

A CONDITIONAL WAVE FUNCTION APPROACH TO REACTIVE SCATTERING

Efrem Bernuz¹, Josep Maria Bofill^{1,2}, Francesc Illas^{2,3}, and Guillermo Albareda^{2,3}

¹ Inorganic and Organic Chemistry Department, University of Barcelona, Barcelona 08028, Spain

² Institute of Theoretical and Computational Chemistry, University of Barcelona, Barcelona 08028, Spain

³ Materials Science and Physycal Chemistry Department, University of Barcelona, Barcelona 08028, Spain



UNIVERSITAT DE
BARCELONA



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Institut de Química Teòrica
i Computacional



ABSTRACT

Recently, a new theoretical approach to solve adiabatic quantum molecular dynamics was presented.¹ It has been shown that the evolution of a N-body nuclear wave function moving on a 3N-dimensional Born-Oppenheimer potential-energy hyper-surface can be rewritten in terms of single-nuclei wave functions evolving nonunitarily on 3-dimensional potential-energy surfaces that depend parametrically on the configuration of an ensemble formed by defined trajectories.²

In Ref. [2], Albareda et al. already showed the advantages of the method for a model porphine. We here further explore the possibilities of the method by applying it to a reactive scattering problem, viz., we study the proton transfer in chlorine methane by means of a 2-dimensional model Hamiltonian.

1. Conditional Born-Oppenheimer Dynamics

Starting from the full electron-nuclear wave function $\Psi(\mathbf{R}, \mathbf{r}, t)$ which must satisfy the time-dependent Schrödinger equation (TDSE), we consider the Born-Huang expansion,

$$\Psi(\mathbf{R}, \mathbf{r}, t) = \sum_{\mu=1}^{\infty} \varphi_{\mathbf{R}}^{\mu}(\mathbf{r}) \chi^{\mu}(\mathbf{R}, t)$$

where we separate the full Schrödinger equation into an electronic $\varphi_{\mathbf{R}}$ and a nuclear part χ for each μ electronic state. Then we include the expression in the TDSE,

$$i\partial_t \chi^{\mu}(\mathbf{R}, t) = (T_n + \text{PES}^{\mu}(\mathbf{R})) \chi^{\mu}(\mathbf{R}, t) + \sum_{\nu=1}^{\infty} C_{\mu\nu}(\mathbf{R}) \chi^{\nu}(\mathbf{R}, t)$$

The Born-Oppenheimer (BO) approximation neglects the coupling terms ($C_{\mu\nu}$), so for a 2-dimensional model, where we only consider the ground state, the derivation of the equation with the conditional wave function (CWF) method is,

$$i\partial_t \chi_{\alpha}^{\text{gr}}(R_1, t) = (T_{R_1}^{\alpha} + \text{PES}^{\text{gr}}(R_1; R_2^{\alpha})) \chi_{\alpha}^{\text{gr}}(R_1, t) + \frac{T_{R_2}^{\alpha} \Psi(R_1, R_2, t)}{\Psi(R_1, R_2, t)} \Big|_{R_1^{\alpha}} + i\nabla_{R_2}^{\alpha} \Psi(R_1, R_2, t) \Big|_{R_1^{\alpha}} R_2^{\alpha}$$

However, this exact model becomes a quasi-on-the-fly dynamics.

3. Conditional BO dynamics with quantum trajectories

In our study, we compare the exact TDSE with the CWF approach, to do so we analyse the reduced density and the reactivity of the system. Trajectories follow the equation,

$$v(R_1, R_2) = \frac{1}{M} \text{Im}(\nabla_{\mathbf{R}} \Psi / \Psi)$$

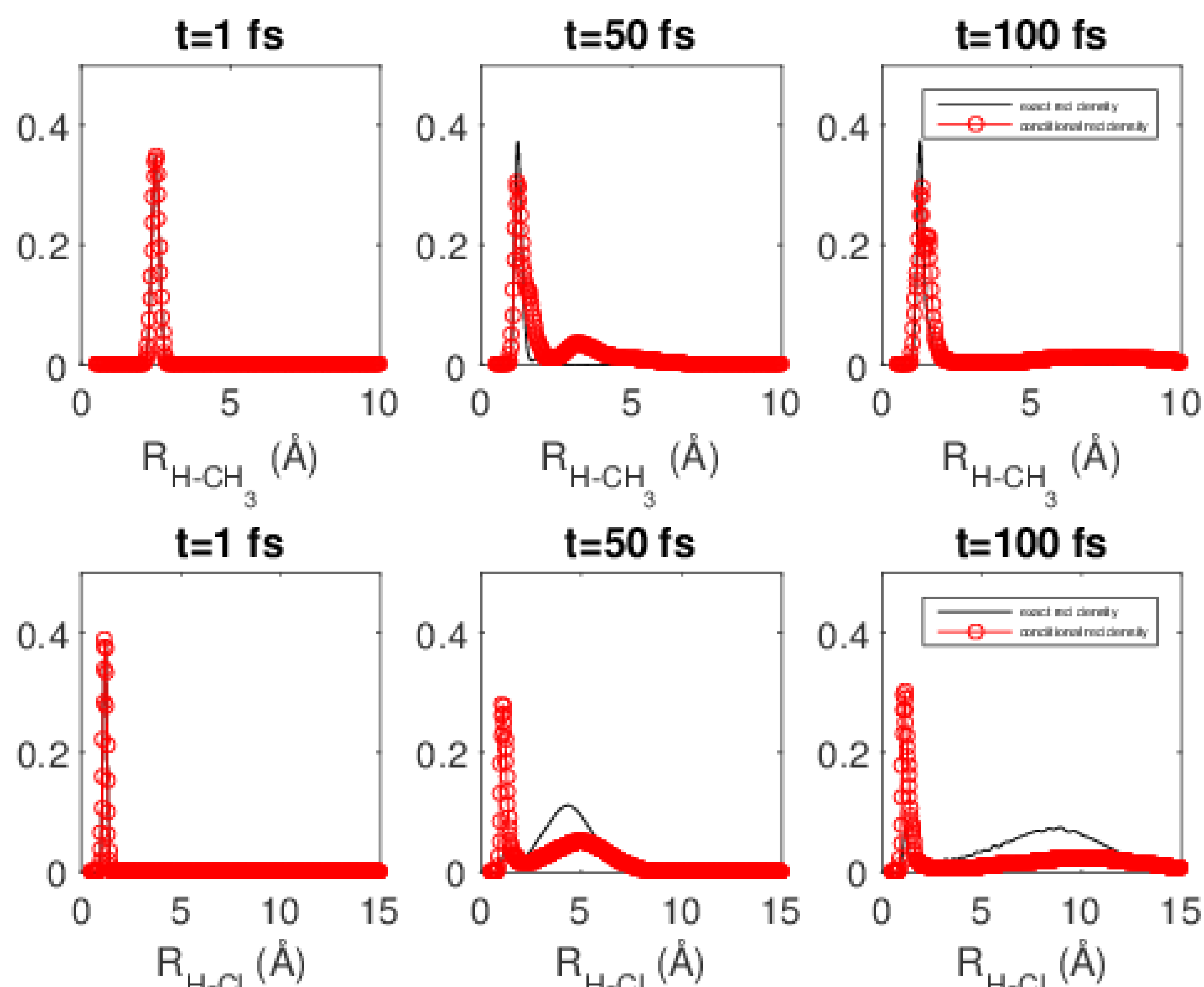


Figure 2. Exact (black) and conditional(red) reduced density for the two dimensions analyzed.

The reactivity of the system,

	Reactive	Non reactive
Exact Solution	95%	5%
Conditional model	62%	38%

6. ACKNOWLEDGMENTS

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2. Potential Energy Surface

We use the potential energy surface (PES) of the chlorine methane proton transfer that was studied by Troya et al.³

$$V(R_{\text{HCl}}, R_{\text{H}(\text{CH}_3)}, R_{\text{Cl}(\text{CH}_3)}) = V_{\text{HCl}}^{(2)}(R_{\text{HCl}}) + V_{\text{H}(\text{CH}_3)}^{(2)}(R_{\text{H}(\text{CH}_3)}) + V_{\text{Cl}(\text{CH}_3)}^{(2)}(R_{\text{Cl}(\text{CH}_3)}) + V_{\text{ClH}(\text{CH}_3)}^{(3)}(R_{\text{HCl}}, R_{\text{CH}_3}, R_{\text{Cl}(\text{CH}_3)})$$

The above expression contains diatomic and triatomic terms.

$$V^{(2)}(\rho) = -D \left(\sum_{n=0}^5 a_n \rho^n \right) \exp(-a_1 \rho)$$

$$V^{(3)}(\rho) = \sum_{i,j,k=0}^{0 \leq i+j+k \leq 3} c_{ijk} \rho_{\text{HCl}}^i \rho_{\text{H}(\text{CH}_3)}^j \rho_{\text{Cl}(\text{CH}_3)}^k * T$$

$$T = \prod_{i=1}^3 [1 - \tanh(Y_i \rho_i / 2)]$$

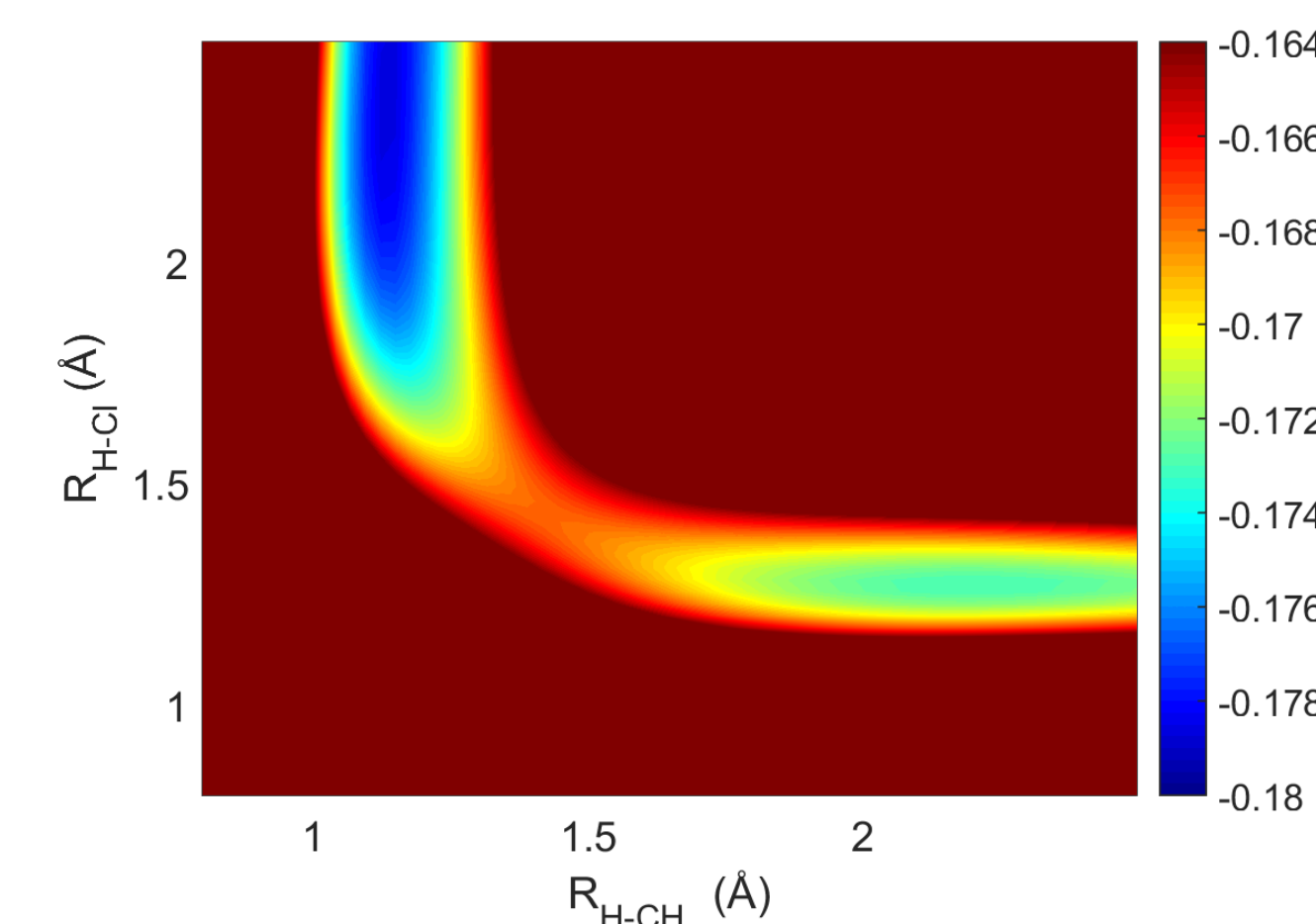


Figure 1. The potential energy surface of the chlorine-methane system

4. Conditional BO dynamics with mixed quantum-classical trajectories

The results in section 3 shows that the approximation of the two-dimensional terms guided the conditional wave function partially incorrect. To improve the conditional approximation we investigate the use of classical trajectories to guide the ensemble of 1-dimensional slices.

$$d_t v(R_1, R_2) = - \frac{\nabla_{R_1} \text{PES}(R_1, R_2)}{M_{R_1}} dt$$

After some test, we find the best results when we use classical trajectories in one degree of freedom and quantum trajectories in the other.⁴

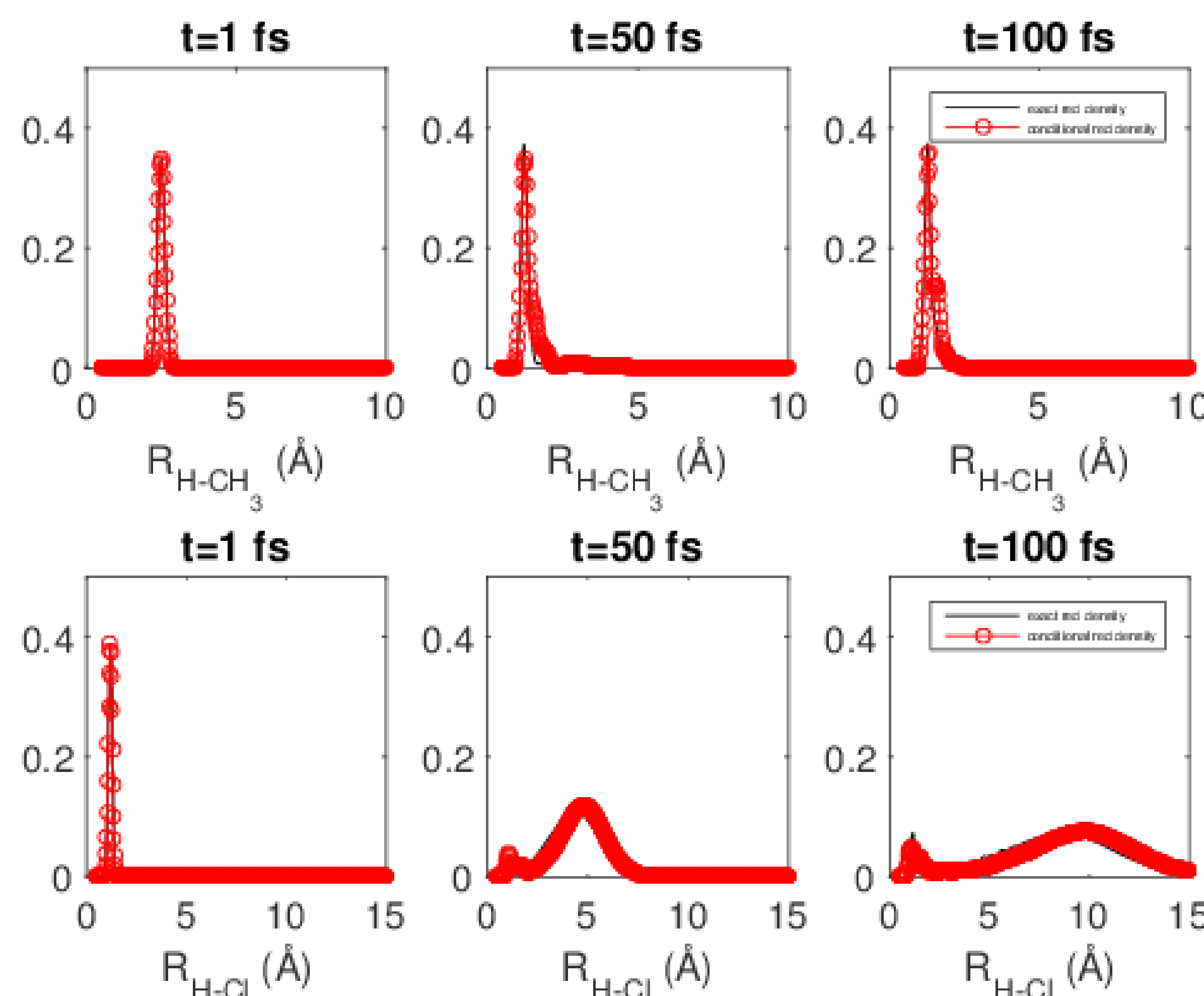


Figure 3. Exact (black) and conditional(red) reduced density with the classical-quantum trajectories.

The reactivity now is almost the same,

	Reactive	Non reactive
Exact Solution	95%	5%
Conditional model	94%	6%

5. CONCLUSIONS

- Due to the approximation of some terms in the exact expression of the CWF model we obtain results a bit far from the exact solution.
- The inclusion of classical trajectories improved the results as we prove analyzing the reduced density and the reactivity of the system.

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