

Time in quantum mechanics: A fresh look at the continuity equation

Axel Schild

ETH Zürich, Laboratorium für Physikalische Chemie, 8093 Zürich, Switzerland

(Received 15 August 2018; published 12 November 2018)

The local conservation of a physical quantity whose distribution changes with time is mathematically described by the continuity equation. The corresponding time parameter, however, is defined with respect to an idealized classical clock. We consider what happens when this classical time is replaced by a nonrelativistic quantum-mechanical description of the clock. From the clock-dependent Schrödinger equation (as an analog of the time-dependent Schrödinger equation) we derive a continuity equation, where, instead of a time derivative, an operator occurs that depends on the flux (probability current) density of the clock. This clock-dependent continuity equation can be used to analyze the dynamics of a quantum system and to study degrees of freedom that may be used as internal clocks for an approximate description of the dynamics of the remaining degrees of freedom. As an illustration, we study a simple model for coupled electron-nuclear dynamics and interpret the nuclei as quantum clock for the electronic motion. We find that whenever the Born-Oppenheimer approximation is valid, the continuity equation shows that the nuclei are the only relevant clock for the electrons.

DOI: [10.1103/PhysRevA.98.052113](https://doi.org/10.1103/PhysRevA.98.052113)

In many physical processes, the state of a system can be described by a density distribution of a physical quantity which is locally conserved, i.e., which is not created or destroyed during the process of interest. The mathematical form of the conservation law for such a density is the continuity equation [1]. It relates changes of the density of the conserved quantity to the divergence of a vector field, called the flux density (or current density). The flux density represents the instantaneous motion of the density and, when integrated over a surface, yields the flow of the density through that surface. As the continuity equation follows from the requirement of continuity alone [1], it is a very important relation for the mathematical description of nature. In nonrelativistic quantum mechanics it holds for the probability density of the particles [2] and occurs, for example, in the hydrodynamic formulation of quantum mechanics [3,4], in time-dependent density functional theory [5], and in the study of nuclear and electron dynamics [6–9]. Continuity is such a basic requirement that the continuity equation can also be used to test theories, models, or numerical calculations for errors by comparing the change of the density distribution to the expected fluxes.

Although the continuity equation is a very general relation, it is typically assumed that the dynamics is parametrized by a unique time; hence the continuity equation is stated accordingly. However, the special status of time in quantum mechanics is currently investigated [10–20] and different approaches are developed that view time mostly as an emergent property, assuming that quantum mechanics is fundamentally timeless. One of these is the Page-Wootters approach [10,21–26], where the timeless universe (a closed system containing all relevant degrees of freedom) is partitioned into a clock and a system of interest. This system has to be entangled with the clock, and there has to exist a good clock in the sense that it has many distinguishable states but little interaction with the system [25]. The concept of time can then be found as a (classical) conditional variable.

In this article, we use a different but related approach which allows us to include quantum-mechanical effects of the clock: In the Briggs-Rost approach [11,15], a closed composite (i.e., consisting of at least two degrees of freedom) universe is also separated into a clock and a system which depends conditionally on (and which is entangled with) the clock. Then, from the time-independent Schrödinger equation (TISE) of the system together with the clock, the time-dependent Schrödinger equation (TDSE) of the system can be obtained in the classical limit for the clock. It follows that the TDSE is a quantum-classical equation. Consequently, the time-dependent continuity equation is a quantum-classical relation, too, and we may ask if a fully quantum-mechanical equivalent can be found.

To investigate this question, we use the Briggs-Rost approach in the language of the exact factorization [15,27], where the joint probability density for system and clock is separated into a marginal probability density for the clock and a conditional probability density for the system, which conditionally depends on the state of the clock. Thus, time has a similar status as it has in the Page-Wootters approach. However, no assumptions or constructions are necessary and all results can directly be derived from the time-independent equation of motion, which in our case is the TISE. This will allow us to find a fully quantum-mechanical continuity equation by replacing the TDSE of the system with a clock-dependent Schrödinger equation (CDSE), which becomes a TDSE in the classical limit of the clock wave function. Instead of a conditional time parameter, both the CDSE and its continuity equation depend on the (quantum) state of the clock.

Such a quantum-mechanical continuity equation is interesting from a fundamental point of view, because it illustrates the quantum-mechanical nature of the clock that is used to track the dynamics of the system. Our focus in this article, however, is to illustrate a possible practical purpose of the quantum-mechanical continuity equation: It can be used to

analyze a dynamics and to find degrees of freedom that can be used as clocks for other degrees of freedom, possibly allowing one to find approximate simulation methods in the spirit of the Born-Oppenheimer approximation. Born-Oppenheimer-type approaches are used in many different ways, e.g., for quantizing constrained systems [28], for Rydberg states [29], for quantum heat transfer [30], for a model of atoms in an oscillator and lattice trap [31], or for the dynamics of H_2 in carbon nanotubes [32]. The clock-dependent continuity equation shows how the approximation works: As an example, we consider a simple model of the coupled electron-nuclear dynamics during a proton-coupled electron transfer process and treat the nuclei as a quantum clock for the electronic motion. In this case, there are two clocks for the electrons: an external clock (to which also the nuclear motion is referred) and an internal clock given by the nuclear wave function. In the continuity equation, the change of the electron density with respect to (w.r.t.) these two clocks shows clearly under which conditions only the internal clock is relevant for the electronic motion. These conditions correspond to situations where the Born-Oppenheimer approximation is applicable, i.e., where the change of the nuclear configuration is enough to represent the electron dynamics. Of course, the conditions for which the Born-Oppenheimer approximation works are well known, but our analysis in terms of different clocks gives both a new point of view on this familiar method, and it allows a generalization of the approach to other problems where similar separations of timescales may be helpful. As a by-product, treating the nuclei as a clock for the electrons also sheds a new light on the riddle of the vanishing electronic flux density in the Born-Oppenheimer approximation [33], as explained below.

I. THE TIME-DEPENDENT CONTINUITY EQUATION

Before developing the idea of time measured by means of a quantum clock, we first review the time-dependent continuity equation in quantum mechanics. Let $\rho(\mathbf{x}|t) \in \mathbb{R}$ be the distribution of a conserved continuous physical quantity depending on spatial coordinates $\mathbf{x} \in \mathbb{R}^3$ and on time t . The change of $\rho(\mathbf{x}|t)$ in some compact volume Ω has to correspond to the flux through the surface $\partial\Omega$ of the volume. This requirement is stated as [1]

$$\partial_t \int_{\Omega} \rho(\mathbf{x}|t) d\mathbf{x} + \int_{\partial\Omega} \mathbf{j}(\mathbf{x}|t) \cdot d\mathbf{S} = 0, \quad (1)$$

where the vector field $\mathbf{j}(\mathbf{x}|t) \in \mathbb{R}^3$ is the flux density (or current density) and where ∂_t is the derivative w.r.t. time. By means of Stokes' theorem and the requirement that (1) is true for any volume, we obtain the continuity equation [1]

$$\partial_t \rho(\mathbf{x}|t) + \nabla_{\mathbf{x}} \cdot \mathbf{j}(\mathbf{x}|t) = 0 \quad (2)$$

with the gradient vector w.r.t. the components of \mathbf{x} denoted as $\nabla_{\mathbf{x}}$. Equation (2) relates changes of $\rho(\mathbf{x}|t)$ in time to the divergence of $\mathbf{j}(\mathbf{x}|t)$. If the state $\psi(\mathbf{x}|t)$ of a particle is described by the TDSE

$$i\hbar \partial_t \psi(\mathbf{x}|t) = \left(\frac{\hbar^2}{2m} [-i\nabla_{\mathbf{x}} + \mathbf{A}(\mathbf{x}|t)]^2 + V(\mathbf{x}|t) \right) \psi(\mathbf{x}|t) \quad (3)$$

with scalar potential $V \in \mathbb{R}$ and vector potential $\mathbf{A} \in \mathbb{R}^3$, and if $|\psi(\mathbf{x}|t)|^2 = \rho(\mathbf{x}|t)$ is the probability density of this particle, the probability flux density $\mathbf{j}(\mathbf{x}|t)$ in the continuity equation (2) is identified with

$$\mathbf{j}(\mathbf{x}|t) = \frac{\hbar}{m} \{ \text{Im}[\bar{\psi}(\mathbf{x}|t) \nabla_{\mathbf{x}} \psi(\mathbf{x}|t)] + \mathbf{A}(\mathbf{x}|t) |\psi(\mathbf{x}|t)|^2 \}, \quad (4)$$

where $\bar{\psi}$ denotes the complex conjugate of ψ .

We note that the flux density $\mathbf{j}(\mathbf{x}|t)$ is defined via (2) only up to the addition of a vector field $\mathbf{j}_{\perp}(\mathbf{x}|t)$ for which $\nabla_{\mathbf{x}} \cdot \mathbf{j}_{\perp}(\mathbf{x}|t) = 0$. Hence, (4) is not a unique definition if only the continuity equation and the TDSE are known [34]. It is, however, the position representation of the quantum-mechanical operator corresponding to the classical flux density, and the continuity equation may be derived from this operator [2].

II. THE CLOCK-DEPENDENT SCHRÖDINGER EQUATION

To describe the system and its clock quantum mechanically, we follow the developments presented in [11,15]. In these articles, it was shown that the TDSE (3) can be obtained from the TISE for the considered system together with the clock that is used to measure the time parameter. Two requirements were necessary: The energy of the clock has to be much larger than that of the system so that its state is negligibly disturbed by the system, and the classical limit has to be taken for the wave function of the clock. Only in this case a time parameter can be defined which corresponds to a “universal” reference time. For our discussion, we do not need to make any of these assumptions, but we keep the clock fully quantum mechanical. Our derivation is based on the exact factorization method [27,35] that was also used in [15], but we explicitly take into account the gauge freedom that appears in this theory.

We start from the TISE

$$\left(-\frac{\hbar^2 \nabla_{\mathbf{R}}^2}{2M} + H_S \right) \psi(\mathbf{R}, \mathbf{r}) = E \psi(\mathbf{R}, \mathbf{r}) \quad (5)$$

for a closed system (the “universe”) with energy E . The Hamiltonian of the system is given as

$$H_S = -\frac{\hbar^2 \nabla_{\mathbf{r}}^2}{2m} + V(\mathbf{R}, \mathbf{r}), \quad (6)$$

where $\mathbf{R}, \mathbf{r} \in \mathbb{R}^3$ are the coordinates of two particles and where the gradients w.r.t. \mathbf{R} and \mathbf{r} are denoted as $\nabla_{\mathbf{R}}$ and $\nabla_{\mathbf{r}}$, respectively. The restriction of the notation to two particles leads to a simplification of the equations. The generalization to many particles is straightforward and is discussed briefly below. The wave function ψ shall be normalized according to

$$\langle \psi(\mathbf{R}, \mathbf{r}) | \psi(\mathbf{R}, \mathbf{r}) \rangle = 1, \quad (7)$$

where $\langle \cdot | \cdot \rangle$ denotes the scalar product w.r.t. coordinates \mathbf{R} and \mathbf{r} . In the exact factorization ansatz [27,36] the wave function is written as a product

$$\psi(\mathbf{R}, \mathbf{r}) = \chi(\mathbf{R}) \phi(\mathbf{r}|\mathbf{R}) \quad (8)$$

of two amplitudes $\chi(\mathbf{R})$ and $\phi(\mathbf{r}|\mathbf{R})$, which fulfill the following properties: The function

$$|\chi(\mathbf{R})|^2 := \langle \psi | \psi \rangle_{\mathbf{r}} \quad (9)$$

is the marginal probability density, which represents the probability of finding a particle of mass M at \mathbf{R} independent of where the particle with mass m is. The symbol $\langle \cdot | \cdot \rangle_r$ indicates the scalar product w.r.t. the coordinate \mathbf{r} only. Also,

$$\phi(\mathbf{r}|\mathbf{R}) := \psi(\mathbf{R}, \mathbf{r})/\chi(\mathbf{R}) \quad (10)$$

yields the conditional probability density $|\phi(\mathbf{r}|\mathbf{R})|^2$ of finding a particle with mass m at \mathbf{r} , given there is a particle with mass M at \mathbf{R} . It obeys the partial normalization condition

$$\langle \phi(\mathbf{r}|\mathbf{R}) | \phi(\mathbf{r}|\mathbf{R}) \rangle_r \stackrel{\perp}{=} 1. \quad (11)$$

This condition has to be valid all values of \mathbf{R} .

Before using the ansatz (8), we would like to comment on two restrictions of the approach. First, writing the wave function $\psi(\mathbf{R}, \mathbf{r})$ as a product of marginal and a conditional amplitude is in general possible for $\psi(\mathbf{R}, \mathbf{r})$ as defined above, but there are situations where this factorization may fail. In particular, there may exist configurations \mathbf{R}_s for which $\psi(\mathbf{R}_s, \mathbf{r}) = 0$ for all \mathbf{r} and thus the marginal amplitude $\chi(\mathbf{R}_s) = 0$, which leads to an ill-defined conditional amplitude $\phi(\mathbf{r}|\mathbf{R}_s)$, cf. (10). Such a situation can be problematic, for example, for Coulomb potentials [37] but may also be relevant in other situations. Second, for (7) to hold with the given TISE, $V(\mathbf{R}, \mathbf{r})$ has to be such that $\psi(\mathbf{R}, \mathbf{r})$ is a bound state. If $V(\mathbf{R}, \mathbf{r})$ would contain only interparticle interactions, it would be necessary to extract the center-of-mass coordinate first and to use only relative coordinates, which would change the kinetic energy operators used in (5) and (6). The effect of both restrictions on the following discussion is not yet known and has to be investigated further.

The function $\chi(\mathbf{R})$ is interpreted as the wave function of the clock, whereas the function $\phi(\mathbf{r}|\mathbf{R})$ is interpreted as the wave function of the system which depends conditionally on the configuration \mathbf{R} of the clock. The equation of motion for the clock is then [27,36]

$$\left(\frac{\hat{\mathbf{P}}^2}{2M} + \epsilon(\mathbf{R}) \right) \chi = E \chi \quad (12)$$

and the equation of motion for the system is

$$\hat{\mathcal{C}}\phi = (\hat{H}_S + \hat{U} - \epsilon(\mathbf{R}))\phi. \quad (13)$$

In the equation for the system, the clock-dependent operator

$$\hat{\mathcal{C}} = \frac{1}{M} \frac{\hat{\mathbf{P}}\chi}{\chi} \cdot \hat{\mathbf{P}}^\dagger \quad (14)$$

and the kinetic operator

$$\hat{U} = \frac{(\hat{\mathbf{P}}^\dagger)^2}{2M} \quad (15)$$

occur, which both operate on the conditional variable \mathbf{R} , because the momentum operator $\hat{\mathbf{P}}$ is defined as

$$\hat{\mathbf{P}} := \hbar(-i\nabla_{\mathbf{R}} + \mathbf{A}) \quad (16)$$

with the Hermitian adjoint

$$\hat{\mathbf{P}}^\dagger = \hbar(i\nabla_{\mathbf{R}} + \mathbf{A}). \quad (17)$$

The real-valued scalar potential $\epsilon(\mathbf{R}) \in \mathbb{R}$ is obtained from these operators as

$$\epsilon(\mathbf{R}) := \langle \phi | \hat{H}_S + \hat{U} - \hat{\mathcal{C}} | \phi \rangle_r, \quad (18)$$

whereas the real-valued vector potential $\mathbf{A}(\mathbf{R}) \in \mathbb{R}^3$ is given by

$$\mathbf{A}(\mathbf{R}) := -i \langle \phi | \nabla_{\mathbf{R}} \phi \rangle_r. \quad (19)$$

The operators $\hat{\mathbf{P}}$ and $\hat{\mathbf{P}}^\dagger$ are Hermitian adjoints for χ w.r.t. \mathbf{R} space, because

$$\langle \hat{\mathbf{P}}\chi | \chi \rangle_{\mathbf{R}} \equiv \int \chi \hat{\mathbf{P}}^\dagger \bar{\chi} d\mathbf{R} = \langle \chi | \hat{\mathbf{P}}\chi \rangle_{\mathbf{R}}, \quad (20)$$

but also for ϕ w.r.t. \mathbf{r} space. If we interpret the definition (19) of the vector potential \mathbf{A} such that \mathbf{A} is a functional of ϕ , we find from the partial normalization condition (11) that $\mathbf{A}[\phi] = -\mathbf{A}[\bar{\phi}]$. It follows that

$$\langle \hat{\mathbf{P}}\phi | \phi \rangle_r = \langle \phi | \hat{\mathbf{P}}\phi \rangle_r = 2\hbar\mathbf{A}[\phi]. \quad (21)$$

We note that if the scalar potential (18) is taken as a functional of ϕ , we have $\epsilon[\phi] = \epsilon[\bar{\phi}]$.

From the ansatz (8), $\chi(\mathbf{R})$ and $\phi(\mathbf{r}|\mathbf{R})$ are defined up to a phase factor $\theta(\mathbf{R})$. Choosing $\theta(\mathbf{R})$ means choosing a gauge, as the equations of motion (12), (13) are unchanged if the marginal amplitude, the conditional amplitude, and the vector potential are replaced by

$$\begin{aligned} \chi'(\mathbf{R}) &= \chi(\mathbf{R})e^{-i\theta(\mathbf{R})}, \\ \phi'(\mathbf{r}|\mathbf{R}) &= \phi(\mathbf{r}|\mathbf{R})e^{i\theta(\mathbf{R})}, \\ \mathbf{A}'(\mathbf{R}) &= \mathbf{A}(\mathbf{R}) + \nabla_{\mathbf{R}}\theta(\mathbf{R}). \end{aligned} \quad (22)$$

For a given state $\chi(\mathbf{R})$ of the clock, (13) yields the state of the system ϕ . If we take

$$\chi(\mathbf{R}) =: e^{-iW(\mathbf{R})} =: |\chi(\mathbf{R})|e^{-iS(\mathbf{R})} \quad (23)$$

with $W(\mathbf{R}) \in \mathbb{C}$ and $S(\mathbf{R}) \in \mathbb{R}$, we can rewrite (13) either as

$$i\hbar\hat{c}_W\phi = (\hat{H}_S + \hat{U} - \epsilon(\mathbf{R}))\phi \quad (24)$$

with

$$\hat{c}_W := \frac{\hbar}{M}(-\nabla_{\mathbf{R}}W + \mathbf{A}) \cdot (\nabla_{\mathbf{R}} - i\mathbf{A}), \quad (25)$$

or as

$$i\hbar\hat{c}_S\phi = (\hat{H}_S + \hat{U} + \hat{u}_S - \epsilon(\mathbf{R}))\phi \quad (26)$$

with

$$\hat{c}_S := \frac{\hbar}{M}(-\nabla_{\mathbf{R}}S + \mathbf{A}) \cdot (\nabla_{\mathbf{R}} - i\mathbf{A}), \quad (27)$$

$$\hat{u}_S := \frac{\hbar^2}{2M} \frac{\nabla_{\mathbf{R}}|\chi|^2}{|\chi|^2} \cdot (i\mathbf{A} - \nabla_{\mathbf{R}}). \quad (28)$$

We note that the above equations can easily be extended to many particles by redefining the coordinates as $\mathbf{R} \in \mathbb{R}^{3n_C}$, $\mathbf{r} \in \mathbb{R}^{3n_S}$ if the clock and system consist of n_C and n_S particles, respectively. The above equations can directly be used if the number of components of the vector quantities is adjusted and if the coordinates are mass-scaled such that only two masses M and m occur. Alternatively, individual vector potentials and flux densities for each particle can be defined.

We call both (24) and (26) the clock-dependent Schrödinger equation (CDSE) in analogy to the TDSE, because they become TDSEs if the classical limit for the clock is taken. How to take this classical limit is discussed in [15], and we only sketch here the steps that need to be done, using some results of an analysis of the adiabatic limit in the exact factorization [38]. First, we introduce a parameter $\mu := \sqrt{m/M}$, which is the ratio of the mass of the system to that of the clock. If the clock is heavy compared to the system (μ is small), the quantization of the clock becomes negligible and the clock behaves classically. We can then expand $W(\mathbf{R})$ in powers of μ ,

$$W(\mathbf{R}) = \frac{1}{\mu} \sum_{n=0}^{\infty} \mu^n W_n(\mathbf{R}). \quad (29)$$

To lowest order in μ , it can be shown [15,38] that the equation of motion for the clock (12) becomes a classical time-independent Hamilton-Jacobi equation and W_0 is the classical real-valued action. Next, we consider the CDSE (24) and use the result of [38] that \hat{U} is of order μ^2 and can be neglected, while \hat{c}_W is of order μ and is kept. By choosing the gauge where the vector potential vanishes, $\mathbf{A} = 0$, the CDSE becomes

$$i\hbar \hat{c}_W \phi \rightarrow i\hbar \frac{\mathbf{P}}{M} \cdot \nabla_{\mathbf{R}} \phi \approx (\hat{H}_S - \epsilon(\mathbf{R}))\phi, \quad (30)$$

where \mathbf{P} is the classical momentum of the clock defined via the derivative $\nabla_{\mathbf{R}} W_0$ of the classical action of the clock. We can now define a time t that parametrized the position \mathbf{R} of the clock, such that the classical momentum is $\mathbf{P} = M \partial_t \mathbf{R}(t)$, and

$$i\hbar \frac{\mathbf{P}}{M} \cdot \nabla_{\mathbf{R}} \phi = i\hbar \partial_t \phi. \quad (31)$$

Thus, (30) is a TDSE.

This sketch of the derivation of the TDSE from the CDSE leaves out many technical details, e.g., the change of the scalar potential $\epsilon(\mathbf{R})$ when the classical limit is taken or how to perform the classical limit in a gauge invariant way, i.e., including the vector potential $\mathbf{A}(\mathbf{R})$. While some of those details are explained in [15,38], some are still open problems and may be rewarding topics for future research. We need not be concerned with them here, however, because we keep the clock fully quantum mechanical and derive the continuity equation for such a quantum clock.

The operators \hat{c}_W and \hat{c}_S have some interesting properties: They are gauge invariant, as a change of gauge (22) yields

$$\hat{c}'_{S/W} \phi'(\mathbf{r}|\mathbf{R}) = e^{i\theta(\mathbf{R})} \hat{c}_{S/W} \phi(\mathbf{r}|\mathbf{R}), \quad (32)$$

and $i\hbar \hat{c}_S$ is (like $i\hbar \partial_t$) Hermitian for ϕ w.r.t. the \mathbf{r} space,

$$\langle \phi | i\hbar \hat{c}_S \phi \rangle_{\mathbf{r}} = \langle i\hbar \hat{c}_S \phi | \phi \rangle_{\mathbf{r}}, \quad (33)$$

because of the normalization condition (11) that ϕ has to fulfill. However, in contrast to ∂_t , the operators $\hat{c}_{W/S}$ are in general complex.

III. TIME-REVERSAL INVARIANCE

Before using the CDSE to derive a continuity equation, we would like to comment on time-reversal invariance and

how it occurs in the CDSE. For the TDSE, it is well known [39] that it is equivalent to either solve the TDSE with time t , or to solve its complex-conjugate equation with time $-t$, provided the sign of a possible vector potential occurring in the canonical momentum operator is changed. Hence, solving the TDSE (3) or solving

$$-i\hbar \partial_{-t} \bar{\psi}(\mathbf{x}, -t) = \left(\frac{\hbar^2}{2m} [i\nabla_{\mathbf{x}} - \mathbf{A}(\mathbf{x}, -t)]^2 \right) \bar{\psi}(\mathbf{x}, -t) \quad (34)$$

for the same initial condition $\psi(\mathbf{x}, t_0)$ yields the same probability density $|\psi|^2$ and, except for a change of sign, the same probability flux density (4).

From the clock-dependent point of view, time-reversal invariance originates from invariance of the TISE of the universe, (5), w.r.t. to complex conjugation. Taking, for example, the complex conjugate of the CDSE (26) yields an equation equivalent to (26), provided one realizes that $\mathbf{A}[\bar{\phi}]$ has to be replaced with $\mathbf{A}[\bar{\phi}] = -\mathbf{A}[\phi]$, and provided one changes the sign of the clock's phase $S(\mathbf{R})$, making it run in the "reverse" direction. In this sense the CDSE is clock-reversal invariant, but this is a rather trivial consequence of the requirement that the universe is in a static state.

IV. THE CLOCK-DEPENDENT CONTINUITY EQUATION

To obtain the fully quantum-mechanical continuity equation for the density $|\phi(\mathbf{r}|\mathbf{R})|^2$ of the system which depends on the system coordinates \mathbf{r} , on the clock coordinates \mathbf{R} , and also on the state of the clock χ , we work with \hat{c}_S and treat it as an analog of the time-derivative operator. Its action on the conditional density $|\phi(\mathbf{r}|\mathbf{R})|^2$ can be defined as

$$\bar{\phi} \hat{c}_S \phi + \phi \hat{c}_S^\dagger \bar{\phi} =: \hat{c} |\phi|^2 \quad (35)$$

with a purely real operator

$$\hat{c} = \frac{\hbar}{M} (-\nabla_{\mathbf{R}} S + \mathbf{A}) \cdot \nabla_{\mathbf{R}}. \quad (36)$$

From the CDSE for ϕ and for its complex conjugate $\bar{\phi}$, we find

$$\begin{aligned} \hat{c} |\phi|^2 + \nabla_{\mathbf{r}} \cdot \mathbf{j}[\phi](\mathbf{r}|\mathbf{R}) + \left(\nabla_{\mathbf{R}} + \frac{\nabla_{\mathbf{R}} |\chi|^2}{|\chi|^2} \right) \cdot \mathbf{J}[\phi, -\mathbf{A}](\mathbf{r}|\mathbf{R}) \\ = 0 \end{aligned} \quad (37)$$

with the flux densities $\mathbf{j}[\phi]$ and $\mathbf{J}[\phi, -\mathbf{A}]$ being of the usual form of (4), given for a general function $f \in \mathbb{C}$ as

$$\mathbf{j}[f] = \frac{\hbar}{m} \text{Im}(\bar{f} \nabla_{\mathbf{r}} f) \quad (38)$$

$$\mathbf{J}[f, \pm \mathbf{A}] = \frac{\hbar}{M} [\text{Im}(\bar{f} \nabla_{\mathbf{R}} f) \pm \mathbf{A} |f|^2]. \quad (39)$$

Here, $\mathbf{j}[\phi]$ appears because of the Hamiltonian \hat{H}_S of the system alone and is the flux density of the system w.r.t. the system variables, while $\mathbf{J}[\phi, -\mathbf{A}]$ appears because of the operator \hat{U} and is the flux density of the system w.r.t. the clock variables. We note that $\mathbf{J}[f, \pm \mathbf{A}]$ (as well as $\mathbf{j}[f]$) are invariant w.r.t. the choice of gauge (22). With these definitions, we can also

write the operator \hat{c} as

$$\hat{c} = \frac{1}{|\chi|^2} \mathbf{J}[\chi, +\mathbf{A}] \cdot \nabla_{\mathbf{R}}. \quad (40)$$

Equation (37) is a clock-dependent continuity equation in the space of the coordinates of the system which, however, depends also conditionally on the coordinates of the clock. Three flux densities occur in this equation: the flux density of the system w.r.t. its coordinates, the flux density of the system w.r.t. the clock coordinates, and, as part of the \hat{c} operator, the flux density of the clock. The \hat{c} operator yields the change of the density $|\phi|^2$ w.r.t. the clock variables, weighted by the velocity components (flux density divided by density) in the respective direction. What is also notable about (37) is that there is a modification of the divergence of $\mathbf{J}[\phi, -\mathbf{A}]$ by the additional term $(\nabla_{\mathbf{R}}|\chi|^2)/|\chi|^2$. This could be avoided if we had used the complex-valued function $W(\mathbf{R})$ instead of the real-valued functions $S(\mathbf{R})$ and $|\chi(\mathbf{R})|$, i.e., if we had used \hat{c}_W instead of \hat{c}_S . The disadvantage of this choice would have been that we could not have written (35) with a real-valued operator \hat{c} acting on $|\phi|^2$.

To obtain a continuity equation for the system alone, we need to average over the degrees of freedom of the clock. This is done by multiplication of (37) with the probability distribution of the clock $|\chi|^2$ and subsequent integration over the clock configurations \mathbf{R} . Due to the modified divergence w.r.t. the clock coordinates, the contribution of the flux density $\mathbf{J}[\phi, -\mathbf{A}]$ cancels,

$$\int |\chi|^2 \left(\nabla_{\mathbf{R}} + \frac{\nabla_{\mathbf{R}}|\chi|^2}{|\chi|^2} \right) \cdot \mathbf{J}[\phi, -\mathbf{A}](\mathbf{r}|\mathbf{R}) d\mathbf{R} = 0, \quad (41)$$

and we obtain

$$\dot{\rho}_S[\chi](\mathbf{r}) + \nabla_{\mathbf{r}} \cdot \mathbf{j}_S[\chi](\mathbf{r}) = 0 \quad (42)$$

with the clock-averaged change of the density defined as

$$\dot{\rho}_S[\chi](\mathbf{r}) := \int |\chi(\mathbf{R})|^2 \hat{c} |\phi(\mathbf{r}|\mathbf{R})|^2 d\mathbf{R} \quad (43)$$

and with the clock-averaged flux density

$$\mathbf{j}_S[\chi](\mathbf{r}) := \int |\chi(\mathbf{R})|^2 \mathbf{j}[\phi](\mathbf{r}|\mathbf{R}) d\mathbf{R}. \quad (44)$$

The clock-dependent continuity equations (37) and (42) are the main results of this article. The equation for the system alone, (42), is especially interesting, as it is the direct analog of the time-dependent continuity equation. Instead of the usual time dependence, there is a functional dependence on the state of the clock χ in both the change of the density $\dot{\rho}_S$ and in the flux density \mathbf{j}_S which takes into account the quantum-mechanical nature of the clock.

The clock-dependent continuity equation (42) can be useful to analyze a quantum dynamics, as illustrated in the next section. However, as we started from a stationary state of the universe, it is not obvious from (37) and (42) how to obtain a nontrivial dynamics of the system. Here, nontrivial means that the terms of the continuity equations are not individually zero. If the universe (which is assumed to be a closed system) is in an eigenstate of zero total angular momentum, its wave function can be chosen to be real and hence both the clock wave function χ and the system wave function ϕ may be

chosen to be real. Then, the (gauge-invariant) flux densities $\mathbf{j}[\phi]$, $\mathbf{J}[\phi, -\mathbf{A}]$, and $\mathbf{J}[\chi, +\mathbf{A}]$ in (37) vanish and there is no dynamics. However, there are cases where there always exists a nonzero vector potential leading to nonzero flux densities, even for eigenstates [40]. This is the case if the universe is in a state of nonzero angular momentum, and then it may be possible to obtain a nontrivial dynamics. We tested a model of a universe having only harmonic interactions, finding that for an eigenstate of the universe with nonzero integer angular momentum, a gauge $\mathbf{A} = 0$ is in general not possible. Nevertheless, after averaging over the clock wave function, we find that the terms in (42) are still individually zero. This test, of course, is not conclusive and further investigations are necessary.

A clock-dependent measurement has, however, not only a system and a clock that are involved, but also an observer which measures both the state of the clock and of the system. Taking the act of measurement into account may lead to a nontrivial dynamics even if the universe is in an eigenstate, and hence may change the interpretation of the clock-dependent continuity equations. It may thus be necessary to take the view of an internal observer that is measuring the state of the clock and of the system, and some ideas of how to obtain such a consistent timeless theory with evolution exist [20].

In the following example application we avoid the question of the origin of the dynamics from a universe-internal point of view altogether by assuming that the dynamics is measured w.r.t. some external classical time (i.e., the dynamics is the solution of a TDSE). This is the typical experimental situation, but it is understood that the lack of a fully internal description is unsatisfying from a fundamental point of view and calls for further research.

V. APPLICATION

To understand the clock-dependent continuity equation better, we consider as an example a molecular dynamics, i.e., a dynamics of nuclei and electrons, which is generated by an external interaction (that need not be present anymore) and which can be described by a TDSE. Our aim is to study the electron dynamics with respect to the external classical time and with respect to the nuclei, which are treated as an internal clock. As the ansatz is similar to the Born-Oppenheimer approach to molecular dynamics, the example allows us to understand better how the Born-Oppenheimer approximation works and shows how the idea of separating “slow” and “fast” degrees of freedom can be transferred to other problems. Additionally, it gives new insights into the puzzling problem that the electronic continuity equation seems to be violated in the limit of the Born-Oppenheimer approximation [33].

The state of the molecule is described by a wave function $\psi(\mathbf{R}, \mathbf{r}|t)$ depending on nuclear coordinates \mathbf{R} , on electronic coordinates \mathbf{r} , and on an external time t , i.e., it is assumed that the considered dynamics is governed by the TDSE

$$i\hbar\partial_t\psi = \left(-\frac{\hbar^2\nabla_{\mathbf{R}}^2}{2M} + \hat{H}_{\text{el}} \right) \psi \quad (45)$$

with electronic Hamiltonian \hat{H}_{el} [corresponding to the system Hamiltonian \hat{H}_S , cf. (5)] containing the electronic kinetic energy operator and the scalar interaction potential. Initialization

of the dynamics and measurement of t can happen by means of a suitable external interaction, e.g., strong ultrashort laser pulses that can act as a good clock [12].

In analogy to (8), we make the factorization ansatz

$$\psi(\mathbf{R}, \mathbf{r}|t) = \chi(\mathbf{R}|t)\phi(\mathbf{r}|\mathbf{R}, t) \quad (46)$$

with partial normalization condition $\langle \phi|\phi \rangle_{\mathbf{r}} \stackrel{!}{=} 1 \forall \mathbf{R}, t$, where the equations of motion are [27]

$$i\hbar\partial_t\chi = \left(-\frac{\hbar^2}{2M}[i\nabla_{\mathbf{R}} + \mathbf{A}(\mathbf{R}|t)]^2 + \epsilon(\mathbf{R}|t) \right)\chi, \quad (47)$$

$$(i\hbar\partial_t + \hat{C})\phi = (\hat{H}_{\text{el}} + \hat{U} - \epsilon(\mathbf{R}|t))\phi, \quad (48)$$

with the time-dependent vector potential $\mathbf{A}(\mathbf{R}|t)$ as defined in (19), with the operators \hat{C} , \hat{U} as defined in (14), (15), and with the time-dependent scalar potential

$$\epsilon(\mathbf{R}|t) = \langle \phi|\hat{H}_{\text{el}} + \hat{U} - \hat{C} - i\hbar\partial_t|\phi \rangle_{\mathbf{r}}. \quad (49)$$

For a change of gauge (22), the time-dependent scalar potential transforms as $\epsilon'(\mathbf{R}|t) = \epsilon(\mathbf{R}|t) + \partial_t\theta(\mathbf{R}, t)$. The continuity equation following from the TDSE for ψ , integrated over \mathbf{R} , gives

$$0 = \langle |\chi|^2\partial_t|\phi|^2 \rangle_{\mathbf{R}} + \langle |\phi|^2\partial_t|\chi|^2 \rangle_{\mathbf{R}} + \langle |\chi|^2\nabla_{\mathbf{r}} \cdot \mathbf{j}[\phi] \rangle_{\mathbf{R}}. \quad (50)$$

Also, (47) is a normal TDSE for $\chi(\mathbf{R}|t)$, and hence the corresponding continuity equation is

$$0 = \partial_t|\chi|^2 + \nabla_{\mathbf{R}} \cdot \mathbf{J}[\chi, \mathbf{A}]. \quad (51)$$

Inserting (51) for $\partial_t|\chi|^2$ in (50) yields the t - and clock-dependent continuity equation

$$0 = \langle |\chi|^2\partial_t|\phi|^2 \rangle_{\mathbf{R}} + \langle \mathbf{J}[\chi, \mathbf{A}] \cdot \nabla_{\mathbf{R}}|\phi|^2 \rangle_{\mathbf{R}} + \nabla_{\mathbf{r}} \cdot \langle |\chi|^2\mathbf{j}[\phi] \rangle_{\mathbf{R}}, \quad (52)$$

where a partial integration was used once for the \mathbf{J} -dependent term. $\langle |\chi|^2\mathbf{j}[\phi] \rangle_{\mathbf{R}}$ is the electronic flux density, and a comparison with (42) shows that $\langle |\chi|^2\partial_t|\phi|^2 \rangle_{\mathbf{R}}$ can be interpreted as the (averaged) change of the electronic density w.r.t. the external time, and $\langle \mathbf{J}[\chi, \mathbf{A}] \cdot \nabla_{\mathbf{R}}|\phi|^2 \rangle_{\mathbf{R}}$ is the change of the electronic density w.r.t. the internal clock.

To illustrate this continuity equation, we consider a model for proton-coupled electron transfer [41] with the parameters of [38]. In this one-dimensional model, two ‘‘ions’’ of infinite mass are located at $\pm L/2$, and a positively charged particle, the nucleus, as well as a negatively charged particle, the electron, are allowed to move along dimensions R and r , respectively. The Hamiltonian for the system is

$$H = -\frac{\mu}{2}\partial_R^2 + \hat{H}_{\text{el}}, \quad (53)$$

where $\mu = m/M$ is the mass ratio between electron and nucleus, and where

$$\hat{H}_{\text{el}} = -\frac{\partial_r^2}{2} + \frac{1}{|R - \frac{L}{2}|} + \frac{1}{|R + \frac{L}{2}|} - \frac{\text{erf}\left(\frac{|r-R|}{R_c}\right)}{|R-r|} - \frac{\text{erf}\left(\frac{|r-\frac{L}{2}|}{R_r}\right)}{|r-\frac{L}{2}|} - \frac{\text{erf}\left(\frac{|r+\frac{L}{2}|}{R_l}\right)}{|r+\frac{L}{2}|}. \quad (54)$$

The parameters are taken to be $L = 19 a_0$, $R_r = R_l = 3.5 a_0$, and we consider different values for R_c . This parameter determines the coupling between the two lowest electronic states in a Born-Oppenheimer description of the dynamics. The respective Born-Oppenheimer potential energy surfaces are shown in Fig. 1 for $R_c = 4.0 a_0$ (weak coupling) and $R_c = 7.0 a_0$ (strong coupling).

As in [38], we choose the initial state to be $\psi(R, r|0) = G(R - R_0, \sigma)\phi_0^{\text{BO}}(r|R)$ with the electronic ground state ϕ_0^{BO} within the Born-Oppenheimer approximation and with Gaussian G centered at $R_0 = 5.0 a_0$ having variance $\sigma^2 = (0.15 a_0)^2\sqrt{2000\mu}$. The specific choice of the parameters for the Gaussian are, however, not important for the following analysis. The initial densities for the choices $\mu^{-1} = 100$ and $\mu^{-1} = 900$ are shown in Fig. 1. We integrate the TDSE (45) by constructing a sparse-matrix representation of the Hamiltonian and by applying the corresponding evolution operator to a vector representation of the wave function using the SciPy sparse matrix functionalities [42]. Videos and further pictures of the dynamics are given in the Supplemental Material [43].

We investigate the mass dependence and coupling-strength dependence of the three terms in the electronic continuity equation (50). To quantify the contributions of each term, we integrate their magnitudes over the whole simulation time. Subsequently, the results are normalized by a factor $1/\kappa$ such that the maximum value of the largest of these quantities, for the simulation with the largest flux, is 1, i.e., we define

$$N_t = \frac{1}{\kappa} \int_0^{t_{\text{max}}} \langle |\chi|^2\partial_t|\phi|^2 \rangle_{\mathbf{R}} dt, \quad (55)$$

$$N_c = \frac{1}{\kappa} \int_0^{t_{\text{max}}} \langle |\chi|^2\hat{C}|\phi|^2 \rangle_{\mathbf{R}} dt, \quad (56)$$

$$N_J = \frac{1}{\kappa} \int_0^{t_{\text{max}}} |\partial_r \langle |\chi|^2\mathbf{j}[\phi] \rangle_{\mathbf{R}}| dt. \quad (57)$$

The larger N_t , N_c , or N_J are, the more flux they correspond to.

The coupling-strength dependence is shown for $\mu^{-1} = 900$ in Fig. 2. From the figure, we see that for strong coupling, both the contributions w.r.t. the external and the internal clock are important. In contrast, for weak coupling N_t becomes negligible compared to the other two terms, i.e., the external clock plays a minor role.

The other relevant factor for the dynamics is the mass ratio. The mass dependence of N_t , N_c , N_J for weak coupling ($R_c = 4 a_0$) is shown in Fig. 3. We see that N_t becomes less and less important with increasing mass. This is a general trend, i.e., for weak couplings and large masses the contribution of the external clock can be neglected, whereas for small masses and/or strong couplings all terms are relevant.

The conditions where only the nucleus as internal clock is relevant for the electron dynamics (large mass ratio, small coupling parameter) are also those for which the Born-Oppenheimer approximation is valid. There, the molecular wave function is written as

$$\psi(\mathbf{R}, \mathbf{r}|t) \approx \chi^{\text{BO}}(\mathbf{R}|t)\phi^{\text{BO}}(\mathbf{r}|\mathbf{R}), \quad (58)$$

with $\phi^{\text{BO}}(\mathbf{r}|\mathbf{R})$ being an eigenfunction of \hat{H}_{el} at a fixed nuclear configuration \mathbf{R} . It can be derived from the exact factorization in the limit of vanishing mass ratio μ

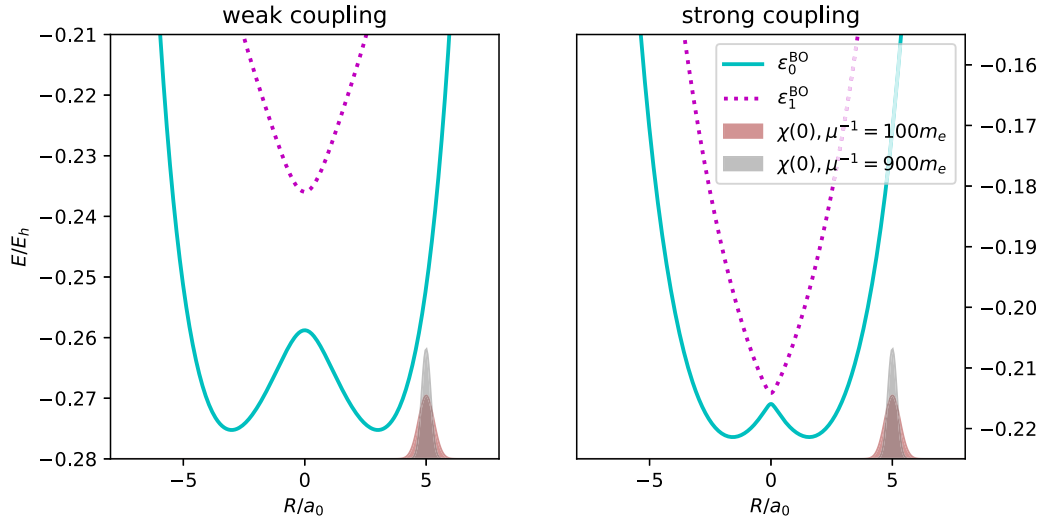


FIG. 1. The two lowest Born-Oppenheimer potential energy surfaces of the proton-coupled electron transfer model as well as the initial nuclear densities $|\chi|^2$ for mass parameters $\mu^{-1} = 100$ and 900 are shown for a case of weak coupling (left, $R_c = 4.0 a_0$) and strong coupling (right, $R_c = 7.0 a_0$).

of electronic and nuclear mass, cf. [38], which leads to the disappearance of $i\hbar\partial_t$, \hat{U} , and \hat{C} in the conditional equation (48).

The Born-Oppenheimer approximation is usually interpreted such that due to their comparably small mass, the electrons react instantaneously to a change in the nuclear position. In this way, the electron density is well approximated by the density of an eigenstate ϕ^{BO} of \hat{H}_{el} at a given nuclear configuration \mathbf{R} . We see the meaning of this interpretation in the vanishing of the contribution $\partial_t|\phi|^2$ to the continuity equation, i.e., in the vanishing of the (direct) dependence of

the electronic density on the external time. However, there is still a motion of the electrons which is given by the electronic flux density $\mathbf{j}[\phi]$, but this motion is induced by the motion of the nuclei. In the continuity equation, this part corresponds to the clock-dependent contribution $\hat{c}|\phi|^2$ (that indirectly depends on t , too), which entirely cancels the divergence of the electronic flux density for large nuclear masses and small coupling strengths.

Typically, the Born-Oppenheimer approximation does not take into account this electronic motion w.r.t. the internal clock of the nuclei. The consequence is that the electronic

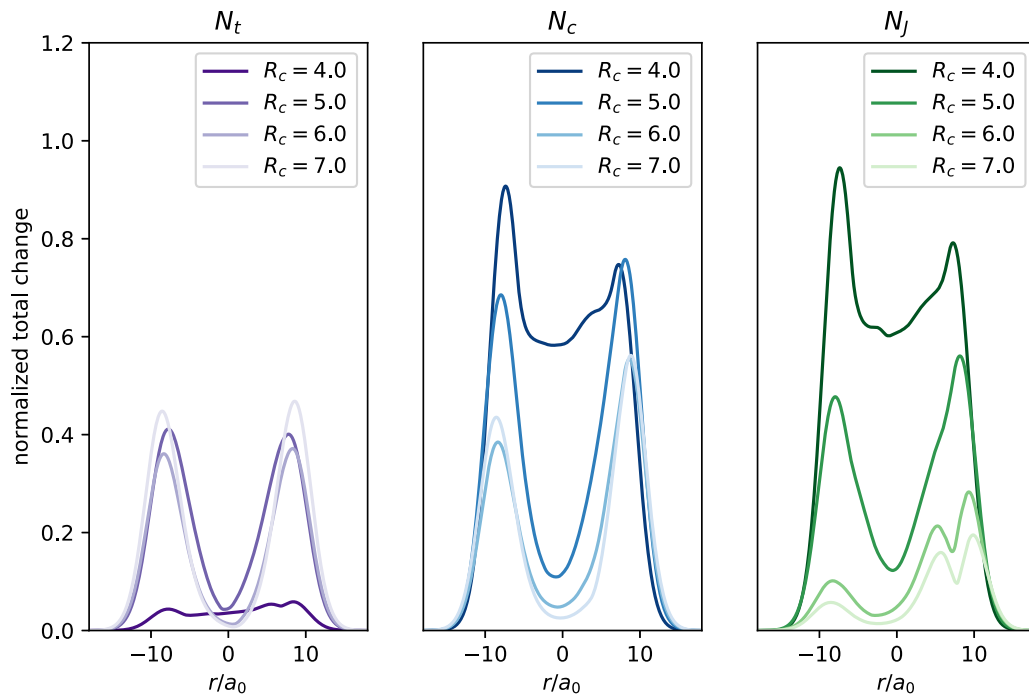


FIG. 2. Measures N_t , N_c , N_j of the three contributions occurring in the continuity equation for the electron density for a mass parameter $\mu^{-1} = 900$, for different coupling parameters R_c .

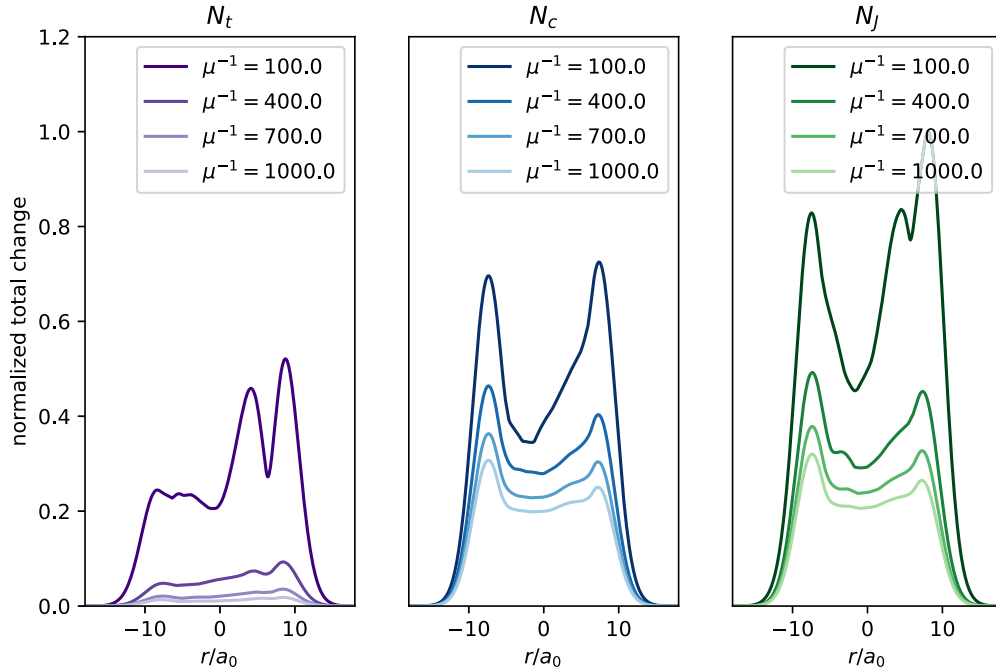


FIG. 3. Measures N_t , N_c , N_J of the three contributions occurring in the continuity equation for the electron density for a coupling parameter $R_c = 4.0 a_0$, for different mass parameters μ^{-1} .

density

$$\rho_{\text{el}}(\mathbf{r}) := \int |\psi|^2 d\mathbf{R} \approx \int |\chi^{\text{BO}}(\mathbf{R}|t)|^2 |\phi^{\text{BO}}(\mathbf{r}|\mathbf{R})|^2 d\mathbf{R} \quad (59)$$

is close to the true density, but the flux density computed with the Born-Oppenheimer wave function is zero [33],

$$\begin{aligned} j_{\text{el}}(\mathbf{r}) &= \frac{\hbar}{m_e} \int \text{Im}(\bar{\psi} \nabla_r \psi) d\mathbf{R} \\ &\approx \frac{\hbar}{m_e} \int |\chi^{\text{BO}}|^2 \text{Im}(\bar{\phi}^{\text{BO}} \nabla_r \phi^{\text{BO}}) d\mathbf{R} \equiv 0. \end{aligned} \quad (60)$$

Comparing (59) and (60), we see that the continuity equation (2) seems to be invalid. A number of investigations [44–47] partly clarify the issue. In view of the results presented above, the failure of the Born-Oppenheimer wave function can be interpreted as the lack of correctly accounting for the motion w.r.t. the internal clock. This interpretation is in line with [47], where it was shown that the electronic flux density can be recovered for conditions where the Born-Oppenheimer approximation is valid if \hat{C} is treated as perturbation, i.e., if the motion is referred to the nuclei being the clock.

We note that a different way to find an approximation for the motion of the electrons relative to the nuclear clock is to replace the CDSE with a TDSE. This can be done by starting from the conditional equation (13), applied to the electron-nuclear problem (i.e., without dependence on the external time t), and taking the classical limit for the nuclear wave function. The results are essentially the equations of motion of Ehrenfest molecular dynamics [48]. We find that a simulation of the electron dynamics using equations of this type, specifically, solving

$$i\hbar \partial_T \phi(r|T) = \hat{H}_{\text{el}}(T) \phi(r|T) \quad (61)$$

for effective time T (which is close to the external time t) defined via the expectation values of nuclear position and momentum, $T := \langle R(t) \rangle / \langle \hat{P}(t) \rangle$, yields a good approximation for the electronic flux density in our models. In the classical limit of the nuclei, the internal classical time T and the external time t are, of course, identical. We note that the electronic Hamiltonian \hat{H}_{el} depends on T in the sense that its dependence on the nuclear position R is replaced by the expectation value $\langle R \rangle$.

VI. CONCLUSION AND OUTLOOK

In this article, we start with the premise that time is obtained in the classical limit of a clock and that the system depends conditionally on the configuration of the clock. From a quantum-mechanical perspective, it follows that there is no time, there are only clocks. We investigate the consequences of this statement on the continuity equation, finding that the flux density of the clock plays a vital role if the clock needs to be treated as a quantum system.

The generalization of the TDSE to a CDSE by means of the exact factorization allows us to define any degree of freedom as a clock. Interpreting part of a quantum system as a clock for the remaining degrees of freedom can be a helpful idea for developing effective simulation methods. The clock-dependent continuity equation (42) or its analog for dynamics referred to an external time, (52), may be used as a tool to analyze a general quantum dynamics for possible degrees of freedom that are amenable to such approximate treatments. Then, one may use a Born-Oppenheimer-like approach based on the separation of timescales, or one may derive other approximations to the CDSE based on the quasiclassical behavior of some degrees of freedom, like Ehrenfest molecular dynamics, where the CDSE is replaced by a TDSE. Our

analysis of a simple model of a coupled electron-nuclear dynamics illustrates the idea of a quantum clock and shows how the Born-Oppenheimer approach works, and might provide some ideas for a timescale separation of other problems.

Finally, an important point that we discussed only briefly here is the origin of the dynamics, i.e., of evolution without time as a fundamental variable. Starting from a stationary state of the universe without reference to an external clock or observer, an internally consistent static theory may be derived. However, the mechanism of how a change of the system happens needs to be explored further. One way that this problem might conceptually be solved is by inclusion

of an internal observer which measures the clock and the properties of the system. In this author's opinion, there is some promising research on this topic, but there is still no relative point of view on time (and space) that yields a fully developed picture of dynamics without time. Thus, further work is needed.

ACKNOWLEDGMENTS

The author is grateful to Basile F. E. Curchod for helpful comments on the manuscript. This research is supported by an Ambizione grant of the Swiss National Science Foundation.

-
- [1] R. Aris, *Vectors, Tensors, and the Basic Equations of Fluid Mechanics* (Dover, New York, 1989).
- [2] T. B. Boykin, An alternative view of the continuity equation in quantum mechanics, *Am. J. Phys.* **68**, 665 (2000).
- [3] E. Madelung, Quantentheorie in hydrodynamischer form, *Z. Phys.* **40**, 322 (1927).
- [4] K. Renziehausen and I. Barth, Many-particle quantum hydrodynamics: Exact equations and pressure tensors, *Prog. Theor. Exp. Phys.* (2018) 013A05.
- [5] E. Runge and E. K. U. Gross, Density-Functional Theory for Time-Dependent Systems, *Phys. Rev. Lett.* **52**, 997 (1984).
- [6] L. A. Nafie, *Vibrational Optical Activity* (Wiley, New York, 2011).
- [7] G. Hermann, B. Paulus, J. F. Pérez-Torres, and V. Pohl, Electronic and nuclear flux densities in the H₂ molecule, *Phys. Rev. A* **89**, 052504 (2014).
- [8] T. Bredtmann, D. J. Diestler, Si-Dian Li, J. Manz, J. F. Pérez-Torres, Wen-Juan Tian, Yan-Bo Wu, Yonggang Yang, and Hua-Jin Zhai, Quantum theory of concerted electronic and nuclear fluxes associated with adiabatic intramolecular processes, *Phys. Chem. Chem. Phys.* **17**, 29421 (2015).
- [9] G. Hermann, C. M. Liu, J. Manz, B. Paulus, J. F. Pérez-Torres, V. Pohl, and J. C. Tremblay, Multidirectional angular electronic flux during adiabatic attosecond charge migration in excited benzene, *J. Phys. Chem. A* **120**, 5360 (2016).
- [10] D. N. Page and W. K. Wootters, Evolution without evolution: Dynamics described by stationary observables, *Phys. Rev. D* **27**, 2885 (1983).
- [11] J. S. Briggs and J. M. Rost, Time dependence in quantum mechanics, *Eur. Phys. J. D* **10**, 311 (2000).
- [12] L. Braun, W. T. Strunz, and J. S. Briggs, Classical limit of the interaction of a quantum system with the electromagnetic field, *Phys. Rev. A* **70**, 033814 (2004).
- [13] J. S. Briggs, S. Boonchui, and S. Khemmani, The derivation of time-dependent Schrödinger equations, *J. Phys. A: Math. Theor.* **40**, 1289 (2007).
- [14] J. S. Briggs and J. M. Feagin, Scattering theory, multiparticle detection, and time, *Phys. Rev. A* **90**, 052712 (2014).
- [15] J. S. Briggs, Equivalent emergence of time dependence in classical and quantum mechanics, *Phys. Rev. A* **91**, 052119 (2015).
- [16] S. Massar, P. Spindel, A. F. Varón, and C. Wunderlich, Investigating the emergence of time in stationary states with trapped ions, *Phys. Rev. A* **92**, 030102 (2015).
- [17] A. Boette, R. Rossignoli, N. Gigena, and M. Cerezo, System-time entanglement in a discrete-time model, *Phys. Rev. A* **93**, 062127 (2016).
- [18] H. Kitada, J. Jeknić-Dugić, M. Arsenijević, and M. Dugić, A minimalist approach to conceptualization of time in quantum theory, *Phys. Lett. A* **380**, 3970 (2016).
- [19] P. Erker, M. T. Mitchison, R. Silva, M. P. Woods, N. Brunner, and M. Huber, Autonomous Quantum Clocks: Does Thermodynamics Limit Our Ability to Measure Time?, *Phys. Rev. X* **7**, 031022 (2017).
- [20] P. Małkiewicz and A. Miroszewski, Internal clock formulation of quantum mechanics, *Phys. Rev. D* **96**, 046003 (2017).
- [21] E. Moreva, G. Brida, M. Gramegna, V. Giovannetti, L. Maccone, and M. Genovese, Time from quantum entanglement: An experimental illustration, *Phys. Rev. A* **89**, 052122 (2014).
- [22] E. Moreva, G. Brida, M. Gramegna, V. Giovannetti, L. Maccone, and M. Genovese, The time as an emergent property of quantum mechanics, A synthetic description of a first experimental approach, *J. Phys.: Conf. Ser.*, **626**, 012019 (2015).
- [23] V. Giovannetti, S. Lloyd, and L. Maccone, Quantum time, *Phys. Rev. D* **92**, 045033 (2015).
- [24] E. Moreva, M. Gramegna, G. Brida, L. Maccone, and M. Genovese, Quantum time: Experimental multitime correlations, *Phys. Rev. D* **96**, 102005 (2017).
- [25] C. Marletto and V. Vedral, Evolution without evolution and without ambiguities, *Phys. Rev. D* **95**, 043510 (2017).
- [26] K. L. H. Bryan and A. J. M. Medved, Realistic clocks for a universe without time, *Found. Phys.* **48**, 48 (2018).
- [27] A. Abedi, N. T. Maitra, and E. K. U. Gross, Exact Factorization of the Time-Dependent Electron-Nuclear Wave Function, *Phys. Rev. Lett.* **105**, 123002 (2010).
- [28] L. Kaplan, N. T. Maitra, and E. J. Heller, Quantizing constrained systems, *Phys. Rev. A* **56**, 2592 (1997).
- [29] F. Remacle and R. D. Levine, On the inverse Born-Oppenheimer separation for high Rydberg states of molecules, *Int. J. Quantum Chem.* **67**, 85 (1998).
- [30] Lian-Ao Wu and D. Segal, Quantum heat transfer: A Born-Oppenheimer method, *Phys. Rev. E* **83**, 051114 (2011).
- [31] O. S. Sørensen and K. Mølmer, Born-Oppenheimer description of two atoms in a combined oscillator and lattice trap, *Phys. Rev. A* **86**, 013625 (2012).
- [32] M. Mondelo-Martell, F. Huarte-Larrañaga, and U. Manthe, Quantum dynamics of H₂ in a carbon nanotube: Separation of time scales and resonance enhanced tunneling, *J. Chem. Phys.* **147**, 084103 (2017).

- [33] I. Barth, H.-C. Hege, H. Ikeda, A. Kenfack, M. Koppitz, J. Manz, F. Marquardt, and G. K. Paramonov, Concerted quantum effects of electronic and nuclear fluxes in molecules, *Chem. Phys. Lett.* **481**, 118 (2009).
- [34] W. B. Hodge, S. V. Migirditch, and W. C. Kerr, Electron spin and probability current density in quantum mechanics, *Am. J. Phys.* **82**, 681 (2014).
- [35] A. Abedi, N. T. Maitra, and E. K. U. Gross, Correlated electron-nuclear dynamics: Exact factorization of the molecular wavefunction, *J. Chem. Phys.* **137**, 22A530 (2012).
- [36] N. I. Gidopoulos and E. K. U. Gross, Electronic non-adiabatic states: Towards a density functional theory beyond the Born–Oppenheimer approximation, *Proc. R. Soc. A* **372**, 20130059 (2014).
- [37] T. Jecko, B. T. Sutcliffe, and R. G. Woolley, On factorization of molecular wavefunctions, *J. Phys. A: Math. Theor.* **48**, 445201 (2015); Corrigendum: On factorization of molecular wavefunctions, **51**, 149501 (2018).
- [38] F. G. Eich and Federica Agostini, The adiabatic limit of the exact factorization of the electron-nuclear wave function, *J. Chem. Phys.* **145**, 054110 (2016).
- [39] A. Messiah, *Quantum Mechanics* (Dover Publications, Inc., Mineola, NY, 1999).
- [40] R. Requist and E. K. U. Gross, Exact Factorization-Based Density Functional Theory of Electrons and Nuclei, *Phys. Rev. Lett.* **117**, 193001 (2016).
- [41] S. Shin and H. Metiu, Nonadiabatic effects on the charge transfer rate constant: A numerical study of a simple model system, *J. Chem. Phys.* **102**, 9285 (1995).
- [42] E. Jones, T. Oliphant, P. Peterson *et al.*, SciPy: Open source scientific tools for Python, (2001), <http://www.scipy.org>.
- [43] See Supplemental Material at <http://link.aps.org/supplemental/10.1103/PhysRevA.98.052113> for movies and further pictures of the dynamics.
- [44] D. J. Diestler, Beyond the Born-Oppenheimer approximation: A treatment of electronic flux density in electronically adiabatic molecular processes, *J. Phys. Chem. A* **117**, 4698 (2013).
- [45] D. J. Diestler, A. Kenfack, J. Manz, B. Paulus, J. F. Pérez-Torres, and V. Pohl, Computation of the electronic flux density in the Born-Oppenheimer approximation, *J. Phys. Chem. A* **117**, 8519 (2013).
- [46] A. Scherrer, R. Vuilleumier, and D. Sebastiani, Nuclear velocity perturbation theory of vibrational circular dichroism, *J. Chem. Theory Comput.* **9**, 5305 (2013).
- [47] A. Schild, F. Agostini, and E. K. U. Gross, Electronic flux density beyond the Born-Oppenheimer approximation, *J. Phys. Chem. A* **120**, 3316 (2016).
- [48] J. C. Tully, Mixed quantum-classical dynamics, *Faraday Discuss.* **110**, 407 (1998).