Towards a full trajectory-based formulation of Molecular Dynamics
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ABSTRACT
In this work we want to provide an answer to the question if a full quantum trajectory-based description of both fermions and bosons in molecular systems can be achieved, and more importantly, if such a formulation would have any advantage with respect to other well established techniques. Our starting point is the so called conditional wave function, whose definition allows for a rigorous splitting of the many-body Schrödinger equation into a set of coupled single-particle conditional equations [1]. Inspired by previous results in the field of mesoscopic electron transport [2], we extend the conditional wavefunction concept into scenarios where both bosonic and fermionic degrees of freedom are present.

BOHMIAN MECHANICS
Non-relativistic quantum particles obey the Time-dependent Schrödinger equation (TDSE)

\[ i\hbar \frac{\partial \Psi(r, t)}{\partial t} = H\Psi(r, t), \]  

and preserve the quantum local continuity equation

\[ \frac{\partial}{\partial t} |\Psi(r, t)|^2 + \sum_{n=1}^{N} \nabla \cdot j_n(r, t) = 0, \]  

being \( j_n(r, t) = \frac{i\hbar}{2m_n} \left( \Psi^\dagger(r, t) \nabla \Psi - \Psi(r, t) \nabla \Psi^\dagger(r, t) \right) \) the \( n \)-th component of the probability current density. Equation (2) suggests defining the following velocity field

\[ v_n(r, t) = \frac{j_n(r, t)}{|\Psi(r, t)|^2}. \]  

Equation (3) together with the quantum equilibrium hypothesis

\[ R(r, t)^2 = \lim_{M \to \infty} \frac{1}{M} \sum_{j=1}^{M} \delta \left( r - x^{(j)}(t) \right), \]  

(R being the modulus of the wavefunction, i.e. \( \Psi = Re \exp(iS/\hbar) \)) constitutes the minimalist postulates, or equivalently, the Analytic formulation of Bohmian Mechanics (BM).

THE CONDITIONAL WAVEFUNCTION
Any Bohmian trajectory \( r_n(t) \) derived from the solution of the N-particle TDSE in (1), can be alternatively computed through the solution of a single-particle conditional TDSE

\[ i\hbar \frac{\partial \Phi_n(r_n, t)}{\partial t} = \left\{ \frac{\hbar^2}{2m_n} \nabla^2 \Phi_n(r_n, t) - \frac{\hbar^4}{2m_n} \nabla^4 \Phi_n(r_n, t) \right\} \Phi_n(r_n, t). \]  

In (5), \( \Phi_n(r_n, t) = \Psi(r_n(t), r_n(t), t) \) is referred to as the \( n \)-th conditional wavefunction, and \( G_n \) and \( J_n \) read

\[ G_n(r, t) = U_n(r_n, t) + \sum_{k=1, k \neq n}^{N} \left\{ \frac{\nabla \cdot S(r, t)}{2m} + \frac{\hbar^2}{2m_n} \nabla^2 \Phi_n(r_n, t) - \left( \nabla \cdot S(r, t) \right) \cdot v_n(r_n(t), t) \right\}, \]  

\[ J_n(r, t) = \sum_{k=1, k \neq n}^{N} \frac{\hbar}{2m} \left( \nabla^2 \Phi_n^2(r_n, t) \cdot v_n(r_n(t), t) - \nabla \cdot \left( \nabla^2 \Phi_n^2(r_n, t) \cdot v_n(r_n(t), t) \right) \right). \]  

1ST. CONDITIONAL ELECTRONIC & NUCLEAR WAVEFUNCTIONS
Our proposal starts with the split up of the whole molecular wavefunction \( \Psi(r, t) \) into conditional electronic, \( \Phi_e(x, t) \), and nuclear, \( \Phi_n(x, t) \), components, obeying respectively the following conditional TDSEs:

\[ i\hbar \frac{\partial \Phi_e(x, t)}{\partial t} = \left\{ \frac{\hbar^2}{2m_e} \nabla^2 \Phi_e(x, t) - \frac{\hbar^4}{2m_e} \nabla^4 \Phi_e(x, t) \right\} \Phi_e(x, t), \]  

\[ i\hbar \frac{\partial \Phi_n(x, t)}{\partial t} = \left\{ \frac{\hbar^2}{2m_n} \nabla^2 \Phi_n(x, t) - \frac{\hbar^4}{2m_n} \nabla^4 \Phi_n(x, t) \right\} \Phi_n(x, t). \]  

In (7), \( r = (x, X) \), and \( x \) and \( X \) are respectively the electronic (with spin) and nuclear (spinless) coordinates. Equations (7) are accurate whenever \( G \) and \( J \) can be approximated to zero order Taylor series. The electronic and nuclear wavefunctions then read \( \Phi_e(x, t) \approx \Phi_e(x(t), t) \cdot \Phi_e(x(t), t) \) and \( \Phi_n(X, t) \approx \Phi_n(x(t), t) \cdot \Phi_n(x(t), t) \).

2ND. SPLITTING UP THE NUCLEAR WAVEFUNCTION
A SIMPLIFIED TEST: TWO-BODY SYSTEM
Approximating \( G \) and \( J \) to zero order Taylor series, the nuclear wavefunction can be further split up into single-nuclei conditional wave functions, \( \Phi_{n}^{a}(X_{a}, t) \), obeying single-particle TDSEs

\[ i\hbar \frac{\partial \Phi_{n}(X_{a}, t)}{\partial t} = \left\{ \frac{\hbar^2}{2m_{a}} \nabla^2 \Phi_{n}(X_{a}, t) - \frac{\hbar^4}{2m_{a}} \nabla^4 \Phi_{n}(X_{a}, t) \right\} \Phi_{n}(X_{a}, t), \]  

being

\[ \Phi_{n}^{a}(X_{a}, t) \approx \Phi_{n}^{a}(X_{a}, t) \cdot \prod_{k=1, k \neq a}^{N} \Phi_{n}^{a}(X_{a}, t), \]  

Again, \( G(t) \) and \( J(t) \) only introduce a global phase factor in each single-nuclei wavefunction.

3RD. SPLITTING UP THE ELECTRONIC WAVEFUNCTION
The next step in the process is to consider the electronic wave function \( \Phi_{e}(x, t) \) as a superposition of single-electron wave functions, \( \Phi_{e}^{a}(x, t) \), that obey the single-particle TDSE:

\[ i\hbar \frac{\partial \Phi_{e}^{a}(x, t)}{\partial t} = \left\{ \frac{\hbar^2}{2m_{e}} \nabla^2 \Phi_{e}^{a}(x, t) - \frac{\hbar^4}{2m_{e}} \nabla^4 \Phi_{e}^{a}(x, t) \right\} \Phi_{e}^{a}(x, t), \]  

The second step in (9) refers to the degree of freedom we are solving, the second one, \( p(t) \), refers to the initial wave function we are considering. The whole electronic wave function, \( \Phi_{e}(x, t) \), can be finally written in terms of \( N_{e} \) conditional wave functions as

\[ \Phi_{e}(x, t) \approx \frac{1}{N_{e}} \sum_{a=1}^{N_{e}} \left( \Phi_{e}^{a}(x, t) \right) \prod_{k=1, k \neq a}^{N_{e}} \Phi_{e}^{a}(x, t) \cdot s(p(t)). \]  

OUTLOOK & FUTURE WORK
The exact separation of a ND Schrödinger equation into N 1D equations comes at the price of introducing two unknown effective potentials, \( G \) and \( J \). Its approximation to lowest order allows us to preserve antisymmetry and a quantitative agreement for two-body system dynamics.

The many-body exponential barrier is still present in equation (12). In order to avoid the computation of huge Slater determinants, we need to seek better guesses for \( G \) and \( J \).

REFERENCES