Topologically correct quantum nonadiabatic formalism for on-the-fly dynamics

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On-the-fly quantum nonadiabatic dynamics for large systems greatly benefits from the adiabatic representation readily available from the electronic structure programs. However, frequently occurring in this representation conical intersections introduce non-trivial geometric or Berry phases which require a special treatment for adequate modelling of the nuclear dynamics. We analyze two approaches for nonadiabatic dynamics using the time-dependent variational principle and the adiabatic representation. The first approach employs adiabatic electronic functions with global parametric dependence on the nuclear coordinates. The second approach uses adiabatic electronic functions obtained only at the centres of moving localized nuclear basis functions (e.g. frozen-width Gaussians). Unless a gauge transformation is used to enforce single-valued boundary conditions, the first approach fails to capture the geometric phase. In contrast, the second approach accounts for the geometric phase naturally because of the absence of the global nuclear coordinate dependence in the electronic functions.

The time-dependent variational principle (TDVP)1–3 provides a very efficient framework for simulating quantum dynamics in large molecular systems. The most powerful aspect of this framework is use of time-dependent basis functions which reduces basis set size requirement compare to that for static basis sets. Two most widely used branches of the TDVP methodology constitute approaches related to the multi-configuration time-dependent Hartree (MCTDH) method4–6 and approaches using frozen-width Gaussian functions.7–13 If the MCTDH-based approaches are more suitable for fixed diabatic models, the frozen Gaussian functions have been extended to simulating nuclear dynamics with the on-the-fly calculation of the electronic potential energy surfaces.7–9,14 Naturally, the adiabatic representation becomes the most straightforward representation for the electronic part of the problem in this case.

One of the most frequent manifestations of the nuclear quantum character is nonadiabatic phenomena where the nuclear dynamics involves several electronic states. TDVP has been successfully extended and applied to modelling nonadiabatic dynamics (NAD). Very frequently NAD becomes necessary because adiabatic electronic potential energy surfaces form conical intersections (CIs).15–18 CIs promote transitions between electronic states and introduce nontrivial geometric phases19–24 that can affect dynamics in profound ways.25–30 It is important to stress that CIs and associated GPs appear only when one uses the adiabatic representation for description of electronic part of the total wave-function. CIs and GPs disappear when the diabatic representation is used, however, physical observables of NAD do not change with the representation. Therefore, the dynamical features that emerge in the diabatic representation due to a nontrivial GP appear in the diabatic or any other representation as well.31,32

One of the simplest signatures of the nontrivial GP introduced by CI is a nodal line appearing in non-stationary nuclear density that moves between minima of a double-well potential with a CI in between the minima (Fig. 1). This nodal line appears due to acquisition of opposite GPs by parts of the wave-packet going around the CI from different sides.26,29,33 This destructive interference can significantly slow down the transfer between the minima and even freeze it completely.26 Of course, any accurate method of quantum dynamics must reproduce the nodal line appearing in this setup. Mead and Truhlar20 shown that to capture the GP in simulations using time-independent nuclear basis functions it is necessary to introduce a complex-valued gauge transformation. This transformation requires some global information about the topology of the potential energy surfaces forming CI and thus poses difficulties in application within the on-the-fly framework, where only local information is available. To address this difficulty, we consider two approaches to formulating TDVP using the adiabatic representation and show how the GP can be accounted
in each of these approaches.

The total non-relativistic molecular Hamiltonian can be written as
\[ \hat{H}(\mathbf{r}, \mathbf{R}) = \hat{T}_N + \hat{H}_e(\mathbf{r}; \mathbf{R}), \]
where \( \hat{T}_N = -\nabla^2_{\mathbf{R}}/2 \) is the kinetic energy of nuclei, \( \hat{H}_e(\mathbf{r}; \mathbf{R}) \) is the electronic Hamiltonian with electronic \( \mathbf{r} \) and nuclear \( \mathbf{R} \) coordinates. \( \hat{H}_e(\mathbf{r}; \mathbf{R}) \) determines the adiabatic electronic wave-functions \( |\phi_s(\mathbf{R})\rangle \) and potential energy surfaces \( E_e^{(s)}(\mathbf{R}) \): \( \hat{H}_e(\mathbf{r}; \mathbf{R})|\phi_s(\mathbf{R})\rangle = E_e^{(s)}(\mathbf{R})|\phi_s(\mathbf{R})\rangle \).

\text{a. Global adiabatic (GA) representation:} The total non-stationary wave-function can be expanded in the adiabatic representation as
\[ \langle \mathbf{r}, \mathbf{R} | \Psi(t) \rangle = \sum_{I,s} C_I^{(s)}(t) \langle \mathbf{R} | G_I^{(s)}(\mathbf{r}) \rangle |\phi_s(\mathbf{R})\rangle, \]
where \( C_I^{(s)} \) are time dependent coefficients, indices \( s \) and \( I \) enumerate the electronic and nuclear coherent states (CSs)
\[ \langle \mathbf{R} | G_I^{(s)}(\mathbf{r}) \rangle = \prod_{j=1}^{N} \left( \frac{\omega_j}{\pi} \right)^{1/4} \exp \left[ -\frac{\omega_j}{2} (R_j - q_j^{(s)}(t))^2 \right] \]
\[ + i\dot{q}_j^{(s)}(t) (R_j - q_j^{(s)}(t)) + \frac{i}{2} \dot{p}_j^{(s)}(t) q_j^{(s)}(t) \]
with time-dependent positions \( q_j^{(s)} = \{q_j^{(s)}\}_{j=1,N} \) and momenta \( p_j^{(s)} = \{p_j^{(s)}\}_{j=1,N} \) \( [N = \text{dim}(\mathbf{R})] \).

Equations of motion (EOM) for positions and momenta of CSs can be obtained using TDVP but resulting EOM would introduce unnecessary complexity for our consideration. Thus, here, we adopt simpler EOM that follow classical dynamics on the adiabatic potential energy surfaces
\[ \dot{q}_j^{(s)} = p_j^{(s)} \]
\[ \dot{p}_j^{(s)} = \left. \frac{\partial E_e^{(s)}(\mathbf{R})}{\partial \mathbf{R}} \right|_{\mathbf{R}=q_j^{(s)}}. \]

This simplifies variation of the total wave-function by restricting it only to the linear coefficients \( C_I^{(s)}(t) \)
\[ \delta \langle \mathbf{r}, \mathbf{R} | \Psi(t) \rangle = \sum_{I,s} [\delta C_I^{(s)}(t)] \langle \mathbf{R} | G_I^{(s)}(\mathbf{r}) \rangle |\phi_s(\mathbf{R})\rangle. \]

Applying the Dirac-Frenkel TDVP\(^2,3\)
\[ \langle \Delta \Psi | \hat{H} - i \partial_t | \Psi \rangle = 0 \]
and substituting the \( \Psi \) and \( \delta \Psi \) expressions from Eqs. (2) and (6) we obtain
\[ \sum_{I,K,ss'} \delta C_I^{(s)}(t) \langle G_I^{(s')}(\mathbf{r}) | \hat{H}_N^{(ss')} - i \partial_t | G_K^{(s')} \rangle C_K^{(s')} = 0, \]
where
\[ \hat{H}_N^{(ss')} = \langle \phi_s(\mathbf{R}) | \hat{H}_e(\mathbf{R}) + \hat{T}_N | \phi_s'(\mathbf{R}) \rangle \]
\[ = E_e^{(s)}(\mathbf{R}) \delta_{ss'} + \hat{T}_N + \hat{\tau}_{ss'}, \]
\[ \hat{\tau}_{ss'} = -i \langle \phi_s(\mathbf{R}) | \nabla_R \phi_{s'}(\mathbf{R}) \rangle \nabla_R \]
\[ - \langle \phi_s(\mathbf{R}) | \nabla_R \phi_{s'}(\mathbf{R}) \rangle / 2. \]

Note that so-called nonadiabatic couplings (NACs) \( \hat{\tau}_{ss'} \) appear as a result of a global dependence of the electronic wave-functions \( \phi_s \) on the nuclear coordinates \( \mathbf{R} \).

Considering independence of \( \delta C_I^{(s)} \) variations, EOM for the coefficients \( C_I^{(s)}(t) \) become
\[ \sum_{K,s'} \langle G_I^{(s)}(\mathbf{R}) | \hat{H}_N^{(ss')} - i \partial_t | G_K^{(s')} \rangle C_K^{(s')} = 0, \]
Rearranging few terms leads to EOM in the form
\[ i \delta C_I^{(s)}(t) = \sum_{I,K} \langle G_I^{(s')}(\mathbf{R}) | G_I^{(s')} \rangle^{-1} \left[ \langle G_I^{(s')} | \hat{H}_N^{(ss')} | G_K^{(s')} \rangle \right] \]
\[ - i \langle \phi_s(\mathbf{R}) | \partial_t G_K^{(s')} \rangle \right] C_K^{(s')} \]
where \( \langle G_I^{(s')} | G_I^{(s')} \rangle^{-1} \) are elements of the inverse CS overlap matrix. Time-derivatives of CSs needed in Eq. (13) are derived using the chain rule
\[ [\partial_t G_K^{(s')} = \left. \frac{\partial G_K^{(s')}}{\partial q_k^{(s')}} \right|_{\mathbf{R}=q_k^{(s')}} q_k^{(s')}(t) + \left. \frac{\partial G_K^{(s')}}{\partial p_k^{(s')}} \right|_{\mathbf{R}=q_k^{(s')}} \dot{p}_k^{(s')}(t). \]

The difficulty associated with a proper treatment of the nuclear dynamics using global adiabatic electronic functions is that \( |\phi_s(\mathbf{R})\rangle \) are double-valued functions with respect to \( \mathbf{R} \) in the CI case. To have a single-valued total wave-function in Eq. (2) the nuclear wave-function must also be double-valued, which is not the case for typical Gaussian-like basis sets [Eq. (3)]. In order to include GP related effects in the nuclear dynamics one needs to substitute the real but double-valued adiabatic electronic wave-functions \( |\phi_s(\mathbf{R})\rangle \) by their complex but single-valued counterparts: \( |\phi_s(\mathbf{R})\rangle = e^{i\phi_s(\mathbf{R})} |\phi_s(\mathbf{R})\rangle \), where \( e^{i\phi_s(\mathbf{R})} \) is a phase factor that changes its sign when \( \mathbf{R} \) follows any curve encircling the CI. This phase factor can be seen as a gauge transformation which is needed when a single-valued basis functions for the nuclear counterpart are used.

\text{b. Moving crude adiabatic (MCA) representation:} Alternatively, EOM can be derived using a different ansatz for the total wave-function
\[ \langle \mathbf{r}, \mathbf{R} | \Psi(t) \rangle = \sum_{I,s} C_I^{(s)}(t) \langle \mathbf{R} | G_I^{(s)}(\mathbf{r}) \rangle |\phi_s(\mathbf{q}_I^{(s)}(t))\rangle, \]
here the electronic functions are evaluated only at the centres of CSs, \( \mathbf{q}_I^{(s)} \), and thus do not depend on the nuclear coordinates \( \mathbf{R} \). To simplify the notation we will denote \( |\phi_s(\mathbf{q}_I^{(s)}(t))\rangle \) as \( |\phi_I^{(s)}\rangle \). Treating CS motion classically [Eqs. (4) and (5)] we repeat the derivation of EOM
for $C_{I}^{(s)}(t)$ in Eq. (15) and obtain

$$i\dot{C}_{I}^{(s')} = \sum_{I,K} \langle G_{I}^{(s')} | \dot{\phi}_{I}^{(s')} | C_{I}^{(s)} \rangle \langle C_{I}^{(s')} | \hat{H}_{IK}^{(s')} | G_{K}^{(s')} \rangle,$$

$$-i \langle \phi_{I}^{(s')} | \hat{G}_{I}^{(s')} | \dot{\phi}_{I}^{(s')} \rangle C_{I}^{(s')} = \frac{i}{\hbar} \langle \phi_{I}^{(s')} | \hat{G}_{I}^{(s')} | \dot{\phi}_{I}^{(s')} \rangle C_{I}^{(s')}.$$

where $\langle G_{I}^{(s')} | \dot{\phi}_{I}^{(s')} | C_{I}^{(s)} \rangle$ are elements of the total inverse overlap matrix, and

$$\hat{H}_{IK}^{(s')} = \langle \phi_{I}^{(s')} | \hat{H}_{I}^{(s')} | \phi_{K}^{(s')} \rangle + \langle \phi_{I}^{(s')} | \hat{G}_{I}^{(s')} | \phi_{K}^{(s')} \rangle \hat{T}_{N}$$

$$-i \langle \phi_{I}^{(s')} | \hat{G}_{I}^{(s')} | \phi_{K}^{(s')} \rangle.$$

Here, the adiabatic electronic functions obtained at different points of nuclear geometry and corresponding to different electronic states are non-orthogonal: $\langle \phi_{I}^{(s')} | \phi_{K}^{(s')} \rangle \neq \delta_{ss'}$ if $I \neq K$. Also, the electronic functions are not eigenfunctions of the electronic Hamiltonian for all values of $\mathbf{R}$, therefore, $\langle \phi_{I}^{(s')} | \hat{H}_{e}^{(s')} | \phi_{K}^{(s')} \rangle$ is a $\mathbf{R}$ and $t$ dependent matrix of functions.

Using the chain rule, the electronic time-derivative couplings in Eq. (17) can be expressed as

$$\langle \phi_{I}^{(s')} | \partial_{t} \phi_{K}^{(s')} \rangle = \langle \phi_{I}^{(s')} | \frac{\partial \phi_{K}^{(s')}}{\partial \phi_{I}^{(s')}} \rangle C_{I}^{(s')}.$$  

Considering the equivalence between dependencies of the MCA electronic functions on centres of CSs and the GA electronic functions on $\mathbf{R}$, the electronic function derivatives in Eq. (18) are similar to the first order derivative part of NACs in Eq. (11). The first order derivative couplings diverge at the point of the CI, however, since the CS centres form a measure zero subset, CSs will never have their centres exactly at the CI seam. Note that in the MCA representation there are no analogues of the second order derivative parts of NACs. The second order derivatives in NACs pose difficulties for integrating EOM due to their $1/R^2$ divergent behavior with the distance from the CI.  

From the GP point of view, the MCA formalism can be thought as a truly diabatic formalism since the electronic functions do not have the dependence on $\mathbf{R}$, and thus problems emerging in the GA representation do not appear here. Nevertheless, due to a parametric dependence of the adiabatic electronic functions on CSs’ centres, the MCA representation has GP’s carried by the electronic functions.  

We illustrate nuclear dynamics in the introduced representations for a 2D-LVC model where formulated EOM can be simulated without additional approximations and where the GP plays a significant role. The total Hamiltonian for 2D-LVC is

$$\hat{H}_{LVC} = \begin{pmatrix} \hat{T}_{N} + V_{11} & V_{12} \\ V_{12} & \hat{T}_{N} + V_{22} \end{pmatrix},$$

where $\hat{T}_{N} = -\frac{1}{2} (\partial^2/\partial x^2 + \partial^2/\partial y^2)$ is the nuclear kinetic energy operator, $V_{11}$ and $V_{22}$ are the diabatic potentials represented by identical 2D parabolas shifted in the $x$-direction by $a$

$$V_{11}(\mathbf{R}) = \frac{e^2}{2} [(x + a)^2 + y^2],$$

$$V_{22}(\mathbf{R}) = \frac{e^2}{2} [(x - a)^2 + y^2].$$

To have the CI in the adiabatic representation, $V_{11}$ and $V_{22}$ are coupled by a linear potential $V_{12}(\mathbf{R}) = cy$. Thus for this example we have $\mathbf{R} = (x, y)$ and the electronic Hamiltonian can be defined as $\hat{H}_{e}(\mathbf{R}) = \sum_{ij} |\varphi_{i} \rangle V_{ij}(\mathbf{R}) |\varphi_{j} \rangle$, where $|\varphi_{i} \rangle$’s are the diabatic electronic states.

Switching to the adiabatic representation is done by rotating the electronic basis into the adiabatic states $|\phi_{1} \rangle = \cos \theta(\mathbf{R}) |\varphi_{1} \rangle + \sin \theta(\mathbf{R}) |\varphi_{2} \rangle,$

$|\phi_{2} \rangle = -\sin \theta(\mathbf{R}) |\varphi_{1} \rangle + \cos \theta(\mathbf{R}) |\varphi_{2} \rangle,$

which diagonalize the potential matrix. $\theta(\mathbf{R})$ is a rotation angle

$$\theta = \frac{1}{2} \arctan \frac{2V_{12}}{V_{22} - V_{11}}.$$  

If we track $\theta$ changes continuously along a contour encircling the CI, it will change by $\pi$, which flips the sign of the phase factor $e^{i\theta}$.  

The nuclear 2D-LVC Hamiltonian in the adiabatic representation is

$$\hat{H}_{\text{adi}} = \begin{pmatrix} \hat{T}_{N} + \hat{\tau}_{11} + \hat{\tau}_{12} & \hat{E}_{e}^{(-)} \\ \hat{\tau}_{21} + \hat{\tau}_{22} & \hat{T}_{N} + \hat{\tau}_{22} \end{pmatrix} + \begin{pmatrix} 0 & \hat{E}_{e}^{(-)} \\ \hat{E}_{e}^{(-)} & 0 \end{pmatrix},$$

where

$$\hat{E}_{e}^{(\pm)} = \frac{1}{2} (V_{11} + V_{22} \pm \frac{1}{2} \sqrt{(V_{11} - V_{22})^2 + 4V_{12}^2}),$$

are the adiabatic energy surfaces and

$$\hat{\tau}_{11} = \hat{\tau}_{22} = \frac{1}{2} \nabla \theta \cdot \nabla \theta$$

$$\hat{\tau}_{12} = \hat{\tau}_{21} = \frac{1}{2} (\nabla^2 \theta + 2\nabla \theta \cdot \nabla \theta)$$

are NACs.

In order to include the GP we use the gauge transformation of the electronic functions that can be seen as a modification of the nuclear Hamiltonian $H_{\text{adi}}^{\text{GP}} = e^{-i\theta} \hat{H}_{\text{adi}} e^{i\theta}$.  

This transformation leads to modification of NACs

$$H_{\text{adi}}^{\text{GP}} = \begin{pmatrix} \hat{T}_{N} + \hat{\tau}_{11}^{\text{GP}} + \hat{\tau}_{12}^{\text{GP}} & \hat{E}_{e}^{(-)} \\ \hat{\tau}_{21}^{\text{GP}} + \hat{\tau}_{22}^{\text{GP}} & \hat{T}_{N} + \hat{\tau}_{22}^{\text{GP}} \end{pmatrix} + \begin{pmatrix} 0 & \hat{E}_{e}^{(-)} \\ \hat{E}_{e}^{(+)} & 0 \end{pmatrix},$$

where

$$\hat{\tau}_{11}^{\text{GP}} = \hat{\tau}_{12}^{\text{GP}} = (\nabla \theta)^2 - \frac{i}{2} (\nabla^2 \theta + 2\nabla \theta \cdot \nabla \theta),$$

$$\hat{\tau}_{12}^{\text{GP}} = \hat{\tau}_{21}^{\text{GP}} = -i (\nabla \theta)^2 + \frac{1}{2} (\nabla^2 \theta + 2\nabla \theta \cdot \nabla \theta).$$
For the MCA representation, the electronic states are calculated as
\[
\phi_I^{(1)}(t) = \cos \theta(q_I^{(1)}) |\varphi_1\rangle + \sin \theta(q_I^{(1)}) |\varphi_2\rangle, \quad (32)
\]
\[
\phi_I^{(2)}(t) = -\sin \theta(q_I^{(2)}) |\varphi_1\rangle + \cos \theta(q_I^{(2)}) |\varphi_2\rangle, \quad (33)
\]
where \(q_I^{(1)}\) and \(q_I^{(2)}\) are centres of corresponding CSs. Therefore, integrals \(\langle \phi_i^{(s)} | H_e(R) | \phi_j^{(s)} \rangle\) for the 2D-LVC model are simply linear combinations of \(V_{ik}(R)\) multiplied by cos and sin functions.

To illustrate the performance of all three approaches in reproducing the GP we simulate nuclear dynamics of the initial wave-function
\[
\langle R | \Psi(t = 0) \rangle = \frac{1}{\sqrt{2}} [\langle R | \phi_1 \rangle + \langle R | \phi_2 \rangle] \quad (34)
\]
that is comprised of two CSs, \(|G_I^{(1)}\rangle = |G_I^{(1)}(q,p_I)\rangle\) centred at the same point \(q = (-1.5,0)\) of the ground potential energy surface, but with momenta \(p_1 = (0.1,0.5)\) and \(p_2 = (0.1,-0.5)\), which have the opposite \(y\)-components. Using three different Hamiltonians, Eqs. (17), (25), and (29), we simulate time-dependent wave-functions and monitor the total nuclear density \(\rho_n(R,t) = Tr_e[\langle R | \Psi(t) \rangle \langle \Psi(t) | R \rangle]\), where \(Tr_e\) is the trace over the electronic coordinates. Figure 2 illustrates that dynamics with the adiabatic Hamiltonian (25) misses the GP, while two other Hamiltonians reproduce the GP induced destructive interference perfectly. However, mechanisms for the destructive interference in the two approaches is quite different: For the GA representation, two CSs acquire different phases from the two approaches is quite different: For the GA representation, electronic functions becomes especially difficult for calculations beyond models. The systematic application of TDVP with the GA electronic functions becomes especially difficult for the on-the-fly calculations, not only because of the necessity to generate the gauge transformation \(e^{i\theta(R)}\) using only local information but also because of the second order derivative NACs whose integrals with Gaussianians are divergent. On both accounts, employing the MCA representation is much more practical: GPs are always carried by the electronic functions and numerically difficult second order derivative NACs never appear in the formalism. Interestingly, in previous works on ab initio multiple spawning (AIMS), the derivation was presented starting with the GA representation but the actual working EOM for the linear coefficients were very similar to the ones obtained in the current work using the MCA representation. This was the result of approximations needed to make AIMS EOM feasible for simulating dynamics in realistic systems.

work provides a rigorous framework of the MCA representation that justifies some of the approximations made in AIMS. Also, the MCA representation can be seen as an effortless realization of a recently proposed on-the-fly diabatization to solve the problem of numerical difficulties in integration of the second order NACs.

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