

Nonadiabatic Ehrenfest dynamics with norm-conserving and ultrasoft pseudopotentials with nuclear velocity corrections on the atomic orbitals within the framework of the projector augmented wave method

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We derive the first-principles Ehrenfest molecular dynamics describing nonadiabatic processes with the inclusion of the nuclear-velocity-dependent phases (also known as electron-translation factors) on the atomic orbital basis. These phases, appearing when nuclei are treated dynamically, affect effective Hamiltonians constructed from localized orbitals. In this work, we focus on the effects on the first-principles pseudopotential Hamiltonian for both the norm-conserving and ultrasoft cases, derived within the projector augmented wave method framework. Peierls-like phases depending on the nuclear velocities appear in the nonlocal part of the potential, while additional nuclear velocity and acceleration-dependent corrections appear in the ultrasoft pseudopotential case. The use of the velocity-including atomic orbital basis enables a Galilean-invariant description of the nonadiabatic Ehrenfest molecular dynamics, removing spurious nonadiabatic couplings that arise from neglecting the nuclear velocity phases in the atomic orbitals.

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I. INTRODUCTION

Effective electronic Hamiltonians are widely used in condensed matter physics to describe the low-energy spectrum of the system and the related physical properties [1]. Within the *ab initio* framework, the use of pseudopotentials enables the achievement of large computational gains with respect to all-electron calculations [2–9]. In the Born-Oppenheimer approximation, effective electronic Hamiltonians are usually derived starting from the all-electron one, at fixed nuclei, and excluding nonadiabatic effects. Even when nonadiabatic effects are included in the nuclear dynamics, the effective electronic Hamiltonians are still usually constructed using atomlike orbitals as if the nuclei were at rest or at most considering the electronic wave function rigidly shifting with the nuclei. This approach introduces discrepancies between the dynamics of the effective models and of the all-electron Hamiltonian. For example, in the context of the nonadiabatic molecular dynamics, spurious couplings arise in the effective Hamiltonian governing the temporal evolution of electronic systems [10–13]. They manifest in the paradox that a motion at constant velocity of an atom can induce electronic transitions [10,11], clearly breaking the principle of Galilean invariance. Analogously, the breaking of Galilean invariance manifests in the violation of nonadiabatic sum rules relating Born effective charges and the interatomic force constant

matrix to the frequency-dependent electromagnetic susceptibility when calculated with pseudopotential Hamiltonians obtained by rigidly shifting the electronic orbitals with the nuclei, as opposed to all-electron ones, as recently pointed out in Ref. [14].

These issues arise from neglecting the nuclear-velocity-dependent phases in atomlike orbitals [10,11,14–16], often called “electron-translation factors” in the literature. The use of the nuclear-velocity-including atomic orbital basis has a long history in the study of atomic collisions, where it was first introduced [17] and saw several developments [15,18–27]. In the study of the properties of molecules and solids, velocity-including atomic orbitals were first introduced by Nafie to assess vibrational circular dichroism (VCD) in Ref. [28] using the complete adiabatic approach [29]. Nuclear-velocity-dependent phases enable nonzero electronic currents and magnetic dipole moments, which, conversely, vanish for the standard real-valued Born-Oppenheimer electronic wave functions, resulting in a vanishing electronic contribution to VCD [30,31]. In this framework, nuclear velocity perturbation theory was developed and implemented, mainly for the purpose of determining VCD spectra [32–35]. It is worth noting that the exact factorization method [36] encodes these effects, as can be appreciated in the classical limit for the nuclear wave function [30].

Besides being essential for correctly describing VCD spectra, the use of the nuclear-velocity-including atomic orbital basis allows for the removal of spurious electronic transitions in the dynamics. This has been shown, at the linear order in the nuclear velocity, in the context of a time-dependent Hartree-Fock dynamics in Refs. [12,13,37,38] and for localized atomic orbitals in Refs. [10,11,16], as well as in the

context of time-dependent density-functional theory linear response theory in Refs. [39,40]. Furthermore, in the framework of the pseudopotential approximation, this approach restores the frequency-dependent sum rules, correctly accounting for nonadiabatic couplings and frequency-dependent vibrational responses within linear response theory and introducing corrections to the linear and angular momentum [14]. Nonetheless, nuclear velocity effects on the wave functions are still neglected in current implementations of first-principles nonadiabatic molecular dynamics [41–48].

The effects of the nuclear motion are also encoded in the electronic problem in the moving Born-Oppenheimer approximation [49] and the phase space method [50], as well as in the exact factorization [36] previously cited. In particular, the phase space method goes beyond the Born-Oppenheimer approximation by parametrizing the electronic states in terms of both the nuclear position and momentum, solving the issue of the spurious nonadiabatic coupling [51] and properly describing the vibrational circular dichroism [52]. Moreover, the inclusion of the effects of the nuclear motion on the electronic system ensures the conservation of the linear and angular momentum in the nonadiabatic dynamics [51,53,54], which otherwise is not guaranteed. The momentum conservation issue is also affected by the electronic basis completeness. For instance, when a truncated basis of adiabatic states is used, the Ehrenfest dynamics require the inclusion of the non-Abelian Berry connection to ensure the momentum conservation [55]. This issue further highlights the necessity of including the nuclear velocity dependence of the electronic orbitals since the adiabatic basis set—used in current implementations—is inadequate for describing dynamically moving atoms.

In this work, we determine the first-principles nonadiabatic semiclassical Ehrenfest dynamics, where nuclei are classical and electrons are quantum mechanical particles [56], within the projector augmented wave (PAW) method framework for both the ultrasoft and norm-conserving cases, using nuclear-velocity-including atomic orbitals. Our approach enables the removal of the spurious contribution in the nonadiabatic Ehrenfest dynamics, recovering the physical results of the all-electron dynamics with the pseudopotential one, where full Galilean invariance is respected. These nuclear velocity dependences manifest as Peierls-like phases appearing in the nonlocal part of the pseudopotential, capturing the response at any order in the nuclear velocity, as already discussed in Ref. [14]. We generalize the results of Ref. [14] to the case of ultrasoft pseudopotentials, and we consider the contributions from the temporal derivatives of the PAW transformation. They generate additional nuclear-velocity- and acceleration-dependent terms relevant in the ultrasoft case that were always neglected in previous studies.

This paper is organized as follows: In Sec. II we introduce the velocity-including atomic orbitals, studying the electronic problem for an isolated nucleus in motion, while in Sec. III we present the semiclassical Ehrenfest Lagrangian formalism used to derive the effective Hamiltonians and the equations of motion for velocity-including atomic orbitals. The standard PAW method is explained in Sec. IV, showing the adiabatic Hamiltonian and the related responses. These instruments allow us to review the currently implemented nonadiabatic PAW Ehrenfest dynamics [41–43] in Sec. IV B. Conversely,

Sec. V is devoted to explaining the PAW method with the velocity-including atomic orbitals, which enables a proper description of the nonadiabatic Ehrenfest dynamics in subsection of Sec. V. Finally, we draw our conclusions in Sec. VI. The Hamiltonians, the electronic temporal dynamics, and the conserved energies are compared with the results from the literature in Table II in Sec. V, which summarizes the main findings of this work.

II. VELOCITY-INCLUDING ATOMIC ORBITALS

Localized atomic orbital bases are usually constructed from the orbitals of isolated atoms with the nucleus fixed in its position. In this paragraph, we establish a localized atomic orbital basis for the case of moving nuclei.

Consider an isolated atom s with the nucleus at rest which, without loss of generality, is located at the origin. The electrons are described by a single-particle all-electron Hamiltonian:

$$\hat{H}_0^{\text{AE}}(\hat{\mathbf{r}}, \hat{\mathbf{p}}) = \frac{\hat{\mathbf{p}}^2}{2m} + V_s(\hat{\mathbf{r}}), \quad (1)$$

where the hat denotes operators, $V_s(\hat{\mathbf{r}})$ is the effective potential acting on the electron, and the subscript s indicates the dependence of the potential on the atomic properties of s . The Hamiltonian is diagonalized by the atomic orbitals $|\phi_{si}^0\rangle$ with energy E_{si} , where i indicates the electronic quantum number and the superscript 0 indicates that the orbitals $|\phi_{si}^0\rangle$ are solutions for the atom at rest at the origin,

$$\hat{H}_0^{\text{AE}}(\hat{\mathbf{r}}, \hat{\mathbf{p}}) |\phi_{si}^0\rangle = E_{si} |\phi_{si}^0\rangle. \quad (2)$$

Usually, localized atomic orbital bases are constructed using $|\phi_{si}^0\rangle$ orbitals, translated to the positions of atoms in the system,

$$|\phi_{si}^{\mathbf{R}_s}\rangle = \hat{T}_{\mathbf{R}_s} |\phi_{si}^0\rangle, \quad (3)$$

which form the basis set $\{|\phi_{si}^{\mathbf{R}_s}\rangle\}_{si}$. We remark that the translation operator $\hat{T}_{\mathbf{R}_s}$ acts on the position eigenstates as $\hat{T}_{\mathbf{R}_s} |\mathbf{r}\rangle = |\mathbf{r} + \mathbf{R}_s\rangle$. The rigid translation of the orbitals assumes that nuclei are static. If the nuclei are moving, with their coordinates explicitly depending on time $\mathbf{R}_s(t)$, the rigidly translated atomic orbitals, in spite of their common use, should be replaced by atomic orbitals accounting for the nuclear motion. In the following, we derive this basis set.

Suppose that, for $t < 0$, the s nucleus, identified by the coordinate $\mathbf{R}_s(t)$, is at rest $[\mathbf{R}_s(t < 0) = \mathbf{0}]$ and that, at $t = 0$, the nucleus starts moving with velocity $\dot{\mathbf{R}}_s(t)$ and acceleration $\ddot{\mathbf{R}}_s(t)$. At $t = 0$, $|\phi_{si}(t)\rangle = |\phi_{si}^0\rangle$; then the time evolution of the atomic orbital $|\phi_{si}(t)\rangle$ for $t > 0$ is determined by the Schrödinger equation with the Hamiltonian $\hat{H}^{\text{AE}}(\hat{\mathbf{r}}, \hat{\mathbf{p}}; \mathbf{R}_s(t))$, which depends on time through the nuclear position $\mathbf{R}_s(t)$,

$$i\hbar \frac{d}{dt} |\phi_{si}(t)\rangle = \hat{H}^{\text{AE}}(\hat{\mathbf{r}}, \hat{\mathbf{p}}; \mathbf{R}_s(t)) |\phi_{si}(t)\rangle, \quad (4)$$

$$\hat{H}^{\text{AE}}(\hat{\mathbf{r}}, \hat{\mathbf{p}}; \mathbf{R}_s(t)) = \frac{\hat{\mathbf{p}}^2}{2m} + V_s[\hat{\mathbf{r}} - \mathbf{R}_s(t)]. \quad (5)$$

For $t > 0$, we suppose that the solution of the above Schrödinger equation [Eq. (4)] is expressed in the form of

$$|\phi_{si}(t)\rangle = e^{i\alpha_s(\hat{\mathbf{r}})} \hat{T}_{\mathbf{R}_s(t)} e^{i\Theta(t)} |\phi'_{si}(t)\rangle, \quad (6)$$

$$\alpha_s(\hat{\mathbf{r}}) = \frac{m}{\hbar} \dot{\mathbf{R}}_s(t) \cdot [\hat{\mathbf{r}} - \mathbf{R}_s(t)], \quad (7)$$

$$\Theta(t) = -\frac{1}{\hbar} \left(E_{si} t - \int_0^t dt' \frac{m |\dot{\mathbf{R}}_s(t')|^2}{2} \right).$$

We remark that the velocity-dependent phase $\alpha_s(\hat{\mathbf{r}})$ does not depend on the choice of the origin of the reference frame. Its time dependence is instantaneous. Conversely, the purely time-dependent phase $\Theta(t)$ and $|\phi'_{si}(t)\rangle$ depend on the system's history. In particular, the phase $\Theta(t)$ depends on the temporal integration of the electron's kinetic energy moving at the velocity of the nucleus.

To obtain the differential equation for $|\phi'_{si}(t)\rangle$, we plug Eq. (6) into Eq. (4). The temporal derivative on the left-hand side is

$$\begin{aligned} \frac{d|\phi_{si}(t)\rangle}{dt} &= e^{i\alpha_s(\hat{\mathbf{r}})} \hat{T}_{\mathbf{R}_s(t)} e^{i\Theta(t)} \left[\frac{d|\phi'_{si}(t)\rangle}{dt} - \frac{i}{\hbar} \left(E_{si} + \dot{\mathbf{R}}_s(t) \cdot \hat{\mathbf{p}} \right. \right. \\ &\quad \left. \left. - m \ddot{\mathbf{R}}_s(t) \cdot \hat{\mathbf{r}} + \frac{m |\dot{\mathbf{R}}_s(t)|^2}{2} \right) |\phi'_{si}(t)\rangle \right], \end{aligned} \quad (8)$$

where we used $\hat{T}_{\mathbf{R}_s(t)}^\dagger \hat{\mathbf{r}} \hat{T}_{\mathbf{R}_s(t)} = \hat{\mathbf{r}} + \mathbf{R}_s(t)$. On the right-hand side of Eq. (4), the application of the Hamiltonian to $|\phi_{si}(t)\rangle$ corresponds to

$$\begin{aligned} \hat{H}^{\text{AE}}(\hat{\mathbf{r}}, \hat{\mathbf{p}}; \mathbf{R}_s(t)) e^{i\alpha_s(\hat{\mathbf{r}})} \hat{T}_{\mathbf{R}_s(t)} \\ = e^{i\alpha_s(\hat{\mathbf{r}})} \hat{T}_{\mathbf{R}_s(t)} \hat{H}^{\text{AE}}(\hat{\mathbf{r}} + \mathbf{R}_s(t), \hat{\mathbf{p}} + m \dot{\mathbf{R}}_s(t); \mathbf{R}_s(t)), \end{aligned} \quad (9)$$

where we used $e^{-i\alpha_s(\hat{\mathbf{r}})} \hat{\mathbf{p}} e^{i\alpha_s(\hat{\mathbf{r}})} = \hat{\mathbf{p}} + m \dot{\mathbf{R}}_s(t)$. Conversely, the purely time-dependent phase factor commutes with the Hamiltonian. By putting together Eqs. (8) and (9), we find that the Schrödinger equation for moving nuclei in Eq. (4) is equivalent to the following equations for $|\phi'_{si}(t)\rangle$ with the boundary condition $|\phi'_{si}(t=0)\rangle = |\phi_{si}^0\rangle$:

$$i\hbar \frac{d|\phi'_{si}(t)\rangle}{dt} = [\hat{H}'^{\text{AE}}(\hat{\mathbf{r}}, \hat{\mathbf{p}}; \ddot{\mathbf{R}}_s(t)) - E_{si}] |\phi'_{si}(t)\rangle, \quad (10)$$

$$\hat{H}'^{\text{AE}}(\hat{\mathbf{r}}, \hat{\mathbf{p}}; \ddot{\mathbf{R}}_s(t)) = \frac{\hat{\mathbf{p}}^2}{2m} + V_s(\hat{\mathbf{r}}) + m \ddot{\mathbf{R}}_s(t) \cdot \hat{\mathbf{r}}. \quad (11)$$

$\hat{H}'^{\text{AE}}(\hat{\mathbf{r}}, \hat{\mathbf{p}}; \ddot{\mathbf{R}}_s(t))$ differs from $\hat{H}_0^{\text{AE}}(\hat{\mathbf{r}}, \hat{\mathbf{p}})$ only by the term $m \ddot{\mathbf{R}}_s(t) \cdot \hat{\mathbf{r}}$, which can be interpreted as the noninertial force acting on the electrons in the frame where the nucleus is at rest. Its effect on the Hamiltonian is analogous to a time-dependent electric field, described by the Stark effect.

If we neglect the nuclear acceleration term $m \ddot{\mathbf{R}}_s(t) \cdot \hat{\mathbf{r}}$ in the Hamiltonian $\hat{H}'^{\text{AE}}(\hat{\mathbf{r}}, \hat{\mathbf{p}}; \ddot{\mathbf{R}}_s(t))$, $|\phi'_{si}(t)\rangle = |\phi_{si}^0\rangle$, implying that $|\phi'_{si}(t)\rangle$ does not depend on the history of the system and that the atomic orbitals for static nuclei $|\phi_{si}^0\rangle$ satisfy Eq. (10).

Therefore, for moving nuclei the atomic orbitals should be expressed in the form of Eq. (6). The purely time-dependent phases, including those depending on the history of the system, do not affect the basis and can be removed. Consequently, we define the velocity-including localized atomic orbital as

$$|\phi_{si}^{\mathbf{R}_s, \mathbf{R}_s}\rangle = e^{i\frac{m}{\hbar} \dot{\mathbf{R}}_s(t) \cdot [\hat{\mathbf{r}} - \mathbf{R}_s(t)]} |\phi_{si}^{\mathbf{R}_s(t)}\rangle. \quad (12)$$

TABLE I. Summary of the notation used for the different kinds of atomic orbitals throughout the paper.

Atomic orbital for level i of atom s	
$ \phi_{si}^0\rangle$	For the atom centered at the origin
$ \phi_{si}^{\mathbf{R}_s}\rangle$	Translated to the fixed atomic equilibrium position
$ \phi_{si}^{\mathbf{R}_s(t)}\rangle$	Translated to the time-dependent atomic position
$ \phi_{si}^{\mathbf{R}_s, \mathbf{R}_s}\rangle$	$ \phi_{si}^{\mathbf{R}_s(t)}\rangle$ times the nuclear-velocity-dependent phase

In the superscript $\mathbf{R}_s, \mathbf{R}_s$ we omit the temporal dependence for brevity since it is clear from the context. The velocity-including basis set $\{|\phi_{si}^{\mathbf{R}_s, \mathbf{R}_s}\rangle\}_{si}$ depends on time instantaneously through the nuclear position $\mathbf{R}_s(t)$ and velocity $\dot{\mathbf{R}}_s(t)$. The temporal derivative of the states is

$$\begin{aligned} \frac{d|\phi_{si}^{\mathbf{R}_s, \mathbf{R}_s}\rangle}{dt} &= \frac{i}{\hbar} e^{i\alpha_s(\hat{\mathbf{r}})} \{ m \ddot{\mathbf{R}}_s(t) \cdot [\hat{\mathbf{r}} - \mathbf{R}_s(t)] \\ &\quad - \dot{\mathbf{R}}_s(t) \cdot \hat{\mathbf{p}} - m |\dot{\mathbf{R}}_s(t)|^2 \} |\phi_{si}^{\mathbf{R}_s(t)}\rangle, \end{aligned} \quad (13)$$

and if we use $e^{i\alpha_s(\hat{\mathbf{r}})} \hat{\mathbf{p}} e^{-i\alpha_s(\hat{\mathbf{r}})} = \hat{\mathbf{p}} - m \dot{\mathbf{R}}_s(t)$,

$$\begin{aligned} \frac{d|\phi_{si}^{\mathbf{R}_s, \mathbf{R}_s}\rangle}{dt} &= \frac{i}{\hbar} \{ m \ddot{\mathbf{R}}_s(t) \cdot [\hat{\mathbf{r}} - \mathbf{R}_s(t)] \\ &\quad - \dot{\mathbf{R}}_s(t) \cdot \hat{\mathbf{p}} \} |\phi_{si}^{\mathbf{R}_s, \mathbf{R}_s}\rangle. \end{aligned} \quad (14)$$

In the construction of the localized atomic orbital basis set, neglecting the nuclear acceleration term, which induces a Stark effect, causes a small error. Indeed, we are excluding the mixing, due to the Stark effect, of the occupied states with orbitals that are not included in the basis set. These contributions are small because of the large energy difference between the occupied states and those excluded from the basis set, becoming increasingly smaller as the basis set is enlarged.

The notation used to indicate the atomic orbitals is summarized in Table I. From now on, we omit the hat unless it is important for context.

III. NONADIABATIC EHRENFEST DYNAMICS

Consider a system of classical nuclei with mass M_s , located at positions $\{\mathbf{R}_s(t)\}$, and quantum electrons. The all-electron single-particle mean-field Hamiltonian $\hat{H}$ presents an effective self-consistent local potential $V(\hat{\mathbf{r}})$, obtained with a density functional theory (DFT) local or semilocal approximation for the exchange-correlation functional. We do not explicitly treat the self-consistent potential since it is local, adding no complications compared with the non-self-consistent case for our purposes. Therefore, the single-particle Hamiltonian of the electron interacting with many nuclei is

$$\hat{H}^{\text{AE}}(\hat{\mathbf{r}}, \hat{\mathbf{p}}; \{\mathbf{R}_s(t)\}) = \frac{\hat{\mathbf{p}}^2}{2m} + V(\hat{\mathbf{r}}). \quad (15)$$

At zero temperature, the system of electrons and nuclei can be described by the real-valued Ehrenfest Lagrangian [56], depending on the independent variables

$$\mathbf{q} = (\{\mathbf{R}_s(t)\}_s, \{|\psi_I(t)\rangle\}_I, \{\langle\psi_I(t)|\}_I),$$

$$\mathcal{L}(\mathbf{q}) = \sum_s \frac{M_s |\dot{\mathbf{R}}_s(t)|^2}{2} - \sum_{I=1}^{N_{\text{el}}} \left[\langle\psi_I(t)| \hat{H}^{\text{AE}} |\psi_I(t)\rangle - \frac{i\hbar}{2} \left(\langle\psi_I(t)| \frac{d}{dt} |\psi_I(t)\rangle - \frac{d}{dt} \langle\psi_I(t)| |\psi_I(t)\rangle \right) \right], \quad (16)$$

$$\mathcal{L}'(\mathbf{q}') = \sum_s \frac{M_s |\dot{\mathbf{R}}_s(t)|^2}{2} - \sum_{I=1}^{N_{\text{el}}} \left[\langle\psi'_I(t)| \mathcal{R}^\dagger(t) \hat{H}^{\text{AE}} \mathcal{R}(t) |\psi'_I(t)\rangle + \frac{i\hbar}{2} \left(\langle\psi'_I(t)| \frac{d\mathcal{R}^\dagger(t)}{dt} \mathcal{R}(t) - \mathcal{R}^\dagger(t) \frac{d\mathcal{R}(t)}{dt} |\psi'_I(t)\rangle \right) + \frac{d}{dt} \langle\psi'_I(t)| \mathcal{R}^\dagger(t) \mathcal{R}(t) |\psi'_I(t)\rangle - \langle\psi'_I(t)| \mathcal{R}^\dagger(t) \mathcal{R}(t) \frac{d}{dt} |\psi'_I(t)\rangle \right], \quad (18)$$

where the independent variables are $\mathbf{q}' = (\{\mathbf{R}_s(t)\}_s, \{|\psi'_I(t)\rangle\}_I, \{\langle\psi'_I(t)|\}_I)$. We do not treat the finite-temperature case directly in the Lagrangian, but it can be obtained with straightforward generalizations. In the following sections, we use Eq. (18) to determine the Ehrenfest Lagrangian for the PAW method with the inclusion of the nuclear velocity phases in the atomic orbitals.

The equations of motion for the nuclear and electronic variables are determined by requiring the action $\mathcal{A} = 1/T \int_0^T \mathcal{L} dt$ to be stationary for a variation of an independent variable of the Lagrangian, i.e., $\frac{\delta \mathcal{A}}{\delta q_i} = 0$. Usually, the Lagrangian depends on $\mathbf{q}$ and $\dot{\mathbf{q}}$, implying that the equations of motion are the Euler-Lagrange equations

$$\frac{\partial \mathcal{L}(\mathbf{q}, \dot{\mathbf{q}})}{\partial q_i} - \frac{d}{dt} \frac{\partial \mathcal{L}(\mathbf{q}, \dot{\mathbf{q}})}{\partial \dot{q}_i} = 0, \quad (19)$$

which are always used in this work for the electronic degrees of freedom (wave functions). The conserved energy is obtained as the Legendre transformation of the Lagrangian

$$E = \sum_i \frac{\partial \mathcal{L}(\mathbf{q}, \dot{\mathbf{q}})}{\partial \dot{q}_i} \dot{q}_i - \mathcal{L}(\mathbf{q}, \dot{\mathbf{q}}). \quad (20)$$

Conversely, the nuclear-velocity dependence of the atomic orbitals may lead to a nuclear-acceleration dependence in the effective model's Lagrangian. Consequently, the Euler-Lagrange equations need to be generalized to higher orders to describe nuclear dynamics. Under the assumption that the highest-order temporal derivative is the second-order one, the Euler-Lagrange equations are generalized as [57–59]

$$\frac{\partial \mathcal{L}(\mathbf{q}, \dot{\mathbf{q}}, \ddot{\mathbf{q}})}{\partial q_i} - \frac{d}{dt} \frac{\partial \mathcal{L}(\mathbf{q}, \dot{\mathbf{q}}, \ddot{\mathbf{q}})}{\partial \dot{q}_i} + \frac{d^2}{dt^2} \frac{\partial \mathcal{L}(\mathbf{q}, \dot{\mathbf{q}}, \ddot{\mathbf{q}})}{\partial \ddot{q}_i} = 0. \quad (21)$$

Specifically, the equations for the nuclear system are obtained by setting $q_i \rightarrow \mathbf{R}_s$. Explicitly, if the Lagrangian also depends on the nuclear acceleration, the forces governing the nuclear dynamics are

$$M_s \ddot{\mathbf{R}}_s(t) = \frac{\partial \mathcal{L}_{\text{el}}}{\partial \mathbf{R}_s} - \frac{d}{dt} \frac{\partial \mathcal{L}_{\text{el}}}{\partial \dot{\mathbf{R}}_s} + \frac{d^2}{dt^2} \frac{\partial \mathcal{L}_{\text{el}}}{\partial \ddot{\mathbf{R}}_s}, \quad (22)$$

where $\mathcal{L}_{\text{el}} = \mathcal{L} - \sum_s \frac{M_s |\dot{\mathbf{R}}_s(t)|^2}{2}$. Even though derivatives of the nuclear acceleration appear in the transformed Lagrangian, the physics of the system is the same as that described

where $|\psi_I(t)\rangle$ are the solutions of Eq. (15) and N_{el} is the number of electrons. In addition, if we apply a transformation that depends on time to the wave function

$$|\psi_I(t)\rangle = \mathcal{R}(t) |\psi'_I(t)\rangle, \quad (17)$$

the Ehrenfest Lagrangian in Eq. (16) is transformed to

by the all-electron Lagrangian, depending only on the nuclear position and velocity, since the two are mapped by the PAW transformation [60]. In the presence of a dependence on second-order derivatives of the variables $\mathbf{q}$ in the Lagrangian, the energy is obtained through Ostrogradsky's construction [57–59] as

$$E = \sum_i \frac{\partial \mathcal{L}(\mathbf{q}, \dot{\mathbf{q}}, \ddot{\mathbf{q}})}{\partial \ddot{q}_i} \ddot{q}_i - \mathcal{L}(\mathbf{q}, \dot{\mathbf{q}}, \ddot{\mathbf{q}}) + \sum_i \left[\left(\frac{\partial \mathcal{L}(\mathbf{q}, \dot{\mathbf{q}}, \ddot{\mathbf{q}})}{\partial \dot{q}_i} - \frac{d}{dt} \frac{\partial \mathcal{L}(\mathbf{q}, \dot{\mathbf{q}}, \ddot{\mathbf{q}})}{\partial \ddot{q}_i} \right) \dot{q}_i \right]. \quad (23)$$

In the absence of an explicit time dependence in the Lagrangian, the total energy is conserved because the time derivative of E is zero along the trajectory of the system. The Lagrangians presented in this work do not have an explicit time dependence. This implies that the energy, obtained either with the usual Hamiltonian formulation in Eq. (20) or with the Ostrogradsky generalization in Eq. (23), is always conserved.

IV. PAW METHOD

The projector augmented wave method, developed in Ref. [6], determines the single-particle pseudo-wave-function $|\tilde{\psi}\rangle$ through a linear transformation $\hat{\mathcal{T}}$ applied to the all-electron wave function,

$$|\psi\rangle = \hat{\mathcal{T}} |\tilde{\psi}\rangle. \quad (24)$$

In the original formulation, with atomic orbitals for nuclei at rest centered at the positions of the nuclei, the linear transformation is defined by selecting a set of all-electron partial waves $|\phi_{si}^{\mathbf{R}_s}\rangle$ obtained by applying the transformation $\hat{\mathcal{T}}$ to the set of pseudopartial waves $|\tilde{\phi}_{si}^{\mathbf{R}_s}\rangle$:

$$\hat{\mathcal{T}} = \hat{\mathbb{1}} + \sum_s \hat{t}^s, \quad \hat{t}^s = \sum_i (|\phi_{si}^{\mathbf{R}_s}\rangle - |\tilde{\phi}_{si}^{\mathbf{R}_s}\rangle) \langle \tilde{\phi}_{si}^{\mathbf{R}_s} |, \quad (25)$$

where the projectors $|\tilde{\phi}_{si}^{\mathbf{R}_s}\rangle$ satisfy the orthogonality relation with the pseudopartial waves $\langle \tilde{\phi}_{si}^{\mathbf{R}_s} | \tilde{\phi}_{s'j}^{\mathbf{R}_{s'}} \rangle = \delta_{ss'} \delta_{ij}$. We further assume that an augmentation region Ω_s around each site $\mathbf{R}_s$ exists where the all-electron partial waves $|\phi_{si}^{\mathbf{R}_s}\rangle$ form a complete set for the valence all-electron wave function. Outside that region, the all-electron and pseudopartial waves coincide, and the pseudoprojectors vanish. Finally, the augmentation regions do not overlap. We consider the nonrelativistic case with

spin-independent projectors for the sake of clarity. Generalizations to a system with spin-orbit coupling can be obtained within the fully relativistic PAW approach of Ref. [61] and do not affect the main findings of this work.

For a complete basis set, if $\mathbf{r} \in \Omega_s$, the following relations hold:

$$\begin{aligned} \sum_i \langle \mathbf{r} | \tilde{\phi}_{si}^{\mathbf{R}_s} \rangle \langle \tilde{p}_{si}^{\mathbf{R}_s} | \tilde{\psi} \rangle &= \langle \mathbf{r} | \tilde{\psi} \rangle, \\ \sum_i \langle \tilde{\psi} | \tilde{p}_{si}^{\mathbf{R}_s} \rangle \langle \tilde{\phi}_{si}^{\mathbf{R}_s} | \mathbf{r} \rangle &= \langle \tilde{\psi} | \mathbf{r} \rangle. \end{aligned} \quad (26)$$

Any local or semilocal operator transforms as [6]

$$\tilde{O} = \hat{T}^\dagger O \hat{T} = O + \sum_{s,ij} |\tilde{p}_{si}^{\mathbf{R}_s}\rangle \Delta O_{ij}^s \langle \tilde{p}_{sj}^{\mathbf{R}_s}|, \quad (27)$$

$$\Delta O_{ij}^s = \langle \phi_{si}^{\mathbf{R}_s} | O | \phi_{sj}^{\mathbf{R}_s} \rangle - \langle \tilde{\phi}_{si}^{\mathbf{R}_s} | O | \tilde{\phi}_{sj}^{\mathbf{R}_s} \rangle, \quad (28)$$

where the second equality requires the use of the identity in the augmentation region as given in Eq. (26), which holds for a complete basis set. The transformation rule for the operators in Eq. (27) implies that the identity operator in the all-electron wave function space transforms as

$$\begin{aligned} S = \hat{T}^\dagger \hat{T} &= \mathbb{1} + \sum_{s,ij} |\tilde{p}_{si}^{\mathbf{R}_s}\rangle Q_{ij}^s \langle \tilde{p}_{sj}^{\mathbf{R}_s}|, \\ Q_{ij}^s &= \langle \phi_{si}^{\mathbf{R}_s} | \phi_{sj}^{\mathbf{R}_s} \rangle - \langle \tilde{\phi}_{si}^{\mathbf{R}_s} | \tilde{\phi}_{sj}^{\mathbf{R}_s} \rangle, \end{aligned} \quad (29)$$

where $\mathbb{1}$ indicates the identity in the pseudo-wave-function space. As a consequence, the pseudo-wave-function is normalized as $\langle \tilde{\psi} | S | \tilde{\psi} \rangle = 1$. In the norm-conserving case, where $\langle \phi_{si}^{\mathbf{R}_s} | \phi_{sj}^{\mathbf{R}_s} \rangle = \langle \tilde{\phi}_{si}^{\mathbf{R}_s} | \tilde{\phi}_{sj}^{\mathbf{R}_s} \rangle$, the identity in the all-electron wave function space is mapped to the identity in the pseudo-wave-function space $S = \mathbb{1}$. The PAW Hamiltonian is analogously obtained as

$$\hat{H}^{\text{PAW}} = \hat{T}^\dagger \hat{H}^{\text{AE}} \hat{T} = \frac{\mathbf{p}^2}{2m} + V^{\text{loc}} + \sum_s v_s^{\text{nl}}. \quad (30)$$

V^{loc} is the local part of the pseudopotential plus, eventually, a DFT self-consistent potential; v_s^{nl} is the nonlocal part of the potential obtained as in Ref. [6]

A. Adiabatic PAW dynamics

In the adiabatic limit, the electronic wave function remains in the ground state, satisfying the eigenvalue equation [5,6,62,63], where H^{PAW} and S are time dependent through the nuclear motion as well as the instantaneous eigenvalues and eigenvectors,

$$H^{\text{PAW}} |\tilde{\psi}_I\rangle = E_I S |\tilde{\psi}_I\rangle. \quad (31)$$

The forces on the ions are [62,64–66]

$$M_s \ddot{\mathbf{R}}_s(t) = \mathbf{F}_s^{\text{HF}} + \mathbf{F}_s^S, \quad (32)$$

$$\mathbf{F}_s^{\text{HF}} = - \sum_{I=1}^{N_{\text{el}}} \langle \tilde{\psi}_I | \frac{\partial H^{\text{PAW}}}{\partial \mathbf{R}_s} | \tilde{\psi}_I \rangle, \quad (33)$$

$$\mathbf{F}_s^S = \sum_{I=1}^{N_{\text{el}}} E_I \langle \tilde{\psi}_I | \frac{\partial S}{\partial \mathbf{R}_s} | \tilde{\psi}_I \rangle, \quad (34)$$

where the first contribution is the standard Hellmann-Feynman force $\mathbf{F}_s^{\text{HF}}$, i.e., the quantum mechanical average over the electronic ground state of the variation of the electronic Hamiltonian due to the nuclear displacement, and the second one, $\mathbf{F}_s^S$, is the force originating from the transformation of the identity operator in the pseudo-wave-function space. In the case of a norm-conserving pseudopotential $\mathbf{F}_s^S$ vanishes, leaving only the $\mathbf{F}_s^{\text{HF}}$ contribution to the forces.

B. Standard nonadiabatic PAW Ehrenfest dynamics

In this subsection, we present the equations of the PAW nonadiabatic Ehrenfest dynamics obtained with the electronic wave function rigidly shifting with the nuclei. These equations were presented in Refs. [41,42,67] and are currently implemented in the GPAW code [43].

The Ehrenfest Lagrangian is obtained using Eq. (18) with the transformation $\hat{T}$, defined in Eq. (25), with the nuclear positions explicitly depending on time $\mathbf{R}_s(t)$:

$$\begin{aligned} \mathcal{L}_R^{\text{PAW}} &= \sum_s \frac{M_s |\dot{\mathbf{R}}_s(t)|^2}{2} - \sum_{I=1}^{N_{\text{el}}} \left[\langle \tilde{\psi}_I(t) | \hat{H}_R^{\text{PAW}} | \tilde{\psi}_I(t) \rangle \right. \\ &\quad \left. + \frac{i\hbar}{2} \left(\frac{d \langle \tilde{\psi}_I(t) |}{dt} S | \tilde{\psi}_I(t) \rangle - \langle \tilde{\psi}_I(t) | S \frac{d | \tilde{\psi}_I(t) \rangle}{dt} \right) \right], \end{aligned} \quad (35)$$

where

$$\hat{H}_R^{\text{PAW}} = \hat{H}^{\text{PAW}} + \frac{i\hbar}{2} \left(\frac{d \hat{T}^\dagger}{dt} \hat{T} - \hat{T}^\dagger \frac{d \hat{T}}{dt} \right). \quad (36)$$

The S -matrix here is time dependent, different from the adiabatic case, due to the time dependence of the nuclear positions $\mathbf{R}_s(t)$ to be used in Eq. (29). As shown in detail in Appendix C, the temporal derivative of the transformation, entering Eq. (36), is [41,42]

$$\frac{d \hat{T}}{dt} = -\frac{i}{\hbar} \sum_s [\dot{\mathbf{R}}_s(t) \cdot \hat{\mathbf{p}}, \hat{T}^s], \quad (37)$$

implying that

$$\begin{aligned} \frac{i\hbar}{2} \left(\frac{d \hat{T}^\dagger}{dt} \hat{T} - \hat{T}^\dagger \frac{d \hat{T}}{dt} \right) &= - \sum_s \dot{\mathbf{R}}_s(t) \cdot \mathbf{C}_s, \\ \mathbf{C}_s &= \sum_{ij} \left(- \left\{ \frac{\hat{\mathbf{p}}}{2}, |\tilde{p}_{si}^{\mathbf{R}_s(t)}\rangle Q_{ij}^s \langle \tilde{p}_{sj}^{\mathbf{R}_s(t)}| \right\} \right. \\ &\quad \left. + |\tilde{p}_{si}^{\mathbf{R}_s(t)}\rangle \Delta \hat{\mathbf{p}}_{ij}^s \langle \tilde{p}_{sj}^{\mathbf{R}_s(t)}| \right), \end{aligned} \quad (38)$$

where $\{\cdot, \cdot\}$ is the anticommutator and Δ is used in the sense of Eq. (28). Therefore, the electronic and nuclear dynamics are obtained from the standard Euler-Lagrange equations [Eq. (19)],

$$i\hbar S \frac{d | \tilde{\psi}_I(t) \rangle}{dt} = \left(H_R^{\text{PAW}} - \frac{i\hbar}{2} \frac{d S}{dt} \right) | \tilde{\psi}_I(t) \rangle, \quad (39)$$

where the effective Hamiltonian governing the electronic dynamics is

$$H_R^{\text{PAW}} - \frac{i\hbar}{2} \frac{dS(t)}{dt} = H^{\text{PAW}} - i\hbar \hat{T}^\dagger \frac{d\hat{T}}{dt},$$

$$-i\hbar \hat{T}^\dagger \frac{d\hat{T}}{dt} = - \sum_{s,ij} \dot{\mathbf{R}}_s(t) \cdot (|\tilde{p}_{si}^{\mathbf{R}_s(t)}\rangle \Delta \hat{\mathbf{p}}_{ij}^s \langle \tilde{p}_{sj}^{\mathbf{R}_s(t)}|$$

$$- |\tilde{p}_{si}^{\mathbf{R}_s(t)}\rangle Q_{ij}^s \langle \tilde{p}_{sj}^{\mathbf{R}_s(t)}| \hat{\mathbf{p}}). \quad (40)$$

Compared to the adiabatic dynamics, Eq. (40) contains an additional time-dependent term, $-i\hbar \hat{T}^\dagger \frac{d\hat{T}}{dt}$. This term introduces coupling between different electronic states, even when the entire system undergoes a global translation at constant speed, breaking Galilean invariance [11]. As shown in Appendix A, the presence of time-dependent S makes it so that the evolution of the pseudo-wave-function is determined by a non-Hermitian operator, $H_R^{\text{PAW}} - \frac{i\hbar}{2} \frac{dS}{dt}$. This allows for the norm conservation of $\langle \tilde{\psi}(t) | S | \tilde{\psi}(t) \rangle$ along the temporal evolution.

According to Eq. (22), the nuclear dynamics is governed by the following equation:

$$M_s \ddot{\mathbf{R}}_s(t) = \mathbf{F}_s^{\text{HF}} + \mathbf{F}_s^{\text{HF}-\dot{\mathbf{R}}} + \mathbf{F}_s^{\text{S}}, \quad (41)$$

where

$$\mathbf{F}_s^{\text{HF}} = - \sum_{I=1}^{N_{\text{el}}} \langle \tilde{\psi}_I(t) | \frac{\partial H_R^{\text{PAW}}}{\partial \mathbf{R}_s} | \tilde{\psi}_I(t) \rangle,$$

$$\mathbf{F}_s^{\text{HF}-\dot{\mathbf{R}}} = \sum_{I=1}^{N_{\text{el}}} \frac{d}{dt} \langle \tilde{\psi}_I(t) | \frac{\partial H_R^{\text{PAW}}}{\partial \dot{\mathbf{R}}_s} | \tilde{\psi}_I(t) \rangle,$$

$$\frac{\partial H_R^{\text{PAW}}}{\partial \dot{\mathbf{R}}_s} = -\mathbf{C}_s,$$

$$\mathbf{F}_s^{\text{S}} = \frac{i\hbar}{2} \sum_{I=1}^{N_{\text{el}}} \left(\langle \tilde{\psi}_I(t) | \frac{\partial S}{\partial \mathbf{R}_s} \frac{d}{dt} | \tilde{\psi}_I(t) \rangle \right.$$

$$\left. - \frac{d}{dt} \langle \tilde{\psi}_I(t) | \frac{\partial S}{\partial \mathbf{R}_s} | \tilde{\psi}_I(t) \rangle \right). \quad (42)$$

$\mathbf{F}_s^{\text{HF}}$ and $\mathbf{F}_s^{\text{S}}$ reduce to Eqs. (33) and (34) in the adiabatic limit, where H_R^{PAW} reduces to H^{PAW} . In addition, in the nonadiabatic dynamics, an additional Hellmann-Feynman contribution, $\mathbf{F}_s^{\text{HF}-\dot{\mathbf{R}}}$, appears due to the nuclear velocity dependence in the electronic part of the Lagrangian, expressed as the time derivative of a Hellmann-Feynman term entailing the nuclear velocity derivative [41].

Finally, according to Eq. (20), the conserved energy is

$$E_R^{\text{PAW}} = \sum_s \frac{M_s}{2} |\dot{\mathbf{R}}_s(t)|^2 + \sum_{I=1}^{N_{\text{el}}} \langle \tilde{\psi}_I(t) | \hat{H}^{\text{PAW}} | \tilde{\psi}_I(t) \rangle, \quad (44)$$

where all the terms that are linear in the derivatives of the independent variables of the Lagrangian cancel.

Norm-conserving case

In the norm-conserving case, where $S = \mathbb{1}$, $Q_{ij}^s = 0$, and

$$\mathbf{C}_s^{\text{NC}} = \sum_{ij} |\tilde{p}_{si}^{\mathbf{R}_s(t)}\rangle \Delta \hat{\mathbf{p}}_{ij}^s \langle \tilde{p}_{sj}^{\mathbf{R}_s(t)}|, \quad (45)$$

the Hamiltonian reduces to

$$H_R^{\text{PAW-NC}} = H^{\text{PAW}} - \sum_s \dot{\mathbf{R}}_s(t) \cdot \mathbf{C}_s^{\text{NC}}. \quad (46)$$

The Schrödinger equation for the pseudo-wave-functions is

$$i\hbar \frac{d}{dt} |\tilde{\psi}_I(t)\rangle = H_R^{\text{PAW-NC}} |\tilde{\psi}_I(t)\rangle. \quad (47)$$

In addition, the nuclear dynamics of Eq. (41) is governed by $\mathbf{F}_s^{\text{HF}}$ and $\mathbf{F}_s^{\text{HF}-\dot{\mathbf{R}}}$, obtained from the derivative of the norm-conserving Lagrangian, since $\mathbf{F}_s^{\text{S}}$ is zero.

V. VELOCITY-INCLUDING PAW

With a procedure analogous to the one followed in Refs. [68–70] for the inclusion of magnetic fields in the PAW method, we define the nuclear-velocity-including PAW transformation operator by substituting the atomic orbitals for fixed nuclei with the velocity-including ones defined in Eq. (12). We assume that the atomic orbitals centered on a nucleus feel only the motion of that nucleus; in other words, atomic orbitals are those obtained as if each nucleus were isolated, and then, we exploit the superposition principle to construct the transformation operator for the entire wave function. The pseudo-wave-function $|\tilde{\psi}\rangle$ is mapped to the velocity-including all-electron one by the transformation operator for velocity-including orbitals $\hat{T}_R$,

$$|\psi\rangle = \hat{T}_R |\tilde{\psi}\rangle, \quad (48)$$

$$\hat{T}_R = \hat{\mathbb{1}} + \sum_s \hat{t}_{\mathbf{R}_s}^s,$$

$$\hat{t}_{\mathbf{R}_s}^s = \sum_i e^{i\alpha_s(\hat{\mathbf{r}})} (|\phi_{si}^{\mathbf{R}_s(t)}\rangle - |\tilde{\phi}_{si}^{\mathbf{R}_s(t)}\rangle) \langle \tilde{p}_{si}^{\mathbf{R}_s(t)}| e^{-i\alpha_s(\hat{\mathbf{r}})}. \quad (49)$$

This expression coincides with the one given in the Supplemental Material of Ref. [14]. In the following, for brevity we indicate the nuclear velocity phase using $\alpha_s(\hat{\mathbf{r}}) = \frac{m}{\hbar} \mathbf{R}_s(t) \cdot [\hat{\mathbf{r}} - \mathbf{R}_s(t)]$, as in Eq. (6).

The transformation operator depends on both the time-dependent nuclear positions and velocities. For a complete basis set, the relations for the standard PAW of Eq. (26), assuming that $\mathbf{r} \in \Omega_s$, are transformed as

$$\sum_i \langle \mathbf{r} | (e^{i\alpha_s(\hat{\mathbf{r}})} |\tilde{\phi}_{si}^{\mathbf{R}_s}\rangle \langle \tilde{p}_{si}^{\mathbf{R}_s}| e^{-i\alpha_s(\hat{\mathbf{r}})}) e^{i\alpha_s(\hat{\mathbf{r}})} | \tilde{\psi} \rangle$$

$$= e^{i\alpha_s(\mathbf{r})} \langle \mathbf{r} | \tilde{\psi} \rangle,$$

$$\sum_i \langle \tilde{\psi} | e^{-i\alpha_s(\hat{\mathbf{r}})} (e^{i\alpha_s(\hat{\mathbf{r}})} |\tilde{\phi}_{si}^{\mathbf{R}_s}\rangle \langle \tilde{p}_{si}^{\mathbf{R}_s}| e^{-i\alpha_s(\hat{\mathbf{r}})}) | \mathbf{r} \rangle$$

$$= \langle \tilde{\psi} | \mathbf{r} \rangle e^{-i\alpha_s(\mathbf{r})}. \quad (50)$$

The transformation of the operators in Eq. (27) (also given in the Supplemental Material of Ref. [14]) is generalized to an expression analogous to the case of the presence of a magnetic field [68]:

$$\tilde{O} = O + \sum_{s,ij} e^{i\alpha_s(\hat{\mathbf{r}})} |\tilde{p}_{si}^{\mathbf{R}_s(t)}\rangle \Delta O_{ij}^{s,\dot{\mathbf{R}}} \langle \tilde{p}_{sj}^{\mathbf{R}_s(t)}| e^{-i\alpha_s(\hat{\mathbf{r}})},$$

$$\Delta O_{ij}^{s,\dot{\mathbf{R}}} = \langle \phi_{si}^{\mathbf{R}_s(t)} | e^{-i\alpha_s(\hat{\mathbf{r}})} O e^{i\alpha_s(\hat{\mathbf{r}})} | \phi_{sj}^{\mathbf{R}_s(t)} \rangle$$

$$- \langle \tilde{\phi}_{si}^{\mathbf{R}_s(t)} | e^{-i\alpha_s(\hat{\mathbf{r}})} O e^{i\alpha_s(\hat{\mathbf{r}})} | \tilde{\phi}_{sj}^{\mathbf{R}_s(t)} \rangle. \quad (51)$$

The identity operator for the velocity-including case is transformed as the generalization of the standard expression given in Eq. (29):

$$S_{\mathbf{R},\dot{\mathbf{R}}} = \hat{\mathcal{T}}_{\mathbf{R}}^\dagger \hat{\mathcal{T}}_{\mathbf{R}} = \mathbb{1} + \sum_{s,ij} e^{i\alpha_s(\hat{\mathbf{r}})} |\tilde{p}_{si}^{\mathbf{R}_s(t)}\rangle \mathcal{Q}_{ij}^s \langle \tilde{p}_{sj}^{\mathbf{R}_s(t)}| e^{-i\alpha_s(\hat{\mathbf{r}})},$$

$$\mathcal{Q}_{ij}^s = \langle \phi_{si}^{\mathbf{R}_s(t)} | \phi_{sj}^{\mathbf{R}_s(t)} \rangle - \langle \tilde{\phi}_{si}^{\mathbf{R}_s(t)} | \tilde{\phi}_{sj}^{\mathbf{R}_s(t)} \rangle. \quad (52)$$

$S_{\mathbf{R},\dot{\mathbf{R}}}$ depends on both the nuclear positions and velocities.

Velocity-including Ehrenfest dynamics

In this subsection, we derive the nonadiabatic Ehrenfest dynamics by using the velocity-including PAW method. The Ehrenfest Lagrangian is obtained using Eq. (18) with the transformation $\hat{\mathcal{T}}_{\mathbf{R}}$, defined in Eq. (49), as

$$\mathcal{L}_{\mathbf{R},\dot{\mathbf{R}}}^{\text{PAW}} = \sum_s \frac{M_s |\dot{\mathbf{R}}_s(t)|^2}{2} - \sum_{I=1}^{N_{\text{el}}} \left[\langle \tilde{\psi}_I(t) | \hat{H}_{\mathbf{R},\dot{\mathbf{R}}}^{\text{PAW}} | \tilde{\psi}_I(t) \rangle \right. \\ \left. + \frac{i\hbar}{2} \left(\frac{d}{dt} \langle \tilde{\psi}_I(t) | S_{\mathbf{R},\dot{\mathbf{R}}} | \tilde{\psi}_I(t) \rangle \right. \right. \\ \left. \left. - \langle \tilde{\psi}_I(t) | S_{\mathbf{R},\dot{\mathbf{R}}} | \frac{d}{dt} \langle \tilde{\psi}_I(t) \rangle \right) \right], \quad (53)$$

where

$$\hat{H}_{\mathbf{R},\dot{\mathbf{R}}}^{\text{PAW}} = \hat{\mathcal{T}}_{\mathbf{R}}^\dagger \hat{H}^{\text{AE}}(\hat{\mathbf{r}}, \hat{\mathbf{p}}; \{\mathbf{R}_s(t)\}) \hat{\mathcal{T}}_{\mathbf{R}} + \frac{i\hbar}{2} \left(\frac{d\hat{\mathcal{T}}_{\mathbf{R}}^\dagger}{dt} \hat{\mathcal{T}}_{\mathbf{R}} - \hat{\mathcal{T}}_{\mathbf{R}}^\dagger \frac{d\hat{\mathcal{T}}_{\mathbf{R}}}{dt} \right). \quad (54)$$

We are going to drop $\{\mathbf{R}_s(t)\}$ in the following. The contribution from the temporal derivative is crucial to obtain

$$\frac{i\hbar}{2} \left(\frac{d\hat{\mathcal{T}}_{\mathbf{R}}^\dagger}{dt} \hat{\mathcal{T}}_{\mathbf{R}} - \hat{\mathcal{T}}_{\mathbf{R}}^\dagger \frac{d\hat{\mathcal{T}}_{\mathbf{R}}}{dt} \right) = -i\hbar \sum_{s,ij} \left(e^{i\alpha_s(\hat{\mathbf{r}})} |\tilde{p}_{si}^{\mathbf{R}_s(t)}\rangle \Delta \mathbf{D}_{ij}^{s,\dot{\mathbf{R}}} \langle \tilde{p}_{sj}^{\mathbf{R}_s(t)}| e^{-i\alpha_s(\hat{\mathbf{r}})} - \left\{ \frac{\mathbf{D}_s}{2}, e^{i\alpha_s(\hat{\mathbf{r}})} |\tilde{p}_{si}^{\mathbf{R}_s(t)}\rangle \mathcal{Q}_{ij}^s \langle \tilde{p}_{sj}^{\mathbf{R}_s(t)}| e^{-i\alpha_s(\hat{\mathbf{r}})} \right\} \right). \quad (59)$$

Explicitly,

$$\Delta \mathbf{D}_{ij}^{s,\dot{\mathbf{R}}} = \frac{i}{\hbar} \left(\langle \phi_{si}^{\mathbf{R}_s(t)} | \{m\ddot{\mathbf{R}}_s(t) \cdot [\hat{\mathbf{r}} - \mathbf{R}_s(t)] - \dot{\mathbf{R}}_s(t) \cdot \hat{\mathbf{p}} - m|\dot{\mathbf{R}}_s(t)|^2 \} | \phi_{sj}^{\mathbf{R}_s(t)} \rangle \right. \\ \left. - \langle \tilde{\phi}_{si}^{\mathbf{R}_s(t)} | \{m\ddot{\mathbf{R}}_s(t) \cdot [\hat{\mathbf{r}} - \mathbf{R}_s(t)] - \dot{\mathbf{R}}_s(t) \cdot \hat{\mathbf{p}} - m|\dot{\mathbf{R}}_s(t)|^2 \} | \tilde{\phi}_{sj}^{\mathbf{R}_s(t)} \rangle \right). \quad (60)$$

Summing Eqs. (55) and (59), we obtain the effective Hamiltonian from Eq. (54):

$$\hat{H}_{\mathbf{R},\dot{\mathbf{R}}}^{\text{PAW}} = \frac{\hat{\mathbf{p}}^2}{2m} + V^{\text{loc}}(\hat{\mathbf{r}}) + \sum_s e^{i\alpha_s(\hat{\mathbf{r}})} v_s^{\text{nl}} e^{-i\alpha_s(\hat{\mathbf{r}})} + \sum_{s,ij} \left(m\ddot{\mathbf{R}}_s(t) \cdot e^{i\alpha_s(\hat{\mathbf{r}})} |\tilde{p}_{si}^{\mathbf{R}_s(t)}\rangle \mathbf{d}_{ij}^s \langle \tilde{p}_{sj}^{\mathbf{R}_s(t)}| e^{-i\alpha_s(\hat{\mathbf{r}})} \right. \\ \left. - \frac{1}{2} \left\{ m\ddot{\mathbf{R}}_s(t) \cdot [\hat{\mathbf{r}} - \mathbf{R}_s(t)] - \dot{\mathbf{R}}_s(t) \cdot \hat{\mathbf{p}} + \frac{m|\dot{\mathbf{R}}_s(t)|^2}{2}, e^{i\alpha_s(\hat{\mathbf{r}})} |\tilde{p}_{si}^{\mathbf{R}_s(t)}\rangle \mathcal{Q}_{ij}^s \langle \tilde{p}_{sj}^{\mathbf{R}_s(t)}| e^{-i\alpha_s(\hat{\mathbf{r}})} \right\} \right). \quad (61)$$

We have defined, following the notation used in Ref. [71], the quantity

$$\mathbf{d}_{ij}^s = \langle \phi_{si}^{\mathbf{R}_s(t)} | [\hat{\mathbf{r}} - \mathbf{R}_s(t)] | \phi_{sj}^{\mathbf{R}_s(t)} \rangle - \langle \tilde{\phi}_{si}^{\mathbf{R}_s(t)} | [\hat{\mathbf{r}} - \mathbf{R}_s(t)] | \tilde{\phi}_{sj}^{\mathbf{R}_s(t)} \rangle. \quad (62)$$

The last line of Eq. (61) contains additional terms compared to the nuclear-velocity-including pseudopotential Hamiltonian given in Ref. [14]. While vanishing in the norm-conserving case, they cannot be neglected for ultrasoft pseudopotentials; however, they do not raise any particular computational issues. Indeed, $\mathbf{d}_{ij}^s$ is easily computed

the correct Hamiltonian. If we use $e^{-i\alpha_s(\hat{\mathbf{r}})} H^{\text{AE}}(\hat{\mathbf{r}}, \hat{\mathbf{p}}) e^{i\alpha_s(\hat{\mathbf{r}})} = H^{\text{AE}}(\hat{\mathbf{r}}, \hat{\mathbf{p}} + m\dot{\mathbf{R}}_s(t))$ and the transformation of the operators expressed in Eq. (51), it follows that (see Appendix B)

$$\hat{\mathcal{T}}_{\mathbf{R}}^\dagger \hat{H}^{\text{AE}}(\hat{\mathbf{r}}, \hat{\mathbf{p}}) \hat{\mathcal{T}}_{\mathbf{R}} = \frac{\hat{\mathbf{p}}^2}{2m} + V^{\text{loc}}(\hat{\mathbf{r}}) + \sum_s e^{i\alpha_s(\hat{\mathbf{r}})} v_s^{\text{nl}} e^{-i\alpha_s(\hat{\mathbf{r}})} \\ + \sum_{s,ij} e^{i\alpha_s(\hat{\mathbf{r}})} |\tilde{p}_{si}^{\mathbf{R}_s(t)}\rangle \Delta \mathcal{H}_{ij}^s \langle \tilde{p}_{sj}^{\mathbf{R}_s(t)}| e^{-i\alpha_s(\hat{\mathbf{r}})}, \quad (55)$$

where

$$\mathcal{H} = H^{\text{AE}}(\hat{\mathbf{r}}, \hat{\mathbf{p}} + m\dot{\mathbf{R}}_s(t)) - H^{\text{AE}}(\hat{\mathbf{r}}, \hat{\mathbf{p}}) \\ = \dot{\mathbf{R}}_s(t) \cdot \hat{\mathbf{p}} + \frac{m}{2} |\dot{\mathbf{R}}_s(t)|^2, \quad (56)$$

and we stress that $\Delta \mathcal{H}_{ij}^s$ is computed as in Eq. (28). To determine the contribution to the Hamiltonian in Eq. (54) originating in the temporal derivatives of the transformation, as expressed in detail in Appendix C, we compute $\frac{d\hat{\mathcal{T}}_{\mathbf{R}}}{dt}$, which, using Eq. (14) and defining

$$\mathbf{D}_s(\hat{\mathbf{r}}, \hat{\mathbf{p}}) = \frac{i}{\hbar} \{m\ddot{\mathbf{R}}_s(t) \cdot [\hat{\mathbf{r}} - \mathbf{R}_s(t)] - \dot{\mathbf{R}}_s(t) \cdot \hat{\mathbf{p}}\}, \quad (57)$$

is expressed as

$$\frac{d\hat{\mathcal{T}}_{\mathbf{R}}}{dt} = \sum_s [\mathbf{D}_s(\hat{\mathbf{r}}, \hat{\mathbf{p}}), \hat{t}_{\mathbf{R}_s}^s]. \quad (58)$$

$\frac{d\hat{\mathcal{T}}_{\mathbf{R}}}{dt}$ vanishes outside each augmentation region Ω_s . As explained in detail in Appendix C, we obtain

in the ultrasoft pseudopotential implementations [66,71]. Also, the term $\{[\hat{\mathbf{r}} - \mathbf{R}_s(t)], e^{i\alpha_s(\hat{\mathbf{r}})} |\tilde{p}_{si}^{\mathbf{R}_s(t)}\rangle \mathcal{Q}_{ij}^s \langle \tilde{p}_{sj}^{\mathbf{R}_s(t)}| e^{-i\alpha_s(\hat{\mathbf{r}})}\}$ is well-defined since it is localized in each augmentation region.

The $\Delta \hat{\mathbf{p}}_{ij}^s$ terms appearing in Eq. (38) are canceled by the momentum translation of the Hamiltonian due to the

TABLE II. Comparison of the Hamiltonians in the ultrasoft and norm-conserving cases, the Schrödinger equation for the electronic nonadiabatic Ehrenfest dynamics, and the conserved energy obtained by either rigidly shifting the electronic orbitals with the nuclei (left column and Refs. [41,42,67]) or applying the nuclear-velocity-dependent phases to the electronic wave function (right column).

Static Hamiltonian	
$\hat{H}^{\text{PAW}} = \frac{\mathbf{p}^2}{2m} + V^{\text{loc}} + \sum_s v_s^{\text{nl}}, \quad \text{Eq. (30)}$	
Refs. [41,42,67]	This work with velocity-including orbitals
Norm-conserving Hamiltonian	
$\hat{H}_{\text{R}}^{\text{PAW-NC}} = \hat{H}^{\text{PAW}} - \sum_{s,ij} \dot{\mathbf{R}}_s(t) \cdot \tilde{p}_{si}^{\mathbf{R}_s(t)}\rangle \Delta \mathbf{p}_{ij}^s \langle \tilde{p}_{sj}^{\mathbf{R}_s(t)} ,$ Eq. (46)	$\hat{H}_{\text{R},\dot{\mathbf{R}}}^{\text{PAW-NC}} = \frac{\mathbf{p}^2}{2m} + V^{\text{loc}} + \sum_s e^{\frac{i}{\hbar} m \dot{\mathbf{R}}_s(t) \cdot \hat{\mathbf{r}}} v_s^{\text{nl}} e^{-\frac{i}{\hbar} m \dot{\mathbf{R}}_s(t) \cdot \hat{\mathbf{r}}},$ Eq. (75) and Ref. [14]
Ultrasoft Hamiltonian	
$\hat{H}_{\text{R}}^{\text{PAW}} = \hat{H}_{\text{R}}^{\text{PAW-NC}} - \sum_{s,ij} \{ \frac{\mathbf{p}}{2}, \tilde{p}_{si}^{\mathbf{R}_s(t)}\rangle Q_{ij}^s \langle \tilde{p}_{sj}^{\mathbf{R}_s(t)} \},$ Eqs. (36) and (38)	$\hat{H}_{\text{R},\dot{\mathbf{R}}}^{\text{PAW}} = \hat{H}_{\text{R},\dot{\mathbf{R}}}^{\text{PAW-NC}} + \sum_{s,ij} (m \ddot{\mathbf{R}}_s(t) \cdot$ $e^{i\alpha_s(\hat{\mathbf{r}})} \tilde{p}_{si}^{\mathbf{R}_s(t)}\rangle \mathbf{d}_{ij}^s \langle \tilde{p}_{sj}^{\mathbf{R}_s(t)} e^{-i\alpha_s(\hat{\mathbf{r}})} - \frac{1}{2} \{ m \ddot{\mathbf{R}}_s(t) \cdot [\hat{\mathbf{r}} - \mathbf{R}_s(t)] - \dot{\mathbf{R}}_s(t) \cdot$ $\hat{\mathbf{p}} + \frac{m \dot{\mathbf{R}}_s(t) ^2}{2}, \quad e^{i\alpha_s(\hat{\mathbf{r}})} \tilde{p}_{si}^{\mathbf{R}_s(t)}\rangle Q_{ij}^s \langle \tilde{p}_{sj}^{\mathbf{R}_s(t)} e^{-i\alpha_s(\hat{\mathbf{r}})} \},$ Eq. (61)
Schrödinger equation for the nonadiabatic Ehrenfest dynamics for ultrasoft pseudopotentials	
$i\hbar S \frac{d \tilde{\psi}_I(t)\rangle}{dt} = (\hat{H}_{\text{R}}^{\text{PAW}} - \frac{i\hbar}{2} \frac{dS}{dt}) \tilde{\psi}_I(t)\rangle, \quad \text{Eq. (39)}$	$i\hbar S_{\text{R},\dot{\mathbf{R}}} \frac{d \tilde{\psi}_I(t)\rangle}{dt} = (\hat{H}_{\text{R},\dot{\mathbf{R}}}^{\text{PAW}} - \frac{i\hbar}{2} \frac{dS_{\text{R},\dot{\mathbf{R}}}}{dt}) \tilde{\psi}_I(t)\rangle, \quad \text{Eq. (63)}$
$S = \mathbb{1} + \sum_{s,ij} \tilde{p}_{si}^{\mathbf{R}_s(t)}\rangle Q_{ij}^s \langle \tilde{p}_{sj}^{\mathbf{R}_s(t)} , \quad \text{Eq. (29)}$	$S_{\text{R},\dot{\mathbf{R}}} = \mathbb{1} + \sum_{s,ij} e^{i\alpha_s(\hat{\mathbf{r}})} \tilde{p}_{si}^{\mathbf{R}_s(t)}\rangle Q_{ij}^s \langle \tilde{p}_{sj}^{\mathbf{R}_s(t)} e^{-i\alpha_s(\hat{\mathbf{r}})}, \quad \text{Eq. (52)},$
with $Q_{ij}^s = \langle \tilde{\phi}_{si}^{\mathbf{R}_s} \tilde{\phi}_{sj}^{\mathbf{R}_s} \rangle - \langle \tilde{\phi}_{si}^{\mathbf{R}_s} \tilde{\phi}_{sj}^{\mathbf{R}_s} \rangle$; in the norm-conserving case $S = \mathbb{1}$, $\frac{dS}{dt} = 0$ [see Eqs. (47) and (76)]	
Conserved energy	
$E_{\text{R}}^{\text{PAW}} = \sum_s \frac{M_s}{2} \dot{\mathbf{R}}_s(t) ^2 + \sum_{l=1}^{N_{\text{el}}} \langle \tilde{\psi}_l(t) \hat{H}^{\text{PAW}} \tilde{\psi}_l(t) \rangle,$ Eq. (44)	$E_{\text{R},\dot{\mathbf{R}}}^{\text{PAW}} = \sum_s \frac{M_s \dot{\mathbf{R}}_s(t) ^2}{2} + \sum_{l=1}^{N_{\text{el}}} \{ \langle \tilde{\psi}_l(t) \hat{H}_{\text{R},\dot{\mathbf{R}}}^{\text{PAW}} \tilde{\psi}_l(t) \rangle$ $- \sum_s [\langle \tilde{\psi}_l(t) \frac{\partial \hat{H}_{\text{R},\dot{\mathbf{R}}}^{\text{PAW}}}{\partial \dot{\mathbf{R}}_s} \cdot \dot{\mathbf{R}}_s(t) + \frac{\partial \hat{H}_{\text{R},\dot{\mathbf{R}}}^{\text{PAW}}}{\partial \dot{\mathbf{R}}_s} \cdot \dot{\mathbf{R}}_s(t) \rangle \tilde{\psi}_l(t) \rangle$ $- \frac{d}{dt} (\langle \tilde{\psi}_l(t) \frac{\partial \hat{H}_{\text{R},\dot{\mathbf{R}}}^{\text{PAW}}}{\partial \dot{\mathbf{R}}_s} \tilde{\psi}_l(t) \rangle) \cdot \dot{\mathbf{R}}_s(t) + \frac{i\hbar}{2} (\frac{d \langle \tilde{\psi}_l(t) }{dt} \frac{\partial S_{\text{R},\dot{\mathbf{R}}}}{\partial \dot{\mathbf{R}}_s} \tilde{\psi}_l(t) \rangle$ $- \langle \tilde{\psi}_l(t) \frac{\partial S_{\text{R},\dot{\mathbf{R}}}}{\partial \dot{\mathbf{R}}_s} \frac{d \tilde{\psi}_l(t)\rangle}{dt}) \cdot \dot{\mathbf{R}}_s(t) \},$ Eq. (73) and Ref. [14] for the norm-conserving limit

nuclear-velocity-dependent phases. This removes the spurious couplings between electronic states present in Eq. (39) that emerge even when the entire system undergoes a global translation at constant speed. The difference between the two formulations can be appreciated in the comparison in Table II.

The electronic dynamics are described by the standard Euler-Lagrange equation [Eq. (19)]:

$$i\hbar S_{\text{R},\dot{\mathbf{R}}} \frac{d|\tilde{\psi}_I(t)\rangle}{dt} = \left(\hat{H}_{\text{R},\dot{\mathbf{R}}}^{\text{PAW}} - \frac{i\hbar}{2} \frac{dS_{\text{R},\dot{\mathbf{R}}}}{dt} \right) |\tilde{\psi}_I(t)\rangle, \quad (63)$$

where

$$\hat{H}_{\text{R},\dot{\mathbf{R}}}^{\text{PAW}} - \frac{i\hbar}{2} \frac{dS_{\text{R},\dot{\mathbf{R}}}}{dt} = \hat{\mathcal{T}}_{\text{R}}^\dagger \hat{H}^{\text{AE}}(\hat{\mathbf{r}}, \hat{\mathbf{p}}) \hat{\mathcal{T}}_{\text{R}} - i\hbar \hat{\mathcal{T}}_{\text{R}}^\dagger \frac{d\hat{\mathcal{T}}_{\text{R}}}{dt}. \quad (64)$$

In the presence of nuclear acceleration contributions in the Lagrangian, the nuclear dynamics is governed by Eq. (22), with the nuclear acceleration terms

$$M_s \ddot{\mathbf{R}}_s(t) = \mathbf{F}_s^{\text{HF}} + \mathbf{F}_s^{\text{HF}-\dot{\mathbf{R}}} + \mathbf{F}_s^{\text{HF}-\ddot{\mathbf{R}}} + \mathbf{F}_s^{\text{S}} + \mathbf{F}_s^{\text{S}-\dot{\mathbf{R}}}. \quad (65)$$

We remark that despite the presence of nuclear acceleration derivatives, the equations of motion of the system are equivalent to those obtained from the all-electron Lagrangian since the two are mapped by the PAW transformation, as proven in Ref. [60]. A nuclear acceleration Hellmann-Feynman force $\mathbf{F}_s^{\text{HF}-\ddot{\mathbf{R}}}$ appears in the equations for the ions compared to Eq. (41). The other Hellmann-Feynman terms have expressions analogous to the ones given in Eqs. (42),

$$\mathbf{F}_s^{\text{HF}} = - \sum_{l=1}^{N_{\text{el}}} \langle \tilde{\psi}_l(t) | \frac{\partial \hat{H}_{\text{R},\dot{\mathbf{R}}}^{\text{PAW}}}{\partial \dot{\mathbf{R}}_s} | \tilde{\psi}_l(t) \rangle,$$

$$\mathbf{F}_s^{\text{HF}-\dot{\mathbf{R}}} = \sum_{l=1}^{N_{\text{el}}} \frac{d}{dt} \langle \tilde{\psi}_l(t) | \frac{\partial \hat{H}_{\text{R},\dot{\mathbf{R}}}^{\text{PAW}}}{\partial \dot{\mathbf{R}}_s} | \tilde{\psi}_l(t) \rangle, \quad (66)$$

$$\mathbf{F}_s^{\text{HF}-\ddot{\mathbf{R}}} = - \sum_{l=1}^{N_{\text{el}}} \frac{d^2}{dt^2} \langle \tilde{\psi}_l(t) | \frac{\partial \hat{H}_{\text{R},\dot{\mathbf{R}}}^{\text{PAW}}}{\partial \dot{\mathbf{R}}_s} | \tilde{\psi}_l(t) \rangle. \quad (67)$$

Crucially, the nuclear velocity derivative entering $\mathbf{F}_s^{\text{HF}-\dot{\mathbf{R}}}$ differs from that of Eq. (42), being

$$\begin{aligned} \frac{\partial \hat{H}_{\mathbf{R},\dot{\mathbf{R}},\ddot{\mathbf{R}}}^{\text{PAW}}}{\partial \dot{\mathbf{R}}_s} &= \frac{im}{\hbar} [\hat{r}_\beta, e^{i\alpha_s(\hat{\mathbf{r}})} v_s^{\text{nl}} e^{-i\alpha_s(\hat{\mathbf{r}})}] + \frac{1}{2} \sum_{ij} \left(\left[\hat{p}_\beta - m\dot{\mathbf{R}}_{s\beta}(t), e^{i\alpha_s(\hat{\mathbf{r}})} |\tilde{p}_{si}^{\mathbf{R}_s(t)}\rangle Q_{ij}^s \langle \tilde{p}_{sj}^{\mathbf{R}_s(t)}| e^{-i\alpha_s(\hat{\mathbf{r}})} \right] \right. \\ &\quad + \frac{im^2}{\hbar} \ddot{\mathbf{R}}_s(t) \cdot [\hat{r}_\beta, e^{i\alpha_s(\hat{\mathbf{r}})} |\tilde{p}_{si}^{\mathbf{R}_s(t)}\rangle \mathbf{d}_{ij}^s \langle \tilde{p}_{sj}^{\mathbf{R}_s(t)}| e^{-i\alpha_s(\hat{\mathbf{r}})}] \\ &\quad \left. - \frac{im}{2\hbar} \left\{ m\ddot{\mathbf{R}}_s(t) \cdot [\hat{\mathbf{r}} - \mathbf{R}_s(t)] - \dot{\mathbf{R}}_s(t) \cdot \hat{\mathbf{p}} + \frac{m|\dot{\mathbf{R}}_s(t)|^2}{2}, [\hat{r}_\beta, e^{i\alpha_s(\hat{\mathbf{r}})} |\tilde{p}_{si}^{\mathbf{R}_s(t)}\rangle Q_{ij}^s \langle \tilde{p}_{sj}^{\mathbf{R}_s(t)}| e^{-i\alpha_s(\hat{\mathbf{r}})}] \right\} \right). \end{aligned} \quad (68)$$

The nuclear acceleration derivative is expressed as

$$\frac{\partial \hat{H}_{\mathbf{R},\dot{\mathbf{R}},\ddot{\mathbf{R}}}^{\text{PAW}}}{\partial \ddot{\mathbf{R}}_s} = m \sum_{ij} e^{i\alpha_s(\hat{\mathbf{r}})} \left(|\tilde{p}_{si}^{\mathbf{R}_s(t)}\rangle \mathbf{d}_{ij}^s \langle \tilde{p}_{sj}^{\mathbf{R}_s(t)}| - \frac{1}{2} \{ [\hat{\mathbf{r}} - \mathbf{R}_s(t)], |\tilde{p}_{si}^{\mathbf{R}_s(t)}\rangle Q_{ij}^s \langle \tilde{p}_{sj}^{\mathbf{R}_s(t)}| \} \right) e^{-i\alpha_s(\hat{\mathbf{r}})}. \quad (69)$$

Additional forces originating from $S_{\mathbf{R},\dot{\mathbf{R}}}$ are $\mathbf{F}_s^S$ [analogous to Eq. (43) and reducing to Eq. (34) in the adiabatic limit] and its nuclear velocity generalization $\mathbf{F}_s^{S-\dot{\mathbf{R}}}$, appearing only in the velocity-including PAW,

$$\mathbf{F}_s^S = \frac{i\hbar}{2} \sum_{I=1}^{N_{\text{el}}} \left(\langle \tilde{\psi}_I(t) | \frac{\partial S_{\mathbf{R},\dot{\mathbf{R}}}}{\partial \mathbf{R}_s} \frac{d|\tilde{\psi}_I(t)\rangle}{dt} - \frac{d|\tilde{\psi}_I(t)\rangle}{dt} \frac{\partial S_{\mathbf{R},\dot{\mathbf{R}}}}{\partial \mathbf{R}_s} |\tilde{\psi}_I(t)\rangle \right), \quad (70)$$

$$\begin{aligned} \mathbf{F}_s^{S-\dot{\mathbf{R}}} &= -\frac{i\hbar}{2} \frac{d}{dt} \sum_{I=1}^{N_{\text{el}}} \left(\langle \tilde{\psi}_I(t) | \frac{\partial S_{\mathbf{R},\dot{\mathbf{R}}}}{\partial \dot{\mathbf{R}}_s} \frac{d|\tilde{\psi}_I(t)\rangle}{dt} \right. \\ &\quad \left. - \frac{d|\tilde{\psi}_I(t)\rangle}{dt} \frac{\partial S_{\mathbf{R},\dot{\mathbf{R}}}}{\partial \dot{\mathbf{R}}_s} |\tilde{\psi}_I(t)\rangle \right), \end{aligned} \quad (71)$$

where, from Eq. (52), the nuclear velocity derivative of $S_{\mathbf{R},\dot{\mathbf{R}}}$ is

$$\frac{\partial S_{\mathbf{R},\dot{\mathbf{R}}}}{\partial \dot{\mathbf{R}}_s} = \sum_{ij} \frac{im}{\hbar} [\hat{\mathbf{r}}, e^{i\alpha_s(\hat{\mathbf{r}})} |\tilde{p}_{si}^{\mathbf{R}_s(t)}\rangle Q_{ij}^s \langle \tilde{p}_{sj}^{\mathbf{R}_s(t)}| e^{-i\alpha_s(\hat{\mathbf{r}})}]. \quad (72)$$

Finally, the conserved energy is computed according to Eq. (23), which holds in the presence of nuclear acceleration terms in the Lagrangian. The complete expression is

$$\begin{aligned} E_{\mathbf{R},\dot{\mathbf{R}},\ddot{\mathbf{R}}}^{\text{PAW}} &= \sum_s \frac{M_s |\dot{\mathbf{R}}_s(t)|^2}{2} + \sum_{I=1}^{N_{\text{el}}} \left\{ \langle \tilde{\psi}_I(t) | \hat{H}_{\mathbf{R},\dot{\mathbf{R}},\ddot{\mathbf{R}}}^{\text{PAW}} | \tilde{\psi}_I(t) \rangle \right. \\ &\quad - \sum_s \left[\langle \tilde{\psi}_I(t) | \frac{\partial \hat{H}_{\mathbf{R},\dot{\mathbf{R}},\ddot{\mathbf{R}}}^{\text{PAW}}}{\partial \dot{\mathbf{R}}_s} \cdot \dot{\mathbf{R}}_s(t) + \frac{\partial \hat{H}_{\mathbf{R},\dot{\mathbf{R}},\ddot{\mathbf{R}}}^{\text{PAW}}}{\partial \ddot{\mathbf{R}}_s} \cdot \ddot{\mathbf{R}}_s(t) | \tilde{\psi}_I(t) \rangle \right. \\ &\quad \left. - \frac{d}{dt} \left(\langle \tilde{\psi}_I(t) | \frac{\partial \hat{H}_{\mathbf{R},\dot{\mathbf{R}},\ddot{\mathbf{R}}}^{\text{PAW}}}{\partial \dot{\mathbf{R}}_s} | \tilde{\psi}_I(t) \rangle \right) \cdot \dot{\mathbf{R}}_s(t) \right. \\ &\quad + \frac{i\hbar}{2} \left(\frac{d|\tilde{\psi}_I(t)\rangle}{dt} \frac{\partial S_{\mathbf{R},\dot{\mathbf{R}}}}{\partial \dot{\mathbf{R}}_s} |\tilde{\psi}_I(t)\rangle \right. \\ &\quad \left. \left. - \langle \tilde{\psi}_I(t) | \frac{\partial S_{\mathbf{R},\dot{\mathbf{R}}}}{\partial \dot{\mathbf{R}}_s} \left| \frac{d|\tilde{\psi}_I(t)\rangle}{dt} \right) \cdot \dot{\mathbf{R}}_s(t) \right] \right\}. \end{aligned} \quad (73)$$

The nuclear velocity and acceleration derivatives are reported explicitly in Eqs. (68), (69), and (72). For a direct comparison of the main results of this work—including the conserved energy—obtained using the nuclear velocity-including atomic orbital basis with those obtained using the rigidly translated atomic orbital basis, see Table II.

Norm-conserving case

In the case of a norm-conserving pseudopotential, $S = 1$, and the augmentation charges are zero, $Q_{ij}^s = 0$. Moreover, for a smooth operator within the augmentation region, such as the position, the matrix elements with the all-electron and pseudopartial waves almost coincide,

$$\langle \phi_{si}^{\mathbf{R}_s} | \hat{\mathbf{r}} | \phi_{sj}^{\mathbf{R}_s} \rangle \approx \langle \tilde{\phi}_{si}^{\mathbf{R}_s} | \hat{\mathbf{r}} | \tilde{\phi}_{sj}^{\mathbf{R}_s} \rangle. \quad (74)$$

As a consequence, the Hamiltonian reduces to the one given by Ref. [14],

$$\hat{H}_{\mathbf{R},\dot{\mathbf{R}}}^{\text{PAW-NC}} = \frac{\hat{\mathbf{p}}^2}{2m} + V^{\text{loc}} + \sum_s e^{\frac{i}{\hbar} m \dot{\mathbf{R}}_s(t) \cdot \hat{\mathbf{r}}} v_s^{\text{nl}} e^{-\frac{i}{\hbar} m \dot{\mathbf{R}}_s(t) \cdot \hat{\mathbf{r}}}. \quad (75)$$

The evolution of the electronic system is determined by

$$i\hbar \frac{d|\tilde{\psi}_I(t)\rangle}{dt} = \hat{H}_{\mathbf{R},\dot{\mathbf{R}}}^{\text{PAW-NC}} |\tilde{\psi}_I(t)\rangle, \quad (76)$$

which guarantees Galilean invariance since the motion at constant velocity of the entire system does not cause any spurious electronic transitions. Indeed, there are no terms in the Hamiltonian mixing different electronic orbitals, overcoming the paradox of the nonadiabatic Ehrenfest dynamics without the nuclear-velocity-dependent phases.

In the nuclear dynamics, the nuclear acceleration contribution to the force is approximately zero, $\mathbf{F}_s^{\text{HF}-\ddot{\mathbf{R}}} \approx 0$, whereas the other two reduce to

$$\mathbf{F}_s^{\text{HF}} = - \sum_{I=1}^{N_{\text{el}}} \langle \tilde{\psi}_I(t) | \frac{\partial \hat{H}_{\mathbf{R},\dot{\mathbf{R}}}^{\text{PAW-NC}}}{\partial \mathbf{R}_s} | \tilde{\psi}_I(t) \rangle, \quad (77)$$

$$\mathbf{F}_s^{\text{HF}-\dot{\mathbf{R}}} = \sum_{I=1}^{N_{\text{el}}} \frac{d}{dt} \langle \tilde{\psi}_I(t) | \frac{\partial \hat{H}_{\mathbf{R},\dot{\mathbf{R}}}^{\text{PAW-NC}}}{\partial \dot{\mathbf{R}}_s} | \tilde{\psi}_I(t) \rangle. \quad (78)$$

These expressions give the force-constant matrix and the Born effective charges presented in Ref. [14], which neglects

the nuclear-acceleration contribution. The conserved energy is

$$E_{\mathbf{R},\dot{\mathbf{R}}}^{\text{PAW-NC}} = \sum_s \frac{M_s |\dot{\mathbf{R}}_s(t)|^2}{2} + \sum_{I=1}^{N_{\text{el}}} \left[\langle \tilde{\psi}_I(t) | \left(\hat{H}_{\mathbf{R},\dot{\mathbf{R}}}^{\text{PAW-NC}} - \sum_s \frac{\partial \hat{H}_{\mathbf{R},\dot{\mathbf{R}}}^{\text{PAW-NC}}}{\partial \dot{\mathbf{R}}_s} \cdot \dot{\mathbf{R}}_s \right) | \tilde{\psi}_I(t) \rangle \right], \quad (79)$$

where, from Eq. (68),

$$\frac{\partial \hat{H}_{\mathbf{R},\dot{\mathbf{R}}}^{\text{PAW-NC}}}{\partial \dot{\mathbf{R}}_s} = \frac{im}{\hbar} [\hat{\mathbf{r}}, e^{i\alpha_s(\hat{\mathbf{r}})} v_s^{\text{nl}} e^{-i\alpha_s(\hat{\mathbf{r}})}]. \quad (80)$$

This coincides with the results of Ref. [14].

VI. CONCLUSIONS

In this work, we constructed the pseudopotential Hamiltonian through a PAW transformation that employs velocity-including atomic orbitals in both the norm-conserving and ultrasoft cases, with the aim of obtaining the nonadiabatic Ehrenfest dynamics, as summarized in Table II. While the local part of the Hamiltonian remains unaffected, Peierls-like phases that depend on the nuclear velocity appear in the nonlocal part of the potential. Additional nuclear velocity and acceleration contributions, depending on the augmentation charge, are also present in the ultrasoft pseudopotential case. Indeed, the nuclear acceleration contributions, previously overlooked in the literature, cannot be neglected in the ultrasoft case, while in the norm-conserving case they are small and can be disregarded. Thus, the use of the nuclear-velocity-including atomic orbitals in the PAW transformation enables the proper reproduction of the all-electron properties in the pseudopotential Hamiltonian when nuclei are moving at any order in the nuclear velocity, addressing specific issues that arise in standard approaches. First of all, since electronic wave functions acquire spherical harmonics components at any order when nuclei are moving, neglecting the nuclear-velocity-dependent phases in the atomic orbitals implies that the static orbital basis set is incomplete, making it inadequate for the description of the all-electron problem. Furthermore, our equations fully restore Galilean invariance through nuclear-velocity-dependent phases that allow for the removal of spurious couplings between different electronic states, which would otherwise appear when the entire system undergoes a global translation. This is highlighted in Table II in the comparison between the electronic dynamics obtained with the rigid translation of electronic orbitals to the time-dependent nuclear positions and the use of the nuclear-velocity-dependent orbitals. Finally, we generalized to ultrasoft pseudopotentials the results of Ref. [14], which is limited to the norm-conserving case, showing that additional nuclear-velocity- and acceleration-dependent contributions have to be accounted for in the assessment of dynamical vibrational responses as the force constant matrix and the Born effective charge tensor. Therefore, our work provides an analytical theoretical framework for future implementation of first-principles nonadiabatic dynamics with pseudopotentials.

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DATA AVAILABILITY

There are no publicly available research data or software supporting this manuscript. Requests for further information or data should be sent to the authors.

APPENDIX A: TEMPORAL EVOLUTION WITH A NON-HERMITIAN HAMILTONIAN AND NORM CONSERVATION

Consider a system in which the electronic part of the Lagrangian is

$$\mathcal{L}_{\text{el}} = - \sum_{I=1}^{N_{\text{el}}} \left[\langle \tilde{\psi}_I(t) | \hat{O}(t) | \tilde{\psi}_I(t) \rangle + \frac{i\hbar}{2} \left(\frac{d \langle \tilde{\psi}_I(t) |}{dt} S | \tilde{\psi}_I(t) \rangle - \langle \tilde{\psi}_I(t) | S | \frac{d \tilde{\psi}_I(t)}{dt} \rangle \right) \right] \quad (A1)$$

and the wave function is normalized such that

$$\langle \tilde{\psi}_I(t) | S | \tilde{\psi}_I(t) \rangle = 1; \quad (A2)$$

then the temporal evolution operator $\hat{O}(t)$ is a non-Hermitian operator,

$$i\hbar S | \dot{\tilde{\psi}}_I(t) \rangle = O(t) | \tilde{\psi}_I(t) \rangle. \quad (A3)$$

In order to prove this, we compute the temporal derivative of the norm,

$$\begin{aligned} \frac{d}{dt} [\langle \tilde{\psi}_I(t) | S | \tilde{\psi}_I(t) \rangle] &= 0, \\ \langle \dot{\tilde{\psi}}_I(t) | S | \tilde{\psi}_I(t) \rangle + \langle \tilde{\psi}_I(t) | S | \dot{\tilde{\psi}}_I(t) \rangle \\ + \langle \tilde{\psi}_I(t) | \frac{dS(t)}{dt} | \tilde{\psi}_I(t) \rangle &= 0. \end{aligned} \quad (A4)$$

Substituting the Schrödinger equations for $| \tilde{\psi}_I(t) \rangle$ and $\langle \tilde{\psi}_I(t) |$, we obtain

$$\langle \tilde{\psi}_I(t) | O(t) - O^\dagger(t) + i\hbar \frac{dS(t)}{dt} | \tilde{\psi}_I(t) \rangle = 0, \quad (A5)$$

following

$$i\hbar \frac{dS(t)}{dt} = O^\dagger(t) - O(t). \quad (A6)$$

In conclusion, a time-dependent S implies that the evolution is not determined by a Hermitian operator. Nonetheless, the temporal evolution preserves the norm defined with the S -matrix. A non-Hermitian evolution operator is needed to conserve this norm.

APPENDIX B: DETAILS OF THE TRANSFORMATION OF OPERATORS WITH THE VELOCITY-INCLUDING PAW

According to Eq. (51) in the main text, the operators transform with the velocity-including PAW transformation as

$$\begin{aligned}\tilde{O} &= O + \sum_{s,ij} e^{i\alpha_s(\hat{\mathbf{r}})} |\tilde{p}_{si}^{\mathbf{R}_s(t)}\rangle \Delta O_{ij}^{s,\dot{\mathbf{R}}} \langle \tilde{p}_{sj}^{\mathbf{R}_s(t)}| e^{-i\alpha_s(\hat{\mathbf{r}})}, \\ \Delta O_{ij}^{s,\dot{\mathbf{R}}} &= \langle \phi_{si}^{\mathbf{R}_s(t)} | e^{-i\alpha_s(\hat{\mathbf{r}})} O e^{i\alpha_s(\hat{\mathbf{r}})} | \phi_{sj}^{\mathbf{R}_s(t)} \rangle - \langle \tilde{\phi}_{si}^{\mathbf{R}_s(t)} | e^{-i\alpha_s(\hat{\mathbf{r}})} O e^{i\alpha_s(\hat{\mathbf{r}})} | \tilde{\phi}_{sj}^{\mathbf{R}_s(t)} \rangle.\end{aligned}\quad (\text{B1})$$

We remark that $\Delta O_{ij}^{s,\dot{\mathbf{R}}}$ and ΔO_{ij}^s in Eq. (28) in the main text indicate the difference between the all-electron and pseudo-wave-function matrix elements with and without the nuclear-velocity-dependent phases in the orbitals, respectively. Adding and subtracting $\sum_{s,ij} e^{i\alpha_s(\hat{\mathbf{r}})} |\tilde{p}_{si}^{\mathbf{R}_s(t)}\rangle \Delta O_{ij}^s \langle \tilde{p}_{sj}^{\mathbf{R}_s(t)}| e^{-i\alpha_s(\hat{\mathbf{r}})}$, we can rewrite Eq. (B1) as

$$\tilde{O} = O + \sum_{s,ij} [e^{i\alpha_s(\hat{\mathbf{r}})} |\tilde{p}_{si}^{\mathbf{R}_s(t)}\rangle \Delta O_{ij}^s \langle \tilde{p}_{sj}^{\mathbf{R}_s(t)}| e^{-i\alpha_s(\hat{\mathbf{r}})} + e^{i\alpha_s(\hat{\mathbf{r}})} |\tilde{p}_{si}^{\mathbf{R}_s(t)}\rangle (\Delta O_{ij}^{s,\dot{\mathbf{R}}} - \Delta O_{ij}^s) \langle \tilde{p}_{sj}^{\mathbf{R}_s(t)}| e^{-i\alpha_s(\hat{\mathbf{r}})}], \quad (\text{B2})$$

where ΔO_{ij}^s is the difference between the all-electron and pseudomatrix elements without the nuclear-velocity-dependent phases, as defined in Eq. (28). The last term contains the difference between the velocity-including and standard cases. It is expressed as

$$\Delta O_{ij}^{s,\dot{\mathbf{R}}} - \Delta O_{ij}^s = \langle \phi_{si}^{\mathbf{R}_s(t)} | e^{-i\alpha_s(\hat{\mathbf{r}})} O e^{i\alpha_s(\hat{\mathbf{r}})} - O | \phi_{sj}^{\mathbf{R}_s(t)} \rangle - \langle \tilde{\phi}_{si}^{\mathbf{R}_s(t)} | e^{-i\alpha_s(\hat{\mathbf{r}})} O e^{i\alpha_s(\hat{\mathbf{r}})} - O | \tilde{\phi}_{sj}^{\mathbf{R}_s(t)} \rangle. \quad (\text{B3})$$

For instance, for an operator depending on the momentum $O(\hat{\mathbf{p}})$, the nuclear-velocity-dependent phase factor causes a shift in momentum, according to the commutation rules between the position and momentum operators, $e^{-i\alpha_s(\hat{\mathbf{r}})} O(\hat{\mathbf{p}}) e^{i\alpha_s(\hat{\mathbf{r}})} = O[\hat{\mathbf{p}} + m\dot{\mathbf{R}}_s(t)]$, implying that

$$\Delta O_{ij}^{s,\dot{\mathbf{R}}} - \Delta O_{ij}^s = \langle \phi_{si}^{\mathbf{R}_s(t)} | O[\hat{\mathbf{p}} + m\dot{\mathbf{R}}_s(t)] - O | \phi_{sj}^{\mathbf{R}_s(t)} \rangle - \langle \tilde{\phi}_{si}^{\mathbf{R}_s(t)} | O[\hat{\mathbf{p}} + m\dot{\mathbf{R}}_s(t)] - O | \tilde{\phi}_{sj}^{\mathbf{R}_s(t)} \rangle. \quad (\text{B4})$$

APPENDIX C: DETAILED CALCULATION OF THE TEMPORAL DERIVATIVE OF THE PAW TRANSFORMATION

The PAW transformation in Eq. (25) for moving nuclei without the nuclear-velocity-dependent phase factors can be expressed as

$$\hat{\mathcal{T}} = \hat{1} + \sum_s \hat{t}_s^s, \quad \hat{t}_s^s = \sum_i (|\phi_{si}^{\mathbf{R}_s(t)}\rangle - |\tilde{\phi}_{si}^{\mathbf{R}_s(t)}\rangle) \langle \tilde{p}_{si}^{\mathbf{R}_s(t)}|, \quad (\text{C1})$$

whereas with the nuclear-velocity-dependent phases, it is expressed as in Eq. (49),

$$\hat{\mathcal{T}}_{\dot{\mathbf{R}}} = \hat{1} + \sum_s \hat{t}_{\dot{\mathbf{R}}}^s, \quad \hat{t}_{\dot{\mathbf{R}}}^s = \sum_i e^{i\alpha_s(\hat{\mathbf{r}})} (|\phi_{si}^{\mathbf{R}_s(t)}\rangle - |\tilde{\phi}_{si}^{\mathbf{R}_s(t)}\rangle) \langle \tilde{p}_{si}^{\mathbf{R}_s(t)}| e^{-i\alpha_s(\hat{\mathbf{r}})}. \quad (\text{C2})$$

By using the equations above, we can also express the difference between the pseudo- and all-electron (local or semilocal) operators as

$$\tilde{O} - O = \sum_s [(\hat{t}_{\dot{\mathbf{R}}}^s)^\dagger O + O \hat{t}_{\dot{\mathbf{R}}}^s + (\hat{t}_{\dot{\mathbf{R}}}^s)^\dagger O \hat{t}_{\dot{\mathbf{R}}}^s]. \quad (\text{C3})$$

By applying the identity for the ket and the bra of the pseudo-wave-function given in Eq. (26) to the first and second terms on the right-hand side, respectively, the expression for the transformation of the PAW operators, given in Eq. (27), is obtained.

In the calculation of the temporal derivatives of the transformation, we consider the nuclear-velocity-including case since the other case is recovered by setting $\alpha(\hat{\mathbf{r}}) = 0$. Therefore, using Eq. (14) and defining

$$\mathbf{D}_s(\hat{\mathbf{r}}, \hat{\mathbf{p}}) = \frac{i}{\hbar} \{m\dot{\mathbf{R}}_s(t) \cdot [\hat{\mathbf{r}} - \mathbf{R}_s(t)] - \dot{\mathbf{R}}_s(t) \cdot \hat{\mathbf{p}}\}, \quad (\text{C4})$$

we obtain

$$\frac{d\hat{\mathcal{T}}_{\dot{\mathbf{R}}}}{dt} = \sum_s [\mathbf{D}_s(\hat{\mathbf{r}}, \hat{\mathbf{p}}), \hat{t}_{\dot{\mathbf{R}}}^s]. \quad (\text{C5})$$

In the absence of the nuclear-velocity-dependent phase factors, we have the same expression with $\dot{\mathbf{R}}_s(t) = 0$. From Eq. (C5), it follows that

$$\hat{\mathcal{T}}_{\dot{\mathbf{R}}}^\dagger \frac{d\hat{\mathcal{T}}_{\dot{\mathbf{R}}}}{dt} = \hat{\mathcal{T}}_{\dot{\mathbf{R}}}^\dagger \sum_s [\mathbf{D}_s(\hat{\mathbf{r}}, \hat{\mathbf{p}}), \hat{t}_{\dot{\mathbf{R}}}^s] = \sum_s [\mathbf{D}_s \hat{t}_{\dot{\mathbf{R}}}^s - \hat{t}_{\dot{\mathbf{R}}}^s \mathbf{D}_s + (\hat{t}_{\dot{\mathbf{R}}}^s)^\dagger \mathbf{D}_s \hat{t}_{\dot{\mathbf{R}}}^s - (\hat{t}_{\dot{\mathbf{R}}}^s)^\dagger \hat{t}_{\dot{\mathbf{R}}}^s \mathbf{D}_s]. \quad (\text{C6})$$

By summing and subtracting $\sum_s (\hat{t}_{\dot{\mathbf{R}}}^s)^\dagger \mathbf{D}_s$,

$$\hat{\mathcal{T}}_{\dot{\mathbf{R}}}^\dagger \frac{d\hat{\mathcal{T}}_{\dot{\mathbf{R}}}}{dt} = \sum_s \{[(\hat{t}_{\dot{\mathbf{R}}}^s)^\dagger \mathbf{D}_s + \mathbf{D}_s \hat{t}_{\dot{\mathbf{R}}}^s + (\hat{t}_{\dot{\mathbf{R}}}^s)^\dagger \mathbf{D}_s \hat{t}_{\dot{\mathbf{R}}}^s] - [(\hat{t}_{\dot{\mathbf{R}}}^s)^\dagger + \hat{t}_{\dot{\mathbf{R}}}^s + (\hat{t}_{\dot{\mathbf{R}}}^s)^\dagger \hat{t}_{\dot{\mathbf{R}}}^s] \mathbf{D}_s\}. \quad (\text{C7})$$

According to Eq. (C3), the two terms on the right-hand side correspond to the augmentation region resolved difference between the all-electron and pseudo-operators $\mathbf{D}_s$ and $\mathbb{1}$. Therefore, by properly applying the identities in the augmentation region given in Eq. (26), like for the transformation of the operators, we obtain, with the hypothesis that augmentation regions do not overlap and by performing the same calculation for $\frac{d\hat{\mathcal{T}}_R^\dagger}{dt}\hat{\mathcal{T}}_R$,

$$\begin{aligned}\hat{\mathcal{T}}_R^\dagger \frac{d\hat{\mathcal{T}}_R}{dt} &= \sum_{s,j} e^{i\alpha_s(\hat{\mathbf{r}})} \left(|\tilde{p}_{si}^{\mathbf{R}_s(t)}\rangle \Delta \mathbf{D}_{ij}^{s,\dot{\mathbf{R}}} \langle \tilde{p}_{sj}^{\mathbf{R}_s(t)}| e^{-i\alpha_s(\hat{\mathbf{r}})} - |\tilde{p}_{si}^{\mathbf{R}_s(t)}\rangle \mathcal{Q}_{ij}^s \langle \tilde{p}_{sj}^{\mathbf{R}_s(t)}| e^{-i\alpha_s(\hat{\mathbf{r}})} \mathbf{D}_s \right), \\ \frac{d\hat{\mathcal{T}}_R^\dagger}{dt} \hat{\mathcal{T}}_R &= \sum_{s,j} \left(-e^{i\alpha_s(\hat{\mathbf{r}})} |\tilde{p}_{si}^{\mathbf{R}_s(t)}\rangle \Delta \mathbf{D}_{ij}^{s,\dot{\mathbf{R}}} \langle \tilde{p}_{sj}^{\mathbf{R}_s(t)}| + \mathbf{D}_s e^{i\alpha_s(\hat{\mathbf{r}})} |\tilde{p}_{si}^{\mathbf{R}_s(t)}\rangle \mathcal{Q}_{ij}^s \langle \tilde{p}_{sj}^{\mathbf{R}_s(t)}| \right) e^{-i\alpha_s(\hat{\mathbf{r}})},\end{aligned}\quad (\text{C8})$$

where, if we use $e^{-i\alpha_s(\hat{\mathbf{r}})} \hat{\mathbf{p}} e^{i\alpha_s(\hat{\mathbf{r}})} = \hat{\mathbf{p}} + m\dot{\mathbf{R}}_s(t)$ in combination with the definition of $\mathbf{D}_s$ given in Eq. (C4),

$$\begin{aligned}\Delta \mathbf{D}_{ij}^{s,\dot{\mathbf{R}}} &= \frac{i}{\hbar} \left\{ \langle \phi_{si}^{\mathbf{R}_s(t)} | m\ddot{\mathbf{R}}_s(t) \cdot [\hat{\mathbf{r}} - \mathbf{R}_s(t)] - \dot{\mathbf{R}}_s(t) \cdot \hat{\mathbf{p}} - m|\dot{\mathbf{R}}_s(t)|^2 | \phi_{sj}^{\mathbf{R}_s(t)} \rangle \right. \\ &\quad \left. - \langle \tilde{\phi}_{si}^{\mathbf{R}_s(t)} | m\ddot{\mathbf{R}}_s(t) \cdot [\hat{\mathbf{r}} - \mathbf{R}_s(t)] - \dot{\mathbf{R}}_s(t) \cdot \hat{\mathbf{p}} - m|\dot{\mathbf{R}}_s(t)|^2 | \tilde{\phi}_{sj}^{\mathbf{R}_s(t)} \rangle \right\}.\end{aligned}\quad (\text{C9})$$

Finally, the contribution to the Lagrangian originating from the temporal derivative of the transformation is

$$\frac{i\hbar}{2} \left(\frac{d\hat{\mathcal{T}}_R^\dagger}{dt} \hat{\mathcal{T}}_R - \hat{\mathcal{T}}_R^\dagger \frac{d\hat{\mathcal{T}}_R}{dt} \right) = -i\hbar \sum_{s,j} \left(e^{i\alpha_s(\hat{\mathbf{r}})} |\tilde{p}_{si}^{\mathbf{R}_s(t)}\rangle \Delta \mathbf{D}_{ij}^{s,\dot{\mathbf{R}}} \langle \tilde{p}_{sj}^{\mathbf{R}_s(t)}| e^{-i\alpha_s(\hat{\mathbf{r}})} - \left\{ \frac{\mathbf{D}_s}{2}, e^{i\alpha_s(\hat{\mathbf{r}})} |\tilde{p}_{si}^{\mathbf{R}_s(t)}\rangle \mathcal{Q}_{ij}^s \langle \tilde{p}_{sj}^{\mathbf{R}_s(t)}| e^{-i\alpha_s(\hat{\mathbf{r}})} \right\} \right). \quad (\text{C10})$$

In the norm-conserving case, where $\mathcal{Q}_{ij}^s = 0$ and $\hat{\mathcal{T}}_R^\dagger \hat{\mathcal{T}}_R = \mathbb{1}$, the temporal derivative terms reduce to

$$\hat{\mathcal{T}}_R^\dagger \frac{d\hat{\mathcal{T}}_R}{dt} = -\frac{d\hat{\mathcal{T}}_R^\dagger}{dt} \hat{\mathcal{T}}_R = \sum_{s,j} e^{i\alpha_s(\hat{\mathbf{r}})} |\tilde{p}_{si}^{\mathbf{R}_s(t)}\rangle \Delta \mathbf{D}_{ij}^{s,\dot{\mathbf{R}}} \langle \tilde{p}_{sj}^{\mathbf{R}_s(t)}| e^{-i\alpha_s(\hat{\mathbf{r}})}. \quad (\text{C11})$$

In the absence of nuclear-velocity-dependent phase factors, the proof is the same with $\dot{\mathbf{R}}_s(t) = 0$ and $\Delta \mathbf{D}_{ij}^{s,\dot{\mathbf{R}}}$ replaced by $\Delta \mathbf{D}_{ij}^s$, which gives, as a result, Eq. (38) in the main text.

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