

Supporting Information to “Ab Initio Nonadiabatic Dynamics with Coupled Trajectories: A Rigorous Approach to Quantum (De)Coherence”

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SI.1 – Summary of the approximations

Classical trajectories

In the coupled-trajectory mixed quantum-classical (CT-MQC) algorithm,^{1,2} classical trajectories are employed to mimic the dynamics of the nuclear wavefunction $\chi(\mathbf{R}, t)$ that evolves according to the time-dependent Schrödinger equation of the exact factorization^{3,4}

$$\left(\sum_{\nu=1}^{N_n} \frac{[-i\hbar\nabla_{\nu} + \mathbf{A}_{\nu}(\mathbf{R}, t)]^2}{2M_{\nu}} + \epsilon(\mathbf{R}, t) \right) \chi(\mathbf{R}, t) = i\hbar\partial_t\chi(\mathbf{R}, t). \quad (\text{S1})$$

The trajectories can be assimilated to a moving grid, therefore it seems more natural to work in a reference frame that moves with the trajectories, i.e., the Lagrangian frame, rather than in the fixed Eulerian frame. In the Lagrangian frame time derivatives are calculated “along the flow”, thus all partial time derivatives have to be replaced by total derivatives, using the chain rule $d/dt = \partial_t + \sum_{\nu} \mathbf{V}_{\nu} \cdot \nabla_{\nu}$. Here, the quantity \mathbf{V}_{ν} is the velocity of the moving grid point, i.e., the velocity of each trajectory which will be determined below.

Writing the nuclear wavefunction in polar form, $\chi(\mathbf{R}, t) = |\chi(\mathbf{R}, t)|e^{(i/\hbar)S(\mathbf{R}, t)}$, the real part of Eq. (S1) yields

$$\frac{\partial}{\partial t}S(\mathbf{R}, t) = - \sum_{\nu=1}^{N_n} \frac{[\nabla_{\nu}S(\mathbf{R}, t) + \mathbf{A}_{\nu}(\mathbf{R}, t)]^2}{2M_{\nu}} - \epsilon(\mathbf{R}, t) + \hbar^2 \sum_{\nu=1}^{N_n} \frac{1}{2M_{\nu}} \frac{\nabla_{\nu}^2|\chi(\mathbf{R}, t)|}{|\chi(\mathbf{R}, t)|}, \quad (\text{S2})$$

a Hamilton-Jacobi equation in the presence of the time-dependent vector potential $\mathbf{A}_{\nu}(\mathbf{R}, t)$ and of a potential term (last term in Eq. (S2)) known in the framework of Bohmian dynamics as quantum potential. The imaginary part of Eq. (S1) yields a continuity equation for the nuclear density. Neglecting the quantum potential, Eq. (S2) becomes a (standard) classical Hamilton-Jacobi equation,

$$\dot{S}(\mathbf{R}, t) = - \sum_{\nu=1}^{N_n} \left[\frac{[\nabla_{\nu}S(\mathbf{R}, t) + \mathbf{A}_{\nu}(\mathbf{R}, t)]^2}{2M_{\nu}} - \mathbf{V}_{\nu} \cdot \nabla_{\nu}S(\mathbf{R}, t) \right] - \epsilon(\mathbf{R}, t), \quad (\text{S3})$$

where \dot{S} stands for the full time derivative of S . The canonical momentum of the moving grid is defined as $M_\nu \mathbf{V}_\nu = \nabla_\nu S_0(\mathbf{R}, t) + \mathbf{A}_\nu(\mathbf{R}, t) = \mathbf{P}_\nu$. Taking the spatial derivative $\nabla_{\nu'}$ on both sides, Eq. (S3) reduces to a classical evolution equation for the characteristics

$$\dot{\mathbf{P}}_\nu(t) \Big|_{\mathbf{R}^{(I)}(t)} = - \nabla_\nu \left(\epsilon(\mathbf{R}, t) + \sum_{\nu'=1}^{N_n} \mathbf{A}_{\nu'}(\mathbf{R}, t) \cdot \frac{\mathbf{P}_{\nu'}(\mathbf{R}, t)}{M_{\nu'}} \right) + \dot{\mathbf{A}}_\nu(\mathbf{R}, t) \Big|_{\mathbf{R}^{(I)}(t)}. \quad (\text{S4})$$

At time t all quantities are evaluated at the grid point $\mathbf{R}^{(I)}(t)$.

Choice of the gauge

The product form the electron-nuclear wavefunction $\Psi(\mathbf{r}, \mathbf{R}, t) = \Phi_{\mathbf{R}}(\mathbf{r}, t) \chi(\mathbf{R}, t)$ is invariant under a (\mathbf{R}, t) -phase transformation⁵⁻⁷ of $\Phi_{\mathbf{R}}(\mathbf{r}, t)$ and $\chi(\mathbf{R}, t)$. In order to fix this gauge freedom, the additional constraint

$$\epsilon(\mathbf{R}, t) + \sum_{\nu=1}^{N_n} \mathbf{A}_\nu(\mathbf{R}, t) \cdot \frac{\mathbf{P}_\nu(\mathbf{R}, t)}{M_\nu} = 0. \quad (\text{S5})$$

is imposed in the CT-MQC scheme. Eq. (S4) thus simplifies to $\dot{\mathbf{P}}_\nu(t) = \dot{\mathbf{A}}_\nu(t)$.

Time-dependent potential energy surface

The expression of the time-dependent potential energy surface is

$$\epsilon(\mathbf{R}, t) = \left\langle \Phi_{\mathbf{R}}(t) \left| \hat{H}_{BO} + \hat{U}_{en}^{coup} - i\hbar \partial_t \right| \Phi_{\mathbf{R}}(t) \right\rangle_{\mathbf{r}}, \quad (\text{S6})$$

with the electron-nuclear coupling operator defined as

$$\hat{U}_{en}^{coup}[\Phi_{\mathbf{R}}, \chi] = \sum_{\nu=1}^{N_n} \left[\frac{(-i\hbar \nabla_\nu - \mathbf{A}_\nu)^2}{2M_\nu} + \frac{1}{M_\nu} \left(\frac{-i\hbar \nabla_\nu \chi}{\chi} + \mathbf{A}_\nu \right) \cdot (-i\hbar \nabla_\nu + \mathbf{A}_\nu) \right]. \quad (\text{S7})$$

Neglecting the first term in the definition of $\hat{U}_{coup}^{en}[\Phi_{\mathbf{R}}, \chi]$ that depends on second-order derivatives of the electronic wavefunction with respect to the nuclear positions, and working in the Lagrangian frame, the approximate expression of the time-dependent potential energy surface, $\epsilon^{apx}(\mathbf{R}, t)$, becomes

$$\epsilon^{apx}(\mathbf{R}, t) = \left\langle \Phi_{\mathbf{R}}(t) \left| \hat{H}_{BO} \right| \Phi_{\mathbf{R}}(t) \right\rangle_{\mathbf{r}} - i\hbar \left\langle \Phi_{\mathbf{R}}(t) \left| \dot{\Phi}_{\mathbf{R}}(t) \right\rangle_{\mathbf{r}} - \sum_{\nu=1}^{N_n} \frac{\mathbf{P}_{\nu}}{M_{\nu}} \cdot \mathbf{A}_{\nu}(\mathbf{R}, t). \quad (\text{S8})$$

Eq. (S8) is obtained by replacing the partial time derivative in Eq. (S6) with the total time derivative of $\Phi_{\mathbf{R}}(\mathbf{r}, t)$. The additional term from the chain rule used above contains ∇_{ν} , which leads to the appearance of the time-dependent vector potential when averaged over the electronic wavefunction.

The Born-Huang expansion

The CT-MQC scheme is based on the Born-Huang expansion of the electronic wavefunction $\Phi_{\mathbf{R}}(\mathbf{r}, t)$,

$$\Phi_{\mathbf{R}}(\mathbf{r}, t) = \sum_l C_l(\mathbf{R}, t) \varphi_{\mathbf{R}}^{(l)}(\mathbf{r}), \quad (\text{S9})$$

where the adiabatic states $\varphi_{\mathbf{R}}^{(l)}(\mathbf{r})$ are the eigenstates of the Hamiltonian \hat{H}_{BO} with eigenvalues $\epsilon_{BO}^{(l)}(\mathbf{R})$. This expansion is inserted in the electronic evolution equation of the exact factorization, i.e.,

$$\left(\hat{H}_{BO} + \hat{U}_{en}^{coup}[\Phi_{\mathbf{R}}, \chi] - \epsilon(\mathbf{R}, t) \right) \Phi_{\mathbf{R}}(\mathbf{r}, t) = i\hbar \partial_t \Phi_{\mathbf{R}}(\mathbf{r}, t). \quad (\text{S10})$$

Furthermore, the partial time derivative of the electronic wavefunction is replaced by the total time derivative, according to $\partial_t \Phi_{\mathbf{R}}(\mathbf{r}, t) \big|_{\mathbf{R}(t)} = \dot{\Phi}_{\mathbf{R}}(\mathbf{r}, t) - \sum_{\nu=1}^{N_n} \frac{\mathbf{P}_{\nu}(t)}{M_{\nu}} \cdot \nabla_{\nu} \Phi_{\mathbf{R}}(\mathbf{r}, t) \big|_{\mathbf{R}(t)}$ (when evaluated along the trajectory). These two operations allow us, starting from Eq. (S10),

to derive a set of coupled partial differential equations for the coefficients $C_l(\mathbf{R}, t)$,

$$\begin{aligned} \dot{C}_l^{(I)}(t) = & \frac{-i}{\hbar} \left[\epsilon_{BO}^{(I)(I)} - \epsilon^{apx(I)}(t) - \sum_{\nu=1}^{N_n} \frac{\mathbf{P}_\nu^{(I)}(t) + i\mathbf{Q}_\nu^{(I)}(t)}{M_\nu} \cdot \mathbf{A}_\nu(t) \right] C_l^{(I)}(t) \\ & - \sum_{\nu=1}^{N_n} \frac{i\mathbf{Q}_\nu^{(I)}(t)}{M_\nu} \nabla_\nu C_l^{(I)}(t) - \sum_{\nu=1}^{N_n} \frac{\mathbf{P}_\nu^{(I)}(t) + i\mathbf{Q}_\nu^{(I)}(t)}{M_\nu} \sum_k C_k^{(I)}(t) \mathbf{d}_{\nu,lk}^{(I)}. \end{aligned} \quad (\text{S11})$$

All quantities labeled by a superscript (I) are evaluated at the position $\mathbf{R}^{(I)}(t)$ of the trajectory at time t , as they depend on nuclear positions. The nonadiabatic coupling vectors have been introduced in the above expression, i.e., $\mathbf{d}_{\nu,lk}^{(I)} = \langle \varphi_{\mathbf{R}^{(I)}(t)}^{(I)} | \nabla_\nu \varphi_{\mathbf{R}^{(I)}(t)}^{(k)} \rangle_{\mathbf{r}}$. In deriving Eq. (S11), we have employed the polar representation of the nuclear wavefunction in the electron-nuclear coupling operator \hat{U}_{en}^{coup} of Eq. (S7), i.e.,

$$\begin{aligned} \frac{-i\hbar \nabla_\nu \chi^{(I)}(t)}{\chi^{(I)}(t)} + \mathbf{A}_\nu^{(I)}(t) &= [\nabla_\nu S^{(I)}(t) + \mathbf{A}_\nu^{(I)}(t)] + i \frac{-\hbar \nabla_\nu |\chi^{(I)}(t)|}{|\chi^{(I)}(t)|} \\ &= \mathbf{P}_\nu^{(I)}(t) + i\mathbf{Q}_\nu^{(I)}(t). \end{aligned} \quad (\text{S12})$$

This equation contains the quantities $\mathbf{P}_\nu^{(I)}(t)$, the classical nuclear momentum, and $\mathbf{Q}_\nu^{(I)}(t)$, the signature quantity of the exact factorization that we have dubbed “quantum momentum”.

The gauge condition (S5) is introduced in Eq. (S11) to obtain

$$\begin{aligned} \dot{C}_l^{(I)}(t) = & \frac{-i}{\hbar} \left[\epsilon_{BO}^{(I)(I)} - \sum_{\nu=1}^{N_n} \frac{i\mathbf{Q}_\nu^{(I)}(t)}{M_\nu} \cdot \mathbf{A}_\nu(t) \right] C_l^{(I)}(t) \\ & - \sum_{\nu=1}^{N_n} \frac{i\mathbf{Q}_\nu^{(I)}(t)}{M_\nu} \nabla_\nu C_l^{(I)}(t) - \sum_{\nu=1}^{N_n} \frac{\mathbf{P}_\nu(t) + i\mathbf{Q}_\nu^{(I)}(t)}{M_\nu} \sum_k C_k^{(I)}(t) \mathbf{d}_{\nu,lk}^{(I)}. \end{aligned} \quad (\text{S13})$$

On the right-hand side of Eq. (S13), the terms that do not contain the quantum momentum $\mathbf{Q}_\nu^{(I)}(t)$ are exactly the same as in the Ehrenfest and surface hopping schemes. An additional approximation is considered at this point, that is, neglecting all terms in the above equation that contain products of the quantum momentum, inducing decoherence, with the nonadiabatic coupling vectors, driving the nonadiabatic population exchange between elec-

tronic states. Such an approximation, easy to relax if not accurate enough, is based on the hypothesis that the nonadiabatic coupling vectors are localized in space such that the two effects, decoherence and population exchange, can be clearly separated in time.

The approximate form of the spatial derivative of the coefficients of the Born-Huang expansion used in the CT-MQC algorithm is $\nabla_\nu C_l^{(I)}(t) = (i/\hbar) \mathbf{f}_{l,\nu}^{(I)}(t) C_l^{(I)}(t)$. The quantity $\mathbf{f}_{l,\nu}^{(I)}(t)$ is the time-integrated adiabatic force

$$\mathbf{f}_{l,\nu}^{(I)}(t) = - \int^t dt' \nabla_\nu \epsilon_{BO}^{(I),(I)}. \quad (\text{S14})$$

With this approximation, the electronic evolution equation (S13) is no longer a partial differential equation, but an ordinary differential equation.

From the definition of the time-dependent vector potential

$$\mathbf{A}_\nu(\mathbf{R}, t) = \langle \Phi_{\mathbf{R}}(t) | -i\hbar \nabla_\nu \Phi_{\mathbf{R}}(t) \rangle_{\mathbf{r}}, \quad (\text{S15})$$

it is easy to see that when the Born-Huang expansion is used for the electronic wavefunction, such spatial derivatives appear. Therefore, related to the discussion just presented, we can now provide the explicit expression of the time-dependent vector potential evaluated along the trajectory I , namely

$$\mathbf{A}_\nu^{(I)}(t) = \sum_l \left| C_l^{(I)}(t) \right|^2 \mathbf{f}_{l,\nu}^{(I)}(t) + \hbar \text{Im} \sum_{l,k} C_l^{(I)*}(t) C_k^{(I)}(t) \mathbf{d}_{\nu,lk}^{(I)}. \quad (\text{S16})$$

It depends on the adiabatic potential energy, via its dependence on $\mathbf{f}_{l,\nu}^{(I)}(t)$, and on the non-adiabatic coupling vectors.

SI.2 – Evaluation of the quantum momentum

The quantum momentum has been introduced in Eq. (S12), and defined as

$$\mathbf{Q}_\nu^{(I)}(t) = \frac{-\hbar \nabla_\nu |\chi^{(I)}(t)|}{|\chi^{(I)}(t)|} = \frac{-\hbar \nabla_\nu |\chi^{(I)}(t)|^2}{2 |\chi^{(I)}(t)|^2}. \quad (\text{S17})$$

It appears as a purely imaginary correction to the (real) classical momentum in the expression of the electron-nuclear coupling operator $\hat{U}_{en}^{coup}[\Phi_{\mathbf{R}}, \chi]$. Here, $|\chi^{(I)}(t)|^2$ stands for the value of the nuclear density evaluated at the position of the I -th trajectory. Due to the presence of the spatial derivative of the nuclear density in Eq. (S17), the quantum momentum clearly encloses information about the “dispersion” of the trajectories in configuration space.

In the derivation of the CT-MQC algorithm, we have adopted a trajectory-based representation of the nuclear evolution. It follows that information about the nuclear density has to be somehow recovered in order to evaluate the quantum momentum. In Ref.,² we have proposed a procedure for determining numerically the quantum momentum, based on the representation of the nuclear density as a sum of Gaussian-shaped wavepackets, one for each electronic state considered in the simulation. In order to make the calculation of the quantum momentum more flexible and adaptable to general situations, we propose in the following a new procedure for its calculation. Such procedure has been implemented in CPMD.⁸

The most natural way of reconstructing the nuclear density $|\chi(\mathbf{R}, t)|^2$ from a distribution of classical trajectories is to express it as a sum of Gaussians, each centered at the position of the trajectories. Therefore, we introduce the quantity

$$g_{\sigma_\nu^{(J)}(t)}(\mathbf{R}_\nu - \mathbf{R}_\nu^{(J)}(t)) = \left(\frac{1}{2\pi\sigma_\nu^{(J)2}(t)} \right)^{\frac{3}{2}} \exp \left(-\frac{[\mathbf{R}_\nu - \mathbf{R}_\nu^{(J)}(t)]^2}{2\sigma_\nu^{(J)2}(t)} \right), \quad (\text{S18})$$

which is a normalized Gaussian centered at $\mathbf{R}_\nu^{(J)}(t)$ with variance $\sigma_\nu^{(J)}(t)$, with \mathbf{R}_ν repre-

senting the three-dimensional position vector corresponding to the nucleus ν . The nuclear density in configuration space can thus be expressed as a (normalized) sum of such Gaussian functions,

$$|\chi(\mathbf{R}, t)|^2 = \frac{1}{N_{tr}} \sum_{J=1}^{N_{tr}} \prod_{\nu=1}^{N_n} g_{\sigma_\nu^{(J)}(t)} \left(\mathbf{R}_\nu - \mathbf{R}_\nu^{(J)}(t) \right), \quad (\text{S19})$$

which becomes

$$|\chi^{(I)}(t)|^2 = \frac{1}{N_{tr}} \sum_{J=1}^{N_{tr}} \prod_{\nu=1}^{N_n} g_{\sigma_\nu^{(J)}(t)} \left(\mathbf{R}_\nu^{(I)}(t) - \mathbf{R}_\nu^{(J)}(t) \right) \quad (\text{S20})$$

when evaluated at time t at the position $\mathbf{R}_\nu^{(I)}(t)$ of the I -th classical trajectory. This is the expression needed to evaluate the quantum momentum. In fact, according to its definition given in Eq. (S17), we can easily derive

$$\mathcal{Q}_\nu^{(I)}(t) = \sum_{J=1}^{N_{tr}} W_\nu^{IJ}(t) \left[\mathbf{R}_\nu^{(I)}(t) - \mathbf{R}_\nu^{(J)}(t) \right] \quad (\text{S21})$$

where

$$W_\nu^{IJ}(t) = \frac{\hbar \prod_{\nu'} g_{\sigma_{\nu'}^{(J)}(t)} \left(\mathbf{R}_{\nu'}^{(I)}(t) - \mathbf{R}_{\nu'}^{(J)}(t) \right)}{2\sigma_\nu^{(J)2}(t) \sum_K \prod_{\nu'} g_{\sigma_{\nu'}^{(K)}(t)} \left(\mathbf{R}_{\nu'}^{(I)}(t) - \mathbf{R}_{\nu'}^{(K)}(t) \right)}. \quad (\text{S22})$$

Performing the sum over the index J , thus over the trajectories, in Eq. (S21), the quantum momentum results

$$\mathcal{Q}_\nu^{(I)}(t) = \alpha_\nu^{(I)}(t) \mathbf{R}_\nu^{(I)}(t) - \mathbf{R}_{0,\nu}^{(I)}(t). \quad (\text{S23})$$

From this derivation, it is clear that evaluating $\mathcal{Q}_\nu^{(I)}(t)$ for the trajectory I requires knowledge of the positions of all trajectories, necessary to perform the summation in Eq. (S21). The trajectories become thus coupled through the quantum momentum.

The quantity $\alpha_\nu^{(I)}(t)$ is evaluated as $\alpha_\nu^{(I)}(t) = \sum_J W_\nu^{IJ}(t)$, whereas the expression of $\mathbf{R}_{0,\nu}^{(I)}(t) = \sum_J W_\nu^{IJ}(t) \mathbf{R}_\nu^{(J)}(t)$ will be simplified below. To this end, let us recall Eq. (4) of the main text, namely the term containing the quantum momentum in the evolution equation for $C_l^{(I)}(t)$. Introducing Eq. (S23), we obtain

$$\dot{C}_{\text{qm}l}^{(I)}(t) = - \sum_{\nu=1}^{N_n} \frac{\alpha_\nu^{(I)} \mathbf{R}_\nu^{(I)}(t) - \mathbf{R}_{0,\nu}^{(I)}}{\hbar M_\nu} \cdot \left[\sum_k \left| C_k^{(I)}(t) \right|^2 \mathbf{f}_{k,\nu}^{(I)}(t) - \mathbf{f}_{l,\nu}^{(I)}(t) \right] C_l^{(I)}(t). \quad (\text{S24})$$

As it appears in Eq. (S23), the quantity $\mathbf{R}_{0,\nu}^{(I)}$ is independent of the state index l . However, due to the approximations introduced in the framework of the exact factorization to derive Eqs. (1) of the main text, this form of the quantum momentum (Eq. (S23)) does not satisfy the physical condition that no population transfer among electronic states should be observed if the nonadiabatic coupling vectors are zero. Therefore, we enforce this condition *for each pair of electronic states* by introducing a different value $\mathbf{R}_{0,\nu}^{(I)} \rightarrow \mathbf{R}_{lk,\nu}^0$ for each pair of states (l, k) . Additionally, we simplify the evaluation of this quantity by imposing that it is independent of the trajectory index I . In fact, based on previous analysis of exact calculations,^{1,2,9} we write the quantum momentum as a sum of *linear* functions having the main contributions in the overlap regions of splitting nuclear wavepackets. Eq. (S24) thus becomes

$$\dot{C}_{\text{qm}l}^{(I)}(t) \simeq - \sum_{\nu=1}^{N_n} \sum_k \frac{\alpha_\nu^{(I)} \mathbf{R}_\nu^{(I)}(t) - \mathbf{R}_{lk,\nu}^0}{\hbar M_\nu} \cdot \left[\mathbf{f}_{k,\nu}^{(I)}(t) - \mathbf{f}_{l,\nu}^{(I)}(t) \right] \left| C_k^{(I)}(t) \right|^2 C_l^{(I)}(t), \quad (\text{S25})$$

where we used the partial normalization condition^{3,4} of the electronic wavefunction $\sum_k |C_k^{(I)}(t)|^2 =$

1. At this point, $\mathbf{R}_{lk,\nu}^0$ can be determined for each pair of states l, k . Notice that the procedure just presented has allowed us to separate the effect of the quantum momentum on the evolution of $C_l^{(I)}(t)$ in a sum of contributions from each state $k \neq l$. This effect is similar to the effect of the nonadiabatic coupling vectors, as the term $\mathbf{d}_{\nu,lk}^{(I)}$ in fact couples the states l and k inducing population transfer between them. The overall effect of the nonadiabatic

coupling vectors on $C_l^{(I)}(t)$ can be summed up over the states $k \neq l$.

For each term of the sum over the state index k in Eq. (S25), we impose that

$$\sum_I \frac{d|C_l^{(I)}(t)|^2}{dt} = \sum_I \sum_\nu 2 \frac{\mathcal{Q}_{lk,\nu}^{(I)}}{\hbar M_\nu} \cdot \left(\mathbf{f}_{k,\nu}^{(I)}(t) - \mathbf{f}_{l,\nu}^{(I)}(t) \right) |C_k^{(I)}(t)|^2 |C_l^{(I)}(t)|^2 = 0 \quad \forall l, k, \quad (\text{S26})$$

where we introduced the symbol $\mathcal{Q}_{lk,\nu}^{(I)} = \alpha_\nu^{(I)} \mathbf{R}_\nu^{(I)} - \mathbf{R}_{lk,\nu}^0$ to indicate the quantum momentum between states l and k . Eq. (S26) guarantees that no population transfer among electronic states should be observed if the nonadiabatic coupling vectors are zero. Indeed, we only require that this condition holds valid for all trajectories, not for each trajectories (notice, in fact, that we introduced the sum over the trajectories). We recall that, as described above, the slope $\alpha_\nu^{(I)}(t)$ of each linear function is determined by summing over J the first term on the right-hand side of Eq. (S21). Eq. (S26) is clearly non-zero if the quantum momentum is different from zero itself. Additionally, it is zero (i) if $|C_l^{(I)}(t)|^2 = 1$, while $|C_k^{(I)}(t)|^2 = 0$ for $k \neq l$ since the term in parenthesis vanishes, and (ii) if $|C_l^{(I)}(t)|^2 = 0$. When all electronic populations are different from either 0 or 1, suitably choosing $\mathbf{R}_{lk,\nu}^0(t)$ in $\mathcal{Q}_{lk,\nu}^{(I)}$ allows us to eliminate spurious population transfer between states k and l if the nonadiabatic coupling vectors between those states are zero.

We further simplify the above expression by imposing that it holds valid for each term of the scalar product (over ν and over the Cartesian components of the vectors), thus obtaining

$$\sum_I \mathcal{Q}_{lk,\nu}^{(I)}(t) \left(f_{k,\nu}^{(I)}(t) - f_{l,\nu}^{(I)}(t) \right) |C_k^{(I)}(t)|^2 |C_l^{(I)}(t)|^2 = 0 \quad \forall l, k, \nu. \quad (\text{S27})$$

Rather than explicitly indicating the dependence on Cartesian indices, we have abandoned the bold-symbol notation, to imply that this is now a scalar condition for the components of the quantum momentum and of the time-integrated adiabatic forces. Thus, the above

condition yields the expression used to determine $R_{lk,\nu}^0(t)$, namely

$$\begin{aligned} R_{lk,\nu}^0(t) &= \sum_I R_\nu^{(I)}(t) \alpha_\nu^{(I)}(t) \frac{\left| C_k^{(I)}(t) \right|^2 \left| C_l^{(I)}(t) \right|^2 \left(f_{k,\nu}^{(I)}(t) - f_{l,\nu}^{(I)}(t) \right)}{\sum_J \left| C_k^{(J)}(t) \right|^2 \left| C_l^{(J)}(t) \right|^2 \left(f_{k,\nu}^{(J)}(t) - f_{l,\nu}^{(J)}(t) \right)} \\ &= \sum_I R_\nu^{(I)}(t) \alpha_\nu^{(I)}(t) \omega_{lk,\nu}^{(I)}(t) \quad \forall l, k, \nu. \end{aligned} \quad (\text{S28})$$

Here, $\omega_{lk,\nu}^{(I)}(t)$ appears as a weight factor. Also, notice from the above expression that $\mathbf{R}_{lk,\nu}^0 = \mathbf{R}_{kl,\nu}^0$, and thus $\mathbf{Q}_{lk,\nu}^{(I)} = \mathbf{Q}_{kl,\nu}^{(I)}$

SI.3 – Linear-response TDDFT

The nonadiabatic schemes presented in the previous sections depend in their implementation on a number of electronic properties like the electronic energies (potential energy surfaces, PES), forces, nonadiabatic couplings and others. The efficient and reliable calculation of these terms is key to the development of *on-the-fly* nonadiabatic molecular dynamics schemes. Matrix elements between electronic states are straightforwardly obtained by means of electronic wavefunction-based methods like, for example, configuration interaction singles (CIS), multireference configuration interaction (MR-CI), and equation-of-motion excitation energy coupled-cluster singles and doubles (EOMEE-CCSD). However, the evaluation of any matrix element within linear-response time-dependent density functional theory (LR-TDDFT) requires a reformulation of these quantities as a functional of the electronic density or, equivalently, of the Kohn-Sham (KS) orbitals. This is necessary since DFT and TDDFT are wavefunction-free theories based exclusively on the electronic density and its representations.

In the next sections, we will briefly present the main LR-TDDFT equations and introduce the concept of *auxiliary many-electron wavefunctions*, which is used to describe all matrix elements required in the nonadiabatic dynamics.

The linear-response equation for TDDFT

The linear response TDDFT equations (using Casida's formulations) can be described as

$$\sum_{kl\tau}^{f_{k\tau}-f_{l\tau}\neq 0} [[\chi^s]_{ij\sigma,kl\tau}^{-1} - K_{ij\sigma,kl\tau}(\omega)] \delta P_{kl\tau}(\omega) = \delta v_{ij\sigma}^{\text{app}}(\omega) \quad (\text{S29})$$

where, formally, $\chi^{-1} = ([\chi^s]^{-1} - \mathbb{K})$, and

$$\begin{aligned} \delta\rho_\sigma(r, \omega) &= \sum_{ij} \delta P_{ij\sigma}(\omega) \phi_{i\sigma}(r) \phi_{j\sigma}^*(r) \\ [\chi^s]_{ij\sigma,kl\tau}^{-1} &= \delta_{\sigma,\tau} \delta_{i,k} \delta_{j,l} \frac{\omega - (\varepsilon_{k\sigma} - \varepsilon_{l\sigma})}{f_{l\sigma} - f_{k\sigma}} \\ K_{ij\sigma,kl\tau}(\omega) &= \int d\mathbf{r} d\mathbf{r}' \frac{\phi_{i\sigma}^*(\mathbf{r}) \phi_{j\sigma}(\mathbf{r}) \phi_{k\tau}(\mathbf{r}') \phi_{l\tau}^*(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} \\ &\quad + \int d(t - t') e^{i\omega(t-t')} \int d\mathbf{r} d\mathbf{r}' \phi_{i\sigma}^*(\mathbf{r}) \phi_{j\sigma}(\mathbf{r}) \frac{\delta^2 \mathcal{A}_{xc}[\rho]}{\delta\rho_\sigma(\mathbf{r}, t) \delta\rho_\tau(\mathbf{r}', t')} \phi_{k\tau}(\mathbf{r}') \phi_{l\tau}^*(\mathbf{r}'). \end{aligned}$$

By ordering the KS orbital basis according to the occupation, we can split Eq. (S29) into *particle-hole* (ph) and *hole-particle* (hp) sectors and rewrite Eq. (S29) in the following form (in the following i, j, k, \dots label occupied- and a, b, c, \dots virtual orbitals)

$$\left(\omega \begin{bmatrix} \mathbb{I} & 0 \\ 0 & -\mathbb{I} \end{bmatrix} - \begin{bmatrix} \mathbb{A}(\omega) & \mathbb{B}(\omega) \\ \mathbb{B}^*(\omega) & \mathbb{A}^*(\omega) \end{bmatrix} \right) \begin{bmatrix} \delta \mathbf{P}(\omega) \\ \delta \mathbf{P}^*(\omega) \end{bmatrix} = \begin{bmatrix} \delta \mathbf{v}(\omega) \\ \delta \mathbf{v}^*(\omega) \end{bmatrix} \quad (\text{S30})$$

where

$$A_{ia\sigma,jb\tau}(\omega) = \delta_{\sigma,\tau} \delta_{i,j} \delta_{a,b} (\varepsilon_{a\tau} - \varepsilon_{i\tau}) + K_{ia\sigma,jb\tau}(\omega), \quad (\text{S31})$$

$$B_{ia\sigma,jb\tau}(\omega) = K_{ia\sigma,bj\tau}(\omega). \quad (\text{S32})$$

The matrix on the left-hand side of Eq. (S30) is the inverse of the susceptibility and therefore the excitation energies ω_n can be obtained from the solution of the generalized eigenvalue

equation

$$\begin{bmatrix} \mathbb{A} & \mathbb{B} \\ \mathbb{B}^* & \mathbb{A}^* \end{bmatrix} \begin{bmatrix} \mathbf{X}_n \\ \mathbf{Y}_n \end{bmatrix} = \omega_n \begin{bmatrix} \mathbb{I} & 0 \\ 0 & -\mathbb{I} \end{bmatrix} \begin{bmatrix} \mathbf{X}_n \\ \mathbf{Y}_n \end{bmatrix} \quad (\text{S33})$$

where we now assume that the matrices \mathbb{A} and \mathbb{B} are frequency independent (adiabatic approximation for the TDDFT kernel, f_{xc}). This equation has paired excitation ($\omega_n > 0$) and de-excitation ($\omega_n < 0$).¹⁰ The usual normalization is

$$\mathbf{X}_n^\dagger \mathbf{X}_n - \mathbf{Y}_n^\dagger \mathbf{Y}_n = \begin{cases} +1, & \omega_n > 0 \\ -1, & \omega_n < 0. \end{cases} \quad (\text{S34})$$

Nuclear forces from LR-TDDFT

LR-TDDFT can become the method of choice for the calculation of excited state PESs to be used in different nonadiabatic molecular dynamics (MD) schemes. In this case, the calculation of nuclear forces within the LR-TDDFT formalism becomes an essential step. Among the different approaches developed for the calculation of analytic derivatives, the Lagrangian method¹¹ is of particular interest because of its numerical efficiency. However, the derivation of LR-TDDFT is technically involved and since it does not bring any new physical insights, we simply refer the interested reader to the rich literature on the subject.^{12–16}

The LR-TDDFT sum-over-states (SOS) formula

In this section we derive a SOS representation of the density-density response function within LR-TDDFT. The starting point is the matrix form of the TDDFT linear response equations in frequency space, Eq. (S30). For a real perturbation of the type $\delta\mathbf{v}'(\omega) = 1/2(\delta\mathbf{v}(\omega) + \delta\mathbf{v}^*(\omega))$ Eq. (S30) leads to¹⁷

$$\Re(\delta\mathbf{P})(\omega) = (\mathbb{A} - \mathbb{B})^{1/2}(\omega^2\mathbb{I} - \Omega(\omega))^{-1}(\mathbb{A} - \mathbb{B})^{1/2}\delta\mathbf{v}'(\omega) \quad (\text{S35})$$

where

$$\Omega = (\mathbb{A} - \mathbb{B})^{1/2}(\mathbb{A} + \mathbb{B})(\mathbb{A} - \mathbb{B})^{1/2} \quad (\text{S36})$$

and

$$\begin{aligned} \Omega_{ij\sigma,kl\tau}(\omega) = & \delta_{\sigma,\tau} \delta_{i,k} \delta_{j,l} (\varepsilon_{l\tau} - \varepsilon_{k\tau})^2 \\ & + 2\sqrt{(f_{i\sigma} - f_{j\sigma})(\varepsilon_{j\sigma} - \varepsilon_{i\sigma})} K_{ij\sigma,kl\tau}(\omega) \sqrt{(f_{k\tau} - f_{l\tau})(\varepsilon_{l\tau} - \varepsilon_{k\tau})}. \end{aligned} \quad (\text{S37})$$

We can therefore define the susceptibility $\chi(\omega)$ as

$$\chi(\omega) = -2(\mathbb{A} - \mathbb{B})^{1/2}(\Omega(\omega) - \omega^2\mathbb{I})^{-1}(\mathbb{A} - \mathbb{B})^{1/2}. \quad (\text{S38})$$

Using the spectral representation of the $(\Omega(\omega) - \omega^2\mathbb{I})^{-1}$, we can write

$$(\Omega(\omega) - \omega^2\mathbb{I})^{-1} = \sum_n \frac{\mathbf{Z}_n \mathbf{Z}_n^\dagger}{\omega_n^2 - \omega^2} \quad (\text{S39})$$

where \mathbf{Z}_n are the eigenvectors of $\Omega(\omega)$

$$\Omega(\omega)\mathbf{Z}_n = \omega_n^2\mathbf{Z}_n \quad (\text{S40})$$

and are related to the eigenvectors of Eq. (S33) according to¹⁰

$$\mathbf{Z}_n = (\mathbb{A} - \mathbb{B})^{-1/2}(\mathbf{X}_n + \mathbf{Y}_n). \quad (\text{S41})$$

Note that in case of a frequency dependent $\Omega(\omega)$, the eigenvectors \mathbf{Z}_n requires the normalization¹⁷

$$\mathbf{Z}_n^\dagger \left(\mathbb{I} - \left[\frac{\partial \Omega(\omega)}{\partial \omega^2} \right] \right) \mathbf{Z}_n = 1 \quad (\text{S42})$$

in order to enforce the residues in the spectral representation (Eq. (S39)) to be equal to one. Finally, we obtain for the susceptibility χ the following SOS representation

$$\chi(\omega) = -2 \sum_n \frac{(\mathbb{A} - \mathbb{B})^{1/2} \mathbf{Z}_n \mathbf{Z}_n^\dagger (\mathbb{A} - \mathbb{B})^{1/2}}{\omega_n^2 - \omega^2}. \quad (\text{S43})$$

Using Eq. (S43), we can now compute the response $\delta\langle\hat{\mathcal{O}}\rangle(\omega)$ of any one-body operator $\hat{\mathcal{O}}$ due to the action of a generic time-dependent perturbation $\hat{v}(\mathbf{r}, t) = \hat{v}'(\mathbf{r})E(t)$. Taking the usual representation of one-body operators in terms of the (Kohn-Sham) creation and annihilation operators

$$\hat{\mathcal{O}} = \sum_{ij\sigma} o_{ij\sigma} \hat{a}_{i\sigma}^\dagger \hat{a}_{j\sigma} \quad (\text{S44})$$

$$\hat{v}' = \sum_{ij\sigma} v'_{ij\sigma} \hat{a}_{i\sigma}^\dagger \hat{a}_{j\sigma} \quad (\text{S45})$$

with $o_{ij\sigma} = \int d\mathbf{r} \hat{\mathcal{O}}(\mathbf{r}) \phi_{i\sigma}^*(\mathbf{r}) \phi_{j\sigma}(\mathbf{r})$ and $v'_{ij\sigma} = \int d\mathbf{r} \hat{v}'(\mathbf{r}) \phi_{i\sigma}^*(\mathbf{r}) \phi_{j\sigma}(\mathbf{r})$, we first get for $\delta\mathcal{O}(\omega) = \delta\langle\hat{\mathcal{O}}\rangle(\omega) = \int d\mathbf{r} \hat{\mathcal{O}}(\mathbf{r}) \delta\rho(\mathbf{r}, \omega)$,

$$\delta\mathcal{O}(\omega) = \sum_{ij\sigma} o_{ij\sigma} \delta P_{ij\sigma}(\omega), \quad (\text{S46})$$

where, according to $\delta\rho(\mathbf{r}, \omega) = \int d\mathbf{r}' v'(\mathbf{r}') E(\omega) \chi(\mathbf{r}, \mathbf{r}', \omega)$,

$$\delta P_{ij\sigma}(\omega) = \sum_{kl\tau} \chi_{ij\sigma, kl\tau}(\omega) v'_{kl\tau} E(\omega). \quad (\text{S47})$$

Therefore, from Eq. (S43) the final LR-TDDFT SOS equation reads

$$\delta\mathcal{O}(\omega) = -2 \sum_n \mathbf{o}^\dagger \frac{(\mathbb{A} - \mathbb{B})^{1/2} \mathbf{Z}_n \mathbf{Z}_n^\dagger (\mathbb{A} - \mathbb{B})^{1/2}}{\omega_n^2 - \omega^2} \mathbf{v}' E(\omega). \quad (\text{S48})$$

As an example, the polarizability defined as $\alpha_{\epsilon_1, \epsilon_2}(\omega) = \frac{\delta\mu_{\epsilon_1}}{E_{\epsilon_2}(t)}$ where ϵ_1 and ϵ_2 are two cartesian directions in space, is measuring the change in dipole $\delta\mu_{\epsilon_1} = -\epsilon_1 \cdot \mathbf{r}$ induced by a

perturbation of the form $v'(r, \omega) = \epsilon_2 \cdot \mathbf{r} E(\omega)$. From Eq. (S48) we get (for $\epsilon_1 = \hat{x}$ and $\epsilon_2 = \hat{z}$)

$$\alpha_{xz}(\omega) = 2 \sum_n \mathbf{x}^\dagger \frac{(\mathbb{A} - \mathbb{B})^{1/2} \mathbf{Z}_n \mathbf{Z}_n^\dagger (\mathbb{A} - \mathbb{B})^{1/2}}{\omega_n^2 - \omega^2} \mathbf{z}, \quad (\text{S49})$$

where the factor 2 comes from the fact that (for symmetry reasons) the summation over ij can be restricted to the terms with $(f_{i\sigma} - f_{j\sigma}) > 0$.

Matrix elements in LR-TDDFT

The derivation of a general formula for the evaluation of matrix elements of one-particle operators in linear-response theory

$$\langle \Phi_0 | \hat{\mathcal{O}} | \Phi_n \rangle \quad (\text{S50})$$

is based on a direct comparison with the same quantity derived using many-body perturbation theory (MBPT). In Eq. (S50), the states $|\Phi_0\rangle$ and $|\Phi_n\rangle$ describe the ground state and n^{th} electronic excited state wavefunctions, respectively.

We start therefore with a short outline of the main linear-response equations in MBPT.

From the definition of the retarded density-density response function¹,

$$\chi(\mathbf{r}, t, \mathbf{r}', t') = \Pi^R(\mathbf{r}, t, \mathbf{r}', t') = -i\theta(t - t') \frac{\langle \Phi_0 | [\hat{\rho}(\mathbf{r}, t), \hat{\rho}(\mathbf{r}', t')] | \Phi_0 \rangle}{\langle \Phi_0 | \Phi_0 \rangle}, \quad (\text{S52})$$

the change of an observable \mathcal{O} , under the influence of a perturbation $v_{\text{ext}}(\mathbf{r}', t')$ in the linear-response regime is given by

$$\delta \mathcal{O}(t) = \int_0^\infty dt' \int d\mathbf{r} \int d\mathbf{r}' o(\mathbf{r}) v_{\text{ext}}(\mathbf{r}', t') \chi(\mathbf{r}, t, \mathbf{r}', t') \quad (\text{S53})$$

¹For the special case of $o(\mathbf{r}) = 1$, we get the density linear-response:

$$\delta \rho(\mathbf{r})(t) = \int_0^\infty dt' \int d\mathbf{r} v^{\text{ext}}(\mathbf{r}', t') \chi^R(\mathbf{r}t, \mathbf{r}'t'). \quad (\text{S51})$$

(here we consider an interaction of the form $\delta v^{ext}(\mathbf{r}', t') = v'(\mathbf{r}')E(t')$). If χ depends only on the difference $(t - t')$, the Fourier transform in time gives

$$\delta\mathcal{O}(\omega) = \int d\mathbf{r} \int d\mathbf{r}' o(\mathbf{r})v'(\mathbf{r}')E(\omega)\chi(\mathbf{r}, \mathbf{r}', \omega). \quad (\text{S54})$$

For finite size systems for which we can construct a discrete set of "quasiparticle" one-electron orbitals to be used in Slater-type many-electron wavefunctions (Hartree-Fock or Kohn-Sham orbitals in most cases), we can introduce the matrix representation

$$\delta\mathcal{O}(\omega) = \sum_{ij\sigma, kl\tau} o_{ij\sigma} \chi_{ij\sigma, kl\tau}(\omega) v'_{kl\tau} E(\omega), \quad (\text{S55})$$

where²

$$\chi_{ij\sigma, kl\tau}(\omega) = \sum_n \left[\frac{\langle \Phi_0 | \hat{a}_{j\sigma}^\dagger \hat{a}_{i\sigma} | \Phi_n \rangle \langle \Phi_n | \hat{a}_{k\tau}^\dagger \hat{a}_{l\tau} | \Phi_0 \rangle}{\omega - \omega_n + i\eta} - \frac{\langle \Phi_0 | \hat{a}_{k\tau}^\dagger \hat{a}_{l\tau} | \Phi_n \rangle \langle \Phi_n | \hat{a}_{j\sigma}^\dagger \hat{a}_{i\sigma} | \Phi_0 \rangle}{\omega + \omega_n + i\eta} \right] \quad (\text{S56})$$

and $\hat{\mathcal{O}} = \sum_{ij\sigma} o_{ij\sigma} \hat{a}_{i\sigma}^\dagger \hat{a}_{j\sigma}$, $\hat{v}' = \sum_{ij\sigma} v'_{ij\sigma} \hat{a}_{i\sigma}^\dagger \hat{a}_{j\sigma}$. Using the symmetry property

$$\langle \Phi_0 | \hat{\mathcal{O}} | \Phi_n \rangle \langle \Phi_n | \hat{v}' E(\omega) | \Phi_0 \rangle = \langle \Phi_0 | \hat{v}' E(\omega) | \Phi_n \rangle \langle \Phi_n | \hat{\mathcal{O}} | \Phi_0 \rangle, \quad (\text{S57})$$

we finally obtain the sum-over-states (SOS) formula

$$\delta\mathcal{O}(\omega) = -2 \sum_n \frac{\omega_n \langle \Phi_0 | \hat{\mathcal{O}} | \Phi_n \rangle \langle \Phi_n | \hat{v}' E(\omega) | \Phi_0 \rangle}{\omega_n^2 - \omega^2}. \quad (\text{S58})$$

Comparing the residues of LR-TDDFT response function Eq. (S48) with the residues of the

$$\int d\mathbf{r} o(\mathbf{r}) \hat{\psi}^\dagger(\mathbf{r}) \hat{\psi}(\mathbf{r}) = \int d\mathbf{r} \sum_{ij\sigma} \phi_{i\sigma}(\mathbf{r}) \phi_{j\sigma}(\mathbf{r}) o(\mathbf{r}) \hat{a}_{i\sigma}^\dagger \hat{a}_{j\sigma} = \sum_{ij\sigma} \left[\int d\mathbf{r} \phi_{i\sigma}(\mathbf{r}) \phi_{j\sigma}(\mathbf{r}) o(\mathbf{r}) \right] \hat{a}_{i\sigma}^\dagger \hat{a}_{j\sigma}$$

MBPT response function Eq. (S58) at equal energy ω_n , we obtain the following identity ³

$$\langle \Phi_0 | \hat{O} | \Phi_n \rangle = \sum_{ij\sigma}^{(f_{i\sigma}-f_{j\sigma})>0} o_{ij\sigma} \langle \Phi_0 | \hat{a}_{i\sigma}^\dagger \hat{a}_{j\sigma} | \Phi_n \rangle \quad (\text{S59})$$

$$= \sum_{ij\sigma}^{(f_{i\sigma}-f_{j\sigma})>0} \frac{1}{\sqrt{\omega_n}} o_{ij\sigma} ((\mathbb{A} - \mathbb{B})^{1/2} \mathbf{Z}_n)_{ij\sigma} . \quad (\text{S60})$$

This equation was derived by Casida¹⁷ and then applied by Tavernelli et al. and Hu et al. for the calculation of the nonadiabatic coupling vectors between the ground state and an excited state. A similar equation was also given in Ref.¹⁸

The auxiliary many-electron wavefunction

It may be useful at this point to investigate the possibility to further simplify the definition and the calculation of matrix elements within LR-TDDFT by means of the definition of a set of "auxiliary" multideterminantal many-electron wavefunctions based on KS orbitals. This route was first explored by Casida¹⁷ to solve the assignment problem of the LR-TDDFT excited state transitions and then further developed by Tavernelli et. al¹⁹ in relation to the calculation of matrix elements in the linear and second-order response regimes.²⁰⁻²²

In Ref.,²¹ we showed that defining the ground state many-electron wavefunction as a Slater determinant of all occupied KS orbitals $\{\phi_i\}_{i=1}^{N_{el}}$

$$\langle \mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3, \dots, \mathbf{r}_{N_{el}} | \tilde{\Phi}_0 \rangle = \frac{1}{\sqrt{N_{el}!}} \det |\phi_1(\mathbf{r}_1) \phi_2(\mathbf{r}_2) \phi_3(\mathbf{r}_3), \dots, \phi_{N_{el}}(\mathbf{r}_{N_{el}})| \quad (\text{S61})$$

³With no Hartree-Fock exchange contribution in the functional, $(\mathbb{A} - \mathbb{B})$ is diagonal and becomes:¹⁰

$$(\mathbb{A} - \mathbb{B})_{ia\sigma, jb\tau} = \delta_{i,j} \delta_{a,b} \delta_{\sigma,\tau} (\varepsilon_{a\tau} - \varepsilon_{i\tau}) .$$

and the excited state wavefunction corresponding to the excitation energy ω_n as

$$\begin{aligned}
\langle \mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3, \dots, \mathbf{r}_{N_{el}} | \tilde{\Phi}_n \rangle &= \sum_{ia\sigma} \sqrt{\frac{\varepsilon_a - \varepsilon_i}{\omega_n}} (\mathbf{Z}_n)_{ia\sigma} \hat{a}_{a\sigma}^\dagger \hat{a}_{i\sigma} \langle \mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3, \dots, \mathbf{r}_{N_{el}} | \tilde{\Phi}_0 \rangle \\
&= \sum_{ia\sigma} C_{ia\sigma}^n \hat{a}_{a\sigma}^\dagger \hat{a}_{i\sigma} \langle \mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3, \dots, \mathbf{r}_{N_{el}} | \tilde{\Phi}_0 \rangle \\
&= \sum_{ia\sigma} C_{ia\sigma}^n \langle \mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3, \dots, \mathbf{r}_{N_{el}} | \tilde{\Phi}_{i\sigma}^{a\sigma} \rangle,
\end{aligned} \tag{S62}$$

we obtain for any one-body operator of the form $\hat{\mathcal{O}} = \sum_{pq\sigma} o_{pq\sigma} \hat{a}_{p\sigma}^\dagger \hat{a}_{q\sigma}$ (where p, q are general indices) the correct linear-response expression for the matrix element $\langle \Phi_0 | \hat{\mathcal{O}} | \Phi_n \rangle$. Eq. (S62) is derived from Eq. (S60) where now the index i runs over all occupied and a over the unoccupied (virtual) KS orbitals and $|\tilde{\Phi}_{i\sigma}^{a\sigma}\rangle$ denotes a singly-excited Slater determinant defined by the transition $i\sigma \rightarrow a\sigma$. This theory was then successfully extended to the case of the calculation of matrix elements between two excited state wavefunctions, $\langle \Phi_n | \hat{\mathcal{O}} | \Phi_m \rangle$ as will be shown in the next section on the calculation of nonadiabatic coupling vectors.

It is important to further stress the fact that both auxiliary functions introduced in Eqs. (S61) and (S62) have only a physical meaning when used within LR-TDDFT for the calculation of matrix elements of the type $\langle \tilde{\Phi}_0 | \hat{\mathcal{O}} | \tilde{\Phi}_n \rangle$ and eventually $\langle \tilde{\Phi}_n | \hat{\mathcal{O}} | \tilde{\Phi}_m \rangle$. The use of this representations of the ground state and excited state KS many-electron wavefunctions in other contexts is not justified.

The nonadiabatic coupling vectors in LR-TDDFT

Traditionally, the computation of the nonadiabatic coupling vectors (NACVs) is carried out using wavefunction-based *ab initio* quantum chemistry approaches, which, however, are not well suited for condensed phase applications and become computationally unaffordable when the dynamics of large molecular systems is considered.

Using the auxiliary many-electron wavefunction approach outlined above we are now in the position to derive an approach for the calculation of nonadiabatic vectors within LR-

TDDFT.

The couplings with the ground state

We start from an alternative definition of the NACV²³ (see also Ch. 5 of Ref.²⁴ for a complete discussion) between the ground (0) state and the n^{th} excited state for a molecular system characterized by nuclear coordinates \mathbf{R} in the configuration space (\mathbb{R}^{3N_n})

$$\mathbf{d}_{0n}^\gamma = \frac{\langle \Phi_0(\mathbf{R}) | \partial_\gamma \hat{\mathcal{H}}_{el} | \Phi_n(\mathbf{R}) \rangle}{E_n^{el}(\mathbf{R}) - E_0^{el}(\mathbf{R})} \quad (\text{S63})$$

where γ is an atomic label, $\hat{\mathcal{H}}_{el}$ is the electronic Hamiltonian, and $\partial_\gamma \hat{\mathcal{H}}_{el} = \partial \hat{\mathcal{H}}_{el} / \partial \mathbf{R}_\gamma$.

Applying the results of the above sections on the evaluation of matrix elements of the form $\langle \Phi_0 | \hat{\mathcal{O}} | \Phi_n \rangle$ in LR-TDDFT to the NACV gives directly the desired expression

$$\mathbf{d}_{0n}^\gamma = \sum_{ij\sigma}^{(f_{i\sigma} - f_{j\sigma}) > 0} \frac{1}{(\omega_n)^{3/2}} h_{ij\sigma}^\gamma ((\mathbb{A} - \mathbb{B})^{1/2} \mathbf{Z}_n)_{ij\sigma} \quad (\text{S64})$$

where $h_{ij\sigma}^\gamma = \int d\mathbf{r} \partial_\gamma \hat{\mathcal{H}}_{el} \phi_{i\sigma}^*(\mathbf{r}) \phi_{j\sigma}(\mathbf{r})$.

This formula for the NACVs within LR-TDDFT was derived several times in the literature using slightly different formalisms. The first derivation was by Chernyak and Mukamel²⁵ using a classical Liouville dynamics for the single-electron density matrix. Later, Tavernelli et al.^{19,20} and Hu et al.^{26,27} arrived to the same result (Eq. (S64)) using the most widely used formulation based on Casida's LR-TDDFT equations.¹⁷

Concerning the numerical implementation of Eq. (S63) several approaches have also been proposed that differ mainly in the choice of the basis set and in the way the implicit dependence of the pseudopotentials on the nuclear positions is treated. Due to the technical nature of this subject, we will not go through the numerical details but better refer to the literature, which is very rich on this subject.^{20,26,28–30}

References

- (1) Min, S. K.; Agostini, F.; Gross, E. K. U. Coupled-Trajectory Quantum-Classical Approach to Electronic Decoherence in Nonadiabatic Processes. *Phys. Rev. Lett.* **2015**, *115*, 073001.
- (2) Agostini, F.; Min, S. K.; Abedi, A.; Gross, E. K. U. Quantum-Classical Non-Adiabatic Dynamics: Coupled- vs. Independent-Trajectory Methods. *J. Chem. Theory Comput.* **2016**, *12*, 2127-2143.
- (3) Abedi, A.; Maitra, N. T.; Gross, E. K. U. Exact Factorization of the Time-Dependent Electron-Nuclear Wave Function. *Phys. Rev. Lett.* **2010**, *105*, 123002.
- (4) Abedi, A.; Maitra, N. T.; Gross, E. K. U. Correlated Electron-Nuclear Dynamics: Exact Factorization of the Molecular Wave-Function. *J. Chem. Phys.* **2012**, *137*, 22A530.
- (5) Abedi, A.; Maitra, N. T.; Gross, E. K. U. Reply to Comment on “Correlated Electron-Nuclear Dynamics: Exact Factorization of the Molecular Wave-Function”. *J. Chem. Phys.* **2013**, *139*, 087102.
- (6) Agostini, F.; Abedi, A.; Suzuki, Y.; Gross, E. K. U. Mixed Quantum-Classical Dynamics on the Exact Time-Dependent Potential Energy Surfaces: A Novel Perspective on Non-Adiabatic Processes. *Mol. Phys.* **2013**, *111*, 3625-3640.
- (7) Abedi, A.; Agostini, F.; Suzuki, Y.; Gross, E. K. U. Dynamical Steps That Bridge Piecewise Adiabatic Shapes in the Exact Time-Dependent Potential Energy Surface. *Phys. Rev. Lett* **2013**, *110*, 263001.
- (8) CPMD, <http://www.cpmd.org/>, Copyright IBM Corp 1990-2015, Copyright MPI für Festkörperforschung Stuttgart 1997-2001.
- (9) Agostini, F.; Min, S. K.; Gross, E. K. U. Semiclassical Analysis of the Electron-Nuclear Coupling in Electronic Non-Adiabatic Processes. *Ann. Phys.* **2015**, *527*, 546-555.

- (10) Casida, M. E. Time-Dependent Density-Functional Theory for Molecules and Molecular Solids. *J. Mol. Struct.: THEOCHEM* **2009**, *914*, 3-18.
- (11) Helgaker, T.; Jørgensen, P. Configuration-Interaction Energy Derivatives in a Fully Variational Formulation. *Theor. Chem. Acc.* **1989**, *75*, 111-127.
- (12) Pulay, P. Analytical Derivative Methods in Quantum Chemistry. *Adv. Chem. Phys.* **1987**, *69*, 241-286.
- (13) Hutter, J. Excited State Nuclear Forces from the Tamm-Dancoff Approximation to Time-Dependent Density Functional Theory within the Plane Wave Basis Set Framework. *J. Chem. Phys.* **2003**, *118*, 3928-3934.
- (14) Deglmann, P.; Furche, F.; Ahlrichs, R. An Efficient Implementation of Second Analytical Derivatives for Density Functional Methods. *Chem. Phys. Lett.* **2002**, *362*, 511-518.
- (15) Rappoport, D.; Furche, F. Analytical Time-Dependent Density Functional Derivative Methods within the RI-*J* Approximation, an Approach to Excited States of Large Molecules. *J. Chem. Phys.* **2005**, *122*, 064105.
- (16) Marx, D.; Hutter, J. *Ab Initio Molecular Dynamics: Basic Theory and Advanced Methods*; Cambridge University Press, 2009.
- (17) Casida, M. E. In *Recent Advances in Density Functional Methods*; Chong, D. P., Ed.; Singapore, World Scientific, 1995; p. 155.
- (18) Chernyak, V.; Mukamel, S. Size-Consistent Quasiparticle Representation of Nonlinear Optical Susceptibilities in Many-Electron Systems. *J. Chem. Phys.* **1996**, *104*, 444-459.
- (19) Tapavicza, E.; Tavernelli, I.; Rothlisberger, U. Trajectory Surface Hopping within Linear Response Time-Dependent Density-Functional Theory. *Phys. Rev. Lett.* **2007**, *98*, 023001.

- (20) Tavernelli, I.; Tapavicza, E.; Rothlisberger, U. Nonadiabatic Coupling Vectors within Linear Response Time-Dependent Density Functional Theory. *J. Chem. Phys.* **2009**, *130*, 124107.
- (21) Tavernelli, I.; Curchod, B. F. E.; Rothlisberger, U. On Nonadiabatic Coupling Vectors in Time-Dependent Density Functional Theory. *J. Chem. Phys.* **2009**, *131*, 196101.
- (22) Tavernelli, I.; Curchod, B. F. E.; Laktionov, A.; Rothlisberger, U. Nonadiabatic Coupling Vectors for Excited States within Time-Dependent Density Functional Theory and Beyond. *J. Chem. Phys.* **2010**, *133*, 194104.
- (23) Epstein, S. Note on Perturbation Theory. *Am. J. Phys.* **1954**, *22*, 613.
- (24) Baer, M. *Beyond Born-Oppenheimer: Electronic Nonadiabatic Coupling Terms and Conical Intersections*; John Wiley & Sons, Inc., 2006.
- (25) Chernyak, V.; Mukamel, S. Density-Matrix Representation of Nonadiabatic Couplings in Time-Dependent Density Functional (TDDFT) Theories. *J. Chem. Phys.* **2000**, *112*, 3572-3579.
- (26) Hu, C.; Hirai, H.; Sugino, O. Nonadiabatic Couplings from Time-Dependent Density Functional Theory: Formulation in the Casida Formalism and Practical Scheme within Modified Linear Response. *J. Chem. Phys.* **2007**, *127*, 064103.
- (27) Hu, C.; Hirai, H.; Sugino, O. Nonadiabatic Couplings from Time-Dependent Density Functional Theory. II. Successes and Challenges of the Pseudopotential Approximation. *J. Chem. Phys.* **2008**, *128*, 154111.
- (28) Send, R.; Furche, F. First-Order Nonadiabatic Couplings from Time-Dependent Hybrid Density Functional Response Theory: Consistent Formalism, Implementation, and Performance. *J. Chem. Phys.* **2010**, *132*, 044107.

- (29) Hu, C.; Sugino, O.; Hirai, H.; Tateyama, Y. Nonadiabatic Couplings from the Kohn-Sham Derivative Matrix: Formulation by Time-Dependent Density-Functional Theory and Evaluation in the Pseudopotential Framework. *Phys. Rev. A* **2010**, *82*, 062508.
- (30) Hu, C.; Komakura, R.; Li, Z.; Watanabe, K. TDDFT Study on Quantization Behaviors of Nonadiabatic Couplings in Polyatomic Systems. *Int. J. Quantum Chem.* **2012**, *113*, 263-271.