

DERIVING EHRENFEST AND BORN-OPPENHEIMER DYNAMICS FROM FIRST PRINCIPLES

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1. INTRODUCTION

There exist several mean-field approximate methods deriving from Time-Dependent Self-Consistent Field (TDSCF) theory which may be used to simulate the electronic and nuclear dynamics in molecules with varying degrees of coupling between the electronic and nuclear components.[2] Mean-field methods (also called ‘single-reference’ methods) are approximations of the exact time-dependent Schrödinger equation using the assumption that a single Slater determinant composed of single particle wavefunctions can represent the system at all times.[1] TDSCF itself is a mean-field approximation based in first principles for total molecular motion including both electronic and nuclear degrees of freedom.[2, 3] However, the dimensionality of the TDSCF problem is such that additional approximations must be made to provide an efficient avenue for calculating time-dependent properties of molecules. To that end, following the derivation of classical molecular dynamics (MD) from the time-dependent Schrödinger equation and choosing certain approximations at different points along this path one can obtain the Ehrenfest dynamics and Born-Oppenheimer Molecular Dynamics (BOMD) methods.[2, 3]

These dynamical simulation techniques are indeed useful for observing time-evolving molecular properties. Such properties often appear to experimental chemists as spectra, but as theorists we may also simulate and predict isolated spectral features or complete spectra with sufficiently accurate and complete models. This motivates the implementation of efficient methods for modeling the dynamics of molecular systems. The aim of this work is to provide detailed derivations for two useful mixed quantum-classical dynamical simulation techniques from first principles – Ehrenfest dynamics and Born-Oppenheimer Molecular Dynamics.

2. TDSCF AND THE BORN-OPPENHEIMER WAVEFUNCTION ANSATZ

We may begin by defining an arbitrary, time-dependent molecular wavefunction $\Psi(\mathbf{r}, \mathbf{R}; t)$ which is postulated to contain all information regarding the nuclear and electronic degrees of freedom for the system. Since we are interested in separating the electronic and nuclear degrees of freedom, we apply the Born-Oppenheimer approximate wavefunction ansatz of the form

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$$(1) \quad \Psi(\mathbf{r}, \mathbf{R}; t) = \phi(\mathbf{r}; t) \chi(\mathbf{R}; t) \exp \left[\frac{i}{\hbar} \int^t E_r(t') dt' \right]$$

where we assume both $\phi(\mathbf{r}; t)$ and $\chi(\mathbf{R}; t)$ are normalized at every time t when integrated over spatial degrees of freedom \mathbf{r} and \mathbf{R} . [3] The phase factor $E_r(t)$ is taken to represent the effective electronic energy for the entire molecular system as given in eq. (2). Within eq. (2) we also define an effective electronic Hamiltonian $\hat{\mathcal{H}}_r(\mathbf{r}, \mathbf{R})$ which determines the interactions between electrons and nuclei as well as electron-electron interactions while neglecting the nuclear kinetic energy.

$$(2) \quad E_r(t) = \langle \phi(\mathbf{r}; t) \chi(\mathbf{R}; t) | \hat{\mathcal{H}}_r(\mathbf{r}, \mathbf{R}) | \phi(\mathbf{r}; t) \chi(\mathbf{R}; t) \rangle$$

The total Hamiltonian is then divided into a nuclear kinetic term, and the effective electronic term $\hat{\mathcal{H}}_r$. It should be noted that $\hat{\mathcal{H}}_r$ is still dependent on the nuclear position observable but has no implicit time dependence in the absence of an applied time-evolving external field as shown by eq. (3).

$$(3) \quad \begin{aligned} \hat{\mathcal{H}}_{total}(\mathbf{r}, \mathbf{R}) &= -\frac{\hbar^2}{2} \sum_I \frac{1}{M_I} \nabla_I^2 - \frac{\hbar^2}{2} \sum_i \frac{1}{m_i} \nabla_i^2 + \hat{V}(\mathbf{r}, \mathbf{R}) \\ &= -\frac{\hbar^2}{2} \sum_I \frac{1}{M_I} \nabla_I^2 + \hat{\mathcal{H}}_r(\mathbf{r}, \mathbf{R}) \end{aligned}$$

$$\hat{\mathcal{H}}_r(\mathbf{r}, \mathbf{R}) = -\frac{\hbar^2}{2} \sum_i \frac{1}{M_i} \nabla_i^2 + \hat{V}_{rR}(\mathbf{r}, \mathbf{R})$$

At this point, it is straightforward to insert our wavefunction ansatz from eq. (1) and the molecular Hamiltonian (eq. (3)) into the Time-Dependent Schrödinger equation to obtain a single-reference approximation to the exact quantum dynamics for the entire system given by eq. (4). This constitutes the TDSCF approximation for this time-evolving system. In the following equations, we will omit explicitly writing the obvious dependencies for notational simplicity as they are already defined in the previous equations.

$$\begin{aligned}
(4) \quad & i\hbar \frac{\partial \Psi}{\partial t} = \hat{\mathcal{H}}_{total} \Psi \\
& \longrightarrow i\hbar \frac{\partial}{\partial t} \left[\phi \chi \exp \left(\frac{i}{\hbar} \int^t E_r(t') dt' \right) \right] = \hat{\mathcal{H}}_{total} \left[\phi \chi \exp \left(\frac{i}{\hbar} \int^t E_r(t') dt' \right) \right] \\
& \longrightarrow i\hbar \left[\frac{\partial \phi}{\partial t} \chi + \phi \frac{\partial \chi}{\partial t} + \frac{i}{\hbar} E_r(t) \phi \chi \right] \exp \left(\frac{i}{\hbar} \int^t E_r(t') dt' \right) = \\
& = \left[-\frac{\hbar^2}{2} \sum_I \frac{1}{M_I} \phi \nabla_I^2 \chi - \frac{\hbar^2}{2} \sum_i \frac{1}{m_i} \chi \nabla_i^2 \phi + \hat{V}_{rR} \phi \chi \right] \exp \left(\frac{i}{\hbar} \int^t E_r(t') dt' \right) \\
& \longrightarrow \boxed{i\hbar \frac{\partial \phi}{\partial t} \chi + \phi \frac{\partial \chi}{\partial t} = -\frac{\hbar^2}{2} \sum_I \frac{1}{M_I} \phi \nabla_I^2 \chi - \frac{\hbar^2}{2} \sum_i \frac{1}{m_i} \chi \nabla_i^2 \phi + \hat{V}_{rR} \phi \chi - E_r(t) \phi \chi.}
\end{aligned}$$

Furthermore, through this wavefunction ansatz we may derive specific effective time-dependent Schrödinger equations for both the electronic and nuclear wavefunctions. This is done by projecting out eq. (4) along the normalized wavefunction $\phi(\mathbf{r}; t)$ in the case of the nuclear effective Schrödinger equation (eq. (5)). Similarly, to obtain the effective electronic Schrödinger equation, the same is done with $\chi(\mathbf{R}; t)$ (eq. (6)).[3]

$$\begin{aligned}
(5) \quad i\hbar \frac{\partial \chi}{\partial t} = & -\frac{\hbar^2}{2} \sum_I \frac{1}{M_I} \nabla_I^2 \chi + \left\{ \int \phi^* \left[-\frac{\hbar^2}{2} \sum_i \frac{1}{m_i} \nabla_i^2 + \hat{V}_{rR} \right] \phi d\mathbf{r} \right\} \chi + \dots \\
& \dots + E_r(t) \chi - i\hbar \left[\int \phi^* \frac{\partial \phi}{\partial t} d\mathbf{r} \right] \chi.
\end{aligned}$$

$$\begin{aligned}
(6) \quad i\hbar \frac{\partial \phi}{\partial t} = & -\frac{\hbar^2}{2} \sum_i \frac{1}{m_i} \nabla_i^2 \phi + \left\{ \int \chi^* \left[-\frac{\hbar^2}{2} \sum_I \frac{1}{M_I} \nabla_I^2 + \hat{V}_{rR} \right] \chi d\mathbf{R} \right\} \phi + \dots \\
& \dots + E_r(t) \phi - i\hbar \left[\int \chi^* \frac{\partial \chi}{\partial t} d\mathbf{R} \right] \phi.
\end{aligned}$$

If we project out eq. (5) in the basis of nuclear wavefunctions then rearrange the terms we obtain

$$\begin{aligned}
(7) \quad & i\hbar \int \phi^* \frac{\partial \phi}{\partial t} d\mathbf{r} + i\hbar \int \chi^* \frac{\partial \chi}{\partial t} d\mathbf{R} - E_r(t) = \int \int \phi^* \chi^* \hat{\mathcal{H}} \chi \phi d\mathbf{r} d\mathbf{R} = E \\
& i\hbar \int \phi^* \frac{\partial \phi}{\partial t} d\mathbf{r} - E_r(t) = E - i\hbar \int \chi^* \frac{\partial \chi}{\partial t} d\mathbf{R}.
\end{aligned}$$

The same equation may be obtained by projecting out eq. (6) in the basis of electronic wavefunctions. It is clear that in order to satisfy eq. (7) the derivative factors on the right

hand sides of eq. (5) and eq. (6) are real-valued as ϕ and χ are assumed to be normalized. Since the total energy must necessarily remain conserved, $\frac{\partial E}{\partial t} = 0$, imposing constraints on the derivative factors in addition to $E_r(t)$. The derivative phase factors need only satisfy eq. (7) and do not need to be symmetric. Thus arbitrary phase factor values may be chosen satisfying eq. (7) such that

$$(8) \quad i\hbar \int \chi^* \frac{\partial \chi}{\partial t} d\mathbf{R} = E$$

and

$$(9) \quad i\hbar \int \phi^* \frac{\partial \phi}{\partial t} d\mathbf{r} = E_r(t).$$

Substituting eq. (8) back into eq. (5) and eq. (9) into eq. (6) we subtract out the energy terms, and recalling the definition of $\hat{\mathcal{H}}_r$ from eq. (3) we arrive at the basic working equations for TDSCF (eq. (10) and eq. (11)).

$$(10) \quad \boxed{i\hbar \frac{\partial \chi}{\partial t} = -\frac{\hbar^2}{2} \sum_I \frac{1}{M_I} \nabla_I^2 \chi + \left[\int \phi^* \hat{\mathcal{H}}_r \phi d\mathbf{r} \right] \chi}$$

and

$$(11) \quad \boxed{i\hbar \frac{\partial \phi}{\partial t} = -\frac{\hbar^2}{2} \sum_i \frac{1}{m_i} \nabla_i^2 \phi + \left[\int \chi^* V_{rR} \chi d\mathbf{R} \right] \phi}$$

From eq. (10) and eq. (11) we have the working equations for TDSCF and can now derive Ehrenfest dynamics and BOMD. It is apparent that energy is able to move not only from nuclei to electrons, but also back from electrons to nuclei. This coupling is apparent in the two working equations where the nuclear potential energy term is calculated from the electronic potential energy surface (PES) derived from integrating the effective electronic Hamiltonian over electronic degrees of freedom. Similarly, the opposite is true for the potential energy integral of the electronic effective equation where the *mean-field* nuclear and electronic potentials are captured in the integral of V_{rR} . [3] From here we may subject the TDSCF equations to further approximation to obtain Ehrenfest dynamics and Born-Oppenheimer Molecular Dynamics. [3, 2]

3. EHRENFEST DYNAMICS

Ehrenfest dynamics follows by taking the classical limit of eq. (10). There are several methods for doing so, but this derivation follows the technique used by Tully and coworkers. [3] We may exactly factorize the nuclear wavefunction in eq. (10) into a product of a time-evolving amplitude function and an exponential phase factor such that

$$(12) \quad \chi(\mathbf{R}; t) = A(\mathbf{R}; t) \exp \left[\frac{i}{\hbar} S(\mathbf{R}; t) \right]$$

where both $A(\mathbf{R}; t)$ and $S(\mathbf{R}; t)$ are assumed to be real-valued functions.[3, 2] Substituting eq. (12) into the nuclear effective Schrödinger equation (eq. (10)), applying the product rule, and separating the real and imaginary terms yields a pair of coupled equations dependent on $A(\mathbf{R}; t)$ and $S(\mathbf{R}; t)$ which, after collecting like terms are given as

$$(13) \quad \frac{\partial S}{\partial t} + \sum_I \frac{1}{M_I} (\nabla_I S)^2 + \left[\int \phi^* \hat{\mathcal{H}}_r \phi d\mathbf{r} \right] = \frac{\hbar^2}{2} \sum_I \frac{1}{M_I} \frac{\nabla_I^2 A}{A}$$

and

$$(14) \quad \frac{\partial A}{\partial t} + \sum_I \frac{1}{M_I} \nabla_I A \cdot \nabla_I S + \sum_I \frac{1}{2M_I} A \nabla_I^2 S = 0.$$

At this point, we may approach the classical limit in the real portion of the equation (eq. (13)) by taking the limit where $\hbar \rightarrow 0$. This yields eq. (15), a classical Hamilton–Jacobi equation of motion which describes motion of a fluid of noninteracting nuclei subject to forces from the electronic PES.[3]

$$(15) \quad \boxed{\frac{\partial S}{\partial t} + \sum_I \frac{1}{M_I} (\nabla_I S)^2 + \left[\int \phi^* \hat{\mathcal{H}}_r \phi d\mathbf{r} \right] = 0.}$$

Additionally, it can be shown by manipulating the imaginary part of eq. (10) by left-multiplying by $2A$ and collecting terms, eq. (14) may be rewritten as the continuity equation eq. (16):

$$(16) \quad \begin{aligned} \frac{\partial}{\partial t} [A^2] + \sum_I \frac{1}{M_I} \nabla_I (A^2 \nabla_I S) &= 0 \\ \frac{\partial}{\partial t} [A^2] + \sum_I \nabla_I J_I &= 0 \\ \boxed{\frac{\partial \rho}{\partial t} + \sum_I \nabla_I J_I} &= 0. \end{aligned}$$

In eq. (16) we define the density current $J_I \equiv \frac{1}{M_I} (A^2 \nabla_I S)$ of the particles.[2] Since the amplitude function $A(\mathbf{R}; t)$ exactly represents the amplitude of the nuclear wavefunction $\chi(\mathbf{R}; t)$ in eq. (12) we defined the time-evolving density function $\rho(\mathbf{R}; t) \equiv |\chi(\mathbf{R}; t)|^2 \equiv A(\mathbf{R}; t)^2$ to describe the particle probability density.[2] Combined, we obtain the last expression in eq. (16) which is a continuity equation showing the conservation of probability

density subject to flow of nuclei as a fluid.[2] Put another way, the continuity equation validates that the swarm of nuclei moving subject to eq. (15) conserve the probability density of the total nuclear wavefunction. In conjunction with eq. (16), eq. (15) describes a set of independent nuclei following trajectories propagating along the effective electronic PES.[3]

However, equations eq. (15) and eq. (16) do not fully describe the classical limit for the nuclei. To achieve this, we can apply a classical ansatz of substituting a delta function $\delta(\{\mathbf{R}\})$ in for $\chi(\mathbf{R}, t)$ at the classical nuclear position \mathbf{R} parametrically dependent on time t . [3] Thus the dependence of $\phi(\mathbf{r}; t)$ on $\chi(\mathbf{R}; t)$ can be included as a parameterized classical position $\{\mathbf{R}\}$ in the effective electronic wavefunction. This classical ansatz is applied as

$$\begin{aligned}
 i\hbar \frac{\partial \phi(\mathbf{r}; t)}{\partial t} &= -\frac{\hbar^2}{2} \sum_i \frac{1}{m_i} \nabla_i^2 \phi(\mathbf{r}; t) + \left[\int \chi^*(\mathbf{R}, t) V_{rR}(\mathbf{r}; \mathbf{R}) \chi(\mathbf{R}, t) d\mathbf{R} \right] \phi(\mathbf{r}; t) \\
 &= -\frac{\hbar^2}{2} \sum_i \frac{1}{m_i} \nabla_i^2 \phi(\mathbf{r}; t) + \left[\int \delta(\mathbf{R}) V_{rR}(\mathbf{r}; \mathbf{R}) \delta(\mathbf{R}) d\mathbf{R} \right] \phi(\mathbf{r}; t) \\
 (17) \qquad \qquad \qquad &= -\frac{\hbar^2}{2} \sum_i \frac{1}{m_i} \nabla_i^2 \phi(\mathbf{r}; t) + V_{rR}(\mathbf{r}; \mathbf{R}) \phi(\mathbf{r}; t) \\
 &= \hat{\mathcal{H}}_r(\mathbf{r}, \mathbf{R}) \phi(\mathbf{r}; t)
 \end{aligned}$$

$$i\hbar \frac{\partial \phi(\mathbf{r}; \mathbf{R}; t)}{\partial t} = \hat{\mathcal{H}}_r(\mathbf{r}; \mathbf{R}) \phi(\mathbf{r}; \mathbf{R}; t)$$

which yields the effective time-dependent Schrödinger equation for the electronic wavefunction subject to parameterized nuclear motion.

Turning our attention back to the nuclei, the total energy must remain constant, This allows us to construct a Newtonian equation of motion describing the change in conjugate momenta to the nuclear positions subject to the effective electronic potential in the classical limit (eq. (18)).[3]

$$(18) \qquad \frac{d\mathbf{p}_I}{dt} = -\nabla_I \left[\int \phi^*(\mathbf{r}, \mathbf{R}; t) \hat{\mathcal{H}}_r(\mathbf{r}, \mathbf{R}) \phi(\mathbf{r}, \mathbf{R}; t) d\mathbf{r} \right]$$

In order to simplify numerical calculations of the effective electronic forces, it is common practice to rewrite the analytic time-derivative of the nuclear momenta to use the Hellmann-Feynman force (eq. (19)). However, this is not rigorously true for wavefunctions that are not eigenfunctions of the effective electronic Hamiltonian, $\hat{\mathcal{H}}_r$.

$$(19) \qquad \frac{d\mathbf{p}_I}{dt} = - \int \phi^*(\mathbf{r}, \mathbf{R}; t) [\nabla_I \hat{\mathcal{H}}_r(\mathbf{r}, \mathbf{R})] \phi(\mathbf{r}, \mathbf{R}; t) d\mathbf{r}.$$

From this, the total energy can now be written as

$$(20) \quad E = \sum_I \frac{1}{2M_I} \mathbf{p}_I^2 + \int \phi^*(\mathbf{r}, \mathbf{R}; t) \hat{\mathcal{H}}_r(\mathbf{r}, \mathbf{R}; t) \phi(\mathbf{r}, \mathbf{R}; t) d\mathbf{r}.$$

We can ensure the energy is conserved by enforcing $\frac{\partial E}{\partial t} = 0$. Applying the time-derivative operator to both sides of eq. (20) we obtain the Newtonian equation of motion eq. (18) again.[3]

The preceding equations for Ehrenfest dynamics are still valid for numerically propagating a wavepacket $\phi(\mathbf{r}, \mathbf{R}; t)$ using eq. (17) along the trajectory obtained from self-consistently solving eq. (19). It also is not necessary to expand the wavefunction in terms of a specific basis set.[3] However, for chemists it is often convenient to work in the familiar adiabatic Molecular Orbital (MO) basis. The adiabatic MO wavefunctions are defined as eigenfunctions of the effective electronic Hamiltonian $\hat{\mathcal{H}}_r(\mathbf{r}, \mathbf{R})$ for fixed values of $\{\mathbf{R}\}$ which are parametrically dependent on time t and slowly vary relative to the electronic motion. Additionally, the Hellman-Feynman theorem is valid in the case of adiabatic wavefunctions and eq. (19) is rigorously correct in the MO basis. The total adiabatic electronic wavefunction $\phi(\mathbf{r}, \mathbf{R}; t)$ may be expanded in terms of a set of stationary state MOs, $\{\psi_j(\mathbf{r}, \mathbf{R}; t)\}$ as

$$(21) \quad \phi(\mathbf{r}, \mathbf{R}, t) = \sum_j c_j(t) \psi_j(\mathbf{r}, \mathbf{R}).$$

where

$$(22) \quad \hat{\mathcal{H}}_r(\mathbf{r}; \mathbf{R}) \psi_j(\mathbf{r}; \mathbf{R}) = \epsilon_j(\mathbf{R}) \psi_j(\mathbf{r}, \mathbf{R}).$$

The quantity $\epsilon_j(\mathbf{R})$ defines the j -th adiabatic, Born-Oppenheimer approximate PES. The amplitudes of the adiabatic states $c_j(t)$ are obtained from substituting the expansion (eq. (21)) into the effective electronic time-dependent Schrödinger equation subject to the average nuclear and electronic potentials (eq. (17)) then using the orthonormality of the MO basis by projecting along the adiabatic MO basis functions $\{\psi_j(\mathbf{r}, \mathbf{R}; t)\}$. We can rewrite the time derivative in terms of the nuclear gradient as $\frac{\partial}{\partial t} \equiv \sum_I \nabla_I \cdot \dot{\mathbf{R}}_I$. This yields a set of coupled differential equations[3]

$$\begin{aligned}
i\hbar \frac{\partial}{\partial t} \left[\sum_j c_j(t) \psi_j(\mathbf{r}, \mathbf{R}) \right] &= \hat{\mathcal{H}}_r(\mathbf{r}, \mathbf{R}) \left[\sum_j c_j(t) \psi_j(\mathbf{r}, \mathbf{R}) \right] \\
i\hbar \left\{ \sum_j [\dot{c}_j(t) \psi_j(\mathbf{r}, \mathbf{R}) + c_j(t) \dot{\psi}_j(\mathbf{r}, \mathbf{R})] \right\} &= \sum_j c_j(t) \epsilon_j(\mathbf{R}) \psi_j(\mathbf{r}, \mathbf{R}) \\
i\hbar \sum_j \dot{c}_j(t) \psi_j(\mathbf{r}, \mathbf{R}) &= \sum_j c_j(t) \epsilon_j(\mathbf{R}) \psi_j(\mathbf{r}, \mathbf{R}) - i\hbar \sum_j c_j(t) \dot{\psi}_j(\mathbf{r}, \mathbf{R}) \\
(23) \quad i\hbar \sum_j \dot{c}_j(t) \int \psi_k^*(\mathbf{r}, \mathbf{R}) \psi_j(\mathbf{r}, \mathbf{R}) d\mathbf{r} &= \\
&= \sum_j c_j(t) \epsilon_j(\mathbf{R}) \int \psi_k^*(\mathbf{r}, \mathbf{R}) \psi_j(\mathbf{r}, \mathbf{R}) d\mathbf{r} - i\hbar \sum_j c_j(t) \int \psi_k^*(\mathbf{r}, \mathbf{R}) \frac{\partial}{\partial t} [\psi_j(\mathbf{r}, \mathbf{R})] d\mathbf{r} \\
i\hbar \dot{c}_j(t) &= c_j(t) \epsilon_j - i\hbar \sum_k c_k(t) \int \psi_k^*(\mathbf{r}, \mathbf{R}) \frac{\partial}{\partial t} [\psi_j(\mathbf{r}, \mathbf{R})] d\mathbf{r} \\
i\hbar \dot{c}_j(t) &= c_j(t) \epsilon_j - i\hbar \sum_{I,k} c_k(t) \dot{\mathbf{R}}_I \int \psi_k^*(\mathbf{r}, \mathbf{R}) [\nabla_I \psi_j(\mathbf{r}, \mathbf{R})] d\mathbf{r} \\
&\quad \boxed{i\hbar \dot{c}_j(t) = c_j(t) \epsilon_j(\mathbf{R}) - i\hbar \sum_{I,k} c_k(t) \dot{\mathbf{R}}_I \cdot d_{kj}^I(\mathbf{R})}.
\end{aligned}$$

The term $d_{kj}^I(\mathbf{R})$ is the nonadiabatic (or vibronic) coupling constructed from two adiabatic basis functions mediated by nuclear motions (or vibrations)[3]

$$(24) \quad d_{kj}^I = \int \psi_k^*(\mathbf{r}, \mathbf{R}) [\nabla_I \psi_j(\mathbf{r}, \mathbf{R})] d\mathbf{r}.$$

The expansion of the wavefunction in the adiabatic basis (eq. (21)) substituted into the total energy expression (eq. (20)) yields the nuclear classical mechanical equations of motion[3]

$$(25) \quad E = \sum_I \frac{1}{2M_I} \mathbf{p}_I^2 + \sum_{jk} c_j^* c_k \int \psi_j^*(\mathbf{r}, \mathbf{R}) \hat{\mathcal{H}}_r(\mathbf{r}, \mathbf{R}) \psi_k(\mathbf{r}, \mathbf{R}) d\mathbf{r}$$

Ensuring total energy is conserved, we take the time derivative of eq. (25) and set it to zero to obtain

$$(26) \quad \dot{\mathbf{R}} \cdot \dot{\mathbf{p}} = - \sum_j |c_j|^2 \frac{dE_j}{dt} - \sum_j \frac{d}{dt} |c_j|^2 E_j.$$

This constrained eq. (26) contains two terms which must be included when implementing Ehrenfest dynamics using an adiabatic basis. The first term on the right-hand side is the weighted average of each adiabatic PES. The occupation of each state $|c_j|^2$ serves as the weight.[3] The second term on the right-hand side of eq. (26) represents the time-dependent changes in amplitude of the electronic wavefunction and is thus the effective force on the classical nuclei from *transitions* between adiabatic electronic states.[3] This can be used to show that from eq. (23) and its complex conjugate,

$$(27) \quad \frac{d}{dt}|c_j|^2 = \sum_k (c_k^* c_j + c_j^* c_k) \dot{\mathbf{R}} \cdot \mathbf{d}_{kj}^I.$$

From eq. (27) and eq. (26) we obtain the equation of motion for the classical particle momenta in terms of the positions subject to the effective electronic PES (eq. (28)). [3]

$$(28) \quad \boxed{\frac{d\mathbf{p}_I}{dt} = - \sum_j |c_j|^2 [\nabla_I \epsilon_j(\mathbf{R})] - \sum_{I,j \neq k} c_k^* c_j [\epsilon_k(\mathbf{R}) - \epsilon_j(\mathbf{R})] \cdot \mathbf{d}_{kj}^I(\mathbf{R}).}$$

In conjunction with the effective electronic time-dependent Schrödinger equation (eq. (29) with dependence on nuclear positions, shown again here for convenience, this constitutes the pair of working equations for Ehrenfest dynamics in an adiabatic basis.

$$(29) \quad \boxed{i\hbar \frac{\partial \phi(\mathbf{r}, \mathbf{R}; t)}{\partial t} = \hat{\mathcal{H}}_r(\mathbf{r}; \mathbf{R}) \phi(\mathbf{r}, \mathbf{R}; t).}$$

It is clear from eq. (28) that the two forces on the classical particles are the gradient of the PES (the Hellman-Feynmann term) and the nonadiabatic coupling term. In particular, the nonadiabatic coupling term is necessary to account for changes in adiabatic state population and the corresponding change in forces on the classical nuclei.[3]

4. BORN-OPPENHEIMER MOLECULAR DYNAMICS

Born-Oppenheimer Molecular Dynamics (BOMD) also derives from the TDSCF equations as well as the approximation of nuclei in the classical limit having fixed positions parametrically dependent on time. However, the wavefunctions are assumed to be stationary states for a fixed nuclear position $\{\mathbf{R}_I\}$ which are unchanged over time in the absence of a perturbation. We may first establish the stationary state and adiabatic approximation by using adiabatic basis functions $\{\phi_j(\mathbf{r}, \mathbf{R})\}$. By definition, the adiabatic electronic wavefunctions are eigenfunctions of the effective electronic Hamiltonian $\hat{\mathcal{H}}_r$ so we can rewrite eq. (17) as a time-independent eigenvalue problem in terms of adiabatic basis functions as

$$(30) \quad \boxed{\hat{\mathcal{H}}_r(\mathbf{r}, \mathbf{R}) |\phi_j(\mathbf{r}, \mathbf{R})\rangle = E_j(\mathbf{R}) |\phi_j(\mathbf{r}, \mathbf{R})\rangle.}$$

Turning our attention to the propagation of nuclei we start from eq. (18), the Newtonian form of the Ehrenfest dynamics nuclear equations of motion subject to the electronic PES.

$$(18) \quad \frac{d\mathbf{p}_I}{dt} = -\nabla_I \left[\int \phi^*(\mathbf{r}, \mathbf{R}; t) \hat{\mathcal{H}}_r(\mathbf{r}, \mathbf{R}) \phi(\mathbf{r}, \mathbf{R}; t) d\mathbf{r} \right]$$

From eq. (18) we can constrain the wavefunctions $\{\phi_k(\mathbf{r}, \mathbf{R})\}$ to be stationary states, unchanged for all time t which may be minimized for a fixed nuclear position $\{\mathbf{R}\}$. Here we rewrite the integral in the more compact, familiar bracket notation.[2]

$$(31) \quad \frac{d\mathbf{p}_I}{dt} = -\nabla_I \min_{\phi_k} \{ \langle \phi_k(\mathbf{r}, \mathbf{R}) | \hat{\mathcal{H}}_r(\mathbf{r}, \mathbf{R}) | \phi_k(\mathbf{r}, \mathbf{R}) \rangle \}.$$

The gradient of the minimum energy $E_k(\mathbf{R})$ for stationary state $\phi_k(\mathbf{r}, \mathbf{R})$ may be computed a number of ways: from the Hartree-Fock method, Kohn-Sham density functional theory, or solving the energy functional directly without diagonalizing the Hamiltonian. Regardless, the nuclei are propagated in the direction of $\dot{\mathbf{p}}(t)$ as obtained from the nuclear gradient of the effective electronic PES. Classical positions may be updated using a symplectic integrator such as Velocity-Verlet. It bears repeating that the nuclear positions have a parametric dependence on time t and it is helpful to rewrite eq. (31) explicitly in terms of the nuclear positions $\{\mathbf{R}_I\}$ (eq. (32)).[2] After the position update, BOMD solves the time-independent Schrödinger equation again for the adiabatic stationary state at the new nuclear positions and yet again propagates the nuclei subject to the gradient of the PES. The equations eq. (30) and eq. (32) constitute the general working equations for BOMD.

$$(32) \quad \boxed{M_I \ddot{\mathbf{R}}_I = -\nabla_I \min_{\phi_k} \{ \langle \phi_k(\mathbf{r}, \mathbf{R}_I) | \hat{\mathcal{H}}_r(\mathbf{r}, \mathbf{R}_I) | \phi_k(\mathbf{r}, \mathbf{R}_I) \rangle \}.$$

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