Time dependent density functional theory for nonadiabatic electronic dynamics.

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Abstract

We show that the time dependent single electron, nuclear density matrix of an interacting electronic system coupled to nuclear degrees of freedom can be exactly reproduced by that of an electronic system with arbitrarily specified electron-electron interactions coupled to the same nuclear degrees of freedom, given the initial density matrix of the interacting system. This formalism enables the construction of rigorous time dependent density functional theories to study nonadiabatic electronic dynamics. We obtain the Runge-Gross and Van Leeuwen theorems as special cases in the adiabatic limit.

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The correlated dynamics of electrons and nuclei drive fundamental mechanisms of chemical reaction dynamics. Most of these mechanisms involve nonadiabatic electron nuclear dynamics, where the adiabatic or Born-Oppenheimer approximation is no longer valid.[1, 2] A central problem in understanding correlated electron-nuclear dynamics is the mutual time evolution of the electron and nuclear quantum subsystems. Nonadiabatic energy and information transfer between the two subsystems plays a fundamental role in correlated electron-nuclear dynamics. Nonadiabatic processes are controlled by nuclear momentum dependent derivative couplings between the electronic and nuclear subsystems. Because of their momentum dependence, these couplings also manifest themselves through complex geometric phase effects, a well known example of which is the Jahn-Teller effect [3, 4]. Nonadiabatic couplings between the two subsystems are also generally off diagonal in the nuclear subspace and introduce nonlocal, history dependent correlations into the electron-nuclear dynamics.

Due to the complexity of the time evolution, developing ab initio methods to model correlated electron-nuclear dynamics has proved to be a challenging problem. Time dependent density functional theory(TDDFT) is a formally exact, successful method developed to understand the dynamical properties of interacting electron systems. This theory relies on the Runge-Gross theorem [5] and its generalization by Van Leeuwen [6], which relate the exact single electron density to the single electron time dependent potential. It is also a computationally tractable method, and hence is a promising approach that could be extended to model correlated electron-nuclear dynamics. TDDFT has recently been extended to model certain open quantum systems [7, 8].

Direct extensions of TDDFT to model correlated electron-nuclear dynamics involve the estimation of only single particle densities and more generally diagonal elements of the system density matrix [9, 10, 11] and are based on extensions of DFT to multicomponent systems [12]. Although they guarantee the correct estimation of these quantities, they are unable to fully account for the dynamical phase correlations due to the nonadiabatic derivative couplings between electronic and nuclear subsystems. These correlations are of fundamental importance to nonadiabatic energy transfer mechanisms that occur in many chemical reaction processes [1]. This is because nonadiabatic phase correlations that arise during the system’s time evolution cannot be fully captured by diagonal density matrix elements. It is also difficult to derive essential simplifying semiclassical approximations to the multicomponent TDDFT framework that are required for tractable computational studies.
We propose a formulation that extends the density functional paradigm to model the time evolution of interacting electron nuclear systems starting from an arbitrary initial density matrix for the entire system. The theory we present is designed to explicitly and exactly capture nonadiabatic effects on correlated electron-nuclear dynamics while simplifying the effects of electron-electron interactions. Our theory also retains off diagonal elements of the density matrix in the nuclear subspace. This property allows our theory to retain information regarding quantum coherences during the system time evolution. Thus, in contrast to the multicomponent DFT approach of Refs.(9)-(11), our theory enables an accurate treatment of dynamical phenomena induced by nonadiabatic transitions during electron-nuclear dynamics. This formalism also allows for the straightforward construction of semiclassical approximations to the nuclear dynamics, and also separably includes the effects of nonadiabatic couplings, thus allowing for approximations to model nonadiabatic electronic dynamics based on traditional TDDFT. To construct this theory, we map the interacting electronic system into a reference system where electron-electron interactions can be specified according to convenience, coupled to nuclear degrees of freedom whose interactions are retained. Let $H(q, R)$ be the combined Hamiltonian of the system, with $\{R, P\}$ labeling the nuclear coordinates and $\{q\}$ the electronic coordinates:

$$H(q, R) = \frac{P^2}{2M} + H_0(q) + V(q; R, t)$$

(1)

$V(q; R, t)$ is the sum of the time dependent single electron-nuclear potential and the purely nuclear-nuclear interaction in the Hamiltonian. The density matrix, $\hat{\rho}(t)$, of the system evolves according to the Liouville equation:

$$i\hbar \frac{\partial}{\partial t} \hat{\rho}(t) = [H, \hat{\rho}(t)]$$

(2)

A key issue is that a theory for nonadiabatic dynamics should be able to evaluate time dependent properties of electronic dynamics while simultaneously retaining information regarding dynamics in the nuclear subspace. A natural physical variable that contains this information is the single electron, reduced nuclear density matrix which is conjugate to the electron-nuclear potential. This matrix is made up of diagonal contributions from the electronic subspace, corresponding to the electronic probability density, while the nuclear part of the density matrix is fully retained. We derive continuity equations for reduced electron-nuclear density and current matrices and relate their time evolution directly to the
electron-nuclear potential, $V(q; R, t)$. A suitable and physically transparent method to derive the continuity equations is obtained from analyzing partial Wigner transforms of the density matrix in the nuclear subspace:

$$\tilde{\rho}(R, P; t) = \int d z \exp \left[ -\frac{i P \cdot z}{\hbar} \right] \langle R + \frac{z}{2}|\rho(t)|R - \frac{z}{2} \rangle \tag{3}$$

The quantum Liouville equation can be written in terms of the partial Wigner transformed density matrix:

$$i\hbar \frac{\partial}{\partial t} \tilde{\rho}(R, P; t) = \left\{ \tilde{H}(R, P), \tilde{\rho}(R, P; t) \right\} \tag{4}$$

The bracket $\left\{ .. \right\}$ is the Wigner-Weyl-Moyal bracket \[13, 14, 15\]. The bracket between two arbitrary operators $A$ and $B$ is defined as:

$$\{ A, B \} = \tilde{A}(R, P) \ast \tilde{B}(R, P) - \tilde{B}(R, P) \ast \tilde{A}(R, P) \tag{5}$$

The Moyal product, '$\ast$', is defined\[14\] as a bilinear product of the Wigner transforms of $\hat{A}$ and $\hat{B}$:

$$\tilde{A}(R, P) \ast \tilde{B}(R, P) = \tilde{A}(R, P) \exp \left[ \frac{\hbar \Lambda}{2i} \right] \tilde{B}(R, P)$$

$$\Lambda(R, P) = \nabla_P \cdot \nabla_R - \nabla_P \cdot \nabla_R \tag{6}$$

The Liouville equation for the partial Wigner transformed density, $\tilde{\rho} \equiv \tilde{\rho}(R, P; t)$, is:

$$i\hbar \frac{\partial \tilde{\rho}}{\partial t} = \left\{ \frac{P^2}{2M} + H_0(q), \tilde{\rho}(t) \right\} + \left\{ \tilde{h}(q; R), \tilde{\rho} \right\} \tag{7}$$

Writing $\Re \equiv \{R, P\}$, single particle electronic variables are defined as traces over $\tilde{\rho}(\Re; t)$:

$$f(x|\Re; t) = Tr_{el} \left\{ \hat{f}(x)\tilde{\rho}(t) \right\} : \hat{f} \equiv \{n, \vec{j}\} \tag{8}$$

The current and density operators are:

$$\hat{n}(x) \equiv \frac{1}{N} \sum_{i=1}^{N} \delta(x - \hat{q}_i) \tag{9}$$

$$\hat{\vec{j}}(x) \equiv \frac{1}{2m} \sum_{i=1}^{N} \{\hat{p}_i, \delta(x - \hat{q}_i)\} \tag{10}$$

We also define the quantities:

$$\tilde{\gamma}_e(x|\Re; t) \equiv Tr_{el} \left\{ \left[ \hat{\vec{j}}(x), H_0(q) \right]\tilde{\rho}_W(\Re; t) \right\}$$

$$i\hat{L}[v](\Re; t) \equiv \frac{P}{M} \cdot \nabla_R + \frac{i}{\hbar} \{v(x; R, t), \} \tag{11}$$
From these definitions, the equation of motion for the single electron density and current are obtained:

\[
\begin{align*}
\left[ \partial_t + i\hat{L}[v](\mathcal{R}, t) \right] n(x|\mathcal{R}, t) &= -\nabla_x \cdot \vec{j}(x|\mathcal{R}, t) \\
\left[ \partial_t + i\hat{L}[v](\mathcal{R}, t) \right] \vec{j}(x|\mathcal{R}, t) &= -\gamma_v(x|\mathcal{R}, t) - \frac{1}{m} \nabla_x v(x; \mathcal{R}, t) * n(x|\mathcal{R}, t)
\end{align*}
\] (12) (13)

In the adiabatic limit, Eqs.(12) and (13) reduce to the traditional continuity and current equations for a system of interacting electrons in an external time dependent potential. However, Eq.(12) and Eq.(13) are more general and include the effect of electron-nuclear nonadiabatic couplings. This is given by the action of the quantum Liouville operator, \( i\hat{L}[v] \) on the single electron distribution functions, \( \{n, j\} \). If the classical limit is taken for the nuclei alone, then the time evolution of the electron density has two contributions, one corresponding to the usual continuity equation in the electronic subspace, and the second from the time evolution of a classical nuclear subspace off which electrons can scatter. A satisfactory reference system would need to reproduce correctly the electronic density \( n(x|\mathcal{R}, t) \). We show that the single electron density matrix and its corresponding current density matrix can be reproduced by several hamiltonians which differ from the original hamiltonian in the strength of their electron-electron correlation, through the construction of an appropriate single electron-nuclear interaction for each such hamiltonian.

**Statement**—Let \( H(q; \mathcal{R}) \) be a Hamiltonian with a single particle electron-nuclear coupling and a electron-electron interaction potential given by the pair \( \{v(x; \mathcal{R}, t), V_{ee}(r)\} \). Given an initial value, \( \{n(x|\mathcal{R}, 0), \vec{j}(x|\mathcal{R}, 0)\} \), and a pair of solutions, \( \{n(x|\mathcal{R}, t), \vec{j}(x|\mathcal{R}, t)\} \) to the current and continuity equations, Eqs.(12) and (13), a second Hamiltonian \( H' \) with an arbitrarily specified electron-electron interaction, \( W_{ee}(r) \), can be constructed to reproduce the solutions, \( \{n(x|\mathcal{R}, t), \vec{j}(x|\mathcal{R}, t)\} \) by modifying its single electron-nuclear potential, \( w(r|\mathcal{R}; t) \).

**Proof**—We present a heuristic and constructive derivation. Assume that there exists a Hamiltonian, \( H' \) with a pair of interactions, \( \{w(x; \mathcal{R}), W_{ee}(q)\} \) from which the single particle density \( n(x|\mathcal{R}; t) \), and current, \( \vec{j}(x|\mathcal{R}; t) \) can be derived. We will show that for an arbitrary two particle electron-electron interaction, \( W_{ee} \), a single particle electron-nuclear coupling \( w \) can be constructed that reproduces the given electron density. By assumption, Eq.(12) and Eq.(13) are satisfied for both the Hamiltonians, \( H(q; \mathcal{R}) \) and \( H'(q; \mathcal{R}) \). For notational convenience, we define \( \zeta(x|\mathcal{R}; t) \equiv v(x|\mathcal{R}; t) - w(x|\mathcal{R}; t) \) and \( \gamma_{vw} = \gamma_v - \gamma_w \). Then
by a process of subtraction, we find that the single particle current and density satisfy:

\[
\vec{\gamma}_{wv}(x|R; t) = \frac{\nabla_x \zeta}{m} \ast n(x|R; t) + \frac{i}{\hbar} \{ \zeta, \vec{j}(x|R; t) \}
\]

(14)

\[
\{ \zeta(x|R; t), n(x|R; t) \} = 0
\]

(15)

Two operators \( A, B \) star commute, i.e the equation, \( A \ast B = B \ast A = 0 \) is satisfied when \( A \) is of the form, \( A = g(x, t) \); or \( A = F(B, \ast) \), where \( F(B, \ast) \) is a function generated from Moyal star product polynomials in \( B \), i.e. \( A = \sum_k g_k(x, t) B \ast B \ast B \ldots k \) times. In addition to these solutions, other functions could exist whose star product commutator with \( B \) is zero. Thus, the solutions to Eq.(15) can be written in the form:

\[
\zeta(x|R; t) = \zeta[x, t; n(x|R; t), \Omega(R; t)]
\]

(16)

Here, \( \Omega(t) \) contains the set of functions which star commute with \( n \), and which cannot be generated from the single particle density \( n \). In analogy with quantum mechanical language, we can say that the set of functions, \( n, \Omega \) form a complete set of commuting variables. To understand the solutions to Eq.(14), we first study it in the approximation where the classical limit is taken for the nuclear variables. In this limit Eq.(14) becomes:

\[
\frac{1}{m} n \nabla_x \zeta + \left\{ \zeta(x|R; t), \vec{j}(x|R; t) \right\}_{PB} = \vec{\gamma}_{wv}(x|R; t)
\]

(17)

Here the bracket, \( \{..\}_{PB} \equiv \nabla_R \cdot \nabla_P - \nabla_P \cdot \nabla_R \) is the classical Poisson bracket defined over the nuclear subspace. Physically, the first term of Eq.(17) is the electronic force due to the change in the single particle potential, while the second term is the nonadiabatic coupling contributions that are a result of varying the electron-nuclear coupling. These two terms add to balance the force contributions due to purely electron-electron correlations. In the absence of the nonadiabatic coupling between electrons and nuclei, the equation reduces to the force acting on the electrons due to the difference in single particle potentials, which exactly compensates for the difference in electron-electron interactions, as in traditional TDDFT. The nonadiabatic coupling adds a new contribution corresponding to exchange of energy between electronic and nuclear degrees of freedom.

We show below that if appropriate spatial boundary conditions are specified, Eq.(14) can be solved in the mixed quantum classical limit (Eq.(17)) at a given time, \( t = 0 \) and these solutions can be propagated to succeeding timesteps in an iterative fashion. To construct an explicit solution of Eq.(17), we define:

\[
\{ \vec{v}_\alpha, \vec{u}_\alpha \} \equiv \left\{ \nabla_{P_\alpha} \vec{j}, \nabla_{R_\alpha} \vec{j} \right\}; \alpha = x, y, z.
\]

(18)
Eq.(17) can be rewritten as:
\[
\nabla_x[n(x | \mathcal{R}; t)\zeta] + \sum_\alpha \left[ \bar{v}_\alpha \nabla R_\alpha - \bar{u}_\alpha \nabla P_\alpha - \nabla_x n \right] \zeta = \gamma_{\text{wv}}(x | \mathcal{R}; t)
\]
\[(19)\]

We define the operator \( \hat{\Lambda} \) and a normalized potential \( \sigma \) as:
\[
i\Lambda(x|\mathcal{R}; t) = \left[ \sum_\alpha \left[ \bar{v}_\alpha \nabla R_\alpha \frac{1}{n} - \bar{u}_\alpha \nabla P_\alpha \frac{1}{n} \right] - \frac{\nabla_x n}{n} \right]
\]
\[
\sigma(x|\mathcal{R}; t) = n(x|\mathcal{R}; t)\zeta(x|\mathcal{R}; t)
\]
\[(20)\]

We also assume that the ratios \( \nabla \cdot \bar{j}/n \) and \( \nabla \cdot n/n \) vanish as \( x \to \pm \infty \). Eq.(17) becomes:
\[
\nabla_x \sigma + i\hat{\Lambda} \sigma = \gamma_{\text{cl}} \gamma_{\text{wv}}
\]
\[(21)\]

This equation can be solved explicitly as follows: Define the operator, \( \hat{\Gamma} \) such that it satisfies:
\[
\nabla_x \hat{\Gamma} = i\hat{\Lambda}(x|\mathcal{R}; t)
\]
\[(22)\]

Then \( \hat{\Gamma} \) is a path ordered exponential in the electronic subspace given by:
\[
\hat{\Gamma}(x | \mathcal{R}; t) \equiv \int d\mathcal{C} \sum_{y \to x} \mathcal{P} \exp \left[ i \int_{y}^{x} \hat{\Lambda}(z|\mathcal{R}; t) \cdot dz \right]
\]
\[(23)\]

\( \mathcal{P} \exp[..] \) in Eq.(23) is the path ordering exponential operator. The operator \( \hat{\Gamma} \) is a path integral over all paths, \( \mathcal{C} : y \to x \), ending in \( (x, t) \) in the electronic subspace. Since this is a symmetric operator it has an inverse, \( \hat{\Gamma}^{-1} \). As a consequence of the boundary conditions, \( \Gamma \) becomes unity as \( x \to \pm \infty \). Eq.(20) is rewritten as:
\[
\hat{\Gamma}^{-1} \nabla_x \hat{\Gamma} \sigma = \gamma_{\text{cl}} \gamma_{\text{wv}}
\]
\[(24)\]

This can be solved to obtain:
\[
\sigma = \hat{\Gamma}^{-1}(x | \mathcal{R}; t) \int_{\mathcal{C}} \hat{\Gamma}(y | \mathcal{R}; t) \gamma_{\text{cl}} \gamma_{\text{wv}}(y | \mathcal{R}; t) \cdot dy
\]
\[(25)\]

Thus, a formal solution for Eq.(17) has been constructed. By requantizing the classical nuclear variables using the Weyl correspondence, a solution can be generated for the fully quantum dynamics, Eq.(14). The solution also has a transparent physical interpretation. The kernel, \( \Gamma^{-1}(x)\Gamma(y) \) contains the "history" of the interactions between the electronic and nuclear degrees of freedom. In the Born-Oppenheimer limit, the path ordering becomes...
unnecessary and the kernel becomes independent of path. Thus, this kernel builds into the effective potential, electronic scattering and nonadiabatic dynamical phase correlations.

We now describe the time propagation of the solutions to Eq. (14) using a method similar to that developed in Ref. [6]. We require as an initial condition, that the initial density matrix of the system is known. Consequently, the quantity, \( \gamma(x|\mathcal{R}; 0) \) and its time derivatives at \( t = 0 \) can be evaluated from the initial value of the density matrix \( \hat{\rho}_W(\mathcal{R}; 0) \). Furthermore we make the assumption that all the relevant potentials and distribution functions are Taylor expandable around the time \( t = 0 \). The Taylor expansions for such functions \( f(x|\mathcal{R}; t) \) are defined by:

\[
f(x|\mathcal{R}; t) = \sum_{m=0}^{\infty} f^{(m)}(0) \frac{t^m}{m!}
\]

(26)

Using this Taylor expansion, Eq. (14) can be rewritten as a system of linear difference equations:

\[
\gamma^{(k)}(0) = \sum_{l=0}^{k} C_l^k \left[ \frac{1}{m} \nabla_x \zeta^{(l)}(0) \ast n^{(k-l)}(0) + \frac{i}{\hbar} \left\{ \zeta^{(l)}(0), \mathbf{j}^{(k-l)}(0) \right\} \right]
\]

(27)

This equation can be solved iteratively. For \( k = 0 \) and \( k = 1 \), the system of equations become:

\[
\gamma^{(0)}(0) = \frac{1}{m} \nabla \zeta^{(0)}(0) \ast n^{(0)}(0) + \frac{i}{\hbar} \left\{ \zeta^{(0)}, \mathbf{j}^{(0)} \right\}
\]

(28)

\[
\gamma^{(1)}(0) = \frac{1}{m} \nabla \zeta^{(1)}(0) \ast n^{(0)}(0) + \frac{1}{m} \nabla \zeta^{(0)}(0) \ast n^{(1)}(0) + \frac{i}{\hbar} \left\{ \zeta^{(1)}, \mathbf{j}^{(0)} \right\} + \left\{ \zeta^{(0)}, \mathbf{j}^{(1)} \right\}
\]

(29)

Eq. (27) has one unknown, \( \zeta^{(0)} \), and all the other quantities are known, given the assumptions made. It has a unique solution, upto a function of only the nuclear coordinates whose Wigner-Moyal bracket with the current \( \mathbf{j}^{(0)}(0) \) is zero. Furthermore, the second equation also has a solution with similar properties, given \( \zeta^{(0)}(0) \), since it also satisfies an equation of the same mathematical form. This argument can be inductively extended to solve for the \( k \)-th time derivative \( \zeta^{k}(0) \), for an arbitrary value of \( k \). Thus, this method provides a constructive time dependent solution to Eq. (14).

We now consider an important special case. When the electronic dynamics of the system is adiabatic, the timescales on which the electronic dynamics occur are much faster than the timescales for nuclear motion. As a result, the time derivative of the single electron-nuclear
density matrix is dominated by electronic dynamics, and the derivatives w.r.t nuclear degrees of freedom can be neglected. This implies that the continuity and current equations become:

$$\partial_t n(x|\mathcal{R};t) \approx -\nabla_x \vec{j}(x|\mathcal{R};t)$$ (30)
$$\partial_t \vec{j}(x|\mathcal{R};t) \approx -\vec{\gamma}_v(x|\mathcal{R};t) - \frac{1}{m} n(x|\mathcal{R};t) \nabla_x v$$ (31)

Eqs.(30) and (31) are of the same form as the equations obtained for a purely electronic time evolution under an external time varying potential, $v$. The Runge-Gross theorem [5] has been generalized to relate the time evolution of a electron density and current $\{n, \vec{j}\}$ to an external potential for systems that satisfy equations of this form [6]. Thus, in the adiabatic limit, Van Leeuwen’s generalization of the Runge-Gross theorem is obtained from this formalism. In conclusion, we have shown that the Runge-Gross theorem can be generalized to describe the correlated nonadiabatic dynamics of an interacting electron-nuclear system. This theory is very general and allows maximal information about the quantum mechanical nuclear variables to be retained. Numerically tractable DFTs can be constructed from the explicit solutions, Eq.(25), by the application of various semiclassical reduction schemes on the nuclear dynamics. For example, for weakly nonadiabatic mixed quantum classical evolution, the nonadiabatic kernels in Eq.(25) can be evaluated using a Monte Carlo approach with the nonadiabatic derivative operators in Eq. (22) being treated as inducing occasional "nonadiabatic transitions" according to a suitable Monte Carlo criterion. The construction of such functionals will be discussed in a future work. This formalism demonstrates that the density functionals required to correctly approximate electronic nonadiabatic dynamics are nonlocal functionals and depend on derivatives in the nuclear position and momentum variables. The nonlocality is reminiscent of the memory dependence found in standard TDDFT [16]. The effective potentials include quantum mechanical coherence and geometric phase factors that are a consequence of the nonadiabatic coupling between nuclear and electronic degrees of freedom.

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[1] L. J. Butler, Ann. Rev. Phys. Chem. 49, 125 (1998).
[2] A. M. Wodtke, J. C. Tully, and D. J. Auerbach, Int. Rev. Phys. Chem. 23, 513 (2004).
[3] C. A. Mead and D. G. Truhlar, J. Chem. Phys. 70, 2284 (1979).

[4] J. Moody, A. Shapere, and F. Wilczek, Geometric Phases in Physics, Eds. A. Shapere and F. Wilczek (World Scientific, Singapore, 1989).

[5] E. Runge and E. K. U. Gross, Phys. Rev. Lett. 52, 997 (1984).

[6] R. van Leeuwen, Phys. Rev. Lett. 82, 3863 (1999).

[7] K. Burke, R. Car, and R. Gebauer, Phys. Rev. Lett. 94, 146803 (2005).

[8] M. Di Ventra and R. D’Agosta, Phys. Rev. Lett. 98, 226403 (2007).

[9] O. Butriy, H. Ebadi, P. L. de Boeij, R. van Leeuwen, and E. K. U. Gross, Phys. Rev. A. 76, 052514 (2007).

[10] T. Kreibich and E. K. U. Gross, Phys. Rev. Lett. 86, 2984 (2001).

[11] T. Kreibich, R. van Leeuwen, and E. K. U. Gross, Phys. Rev. A. 78, 022501 (2008).

[12] T. C. Li and P. Q. Tong, Phys. Rev. A. 34, 529 (1986).

[13] E. P. Wigner, Phys. Rev. 40, 749 (1932).

[14] J. E. Moyal, Proc. Camb. Phil. Soc. 45, 99 (1949).

[15] H. J. Groenwald, Physica. 12, 405 (1946).

[16] N. T. Maitra, K. Burke, and C. Woodward, Phys. Rev. Lett. 89, 023002 (2002).