [62–64] following the scheme of Eqs. (1.18), (1.19) and (1.20). However, evaluating the gradient of the force is an important source of numerical error and the second scheme was considered. Alternatively, to avoid these drawbacks, one can re-derive this set of equations in complex form [65–72], by considering a complex phase field, which already include information about the amplitude of the wave function [188].

1.3.2. Nonlocality and entanglement

Dealing with many-body problems, as it is the case when molecular systems are involved, unavoidably leads to the question of the appearance of quantum correlations among the different degrees of freedom necessary to specify the (quantum)
state of the system. Typically the series of approximations that are considered to tackle these problems (starting from the Born-Oppenheimer one, whenever it is required) implies a breach of such correlations. Although this is an efficient route from a problem-solving viewpoint, physically it means there is a certain loss of quantum coherence in the system, which is not going to be shared anymore by the different separated parts. In other words, the degree of entanglement [178, 179] between such parts is totally lost – whatever happens to one of the parts of the full system will only have classical-like consequences on the others, and vice versa.

To better understand the implications of entanglement and the possibility to nonlocally share information among different parts of a quantum system is precisely through Bohmian mechanics. Consider the $N$-body wave function in the position space

$$\Psi(\vec{r}_1, \vec{r}_2, \ldots, \vec{r}_N, t) = R(\vec{r}_1, \vec{r}_2, \ldots, \vec{r}_N, t) e^{iS(\vec{r}_1, \vec{r}_2, \ldots, \vec{r}_N, t)/\hbar}. \quad (1.24)$$

The reduced single-particle probability density for the $i$th particle (or, in general, degree of freedom) is defined as

$$\tilde{\rho}_i(\vec{r}_i, t) = \int \cdots \int \rho(\vec{r}_1, \vec{r}_2, \ldots, \vec{r}_N, t) d\vec{r}_1 d\vec{r}_2 \cdots d\vec{r}_{i-1} d\vec{r}_{i+1} \cdots d\vec{r}_N, \quad (1.25)$$

where $\rho = R^2$. This reduced probability density describes the statistics of the $i$th particle ignoring the statistics of the remaining particles, although due to the correlation among them any change in the configuration of the system will have consequences on this particle. To this particle we can also assign an equation of motion,

$$\vec{v}_i = \frac{\vec{\nabla}_i S}{m}, \quad (1.26)$$

which takes into account the full wave function and therefore the motion of the other particles. This procedure gives rise to a set of $N$ equations of motion coupled through the “wholistic” phase $S$, where the evolution of a particle will be strongly nonlocally influenced by the others (apart from other classical like interactions through $V$). This entanglement becomes more apparent through the quantum potential,

$$Q = -\frac{\hbar^2}{2m} \sum_{i=1}^{N} \frac{\nabla_i^2 R}{R}, \quad (1.27)$$

where $Q = Q(\vec{r}_1, \vec{r}_2, \ldots, \vec{r}_N, t)$, which is nonseparable and therefore strongly nonlocal.

As a simple illustration of these ideas, consider the case of two particles which interact, at some time, through a potential $V$. The two-particle wave function describing this system is

$$\Psi(x, y, t) = R(x, y, t) e^{iS(x, y, t)/\hbar}, \quad (1.28)$$

with $\rho(x, y, t) = R^2(x, y, t)$ being the total probability density, and $\tilde{\rho}_1(x, t)$ and $\tilde{\rho}_2(y, t)$ the reduced probability densities associated with each particle. The trajectories for these particles are obtained from

$$\vec{v}_1 = \frac{1}{m} \frac{\partial S(x, y, t)}{\partial x}, \quad \vec{v}_2 = \frac{1}{m} \frac{\partial S(x, y, t)}{\partial y}, \quad (1.29)$$
which are implicitly influenced by the quantum potential
\[
Q(x, y, t) = -\frac{\hbar^2}{2m} \frac{1}{R(x, y, t)} \left[ \frac{\partial^2 R(x, y, t)}{\partial x^2} + \frac{\partial^2 R(x, y, t)}{\partial y^2} \right].
\]

According to Schrödinger [178, 179], after the interaction, even if the two particles are very far apart from one another, the wave function (1.28) becomes non-factorizable, i.e.,
\[
\Psi(x, y, t) = \psi(x, t) \otimes \psi(y, t),
\]
and the motion of both particles will remain entangled. Different works in the literature analyze the trajectory correlation among entangled particles [189–195], the most recent one within the many-body context of transport phenomena in mesoscopic systems [196].

This does not happen, however, when the wave function is factorizable in terms of single-particle partial wave functions,
\[
\Psi(x, y, t) = \psi_1(x, t) \psi_2(y, t) = R_1(x, t) R_2(y, t) e^{[S_1(x,t)+S_2(y,t)]/\hbar},
\]
since \(\rho(x, y, t) = \rho_1(x, t) \rho_2(y, t)\) is a direct product of (partial) densities, while the particles’ equations of motion,
\[
\vec{v}_1 = \frac{1}{m} \frac{\partial S_1(x, t)}{\partial x}, \quad \vec{v}_2 = \frac{1}{m} \frac{\partial S_2(y, t)}{\partial y}
\]
are uncoupled. This can also be readily inferred from the quantum potential, which is fully separable:
\[
Q(x, y, t) = -\frac{\hbar^2}{2m} \frac{1}{R_1(x, t)} \frac{\partial^2 R_1(x, t)}{\partial x^2} = \frac{\hbar^2}{2m} \frac{1}{R_2(y, t)} \frac{\partial^2 R_2(y, t)}{\partial y^2}
\]
\[
= Q_1(x, t) + Q_2(y, t),
\]
In general, for an \(N\)-particle wave function,
\[
\Psi(\vec{r}_1, \vec{r}_2, \ldots, \vec{r}_N, t) = \Pi_{i=1}^N \psi_i(\vec{r}_i, t) = \Pi_{i=1}^N R_i(\vec{r}_i, t) e^{iS_i(\vec{r}_i,t)/\hbar},
\]
the ith-particle equation of motion is
\[
\vec{v}_i = \frac{\nabla_{\vec{r}_i} S_i}{m},
\]
and the total quantum potential will be given by the direct addition of the quantum potentials associated with each separate particle,
\[
Q = -\frac{\hbar^2}{2m} \sum_{i=1}^N \frac{\nabla^2_{\vec{r}_i} R_i}{R_i} = \sum_{i=1}^N Q_i.
\]

After using the Born-Oppenheimer approximation, splitting electronic from nuclear degrees of freedom, the essence of electronic structure methodologies is precisely finding the electronic configuration of molecular systems by appealing to the idea of separability, from \textit{ab initio} methods (wave function approach) to the density functional theory (probability density approach). Of course, once an optimal basis set is found, correlations will appear when appealing to the appropriate symmetrization conditions. For example, in the case of \textit{ab initio} methodologies,
Slater determinants are considered to provide the correct symmetry to the linear combinations of orbitals formed to describe the configuration of the corresponding molecular system (see Sec. 1.2.2).

There is another interesting issue concerning correlation and the Born-Oppenheimer approximation. Notice that although Eq. (1.6) is separable, due to the dependence of the electronic coordinates, \( \vec{r}_i \), on the nuclear ones, \( \vec{R}_A \), the eventual trajectories for the electrons will depend on the nuclei positions (in agreement with the fact that the potential energy surface varies throughout space), but the same will not happen for the nuclear trajectories with respect to the electrons. Again here we find the problem of the back-reaction, although this time it is within the Bohmian context.

1.3.3. Weak values and equations of change

In the recent years, the concept of weak value [197] has been a subject of much interest, getting some popularity within the quantum metrology and quantum foundations communities. For example, by means of measurements of the weak value it is possible to perform tomography of the quantum state associated with a single photon [198] and also to determine the streamlines describing the (averaged) flow of probability in Young’s two slit experiment [183]. However, this idea, now in fashion, is directly related to the well-known quantum flux [181, 182] and to the averaging of two-state transition probabilities [199, 200]. However, the essence behind this idea can be traced back to 1970s, to a work published by Hirschfelder [201], where we also find a certain connection to the later application of quantum hydrodynamics to time-dependent DFT (see Sec. 1.4.1). According to this author, the framework presented in this work facilitates the study of problems involving external electric and magnetic fields (as seen in previous section) by grounding it on the concept of equation of change for arbitrary quantum-mechanical properties in configuration space. These equations can be used to study the energy flow from one part of a molecule to another, the nature of molecular collisions or the magnetic properties of molecules. The first two cases are somehow summarized by the applications which will be discussed in next section regarding the molecular dynamics. The third type of application, on the other hand, has been exploited in the literature by different authors [202–212] to understand the magnetic properties of molecules within a framework that encompasses electronic structure and topology.

Although in a brief manner, let us here consider how the ideas underlying quantum hydrodynamics emerge in a very elegant fashion within the framework proposed by Hirschfelder [201]. To start with, let us define an arbitrary property \( S \equiv \Psi_1^\dagger \hat{O} \Psi_2 \) (do not confuse this calligraphic \( S \) denoting a certain property with the normal \( S \) referring to the phase of a wave function), where both \( \Psi_1 \) and \( \Psi_2 \) satisfy the same time-dependent Schrödinger equation (i.e., both are governed by the same Hamiltonian) and \( \hat{O} \) is an (arbitrary) operator associated with a quantum observable. If \( \Psi_2 = \Psi_1 \), the integral of \( S \) over configuration space, denoted by \( \tilde{S} \), describes the expectation value associated with \( \hat{O} \), while for \( \Psi_2 \neq \Psi_1 \), \( \tilde{S} \) gives a transition probability or rate (from the state \( \Psi_1 \) to a state \( \Psi_2 \)) governed by \( \hat{O} \). It can
be easily shown that \( S \) satisfies the equation of change

\[
\frac{\partial}{\partial t} (\Psi_1^* \hat{O} \Psi_2) = \Psi_1^* \left\{ \frac{\partial \hat{O}}{\partial t} - \frac{i}{\hbar} [\hat{O}, \hat{H}] \right\} \Psi_2 - \frac{i}{\hbar} \left[ \Psi_1^* \hat{H} \hat{O} \Psi_2 - (\hat{H} \Psi_1)^\dagger \hat{O} \Psi_2 \right].
\]  
(1.38)

Specifically, for a Hamiltonian

\[
\hat{H} = \frac{\hat{p}^2}{2m} + \hat{V}(\vec{r}),
\]

(1.39)

it can be shown [201] that Eq. (1.38) takes the functional form

\[
\frac{\partial}{\partial t} (\Psi_1^* \hat{O} \Psi_2) + \vec{\nabla} \cdot \vec{F} = \mathcal{K},
\]

(1.40)

where

\[
\vec{F} = \frac{1}{2} \left[ \Psi_1^* \hat{O} \Psi_2 - (\hat{r} \Psi_1)^\dagger \hat{O} \Psi_2 \right],
\]

(1.41)

and

\[
\mathcal{K} = \Psi_1^* \left\{ \frac{\partial \hat{O}}{\partial t} - \frac{i}{\hbar} [\hat{O}, \hat{H}] \right\} \Psi_2
\]

(1.42)

are, respectively, the flux of \( S \) and its rate of production, and

\[
\hat{r} = -\frac{i}{\hbar} [\hat{r}, \hat{H}] = \frac{\hat{p}}{m}.
\]

(1.43)

Now, if \( \hat{O} \) is a linear Hermitian operator, physically the most significant form of \( S \) will be

\[
S = \text{Re}[\Psi_1^* \hat{O} \Psi_2] = \frac{1}{2} \left[ \Psi_1^* \hat{O} \Psi_2 + (\hat{O} \Psi_1)^\dagger \Psi_2 \right].
\]

(1.44)

This is because \( S \), as given by (1.44), can be considered itself an observable associated with a certain linear Hermitian operator, \( \hat{O}^H \), in such a way that the integral over configuration space of \( \Psi_1^* \hat{O}^H \Psi_2 \) is precisely (1.44). In particular, this associated operator reads as

\[
\hat{O}^H(\vec{r}, \vec{r}') = \frac{1}{2} \left[ \hat{O}(\vec{r}') \delta(\vec{r}' - \vec{r}) + \delta(\vec{r}' - \vec{r}) \hat{O}(\vec{r}) \right],
\]

(1.45)

and therefore one readily notices

\[
\int \Psi_1^* (\vec{r}') \hat{O}^H(\vec{r}, \vec{r}') \Psi_2(\vec{r}') d\vec{r}' = \frac{1}{2} \text{Re}[\Psi_1^* \hat{O} \Psi_2].
\]

(1.46)

Because \( S \) is an observable with respect to a linear Hermitian operator, it is called a subobservable, which obeys the equation of change

\[
\frac{\partial}{\partial t} \text{Re}[\Psi_1^* \hat{O} \Psi_2] = \text{Re} \left[ \Psi_1^* \frac{\partial \hat{O}}{\partial t} \Psi_2 \right] + \frac{1}{\hbar} \text{Im} \left[ \Psi_1^* \hat{O} \hat{H} \Psi_2 - (\hat{H} \Psi_1)^\dagger \hat{O} \Psi_2 \right].
\]

(1.47)

Note that this equation is precisely the expectation value of \( \hat{O}^H \).

Let us now consider the expression (1.44) for \( S \) and the particular case \( \Psi_2 = \Psi_1 = \Psi \). If \( \hat{O} = \mathbb{I} \), the subobservable corresponds to the probability density
$S = \Psi^* \Psi = \rho$. Substituting this condition into Eq. (1.47), we find the well-known continuity equation,

$$\frac{\partial \rho}{\partial t} + \vec{\nabla} \cdot \vec{J} = 0, \quad (1.48)$$

where

$$\vec{J} \equiv \operatorname{Re}\{\Psi^* \dot{\Psi}\} = \left(\frac{\hbar}{2m}\right) \left(\Psi^* \vec{\nabla} \Psi - \Psi \vec{\nabla} \Psi^*\right) \quad (1.49)$$

is the quantum probability density current or quantum flux (see Sec. 1.3). The equation of change for this latter quantity is obtained assuming $\hat{O} = \hat{p}/m$:

$$\frac{\partial \vec{J}}{\partial t} + \vec{\nabla} \cdot \vec{F} = -\frac{1}{m} \rho \vec{\nabla} V, \quad (1.50)$$

where

$$\vec{F} = \frac{1}{4m^2} \left[ \Psi^* \hat{p} \hat{p} \Psi + \Psi \hat{p} \hat{p} \Psi^* + (\hat{p} \Psi)^\dagger (\hat{p} \Psi) + (\hat{p} \Psi^*)^\dagger (\hat{p} \Psi)^\dagger \right] \quad (1.51)$$

is a tensor quantity accounting for the flux of the quantum probability density current. According to London [38], the velocity $\vec{v}$, as defined in Sec. 1.3, cannot be a subobservable since there is no linear Hermitian operator $\hat{O}^H$ for which $\vec{v}$ is an expectation value. However, an equation of motion for this quantity can be obtained using both (1.48) and (1.50), which reads as

$$m\rho \frac{d\vec{v}}{dt} = -\rho \vec{\nabla} V - \vec{\nabla} \cdot \vec{P}. \quad (1.52)$$

As can be readily noticed, this equation is (1.19), which arises when its right-hand side is conveniently rearranged in terms of the effective potential. As it is given, (1.52) describes an incompressible fluid, with

$$\vec{P} = -\left(\frac{\hbar^2}{4m}\right) \rho \vec{\nabla} \ln \rho = m\vec{F} - \frac{m}{\rho} \vec{J} \vec{J} \quad (1.53)$$

being the quantum pressure tensor introduced by Takabayasi in the 1950s [10, 11], whose effects will be discussed in Sec. 1.4.3.

### 1.4. Applications

Covering all aspects of the topic under consideration would take more than a single chapter due to the many different applications that have been developed in the literature. Thus, instead of trying to go for such an ambitious programme, the following sections are aimed at providing an illustration on how Bohmian mechanics has been or can be used to tackle different problems related to the aspects described in Sec. 1.2.
1.4. Applications

1.4.1. Time-dependent DFT: The quantum hydrodynamic route

Although it is not well known in the Bohmian literature, one of the former (and earlier) applications of Bohmian mechanics in its hydrodynamic version was the design of time-dependent DFT algorithms [213–233]. The formal grounds of this approach, known as quantum fluid dynamics DFT (QFD-DFT), rely on a set of hydrodynamical equations [214–218], having the advantage of being able to deal with dynamical processes evolving in time in terms of single-particle time-dependent equations [227–232]. As happens with time-independent DFT, the density is also determined by solving a single-particle non-interacting time-dependent Schrödinger equation [217], which approximately, but rather accurately, deals with both static and dynamic correlations between electrons. This methodology thus facilitates the computation of ab initio electron densities for \( N \)-electron systems, with the advantage of delivering both density and energy with a superior accuracy to HF methods at a comparable computational overload. For a more detailed historical account on this approach and its achievements, the interested reader may consult Ref. [234].

In order to understand how QFD-DFT works, consider the polynuclear and polyelectronic time-dependent Schrödinger equation,

\[
\hat{H}\Psi(\mathbf{\vec{R}}_1, \mathbf{\vec{R}}_2, \ldots, \mathbf{\vec{R}}_M, q_1, q_2, \ldots, q_N, t) = i\hbar \frac{\partial \Psi(\mathbf{\vec{R}}_1, \mathbf{\vec{R}}_2, \ldots, \mathbf{\vec{R}}_M, q_1, q_2, \ldots, q_N, t)}{\partial t}. \tag{1.54}
\]

As in time-independent DFT, the purpose of time-dependent DFT is to provide solutions to the electronic part of \( \Psi \), also assumed to be separable, as \( \Phi \), although now

\[
|\phi_{e,N}(q_1, q_2, \ldots, q_N, t)|^2 dq_1 dq_2 \cdots dq_N dt. \tag{1.55}
\]

represents the probability that electrons 1, 2, \ldots, \( N \) will be found simultaneously within the volume elements \( dq_1, dq_2, \ldots, dq_N \), respectively, during the time interval \( dt \). Taking this into account and then further proceeding as in DFT, one finds that the time-dependent polyelectronic wave function can be expressed as a combination of product of single monoelectronic time-dependent states,

\[
\phi_{e,N}(q_1, q_2, \ldots, q_N, t) \rightarrow \prod_{i=1}^{N} \phi_{0,i}(q_i, t). \tag{1.56}
\]

and time plays the role of a parameter. In this regard, considering different times could be associated, within the time-independent DFT approach, with assuming different states, each labeled with a different index \( k \). The process to obtain the electronic density is thus similar to that in time-independent DFT, but considering subsequent times, which is done within the quantum hydrodynamics framework, where the quantum probability is understood as a quantum fluid.

As an illustration of the method, we are going to analyze the calculation of a density for an \( N \)-electron system under the influence of an external time-dependent periodic force, formerly studied by Bartolotti [214–216]. In the time-independent case, assuming the electrons are noninteracting, we need \( N \) orbitals to describe the electrons, this being equivalent to assume that each electron can be described by \( N \) different orthonormal orbitals \( \phi_i \) (i.e., \( \langle \phi_i | \phi_k \rangle = \delta_{ik} \)), and therefore

\[
\sum_{i=1}^{N} |\phi_i(\mathbf{\vec{r}})|^2 = \rho(\mathbf{\vec{r}}) \tag{1.57}
\]
is the “exact” density of the system. As in standard DFT \[235\], the \( \phi_i \) are obtained after minimization of the kinetic energy of the \( N \)-electron system, 

\[
T_s[\{\phi_i\}] = -\frac{1}{2} \sum_{i=1}^{N} \int \phi_i(\vec{r}) \left( \nabla^2 \phi_i(\vec{r}) \right) d\vec{r},
\]

(1.58)

which renders the Euler-Lagrange equation

\[
-\frac{1}{2} \nabla^2 \phi_i + v_{\text{eff}} \phi_i = \epsilon_i \phi_i.
\]

(1.59)

As can be noticed, (1.59) is a single-particle time-independent Schrödinger equation, where \( v_{\text{eff}} \) is an effective potential including the external (nuclear) interaction as well as the averaged action of the remaining \( N-1 \) electrons, and \( \epsilon_i \) is the associated eigenenergy — \( \epsilon_i \) can also be interpreted as the Lagrange multiplier that insures (1.57) is satisfied by the \( \phi_i \). Also note in (1.59) that, if this equation is divided by \( \phi_i \), it will read as

\[
Q_i + v_{\text{eff}} = \epsilon_i,
\]

(1.60)

where

\[
Q_i(\vec{r}) = -\frac{1}{2} \frac{\nabla^2 \phi_i(\vec{r})}{\phi_i(\vec{r})}
\]

(1.61)

is the effective quantum potential associated with the state \( \phi_i \). This means that the sum of this quantum potential to the effective one results in the bound-state energy \( \epsilon_i \).

Now, in the time-dependent case, consider the system is described by the (time-dependent) orbitals \( \phi_i(\vec{r}, t) \), from which we want to obtain the (time-dependent) density \( \rho(\vec{r}, t) \). In polar form this orbitals read as

\[
\phi_i(\vec{r}, t) = R_i(\vec{r}, t) \ e^{iS_i(\vec{r}, t)},
\]

(1.62)

with

\[
\int \int \ R_i(\vec{r}, t) R_k(\vec{r}, t) d\vec{r} = \delta_{ik},
\]

(1.63)

where \( \int \int \) denotes a time-averaged integration over one period of time. The kinetic energy associated with this (noninteracting) \( N \)-electron system reads \[215\] as

\[
T_s[\{R_i, S_i\}]_t = -\frac{1}{2} \sum_{i=1}^{N} \int \left\{ R_i(\vec{r}, t) \nabla^2 R_i(\vec{r}, t) - R_i^2(\vec{r}, t) \left( \nabla S_i(\vec{r}, t) \right)^2 \right\} d\vec{r}.
\]

(1.64)

Here, the constraints are

\[
\sum_{i=1}^{N} R_i^2(\vec{r}, t) = \rho(\vec{r}, t),
\]

(1.65)

as in the time-independent case, and the conservation of the number of particles,

\[
\sum_{i=1}^{N} \frac{\partial R_i^2}{\partial t} \left( = \frac{\partial \rho}{\partial t} \right) = -\nabla \cdot J,
\]

(1.66)
where $\vec{J}$ is the single-particle quantum probability density current vector. Thus, after minimizing (1.64) with respect to the $R_i$ (subjected to the previous constraints), we find the Euler-Lagrange equation

$$-\frac{1}{2} \nabla^2 R_i + v_{\text{eff}} R_i = \epsilon_i R_i. \quad (1.67)$$

where $v_{\text{eff}}(\vec{r}, t)$ is the Lagrange multiplier associated with the constraint defined in (1.65), and the $\epsilon_i(\vec{r}, t)$ are the Lagrange multipliers associated with the conservation of the number of particles, given by (1.63) and (1.66). The $\epsilon_i(\vec{r}, t)$ can be split out as a sum of two terms,

$$\epsilon_i(\vec{r}, t) = \epsilon_i^{(0)} + \epsilon_i^{(1)}(\vec{r}, t), \quad (1.68)$$

where $\epsilon_i^{(0)}$ arise from the normalization constraint and $\epsilon_i^{(1)}$ are the Lagrange multipliers associated with the charge-current conservation defined by (1.66). Also note that, analogously to (1.59), (1.67) can now be expressed as

$$Q_i(\vec{r}, t) = -\frac{1}{2} \nabla^2 R_i(\vec{r}, t) \quad (1.69)$$

if we divide by $R_i$, where $Q_i$ is the time-dependent effective quantum potential associated with the state $\phi_i$.

On the other hand, minimizing $T_i[\{R_i, S_i\}]$ with respect to $S_i$, subject to the constraint

$$\frac{\partial S_i}{\partial t} = -\epsilon_i, \quad (1.70)$$

gives rise to the Euler-Lagrange equation

$$\frac{\partial R_i^2}{\partial t} + \vec{\nabla} \cdot (R_i^2 \vec{\nabla} S_i) = 0. \quad (1.71)$$

The scheme based on the coupled equations (1.67) and (1.71) thus provides a means of determining the exact time-dependent density of the system, noticing that

$$\vec{J}(\vec{r}, t) = \sum_{i=1}^N R_i^2(\vec{r}, t) \vec{\nabla} S_i(\vec{r}, t). \quad (1.72)$$

Moreover, if the time-dependence is turned off, the QFD-DFT approach correctly reduces to the standard time-independent DFT results: since $\vec{\nabla} S_i$ vanishes, (1.66), (1.70) and (1.71) will be identically satisfied and (1.64) will reduce to the time-independent kinetic energy of the $N$-electron system.

More recently, Elsayed et al. [236] have proposed a Bohmian-based many-body approach to study the breathing dynamics of a many-boson system enclosed in a trap with both long and short range interactions, without appealing to typical mean-field approximations [237, 238]. This approach is based on the concept of conditional wave function [196] and its accuracy has been tested by comparing with the standardized, numerically exact multiconfigurational time-dependent Hartree (MCDTH) method [239].
Figure 1.1. (a) Contour plot of the Müller-Brown potential energy surface and reaction path (green thick line) joining the reactants minimum with the products one. In the way how the surface is defined, the black contours represent equipotential lines for negative values of the energy, while the gray ones stand for positive energies; the zero-energy separatrix appears as a dashed line. (b) Energy profile along the reaction path. In both panels, the maxima indicate the position of transition states (\(TS\)) and are denoted by red circles, while the minima associated with the different molecular states (\(M\)) are indicated with blue squares.

1.4.2. Bound system dynamics: Chemical reactivity

As an example of bound dynamics describing a chemical reaction, let us consider a prototype potential model in reaction-path finding, namely the Müller-Brown potential energy surface [240–244]. As seen in Fig. 1.1(b), this potential energy surface has three minima (blue squares), \(M_1\), \(M_2\) and \(M_3\), corresponding to the products, intermediate and reactants states, respectively, and two transition states (red circles), \(TS_1\) and \(TS_2\), separating products from pre-equilibrium and the latter from reactants, respectively. The physical meaning of these singular points is better understood by inspecting the energy profile displayed in Fig. 1.1(b). This profile is taken along the reaction path (green line), plotted as a function of the arc-length, which is defined in simple (and standard) terms as

\[
s(x, y) \approx \sum_{i=1}^{N} \sqrt{\Delta x_i^2 + \Delta y_i^2} = \sum_{i=1}^{N} \sqrt{(x_i - x_{i-1})^2 + (y_i - y_{i-1})^2},
\]

where the initial point of the curve, \((x_0, y_0)\), is \(M_3\), the final point is \(M_1\), and \((x, y) = (x_N, y_N)\) is some intermediate point along the path. Furthermore, the reaction path in this case corresponds to the steepest descent curve from the relative maxima (\(TSs\)) to the adjacent minima (\(Ms\)).

Regarding the dynamical analysis, the Müller-Brown potential energy surface is assumed to describe a process governed by a proton transfer, for instance, Schrödinger’s equation is applied to a particle with mass \(m = 1,836\) (atomic units, where \(m_e = 1\) is the electron mass). Quantum-mechanically, the initial state is specified by an initial Gaussian wave packet,

\[
\Psi_0(x, y) = \frac{1}{\sqrt{2\pi \sigma x \sigma y}} e^{-(x-x_0)^2/4\sigma_x^2-(y-y_0)^2/4\sigma_y^2+i p_x(x-x_0)/\hbar+i p_y(y-y_0)/\hbar},
\]

(1.74)
1.4. Applications

with $\sigma_x^2 = \sigma_y^2 = \sigma_0^2 = 0.0125$ and $(p_{x,0}, p_{y,0}) = (-p_0, p_0)$. Physically, from a classical viewpoint, this wave packet is assumed to represent a Gaussian random distribution of initial positions around the minimum of the products state, and a (Gaussian) Boltzmann distribution of initial momenta [which can be readily obtained from the momentum representation of the wave packet \(1.74\)], with dispersion $\hbar/2\sigma_0$ along both directions and average momenta $(p_{x,0}, p_{y,0})$.

The value $p_0$ is considered as a control parameter to determine the effectiveness of the transfer process as a function of the initial energy carried by the proton. The initial conditions for the Bohmian trajectories are obtained by randomly sampling

\[
\rho_0 = |\Psi_0|^2 \delta(p_x - p_{x,0}) \delta(p_y - p_{y,0}).
\]

To compare with, alternative classical statistical simulations are also considered in order to emphasize different quantum-classical aspects. To this end, two samples of classical trajectories are considered. In one of them, trajectories are initially distributed according to the Wigner distribution associated with \(1.74\),

\[
\rho_{0,cl}^{(1)} = \rho_W(x, p_x, y, p_y) 
\propto e^{-(x-x_0)^2/2\sigma_x^2-(p_x-p_{x,0})^2/\hbar^2-(y-y_0)^2/2\sigma_y^2-(p_y-p_{y,0})^2/\hbar^2}.
\]

This distribution introduces a dispersion in momenta such that the classical average energy,

\[
\bar{E}_{cl} = \int E(x, p_x, y, p_y) \rho_W(x, p_x, y, p_y) dxdydp_xdp_y
\]

\[
= \frac{p_0^2}{m} + \bar{V} + \bar{\delta}
\]

\[
\approx \frac{1}{N} \sum_{i=1}^N E_i(x_{i,0}, y_{i,0}),
\]

coincides with the (quantum) expectation value of the energy, \(\bar{E}_q = \langle \hat{H} \rangle\). In Eq. \(1.76\), $\bar{V} = \sum_{i=1}^N V_i(x_{i,0}, y_{i,0})/N$ is the average value of the potential energy, $\bar{\delta} = \hbar^2/4m\sigma^2$ is a sort of internal energy related to the spreading ratio of a Gaussian wave packet \(245\), and the last sum runs over all (classical/quantum) particles considered [with \((x_{i,0}, y_{i,0})\) denoting their corresponding initial positions]. In the second ensemble, the classical trajectories are distributed according to $\rho_{0,cl}^{(2)} = \rho_0$, just as in the Bohmian case. By means of a simple calculation, it can be shown that $\bar{\delta}$ vanishes and therefore the average (ensemble) energy becomes smaller.

The first calculation considered is a measure of reaction probabilities, which provides information about the amount of products formed with time, as well as the formation rate or reaction velocity if we measure the slope of such a function. The reaction probability is defined in the form of a restricted norm \(244, 246\),

\[
\mathcal{P}(t) \equiv \int_\Sigma |\Psi(x, y, t)|^2 dxdy,
\]

where $\Sigma$ is the space region above the border line separating products from pre-equilibrium/reactants, here chosen to be

\[
y_{R\rightarrow P}(x) = 0.8024x + 1.2734.
\]
From a Bohmian viewpoint, Eq. (1.77) has to be interpreted \[244, 246\] as the fraction of trajectories \(N_{\Sigma}\) that penetrate into \(\Sigma\) at a time \(t\) with respect to the total number \(N\) initially considered,

\[
W(t) \equiv \frac{N_{\Sigma}(t)}{N}.
\]  

(1.79)

This quantity will approach \(\mathcal{P}(t)\) in the limit \(N \to \infty\) whenever the initial conditions of the trajectories will be sampled according to \(\rho_0\). Classically, the analog of Eq. (1.79) is also considered to determine a classical rate of production of products, using a subscript “cl” to distinguish this quantity from its quantum-mechanical counterpart [i.e., \(W_{cl}(t)\) for the classical fraction]. Probability can flow backwards from products to reactants \[1–3\], mainly in bound potentials, thus leading to multiple crossings of \(y_{R \to P}(x)\) by the same quantum/classical trajectory. However, working with individual trajectories brings in an advantageous feature: one can determine uniquely when a single particle is in the products region, and therefore neglect its count in (1.79) at subsequent times. Hence, another interesting quantity is the fraction of trajectories going from reactants to products without recrossing the border line at subsequent times,

\[
\bar{W}(t) \equiv \frac{\bar{N}_{\Sigma}(t)}{N}.
\]  

(1.80)

Assuming one could extract the products formed during the reaction by some chemical or physical procedure, \(\bar{W}(t)\) would provide the maximum amount of products at each time and, at \(t \to \infty\), it would render the maximum amount of products which can be extracted from the reaction given a certain initial state.

The fractions \(W\) (solid line) and \(\bar{W}\) (dashed line) are displayed in Figs. 1.2.(a) and (b) for \(p_0 = 4\) and \(p_0 = 10\), respectively. In each panel the three different initial distributions mentioned above are shown: Bohmian trajectories according to \(\rho_0\) (circles) and classical trajectories according to \(\rho^{(1)}_{0,cl}\) (triangles) and \(\rho^{(2)}_{0,cl}\) (inverted triangles), using a total of \(5 \times 10^4\) trajectories in all cases. For \(p_0 = 4\), \(E - \delta\) is well below \(TS_2\) and \(TS_1\), and therefore dynamics should mainly proceed via tunneling according to standard quantum mechanics. This means that one would expect \(W\) to be larger asymptotically than \(W^{(1)}_{cl}\) and \(W^{(2)}_{cl}\). However, in Fig. 1.2(a) we observe that \(W\) is between \(W^{(1)}_{cl}\) and \(W^{(2)}_{cl}\), i.e., there is an excess of classical trajectories which can pass the transition states and reach products. The reason for this behavior is that classical distributions can explore many initial conditions, which eventually may imply energies of individual trajectories higher than the energy of the transition states. Eventually this leads to the formation of products even in cases where the average (ensemble) energy is below the energy of the transition states. This effect will be more relevant in the case of trajectories distributed according to \(\rho^{(1)}_{0,cl}\) than in the case of \(\rho^{(2)}_{0,cl}\). On the other hand, for Bohmian trajectories the dynamics is very different due to the presence of the quantum potential: for low \(p_0\), the wave packet spreads faster than it propagates \[245\], thus favoring the formation of ripples by interference which will hinder the passage of Bohmian trajectories to products — remember that in Bohmian mechanics tunneling cannot be understood as in standard quantum mechanics, but as a process mediated by an
"effective" time-dependent barrier \([247]\), \(V_{\text{eff}}\). Nevertheless, in both cases, quantum and classical, we note that the maximum formation of products, \(\bar{W}\) is almost the same as \(W\).

For \(p_0 = 10\), however, \(\bar{E} - \bar{\delta}\) is above \(TS_1\), and hence a larger amount of products is expected, as it can be seen in Fig.\[1.2\]b, where we observe that the Bohmian distribution and the classical one \(\rho_{0,\text{cl}}^{(1)}\) provide similar values (although the latter goes below the former). In this case, although tunneling may still be active, the direct passage is going to control the dynamics in both cases, classical and quantum-mechanical. Note that in the Bohmian case the propagation is now faster than the spreading of the wave packet, and therefore more trajectories can be promoted to products before interference starts to influence the dynamics. Regarding \(\bar{W}\), we find a trend similar to \(W\), but the difference between the asymptotic values of these magnitudes has increased due to the larger energy (in average) carried by the par-
articles, which favors the recrossing. Only for the distribution $\rho_{0,cl}^{(2)}$ such a difference is negligible, since there is not much energy in excess.

In order to compare the maximum amount of products formed in a more general way, in Fig. 1.2.c there is a comparison among the three initial distributions for a range of $p_0$. As can be noticed, the formation of products is more efficient classically than quantum-mechanically for low values of $p_0$, while this behavior changes as $p_0$ becomes larger (the switching appears [244] for $p_0 \sim 8$, just when $\bar{E}$ approximately coincides with the energy of the transition state $T_1$, which connects the pre-equilibrium with products).

The dynamics associated with the process here described is illustrated in Fig. 1.3, where a series of snapshots display the time-evolution of the probability density associated with a Gaussian wave packet (equally spaced darker contours) starting on the reactants minimum with $p_0 = 9$. As time proceeds the wave packet evolves essentially along the direction indicated by the reaction path (thicker solid line). However, as can be seen particularly in the plots at $t = 100, 200$ and $300$, the motion of the wave packet is quite similar to that shown by a water stream when flowing along a river bed, trying to burst its banks each time it reaches a meander. Specifically, at $t = 300$ we observe that the main stream deviates remarkably from the reaction path, although later this quantum fluid gets back and moves towards the products region (see plot at $t = 500$). This deviation beyond the reaction path, which becomes larger with $p_0$, was called quantum bobsled effect by Marcus [248]. This effect, observed by McCullough and Wyatt [1–3] when studying the dynamics of the collinear H+H$_2$ reaction dynamics, arises from a direct analogy to the deviation undergone by a bobsled from the center of the track where it moves through due to its inertia (a positive centrifugal effect, according to Marcus [248]). Following with the analogy of the river, we observe that, after some time, when the passage to products has occurred the quantum fluid evolves more slowly and only shape changes are noticeable, just the same case after a region of “brave waters”. At this stage, if the dynamics continues, there can be some evolution from products to reactants (and vice versa), but there are no important inertial effects.

The information provided by the probability density results very valuable in order to determine the evolution of the system. However, Bohmian trajectories present some advantages which cannot be noticed studying only the wave packet dynamics. The case analyzed here is a clear example. Instead of displaying trajectories, which would result quite messy after some time, we have superimposed an arrow map on the region occupied by the wave packet at each time. The direction of the arrows indicate at each particular point of space the directionality of the vector field $\vec{v}$, and therefore the local direction of the flow (in this regard, Bohmian trajectories will be tangent to these vectors). According to these maps, we observe how from a situation where all the arrows are aligned along the same direction at $t = 0$, we pass to another at $t = 100$ where part of the arrows point downwards and part along the direction indicated by the reaction path. This happens precisely because the wave packet has collided with the first “meander”; something similar can be seen at $t = 200$, when the wave packet collides with the second “meander”, and so on. The arrows also allow us to detect the presence of quantum
Figure 1.3. Time-evolution of the probability density (red contours) associated with an initial Gaussian wave packet starting on the reactants minimum with $p_0 = 9$ (see text for details). The superimposed (blue) arrows show the directionality of the quantum flux, thus providing a clue on the ensemble (Bohmian) trajectory dynamics. Several contours of the Muller-Brown potential energy surface (with the same meaning as in Fig. 1.3) as well as the reaction path have also been included for a better understanding of the time-evolution of the probability density and the associated flux.
Figure 1.4. (a) Contour plot of the probability density associated with an electron crossing the two slits modeled by the potential energy surface (1.81) at the end of the simulation, i.e., the time when the interference pattern is already formed [119, 185]. Given the high-backscattering component, for a better understanding the contours are truncated to a certain value that allows an optimal visualization of the transferred density. Moreover, the contour plot of the potential energy surface is also displayed, with black contours for equipotentials lesser than or equal to $\langle E \rangle_i \approx 500$, and gray for higher values. (b) Angular distribution of the intensity computed at the end of the simulation (see text for details).

vorticity [12, 249, 250], i.e., the vortical motion that appears whenever the wave function displays a node. In this case, the arrows twist around the node, giving rise to a quantum whirlpool effect [1–3].

1.4.3. Scattering dynamics: Young’s two-slit experiment

In order to illustrate a practical application of Bohmian mechanics now in the case of a scattering system, we are going to consider a model of Young’s experiment with electrons where the interaction between the electrons and the two slits is described by a repulsive potential energy surface (barrier) [119, 185],

$$V(x, y) = \left( V_0 - \frac{1}{2} m \omega^2 y^2 + \frac{m^2 \omega^4 y^4}{16 V_0} \right) e^{-x^2/\alpha^2} ,$$

(1.81)

where $\alpha = 25$, $\omega = 600$, $V_0 = 8000$, and $m$ is the electron mass. As the ingoing wave function we consider a quasi-plane or quasi-monochromatic initial wave function, with energy $\langle E \rangle_i \approx 500$, which is constructed by linearly superimposing a series of identical Gaussian wave packets along the direction parallel to the $y$-axis. This wave function is then launched perpendicularly to the double-slit from a distance $\langle x \rangle_0 = -400$ (far enough from the potential energy surface, where $V \approx 0$). The interest in this kind of models relies on the fact that physical diffracting systems are constituted by atoms or molecules which interact with the diffracted electrons, and therefore a description of the experiment including the interaction potentials or potential energy surfaces results closer to the real experiment [251–254]. In Fig. 1.4(a), a contour plot of the probability density after the collision and diffraction from the two slits is shown. As can be noted, for this incidence energy, there is a large portion of the wave function which is back-scattered,
1.4. Applications

Figure 1.5. Bohmian trajectories illustrating the probability flow in the Young-type experiment with the potential energy surface (1.81). Three different sets of initial conditions have been chosen, which are shown in the three corresponding panels. In these panels, the initial value along the $y$ direction is always the same, with $x_0$ ranging from 0 to about 500, while the three specific values have been chosen for $y_0$ with respect to the initial probability density: (a) at the rearmost part, (b) at the center, and (c) in the foremost part (see text for details). The propagation is up to the final time in the simulation, which corresponds to the case shown in Fig. 1.4. For a better visualization in panels (a) and (b), only the back-scattered or diffracted part of the trajectories has been plotted. Moreover, the contour plot of the potential energy surface is also displayed, with black contours for equipotential lines lesser than or equal to $\langle E \rangle_i \simeq 500$, and gray for higher values.

while an angular distribution of very well-defined diffracted (forward-scattered) peaks appear behind the slits (for $y > 0$). The corresponding angular diffraction pattern is represented in Fig. 1.4(b), where the Gaussian-like envelope can be associated with the particular form chosen for the “holes” of the slits [144, 185].

In order to understand the dynamics that is taking place within this diffraction scenario (but that can also be extrapolated to any other scattering scenario), now we consider it under a Bohmian or quantum hydrodynamical, where the probability density describes a swarm of noninteracting particles. Thus, consider the three panels of Fig. 1.5, where only a half of the trajectories (those corresponding
to the upper slit) has been represented to make clearer the figures (moreover, their incident parts are not shown either) taking advantage of the reflection symmetry with respect to $y = 0$ — in Bohmian mechanics, the trajectories coming from each slit cannot intersect because of the *non-crossing flux* property [245] (see below). The ensembles of trajectories in each panel have been chosen to sample three regions of the initial probability density, i.e., varying their initial position $y_0$, but with the same $x_0$-position: (a) $x_0 = \langle x \rangle_0 - 100$, (b) $x_0 = \langle x \rangle_0$, and (c) $x_0 = \langle x \rangle_0 + 100$. As can be readily seen, the initial position is fundamental in the quantum dynamics displayed by the trajectories, for it leads to very different behaviors due to the action of $Q$, something which does not happen in classical mechanics (provided classical trajectories are launched far enough from the interaction region, their behavior would be independent on their $x_0$-position [246]). Note that those trajectories launched at distances further away from the double-slit barrier will not reach it [see Fig. 1.5(a)], while only those started at closer distances will be able to surmount it [see Fig. 1.5(c)]. In the case of the trajectories started at intermediate positions [see Fig. 1.5(b)], they will remain near the barrier until the “pressure” exerted by those coming behind will diminish and either they will be able to move backwards or pass through the slits. This is a general effect which can also be observed in other scattering problems [246, 249], which can be understood in terms of a sort of *quantum pressure* (within a hydrodynamical viewpoint). The presence of a quantum pressure can be better understood when the quantum Euler equation (1.19) is recast in terms of the velocity components. Then, the quantum force (arising from the quantum potential) can be rearranged [10–12] as

$$F_i = \frac{1}{\rho} \frac{\partial \sigma_{ik}}{\partial r_k},$$  

(1.82)

where $i, k = x, y, z$, with

$$\sigma_{ik} = -\frac{\hbar^2 \rho}{4m} \frac{\partial^2 \ln \rho}{\partial r_i \partial r_k}$$  

(1.83)

being a quantum pressure tensor, in analogy to the classical pressure tensor $p \delta_{ik}$. Thus, taking into account this hydrodynamical scenario, it is clear that electrons will tend to move towards those regions with lower values of the quantum pressure.

The number of particles passing through the slits is a function of the energy $E_i$ as well as the particular form of the potential energy surface. However, given a configuration of the potential energy surface, it is clear that for a certain incidence energy, those electrons associated with the rearmost part of the incident probability density (swarm) will be more likely to get diffracted. The fraction of diffracted electrons will then increase as the incidence energy also increases, which means that electrons coming from layers behind will also start to get diffracted. But, more importantly, by means of this Bohmian picture we are able to determine which electrons are going to contribute to diffraction and, more specifically, to which diffraction peak [255], something that cannot be known within the standard quantum framework. As seen in Fig. 1.5(c), the interference behind the slits manifests by grouping or channeling the trajectories along the diffraction angles (along which
electrons display an essentially free motion) undergoing a strong “repulsive”-like behavior whenever they approach regions of fast variation of the quantum potential. The formation of these channels within the so-called Fraunhofer region [255] is a direct consequence of the information that the quantum potential transmits to particles about the status of each slit (either open or close). This is also related with the non-crossing flux property [245] of Bohmian mechanics mentioned above, which arises from the fact that two (Bohmian) trajectories cannot coincide on the same space point at the same time due to the single-valuedness of $S$ (except on a nodal point). In this way, for the symmetric (with respect to the $y = 0$) double slit we are considering, all those trajectories started above $y = 0$ will not be able to cross to the region $y < 0$, for this would violate the non-crossing flux property.

1.4.4. Effective dynamical treatments: Decoherence and reduced Bohmian trajectories

An interesting description of Bohmian mechanics arises from the field of decoherence and the theory of open quantum systems. 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, $\hat{\rho}(t)$, 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 $\hat{\rho}(t) \equiv |\Psi(t)\rangle\langle\Psi(t)|$ over the $3N$ environment degrees of freedom, $\{\vec{r}_i\}_{i=1}^N$,

$$\hat{\rho}(\vec{r},\vec{r}',t) = \int (\vec{r},\vec{r}_1,\vec{r}_2,\ldots,\vec{r}_N|\Psi(t)\rangle\langle\Psi(t)|\vec{r}',\vec{r}_1,\vec{r}_2,\ldots,\vec{r}_N) \, d\vec{r}_1 \, d\vec{r}_2 \cdots d\vec{r}_N. \quad (1.84)$$

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

$$\vec{J}(\vec{r},t) \equiv \hbar m \Im\left[\vec{\nabla} \hat{\rho}(\vec{r},\vec{r}',t)\right]|_{\vec{r}'=\vec{r}}, \quad (1.85)$$

which satisfies the continuity equation

$$\dot{\hat{\rho}} + \nabla \cdot \vec{J} = 0. \quad (1.86)$$

In Eq. (1.86), $\hat{\rho}$ is the diagonal element [i.e., $\hat{\rho} \equiv \hat{\rho}(\vec{r},\vec{r},t)$] of the reduced density matrix and gives the measured intensity [256].

Taking into account Eqs. (1.85) and (1.86), now we define the velocity field, $\vec{r}$, associated to the (reduced) system dynamics as

$$\vec{J} = \hat{\rho} \vec{r}, \quad (1.87)$$

which is analogous to the Bohmian velocity field. Now, from Eq. (1.87), we define a new class of quantum trajectories as the solutions to the equation of motion

$$\dot{\vec{r}} \equiv \hbar m \frac{\Im[\nabla \hat{\rho}(\vec{r},\vec{r}',t)]}{\Re[\hat{\rho}(\vec{r},\vec{r}',t)]}|_{\vec{r}'=\vec{r}}. \quad (1.88)$$

These new trajectories are the so-called reduced quantum trajectories [194, 195], which are only related to the system reduced density matrix. As shown in [194,
the dynamics described by Eq. (1.88) leads to the correct intensity [with its
time-evolution being described by Eq. (1.86)] when the statistics of a large num-
ber of particles is considered. Moreover, it is also straightforward to show that
Eq. (1.88) reduces to the well-known expression for the velocity field in Bohmian
mechanics when there is no interaction with the environment. An application of
this approach to the analysis of dephasing by incoherence in Young’s experiment
and its influence on the transverse momentum transfer [257] can be found in [258].

1.4.5. Pathways to complex molecular systems: Mixed Bohmian-
classical mechanics

As mentioned in Sec. 1.2.4, there are different hybrid approaches to deal with many
degree-of-freedom systems, where the system degrees of freedom are described
quantum-mechanically while the bath ones are accounted for classically. Among
them, we find methods such as the mean-field approximation [159] or the surface
hopping trajectories [160]. In all these methods, the key point is the implementa-
tion of the so-called backreaction [259], i.e., the action of the system over the bath,
since the contrary is simple and it is usually done in terms of a time-dependent po-
tential which is function of the bath coordinates (following the Born-Oppenheimer
approximation scheme). Here, we are going to analyze this problem within the
framework of the so-called mixed quantum-Bohmian approach [260–263].

Consider two interacting systems $X$ and $Y$ (or degrees of freedom), each spec-
dified by the coordinates $x$ and $y$, respectively, and with associated masses $m_x$ and
$m_y$. Proceeding as in Sec. 1.3, with the polar ansatz (1.11) and the corresponding
two-dimensional Schrödinger equation, Eqs. (1.12) and (1.13) read as

$$\frac{\partial S}{\partial t} + \frac{1}{2m_x} \left( \frac{\partial S}{\partial x} \right)^2 + \frac{1}{2m_y} \left( \frac{\partial S}{\partial y} \right)^2 = -V_{\text{eff}}, \quad (1.89)$$
$$\frac{\partial R^2}{\partial t} + \frac{1}{m_x} \frac{\partial S}{\partial x} \frac{\partial R^2}{\partial x} + \frac{1}{m_y} \frac{\partial S}{\partial y} \frac{\partial R^2}{\partial y} = -R^2 \left( \frac{1}{m_x} \frac{\partial^2 S}{\partial x^2} + \frac{1}{m_y} \frac{\partial^2 S}{\partial y^2} \right), \quad (1.90)$$

where the quantum potential has the form

$$Q(x,y,t) = -\frac{\hbar^2}{2m_x} \frac{1}{R} \frac{\partial^2 R}{\partial x^2} - \frac{\hbar^2}{2m_y} \frac{1}{R} \frac{\partial^2 R}{\partial y^2}, \quad (1.91)$$

which is non-factorizable (see Sec. 1.3.2). Let us recast Eq. (1.89) in its Eulerian
form by applying the operators $\partial / \partial x$ and $\partial / \partial y$ to both sides of this equation. This
gives rise to two coupled equations,

$$\frac{\partial}{\partial t} \left( \frac{\partial S}{\partial x} \right) + v_x \frac{\partial^2 S}{\partial x^2} + v_y \frac{\partial^2 S}{\partial y \partial x} = -\frac{\partial V_{\text{eff}}}{\partial x}, \quad (1.92)$$
$$\frac{\partial}{\partial t} \left( \frac{\partial S}{\partial y} \right) + v_y \frac{\partial^2 S}{\partial y^2} + v_x \frac{\partial^2 S}{\partial x \partial y} = -\frac{\partial V_{\text{eff}}}{\partial y}, \quad (1.93)$$

where $v_x = p_x / m_x = (1/m_x)(\partial S / \partial x)$ and $v_y = p_y / m_y = (1/m_y)(\partial S / \partial y)$. Taking
into account the definition of the Lagrange time derivative (see Sec. 1.3), these two
equations can be recast in a more familiar Newtonian form,
\[ m_x \frac{d^2 x}{dt^2} = -\frac{\partial V_{\text{eff}}}{\partial x}, \]  
\[ m_y \frac{d^2 y}{dt^2} = -\frac{\partial V_{\text{eff}}}{\partial y}. \] (1.94)

So far no approximation has been invoked. Let us now consider, for instance, that \( m_y \gg m_x \), which physically means that for the timescale ruling the behavior of \( X \), the system \( Y \) behaves almost classically. This slower evolution along the \( y \) coordinate means that the second space-derivatives of \( S \) and \( R \) with respect to this coordinate will be negligible. Accordingly, Eqs. (1.92) and (1.93) can be recast as
\[ \frac{\partial}{\partial t} \left( \frac{\partial S}{\partial x} \right) + \frac{1}{m_x} \frac{\partial \tilde{S}}{\partial x} \frac{\partial^2 \tilde{S}}{\partial x^2} + \frac{1}{m_y} \frac{\partial \tilde{S}}{\partial y} \frac{\partial^2 \tilde{R}}{\partial y \partial x} = -\frac{\partial \tilde{V}_{\text{eff}}}{\partial x}, \] (1.96)
\[ \frac{\partial}{\partial t} \left( \frac{\partial S}{\partial y} \right) + \frac{1}{m_x} \frac{\partial \tilde{S}}{\partial x} \frac{\partial^2 \tilde{S}}{\partial x \partial y} - \frac{\partial \tilde{V}_{\text{eff}}}{\partial y}, \] (1.97)

where \( \tilde{S} \) and \( \tilde{R} \) denote the approximate values of \( S \) and \( R \), respectively. In these equations, \( \tilde{V}_{\text{eff}} \) is the corresponding approximate effective potential, with
\[ \tilde{Q}(x, t|y) = -\frac{\hbar^2}{2m_x} \frac{1}{\tilde{R}} \frac{\partial^2 \tilde{R}}{\partial x^2}, \] (1.98)

where \((x, t|y)\) means that \( \tilde{Q} \) depends on \( y \) implicitly through a sort of parametrization — as it also happens in the Born-Oppenheimer approximation (see Sec. 1.2.1). On the other hand, (1.90) becomes the approximate continuity equation,
\[ \frac{\partial \tilde{R}^2}{\partial t} + \frac{\partial}{\partial x} \left( \frac{\tilde{R}^2 \partial \tilde{S}}{m_x \partial x} \right) + \frac{1}{m_y} \frac{\partial \tilde{S}}{\partial y} \frac{\partial \tilde{R}^2}{\partial y} = 0. \] (1.99)

Evaluating (1.96) and (1.99) along the quasi-classical trajectory \( y(t) \) allows us to define the pseudo-Lagrangian time derivative operator
\[ \frac{d}{dt} = \frac{\partial}{\partial t} + v_y \frac{\partial}{\partial y}, \] (1.100)
and therefore to recast those equations as
\[ \frac{d}{dt} \left( \frac{\partial \tilde{S}}{\partial x} \right) + \left( \frac{1}{m_x} \frac{\partial \tilde{S}}{\partial x} \right) \frac{\partial^2 \tilde{S}}{\partial x^2} = -\frac{\partial \tilde{V}_{\text{eff}}}{\partial x}, \] (1.101)
\[ \frac{d \tilde{R}^2}{dt} + \frac{\partial}{\partial x} \left( \tilde{R}^2 \frac{\partial \tilde{S}}{m_x \partial x} \right) = 0, \] (1.102)
which satisfy the pseudo-Schrödinger equation
\[ i\hbar \frac{d \tilde{\Psi}(x, y(t), t)}{dt} = \left[ -\frac{\hbar^2}{2m_s} \frac{\partial^2}{\partial x^2} + V(x, y(t)) \right] \tilde{\Psi}(x, y(t), t), \] (1.103)
where \( \tilde{\Psi} = \tilde{R} e^{i \tilde{S}/\hbar} \). As can be noticed, the dimensionality of the full quantum problem reduces to the (subspace) dimensionality associated with \( X \), since the classical-like coordinate \( y \) acts as a time-dependent parameter (the external potential \( V \) has
become time-dependent in virtue of this parametrization). On the other hand, \( Y \) evolves according to a quasi-classical Newtonian equation,

\[
m_y \frac{d^2 y}{dt^2} = \frac{\partial}{\partial y} \left( V(x, y, t) + \tilde{Q}(x, t|y) \right),
\]

which arises from Eq. (1.97) after applying the pseudo-Lagrangian operator [note that it can also be obtained from Eq. (1.95) after the corresponding approximation is considered] and is integrated after getting the solution \( \tilde{\Psi}(x, y(t), t) \) from (1.103).

As briefly mentioned above, the method here described constitutes a sort of translation of the Born-Oppenheimer rule to the case of slow and fast degrees of freedom. This quantum-classical approach is commonly used when dealing with quantum open systems, whenever some degrees of freedom display a slower dynamics than other, which are faster and in many cases can be treated even as a surrounding noise function (thermal bath). Within the Bohmian literature, approaches to deal with the many-body problem have been suggested, for instance, by Garashchuk and Rassolov [264–266], Bittner [267], Makri [268–270] and, more recently, Franco [271].

1.5. Concluding remarks

Looking back, if there is a healthy and increasing interest at present in Bohmian mechanics, it could be said it partly comes from the important numerical work developed by Wyatt and colleagues since the end of the 1990s. Up to that time Bohmian mechanics had been applied to some physical cases of interest, disproving that trajectories were not incompatible at all with quantum mechanics beyond just metaphysical discussions. From a pragmatic viewpoint, leaving aside interpretational issues concerning hidden variables, the reality of the wave function and the quantum realm, such important contributions were probably marginalized because, in the end, they were only another way to describe what was already known. If a formulation renders the same, what is it worth for? Beyond quantum foundations aspects, this might have been a wondering question — a rather reasonable and understandable one, after all — in people’s minds (reviewers, many of them) that made them reluctant to accept a trajectory-based description of quantum phenomena. Notice that something similar also happened when the first time-dependent quantum-mechanical simulations started appearing by the end of the 1960s [272], making possible the impossible, namely providing a neat and unambiguous visualization of the full quantum process, since the initial state up to the final one. Quantum mechanics was not a “black box” anymore, as claimed by Bohr and followers over decades. With time it was understood that these pictures detailing the process could be used to extract valuable information about it, which could not be done (or not, at least, in an easy manner) with the other more widespread time-independent techniques. Nowadays this type of simulations constitute a consolidated standard tool to approach quantum-mechanical systems, from simple academic-type problems to very complex ones. Something similar has also happened with Bohmian mechanics as soon as it has started being
perceived as a worth exploring and exploiting numerical methodology, particularly in Chemistry, as Wyatt and other pioneers in the field have shown along the about last twenty years. In this regard, it is possible to find Bohmian-based algorithms to determine electronic structure as well as to describe the dynamics of many-body systems.

Besides the computational aspect, the interpretational one has also gained in relevance over the last decades, just as soon as relatively complex (more realistic) problems have started being considered, from atomic and molecular scattering to nanodevices, from nonlinear optics to electron microscopy. For years, molecular dynamics and statistics have mainly relied on the computation of classical trajectories (based on both Newtonian and Hamiltonian schemes) and, in general, the tools of classical mechanics. Good for the purpose, but approximate (at different degrees, depending on the method and/or problem considered) because they lack the essence of quantum mechanics, namely coherence and all the related properties, such as interference, tunneling, or entanglement. With the extensive use and application of quantum mechanics in the development of electronic structure methods, first, and then in molecular dynamics through wave-packet propagation methods, better and more accurate solutions were obtained, of course. However, interpretations of the corresponding outcomes still had to make use of classical argumentations based on the longstanding quantum-classical correspondence thinking established by Bohr back in the 1920s. Bohmian mechanics has allowed to change the landscape, providing a correct trajectory-based interpretation for quantum phenomena (compared to classical approaches), that is, in consonance with the evolution of the corresponding wave functions and without introducing any extra ad hoc artifacts (e.g., quantization rules over classical ensembles). Of course, this does not mean at all that we should now make the mistake of only seeking for Bohmian trajectories to the detriment of trying to still establish bridges between quantum and classical dynamics with the aid of classical trajectories. So far, the quantum world has been and still is disconcerting and challenging to us (and perhaps it will remain so for long), hence any tool to explore it should always be welcome rather than banned.

Getting back to Chemistry, it is perhaps pertinent to conclude this Chapter quoting the very last paragraph of Walter Kohn’s Nobel Lecture [273]:

Looking into the future I expect that wavefunction-based and density based theories will, in complementary ways, continue not only to give us quantitatively more accurate results, but also contribute to a better physical/chemical understanding of the electronic structure of matter.

Probably Bohmian mechanics, that is, the hydrodynamic picture of quantum mechanics will play a major role in this regard. This is something yet to come, although some signs are already on the way, principally the change in the perception we have at present of this approach.
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References

[1] E. A. McCullough and R. E. Wyatt, *Quantum dynamics of the collinear (H, H₂) reaction*, J. Chem. Phys. 51, 1253 (1969).
[2] E. A. McCullough and R. E. Wyatt, *Dynamics of the collinear H + H₂ reaction. I. Probability density and flux*, J. Chem. Phys. 54, 3378 (1971).
[3] E. A. McCullough and R. E. Wyatt, *Dynamics of the collinear H + H₂ reaction. II. Energy analysis*, J. Chem. Phys. 54, 3392 (1971).
[4] J. O. Hirschfelder, A. C. Christoph, and W. E. Palke, *Quantum mechanical streamlines. I. Square potential barrier*, J. Chem. Phys. 61, 5435 (1974).
[5] J. O. Hirschfelder, C. J. Goebel, and L. W. Bruch, *Quantized vortices around wavefunction nodes. II*, J. Chem. Phys. 61, 5456 (1974).
[6] J. O. Hirschfelder and K. T. Tang, *Quantum mechanical streamlines. III. Idealized reactive atom-diatomic molecule collision*, J. Chem. Phys. 64, 5456 (1974).
[7] D. Bohm, *A suggested interpretation of the quantum theory in terms of “hidden” variables. I*, Phys. Rev. 85, 166 (1952).
[8] D. Bohm, *A suggested interpretation of the quantum theory in terms of “hidden” variables. II*, Phys. Rev. 85, 180 (1952).
[9] D. Bohm, *Proof that probability density approaches |ψ|² in causal interpretation of the quantum theory*, Phys. Rev. 89, 458 (1953).
[10] T. Takabayasi, *On the formulation of quantum mechanics associated with classical pictures*, Prog. Theor. Phys. 8, 143 (1952).
[11] T. Takabayasi, *Remarks on the formulation of quantum mechanics with classical pictures and on relations between linear scalar fields and hydrodynamical fields*, Prog. Theor. Phys. 9, 187 (1953).
[12] P. R. Holland, *The Quantum Theory of Motion* (Cambridge University Press, Cambridge 1993).
[13] D. Dürr, *Bohmische Mechanik als Grundlage der Quanten-mechanik* (Springer, Berlin, 2001).
[14] D. Dürr and S. Teufel, *Bohmian Mechanics* (Springer, Berlin, 2009).
[15] R. E. Wyatt, *Quantum Dynamics with Trajectories* (Springer, New York, 2005).
[16] A. S. Sanz and S. Miret-Artés, *A Trajectory Description of Quantum Processes. I. Fundamentals*, Lecture Notes in Physics 880 (Springer, Berlin, 2012).
[17] A. S. Sanz and S. Miret-Artés, *A Trajectory Description of Quantum Processes. II. Applications*, Lecture Notes in Physics 831 (Springer, Berlin, 2014).
[18] A. S. Sanz, *Bohm’s approach to quantum mechanics: Alternative theory or practical picture?*, preprint [arXiv:1707.00609] (2017).
[19] E. Madelung, *Quantentheorie in hydrodynamischer Form*, Z. Physik 40, 332 (1926).
[20] P. K. Chattaraj, *Quantum Trajectories* (CRC Taylor and Francis, New York, 2010).
[21] K. H. Hughes and G. Parlant, *Quantum Trajectories* (CCP6, Daresbury, UK, 2011).
[22] J. P. Dowling and G. J. Milburn, *The second quantum revolution*, Phil. Trans. R. Soc. Lond. A 361, 1655 (2003).
[23] M. A. Nielsen and I. L. Chuang, *Quantum Computation and Quantum Information* (Cambridge University Press, Cambridge, 2000).
[24] J. Olson, Y. Cao, J. Romero, P. Johnson, P.-L. Dallaire-Demers, N. Sawaya, P. Narang, I. Kivlichan, M. Wasielewski and A. Aspuru-Guzik, *Quantum information and computation for Chemistry*, NSF Workshop Report, [arXiv:1706.05413] (2016).
1.5. Concluding remarks

[25] M. E. Eberhart, Quantum mechanics and molecular design in the twenty first century, Found. Chem. 4, 201 (2002).
[26] M. E. Eberhart and D. P. Clougherty, Looking for design in materials design, Nat. Mater. 3, 659 (2004).
[27] A. Lehmann and C. D. Maranas, Molecular design using quantum chemical calculations for property estimation, Ind. Eng. Chem. Res. 43, 3419 (2004).
[28] T. Zhou, D. Huang, and A. Caflisch, Quantum mechanical methods for drug design, Curr. Top. Med. Chem. 10, 33 (2010).
[29] M. Pavone, A. M. Ritzmann, and E. A. Carter, Quantum-mechanics-design principles for solid oxide fuel cell cathode materials, Energy Environ. Sci. 4, 4933 (2011).
[30] N. Lambert, Y.-N. Chen, Y.-C. Cheng, C.-M. Li, G.-Y. Chen, and F. Nori, Quantum biology, Nat. Phys. 9, 10 (2012).
[31] Th. Ritz, S. Adem, and K. Schulten, A model for photoreceptor-based magnetoreception in birds, Biophys. J. 78, 707 (2000).
[32] G. S. Engel, T. R. Calhoun, E. L. Read, T.-K. Ahn, T. Mančal, Y.-C. Cheng, R. E. Banken- ship, and G. R. Fleming, Evidence for wavelike energy transfer through quantum coherence in photosynthetic systems, Nature 446, 782 (2007).
[33] M. Sarovar, A. Ishizaki, G. R. Fleming, and K. B. Whaley, Quantum entanglement in photosynthetic light-harvesting complexes, Nat. Phys. 6, 462 (2010).
[34] I. Bialynicki-Birula, M. Cieplak, and J. Kamisnki, Theory of Quanta (Oxford University Press, Oxford, 1992).
[35] R. Fürth, Über einige Beziehungen zwischen klassischer Statistik und Quantenmechanik, Z. Physik 81, 143 (1933).
[36] G. G. Comisar, Brownian-motion model of nonrelativistic quantum mechanics, Phys. Rev. 138, B1332 (1965).
[37] L. Landau, The theory of superfluidity of helium II, J. Phys. (USSR) 5, 71 (1941).
[38] F. London, Planck’s constant and low temperature transfer, Rev. Mod. Phys. 17, 310 (1945).
[39] L. de Broglie, Remarques sur la nouvelle Mécanique ondulatoire, Compt. Rend. 183, 273 (1926).
[40] L. de Broglie, Sur la possibilité de relier les phénomènes d'interférence et de diffraction à la théorie des quanta de lumière, Compt. Rend. 183, 447 (1926).
[41] L. de Broglie, Sur le rôle des ondes continues Ψ en Mécanique ondulatoire, Compt. Rend. 185, 380 (1927).
[42] T. H. Solomon, E. R. Weeks, and H. L. Swinney, Observation of anomalous diffusion and Lévy flights in a two-dimensional rotating flow, Phys. Rev. Lett. 71, 3975 (1993).
[43] J. C. Sommerer, H.-C. Ku, and H. E. Gilreath, Experimental evidence for chaotic scattering in a fluid wake, Phys. Rev. Lett. 77, 5055 (1996).
[44] A. S. Sanz and S. Miret-Artés, Quantum phase analysis with quantum trajectories: A step towards the creation of a Bohmian thinking, Am. J. Phys. 80, 525 (2012).
[45] A. S. Sanz, Quantumness beyond quantum mechanics, J. Phys.: Conf. Ser. 361, 012016 (2012).
[46] Y. Couder, S. Protière, E. Fort, and A. Boudaoud, Dynamical phenomena: Walking and orbiting droplets, Nature 437, 208 (2005).
[47] S. Protière, A. Boudaoud, Y. Couder, Particle-wave association on a fluid interface, J. Fluid. Mech. 554, 85 (2006).
[48] Y. Couder and E. Fort, Single-particle diffraction and interference at a macroscopic scale, Phys. Rev. Lett. 97, 154101 (2006).
[49] S. Protière and Y. Couder, Orbital motion of bouncing drops, Phys. Fluid. 18, 091114 (2006).
[50] A. Eddi, E. Fort, F. Moisy, and Y. Couder, Unpredictable tunneling of a classical wave-particle association, Phys. Rev. Lett. 102, 240401 (2009).
[51] E. Fort, A. Eddi, A. Boudaoud, J. Moukhtar, and Y. Couder, Path-memory induced quantization of classical orbits, Proc. Natl. Acad. Sci. USA 108, 17515 (2010).
[52] Y. Couder, A. Boudaoud, S. Protière, and E. Fort, Walking droplets: A form of wave-
particle duality at macroscopic scale?, Europhys. News 41, 14 (2010).

[53] J. W. M. Bush, Quantum mechanics writ large, Proc. Natl. Acad. Sci. USA 107, 17455 (2010).

[54] D. M. Harris, J. Moukhtar, E. Fort, Y. Couder, and J. W. M. Bush, Wavelike statistics from pilot-wave dynamics in a circular corral, Phys. Rev. E 88, 011001(R) (2013).

[55] J. W. M. Bush, Pilot-wave hydrodynamics, Annu. Rev. Fluid Mech. 47, 269 (2015).

[56] W. H. Zurek and J. A. Wheeler, Quantum Theory of Measurement (Princeton University Press, Princeton, NJ, 1983).

[57] B. G. Englert, M. O. Scully, G. Süssmann, and H. Walther, Surrealistic Bohm trajectories, Z. Naturforsch. 47a, 1175 (1992).

[58] R. Courant and D. Hilbert, Methods of Mathematical Physics (Wiley-Interscience, New York, 1966).

[59] H. Weyl, Quantenmechanik und Gruppentheorie, Z. Phys. 46, 1 (1927).

[60] E. P. Wigner, On the quantum correction for thermodynamic equilibrium, Phys. Rev. 40, 749 (1932).

[61] J. E. Moyal, Quantum mechanics as a statistical theory, Math. Proc. Cambridge Philos. Soc. 45, 99 (1949).

[62] R. E. Wyatt, Quantum wavepacket dynamics with trajectories: wavefunction synthesis along quantum paths, Chem. Phys. Lett. 313, 189 (1999).

[63] C. L. Lopreore and R. E. Wyatt, Quantum wave packet dynamics with trajectories, Phys. Rev. Lett. 82, 5190 (1999).

[64] C. L. Lopreore and R. E. Wyatt, Quantum wave packet dynamics with trajectories: reflections on a downhill ramp potential, Chem. Phys. Lett. 325, 73 (2000).

[65] Y. Goldfarb, I. Degani, and D. J. Tannor, Bohmian mechanics with complex action: A new trajectory-based formulation of quantum mechanics, J. Chem. Phys. 125, 231103 (2006).

[66] Y. Goldfarb and D. J. Tannor, Interference in Bohmian mechanics with complex action, J. Chem. Phys. 127, 161101 (2007).

[67] Y. Goldfarb, J. Schiff, and D. J. Tannor, Unified derivation of Bohmian methods and the incorporation of interference effects, J. Chem. Phys. 111, 10416 (2007).

[68] Y. Goldfarb, I. Degani, and D. J. Tannor, Semiclassical approximation with zero velocity trajectories, Chem. Phys. 338, 106 (2007).

[69] C.-C. Chou and R. E. Wyatt, Computational method for the quantum Hamilton-Jacobi equation: Bound states in one dimension, J. Chem. Phys. 125, 174103 (2006).

[70] C.-C. Chou and R. E. Wyatt, Quantum trajectories in complex space: One-dimensional stationary scattering problems, J. Chem. Phys. 128, 154106 (2008).

[71] C.-C. Chou and R. E. Wyatt, Quantum streamlines within the complex quantum Hamilton-Jacobi formalism, J. Chem. Phys. 129, 124113 (2008).

[72] C.-C. Chou and R. E. Wyatt, Complex-extended Bohmian mechanics, J. Chem. Phys. 132, 134102 (2010).

[73] J. S. Bell, Speakable and Unspeakable in Quantum Mechanics (Cambridge University Press, Cambridge, 1987).

[74] M. Born and J. R. Oppenheimer, Zur Quantentheorie der Molekeln, Ann. Physik 84, 457 (1927).

[75] B. H. Bransden and C. J. Joachain, Physics of Atoms and Molecules (Longman Scientific & Technical, Essex, 1983).

[76] I. N. Levine, Quantum Chemistry (Prentice Hall, Upper Saddle River, NJ, 2000), 5th Ed.

[77] A. Szabo and N. S. Ostlund, Modern Quantum Chemistry (Dover, Publications, Mineola, NY, 1996).

[78] P. Fulde, Electron Correlations in Molecules and Solids (Springer, Berlin, 2002), 3rd Ed.

[79] W. Koch and M. C. Holthausen, A Chemist’s Guide to Density Functional Theory (Wiley-VCH, Weinheim, 2001), 2nd Ed.

[80] R. M. Martin, Electronic Structure. Basic Theory and Practical Methods (Cambridge Uni-
1.5. Concluding remarks

[81] I. G. Kaplan, *Intermolecular Interactions: Physical Picture, Computational Methods and Model Potentials* (John Wiley & Sons, Chichester, 2006).

[82] J. Z. H. Zhang, *Theory and Application of Quantum Molecular Dynamics* (World Scientific, Singapore, 1999).

[83] D. J. Tannor, *Introduction to Quantum Mechanics* (University Science Books, Sausalito, CA, 2006).

[84] W. H. Louisell, *Quantum Statistical Properties of Radiation* (John Wiley & Sons, New York, 1973).

[85] D. A. McQuarrie, *Statistical Mechanics* (Harper & Row, New York, 1976).

[86] U. Weiss, *Quantum Dissipative Systems* (World Scientific, Singapore, 2008), 3rd Ed.

[87] H.-P. Breuer and F. Petruccione, *The Theory of Open Quantum Systems* (Oxford University Press, New York, 2002).

[88] H. Carmichael, *An Open Systems Approach to Quantum Optics* (Springer-Verlag, Berlin, 1993).

[89] I. Percival, *Quantum State Diffusion* (Cambridge University Press, Cambridge, 1998).

[90] H. Nakai, *Simultaneous determination of nuclear and electronic wave functions without Born-Oppenheimer approximation: Ab initio NO+MO/HF theory*, Int. J. Quantum Chem. 86, 511 (2002).

[91] H. Nakai, *Nuclear orbital plus molecular orbital theory: Simultaneous determination of nuclear and electronic wave functions without Born-Oppenheimer approximation*, Int. J. Quantum Chem. 107, 2849 (2007).

[92] L. Veis, J. Višňák, H. Nishizawa, H. Nakai, and J. Pittner, *Quantum chemistry beyond Born-Oppenheimer approximation on a quantum computer: A simulated phase estimation study*, Int. J. Quantum Chem. 116, 1328 (2016).

[93] M. Head-Gordon, *Quantum chemistry and molecular processes*, J. Phys. Chem. 100, 13213 (1996).

[94] S. S. Shaik and P. C. Hiberty, *A Chemist’s Guide to Valence Bond Theory* (Wiley-Interscience, New Jersey, 2007).

[95] L. Pauling, *The application of the quantum mechanics to the structure of the hydrogen molecule and hydrogen molecule-ion and to related problems*, Chem. Rev. 5, 173 (1928).

[96] L. Pauling, *The nature of the chemical bond. Application of results obtained from the quantum mechanics and from a theory of paramagnetic susceptibility to the structure of molecules*, J. Am. Chem. Soc. 53, 1367 (1931).

[97] K. Blum, *Density Matrix Theory and Applications* (Plenum Press, New York, 1981).

[98] L. H. Thomas, *The calculation of atomic fields*, Proc. Cambridge Phil. Soc. 23, 542 (1927).

[99] E. Fermi, *Un metodo statistico per la determinazione di alcune propriet`a dell’atomo*, Rend. Accad. Naz. Lincei 6, 602 (1927).

[100] M. A. L. Marques and E. K. U. Gross, *Time-dependent density functional theory*, Annu. Rev. Phys. Chem. 55, 427 (2004).

[101] S. Botti, A. Schindlmayr, R. Del Sole, and L. Reining, *Time-dependent density-functional theory for extended systems*, Rep. Prog. Phys. 70, 357 (2007).

[102] H. Nakatsuji, *Equation for direct determination of density matrix*, Phys. Rev. A 14, 41 (1976).

[103] H. Nakatsuji and K. Yasuda, *Direct determination of the quantum-mechanical density matrix using the density equation*, Phys. Rev. Lett. 76, 1039 (1996).

[104] K. Yasuda and H. Nakatsuji, *Direct determination of the quantum-mechanical density matrix using the density equation*, Phys. Rev. A 56, 2648 (1997).

[105] C. Valdemoros, *Approximating the 2nd-order reduced density-matrix in terms of the 1st-order one*, Phys. Rev. A 45, 4462 (1992).

[106] C. Valdemoros, *Contracting and calculating traces over the N-electron space: Two powerful tools for obtaining averages*, Int. J. Quantum Chem. 60, 131 (1996).

[107] C. Valdemoros, *Electron Correlation and Reduced Density Matrices, in Correlation and Localization*, P. R. Surjan (Ed.) (Springer, Berlin, 1999), pp. 187-200.
[108] C. Valdemoro, L. M. Tel, D. R. Alcoba, E. Pérez-Romero, and F. J. Casquero, Some basic properties of the correlation matrices, Int. J. Quantum Chem. 90, 1555 (2002).
[109] D. R. Alcoba and C. Valdemoro, Spin structure and properties of the correlation matrices corresponding to pure spin states: Controlling the S-representability of these matrices, Int. J. Quantum Chem. 102, 629 (2005).
[110] E. R. Davidson, Reduced Density Matrices in Quantum Chemistry (Academic Press, New York, 1976).
[111] A. J. Coleman and V. I. Yukalov, Reduced Density Matrices: Coulson’s Challenge (Springer-Verlag, New York, 2000).
[112] J. Cioslowski (Ed.), Many-Electron Densities and Reduced Density Matrices (Kluwer, Dordrecht, 2000).
[113] D. A. Mazziotti, Contracted Schrödinger equation: Determining quantum energies and two-particle density matrices without wave functions, Phys. Rev. A 57, 4219 (1998).
[114] D. A. Mazziotti, Pursuit of N-representability for the contracted Schrödinger equation through density-matrix reconstruction, Phys. Rev. A 60, 3618 (1999).
[115] D. A. Mazziotti, Anti-Hermitian contracted Schrödinger equation: Direct determination of the two-electron reduced density matrices of many-electron molecules, Phys. Rev. Lett. 97, 143002 (2006).
[116] D. A. Mazziotti (Ed.), Reduced-Density-Matrix Mechanics with Applications to Many-Electron Atoms and Molecules, Adv. Chem. Phys. 134 (Wiley, New York, 2007).
[117] P. Sherwood, Hybrid Quantum Mechanics/Molecular Mechanics Approaches, in Modern Methods and Algorithms of Quantum Chemistry, J. Grotendorst (Ed.) (John von Neumann Institute for Computing, Jülich, 2000), 2nd Ed.
[118] M. Born and E. Wolf, Principles of Optics (Cambridge University Press, Cambridge, 1999), 7th Ed.
[119] R. Guantes, A. S. Sanz, J. Margalef-Roig, and S. Miret-Artés, Atom-surface diffraction: a trajectory description, Surf. Sci. Rep. 53, 199 (2004).
[120] A.S. Sanz and S. Miret-Artés, Selective adsorption resonances: Quantum and stochastic approaches, Phys. Rep. 451, 37 (2007).
[121] P. M. Morse and H. Feshbach, Methods of Theoretical Physics (McGraw Hill, New York, 1953).
[122] M. Razavy, Quantum Theory of Tunneling (World Scientific, New Jersey, 2003).
[123] J. Ankerhold, Quantum Tunneling in Complex Systems in Springer Tracts in Modern Physics 224 (Springer, New York, 2007).
[124] H. Jeffreys, On certain approximate solutions of linear differential equations of the second order, Proc. London Math. Soc. (2), 23, 428 (1925).
[125] G. Wentzel, Eine Verallgemeinerung der Quantenbedingungen für die Zwecke der Wellenmechanik, Z. Physik 38, 518 (1926).
[126] H. A. Kramers, Wellenmechanik und halbzahlige Quantisierung, Z. Physik 39, 828 (1926).
[127] L. Brillouin, La mécanique ondulatoire de Schrödinger; une méthode générale de résolution par approximations successives, Comptes Rendus 183, 24 (1926).
[128] L. Brillouin, Sur un type général de problèmes, permettant la séparation des variables dans la mécanique ondulatoire de Schrödinger, Comptes Rendus 183, 270 (1926).
[129] C. Cerjan (Ed.), Numerical Grid Methods and Their Application to Schrödinger’s Equation (Kluwer Academic, Amsterdam, 1993).
[130] N. J. Giordano, Computational Physics (Prentice Hall, Upper Saddle River, NJ, 1997).
[131] M. C. Gutzwiller, Chaos in Classical and Quantum Mechanics (Springer-Verlag, New York, 1990).
[132] E. J. Heller, Bound-state eigenfunctions of classically chaotic Hamiltonian systems: Scars of periodic orbits, Phys. Rev. Lett. 53, 1515 (1984).
[133] R. G. Newton, Scattering Theory of Waves and Particles (McGraw-Hill, New York, 1966).
[134] M. S. Child, Molecular Collision Theory (Dover, New York, 1996).
[135] C. J. Ray and J. M. Bowman, Quasiclassical trajectory calculations of He-LiF(001) diffraction scattering, J. Chem. Phys. 63, 5231 (1975).
1.5. Concluding remarks

[136] C. J. Ray and J. M. Bowman, *Quasiclassical studies of rigid rotor-solid surface diffraction scattering*, J. Chem. Phys. 66, 1122 (1976).

[137] D. Farías, C. Díaz, P. Rivière, H. F. Busnego, P. Nieto, M. F. Somers, G. J. Kroes, A. Salin, and F. Martín, *In-plane and out-of-plane diffraction of H₂ from metal surfaces*, Phys. Rev. Lett. 93, 246104 (2004).

[138] C. Díaz, M. F. Somers, G. J. Kroes, H. F. Busnego, A. Salin, and F. Martín, *Quantum and classical dynamics of H₂ scattering from Pd(111) at off-normal incidence*, Phys. Rev. B 72, 035401 (2005).

[139] C. Díaz, H. F. Busnego, P. Rivière, D. Farías, P. Nieto, M. F. Somers, G. J. Kroes, A. Salin, and F. Martín, *A classical dynamics method for H₂ diffraction from metal surfaces*, J. Chem. Phys. 122, 154706 (2005).

[140] G. Delgado-Barrio, P. Villarreal, P. Mareca, and G. Albelda, *Three-dimensional vibrational predissociation of the van der Waals complex He···I₂(B). A quasiclassical study*, J. Chem. Phys. 78, 280 (1983).

[141] J. Rubayo-Soneira, A. García-Vela, G. Delgado-Barrio, and P. Villarreal, *Vibrational predissociation of I₂-Ne. A quasiclassical dynamical study*, Chem. Phys. Lett. 243, 236 (1995).

[142] A. García-Vela, J. Rubayo-Soneira, G. Delgado-Barrio, and P. Villarreal, *Quasiclassical dynamics of the I₂-Ne² vibrational predissociation: A comparison with experiment*, J. Chem. Phys. 104, 8405 (1996).

[143] C. Leforestier, R. H. Bisseling, C. Cerjan, M. D. Feit, R. Friesner, A. Guldberg, A. Hammerich, G. Jolicard, W. Karrlein, H.-D. Meyer, N. Lipkin, 0. Roncero, and R. Kosloff, *A comparison of different propagation schemes for the time dependent Schrödinger equation*, J. Comp. Phys. 94, 59 (1991).

[144] A. S. Sanz, F. Borondo, and S. Miret-Artés, *Particle diffraction studied using quantum trajectories*, J. Phys.: Condens. Matter 14, 6109 (2002).

[145] V. B. Magalinskii, *Dynamical model in the theory of the Brownian motion*, Sov. Phys. JETP-USSR 9, 1381 (1959).

[146] A. O. Caldeira and A. J. Leggett, *Influence of dissipation on quantum tunneling in macroscopic systems*, Phys. Rev. Lett. 46, 211 (1981).

[147] A. O. Caldeira and A. J. Leggett, *Quantum tunneling in a dissipative system*, Ann. Phys. (NY) 149, 374 (1983).

[148] R. K. Wangsness and F. Bloch, *The dynamical theory of nuclear induction*, Phys. Rev. 89, 728 (1953).

[149] A. G. Redfield, *On the theory of relaxation processes*, IBM J. Res. Develop. 1, 19 (1957).

[150] A. G. Redfield, *The theory of relaxation processes*, Adv. Magn. Reson. 1, 1 (1965).

[151] W. T. Pollard, A. K. Felts, and R. A. Friesner, *The Redfield Equation in Condensed-Phase Quantum Dynamics*, Adv. Chem. Phys. 93, 77 (1996).

[152] G. W. Ford, M. Kac, and P. Mazur, *Statistical mechanics of assemblies of coupled oscillators*, J. Math. Phys. 6, 504 (1965).

[153] G. W. Ford and M. Kac, *On the quantum Langevin equation*, J. Stat. Phys. 46, 803 (1987).

[154] R. P. Feynman, *Space-time approach to non-relativistic quantum mechanics*, Rev. Mod. Phys. 20, 367 (1948).

[155] R. P. Feynman and A. R. Hibbs, *Quantum Mechanics and Path Integrals* (McGraw-Hill, New York, 1965).

[156] R. P. Feynman, *Statistical Mechanics* (W. A. Benjamin, Reading, MA, 1972).

[157] L. S. Schulman, *Techniques and Applications of Path Integrals* (Wiley, New York, 1981).

[158] A. S. Sanz, *Effective Markovian description of decoherence in bound systems*, Can. J. Chem., 92, 168 (2014).

[159] G. D. Billing, *Classical path method in inelastic and reactive scattering*, Int. Rev. Phys. Chem. 13, 309 (1994).

[160] C. C. Tully, *Nonadiabatic molecular-dynamics*, Int. J. Quantum Chem. 25, 299 (1991).

[161] W. H. Miller, *Semiclassical theory of atom-diatom collisions: Path integrals and the classical S matrix*, J. Chem. Phys. 53, 1949 (1970).

[162] W. H. Miller, *Classical S matrix: Numerical application to inelastic collisions*, J. Chem. Phys.
Phys. 53, 3578 (1970).
[163] W. H. Miller, Quantum and semiclassical theory of chemical reaction rates, Faraday Discuss. 110, 1 (1998).
[164] W. H. Miller, The semiclassical initial value representation: A potentially practical way for adding quantum effects to classical molecular dynamics simulations, J. Phys. Chem. A 105, 2942 (2001).
[165] W. H. Miller and B. M. D. D. Jansen op de Haar, A new basis set method for quantum scattering calculations, J. Chem. Phys. 86, 6213 (1987).
[166] J. Z. H. Zhang, S.-I. Chu, and W. H. Miller, Quantum scattering via the S-matrix version of the Kohn variational principle, J. Chem. Phys. 88, 6233 (1988).
[167] M. A. Sepúlveda and F. Grossmann, Time-dependent semiclassical mechanics, Adv. Chem. Phys. 96, 191 (1996).
[168] N. Makri, Quantum dissipative dynamics: A numerically exact methodology, J. Phys. Chem. A 102, 4414 (1998).
[169] J. Ankerhold, M. Salter, and E. Pollak, A study of the semiclassical initial value representation at short times, J. Chem. Phys. 116, 5925 (2002).
[170] E. Pollak and J. Shao, Systematic improvement of initial value representations of the semiclassical propagator, J. Phys. Chem. A 107, 7112 (2003).
[171] E. Pollak and S. Miret-Artés, Thawed semiclassical IVR propagators, J. Phys. A 37, 9669 (2004).
[172] S. Nielsen, R. Kapral, and G. Ciccotti, Non-adiabatic dynamics in mixed quantum-classical systems, J. Stat. Phys. 101, 225 (2000).
[173] R. Car and M. Parrinello, Unified approach for molecular dynamics and density-functional theory, Phys. Rev. Lett. 55, 2471 (1985).
[174] T. D. Kuhne, M. Krack, F. R. Mohamed, and M. Parrinello, Efficient and accurate Car-Parrinello-like approach to Born-Oppenheimer molecular dynamics, Phys. Rev. Lett. 98, 066401 (2007).
[175] E. Nelson, Derivation of the Schrödinger equation from Newtonian mechanics, Phys. Rev. 150, 1079 (1966).
[176] J. S. Bell, On the problem of hidden variables in quantum mechanics, Rev. Mod. Phys. 38, 447 (1966).
[177] A. S. Sanz and S. Miret-Artés, Aspects of nonlocality from a quantum trajectory perspective: A WKB approach to Bohmian mechanics, Chem. Phys. Lett. 445, 350 (2007).
[178] E. Schrödinger, Discussion of probability relations between separated systems, Proc. Cambridge Phil. Soc. 31, 555 (1935).
[179] E. Schrödinger, Probability relations between separated systems, Proc. Cambridge Phil. Soc. 32, 446 (1936).
[180] A. S. Sanz and S. Miret-Artés, On the unique mapping relationship between initial and final quantum states, Ann. Phys. 339, 11 (2013).
[181] D. Bohm, Quantum Theory (Prentice-Hall, New York, 1951).
[182] L. I. Schiff, Quantum Mechanics (McGraw-Hill, Singapore, 1968), 3rd Ed.
[183] S. Kocsis, B. Braverman, S. Ravets, M. J. Stevens, R. P. Mirin, L. K. Shalm and A. M. Steinberg, Observing the average trajectories of single photons in a two-slit interferometer, Science, 332, 1170 (2011).
[184] A. S. Sanz, M. Davidović, M. Božić, and S. Miret-Artés, Understanding interference experiments with polarized light through photon trajectories, Ann. Phys. 325, 763 (2010).
[185] A. S. Sanz and S. Miret-Artés, Atom-Surface Diffraction: A Quantum Trajectory Description, in Quantum Dynamics of Complex Molecular Systems, D. A. Micha and I. Burghardt (Eds.) (Springer, Berlin, 2007).
[186] P. M. Gerhardt, R. J. Gross, and J. I. Hochstein, Fundamentals of Fluid Mechanics (Addison-Wesley, New York, 1992).
[187] J. H. Spurk, Fluid Mechanics (Springer-Verlag, Berlin, 1997).
[188] A. Benseny, G. Albareda, A. S. Sanz, J. Mompart, and X. Oriols, Applied Bohmian mechanics, Eur. Phys. J. D 68, 286 (2014).
1.5. Concluding remarks

[189] C. Dewdney, Nonlocally correlated trajectories two-particle quantum mechanics, Found. Phys. 18, 867 (1988).

[190] M. M. Lam and C. Dewdney, Locality and nonlocality in correlated two-particle interferometry, Phys. Lett. A 150, 127 (1990).

[191] E. Guay and L. Marchildon, Two-particle interference in standard and Bohmian quantum mechanics, J. Phys. A 36, 5617 (2003).

[192] K. Na and R. E. Wyatt, Quantum hydrodynamic analysis of decoherence: quantum trajectories and stress tensor, Phys. Lett. A 306, 97 (2002).

[193] K. Na and R. E. Wyatt, Quantum hydrodynamic analysis of decoherence, Phys. Scr. 67, 169 (2003).

[194] A.S. Sanz and F. Borondo, A quantum trajectory description of decoherence, Eur. Phys. J. D 44, 319 (2007).

[195] A.S. Sanz and F. Borondo, Contextuality, decoherence and quantum trajectories, Chem. Phys. Lett. 478, 301 (2009).

[196] X. Oriols, Quantum-trajectory approach to time-dependent transport in mesoscopic systems with electron-electron interactions, Phys. Rev. Lett. 98, 066803 (2007).

[197] Y. Aharonov, D. Z. Albert, and L. Vaidman, How the result of a measurement of a component of the spin of a spin $^{-1/2}$ particle can turn out to be 100, Phys. Rev. Lett. 60, 1351 (1988).

[198] J. S. Lundeen, B. Sutherland, A. Patel, C. Stewart, and Ch. Bamber, Direct measurement of the quantum wavefunction, Nature 474, 188 (2011).

[199] H. M. Wiseman, Grounding Bohmian mechanics in weak values an bayesianism, New J. Phys. 9, 165 (2007).

[200] B. J. Hiley, Weak values: Approach through the Clifford and Moyal algebras, J. Phys.: Conf. Ser. 361, 012014 (2012).

[201] J. O. Hirschfelder, Quantum mechanical equations of change. I, J. Chem. Phys. 68, 5151 (1978).

[202] R. F. W. Bader, Quantum topology of molecular charge distributions. III. The mechanics of an atom in a molecule, J. Chem. Phys. 73, 2871 (1980).

[203] J. A. N. F. Gomes, Delocalized magnetic currents in benzene, J. Chem. Phys. 78, 3133 (1983).

[204] J. A. N. F. Gomes, Topological elements of the magnetically induced orbital current densities, J. Chem. Phys. 78, 4585 (1983).

[205] P. Lazzeretti, Ring currents, Prog. Nuc. Mag. Res. Spect. 36, 1 (2000).

[206] S. Pelloni, F. Faglioni, R. Zanasi, and P. Lazzeretti, Topology of magnetic-field-induced current-density field in diatropic monocyclic molecules, Phys. Rev. A 74, 012506 (2006).

[207] S. Pelloni, P. Lazzeretti, and R. Zanasi, Spatial ring current model of the [2.2]paracyclophane molecule, J. Phys. Chem. A 111, 3110 (2007).

[208] S. Pelloni, P. Lazzeretti, and R. Zanasi, Topological models of magnetic field induced current density field in small molecules, Theor. Chem. Acc. 123, 353 (2009).

[209] S. Pelloni and P. Lazzeretti, Spatial ring current model for the prismane molecule, J. Phys. Chem. A 112, 5175 (2008).

[210] S. Pelloni and P. Lazzeretti, Topology of magnetic-field induced electron current density in the cubane molecule, J. Chem. Phys. 128, 194305 (2008).

[211] S. Pelloni and P. Lazzeretti, Ring current models for acetylene and ethylene molecules, Chem. Phys. 356, 153 (2009).

[212] I. García Cuesta, A. Sánchez de Merás, S. Pelloni, and P. Lazzeretti, Understanding the ring current effects on magnetic shielding of hydrogen and carbon nuclei in naphthalene and anthracene, J. Comput. Chem. 30, 551 (2009).

[213] F. Bloch, Bremsvermögen von Atomen mit mehreren Elektronen, Z. Physik 81, 363 (1933).

[214] L. J. Bartolotti and J.C. Mollmann, 4th order time-dependent variational perturbation-theory based on the hydrodynamic analogy, Mol. Phys. 38, 1359 (1979).

[215] L. J. Bartolotti, Time-dependent extension of the Hohenberg-Kohn-Levy energy-density functional, Phys. Rev. A 24, 1661 (1981).
[216] L. J. Bartolotti, *Time-dependent Kohn-Sham density-functional theory*, Phys. Rev. A 26, 2243 (1982).

[217] E. Runge and E. K. U. Gross, *Density-functional theory for time-dependent systems*, Phys. Rev. Lett. 52, 997 (1984).

[218] B. M. Deb and S. K. Ghosh, *Schrödinger fluid-dynamics of many-electron systems in a time-dependent density-functional framework*, J. Chem. Phys. 77, 342 (1982).

[219] B. M. Deb and P. K. Chattaraj, *How can density functional theory be excited from the ground state?*, Proc. Indian Acad. Sci. 99, 67 (1987).

[220] B. M. Deb and P. K. Chattaraj, *Quantum fluid density functional theory of time-dependent phenomena – ion atom collisions*, Chem. Phys. Lett. 148, 550 (1988).

[221] B. M. Deb and P. K. Chattaraj, *Density-functional and hydrodynamical approach to ion-atom collisions through a new generalized nonlinear Schrödinger equation*, Phys. Rev. A 39, 1696 (1989).

[222] B. M. Deb, P. K. Chattaraj, and S. Mishra, *Time-dependent quantum-fluid density-functional study of high-energy proton-helium collisions*, Phys. Rev. A 43, 1248 (1991).

[223] B. Kr. Dey and B. M. Deb, *Time-dependent quantum fluid-dynamics of the photoionization of the he atom under an intense laser field*, Int. J. Quant. Chem. 56, 707 (1995).

[224] B. Kr. Dey and B. M. Deb, *A theoretical study of the high-order harmonics of a 200 nm laser from H²⁺ and HeH⁺*, Chem. Phys. Lett. 276, 157 (1997).

[225] B. Kr. Dey and B. M. Deb, *Stripped ion-helium atom collision dynamics within a time-dependent quantum fluid density functional theory*, Int. J. Quant. Chem. 67, 251 (1998).

[226] G. P. Lawes and N. H. March, *Approximate differential-equation for calculating the electron-density in closed shell atoms and in molecules*, Phys. Scr. 21, 402 (1980).

[227] B. M. Deb and S. K. Ghosh, *New method for the direct calculation of electron-density in many-electron systems I. application to closed-shell atoms*, Int. J. Quantum Chem. 23, 1 (1983).

[228] M. Levy, J. P. Pardew, and V. Sahni, *Exact differential equation for the density and ionization energy of a many-particle system*, Phys. Rev. A 30, 2745 (1984).

[229] N. H. March, *The local potential determining the square root of the ground-state electron-density of atoms and molecules from the Schrödinger equation*, Phys. Lett. A 113, 476 (1986).

[230] G. Hunter, *The exact one-electron model of molecular-structure*, Int. J. Quantum Chem. 29, 197 (1986).

[231] M. Levy and H. Ou-Yang, *Exact properties of the Pauli potential for the square root of the electron density and the kinetic energy functional*, Phys. Rev. A 38, 625 (1988).

[232] M. McClendon, *Real-space diffusion theory of multiparticle quantum systems*, Phys. Rev. A 38, 5851 (1988).

[233] A. S. Sanz, X. Giménez, J. M. Bofill, and S. Miret-Artés, *Time-dependent Density Functional Theory from a Bohmian Perspective*, in *Chemical Reactivity Theory*, P. K. Chattaraj (Ed.) (Taylor & Francis, New York, 2009).

[234] W. Kohn and L. J. Sham, *Self-consistent equations including exchange and correlation effects*, Phys. Rev. 140, A1133 (1965).

[235] T. A. Elsayed, K. Mølmer, and L. B. Madsen, *Solving the quantum many-body problem with Bohmian trajectories*, preprint arXiv:1706.00818v1 (2017).

[236] O. E. Alon, A. I. Streltsov and L. S. Cederbaum, *Multiconfigurational time-dependent Hartree method for bosons: Many-body dynamics of bosonic systems*, Phys. Rev. A 77, 033613 (2008).

[237] V. Bolsinger, S. Kronke and P. Schmelcher, *Beyond mean-field dynamics of ultra-cold bosonic atoms in higher dimensions: Facing the challenges with a multiconfigurational approach*, J. Phys. B 50, 034003 (2017).

[238] M. H. Beck, A. Jäckle, G. Worth and H.-D. Meyer, *The multiconfiguration time-dependent Hartree (MCTDH) method: A high efficient algorithm for propagating wavepackets*, Phys.
1.5. Concluding remarks

[240] K. Müller and L. D. Brown, *Location of saddle points and minimum energy paths by a constrained simplex optimization procedure*, Theor. Chim. Acta **53**, 75 (1979).

[241] R. Crehuet and J. M. Bofill, *The reaction path intrinsic reaction coordinate method and the Hamilton-Jacobi theory*, J. Chem. Phys. **122**, 234105 (2005).

[242] A. Aguilar-Mogas, X. Giménez, and J. M. Bofill, *Finding reaction paths using the potential energy as reaction coordinate*, J. Chem. Phys. **128**, 104102 (2008).

[243] W. Quapp, *Chemical reaction paths and calculus of variations*, Theor. Chem. Account. **121**, 227 (2008).

[244] A. S. Sanz, X. Giménez, and J. M. Bofill, *Understanding chemical reactions within a generalized Hamilton-Jacobi framework*, Chem. Phys. Lett. **478**, 89 (2009); Erratum Chem. Phys. Lett. **488**, 235 (2010).

[245] A. S. Sanz and S. Miret-Artés, *A trajectory-based understanding of quantum interference*, J. Phys. A **41**, 435303 (2008).

[246] A. S. Sanz and S. Miret-Artés, *Quantum trajectories in elastic atom-surface scattering: Threshold and selective adsorption resonances*, J. Chem. Phys. **122**, 014702 (2005).

[247] A. S. Sanz, F. Borondo, and S. Miret-Artés, *Understanding chemical reactions within a generalized Hamilton-Jacobi framework*, Chem. Phys. Lett. **478**, 89 (2009); Erratum Chem. Phys. Lett. **488**, 235 (2010).

[248] A. S. Sanz, F. Borondo, and S. Miret-Artés, *Quantum trajectories in elastic atom-surface scattering with single adsorbates: The role of quantum vortices*, J. Chem. Phys. **120**, 8794 (2004).

[249] R. E. Grisenti, W. Schöllkopf, J. P. Toennies, G. C. Hegerfeldt, and T. Köhler, *Determination of atom-surface van der Waals potentials from transmission-grating diffraction intensities*, Phys. Rev. Lett. **85**, 2284 (2000).

[250] R. E. Grisenti, W. Schöllkopf, J. P. Toennies, J. R. Manson, T. A. Savas, and H. I. Smith, *He-atom diffraction from nanostructure transmission gratings: The role of imperfections*, Phys. Rev. A **61**, 033608 (2000).

[251] A. S. Sanz, F. Borondo, and S. Miret-Artés, *Loss of coherence in double-slit diffraction experiments*, Phys. Rev. A **71**, 42103 (2005).

[252] A. S. Sanz, M. Davidovič, and M. Božič, *Full quantum mechanical analysis of atomic three-grating Mach-Zehnder interferometry*, Ann. Phys. **353**, 205 (2015).

[253] O. V. Prezhdo and C. Brooksby, *Relationship between quantum decoherence times and solution dynamics in condensed phase chemical systems*, Phys. Rev. Lett. **86**, 3215 (2001).

[254] E. Gindensperger, C. Meier, and J. A. Beswick, *Mixing quantum and classical dynamics using Bohmian trajectories*, J. Chem. Phys. **113**, 9369 (2000).

[255] E. Gindensperger, C. Meier, and J. A. Beswick, *Quantum-classical dynamics including continuum states using quantum trajectories*, J. Chem. Phys. **116**, 8 (2002).

[256] E. Gindensperger, C. Meier, J. A. Beswick, and M. -C. Heitz, *Quantum-classical description of rotational diffractive scattering using Bohmian trajectories: Comparison with full quantum wave packet results*, J. Chem. Phys. **116**, 10051 (2002).

[257] C. Meier and J. A. Beswick, *Femtosecond pump-probe spectroscopy of I₂ in a dense rare gas environment: A mixed quantum/classical study of vibrational decoherence*, J. Chem. Phys.
[264] S. Garashchuk and V. Rassolov, Semiclassical dynamics based on quantum trajectories, Chem. Phys. Lett. 364, 562 (2002).
[265] S. Garashchuk and V. Rassolov, Modified quantum trajectory dynamics using a mixed wave function representation, J. Chem. Phys. 121, 8711 (2004).
[266] S. Garashchuk, V. Rassolov, and O. Prezhdo, Semiclassical Bohmian dynamics, Rev. Comput. Chem. 27, 287 (2011).
[267] E. R. Bittner, Quantum initial value representation using approximate Bohmian trajectories, J. Chem. Phys. 119, 1358 (2003).
[268] Y. Zhao and N. Makri, Bohmian versus semiclassical description of interference phenomena, J. Chem. Phys. 119, 60 (2003).
[269] J. Liu and N. Makri, Forward-backward quantum dynamics for time correlation functions, J. Phys. Chem. A 108, 806 (2004).
[270] J. Liu and N. Makri, Monte Carlo Bohmian dynamics from trajectory stability properties, J. Phys. Chem. A 108, 5408 (2004).
[271] B. Gu and I. Franco, Partial hydrodynamic representation of quantum molecular dynamics, J. Chem. Phys. 146, 194104 (2017).
[272] A. Goldberg, H. M. Schey, and J. L. Schwartz, Computer-generated motion pictures of one-dimensional quantum-mechanical transmission and reflection phenomena, Am. J. Phys. 36, 454 (1968).
[273] http://nobelprize.org/nobel_prizes/chemistry/laureates/1998/kohn-lecture.pdf