

# Introduction to Ab Initio Mean-Field Electronic Dynamics Methods<sup>1</sup>

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The development and synthesis of novel photoluminescent materials, medicines, photovoltaic devices, and structural materials all require an understanding of nonequilibrium, dynamical electronic and vibrational phenomena at the molecular level. As a result, theoretical chemistry and physics research groups studying quantum dynamics, and in particular electronic dynamics, often enjoy extensive collaboration with experimental chemists, physicists, and materials engineers. Accordingly, while the bodies of literature on the subjects of electronic dynamics and coupled electronic-nuclear dynamics are indeed extensive, there are few self-contained accounts of these time-domain dynamics methods and how they may be derived from one another. This work aims to introduce the methods of Time-Dependent Self-Consistent Field (TDSCF) theory, Real-Time Time-Dependent Density Functional Theory (RT-TDDFT), Ehrenfest dynamics both in general and as an extension of the RT-TDDFT method, and finally the more familiar and extensively studied Born-Oppenheimer Molecular Dynamics. TDSCF is quite expensive but nevertheless lays the groundwork for all other Born-Oppenheimer approximate wavefunction- and density-functional-based methods employed today and therefore it is included in this work for the sake of completeness.

This text assumes a working knowledge of basic quantum chemistry and the associated mathematics. Some good texts to work through before diving into the field of mixed quantum-classical dynamics include *Modern Quantum Chemistry* by Attila Szabo and Neil Ostlund<sup>2</sup> and the two-volume set *Quantum Mechanics* by Claude Cohen-Tannoudji.<sup>3</sup>

## Introduction

THE VAST MAJORITY of physically interesting problems and systems in quantum chemistry exist in nonequilibrium states despite the preponderance of quantum chemical methods focusing only on time-independent **TO DO** ► CITE Kohn-Sham, Hartree-Fock, etc ◄ or stationary states. Chemical reactions occur as a response to perturbations to the equilibrium states of the electrons surrounding molecules, particularly in the valence orbitals. Of course, this would at first glance appear to be a straightforward and simple application of perturbative methods to solve such nonequilibrium problems. Indeed, a great deal of literature exists on perturbative methods such as time-dependent

<sup>1</sup> Heavily based on the derivations of these methods found in the published work of John C. Tully, Bernhard Schlegel, and Xiaosong Li; as well as a book written by Dominik Marx and Jürg Hutter.

<sup>2</sup> Attila Szabo and Neil Ostlund. *Modern Quantum Chemistry: Introduction to Advanced Electronic Structure Theory*. Dover Publications, Mineola, New York, second reprinting edition, 1996

<sup>3</sup> Claude Cohen-Tannoudji, Bernard Diu, and Franck Laloe. *Quantum Mechanics*. Hermann and John Wiley & Sons. Inc., Paris, France, first edition, 1977

These are such canonical texts in the field of quantum chemistry that they should be available at any modest university library!

Hartree-Fock (TDHF) [TO DO ▶ CITE Li2004 ◀](#) and linear-response time-dependent density functional theory (LR-TDDFT) [TO DO ▶ CITE MHG and Dreuw, Runge and Gross, etc. ◀](#), among other response theories, for treating excited electronic states of molecules. [TO DO ▶ CITE ◀](#) These are indeed powerful and efficient methods, yet they tend to fail in the limit of high-intensity external fields. [TO DO ▶ CITE ◀](#) Moreover, they are currently unable to treat the dynamics of superposition states and thus are unsuitable for tracking the time-resolved behavior of coherent electronic excited states. [TO DO ▶ CITE ◀](#) Naturally, this has motivated the development of *time-resolved* methods for studying electronic dynamics, and indeed even coupled nuclear-electronic dynamics. At the core of these methods resides time-dependent self-consistent field (TDSCF) theory, a mean-field approximation of full, coupled nuclear-electronic dynamics in molecules.<sup>4</sup>

There exist several mean-field approximate methods deriving from TDSCF which may be used to simulate the electronic and nuclear dynamics in molecules with varying degrees of explicit coupling between the electronic and nuclear components. TDSCF itself is a mean-field approximation based in first principles for total molecular motion including both electronic and nuclear degrees of freedom. 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.<sup>5</sup> Following an alternate path of approximations, by fixing the nuclei as point particles and applying the density formalism, one may also treat the purely-electronic dynamics affordably in the limit where time-scales of electronic motion are substantially shorter than that of the nuclei, arriving at the Modified-Midpoint Unitary Transformation Time-Dependent Hartree-Fock (MMUT-TDHF) and Real-Time Time-Dependent Density Functional Theory (RT-TDDFT) methods. [TO DO ▶ CITE Li TDHF and Li RT ◀](#) Still more convenient is the fact that the RT-TDDFT method may be directly derived from the implementation of Ehrenfest dynamics in the DFT framework. [TO DO ▶ CITE Li and Tully, Ehrenfest ◀](#)

These dynamical simulation techniques are indeed useful for observing time-evolving molecular properties via various quantum observables. 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 model chemistries and approximate methods. This

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 multiple single particle wavefunctions can represent the system at all times.

<sup>4</sup> Andreas Dreuw and Martin Head-Gordon. Single-reference ab initio methods for the calculation of excited states of large molecules. *Chem. Rev.*, 105:4009 – 4037, 2005

<sup>5</sup> Dominik Marx and Jurg Hutter. *Ab Initio Molecular Dynamics*. Cambridge University Press, New York, first edition, 2009; and John C. Tully. Mixed quantum-classical dynamics. *Faraday Discussions*, 110:407 – 419, 1998

naturally has motivated the implementation of evermore efficient methods for modeling the dynamics of molecular systems from first principles. The aim of this work is to provide detailed, annotated derivations for a suite of fully *ab initio*<sup>6</sup> and mixed quantum-classical dynamical (MQD) simulation techniques from first principles. An additional objective is to illustrate the relationships between these methods as one moves through successive approximations and *ansätze*<sup>7</sup> from the fully *ab initio* regime up towards classical approaches<sup>8</sup> in the continuum limit. What should soon be obvious is that this set of techniques – enjoying widespread application in the discovery and characterization of novel materials and molecular systems – derives from one source, each only differing by the choices of approximations one makes. In order to make the most effective use of these techniques as a dynamicist, it is of great utility to understand their advantages and limitations from this viewpoint.

Finally, while a general theoretical understanding of these methods is of great importance for their practical application, there are a number of variations of each of these techniques. Accordingly, we will first approach the methods from first-principles in a general sense, but succeeding subsections will discuss the working equations as they are applied in specific basis formalisms. In general, while the methods are formally basis-agnostic, the choice of basis is itself wholly dependent on the types of systems one is modeling. For example, in the quantum chemistry community one is primarily interested in the molecular valence orbitals, thus Gaussian-type basis sets are often the de facto choice for numerical simulations. Therefore, this work primarily focuses on these when formulating the methods from the general derivations.

### *Time-Dependent Self-Consistent Field Theory*

WE 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

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

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  $\mathbf{R}$ . The phase factor  $E_r(t)$  is taken to represent the effective electronic energy

<sup>6</sup> AB INITIO is synonymous here with “from first principles”.

<sup>7</sup> ANSÄTZE is the plural form of the German *ansatz*, meaning “initial placement of a tool at a work piece” – or in other words, an *approach*. *Ansatz* is a frequently used keyword in physics and quantum chemistry to mean “an educated guess later verified by results”.

<sup>8</sup> e. g., molecular mechanics (MM), molecular dynamics (MD), etc.

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.

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

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).

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

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

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.

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

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)).

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

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

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

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

$$i\hbar \int \phi^* \frac{\partial \phi}{\partial t} d\mathbf{r} - E_r(t) = E - i\hbar \int \chi^* \frac{\partial \chi}{\partial t} d\mathbf{R}.$$

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  $\phi$  and  $\chi$  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

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

and

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

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)).

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

and

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

From eq. (10) and eq. (11) we have the working equations for TD-SCF and can now derive Real-Time TDDFT, Ehrenfest dynamics, and BOMD. It is apparent from the coupled TDSCF equations 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  $V_{rR}$ . From here we may subject the TDSCF equations to further approximations to obtain Real-Time TDDFT, Ehrenfest dynamics and Born-Oppenheimer Molecular Dynamics.<sup>9</sup>

## Time-Dependent Hartree-Fock (TDHF)

### Background

WE HAVE SEEN ALREADY the utility in decoupling the nuclear and electronic degrees of freedom by way of the Born-Oppenheimer wavefunction *ansatz*, however the computational expense of directly propagating all degrees of freedom in the TDSCF method – as stated before – sharply impacts its utility in calculating the properties of even modestly sized systems consisting of more than a few light atoms. Accordingly, in order to actually use this framework for research applications in support of experiment, successive approximations must be carefully taken and different approaches for integrating the electronic dynamics should be explored. To this end, the *Modified-Midpoint Unitary Transformation Time-Dependent Hartree-Fock* method was developed and implemented as a less computationally demanding extension of Time-Dependent Hartree-Fock, which is itself less demanding than other available methods<sup>10</sup> for treating non-adiabatic,

<sup>9</sup> John C. Tully. Mixed quantum-classical dynamics. *Faraday Discussions*, 110:407 – 419, 1998; and Dominik Marx and Jurg Hutter. *Ab Initio Molecular Dynamics*. Cambridge University Press, New York, first edition, 2009

<sup>10</sup> e.g., Multiple Configuration Self-Consistent Field (MCSCF) methods or TDSCF with nuclear dynamics treated quantum-mechanically

multi-electron processes in molecular systems interacting with light. It is also able to qualitatively capture much of the physics in non-adiabatic dynamical processes and follow dynamics of electronic superposition states, albeit in a less quantitatively accurate manner than MCSCF. **TO DO** ▶ *CITE Li, Markevitch, etc. 2004* ◀

### *Modified-Midpoint Unitary Transformation (MMUT)-TDHF*

**TO DO** ▶ *derive it here from TDSCF* ◀

### *Real-Time Time-Dependent Density Functional Theory*

**TO DO** ▶ *Introduce the initial approximations and formalism for the Real-Time TDDFT method here.* ◀

FOLLOWING DIRECTLY FROM MMUT-TDHF we may exploit the favorable computational scaling of density functional theory (DFT) methods to make the simulation of electronic state time-evolution still more efficient. This leads us to the Real-Time Time-Dependent Density Functional (RT-TDDFT) theory. **JJR** ▶ *It ties directly into the Ehrenfest method as it's implemented in Gaussian with DFT* ◀

### *The Density Formalism and Time-Dependent Density Functional Theory*

**TO DO** ▶ *Add a quick overview of TDDFT and how it leads to RT-TDDFT* ◀

### *The Real-Time Time-Dependent Density Functional Theory*

**TO DO** ▶ *Describe the theory in more detail including the Magnus expansion, unitary propagation, interpretations of the working equations, and classical and semiclassical analogues.* ◀

### *Ehrenfest Dynamics*

#### *Background and Ehrenfest's Theorem*

**TO DO** ▶ *Some background on Ehrenfest dynamics goes here. Discuss its origins and why it's called "Ehrenfest dynamics" here as well as basic starting assumptions and approximations from TDSCF.* ◀

#### *Ehrenfest Dynamics General Derivation*

EHRENFEST DYNAMICS FOLLOWS, in general, from TDSCF 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.<sup>11</sup> 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

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

where both  $A(\mathbf{R};t)$  and  $S(\mathbf{R};t)$  are assumed to be real-valued functions.<sup>12</sup> 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

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

and

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

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.<sup>13</sup>

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

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):

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

$$\boxed{\frac{\partial \rho}{\partial t} + \sum_I \nabla_I J_I = 0.}$$

In eq. (16) we define the density current  $J_I \equiv \frac{1}{M_I} (A^2 \nabla_I S)$  of the particles.<sup>14</sup> Since the amplitude function  $A(\mathbf{R};t)$  exactly represents the amplitude of the nuclear wavefunction  $\chi(\mathbf{R};t)$  in eq. (12) we

<sup>11</sup> John C. Tully. Mixed quantum-classical dynamics. *Faraday Discussions*, 110:407 – 419, 1998

<sup>12</sup> John C. Tully. Mixed quantum-classical dynamics. *Faraday Discussions*, 110:407 – 419, 1998; and Dominik Marx and Jurg Hutter. *Ab Initio Molecular Dynamics*. Cambridge University Press, New York, first edition, 2009

<sup>13</sup> John C. Tully. Mixed quantum-classical dynamics. *Faraday Discussions*, 110:407 – 419, 1998

<sup>14</sup> Dominik Marx and Jurg Hutter. *Ab Initio Molecular Dynamics*. Cambridge University Press, New York, first edition, 2009



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.<sup>15</sup> 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.<sup>16</sup> 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.<sup>17</sup>

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  $t$ .<sup>18</sup> 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

$$\begin{aligned}
 i\hbar \frac{\partial \phi(\mathbf{r};t)}{\partial t} &= -\frac{\hbar^2}{2} \sum_i \frac{1}{m_i} \nabla_i^2 \phi(\mathbf{r};t) + \left[ \int \chi^*(\mathbf{R},t) V_{rR}(\mathbf{r};\mathbf{R}) \chi(\mathbf{R},t) d\mathbf{R} \right] \phi(\mathbf{r};t) \\
 &= -\frac{\hbar^2}{2} \sum_i \frac{1}{m_i} \nabla_i^2 \phi(\mathbf{r};t) + \left[ \int V_{rR}(\mathbf{r};\mathbf{R}) \delta(\mathbf{R} - \mathbf{R}') d\mathbf{R}' \right] \phi(\mathbf{r};t) \\
 &= -\frac{\hbar^2}{2} \sum_i \frac{1}{m_i} \nabla_i^2 \phi(\mathbf{r};t) + V_{rR}(\mathbf{r};\mathbf{R}) \phi(\mathbf{r};t) \\
 &= \hat{\mathcal{H}}_r(\mathbf{r},\mathbf{R}) \phi(\mathbf{r};t) \\
 \boxed{i\hbar \frac{\partial \phi(\mathbf{r};\mathbf{R};t)}{\partial t} = \hat{\mathcal{H}}_r(\mathbf{r};\mathbf{R}) \phi(\mathbf{r};\mathbf{R};t)} \\
 &\quad (17)
 \end{aligned}$$

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)).<sup>19</sup>

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

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

<sup>15</sup> Dominik Marx and Jurg Hutter. *Ab Initio Molecular Dynamics*. Cambridge University Press, New York, first edition, 2009

<sup>16</sup> Dominik Marx and Jurg Hutter. *Ab Initio Molecular Dynamics*. Cambridge University Press, New York, first edition, 2009

<sup>17</sup> John C. Tully. Mixed quantum-classical dynamics. *Faraday Discussions*, 110:407 – 419, 1998

<sup>18</sup> John C. Tully. Mixed quantum-classical dynamics. *Faraday Discussions*, 110:407 – 419, 1998

Note that in eq. (17), the delta function behaves almost as a “mask” or “filter” such that

$$\int V_{rR}(\mathbf{r};\mathbf{R}) \delta(\mathbf{R} - \mathbf{R}') d\mathbf{R}' = \begin{cases} V_{rR}(\mathbf{r};\mathbf{R}) & \text{if } \mathbf{R} \equiv \mathbf{R}' \\ 0 & \text{if } \mathbf{R} \neq \mathbf{R}' \end{cases}$$

<sup>19</sup> John C. Tully. Mixed quantum-classical dynamics. *Faraday Discussions*, 110:407 – 419, 1998

force (eq. (19)). However, this is not rigorously true for wavefunctions that are not eigenfunctions of the effective electronic Hamiltonian,  $\hat{\mathcal{H}}_r$ .

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

From this, the total energy can now be written as

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

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.<sup>20</sup>

<sup>20</sup> John C. Tully. Mixed quantum-classical dynamics. *Faraday Discussions*, 110:407 – 419, 1998

### *Ehrenfest Dynamics in the Gaussian-type Orbital Basis*

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.<sup>21</sup> 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

<sup>21</sup> John C. Tully. Mixed quantum-classical dynamics. *Faraday Discussions*, 110:407 – 419, 1998

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

where

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

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  $\frac{\partial}{\partial \mathbf{I}} \equiv \sum_I \nabla_I \cdot \dot{\mathbf{R}}_I$ . This yields a set of coupled differential equations<sup>22</sup>

<sup>22</sup> John C. Tully. Mixed quantum-classical dynamics. *Faraday Discussions*, 110:407 – 419, 1998

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

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)<sup>23</sup>

<sup>23</sup> John C. Tully. Mixed quantum-classical dynamics. *Faraday Discussions*, 110:407 – 419, 1998

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

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<sup>24</sup>

<sup>24</sup> John C. Tully. Mixed quantum-classical dynamics. *Faraday Discussions*, 110:407 – 419, 1998

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

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

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

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.<sup>25</sup> 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.<sup>26</sup> This can be used to show that from eq. (23) and its complex conjugate,

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

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)).<sup>27</sup>

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

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.

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

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.<sup>28</sup>

### Ehrenfest Dynamics Derived from Real-Time TDDFT

**TO DO** ► Add derivation from RT-TDDFT (Cite Li and Tully and coworkers here) in the density-formalism here and explain how it saves on cost and implementation time to use the RT infrastructure to propagate the system in the Ehrenfest method. ◀

### 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

<sup>25</sup> John C. Tully. Mixed quantum-classical dynamics. *Faraday Discussions*, 110:407 – 419, 1998

<sup>26</sup> John C. Tully. Mixed quantum-classical dynamics. *Faraday Discussions*, 110:407 – 419, 1998

<sup>27</sup> John C. Tully. Mixed quantum-classical dynamics. *Faraday Discussions*, 110:407 – 419, 1998

<sup>28</sup> John C. Tully. Mixed quantum-classical dynamics. *Faraday Discussions*, 110:407 – 419, 1998

$\{\phi_j(\mathbf{r}, \mathbf{R})\}$ . 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

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

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.

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

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.<sup>29</sup>

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

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)).<sup>30</sup> 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.

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

<sup>29</sup> Dominik Marx and Jurg Hutter. *Ab Initio Molecular Dynamics*. Cambridge University Press, New York, first edition, 2009

<sup>30</sup> Dominik Marx and Jurg Hutter. *Ab Initio Molecular Dynamics*. Cambridge University Press, New York, first edition, 2009

*Applications of These Methods*

TDSCF

RT-TDDFT

*Ehrenfest Dynamics**Born-Oppenheimer Molecular Dynamics**Some Remarks**Acknowledgements*

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