

# 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)

$$i\hbar \frac{\partial \Psi(\mathbf{r}, t)}{\partial t} = \hat{H} \Psi(\mathbf{r}, t), \quad (1)$$

and preserve the quantum local continuity equation

$$\frac{\partial}{\partial t} |\Psi(\mathbf{r}, t)|^2 + \sum_{a=1}^N \nabla_a \cdot \mathbf{j}_a(\mathbf{r}, t) = 0, \quad (2)$$

being  $\mathbf{j}_a(\mathbf{r}, t) = i\hbar/2m_a(\Psi \nabla_a \Psi^* - \Psi^* \nabla_a \Psi)$  the  $a$ -th component of the probability current density. Equation (2) suggests defining the following velocity field

$$\mathbf{v}_a(\mathbf{r}, t) = \frac{\mathbf{j}_a(\mathbf{r}, t)}{|\Psi(\mathbf{r}, t)|^2}. \quad (3)$$

Equation (3) together with the quantum equilibrium hypothesis

$$R(\mathbf{r}, t_0)^2 = \lim_{M \rightarrow \infty} \frac{1}{M} \sum_{j=1}^M \prod_{a=1}^N \delta(\mathbf{r}_a - \mathbf{x}_a^j[t_0]), \quad (4)$$

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

## THE CONDITIONAL WAVEFUNCTION

Any Bohmian trajectory  $\mathbf{r}_a[t]$  derived from the solution of the  $N$ -particle TDSE in (1), can be alternatively computed through the solution of a single-particle conditional TDSE

$$i\hbar \frac{\partial \Phi_a(\mathbf{r}_a, t)}{\partial t} = \{\hat{T}_a + U_a(\mathbf{r}_a, \mathbf{r}_b[t], t) + G_a(\mathbf{r}_a, \mathbf{r}_b[t], t) + iJ_a(\mathbf{r}_a, \mathbf{r}_b[t], t)\} \Phi_a(\mathbf{r}_a, t). \quad (5)$$

In (5),  $\Phi_a(\mathbf{r}_a, t) = \Psi(\mathbf{r}_a, \mathbf{r}_b[t], t)$  is referred to as the  $a$ -th conditional wavefunction, and  $G_a$  and  $J_a$  read

$$G_a(\mathbf{r}, t) = U_b(\mathbf{r}_b, t) + \sum_{k=1, k \neq a}^N \left\{ \frac{(\nabla_k S(\mathbf{r}, t))^2}{2m_k} - \frac{\hbar^2}{2m_k} \frac{\nabla_k^2 R(\mathbf{r}, t)}{R(\mathbf{r}, t)} - (\nabla_k S(\mathbf{r}, t)) \cdot \mathbf{v}_k(\mathbf{r}[t], t) \right\}, \quad (6a)$$

$$J_a(\mathbf{r}, t) = \sum_{k=1, k \neq a}^N \frac{\hbar}{2R^2(\mathbf{r}, t)} \left\{ \nabla_k R^2(\mathbf{r}, t) \cdot \mathbf{v}_k(\mathbf{r}[t], t) - \nabla_k (R^2(\mathbf{r}, t) \cdot \mathbf{v}(\mathbf{r}, t)) \right\}. \quad (6b)$$

## 1ST. CONDITIONAL ELECTRONIC & NUCLEAR WAVEFUNCTIONS

Our proposal starts with the split up of the whole molecular wavefunction  $\Psi(\mathbf{r}, t)$  into conditional electronic,  $\tilde{\Phi}_{el}(\mathbf{x}, t)$ , and nuclear,  $\tilde{\Phi}_{nu}(\mathbf{X}, t)$ , components, obeying respectively the following conditional TDSEs:

$$i\hbar \frac{\partial \tilde{\Phi}_{el}(\mathbf{x}, t)}{\partial t} = \{\hat{T}_{el} + V_{el-el}(\mathbf{x}) + V_{el-nu}(\mathbf{x}, \mathbf{X}[t])\} \tilde{\Phi}_{el}(\mathbf{x}, t), \quad (7a)$$

$$i\hbar \frac{\partial \tilde{\Phi}_{nu}(\mathbf{X}, t)}{\partial t} = \{\hat{T}_{nu} + V_{nu-nu}(\mathbf{X}) + V_{el-nu}(\mathbf{x}[t], \mathbf{X})\} \tilde{\Phi}_{nu}(\mathbf{X}, t). \quad (7b)$$

In (7),  $\mathbf{r} = \{\mathbf{x}, \mathbf{X}\}$ , and  $\mathbf{x}$  and  $\mathbf{X}$  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  $\Phi_{el}(\mathbf{x}, t) \approx \tilde{\Phi}_{el}(\mathbf{x}, t) \cdot \tilde{\Phi}_{nu}(\mathbf{X}[t], t)$  and  $\Phi_{nu}(\mathbf{X}, t) \approx \tilde{\Phi}_{nu}(\mathbf{X}, t) \cdot \tilde{\Phi}_{el}(\mathbf{x}[t], t)$ .

## 2ND. SPLITTING UP THE NUCLEAR WAVEFUNCTION

Approximating  $G$  and  $J$  to zero order Taylor series, the nuclear wavefunction can be further split up into  $N_{nu}$  conditional wave functions,  $\Phi_a^{nu}(\mathbf{X}_a, t)$ , obeying single-particle TDSEs:

$$i\hbar \frac{\partial \tilde{\Phi}_a^{nu}}{\partial t} = \{\hat{T}_a(\mathbf{P}_a) + V_{nu-nu}(\mathbf{X}_a, \mathbf{X}_b[t]) + V_{el-nu}(\mathbf{x}[t], \mathbf{X}_a)\} \tilde{\Phi}_a^{nu}, \quad (8)$$

being

$$\Phi_a^{nu}(\mathbf{X}_a, t) \approx \tilde{\Phi}_a^{nu}(\mathbf{X}_a, t) \cdot \prod_{k=1, k \neq a}^{N_{nu}} \tilde{\Phi}_k^{nu}(\mathbf{X}_k[t], t), \quad (9)$$

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

## 3RD. SPLITTING UP THE ELECTRONIC WAVEFUNCTION

Now, the modulus of the wave function tends to zero,  $R(\mathbf{x}_a, \mathbf{x}_b[t], t) \rightarrow 0$ , every position where  $\mathbf{x}_a \rightarrow \mathbf{x}_k[t]$ , i.e.  $G_a(\mathbf{x}_a, \mathbf{x}_b[t], t)$  and  $J_a(\mathbf{x}_a, \mathbf{x}_b[t], t)$  have asymptotes at  $\mathbf{x}_a \rightarrow \mathbf{x}_k[t]$ . So, in principle we should estimate  $G$  and  $J$  at least beyond its zero order value. However, by the linearity of the TDSE, we can write  $\Phi_{el}(\mathbf{x}, t)$  at any time as a Slater determinant:

$$\Phi_{el}(\mathbf{x}, t) = \frac{1}{N_{el}!} \sum_{l=1}^{N_{el}!} \Phi_{p(l)}^{el}(\mathbf{x}_{p(l)}, t) \cdot s(\mathbf{p}(l)). \quad (10)$$

Thus, since each wave function  $\Phi_{p(l)}^{el}(\mathbf{x}_{p(l)}, t)$  does not contain any symmetry information, it can be computed by following the previous algorithm (approximating  $G$  and  $J$  to zero order), i.e.

$$i\hbar \frac{\partial \tilde{\Phi}_{a,p(l)a}^{el}}{\partial t} = \{\hat{T}_a + V_{el-el}(\mathbf{x}_a, \mathbf{x}_b[p(l), t]) + V_{el-nu}(\mathbf{x}_a, \mathbf{X}[t], t)\} \tilde{\Phi}_{a,p(l)a}^{el}. \quad (11)$$

The first subindex  $a$  in (11) refers to the degree of freedom we are solving, the second one,  $p(l)_a$ , refers to the initial wave function we are considering. The whole electronic wave function,  $\Phi_{el}(\mathbf{x}, t)$ , can be finally written in terms of  $N_{el}$  conditional wave functions as

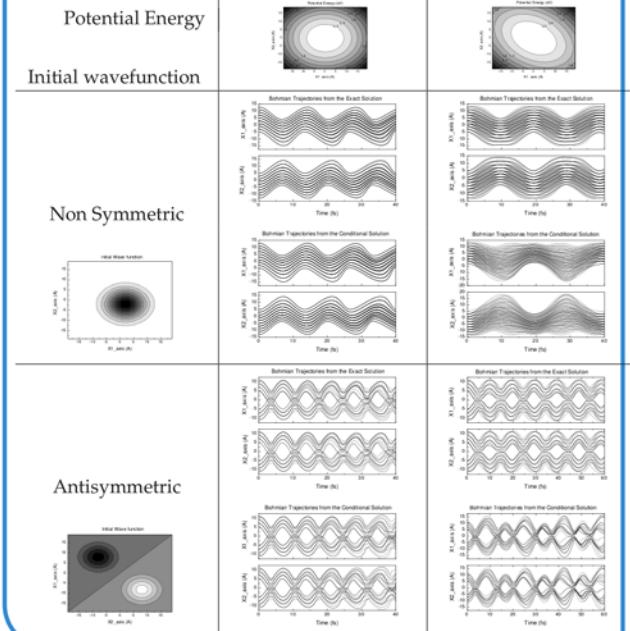
$$\Phi_a^{el}(\mathbf{x}_a, t) \approx \frac{1}{N_{el}!} \sum_{l=1}^{N_{el}!} \left\{ \tilde{\Phi}_{a,p(l)a}^{el}(\mathbf{x}_a, t) \prod_{k=1, k \neq a}^{N_{el}} \tilde{\Phi}_{k,p(l)k}^{el}(\mathbf{x}_k[t], t) \right\} \cdot s(\mathbf{p}(l)). \quad (12)$$

It is worth noticing that phases in (12) are no longer global so they cannot be disregarded.

## REFERENCES

[1] X. Oriols, Phys. Rev. Lett. 98, 066803 (2007). [2] G. Albareda et al. Phys. Rev. B 79, 075315 (2009).

## A SIMPLE TEST: TWO-BODY SYSTEM



## 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,  $G$  &  $J$ . 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  $G$  &  $J$ .