

Atom-Centered Density Matrix Propagation (ADMP): Generalizations Using Bohmian Mechanics[†]

Srinivasan S. Iyengar,^{*,‡} H. Bernhard Schlegel,[§] and Gregory A. Voth[‡]

Department of Chemistry and Henry Eyring Center for Theoretical Chemistry, 315 S. 1400 E. Rm. 2020, University of Utah, Salt Lake City, Utah 84112-0850, and Department of Chemistry, Wayne State University, Detroit, Michigan 48202-3489

Received: March 12, 2003; In Final Form: May 8, 2003

We present a generalization for the atom-centered density matrix propagation (ADMP) approach to ab initio molecular dynamics that allows for a quantum-mechanical treatment of the nuclear degrees of freedom while adiabatically time-propagating the electronic degrees of freedom. This generalization uses the Bohmian approach to quantum mechanics. The regular ADMP equations are seen to arise in the special case of the $\hbar \rightarrow 0$ limit of the current formalism. Semiclassical approximations are also discussed, and rigorous error estimates are provided to define the accuracy of the current formalism.

1. Introduction

The fundamental equation in nonrelativistic quantum mechanics is the time-dependent Schrödinger equation (TDSE),¹ and this is the starting point for a number of different methods in both gas-phase^{2–5} and condensed-phase quantum dynamics.⁶ In most cases the Born–Oppenheimer approximation is invoked, and this allows for propagation of the nuclei (quantum-mechanically, classically, or semiclassically) on a fitted adiabatic electronic surface that is obtained either from highly accurate and demanding electronic structure calculations or from parametrizations of the associated electronic surfaces. In the former case, the number of electronic structure calculations required can be very large depending upon the size of the system, and it is in this regard that “on-the-fly” approaches to dynamics of nuclei and electrons^{7–13} have become popular, leading to the field of ab initio molecular dynamics. Here, approximations to the electronic structure are calculated as needed, as the nuclear configurations are propagated to simulate dynamics on the Born–Oppenheimer surface.

For performing such direct ab initio classical trajectory calculations on large systems, Born–Oppenheimer (BO) dynamics methods^{10,11,13,14} and the extended Lagrangian (EL) approach^{9,12,15–19} constitute two important categories. Here the electronic structure is treated simultaneously with nuclear motion. For BO methods, the electronic structure is converged at each time step in the propagation. In the EL approach, the wave function is propagated with the classical nuclear degrees of freedom using an extended Lagrangian procedure^{20,21} and by adjusting the relative time scales of the electronic and nuclear motions. The Car–Parrinello (CP) method^{9,15,16} is the best known example of the extended Lagrangian molecular dynamics approach.

Traditionally, CP calculations employ Kohn–Sham density functional theory (DFT) orbitals expanded in plane-wave basis

sets (occasionally augmented with Gaussian orbitals^{22,23}). Recently^{12,17–19} we have described the theory, implementation, and initial applications of an extended Lagrangian molecular dynamics method that employs atom-centered Gaussian basis functions and one-particle density matrix propagation. This method is called atom-centered density matrix propagation (ADMP). The dynamics of chemical systems such as large water clusters and gas-phase reactions are more readily described by atom-centered basis sets than with plane waves. Furthermore, the calculations scale as $O(N)$ for large systems, where N is the number of electrons, because ADMP is based on linear scaling DFT code.²⁴ The ADMP method has recently been extended for QM/MM treatments for biological systems²⁵ and for calculations on periodic systems employing atom-centered functions.²⁶ Interesting applications such as solvation of excess protons in water clusters,²⁷ hydroxyl-stretch red-shifts in chloride–water clusters,¹⁸ and product distributions in gas-phase chemical reactions¹⁸ have already been studied. ADMP trajectories of the order of picoseconds show stable dynamics, and the adiabaticity can be controlled effectively in these systems without thermostats. The important conceptual and computational differences between ADMP and other Gaussian basis set based implementations^{28–31} of the Car–Parrinello formalism have been discussed in detail in ref 18.

The ADMP method has a number of attractive features. Systems can be simulated by accurately treating all electrons or by using pseudopotentials. Through the use of a tensorial fictitious mass and smaller values of the mass, reasonably large time steps can be employed, and lighter atoms such as hydrogens need not be replaced with heavier isotopes. A wide variety of exchange–correlation functionals can be utilized, including hybrid density functionals. Atom-centered functions can be used with the correct physical boundary conditions for molecules, polymers, surfaces, and solids, without the need to treat replicated images in order to impose 3D periodicity. Consequently, charged systems and QM/MM models of biological systems can be treated as easily as neutral molecules, whereas special handling is needed for charged systems in most implementations of the plane-wave Car–Parrinello method because they are treated as periodic systems. Deviation from

[†] Part of the special issue “Donald J. Kouri Festschrift”.

^{*} Corresponding author. E-mail: iyengar@hec.utah.edu. Address after July 2003: Department of Chemistry, Indiana University, 800 E. Kirkwood Ave., Bloomington, IN 47405-7102.

[‡] University of Utah.

[§] Wayne State University.

the Born–Oppenheimer surface and the mixing of fictitious and real kinetic energies can also be rigorously controlled on-the-fly in ADMP. Because of fewer basis functions per atom, larger time steps, and its asymptotic $O(N)$ scaling, reasonable computational efficiency can be achieved with the ADMP method.

In the current paper we have undertaken a formal description and generalization of the ADMP approach to treat adiabatic quantum dynamics of the nuclear degrees of freedom and electronic variables. BO and EL methods are successful in simulating classical molecular dynamics. EL methods are more efficient than BO methods, because they avoid the work of converging the electronic structure calculation at each step in the classical trajectory. However, the electronic structure needs to be propagated in a manner comparable with the nuclei, so that energy is conserved. Hence, the Lagrangian equations of motion for the nuclei are extended by adding the electronic degrees of freedom and giving them a fictitious mass, μ , and kinetic energy. With an appropriate choice of fictitious mass, the molecular dynamics can be calculated efficiently and accurately. In the limit as $\mu \rightarrow 0$, EL dynamics is identical to BO dynamics.^{17–19} Basic features of ADMP are discussed in section 2. Further details can be found in refs 12 and 17–19. To develop a comparable conservative dynamics scheme that simulates the quantum dynamics of nuclear motions, we must propagate the electronic degrees of freedom using the same Hamiltonian as that for the nuclear degrees of freedom. Because of its close relation to classical trajectories, we chose to use the Bohmian dynamics^{32–39} approach for this purpose. In recent years,^{38,40–50} Bohmian mechanics has been actively studied in connection with quantum dynamics. In section 3 we follow Bohm’s approach to quantum mechanics^{32–39} to extend the ADMP equations. This generalization of ADMP, discussed in section 4, allows for a quantum-mechanical treatment of nuclei on an approximation to the adiabatic electronic surface. The salient feature of this approach is that it includes simultaneous propagation of the electronic variables with the (quantum) nuclear degrees of freedom and is based on a formalism (ADMP) that scales as $O(N)$ with system size. In the limit as $\hbar \rightarrow 0$, we recover the classical ADMP equations, and as the magnitude of the fictitious variables introduced in ADMP gets small, the current approach is equivalent to quantum dynamics of the nuclei on the Born–Oppenheimer surface. Semiclassical approximations to this description are outlined, and alternate initial conditions are also discussed. In section 5, we discuss some error estimates to bound the formalism, and finally in section 6 we present our conclusions.

2. Atom-Centered Density Matrix Propagation (ADMP) Using an Extended Lagrangian Approach

The Lagrangian for propagation of the density matrix is simplest in an orthonormal basis and can be written as

$$\mathcal{L}_{\text{ADMP}} = \frac{1}{2} \text{Tr}(\mathbf{V}^T \mathbf{M} \mathbf{V}) + \frac{1}{2} \text{Tr}([\underline{\mu}^{1/4} \mathbf{W} \underline{\mu}^{1/4}]^2) - E(\mathbf{R}, \mathbf{P}) - \text{Tr}[\Lambda(\mathbf{P}\mathbf{P} - \mathbf{P})] \quad (1)$$

where \mathbf{R} , \mathbf{V} , and \mathbf{M} are the nuclear positions, velocities, and masses, respectively, and \mathbf{P} , \mathbf{W} , and $\underline{\mu}$ are the density matrix, the density matrix velocity, and the fictitious mass tensor for the electronic degrees of freedom, respectively. The Lagrangian multiplier matrix Λ is used to impose N -representability (i.e., constraints on the total number of electrons and the idempotency of the one-particle density matrix). The energy is calculated using the McWeeny purification of the density, $\hat{\mathbf{P}} = 3\mathbf{P}^2 - 2\mathbf{P}^3$.

The Euler–Lagrange equations of motion for the nuclei and density matrix are

$$\mathbf{M} \frac{d^2 \mathbf{R}}{dt^2} = - \left. \frac{\partial E(\mathbf{R}, \mathbf{P})}{\partial \mathbf{R}} \right|_{\mathbf{P}} \quad (2)$$

and

$$\underline{\mu}^{1/2} \frac{d^2 \mathbf{P}}{dt^2} \underline{\mu}^{1/2} = - \left[\left. \frac{\partial E(\mathbf{R}, \mathbf{P})}{\partial \mathbf{P}} \right|_{\mathbf{R}} + \Lambda \mathbf{P} + \mathbf{P} \Lambda - \Lambda \right] \quad (3)$$

Equations 2 and 3 are classical, in the sense that they are derived from the Lagrangian in eq 1 by using the stationary action principle of classical mechanics.⁵¹ Correspondingly, as outlined in ref 17, the conjugate ADMP Hamiltonian for the Lagrangian in eq 1 is given by

$$\begin{aligned} \mathcal{H}_{\text{ADMP}} &= \text{Tr}(\mathcal{W} \mathbf{W}) + \text{Tr}(\mathcal{V}^T \mathbf{V}) - \mathcal{L}_{\text{ADMP}} \\ &= \frac{1}{2} \text{Tr}(\mathcal{V}^T \mathbf{M}^{-1} \mathcal{V}) + \frac{1}{2} \text{Tr}(\mathcal{W} \underline{\mu}^{-1/2} \mathcal{W} \underline{\mu}^{-1/2}) + \\ &\quad E(\mathbf{R}, \mathbf{P}) + \text{Tr}[\Lambda(\mathbf{P}\mathbf{P} - \mathbf{P})] \quad (4) \end{aligned}$$

where \mathcal{W} is the conjugate momentum of \mathbf{P} :

$$\mathcal{W} = \frac{\partial \mathcal{L}_{\text{ADMP}}}{\partial \mathbf{W}} = \underline{\mu}^{1/2} \mathbf{W} \underline{\mu}^{1/2} \quad (5)$$

and \mathcal{V} is the conjugate momentum of \mathbf{R} :

$$\mathcal{V} = \frac{\partial \mathcal{L}_{\text{ADMP}}}{\partial \mathbf{V}} = \mathbf{M} \mathbf{V} \quad (6)$$

The density and nuclear velocities may also be written using the Poisson bracket of the Hamiltonian in eq 4:

$$\mathbf{W} = \{\mathbf{P}, \mathcal{H}_{\text{ADMP}}\} \quad (7)$$

and

$$\mathbf{V} = \{\mathbf{R}, \mathcal{H}_{\text{ADMP}}\} \quad (8)$$

where $\{\dots, \dots\}$ is the classical Poisson bracket. Equations 7 and 8 will be used in later discussions in this paper. The classical Liouville operator is also given by the Poisson bracket:⁵¹

$$\begin{aligned} \iota \mathcal{L} &= \{\mathcal{H}_{\text{ADMP}}, \dots\} \\ &= \left[\frac{\partial \mathcal{H}_{\text{ADMP}}}{\partial \mathbf{R}} \frac{\partial}{\partial \mathcal{V}} - \frac{\partial \mathcal{H}_{\text{ADMP}}}{\partial \mathcal{V}} \frac{\partial}{\partial \mathbf{R}} \right] + \\ &\quad \left[\frac{\partial \mathcal{H}_{\text{ADMP}}}{\partial \mathbf{P}} \frac{\partial}{\partial \mathcal{W}} - \frac{\partial \mathcal{H}_{\text{ADMP}}}{\partial \mathcal{W}} \frac{\partial}{\partial \mathbf{P}} \right] \\ &= \left[\left. \frac{\partial E(\mathbf{R}, \mathbf{P})}{\partial \mathbf{R}} \right|_{\mathbf{P}} \frac{\partial}{\partial \mathcal{V}} - \mathbf{V} \frac{\partial}{\partial \mathbf{R}} \right] + \\ &\quad \left[\left[\left. \frac{\partial E(\mathbf{R}, \mathbf{P})}{\partial \mathbf{P}} \right|_{\mathbf{R}} + \Lambda \mathbf{P} + \mathbf{P} \Lambda - \Lambda \right] \frac{\partial}{\partial \mathcal{W}} - \mathbf{W} \frac{\partial}{\partial \mathbf{P}} \right] \\ &= \iota \mathcal{L}_{\mathbf{R}} + \iota \mathcal{L}_{\mathbf{P}} \quad (9) \end{aligned}$$

and eqs 3 and 4 are completely equivalent to the classical Liouville equation, with the Liouville operator in eq 9. These equations can be integrated using a Trotter factorization of the Liouville propagator, $\exp(-\iota \mathcal{L} t)$, and as an example, the third-order Trotter factorization (the velocity Verlet algorithm^{52,53}) has the form:

$$\mathbf{P}_{i+1} = \mathbf{P}_i + \mathbf{W}_i \Delta t - \frac{\Delta t^2}{2} \underline{\mu}^{-1/2} \left[\frac{\partial E(\mathbf{R}_i, \mathbf{P}_i)}{\partial \mathbf{P}} \right]_{\mathbf{R}} + \Lambda_i \mathbf{P}_i + \mathbf{P}_i \Lambda_i - \Lambda_i \mu^{-1/2} \quad (10)$$

$$\mathbf{W}_{i+1/2} = \mathbf{W}_i - \frac{\Delta t}{2} \underline{\mu}^{-1/2} \left[\frac{\partial E(\mathbf{R}_i, \mathbf{P}_i)}{\partial \mathbf{P}} \right]_{\mathbf{R}} + \Lambda_i \mathbf{P}_i + \mathbf{P}_i \Lambda_i - \Lambda_i \mu^{-1/2} = \frac{\mathbf{P}_{i+1} - \mathbf{P}_i}{\Delta t} \quad (11)$$

$$\mathbf{W}_{i+1} = \mathbf{W}_{i+1/2} - \frac{\Delta t}{2} \underline{\mu}^{-1/2} \left[\frac{\partial E(\mathbf{R}_{i+1}, \mathbf{P}_{i+1})}{\partial \mathbf{P}} \right]_{\mathbf{R}} + \Lambda_{i+1} \mathbf{P}_{i+1} + \mathbf{P}_{i+1} \Lambda_{i+1} - \Lambda_{i+1} \mu^{-1/2} \quad (12)$$

The Lagrangian multiplier matrixes are determined by an iterative scheme^{12,17} so that \mathbf{P}_{i+1} and \mathbf{W}_{i+1} satisfy the idempotency constraint, $\mathbf{P}^2 = \mathbf{P}$, and its time derivative, $\mathbf{P}\mathbf{W} + \mathbf{W}\mathbf{P} = \mathbf{W}$.

Equations 10–12 only represent one set of numerical solutions to eqs 2 and 3. Other (perhaps more accurate) solutions may be obtained by considering higher order Trotter factorizations of the Liouville propagator, $\exp(-L\mathcal{L}t)$. The higher order integrator will, however, require higher order derivatives of energy, and these could, in general, be cumbersome to obtain.

The fictitious electronic kinetic energy in eq 1 (second term) has been shown^{17,19} to be proportional to deviations from the Born–Oppenheimer surface, and it has also been shown that the fictitious mass is proportional to the commutator of the electronic Hamiltonian and the density matrix.¹⁹ In all current implementations of the ADMP approach,^{12,17,18,25,27} the fictitious kinetic energy is a very small fraction of the total energy of the system, and this leads to a computationally effective and accurate^{18,25,27} approach to model dynamics on the Born–Oppenheimer surface.

3. ADMP Equations with Bohmian Mechanics

Rigorous connections between classical and quantum mechanics can be derived from two different perspectives: (a) the concepts of Bohmian mechanics first derived by Madelung³² and de Broglie,^{33–36} and later by Bohm,³⁷ and (b) the concepts of path integrals due to Feynman.⁵⁴ In the first case, the starting point is the time-dependent Schrödinger equation. Upon invoking the phase-amplitude relation for the time-dependent wave function, the real and imaginary parts may be separated to yield (i) an equation of a form similar to the classical continuity equation, and (ii) an equation that is known as the quantum Hamilton–Jacobi equation. The latter differs from its classical counterpart by the presence of a “quantum force” that depends on \hbar . In the limit that $\hbar \rightarrow 0$, the classical Hamilton–Jacobi (and hence the Newton) equation is recovered. This presents one exact approach to obtain the classical equations of motion from the time-dependent Schrödinger equation in the $\hbar = 0$ limit. When \hbar is not zero (quantum mechanics), the quantum force couples the quantum Hamilton–Jacobi equation and the continuity equation. Solutions to this coupled set of equations comprise the Bohmian approach to quantum dynamics,^{40–48} where an ensemble of classical coordinates are propagated, each obeying the quantum Hamilton–Jacobi equation; however, each classical system has a probability density given by the continuity equation, and this probability density enters into the quantum force. Thus, Bohmian dynamics comprises the propagation of a set of classical systems with associated time-dependent

probabilities and has been referred to as the “quantum-trajectory method”^{41–47} in recent literature. Significant differences between Bohmian mechanics and the conventional Copenhagen interpretation of quantum mechanics are discussed in a recent monograph.³⁸

In this section, we exploit the rigorous Bohmian mechanics framework to obtain a quantum analogue for the ADMP eqs 2 and 3; that is, we will construct a set of equations formally equivalent to the time-dependent Schrödinger equation for the nuclei within the ADMP approximation. This set of equations will then be shown to reduce to eqs 2 and 3 as $\hbar \rightarrow 0$. When $\hbar \neq 0$, the set of equations derived here provides a new quantum dynamics approach for the simultaneous propagation of “quantum” nuclei and approximate adiabatic electronic states. As in the classical ADMP method, the dynamics of the electronic variables is fictitious but its deviations from the Born–Oppenheimer limit can be controlled. Numerical applications of our approach will be studied in future publications.

As discussed in the previous section, eqs 2 and 3 are strictly classical equations of motion, albeit involving parameters such as the electronic density matrix which give a description of the quantum mechanical nature of electrons. To generalize these equations of motion, we start by writing the quantum-mechanical analogue of the ADMP Hamiltonian in eq 4. This we do by replacing the classical nuclear and density matrix momenta with their respective operator forms. It is conceptually straightforward to write down the quantization of the nuclear momentum operator in eq 4:

$$\mathcal{V} \rightarrow -i\hbar \frac{\partial}{\partial \mathbf{R}} \quad (13)$$

The quantization appropriate for the second term in eq 4, that is, the fictitious density matrix kinetic energy, is however tricky. Since the ADMP formalism outlined in the previous section has been shown to provide a numerically efficient propagation scheme of classical nuclei and adiabatic electronic parameters on the Born–Oppenheimer surface, we wish to derive a quantization scheme that is consistent with ADMP. ADMP effectively treats the nuclear and density matrix coordinates on an equal classical footing. To obtain a quantization scheme that treats the nuclear and density matrix coordinates on a consistent quantum-mechanical footing, we quantize the density matrix momentum in eq 4 as

$$\mathcal{W} \rightarrow -i\hbar \frac{\partial}{\partial \mathbf{P}} \quad (14)$$

(We will argue that the quantization proposed in eqs 13 and 14 is consistent with Dirac quantization of classical Hamiltonians.⁵³) This yields a quantum-mechanical analogue for the scalar mass ADMP Hamiltonian as

$$\mathcal{H}_{\text{ADMP}}^{\text{QM}} = - \sum_i \sum_{j=1}^3 \frac{\hbar^2}{2\mathbf{M}_i} \frac{\partial^2}{\partial \mathbf{R}_{i,j}^2} - \frac{\hbar^2}{2\mu} \sum_{ij} \frac{\partial^2}{\partial \mathbf{P}_{i,j}^2} + E(\mathbf{R}, \mathbf{P}) + \text{Tr}[\Lambda(\mathbf{P}\mathbf{P} - \mathbf{P})] \quad (15)$$

We represent the scalar form of the fictitious mass as μ , as in our earlier publications.^{12,17} Here, the second term on the right-hand side is the quantum-mechanical form of the fictitious electronic kinetic energy. Note further that the quantization scheme introduced in eqs 13–15 is consistent with Dirac quantization of classical Hamiltonians,⁵⁵ since the quantum-mechanical velocity corresponding to \mathbf{P} satisfies

$$\frac{d\mathbf{P}}{dt} = \frac{1}{i\hbar}[\mathbf{P}, \mathcal{H}_{\text{ADMP}}^{\text{QM}}] = -\frac{1}{\mu}i\hbar \frac{\partial}{\partial \mathbf{P}} \quad (16)$$

where [..., ...] is the commutator. Note the similarity between eqs 7 and 16; eq 16 obeys the {..., ...} \rightarrow $(1/i\hbar)[\dots, \dots]$ correspondence rule of Dirac.⁵⁵ Thus, eq 15 is the Dirac quantized⁵⁵ form of eq 4. Further note that eq 7 is a classical Hamilton's equation of motion, whereas eq 16 represents the corresponding Heissenberg form.

As the quantum analogue of the fictitious kinetic energy term goes to zero, the Hamiltonian in eq 15 approximates the adiabatic quantum Hamiltonian of the system (i.e., quantum-mechanical nuclei on an approximation to the adiabatic, Born–Oppenheimer, electronic surface given by the energy functional $E(\mathbf{R}, \mathbf{P})$). This is seen from the fact that approximations to the true kinetic energy of the electrons, the electron–electron repulsion contribution, the electron–nuclear attraction, and the nuclear–nuclear repulsion, including approximations to electron correlation effects (all within a single-determinantal approximation such as DFT), are already included in the energy functional $E(\mathbf{R}, \mathbf{P})$. The last term in eq 15 is trivially zero when the density matrix, \mathbf{P} , is N -representable. When the density matrix is not exactly N -representable, this term contributes an energy penalty and hence may be considered to be part of the energy functional. Hence, eq 15 is as an effective approximation to the adiabatic quantum Hamiltonian of the system, that gets better as the second term, the quantum analogue of the fictitious kinetic energy, goes to zero. A detailed analysis of the expectation of the quantum analogue of the fictitious kinetic energy and the conditions under which this quantity may be bounded are discussed in section 5.

It is also important to mention here that other extended Lagrangian ideas (with holonomic constraints) may also be written in a quantum-mechanical form analogous to eq 15. For example, it may be noted that this is the case for the Car–Parrinello extended Lagrangian. However, whether an arbitrary extended Lagrangian is a good approximation to a quantum Hamiltonian of the system, or not, depends on the nature of the constraints included in the extended Lagrangian.

If χ is the complex time-dependent wave function given by the time-dependent Schrödinger equation for the Hamiltonian in eq 15, then χ may be expressed as

$$\chi \equiv \mathcal{R}_{\mathbf{R}, \mathbf{P}} \exp(i\mathcal{S}/\hbar) \quad (17)$$

where $\mathcal{R}_{\mathbf{R}, \mathbf{P}}$ and \mathcal{S} are scalar real functions of both \mathbf{R} and \mathbf{P} . It should also be noted here that since the wave function χ is a function of the variables \mathbf{R} and \mathbf{P} , the quantity $\chi^* \chi = [\mathcal{R}_{\mathbf{R}, \mathbf{P}}]^2 \equiv [\mathcal{R}_{\mathbf{R}, \mathbf{P}}]$ reflects the probability density of the classical system, $\{\mathbf{R}, \mathbf{P}\}$. The quantum system, χ , is created from the classical system with an associated probability. Hence, we can already see that in this formalism there will be a need to have many classical systems, each with associated probabilities to simulate the quantum system. (Note that in ADMP, \mathbf{R} and \mathbf{P} are both free variables, unlike in Born–Oppenheimer dynamics, where \mathbf{P} is fixed by an SCF procedure for a given \mathbf{R} . Hence, the associated probability function in ADMP needs to be a function of both \mathbf{R} and \mathbf{P} .)

Using eqs 15 and 17 in the time-dependent Schrödinger equation

$$i\hbar \frac{\partial}{\partial t} \chi = \mathcal{H}_{\text{ADMP}}^{\text{QM}} \chi \quad (18)$$

and separating real and imaginary parts, we obtain

$$\begin{aligned} \frac{\partial \mathcal{S}}{\partial t} - \left\{ \sum_i \sum_{j=1}^3 \frac{\hbar^2}{2\mathbf{M}_i} \frac{1}{\mathcal{R}_{\mathbf{R}, \mathbf{P}}} \frac{\partial^2 \mathcal{R}_{\mathbf{R}, \mathbf{P}}}{\partial \mathbf{R}_{i,j}^2} \right\} + \\ \left\{ \sum_{i,j} \frac{\hbar^2}{2\mu} \frac{1}{\mathcal{R}_{\mathbf{R}, \mathbf{P}}} \frac{\partial^2 \mathcal{R}_{\mathbf{R}, \mathbf{P}}}{\partial \mathbf{P}_{i,j}^2} \right\} + \left[\sum_i \sum_{j=1}^3 \frac{1}{2\mathbf{M}_i} \left(\frac{\partial \mathcal{S}}{\partial \mathbf{R}_{i,j}} \right)^2 + \right. \\ \left. \sum_{i,j} \frac{1}{2\mu} \left(\frac{\partial \mathcal{S}}{\partial \mathbf{P}_{i,j}} \right)^2 \right] + \{E(\mathbf{R}, \mathbf{P}) + \text{Tr}[\Lambda(\mathbf{P}\mathbf{P} - \mathbf{P})]\} = 0 \quad (19) \end{aligned}$$

from the real part of the time-dependent Schrödinger equation and

$$\begin{aligned} \frac{\partial \mathcal{R}_{\mathbf{R}, \mathbf{P}}}{\partial t} + \left\{ \sum_{i,j} \frac{1}{\mu} \left(\frac{\partial \mathcal{R}_{\mathbf{R}, \mathbf{P}}}{\partial \mathbf{P}_{i,j}} \right) \left(\frac{\partial \mathcal{S}}{\partial \mathbf{P}_{i,j}} \right) + \sum_{i,j} \frac{1}{2\mu} \mathcal{R}_{\mathbf{R}, \mathbf{P}} \frac{\partial^2 \mathcal{S}}{\partial \mathbf{P}_{i,j}^2} \right\} + \\ \left\{ \sum_i \sum_{j=1}^3 \frac{1}{\mathbf{M}_i} \left(\frac{\partial \mathcal{R}_{\mathbf{R}, \mathbf{P}}}{\partial \mathbf{R}_{i,j}} \right) \left(\frac{\partial \mathcal{S}}{\partial \mathbf{R}_{i,j}} \right) + \sum_i \sum_{j=1}^3 \frac{1}{2\mathbf{M}_i} \mathcal{R}_{\mathbf{R}, \mathbf{P}} \frac{\partial^2 \mathcal{S}}{\partial \mathbf{R}_{i,j}^2} \right\} = 0 \quad (20) \end{aligned}$$

from the imaginary part. In the limit as $\hbar \rightarrow 0$, eq 19 yields a form identical to the classical Hamiltonian–Jacobi equation,⁵¹ when the function \mathcal{S} is interpreted^{37,39,56,57} as the action variable

$$\mathcal{S} = \int \mathcal{L}_{\text{ADMP}} dt \quad (21)$$

Furthermore, when \mathcal{S} is the action variable, using eqs 2 and 3, we may redefine the partial derivatives involving the action variable as

$$\frac{1}{\mathbf{M}_i} \left(\frac{\partial \mathcal{S}}{\partial \mathbf{R}_{i,j}} \right) \equiv \mathbf{V}_{i,j} \quad (22)$$

and for the scalar fictitious mass case

$$\frac{1}{\mu} \left(\frac{\partial \mathcal{S}}{\partial \mathbf{P}_{i,j}} \right) \equiv \mathbf{W}_{i,j} \quad (23)$$

and hence, the last four terms on the right-hand side of eq 19 are together exactly equal to the ADMP Hamiltonian of eq 4, that is,

$$\mathcal{H}_{\text{ADMP}} \equiv \sum_i \sum_{j=1}^3 \frac{1}{2\mathbf{M}_i} \left(\frac{\partial \mathcal{S}}{\partial \mathbf{R}_{i,j}} \right)^2 + \sum_{i,j} \frac{1}{2\mu} \left(\frac{\partial \mathcal{S}}{\partial \mathbf{P}_{i,j}} \right)^2 + E(\mathbf{R}, \mathbf{P}) + \text{Tr}[\Lambda(\mathbf{P}\mathbf{P} - \mathbf{P})] \quad (24)$$

Hence, differentiating eq 19 with \mathbf{R} and \mathbf{P} , and assuming that \mathbf{R} and \mathbf{P} are independent variables as is the case for adiabatic separation, yields the corresponding Newton-like equations in matrix form as

$$\mathbf{M} \frac{d^2 \mathbf{R}}{dt^2} = - \frac{\partial E(\mathbf{R}, \mathbf{P})}{\partial \mathbf{R}} \Big|_{\mathbf{P}} + \frac{\partial}{\partial \mathbf{R}} \left[\sum_i \sum_{j=1}^3 \frac{\hbar^2}{2\mathbf{M}_i} \frac{1}{\mathcal{R}_{\mathbf{R}, \mathbf{P}}} \frac{\partial^2 \mathcal{R}_{\mathbf{R}, \mathbf{P}}}{\partial \mathbf{R}_{i,j}^2} \right] \quad (25)$$

and

$$\mu \frac{d^2 \mathbf{P}}{dt^2} = - \left[\frac{\partial E(\mathbf{R}, \mathbf{P})}{\partial \mathbf{P}} \right]_{\mathbf{R}} + \Lambda \mathbf{P} + \mathbf{P} \Lambda - \Lambda + \frac{\partial}{\partial \mathbf{P}} \left[\sum_{ij} \frac{\hbar^2}{2\mu} \frac{1}{\mathcal{R}_{\mathbf{R}, \mathbf{P}}} \frac{\partial^2 \mathcal{R}_{\mathbf{R}, \mathbf{P}}}{\partial \mathbf{P}_{ij}^2} \right] \quad (26)$$

where the total time derivatives in eqs 25 and 26 are obtained from the sum of the partial time derivative of \mathcal{J} in eq 19 and the gradient terms arising from the fourth and fifth terms in eq 19 (or the first and second terms on the right-hand side of eq 24). The latter terms are similar to the convective forces arising in computational fluid dynamics,³⁹ and due to this reason the equations of Bohmian mechanics have been called the hydrodynamic formulation of quantum mechanics in recent literature.⁴³ As $\hbar \rightarrow 0$, eqs 25 and 26 yield the classical ADMP equations of motion.

4. Discussion of the Quantum ADMP Equations

To proceed further with the discussion when $\hbar \neq 0$, we first make the substitution $\mathcal{P}_{\mathbf{R}, \mathbf{P}} = \mathcal{R}_{\mathbf{R}, \mathbf{P}}^2$ in eq 20 to obtain

$$\frac{\partial [\mathcal{P}_{\mathbf{R}, \mathbf{P}}]}{\partial t} + \left[\sum_{ij} \frac{\partial}{\partial \mathbf{P}_{ij}} (\mathcal{P}_{\mathbf{R}, \mathbf{P}} \mathbf{W}_{ij}) \right] + \left[\sum_{i,j=1}^3 \frac{\partial}{\partial \mathbf{R}_{ij}} (\mathcal{P}_{\mathbf{R}, \mathbf{P}} \mathbf{V}_{ij}) \right] = 0 \quad (27)$$

which has a form identical to that of the continuity equation (or conservation of flux equation) of classical mechanics. This can be seen from the fact that $\mathcal{P}_{\mathbf{R}, \mathbf{P}}$ is the probability density measuring the probability of the nuclear positions being at \mathbf{R} and the density matrix being \mathbf{P} . Hence, the quantities $\mathcal{P}_{\mathbf{R}, \mathbf{P}} \mathbf{V}$ and $\mathcal{P}_{\mathbf{R}, \mathbf{P}} \mathbf{W}$ represent the probability flux of the nuclei and density matrix, respectively.

It is important to note here the significance of the probability function in eq 27. This function represents the probability of the classical event $\{\mathbf{R}, \mathbf{P}\}$. Thus, each nuclear configuration is free to have its own density matrix (and hence its own electronic structure configuration which could, in general, be different from those realized by other nuclear configurations), the probability of which is given by $\mathcal{P}_{\mathbf{R}, \mathbf{P}}$. It may be noted here that other approaches in the literature⁵⁸ also allow simultaneous propagation of multiple electronic wave function states along with multiple nuclear configurations, one electronic wave function state per nuclear configuration, to simulate quantum dynamics on an adiabatic electronic surface. In this sense there is an appealing similarity between the current approach and path integral based approaches.⁵⁸

Now, using the definition of the total time derivative as the sum of the partial time derivative and gradient terms, we may rewrite eq 27 as

$$\frac{d \mathcal{P}_{\mathbf{R}, \mathbf{P}}}{dt} + \mathcal{P}_{\mathbf{R}, \mathbf{P}} \left[\sum_{ij} \frac{\partial \mathbf{W}_{ij}}{\partial \mathbf{P}_{ij}} + \sum_{i,j=1}^3 \frac{\partial \mathbf{V}_{ij}}{\partial \mathbf{R}_{ij}} \right] = 0 \quad (28)$$

which can be integrated to obtain

$$\mathcal{P}_{\mathbf{R}, \mathbf{P}}(t+\delta t) = \exp \left\{ -\delta t \left[\sum_{ij} \frac{\partial \mathbf{W}_{ij}}{\partial \mathbf{P}_{ij}} + \sum_{i,j=1}^3 \frac{\partial \mathbf{V}_{ij}}{\partial \mathbf{R}_{ij}} \right] \right\} \mathcal{P}_{\mathbf{R}, \mathbf{P}}(t) \quad (29)$$

Using the probability density, we may rewrite eqs 25 and 26 as

$$\mathbf{M} \frac{d^2 \mathbf{R}}{dt^2} = - \left[\frac{\partial E(\mathbf{R}, \mathbf{P})}{\partial \mathbf{R}} \right]_{\mathbf{P}} + \frac{\partial}{\partial \mathbf{R}} \left[\sum_{i,j=1}^3 \sum_{4M_i} \frac{\hbar^2}{4M_i} \left\{ \frac{1}{\mathcal{P}_{\mathbf{R}, \mathbf{P}}} \frac{\partial^2 \mathcal{P}_{\mathbf{R}, \mathbf{P}}}{\partial \mathbf{R}_{ij}^2} - \frac{1}{2\mathcal{P}_{\mathbf{R}, \mathbf{P}}^2} \left(\frac{\partial \mathcal{P}_{\mathbf{R}, \mathbf{P}}}{\partial \mathbf{R}_{ij}} \right)^2 \right\} \right] \quad (30)$$

and

$$\mu \frac{d^2 \mathbf{P}}{dt^2} = - \left[\frac{\partial E(\mathbf{R}, \mathbf{P})}{\partial \mathbf{P}} \right]_{\mathbf{R}} + \Lambda \mathbf{P} + \mathbf{P} \Lambda - \Lambda + \frac{\partial}{\partial \mathbf{P}} \left[\sum_{ij} \frac{\hbar^2}{4\mu} \left\{ \frac{1}{\mathcal{P}_{\mathbf{R}, \mathbf{P}}} \frac{\partial^2 \mathcal{P}_{\mathbf{R}, \mathbf{P}}}{\partial \mathbf{P}_{ij}^2} - \frac{1}{2\mathcal{P}_{\mathbf{R}, \mathbf{P}}^2} \left(\frac{\partial \mathcal{P}_{\mathbf{R}, \mathbf{P}}}{\partial \mathbf{P}_{ij}} \right)^2 \right\} \right] \quad (31)$$

As stated earlier, eqs 30 and 31 yield the ADMP equations when $\hbar \rightarrow 0$. However, when $\hbar \neq 0$, eqs 29–31 provide the nucleus of an alternate approach to perform quantum dynamics within the approximation to the quantum Hamiltonian specified in eq 15; hence, these equations provide a quantum generalization for ADMP in the Hamilton–Jacobi form. When $\hbar \neq 0$, by comparing eqs 30 and 31 with eqs 2 and 3, we observe that the nuclear and density matrix dynamics are influenced by additional \hbar -dependent “quantum forces”

$$\begin{aligned} \mathcal{Q}_{\mathbf{R}, i, j} &= \frac{\partial}{\partial \mathbf{R}_{i, j}} \left[\sum_{i,j=1}^3 \sum_{4M_i} \frac{\hbar^2}{4M_i} \left\{ \frac{1}{\mathcal{P}_{\mathbf{R}, \mathbf{P}}} \frac{\partial^2 \mathcal{P}_{\mathbf{R}, \mathbf{P}}}{\partial \mathbf{R}_{ij}^2} - \frac{1}{2\mathcal{P}_{\mathbf{R}, \mathbf{P}}^2} \left(\frac{\partial \mathcal{P}_{\mathbf{R}, \mathbf{P}}}{\partial \mathbf{R}_{ij}} \right)^2 \right\} \right] \\ &= \sum_{i,j=1}^3 \sum_{4M_i} \frac{\hbar^2}{4M_i} \left[\frac{1}{\mathcal{R}_{\mathbf{R}, \mathbf{P}}^2} \left(\mathcal{R}_{\mathbf{R}, \mathbf{P}} \frac{\partial^3 \mathcal{R}_{\mathbf{R}, \mathbf{P}}}{\partial \mathbf{R}_{i, j} \partial \mathbf{R}_{i, j}^2} - \frac{\partial^2 \mathcal{R}_{\mathbf{R}, \mathbf{P}}}{\partial \mathbf{R}_{i, j}^2} \frac{\partial \mathcal{R}_{\mathbf{R}, \mathbf{P}}}{\partial \mathbf{R}_{i, j'}} \right) \right] \quad (32) \end{aligned}$$

and

$$\begin{aligned} \mathcal{Q}_{\mathbf{P}, i, j} &= \frac{\partial}{\partial \mathbf{P}_{i, j}} \left[\sum_{ij} \frac{\hbar^2}{4\mu} \left\{ \frac{1}{\mathcal{P}_{\mathbf{R}, \mathbf{P}}} \frac{\partial^2 \mathcal{P}_{\mathbf{R}, \mathbf{P}}}{\partial \mathbf{P}_{ij}^2} - \frac{1}{2\mathcal{P}_{\mathbf{R}, \mathbf{P}}^2} \left(\frac{\partial \mathcal{P}_{\mathbf{R}, \mathbf{P}}}{\partial \mathbf{P}_{ij}} \right)^2 \right\} \right] \\ &= \sum_{ij} \frac{\hbar^2}{4\mu} \left[\frac{1}{\mathcal{R}_{\mathbf{R}, \mathbf{P}}^2} \left(\mathcal{R}_{\mathbf{R}, \mathbf{P}} \frac{\partial^3 \mathcal{R}_{\mathbf{R}, \mathbf{P}}}{\partial \mathbf{P}_{i, j} \partial \mathbf{P}_{i, j}^2} - \frac{\partial^2 \mathcal{R}_{\mathbf{R}, \mathbf{P}}}{\partial \mathbf{P}_{i, j}^2} \frac{\partial \mathcal{R}_{\mathbf{R}, \mathbf{P}}}{\partial \mathbf{P}_{i, j'}} \right) \right] \quad (33) \end{aligned}$$

where, for simplicity, we have presented the results in terms of $\mathcal{R}_{\mathbf{R}, \mathbf{P}}$. A few comments regarding eqs 32 and 33 are now in order. Equation 32 allows the instantaneous shape of the nuclear wave packet (determined by the classical configurations and the associated probabilities) to determine the dynamics of each classical component comprising the wave packet. That is, the nuclear wave packet configuration at time t determines the nuclear wave packet at the next instant by constraining the dynamics of the nuclear coordinates through the quantum force in eq 32 and the associated probabilities through eq 29. The interpretation of eq 33 is as follows. In classical ADMP, \mathbf{P} and \mathbf{R} are both free dynamical variables, as compared to

Born–Oppenheimer dynamics, where \mathbf{R} is free but \mathbf{P} is determined from an SCF procedure for every given \mathbf{R} , and is hence not free. Therefore, in a Bohmian implementation in Born–Oppenheimer dynamics, the corresponding density matrix dynamics is influenced by the quantum force on the nuclei, which in turn affects the SCF procedure, by yielding wave functions that are different from those in the absence of the quantum force. Equation 33 performs a similar function in the current formalism by restricting the density matrix dynamics and the nuclear dynamics in a unified fashion. These quantum forces make the eqs 29–31 equivalent to the time-dependent Schrödinger equation for the Hamiltonian in eq 15. Of course, in large systems it is not necessary that all components be treated quantum-mechanically, and in such cases the appropriate values for the quantum forces (zero or otherwise) may be chosen.

We may construct a propagation scheme based on eqs 29–31 as follows. Since eq 29 represents the propagation of the probability density of a classical system, $\{\mathbf{R}, \mathbf{P}\}$, which in turn is obtained from solving eqs 30 and 31, it is important to note that we may consider here an ensemble of classical systems given by $\{\mathbf{R}_I, \mathbf{P}_I\}$, each system having an associated probability of $\mathcal{P}_{\mathbf{R}_I, \mathbf{P}_I}$. The collection of these classical systems and their probabilities together provide an approximation to the time-dependent wave function χ , at any given time. Each element of the ensemble, $\{\mathbf{R}_I, \mathbf{P}_I\}$, is to be propagated according to eqs 30 and 31, with the associated quantum forces to be determined at every instant by eq 29. Thus, we may consider an ensemble of initial nuclear configurations $\{\mathbf{R}_I^{i=0}\}$ with corresponding initial velocities $\{\mathbf{V}_I^{i=0}\}$. We may further assume that each nuclear configuration has an associated density matrix, leading to the family of initial density matrixes $\{\mathbf{P}_I^{i=0}\}$ with velocities $\{\mathbf{W}_I^{i=0}\}$. (Note that the uppercase subscripts refer to the configuration number in the ensemble, the superscript refers to the time index, and elsewhere in the paper we have used lower case subscripts to refer to the matrix elements of nuclear and density matrixes.) The probability for each nuclear-density matrix state is $\mathcal{P}_{\mathbf{R}_I^{i=0}, \mathbf{P}_I^{i=0}}$, which may be chosen by associating Boltzmann weights to each nuclear-density matrix configuration (i.e., all density matrix elements belonging to the same nuclear configuration have the same probability). Together, $\mathcal{P}_{\mathbf{R}_I^{i=0}, \mathbf{P}_I^{i=0}}$ along with $\{\mathbf{R}_I^{i=0}\}$ and $\{\mathbf{P}_I^{i=0}\}$ represent an approximation to the initial wave packet of the nuclear-electronic system. To obtain the system configuration at the next time step, it is first necessary to calculate the quantum forces in eqs 32 and 33 and the probability density $\mathcal{P}_{\mathbf{R}_I^{i=\Delta t}, \mathbf{P}_I^{i=\Delta t}}$ from eq 29, which is required to construct the velocities at time Δt , as will be seen below.

The quantum forces may be obtained from numerical differentiation of the multidimensional surface of $\mathcal{P}_{\mathbf{R}_I^{i=0}, \mathbf{P}_I^{i=0}}$ using well-known approximations such as the DAFs⁵⁹ or the moving weighted least squares (MWLS) approach⁶⁰ to differentiate functions on an unstructured grid. (Note that the probability density is a $(3N + MM)$ dimensional surface for N atoms and M basis functions.) For this purpose it may be required to obtain a suitable fit of the probability function with respect to the nuclear coordinates and density matrix elements using some basis functions whose derivatives are already known (for example, Gaussians or DAFs). At this point, it would also be important to evaluate if appropriate sampling of the probability density $\mathcal{P}_{\mathbf{R}_I^{i=0}, \mathbf{P}_I^{i=0}}$ is maintained; if not, a larger number of classical systems, $\{\mathbf{R}_I^{i=0}, \mathbf{P}_I^{i=0}\}$, would have to be chosen. Once the fit and the derivatives are obtained, the quantum forces may be calculated. (It is important to note that mixed third derivatives

are necessary to determine the quantum forces; hence, this calculation is perhaps the most critical part of the algorithm for both accuracy and computational efficiency.) To obtain $\mathcal{P}_{\mathbf{R}_I^{i=\Delta t}, \mathbf{P}_I^{i=\Delta t}}$, it is necessary to propagate eq 29. This again is to be achieved from $(3N + MM)$, one-dimensional fits to obtained derivatives of the kind $(\partial \mathbf{W}_{ij} / \partial \mathbf{P}_{ij})$ and $(\partial \mathbf{V}_{ij} / \partial \mathbf{R}_{ij})$. (Note that these fits are each one-dimensional.) Once the quantum forces and $\mathcal{P}_{\mathbf{R}_I^{i=\Delta t}, \mathbf{P}_I^{i=\Delta t}}$ are determined, eqs 30 and 31 may be integrated using the velocity Verlet procedure. For the density matrix propagation, these equations are

$$\mathbf{P}_I^{i+1} = \mathbf{P}_I^i + \mathbf{W}_I^i \Delta t - \frac{\Delta t^2}{2\mu} \left[\frac{\partial E(\mathbf{R}_I^i, \mathbf{P}_I^i)}{\partial \mathbf{P}} \right]_{\mathbf{R}} - \mathcal{Q}_{\mathbf{P}_I^i} + \Lambda_I^i \mathbf{P}_I^i + \left. \mathbf{P}_I^i \Lambda_I^i - \Lambda_I^i \right] \quad (34)$$

$$\mathbf{W}_I^{i+1/2} = \mathbf{W}_I^i - \frac{\Delta t}{2\mu} \left[\frac{\partial E(\mathbf{R}_I^i, \mathbf{P}_I^i)}{\partial \mathbf{P}} \right]_{\mathbf{R}} - \mathcal{Q}_{\mathbf{P}_I^i} + \Lambda_I^i \mathbf{P}_I^i + \mathbf{P}_I^i \Lambda_I^i - \left. \Lambda_I^i \right] = \frac{\mathbf{P}_I^{i+1} - \mathbf{P}_I^i}{\Delta t} \quad (35)$$

$$\mathbf{W}_I^{i+1} = \mathbf{W}_I^{i+1/2} - \frac{\Delta t}{2\mu} \left[\frac{\partial E(\mathbf{R}_I^{i+1}, \mathbf{P}_I^{i+1})}{\partial \mathbf{P}} \right]_{\mathbf{R}} - \mathcal{Q}_{\mathbf{P}_I^{i+1}} + \left. \Lambda_I^{i+1} \mathbf{P}_I^{i+1} + \mathbf{P}_I^{i+1} \Lambda_I^{i+1} - \Lambda_I^{i+1} \right] \quad (36)$$

Note that, to get \mathbf{W}_I^{i+1} , an approximation to $\mathcal{Q}_{\mathbf{P}_I^{i+1}}$, that is, the quantum force on the density matrix at the next time step, is necessary. This is obtained by first propagating the density using eq 29 to obtain $\mathcal{P}_{\mathbf{R}_I^{i=\Delta t}, \mathbf{P}_I^{i=\Delta t}}$. Then the new density may be differentiated with respect to \mathbf{P}_I^{i+1} , as outlined above to yield the new quantum force. This process is to be repeated for the nuclear coordinates to obtain

$$\mathbf{R}_I^{i+1} = \mathbf{R}_I^i + \mathbf{V}_I^i \Delta t - \frac{\Delta t^2}{2} \mathbf{M}^{-1} \left[\frac{\partial E(\mathbf{R}_I^i, \mathbf{P}_I^i)}{\partial \mathbf{R}} \right]_{\mathbf{P}} - \mathcal{Q}_{\mathbf{R}_I^i} \quad (37)$$

$$\mathbf{V}_I^{i+1/2} = \mathbf{V}_I^i - \frac{\Delta t}{2} \mathbf{M}^{-1} \left[\frac{\partial E(\mathbf{R}_I^i, \mathbf{P}_I^i)}{\partial \mathbf{R}} \right]_{\mathbf{P}} - \mathcal{Q}_{\mathbf{R}_I^i} = \frac{\mathbf{R}_I^{i+1} - \mathbf{R}_I^i}{\Delta t} \quad (38)$$

$$\mathbf{V}_I^{i+1} = \mathbf{V}_I^{i+1/2} - \frac{\Delta t}{2} \mathbf{M}^{-1} \left[\frac{\partial E(\mathbf{R}_I^{i+1}, \mathbf{P}_I^{i+1})}{\partial \mathbf{R}} \right]_{\mathbf{P}} - \mathcal{Q}_{\mathbf{R}_I^{i+1}} \quad (39)$$

Here again, $\mathcal{Q}_{\mathbf{R}_I^{i+1}}$ is obtained by differentiating the new density.

One choice of initial conditions for the probability function was discussed above, wherein, at $t = 0$, the probability of the classical $\{\mathbf{R}, \mathbf{P}\}$ system was chosen according to Boltzmann weight. Another, perhaps conceptually more appealing, set of initial conditions may be obtained as follows. Suppose we require that the quantum force in eq 31 be zero for the density matrixes at time $t = 0$. This may be achieved by requiring

$$\frac{1}{\mathcal{P}_{\mathbf{R}, \mathbf{P}}} \frac{\partial^2 \mathcal{P}_{\mathbf{R}, \mathbf{P}}}{\partial \mathbf{P}_{ij}^2} - \frac{1}{2\mathcal{P}_{\mathbf{R}, \mathbf{P}}^2} \left(\frac{\partial \mathcal{P}_{\mathbf{R}, \mathbf{P}}}{\partial \mathbf{P}_{ij}} \right)^2 = \text{constant} \quad (40)$$

for all i, j , which makes the quantum force on each density

matrix zero at the initial step. Equation 40 is a second-order nonlinear differential equation, but it is possible to reduce this to a first-order Bernoulli-type equation of power (-1) , which can be solved analytically. The solution is

$$\mathcal{P}_{\mathbf{R},\mathbf{P}} = \frac{\exp\{C\mathbf{P}_{ij} - E\}}{2} [D^2 \exp\{-2(C\mathbf{P}_{ij} - E)\} + 1] \quad (41)$$

where C , D , and E are constants; C is related to the right-hand side in eq 40, whereas D and E are constants of integration. Initial conditions similar to those of eq 40 can also be obtained for the nuclear degrees of freedom.

The fact that the condition for zero quantum force corresponds to a Bernoulli-type differential equation is a rather intriguing physical result. Since the Bernoulli equation in fluid dynamics corresponds to a fluid devoid of any rotations and viscosity, it is possible to negate this flow by transforming to a Lagrangian (rather than an Eulerian) frame of reference. The solution in eq 41 reflects a new frame of reference where the quantum force on the density matrix is zero. However, at subsequent time steps the probability function is propagated as per eq 29, and the probability function at all times does not, in general, satisfy eq 41. This is because the probability flux terms in eq 29 will in general allow the probability function to deviate from an internal rotation and viscosity-free environment. The continuity equation allows for viscous and rotational dynamics depending upon the nature of the flux term, which is determined by the energy functional, $E(\mathbf{R},\mathbf{P})$. Hence, the quantum force deviates from zero during the propagation, and in fact it deviates by an amount proportional to δt . Therefore, only in the limit of very small time steps, and with initial conditions for the probability distribution as in eq 40, the solutions to eqs 29–31 yield trajectories that are identical to those obtained when the nuclei are propagated as per the Bohmian dynamics eq 30 and the density matrix elements follow the classical ADMP dynamics eq 3 (with no quantum force). Hence, for finite time steps, the forces on a propagation scheme that allows Bohmian dynamics of nuclei as per eq 30 but only accounts for the density matrix dynamics within the classical ADMP equations (i.e., without any quantum force, by assuming eq 40 to be valid at all times) deviate from those of a conservative system by an amount proportional to δt and hence will not conserve the energy.

A consequence of this argument is as follows. Consider an alternate form of eq 15 where the second term is substituted by the fictitious kinetic energy in eq 4. (That is Dirac quantization is only invoked for the nuclear degrees of freedom but not for the density matrix degrees of freedom.) This Hamiltonian will give rise to precisely the same equations discussed in the preceding paragraph, where the nuclear dynamics follows the Bohmian eqs 30 and 29, while the density matrix dynamics is given by the classical ADMP eq 3. From the arguments discussed above, such a scheme will not conserve energy unless the time steps are very small. Furthermore, there would be just one density matrix being propagated as per eq 3, whereas eqs 30 and 29 would allow many different nuclear configurations to be propagated. This would imply that the electronic structures in all the separate nuclear configurations at a given time are described by the same density matrix whose dynamics is given by eq 3. This is clearly nonphysical. The current quantization scheme in eq 15 helps

alleviate such problems. It is important to note that this situation is, however, different from the one discussed in the previous paragraph which considers the dynamics of many density matrixes, each satisfying the initial condition in eq 40. In that case, completely neglecting the quantum force on the density matrix gives rise to a deviation proportional to δt and depending on the energy functional.

We conclude this section by stating one critical feature in the above formalism. The variable \mathcal{J} in eq 17 is not defined when the probability function $\mathcal{P}_{\mathbf{R},\mathbf{P}}$ becomes zero at some point during the trajectory (i.e., when a node develops in the wave function during the propagation scheme). This does not, in principle, present any problem,³⁹ since a trajectory that is started with $\mathcal{P}_{\mathbf{R},\mathbf{P}} \neq 0$ can never pass through a nodal surface. However, this does present a problem of optimal sampling of the probability function; that is, the two regions separated by a node that develops during a propagation may not have the same sampling, in terms of the presence of the classical trajectory elements, and in some cases it is foreseeable that regions beyond the node may not have the requisite sampling. This problem may be alleviated by (i) using the probability density fit to determine the development of a new node during the calculation or (ii) evaluating the fit on all sides of the node and resampling the distribution with more classical points $\{\mathbf{R},\mathbf{P}\}$ to spawn new trajectories, if necessary.

Alternate, approximate, computational schemes may also be obtained by invoking semiclassical approximations to eqs 29–31 or to eq 15 directly. For example, WKB-type approximations for eqs 29–31 may be obtained by ignoring the quantum forces in eqs 30 and 31, and solutions to every $\mathcal{P}_{\mathbf{R},\mathbf{P}}$ may be obtained by invoking the stationarity condition. However, complex boundary matching algorithms will be required to obtain dynamical behavior as a continuous function of incident energy, even at energies close to the classical turning point.

Another semiclassical scheme can be derived by invoking the Ehrenfest theorem, which allows the center of the nuclear-density matrix wave packet to move under the influence of an average force, with the average force being calculated from all the points on the classical set $\{\mathbf{R},\mathbf{P}\}$. However, the sum of the quantum forces over the entire trajectory is proportional only to the time step, δt , and hence, only the classical part of the potential in eqs 30 and 31 is required to calculate such an average. Hence, this approach should provide a reasonable and computationally efficient approximation to the above formalism. It should also be noted that, in the Ehrenfest theorem form where the center of the wave packet is propagated under the influence of an average force, the current approach shares conceptual similarities with the centroid molecular dynamics (CMD) approach^{61,62} to quantum dynamics in the condensed phase.

5. Analysis of the Quantum Fictitious Kinetic Energy

The algorithm presented in the previous section becomes exact as the expectation value of the quantum analogue of the fictitious kinetic energy tends to zero, as was discussed in the paragraphs following eq 15. In this section we conduct a detailed analysis of the second term in eq 15, that is, the quantum fictitious kinetic energy. Using eqs 15, 17, and 23, the expectation value of the quantum fictitious energy is given by

$$\begin{aligned}
\left\langle \chi \left| \frac{\hbar^2}{2\mu} \sum_{ij} \frac{\partial^2}{\partial \mathbf{P}_{ij}^2} \right| \chi \right\rangle &= - \sum_I \mathcal{R}_{\mathbf{R}_I, \mathbf{P}_I} \frac{\hbar^2}{2\mu} \sum_{ij} \left[\frac{\partial^2 \mathcal{R}_{\mathbf{R}_I, \mathbf{P}_I}}{\partial \mathbf{P}_{ij}^2} + \right. \\
& 2 \frac{\iota}{\hbar} \frac{\partial \mathcal{R}_{\mathbf{R}_I, \mathbf{P}_I}}{\partial \mathbf{P}_{ij}} \frac{\partial \mathcal{J}}{\partial \mathbf{P}_{ij}} - \frac{1}{\hbar^2} \mathcal{R}_{\mathbf{R}_I, \mathbf{P}_I} \left(\frac{\partial \mathcal{J}}{\partial \mathbf{P}_{ij}} \right)^2 + \left. \frac{\iota}{\hbar} \mathcal{R}_{\mathbf{R}_I, \mathbf{P}_I} \frac{\partial^2 \mathcal{J}}{\partial \mathbf{P}_{ij}^2} \right] \\
&= - \sum_I \mathcal{R}_{\mathbf{R}_I, \mathbf{P}_I} \sum_{ij} \left[\frac{\hbar^2}{2\mu} \frac{\partial^2 \mathcal{R}_{\mathbf{R}_I, \mathbf{P}_I}}{\partial \mathbf{P}_{ij}^2} + \right. \\
& \left. \iota \hbar \frac{\partial \mathcal{R}_{\mathbf{R}_I, \mathbf{P}_I}}{\partial \mathbf{P}_{ij}} \mathbf{W}_{ij} - \frac{\mu}{2} \mathcal{R}_{\mathbf{R}_I, \mathbf{P}_I} \mathbf{W}_{ij}^2 + \frac{\iota \hbar}{2} \mathcal{R}_{\mathbf{R}_I, \mathbf{P}_I} \frac{\partial \mathbf{W}_{ij}}{\partial \mathbf{P}_{ij}} \right] \quad (42)
\end{aligned}$$

where we have used the fact that the sum over all the classical trajectories is equivalent to the integral over all space. The absolute expectation value of the quantum fictitious energy is then given by

$$\begin{aligned}
\left\langle \chi \left| \frac{\hbar^2}{2\mu} \sum_{ij} \frac{\partial^2}{\partial \mathbf{P}_{ij}^2} \right| \chi \right\rangle^2 &= \\
& \left[\sum_I \sum_{ij} \left(\frac{\hbar^2}{2\mu} \mathcal{R}_{\mathbf{R}_I, \mathbf{P}_I} \frac{\partial^2 \mathcal{R}_{\mathbf{R}_I, \mathbf{P}_I}}{\partial \mathbf{P}_{ij}^2} - \frac{\mu}{2} \mathcal{R}_{\mathbf{R}_I, \mathbf{P}_I}^2 \mathbf{W}_{ij}^2 \right) \right]^2 + \\
& \left[\sum_I \sum_{ij} \left(\hbar \mathcal{R}_{\mathbf{R}_I, \mathbf{P}_I} \frac{\partial \mathcal{R}_{\mathbf{R}_I, \mathbf{P}_I}}{\partial \mathbf{P}_{ij}} \mathbf{W}_{ij} + \frac{\hbar}{2} \mathcal{R}_{\mathbf{R}_I, \mathbf{P}_I}^2 \frac{\partial \mathbf{W}_{ij}}{\partial \mathbf{P}_{ij}} \right) \right]^2 \quad (43)
\end{aligned}$$

The second, third, and fourth terms in the above equation are proportional to μ , \mathbf{W} , and the derivative of \mathbf{W} . Let us compare this with the adiabaticity index obtained in refs 17 and 19, that allows us to ascertain the deviations of ADMP trajectories from the Born–Oppenheimer surface:

$$\frac{d\mathcal{H}_{\text{fict}}}{dt} = \text{Tr} \left[\frac{\partial \mathcal{H}_{\text{fict}}}{\partial \mathcal{W}} \frac{d\mathcal{W}}{dt} \right] = \text{Tr} \left[\mathbf{W} \underline{\mu}^{1/2} \frac{d\mathbf{W}}{dt} \underline{\mu}^{1/2} \right] \quad (44)$$

It has been shown in ref 19 that this quantity is proportional to deviations from the Born–Oppenheimer surface in ADMP simulations, and in the limit that the quantity on the right-hand side of eq 44 goes to zero, the ADMP simulation attains the Born–Oppenheimer dynamics limit. Interestingly, the last three terms in eq 43 are proportional to the same quantities as the quantity in eq 44. The first term in eq 43 is also proportional to the same quantities, and this can be seen from the following analysis. Using eq 29, under the condition of small time steps

$$\begin{aligned}
\frac{\hbar^2}{2\mu} \mathcal{R}_{\mathbf{R}_I, \mathbf{P}_I} \frac{\partial^2 \mathcal{R}_{\mathbf{R}_I, \mathbf{P}_I}}{\partial \mathbf{P}_{kl}^2} &= \delta t \frac{\hbar^2}{2\mu} \mathcal{R}_{\mathbf{R}_I, \mathbf{P}_I}^2 \left[\frac{\delta t}{4} \frac{\partial}{\partial \mathbf{P}_{kl}} \frac{\partial}{\partial \mathbf{P}_{ij}} \sum \frac{\partial \mathbf{W}_{ij}}{\partial \mathbf{P}_{ij}} \right]^2 - \\
& \frac{1}{2} \left[\frac{\partial^2}{\partial \mathbf{P}_{kl}^2} \sum \frac{\partial \mathbf{W}_{ij}}{\partial \mathbf{P}_{ij}} \right] \quad (45)
\end{aligned}$$

When the magnitudes of δt and μ are simultaneously reduced, the above expression is proportional to δt and other higher order derivatives of \mathbf{W} , which are required to be finite, as for the quantity in eq 44. All the terms in eq 43 are proportional to the same quantities that determine the deviation of classical ADMP from Born–Oppenheimer dynamics, that is, μ , \mathbf{W} , and the

derivative of \mathbf{W} as seen in eq 44. All of these quantities can be calculated at every instant during the dynamics to ascertain the required deviations, just as in normal ADMP simulations, where eq 44 is used to ascertain the deviations of ADMP from Born–Oppenheimer dynamics.

Another important conclusion that can be derived from eq 45 is based on the following expression for the quantum force on the density matrix,

$$\begin{aligned}
\sum_{kl} \frac{\hbar^2}{2\mu} \frac{1}{\mathcal{R}_{\mathbf{R}_I, \mathbf{P}_I}} \frac{\partial^2 \mathcal{R}_{\mathbf{R}_I, \mathbf{P}_I}}{\partial \mathbf{P}_{kl}^2} &= \frac{1}{\mathcal{P}_{\mathbf{R}_I, \mathbf{P}_I}} \sum_{kl} \frac{\hbar^2}{2\mu} \mathcal{R}_{\mathbf{R}_I, \mathbf{P}_I} \frac{\partial^2 \mathcal{R}_{\mathbf{R}_I, \mathbf{P}_I}}{\partial \mathbf{P}_{kl}^2} \\
&= \sum_{kl} \delta t \frac{\hbar^2}{2\mu} \left[\frac{\delta t}{4} \frac{\partial}{\partial \mathbf{P}_{kl}} \frac{\partial}{\partial \mathbf{P}_{ij}} \sum \frac{\partial \mathbf{W}_{ij}}{\partial \mathbf{P}_{ij}} \right]^2 - \\
& \frac{1}{2} \left[\frac{\partial^2}{\partial \mathbf{P}_{kl}^2} \sum \frac{\partial \mathbf{W}_{ij}}{\partial \mathbf{P}_{ij}} \right] \quad (46)
\end{aligned}$$

Again the magnitude of the quantum force depends on the same parameters that determine the magnitude of the quantum fictitious kinetic energy and the adiabaticity index in eq 44.

6. Conclusions

In this paper we have (i) proved that the recently developed ADMP approach to ab initio molecular dynamics is the classical analogue of a special approximation to the quantum Hamiltonian and (ii) derived a new approach based on this connection that allows the study of quantum nuclear dynamics on an adiabatic electronic surface. The new approach, being based on ADMP, allows for accurate treatment of the electronic variables within the formalism of DFT, while simultaneously propagating the same with the nuclear degrees of freedom. Semiclassical development of the resultant equations is also an interesting and computationally efficient possibility.

The computational scaling of the classical ADMP procedure is $O(N)$ for large systems, where N is the number of electrons. As a result, the approach derived here scales as $O(N)$ times the number of classical trajectories required to sample the quantum potential energy surface. The latter is a function of the ruggedness of the potential energy surface and is determined on the basis of the accuracy required for the quantum potentials.

The calculation of the quantum forces is expected to be one major computational bottleneck in the methodology. This requires a multidimensional fit that could be cumbersome to achieve. However, such problems have been addressed to some degree in computational fluid dynamics and may not present an intractable problem in the current approach. Furthermore, this problem may be circumvented to a certain extent using semiclassical approximations to the current approach. These issues will be explored in future publications.

Acknowledgment. This work was supported by the Office of Naval Research (G.A.V.), National Science Foundation Grant CHE-0131157 (H.B.S.), and Gaussian, Inc.

References and Notes

- (1) Goldberger, M. L.; Watson, K. M. *Collision Theory*; Wiley: New York, 1964.
- (2) Zhang, D. H.; Zhang, J. Z. H. In *Dynamics of Molecules and Chemical Reactions*; Wyatt, R. E., Zhang, J. Z. H., Eds.; Marcel Dekker Inc.: New York, New York, 1996; pp 231–276.

- (3) Neuhauser, D.; Judson, R. S.; Baer, M.; Kouri, D. J. In *Advances in Molecular Vibrations and Collision Dynamics*; Bowman, J. M., Ed.; JAI Press: Greenwich, CT, 1994; Vol. 2B.
- (4) Mowrey, R. C.; Kouri, D. J. *J. Chem. Phys.* **1986**, *84*, 6466.
- (5) Kosloff, R. *Annu. Rev. Phys. Chem.* **1994**, *45*, 145.
- (6) Berne, B. J.; Ciccotti, G.; Coker, D. F., Eds. *Classical and quantum dynamics in condensed phase simulations*; World Scientific: London, 1997.
- (7) Wang, I. S. Y.; Karplus, M. *J. Am. Chem. Soc.* **1973**, *95*, 8160.
- (8) Leforestier, C. *J. Chem. Phys.* **1978**, *68*, 4406.
- (9) Car, R.; Parrinello, M. *Phys. Rev. Lett.* **1985**, *55*, 2471.
- (10) Payne, M. C.; Teter, M. P.; Allan, D. C.; Arias, T. A.; Joannopoulos, J. D. *Rev. Mod. Phys.* **1992**, *64*, 1045.
- (11) Deumens, E.; Diz, A.; Longo, R.; Öhrn, Y. *Rev. Mod. Phys.* **1994**, *66*, 917.
- (12) Schlegel, H. B.; Millam, J. M.; Iyengar, S. S.; Voth, G. A.; Daniels, A. D.; Scuseria, G. E.; Frisch, M. J. *J. Chem. Phys.* **2001**, *114*, 9758.
- (13) Schlegel, H. B. *J. Comput. Chem.*, accepted.
- (14) Bolton, K.; Hase, W. L.; Peslherbe, G. H. World Scientific: Singapore, 1998; chapter Direct Dynamics of Reactive Systems, p 143.
- (15) Remler, D. K.; Madden, P. A. *Mol. Phys.* **1990**, *70*, 921.
- (16) Marx, D.; Hutter, J. John vonNeumann Institute for Computing: Julich, 2000; Vol. 1, chapter Ab Initio Molecular Dynamics: Theory and Implementation, p 301.
- (17) Iyengar, S. S.; Schlegel, H. B.; Millam, J. M.; Voth, G. A.; Scuseria, G. E.; Frisch, M. J. *J. Chem. Phys.* **2001**, *115*, 10291.
- (18) Schlegel, H. B.; Iyengar, S. S.; Li, X.; Millam, J. M.; Voth, G. A.; Scuseria, G. E.; Frisch, M. J. *J. Chem. Phys.* **2002**, *117*, 8694.
- (19) Iyengar, S. S.; Schlegel, H. B.; Voth, G. A.; Millam, J. M.; Scuseria, G. E.; Frisch, M. J. Special issue of *Isr. J. Chem.*, in press.
- (20) Anderson, H. C. *J. Chem. Phys.* **1980**, *72*, 2384–2393.
- (21) Parrinello, M.; Rahman, A. *Phys. Rev. Lett.* **1980**, *45*, 1196–1199.
- (22) Lippert, G.; Hutter, J.; Parrinello, M. *Theor. Chem. Acc.* **1999**, *103*, 124.
- (23) Lippert, G.; Hutter, J.; Parrinello, M. *Mol. Phys.* **1997**, *92*, 477.
- (24) Scuseria, G. E. *J. Phys. Chem. A* **1999**, *103*, 4782.
- (25) Rega, N.; Iyengar, S. S.; Voth, G. A.; Schlegel, H. B.; Frisch, M. J. Manuscript in preparation.
- (26) Iyengar, S. S.; Kudin, K. N.; Schlegel, H. B.; Voth, G. A.; Scuseria, G. E.; Frisch, M. J. Manuscript in preparation.
- (27) Iyengar, S. S.; Day, T. J. F.; Petersen, M. K.; Voth, G. A. *Nature*, submitted.
- (28) Gibson, D. A.; Ionova, I. V.; Carter, E. A. *Chem. Phys. Lett.* **1995**, *240*.
- (29) Hartke, B.; Carter, E. A. *J. Chem. Phys.* **1992**, *97*, 6569.
- (30) Hartke, B.; Carter, E. A. *Chem. Phys. Lett.* **1992**, *189*, 358.
- (31) Martyna, G.; Cheng, C.; Klein, M. L. *J. Chem. Phys.* **1991**, *95*, 1318.
- (32) Madelung, E. Z. *Phys.* **1926**, *40*, 322.
- (33) de Broglie, L. *An introduction to the study of wave mechanics*; E. P. Dutton and Company, Inc.: New York, 1930.
- (34) de Broglie, L. *Compt. Rend.* **1926**, *183*, 447.
- (35) de Broglie, L. *Compt. Rend.* **1927**, *184*, 273.
- (36) de Broglie, L. *Compt. Rend.* **1927**, *185*, 380.
- (37) Bohm, D. *Phys. Rev.* **1952**, *85*, 166.
- (38) Cushing, J. T.; Fine, A.; Goldstein, S., Eds. *Bohmian Mechanics: An appraisal*; Kluwer: Boston, 1996.
- (39) Holland, P. R. *The Quantum Theory of Motion*; Cambridge: New York, 1993.
- (40) Day, B. K.; Askar, A.; Rabitz, H. A. *J. Chem. Phys.* **1998**, *109*, 8770.
- (41) Lopreore, C. L.; Wyatt, R. E. *Phys. Rev. Lett.* **1999**, *82*, 5190.
- (42) Wyatt, R. E. *Chem. Phys. Lett.* **1999**, *313*, 189.
- (43) Wyatt, R. E. *J. Chem. Phys.* **1999**, *111*, 4406.
- (44) Wyatt, R. E.; Kouri, D. J.; Hoffman, D. K. *J. Chem. Phys.* **2000**, *112*, 1070.
- (45) Bittner, E. R.; Wyatt, R. E. *J. Chem. Phys.* **2000**, *113*, 8888.
- (46) Wyatt, R. E.; Bittner, E. R. *J. Chem. Phys.* **2000**, *113*, 8898.
- (47) Wyatt, R. E. *J. Chem. Phys.* **2002**, *117*, 9569.
- (48) Burant, J. C.; Tully, J. C. *J. Chem. Phys.* **2000**, *112*, 6097.
- (49) Garashchuk, S.; Rassolov, V. A. *Chem. Phys. Lett.* **2002**, *364*, 562–567.
- (50) Garashchuk, S.; Rassolov, V. A. *J. Chem. Phys.* **2003**, *118*, 2482.
- (51) Goldstein, H. *Classical Mechanics*; Addison-Wesley Press: Cambridge, MA, 1980.
- (52) Swope, W. C.; Andersen, H. C.; Berens, P. H.; Wilson, K. R. *J. Chem. Phys.* **1982**, *76*, 637.
- (53) Tuckerman, M. E.; Parrinello, M. *J. Chem. Phys.* **1994**, *101*, 1302.
- (54) Feynman, R. P.; Hibbs, A. R. *Quantum mechanics and path integrals*; McGraw-Hill: New York, 1965.
- (55) Dirac, P. A. M. *The Principles of Quantum Mechanics*; Vol. 27 of The International series of monographs on Physics; Oxford University Press: New York, fourth edition ed., 1958.
- (56) de Broglie, L. *C. R. Acad. Sci. Paris* **1926**, *183*, 447.
- (57) de Broglie, L. *C. R. Acad. Sci. Paris* **1927**, *184*, 273.
- (58) Pavese, M.; Berard, D. R.; Voth, G. A. *Chem. Phys. Lett.* **1999**, *300*, 93–98.
- (59) Hoffman, D. K.; Nayar, N.; Sharafeddin, O. A.; Kouri, D. J. *J. Phys. Chem.* **1991**, *95*, 8299.
- (60) Lancaster, P.; Salkauskas, K. *Curve and Surface Fitting*; Academic: New York, 1986.
- (61) Jang, S.; Voth, G. A. *J. Chem. Phys.* **1999**, *111*, 2357.
- (62) Jang, S.; Voth, G. A. *J. Chem. Phys.* **1999**, *111*, 2371.