Nonadiabatic *ab initio* Quantum Dynamics without Potential Energy Surfaces (Supplemental Information)

Guillermo Albareda,[1,2,*] Aaron Kelly,[1,3,†] and Angel Rubio[1,4,‡]

[1] *Max Planck Institute for the Structure and Dynamics of Matter and Center for Free-Electron Laser Science, Luruper Chaussee 149, 22761 Hamburg, Germany*

[2] *Institute of Theoretical and Computational Chemistry, University of Barcelona, Martí i Franquès 1-11, 08028 Barcelona, Spain*

[3] *Department of Chemistry, Dalhousie University, Halifax, Canada B3H 4R2*

[4] *Center for Computational Quantum Physics (CCQ), Flatiron Institute, 162 Fifth avenue, New York NY 10010*

(Dated: February 6, 2019)

Appendix A: Simulation Details

In the flowchart of Fig. A we give a schematic description of the steps to be performed to implement the ICWF algorithm, namely:

1. Sample initial positions, $\{\mathbf{r}^\alpha(0), \mathbf{R}^\alpha(0)\}$, from the initial probability density $|\Psi(\mathbf{r}, \mathbf{R}, 0)|^2$ for each of the M trajectories. This can be done, e.g., by using an importance sampling technique. Here, we chose the initial trajectory positions to be (stochastically) Monte Carlo-sampled from $|\Psi(\mathbf{r}, \mathbf{R}, 0)|^2$.
2. Use the M positions $\{\mathbf{r}^\alpha(0), \mathbf{R}^\alpha(0)\}$ to evaluate the $2M$ conditional wavefunctions, $\{\psi_1^\alpha(\mathbf{r}, 0), \psi_2^\alpha(\mathbf{R}, 0)\}$, as prescribed in Eqs. (3) and (4). The coefficients $\mathbf{C}(0)$ at the initial time can be found by inverting the equation $\sum_\alpha C^\alpha(0)\psi_1^\alpha(\mathbf{r}, 0)\psi_2^\alpha(\mathbf{R}, 0) = \Psi(\mathbf{r}, \mathbf{R}, 0)$. The initial velocity fields $\{\dot{\mathbf{r}}^\alpha(0), \dot{\mathbf{R}}^\alpha(0)\}$ can be then evaluated according to Eqs. (10) and (11).
3. Propagate the Hermitian CWF equations of motion according to Eqs. (5) and (6) by simply neglecting the complex potentials $\eta_1^\alpha(\mathbf{r}, t)$ and $\eta_2^\alpha(\mathbf{R}, t)$.
4. Solve the equation of motion for the coefficients $\mathbf{C}(t)$ using Eq. (8) together with the definitions in Eq. (9).
5. Evaluate the velocity fields using Eqs. (10) and (11), and then propagate the M trajectories $\{\mathbf{r}^\alpha(t), \mathbf{R}^\alpha(t)\}$.
6. Repeat the procedure starting from point 3. until the end of the simulation.

Step 4. in the implementation is what distinguishes the ICWF approach from independent trajectory methods such as its lowest order version, the HCWF approach. For all CWFs, the time integration has to be performed simultaneously. The parallelization of the algorithm is thus essential for numerical efficiency.

General observables can be written in terms of a CWFs by making use of the Ansatz in Eq. (7). In particular, the performance of the proposed method is assessed by computing the adiabatic populations:

$$P_m(t) = \int d\mathbf{R} |\chi^{(m)}(\mathbf{R}, t)|^2 = \int d\mathbf{R} \left| \sum_\alpha^M C_\alpha \psi_2^\alpha \int d\mathbf{r} \Phi_{\mathbf{R}}^{(m)}(\mathbf{r}) \psi_1^\alpha \right|^2 , \tag{A.1}$$

an indicator of decoherence:

$$D_{nm}(t) = \int d\mathbf{R} |\chi^{(m)}(\mathbf{R}, t)|^2 |\chi^{(n)}(\mathbf{R}, t)|^2 = \int d\mathbf{R} \left| \sum_\alpha^M C_\alpha \psi_2^\alpha \int d\mathbf{r} \Phi_{\mathbf{R}}^{(m)}(\mathbf{r}) \psi_1^\alpha \right|^2 \left| \sum_\alpha^M C_\alpha \psi_2^\alpha \int d\mathbf{r} \Phi_{\mathbf{R}}^{(n)}(\mathbf{r}) \psi_1^\alpha \right|^2 , \tag{A.2}$$

and the reduced nuclear/photonic probability density:

$$\rho(\mathbf{R}, t) = \int d\mathbf{r} |\Psi(t)|^2 = \sum_{\alpha', \alpha}^M C_{\alpha'}^* C_\alpha \psi_2^{\alpha' *} \psi_2^\alpha \int d\mathbf{r} \psi_1^{\alpha' *} \psi_1^\alpha . \tag{A.3}$$

* guillermo.albareda@mpsd.mpg.de

† aaron.kelly@dal.ca

‡ angel.rubio@mpsd.mpg.de

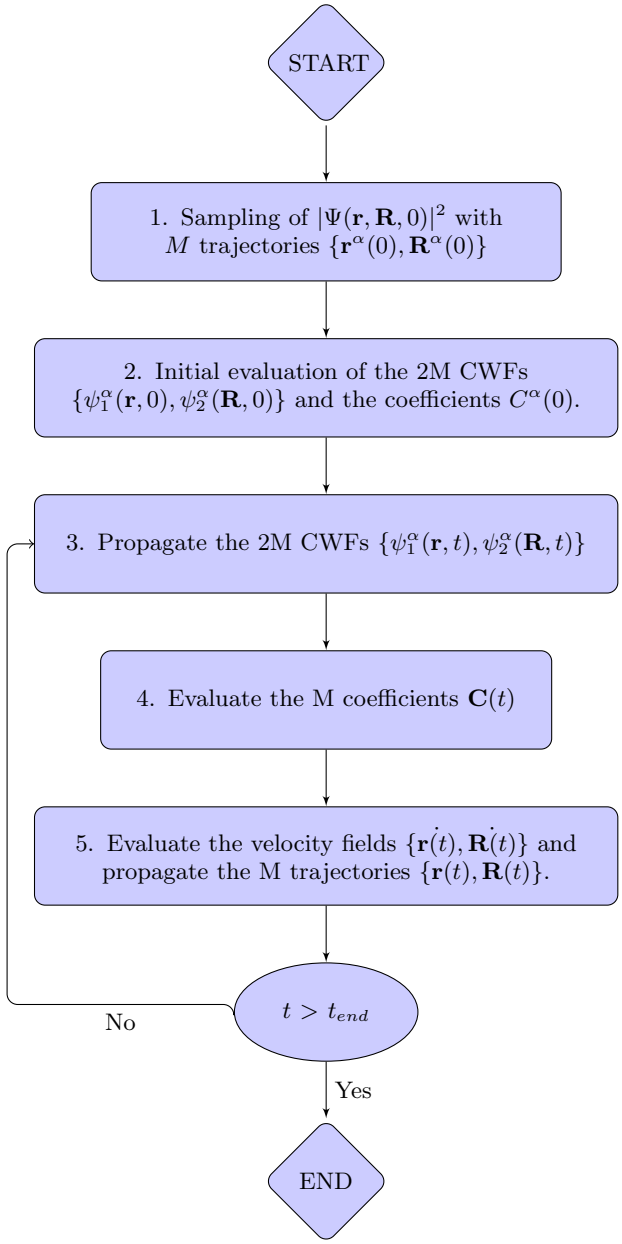

FIG. 1. Flowchart describing the numerical implementation of the ICWF method.