Non-Adiabatic Dynamics with Conditional Wave Functions

Guillermo Albareda[1], Heiko Appel[1], Ignacio Franco[2], Ali Abedi[3], and Angel Rubio[1,4]

[1]Fritz-Haber-Institut der Max-Planck-Gesellschaft - Berlin, Germany; [2]Department of Chemistry, University of Rochester - Rochester, USA; [3]Max-Planck Institut für Mikrostrukturphysik - Halle, Germany; [4]NanoBio Spectroscopy Group and ETSF, UPV - San Sebastián, Spain

MAX-PLANCK-GESELLSCHAFT

Abstract

By projecting the Schrödinger equation on the actual configuration of an infinite set of electronic trajectories, an ensemble of conditional equations of motion for the nuclei is obtained. These equations do not rely on any tracing-out of degrees of freedom and their propagation does not require a prior knowledge of the involved potential-energy surfaces. Using an exact factorization of the full molecular wave function, we establish a formal connection with the recently proposed exact potential energy surfaces. This connection is used to gain insight from a simplified propagation scheme, which is demonstrated to capture non-adiabatic dynamics accurately in the limit of weak nuclear splitting. For pronounced branchings, we show how this simple algorithm partially captures dynamical steps between adiabatic surfaces.

Bohmian Mechanics

The electron-nuclear wave function evolving under a time-dependent external potential obeys the following TDSE

$$i\partial_t \Psi(\underline{\mathbf{r}},\underline{\mathbf{R}},t) = \Big\{\hat{T}_e(\underline{\mathbf{r}}) + \hat{T}_n(\underline{\mathbf{R}}) + \hat{W}(\underline{\mathbf{r}},\underline{\mathbf{R}},t)\Big\}\Psi(\underline{\mathbf{r}},\underline{\mathbf{R}},t). \quad (1)$$

Equation (1) satisfies a continuity equation,

$$\partial_t|\Psi|^2 + \sum_{\xi=1}^{N_e}\nabla_\xi\big(|\Psi|^2\cdot\mathbf{v}^e_\xi\big) + \sum_{\nu=1}^{N_n}\nabla_\nu\big(|\Psi|^2\cdot\mathbf{v}^n_\nu\big) = 0, \quad (2)$$

where $\mathbf{v}^e_\xi(\underline{r},\underline{\mathbf{R}},t) = \mathbf{j}_\xi/|\Psi|^2$ and $\mathbf{v}^n_\nu(\underline{\mathbf{r}},\underline{\mathbf{R}},t) = \mathbf{J}_\nu/|\Psi|^2$, and $\mathbf{j}_\xi(\underline{\mathbf{r}},\underline{\mathbf{R}},t)$ and $\mathbf{J}_\nu(\underline{\mathbf{r}},\underline{\mathbf{R}},t)$ are respectively the $\xi,\nu-$th components of the electronic and nuclear probability current densities.

Sampling the initial wave function, $\Psi(\underline{\mathbf{r}},\underline{\mathbf{R}},t_0)$, according to the *Quantum Equilibrium Hypothesis* [1],

$$|\Psi(t_0)|^2 = \lim_{\Omega\to\infty}\frac{1}{\Omega}\sum_{\alpha=1}^{\Omega}\delta(\underline{\mathbf{r}}-\underline{\mathbf{r}}^\alpha(t_0))\delta(\underline{\mathbf{R}}-\underline{\mathbf{R}}^\alpha(t_0)), \quad (3)$$

guarantees that any observable can be exactly computed, at any time, from the following trajectories:

$$\mathbf{r}^\alpha_\xi(t) = \mathbf{r}^\alpha_\xi(t_0) + \int_{t_0}^t \mathbf{v}^e_\xi(\underline{\mathbf{r}}^\alpha(t'),\underline{\mathbf{R}}^\alpha(t'),t')dt', \quad (4)$$

$$\mathbf{R}^\alpha_\nu(t) = \mathbf{R}^\alpha_\nu(t_0) + \int_{t_0}^t \mathbf{v}^n_\nu(\underline{\mathbf{r}}^\alpha(t'),\underline{\mathbf{R}}^\alpha(t'),t')dt'. \quad (5)$$

The Conditional Wave Function

Theorem.— Any nulcear trajectory, $\mathbf{R}^\alpha_\nu$, can be equivalently obtained from the following *non-unitary conditional wave functions*,

$$\psi_n(\underline{\mathbf{R}},t;\underline{\mathbf{r}}^\alpha) = (\hat{P}^\alpha_e\otimes\hat{1})\Psi(\underline{\mathbf{r}},\underline{\mathbf{R}},t), \quad (6)$$

being $\hat{P}^\alpha_e = |\underline{\mathbf{r}}^\alpha\rangle\langle\underline{\mathbf{r}}^\alpha|$ projectors acting on the electronic subspace and fulfilling an overall unitary condition, $\sum_{\alpha=1}^{\infty}\hat{P}^\alpha_e = \hat{1}$. The wave functions in (6) evolve *non-unitarily* obeying:

$$id_t\psi_n(\underline{\mathbf{R}},t;\underline{\mathbf{r}}^\alpha) = \Big\{\hat{T}_n + \hat{W}(\underline{\mathbf{r}}^\alpha,\underline{\mathbf{R}},t)\Big\}\psi_n(\underline{\mathbf{R}},t;\underline{\mathbf{r}}^\alpha) + \hat{T}_e\Psi(\underline{\mathbf{r}},\underline{\mathbf{R}},t)\Big|_{\underline{\mathbf{r}}^\alpha} + i\sum_{\xi=1}^{N_e}\nabla_\xi\Psi(\underline{\mathbf{r}},\underline{\mathbf{R}},t)\Big|_{\underline{\mathbf{r}}^\alpha}\cdot\dot{\mathbf{r}}^\alpha_\xi. \quad (7)$$

Notice that the above decomposition can be subsequently used to split up equation (7) into single-particle conditional wave functions of the same species $\psi_{n,\nu}(\mathbf{R}_\nu,t;\underline{\mathbf{r}}^\alpha,\underline{\mathbf{R}}^\alpha_{-\nu})$ [2,3].

Connection with the exact TDPES

Corollary.— Factorizing the full wave function as $\Psi(\underline{\mathbf{r}},\underline{\mathbf{R}},t) = \Phi_{\underline{\mathbf{R}}}(\underline{\mathbf{r}},t)\chi(\underline{\mathbf{R}},t)$, the exact solution of (7) can be rewritten in terms of *unitary electronic and nuclear wave functions*, $\Phi_{\underline{\mathbf{R}}^\alpha}(\underline{\mathbf{r}},t)$ and $\chi(\underline{\mathbf{R}},t)$, obeying

$$id_t\Phi_{\underline{\mathbf{R}}^\alpha}(\underline{\mathbf{r}},t) = \Bigg\{\hat{T}_e + \hat{W}(\underline{\mathbf{r}},\underline{\mathbf{R}}^\alpha,t) - i\frac{\partial_t\chi(\underline{\mathbf{R}}^\alpha,t)}{\chi(\underline{\mathbf{R}}^\alpha,t)} + \frac{\hat{T}_n\Psi}{\Psi}\Bigg|_{\underline{\mathbf{R}}^\alpha} + i\sum_{\nu=1}^{N_n}\frac{\nabla_\nu\Phi_{\underline{\mathbf{R}}}}{\Phi_{\underline{\mathbf{R}}}}\Bigg|_{\underline{\mathbf{R}}^\alpha}\cdot\dot{\mathbf{R}}^\alpha_\nu\Bigg\}\Phi_{\underline{\mathbf{R}}^\alpha}(\underline{\mathbf{r}},t), \quad (8)$$

$$i\partial_t\chi(\underline{\mathbf{R}},t) = \Bigg\{\sum_{\nu=1}^{N_n}\frac{1}{2M_\nu}\big(-i\nabla_\nu + \mathbf{A}_\nu(\underline{\mathbf{R}},t)\big)^2 + W^n_{ext}(\underline{\mathbf{R}},t) + \epsilon(\underline{\mathbf{R}},t)\Bigg\}\chi(\underline{\mathbf{R}},t), \quad (9)$$

where $\mathbf{A}_\nu(\underline{\mathbf{R}},t)$ and $\epsilon(\underline{\mathbf{R}},t)$ are respectively the time-dependent Berry connections and the exact TD-PES defined in [4]. Notice that $\dot{\mathbf{R}}^\alpha_\nu = \mathbf{v}^n_\nu(\underline{\mathbf{r}}^\alpha,\underline{\mathbf{R}}^\alpha,t)$, and cannot be computed from $\chi(\underline{\mathbf{R}},t)$ alone.

An Hermitian Propagation Scheme

We consider the hermitian limit of (7). We then introduce an auxiliary conditional wave function $\psi_e(\underline{\mathbf{r}},t;\underline{\mathbf{R}}^\alpha) = (\hat{1}\otimes\hat{P}^\alpha_n)\Psi(\underline{\mathbf{r}},\underline{\mathbf{R}},t)$ approximated also to evolve unitarily. We are left with two coupled equations of motion:

$$id_t\psi_n(\underline{\mathbf{R}},t;\underline{\mathbf{r}}^\alpha) = \Big\{\hat{T}_n + \hat{W}(\underline{\mathbf{r}}^\alpha,\underline{\mathbf{R}},t)\Big\}\psi_n(\underline{\mathbf{R}},t;\underline{\mathbf{r}}^\alpha), \quad (10)$$

$$id_t\psi_e(\underline{\mathbf{r}},t;\underline{\mathbf{R}}^\alpha) = \Big\{\hat{T}_e + \hat{W}(\underline{\mathbf{r}},\underline{\mathbf{R}}^\alpha,t)\Big\}\psi_e(\underline{\mathbf{r}},t;\underline{\mathbf{R}}^\alpha), \quad (11)$$

Equations (10) and (11) are formally equivalent to solve an approximated equation of motion for $\tilde{\Phi}_{\underline{\mathbf{R}}^\alpha}(\underline{\mathbf{r}},t)$

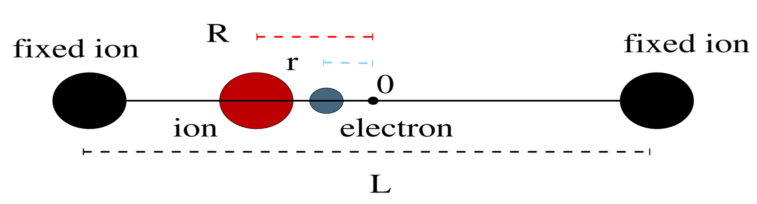
$$id_t\tilde{\Phi}_{\underline{\mathbf{R}}^\alpha} = \Bigg\{\hat{T}_e + \hat{W}(\underline{\mathbf{r}},\underline{\mathbf{R}}^\alpha,t) - i\frac{\partial_t\tilde{\chi}(\underline{\mathbf{R}}^\alpha,t)}{\tilde{\chi}(\underline{\mathbf{R}}^\alpha,t)}\Bigg\}\tilde{\Phi}_{\underline{\mathbf{R}}^\alpha}, \quad (12)$$

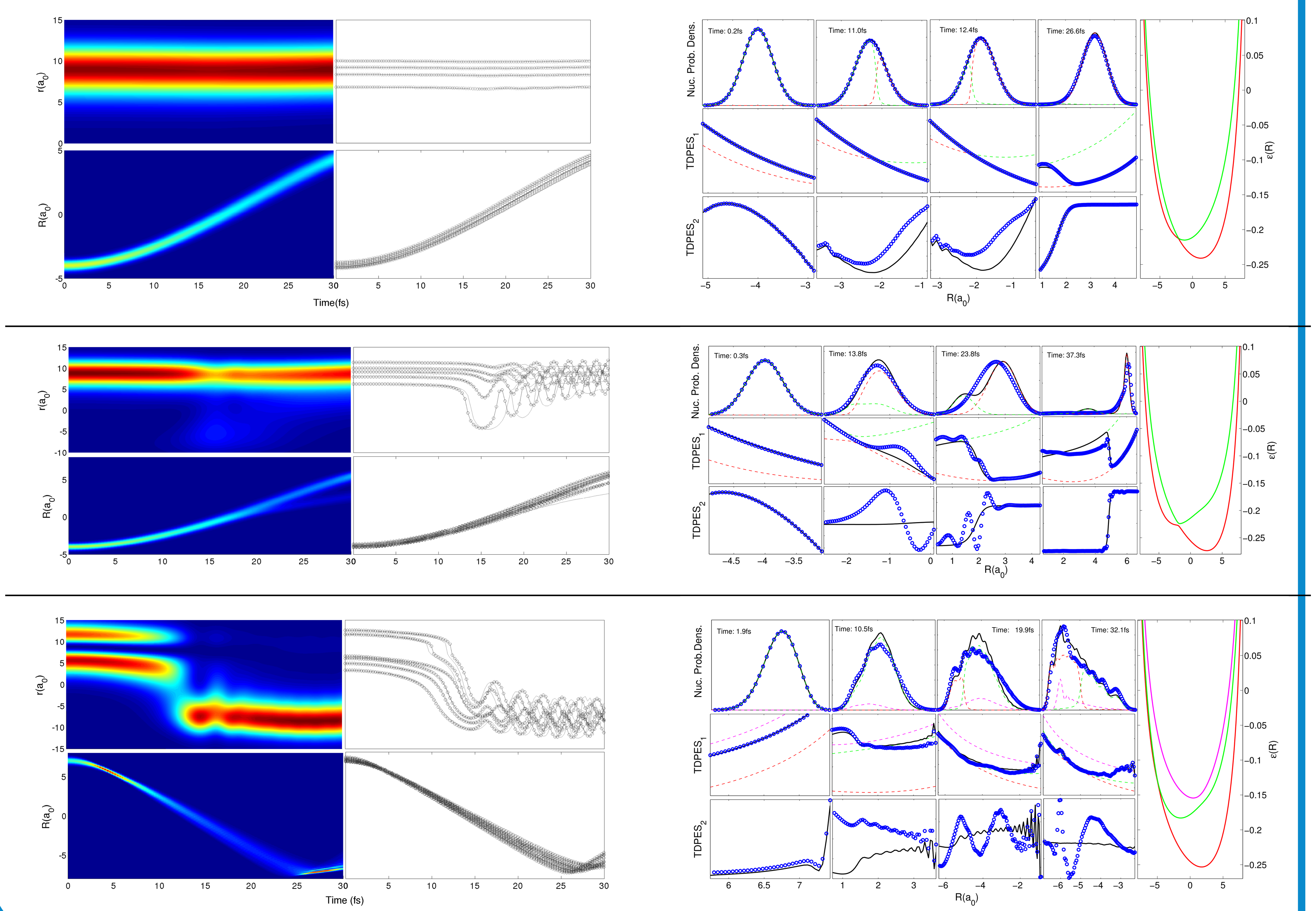
together with an equation of motion for $\tilde{\chi}(\underline{\mathbf{R}},t)$ identical to (9) but with an approximated TDPES, $\tilde{\epsilon}(\underline{\mathbf{R}},t)$, defined as

$$\tilde{\epsilon}(\underline{\mathbf{R}},t) = \epsilon(\underline{\mathbf{R}},t) - \Bigg\langle\hat{T}_e - i\sum_{\xi=1}^{N_e}\frac{\nabla_\xi\tilde{\Phi}_{\underline{\mathbf{R}}}}{\tilde{\Phi}_{\underline{\mathbf{R}}}}\Bigg|_{\underline{\mathbf{r}}^\alpha}\cdot\dot{\mathbf{r}}^\alpha\Bigg\rangle_{\underline{\mathbf{r}}^\alpha}. \quad (13)$$

Test Model: the Shin-Metiu Hamiltonian

$$\hat{W}(r,R) = \frac{1}{|\frac{L}{2}-R|} + \frac{1}{|\frac{L}{2}+R|} - \frac{erf\big(\frac{|R-r|}{R_f}\big)}{|R-r|} - \frac{erf\big(\frac{|r-\frac{L}{2}|}{R_r}\big)}{|r-\frac{L}{2}|} - \frac{erf\big(\frac{|r+\frac{L}{2}|}{R_l}\big)}{|r+\frac{L}{2}|}. \quad (14)$$





Future Work

We are currently trying to improve the algorithm by including some non-hermitian effects into equations (10) and (11). The conditional decomposition used in this work can be, in principle, formulated within any scheme with an underlying continuity equation. In this regard, we have also started to derive a set of conditional equations of motion departing from the time-dependent Kohn-Sham scheme for multi-component systems [6].

References

[1] S. Goldstein, and W. Struyve, J. Stat. Phys. **128**, 1197 (2007). [2] X. Oriols, Phys. Rev. Lett. **98**, 066803 (2007). [3] G. Albareda, J. Suñé, and X. Oriols Phys. Rev. B **79**, 075315 (2009). [4] A. Abedi, N. T. Maitra, and E. K. U. Gross, Phys. Rev. Lett. **105**, 123002 (2010). [5] S. Shin and H. Metiu, J. Chem. Phys. **102**, 9285 (1995). [6] O. Butriy et al., Phys. Rev. A **76**, 052514 (2007).