Optimal control theory for quantum-classical systems: Ehrenfest molecular dynamics based on time-dependent density-functional theory

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Abstract

We derive the fundamental equations of an optimal control theory for systems containing both quantum electrons and classical ions. The system is modeled with Ehrenfest dynamics, a non-adiabatic variant of molecular dynamics. The general formulation, that needs the fully correlated many-electron wavefunction, can be simplified by making use of time-dependent density-functional theory. In this case, the optimal control equations require some modifications that we will provide. The abstract general formulation is complemented with the simple example of the H_2^+ molecule in the presence of a laser field.

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1. Introduction

Molecular dynamics (MD) [1, 2] is the field of physical modeling dedicated to atomistic simulations of condensed matter systems. Due to the impossibility of a full quantum treatment for all particles, the nuclei are considered to be classical, whereas the electrons must retain their quantum nature. This classical description of the nuclear system is of course an approximation, and in many circumstances it is necessary to employ nuclear wave packets to study the dynamics of molecules and other condensed matter systems. The term 'MD', however, is traditionally reserved for the models in which the nuclei are fully classical. Therefore, the problem addressed by MD is that of the evolution of a mixed system composed of a classical and a quantum subsystem.

The level of theory used to describe the electrons differs in the various MD schemes, ranging from detailed first principles approaches [3], to the so-called 'classical' MD force fields [4–6], in which the electronic subsystem is in fact integrated out, and the remaining ions interact with classical forces that have been carefully parameterized over the years to somehow contain the lost electronic influence. In this latter case, the only equations to follow are Newton's laws for the nuclei, and, at least operationally, there is no longer a mixed system—though, originally, the full system is mixed.

Another broad division in MD can be established between adiabatic and non-adiabatic models. In the former, the electronic system is considered to be, at all times, at the ground state (or, perhaps, at some fixed excited state) corresponding to the instantaneous nuclear configuration. In non-adiabatic MD, transitions between electronic states are allowed. These are the cases that, strictly speaking, necessitate a genuine mixed quantum-classical approach. Not surprisingly, these non-adiabatic problems are the most computationally challenging, since they require an *ab initio* electronic structure model.

Yet another classification of MD studies can be established with respect to the properties of the system that one wishes to study via the simulations. Originally, the objects of investigation were assumed to be the equilibrium properties in the canonical ensemble of macroscopic systems. However, the out-of-equilibrium dynamics of molecules in the presence of high intensity fields has become of enormous interest in the last decades due to the experimental advances in that area. When laser pulses are to be considered, one needs a first-principles non-adiabatic model, especially if the pulses have high intensities and the frequencies are visible or higher, i.e. of the order of typical electronic excitations.

In this work, we are interested in non-equilibrium laser–matter interaction experiments, that require a non-adiabatic first principles model. Ehrenfest dynamics is one of such models. It can be derived by taking two consecutive approximations: first, an electronic-nuclear separation of the full quantum wavefunction leads to the usually called 'time-dependent self-consistent field' model [7]; then, the short wave asymptotics of Wentzel, Kramers and Brillouin (WKB) [8–10] is used to take the classical limit for the nuclear degrees of freedom. A discussion on its justification and validity can be found in [11]. The term 'Ehrenfest dynamics' is not of universal use—for example, in this aforementioned work of Bornemann *et al* [11], the scheme is simply called 'mixed quantum-classical dynamics'. The use of Ehrenfest's name is due to the fact that the classical equation of motion for the nuclei can be obtained as an application of his famous theorem [12].

Since, for practical implementations, the many-electron wavefunction cannot be directly handled, it is necessary to model the quantum dynamics with some electronic structure theory, such as for example time-dependent density-functional theory (TDDFT) [13, 14]. Ehrenfest MD based on TDDFT was first attempted by Theilhaber [15] for (external) field-free problems, and afterwards its utility to laser–matter irradiation has been repeatedly demonstrated—see, e.g. [16–22]. Note, however, that TDDFT is, in practice, only an approximate theory (as some of its ingredients—most notably the 'exchange and correlation functional'—are unknown), and the range of applicability of the state-of-the-art TDDFT schemes for high intensity field problems is still an area to be investigated. In particular, with control problems in mind, see the recent works of Raghunathan and Nest [23, 24].

In any case, once one has decided on a technique to describe the evolution of molecules in the presence of intense laser pulses, it becomes possible to attempt the inverse problem: given a desired behavior for the system, finding what is the external perturbation that induces it. This type of problem is the topic of 'control' theories. Quantum optimal control theory (QOCT) [25, 26], in particular, has been developed over the last decades to answer the question of

what are the best external handles to manipulate a quantum system in order to achieve a pre-defined target.

QOCT has been applied to many systems for various purposes; in the molecular physics field, most of the previous QOCT works have addressed the motion of nuclear wave packets, on one or a few potential energy surfaces, in the presence of femtosecond laser pulses. If a sufficient number of surfaces is included in the model, and their non-adiabatic couplings properly treated, this procedure is very precise. However, the computational cost of pre-computing the surfaces with a good theory level, in addition to the cost of the propagation of the nuclear wave packets, makes it rather hard to apply. If the classical approximation for the nuclei is good enough, a mixed quantum-classical treatment is appropriate. A QOCT for mixed systems would be necessary for these cases.

In a previous work [27], we have already studied the selective bond breaking of molecules by making use of the Ehrenfest model. The method of optimization, however, consisted of a simple gradient-free algorithm that does not employ one of the essential results of QOCT: the computation of the gradient of the target functional with respect to the field control parameters. Recently, we have also presented the combination of QOCT with TDDFT [28], which permits to directly control the electronic motion, which occurs in the attosecond time scale, by employing TDDFT to reduce the computational complexity of a full quantum electron dynamics. This combination of QOCT with TDDFT did not consider the nuclear movement, and as demonstrated in [27] and more recently in [29], this can only be valid if very short laser pulses are considered.

In this work, we establish an optimal control framework for mixed systems composed of quantum electrons and classical ions, modeled with the Ehrenfest dynamics. The general framework is presented in section 2, and it employs the fully correlated many-electron wavefunctions. In order to establish a more manageable practical formalism, we replace in section 3 that many-electron wavefunction by the single-particle orbitals that emerge of TDDFT, combining the formalism presented in [29] with that of section 2. Finally, in section 4 the abstract general formulation is complemented with the simple example of the H_2^+ molecule in the presence of a laser field. Atomic units will be used throughout the paper.

2. OCT for a general Ehrenfest system

The state of a quantum-classical Ehrenfest system is specified by a set of classical conjugated position and momenta variables $\{q_a, p_a\}_a$, and a wavefunction Ψ. The dynamics of this system is determined by a Hamiltonian $\hat{H}[q, p, u, t]$, which is a linear Hermitian operator in the Hilbert space of wavefunctions, and simultaneosly depends on the set of classical variables (we will denote q to the full set of q_a variables, and likewise p to the set of p_a variables). In general, the Hamiltonian may also be time-dependent, and we consider its precise form to be determined by a set of M real parameters $u_1, \ldots, u_M \equiv u$, which constitute the 'control' parameters. Usually, one separates out a classical-only part, i.e. a part of the Hamiltonian that is a function of only the classical variables:

$$\hat{H}[q, p, u, t] = H_{\text{clas}}[q, p, u, t]\hat{I} + \hat{H}_{\text{quantum}}[q, p, u, t]. \tag{1}$$

For example, one may include in H_{clas} the classical kinetic energy, the interaction among the classical particles, or the action of external fields on those classical particles. This choice, however, is somehow arbitrary, and the inclusion or not of any of these purely classical terms into the quantum part merely leads to different but physically irrelevant global time-dependent phase factors in the wavefunction.

The dynamics is determined by this Hamiltonian through the following set of 'Ehrenfest' equations:

$$\dot{q}_a(t) = \frac{\partial H_{\text{clas}}}{\partial p_a}[q(t), p(t), u, t] + \langle \Psi(t)|\frac{\partial \hat{H}_{\text{quantum}}}{\partial p_a}[q(t), p(t), u, t]|\Psi(t)\rangle \tag{2}$$

$$\dot{p}_a(t) = -\frac{\partial H_{\text{clas}}}{\partial q_a}[q(t), p(t), u, t] - \langle \Psi(t)|\frac{\partial \hat{H}_{\text{quantum}}}{\partial q_a}[q(t), p(t), u, t]|\Psi(t)\rangle \tag{3}$$

$$\dot{\Psi}(x, t) = -i\hat{H}_{\text{quantum}}[q(t), p(t), u, t]\Psi(x, t), \tag{4}$$

complemented by a suitable set of initial conditions, $q_a(0) = q_{a0}$, $p_a(0) = p_{a0}$, $\Psi(0) = \Psi_0$. The full set of quantum variables is denoted collectively by x. If the Hamiltonian is Hermitian, the norm of the quantum state is preserved along the evolution ($\langle \Psi(t)|\Psi(t)\rangle = 1$ at all times), and the previous equations can be more compactly rewritten as:

$$\dot{q}_a(t) = \langle \Psi(t)|\frac{\partial \hat{H}}{\partial p_a}[q(t), p(t), u, t]|\Psi(t)\rangle \tag{5}$$

$$\dot{p}_a(t) = -\langle \Psi(t)|\frac{\partial \hat{H}}{\partial q_a}[q(t), p(t), u, t]|\Psi(t)\rangle \tag{6}$$

$$\dot{\Psi}(x, t) = -i\hat{H}_{\text{quantum}}[q(t), p(t), u, t]\Psi(x, t), \tag{7}$$

since

$$\frac{\partial H_{\text{clas}}}{\partial q_a}[q(t), p(t), u, t] = \langle \Psi(t)|\frac{\partial H_{\text{clas}}}{\partial q_a}[q(t), p(t), u, t]\hat{I}|\Psi(t)\rangle,$$

$$\frac{\partial H_{\text{clas}}}{\partial p_a}[q(t), p(t), u, t] = \langle \Psi(t)|\frac{\partial H_{\text{clas}}}{\partial p_a}[q(t), p(t), u, t]\hat{I}|\Psi(t)\rangle. \tag{8}$$

The purpose is to induce a given behavior of the system, e.g. the cleavage of a chemical bond, the ionization of the system, or the population of some electronic excited state. This can be formulated as the maximization of a 'target' functional that depends on the system variables, i.e. the classical coordinates and the quantum wavefunction, $F = F[q, p, \Psi]$. Thus, if for example the goal is to break a chemical bond and q_a is the classical coordinate that represents the distance between the two atoms that form that bond, the functional may simply be $F[q, p, \Psi] = q_a^2(T)$. In other words, we want that the distance between the two atoms is as large as possible at the final propagation time T. If the goal is the population of the electronic excited state Ψ_I, then the functional to maximize could be: $F[q, p, \Psi] = |\langle \Psi(T)|\Psi_I\rangle|^2$.

Those two examples have assumed that the target functional depends only on the state of the system at the final propagation time T. This need not be the case, as we might be interested in controlling the behavior of the system during the action of the external field. The functional F is in principle a functional of the full temporal evolution of the system. However, it is mathematically convenient to separate the 'terminal' part (if it exists) from the rest, i.e.:

$$F[q, p, \Psi, u] = F^{\text{td}}[q, p, \Psi, u] + F^{\text{term}}[q(T), p(T), \Psi(T), u]. \tag{9}$$

This division separates a 'time-dependent' functional F^{td} that verifies the following property: the functional derivatives $\frac{\delta F}{\delta q_a(t)}$, $\frac{\delta F}{\delta p_a(t)}$ and $\frac{\delta F}{\delta \Psi^*(x,t)}$ are continuous functions in time. The presence of a 'terminal' part F^{term} on the contrary implies that the functional derivative

of F will have a delta-function at time T: for example, if $F[q, p, \Psi] = q_a^2(T)$, then $\frac{\delta F}{\delta q_a(t)} = 2q_a(t)\delta(t - T)$. One could think of more complex situations in which discontinuities arise at different instants in time, however virtually all interesting cases may be formulated as given above. In fact, in order to simplify the following derivations, we will assume that F^{td} is null, and will work only with terminal targets.

The specification of u obviously determines the system evolution, i.e. $u \rightarrow q[u], p[u], \Psi[u]$. One must find the control u that induces an evolution of the system that maximizes F. In consequence, the problem is reduced to that of maximizing the function:

$$G[u] = F[q[u], p[u], \Psi[u], u]. \tag{10}$$

The maximization of any function is greatly simplified if we have an efficient expression to compute its gradient. In the following, we will derive such an expression. For this purpose, it is convenient to introduce an auxiliary quantum-classical system, that we will characterize by the dynamical variables $\tilde{q}$, $\tilde{p}$, and χ. In the language of Pontryagin's minimum principle [30] (that is at the root of most optimal control developments), this auxiliary state is usually called a *costate*. It is employed to define a new functional J, given by:

$$J[q, p, \tilde{q}, \tilde{p}, \Psi, \chi, u] = F[q, p, \Psi, u] + L[q, p, \tilde{q}, \tilde{p}, \Psi, \chi, u], \tag{11}$$

where the functional L, sometimes called the *Lagrangian*, is defined as:

$L[q, p, \tilde{q}, \tilde{p}, \Psi, \chi, u] =$

$$
-\sum_a \int_0^T dt \; \tilde{p}_a(t) \left(\dot{q}_a(t) - \langle \Psi(t)| \frac{\partial \hat{H}}{\partial p_a}[q(t), p(t), u, t]|\Psi(t)\rangle \right)
$$
$$
+\sum_a \int_0^T dt \; \tilde{q}_a(t) \left(\dot{p}_a(t) + \langle \Psi(t)| \frac{\partial \hat{H}}{\partial q_a}[q(t), p(t), u, t]|\Psi(t)\rangle \right)
$$
$$
-2\,\text{Re} \int_0^T dt \; \langle \chi(t)| \frac{d}{dt} + i\hat{H}_{\text{quantum}}[q(t), p(t), u, t]|\Psi(t)\rangle. \tag{12}
$$

This definition is designed to fulfill the following property: the equations of motion (2)–(4) are retrieved by taking functional derivatives with respect to the new variables and equating them to zero, i.e.:

$$\frac{\delta J}{\delta \tilde{q}_a(t)} = 0 \quad \Rightarrow \quad u \rightarrow q_a[u], \tag{13}$$

$$\frac{\delta J}{\delta \tilde{p}_a(t)} = 0 \quad \Rightarrow \quad u \rightarrow p_a[u], \tag{14}$$

$$\frac{\delta J}{\delta \chi^*(x, t)} = 0 \quad \Rightarrow \quad u \rightarrow \Psi[u]. \tag{15}$$

In analogy, we may define a set of equations of motion for the costate variables: we define them to be the result of setting the functional derivatives of J with respect to q, p and Ψ to zero:

$$\frac{\delta J}{\delta q_a(t)} = 0 \quad \Rightarrow \quad u \rightarrow \tilde{q}_a[u], \tag{16}$$

$$\frac{\delta J}{\delta p_a(t)} = 0 \quad \Rightarrow \quad u \rightarrow \tilde{p}_a[u], \tag{17}$$

$$\frac{\delta J}{\delta \Psi^*(x, t)} = 0 \quad \Rightarrow \quad u \rightarrow \chi[u]. \tag{18}$$

In order to compute these functional derivatives, it is better to rewrite the Lagrangian function as:

$$L[q, p, \tilde{q}, \tilde{p}, \Psi, \chi, u] = \sum_a \int_0^T dt \ (\tilde{q}_a(t)\dot{p}_a(t) - \tilde{p}_a(t)\dot{q}_a(t))$$

$$+ \int_0^T dt \ \langle\Psi(t)|D_{\tilde{q}(t),\tilde{p}(t)}\hat{H}[q(t), p(t), u, t]|\Psi(t)\rangle$$

$$-2\,\mathrm{Re}\int_0^T dt \ \langle\chi(t)|\frac{d}{dt} + i\hat{H}_{\text{quantum}}[q(t), p(t), u, t]|\Psi(t)\rangle, \tag{19}$$

where the differential operator $D_{\tilde{q}(t),\tilde{p}(t)}$ is defined as:

$$D_{\tilde{q}(t),\tilde{p}(t)} = \sum_a \left(\tilde{q}_a(t)\frac{\partial}{\partial q_a} + \tilde{p}_a(t)\frac{\partial}{\partial p_a}\right). \tag{20}$$

The resulting equations of motion (16)–(18) are:

$$\dot{\tilde{q}}_a(t) = \langle\Psi(t)|\ D_{\tilde{q}(t),\tilde{p}(t)}\frac{\partial\hat{H}}{\partial p_a}[q(t), p(t), u, t]\ |\Psi(t)\rangle$$

$$- 2\mathrm{Re}\ i\langle\chi(t)|\frac{\partial\hat{H}_{\text{quantum}}}{\partial p_a}[q(t), p(t), u, t]|\Psi(t)\rangle, \tag{21}$$

$$\dot{\tilde{p}}_a(t) = -\langle\Psi(t)|\ D_{\tilde{q}(t),\tilde{p}(t)}\frac{\partial\hat{H}}{\partial q_a}[q(t), p(t), u, t]\ |\Psi(t)\rangle$$

$$+ 2\,\mathrm{Re}\ i\langle\chi(t)|\frac{\partial\hat{H}_{\text{quantum}}}{\partial q_a}[q(t), p(t), u, t]|\Psi(t)\rangle, \tag{22}$$

$$\dot{\chi}(x, t) = -i\hat{H}_{\text{quantum}}^\dagger[q(t), p(t), u, t]\chi(x, t)$$

$$+ D_{\tilde{q}(t),\tilde{p}(t)}\hat{H}_{\text{quantum}}[q(t), p(t), u, t]\Psi(x, t), \tag{23}$$

$$\tilde{q}_a(T) = -\frac{\partial F^{\text{term}}}{\partial p_a}[q(T), p(T), \Psi(T)], \tag{24}$$

$$\tilde{p}_a(T) = \frac{\partial F^{\text{term}}}{\partial q_a}[q(T), p(T), \Psi(T)], \tag{25}$$

$$\chi(x, T) = \frac{\delta F^{\text{term}}[q(T), p(T), \Psi(T)]}{\delta\Psi^*(x, T)}. \tag{26}$$

These equations establish the map $u \to \{\tilde{q}[u], \tilde{p}[u], \chi[u]\}$. We may now proceed to compute the gradient of G. First, note that, for any value of u, the Lagrangian function vanishes when we use as arguments the mapped variables, i.e.:

$$L[q[u], p[u], \tilde{q}[u], \tilde{p}[u], \Psi[u], \chi[u], u] = 0, \tag{27}$$

and therefore:

$$G[u] = J[q[u], p[u], \Psi[u], \tilde{q}[u], \tilde{p}[u], \chi[u], u]. \tag{28}$$

The gradient may now be computed by employing the chain rule:

$$\frac{\partial G}{\partial u_m} = \sum_a \frac{\delta J}{\delta q_a}\frac{\delta q_a}{\delta u_m} + \sum_a \frac{\delta J}{\delta p_a}\frac{\delta p_a}{\delta u_m} + \frac{\delta J}{\delta\Psi^*}\frac{\delta\Psi^*}{\delta u} + \frac{\delta J}{\delta\Psi}\frac{\delta\Psi}{\delta u}$$

$$+ \sum_a \frac{\delta J}{\delta\tilde{q}_a}\frac{\delta\tilde{q}_a}{\delta u_m} + \sum_a \frac{\delta J}{\delta\tilde{q}_a}\frac{\delta\tilde{p}_a}{\delta u_m} + \frac{\delta J}{\delta\chi^*}\frac{\delta\chi^*}{\delta u} + \frac{\delta J}{\delta\chi}\frac{\delta\chi}{\delta u} + \frac{\partial J}{\partial u_m}. \tag{29}$$

In this expression, however, all the terms in the right-hand side are zero, except for the last one (the explicit derivative of J with respect to u_m). This is so because of the manner in which we have defined the maps $u \to \{q[u], p[u], \Psi[u], \tilde{q}[u], \tilde{p}[u], \tilde{\chi}[u]\}$, i.e. equations (13)–(15) and (16)–(18), which prescribe that all functional derivatives with respect to the state and costate variables are zero. In consequence, the derivative of G with respect to any of the parameters u_m reduces to only the explicit partial derivative of J with respect to u_m, i.e. (with a more detailed notation):

$$\frac{\partial G}{\partial u_m}[u] = \left. \frac{\partial J[q, p, \Psi, \tilde{q}, \tilde{p}, \chi, u]}{\partial u_m} \right|_{q=q[u], p=p[u], \Psi=\Psi[u], \tilde{q}=\tilde{q}[u], \tilde{p}=\tilde{p}[u], \chi=\chi[u]}. \qquad (30)$$

By making use of the definition of J (equation (11)) and of L (equation (12)), the gradient of G may be finally expanded to:

$$\frac{\partial G}{\partial u_m}[u] = \left. \frac{\partial F}{\partial u_m}[q, p, \Psi, u] \right|_{q=q[u](t), p=p[u](t), \Psi=\Psi[u](t)}$$
$$+ \int_0^T dt \ \langle \Psi[u](t) | D_{\tilde{q}[u](t), \tilde{p}[u](t)} \frac{\partial \hat{H}}{\partial u_m}[q[u](t), p[u](t), u, t] | \Psi[u](t) \rangle$$
$$+ 2 \,\text{Im} \int_0^T dt \ \langle \chi[u](t) | \frac{\partial \hat{H}_{\text{quantum}}}{\partial u_m}[q[u](t), p[u](t), u, t] | \Psi[u](t) \rangle. \qquad (31)$$

3. OCT for an Ehrenfest-TDDFT system

In order to obtain the control equations for the case of Ehrenfest dynamics in combination with TDDFT, some modifications need to be done to the previous scheme. In this section we derive the necessary equations, which essentially consist of combining the formalism developed in [29], with the formalism of the previous section.

In TDDFT, the real interacting system of electrons is substituted by a fictitious system of non-interacting electrons whose density is, by definition, equal to the real density. Therefore, instead of one correlated wavefunction we now have a Slater determinant. In order to simplify the formalism, we will consider a spin-compensated system with an even number N of electrons doubly occupying $N/2$ orbitals φ_i. The one-body density of this Slater determinant is given by;

$$n(\vec{r}, t) \equiv n_t(\vec{r}) = \sum_{j=1}^{N/2} 2|\varphi_j(\vec{r}, t)|^2. \qquad (32)$$

The one-particle Hamiltonian that governs the motion of the non-interacting electrons is a functional of this density, and is given the name of 'Kohn–Sham (KS) Hamiltonian'. In this context, it also depends on the classical variables (q, p), and on the control parameters u. The full Hamiltonian that takes the place of the one in equation (1) may in this case be written as:

$$\hat{H}[q, p, u, t] = H_{\text{clas}}[q, p, u, t]\hat{I} + \sum_{i=1}^{N} \hat{H}_{\text{KS}}^{(i)}[q, p, n_t, u, t], \qquad (33)$$

where $\hat{H}_{\text{KS}}^{(i)}[q, p, n_t, u, t]$ is the one-particle KS Hamiltonian, acting on particle i. Note that this Hamiltonian depends on the electronic density at time t, n_t. This is in fact an approximation—the *adiabatic* approximation—which we take here because it simplifies the notation of the results given below, and because the vast majority applications of TDDFT up to now use it. The most common form of this KS Hamiltonian is:

$$\hat{H}_{\text{KS}}[q, p, n_t, u, t] = -\tfrac{1}{2}\nabla^2 + v_0(\vec{r}, q(t)) + v_{\text{Hartree}}[n_t](\vec{r}) + v_{\text{xc}}[n_t](\vec{r}) + v_{\text{ext}}(\vec{r}, u, t), \qquad (34)$$

where (1) $v_0(\vec{r}, q(t))$ is the quantum-classical potential interaction term, that normally depends only on the classical positions $q(t)$ (this fact is not relevant for the following derivations); (2) v_{Hartree} is the classical electrostatic potential created by the density n_t:

$$v_{\text{Hartree}}[n_t](\vec{r}) = \int \mathrm{d}^3 r \, \frac{n_t(\vec{r})}{\vec{r} - \vec{r}} \tag{35}$$

(3) $v_{\text{xc}}[n_t](\vec{r})$ is the exchange and correlation potential functional, whose exact form is unknown and must be approximated; and (4) $v_{\text{ext}}(\vec{r}, u, t)$ is the external potential, whose form depends on the parameters u—i.e. this is in fact the *control* term that we can manipulate.

The corresponding equations of motion are:

$$\dot{q}_a(t) = \frac{\partial H_{\text{clas}}}{\partial p_a}[q(t), p(t), u, t] + \sum_{j=1}^{N/2} 2\langle \varphi_j(t)| \frac{\partial \hat{H}_{\text{KS}}}{\partial p_a}[q(t), p(t), u, t]|\varphi_j(t)\rangle \tag{36}$$

$$\dot{p}_a(t) = -\frac{\partial H_{\text{clas}}}{\partial q_a}[q(t), p(t), u, t] - \sum_{j=1}^{N/2} 2\langle \varphi_j(t)| \frac{\partial \hat{H}_{\text{KS}}}{\partial q_a}[q(t), p(t), u, t]|\varphi_j(t)\rangle \tag{37}$$

$$\dot{\varphi}_j(\vec{r}, t) = -\mathrm{i}\hat{H}_{\text{KS}}[q(t), p(t), u, t]\varphi_j(\vec{r}, t). \tag{38}$$

Here we have assumed the following: the derivatives $\frac{\partial \hat{H}_{\text{KS}}}{\partial q_a}$ and $\frac{\partial \hat{H}_{\text{KS}}}{\partial p_a}$ do not depend on the electronic density. The reason is that the density is included in the KS Hamiltonian through the Hartree and exchange-correlation potentials, which do not depend (explicitly) on the classical variables. This fact can immediately be seen in equation (34). In fact, it will later be useful to split the KS Hamiltonian in the following manner:

$$\hat{H}_{\text{KS}}[q(t), p(t), n_t, u, t] = \hat{H}_{\text{KS}}^0[q(t), p(t), u, t] + \hat{V}_{\text{Hxc}}[n_t]. \tag{39}$$

The previous equations (36)–(38) determine the evolution of the system, given a choice for the control parameters: $u \rightarrow \{q[u], p[u], \varphi[u]\}$. The goal, as in previous section, is to maximize a function G defined in terms of a functional of the system behavior:

$$G[u] = F^{\text{term}}[q[u](T), p[u](T), \varphi[u](T), u]. \tag{40}$$

Once again, we have assumed that this target depends only on the final state of the system. The computation of the gradient of this function proceeds as in previous section, by defining a suitable extended functional, depending on a set of costate variables $\tilde{q}, \tilde{p}, \chi$:

$$J[q, p, \varphi, \tilde{q}, \tilde{p}, \chi, u] = F^{\text{term}}[q, p, \varphi, u] + L[q, p, \varphi, \tilde{q}, \tilde{p}, \chi, u] \tag{41}$$

with the help of the following Lagragian:

$$\begin{aligned}
L[q, p, \varphi, \tilde{q}, \tilde{p}, \chi, u] = &-\sum_a \int_0^T \mathrm{d}t \, \tilde{p}_a(t) \left(\dot{q}_a(t) - \frac{\partial H_{\text{clas}}}{\partial p_a}[q(t), p(t), u, t] \right. \\
&\left. -\sum_{j=1}^{N/2} 2\langle \varphi_j(t)| \frac{\partial \hat{H}_{\text{KS}}}{\partial p_a}[q(t), p(t), u, t]|\varphi_j(t)\rangle \right) \\
&+\sum_a \int_0^T \mathrm{d}t \, \tilde{q}_a(t) \left(\dot{p}_a(t) + \frac{\partial H_{\text{clas}}}{\partial q_a}[q(t), p(t), u, t] \right. \\
&\left. +\sum_{j=1}^{N/2} 2\langle \varphi_j(t)| \frac{\partial \hat{H}_{\text{KS}}}{\partial q_a}[q(t), p(t), u, t]|\varphi_j(t)\rangle \right) \\
&-2\,\text{Re} \sum_{j=1}^{N/2} \int_0^T \mathrm{d}t \, \langle \chi_j(t)| \frac{\mathrm{d}}{\mathrm{d}t} + \mathrm{i}\hat{H}_{\text{KS}}[q(t), p(t), n_t, u, t]|\varphi_j(t)\rangle.
\end{aligned} \tag{42}$$

The functional derivatives of J with respect to the new variables $\tilde{q}$, $\tilde{p}$ and χ, set to zero, lead to the equations of motion of the system. In order to get the equations of motion for the new variables, we must compute and set to zero the functional derivatives of J with respect to the original system variables. In order to do this, it is helpful to rewrite the Lagrangian as:

$$
L[q, p, \tilde{q}, \tilde{p}, \varphi, \chi, u] = \sum_a \int_0^T dt \; (\tilde{q}_a(t)\dot{p}_a(t) - \tilde{p}_a(t)\dot{q}_a(t))
$$

$$
+ \int_0^T dt \; D_{q(t),p(t)} H_{\text{clas}}[q(t), p(t), u, t]
$$

$$
+ \sum_{j=1}^{N/2} \int_0^T dt \; 2\langle \varphi_j(t) | D_{q(t),p(t)} \hat{H}_{\text{KS}}[q(t), p(t), u, t] | \varphi_j(t) \rangle
$$

$$
- 2 \operatorname{Re} \sum_{j=1}^{N/2} \int_0^T dt \; \langle \chi_j(t) | \frac{d}{dt} + i\hat{H}_{\text{KS}}^0[q(t), p(t), n_t, u, t] | \varphi_j(t) \rangle. + L^{\text{Hxc}}[\varphi, \chi].
$$

$$(43)$$

In this expression, we have separated out the part that contains the nonlinear Hartree, exchange and correlation terms:

$$
L^{\text{Hxc}}[\varphi, \chi] = -2 \operatorname{Re} i \sum_{j=1}^{N/2} \int_0^T dt \; \langle \chi_j(t) | \hat{V}_{\text{Hxc}}[n_t] | \varphi_j(t) \rangle.
$$

$$(44)$$

The functional derivatives of this term with respect to the KS orbitals are:

$$
\frac{\delta L^{\text{Hxc}}}{\delta \varphi_l^*(\vec{r}, t)} = \varphi_l(\vec{r}, t) 4 \operatorname{Im} \sum_{j=1}^{N/2} \int d^3r' \chi_j^*(\vec{r}, t) f_{\text{Hxc}}[n_t](\vec{r}, \vec{r}') \varphi_j(\vec{r}', t) + i v_{\text{Hxc}}[n_t](\vec{r}) \chi_l(\vec{r}, t).
$$

$$(45)$$

If we now define the following set of operators:

$$
\hat{K}_{lj}[\varphi(t)] \psi(\vec{r}) = -4i\varphi_l(\vec{r}, t) \operatorname{Im} \int d^3r' \psi(\vec{r}) f_{\text{Hxc}}[n_t](\vec{r}, \vec{r}') \varphi_j(\vec{r}, t),
$$

$$(46)$$

we may rewrite the previous functional derivative as:

$$
\frac{\delta L^{\text{Hxc}}}{\delta \varphi_l^*(\vec{r}, t)} = i \sum_{j=1}^{N/2} \hat{K}_{lj}[\varphi(t)] \chi_j(\vec{r}, t) + i v_{\text{Hxc}}[n_t](\vec{r}) \chi_l(\vec{r}, t).
$$

$$(47)$$

Aided with this expression, we may now write the resulting equations of motion by taking the functional derivatives of J with respect to the state variables:

$$
\dot{\tilde{q}}_a(t) = \frac{\partial}{\partial p_a} D_{q(t),p(t)} H_{\text{class}}[q(t), p(t), u, t]
$$

$$
+ \sum_{j=1}^{N/2} 2\langle \varphi_j(t) | \frac{\partial}{\partial p_a} D_{q(t),p(t)} \hat{H}_{\text{KS}}[q(t), p(t), u, t] | \varphi_j(t) \rangle
$$

$$
- 2 \operatorname{Re} i \sum_{j=1}^{N/2} \langle \chi_j(t) | \frac{\partial}{\partial p_a} \hat{H}_{\text{KS}}[q(t), p(t), u, t] | \varphi_j(t) \rangle,
$$

$$(48)$$

$$\dot{p}_a(t) = -\frac{\partial}{\partial q_a} D_{q(t),p(t)} H_{\mathrm{class}}[q(t), p(t), u, t]$$

$$-\sum_{j=1}^{N/2} 2\langle\varphi_j(t)|\frac{\partial}{\partial q_a} D_{q(t),p(t)}\hat{H}_{\mathrm{KS}}[q(t), p(t), u, t]|\varphi_j(t)\rangle$$

$$+2\,\mathrm{Re}\,\mathrm{i}\sum_{j=1}^{N/2}\langle\chi_j(t)|\frac{\partial}{\partial q_a}\hat{H}_{\mathrm{KS}}[q(t), p(t), u, t]|\varphi_j(t)\rangle, \tag{49}$$

$$\dot{\chi}_j(\vec{r}, t) = -\mathrm{i}\hat{H}_{\mathrm{KS}}[q(t), p(t), n_t, u, t]\chi_j(\vec{r}, t) - \mathrm{i}\sum_{k=1}^{N/2} K_{jk}[\varphi(t)]\chi_k(\vec{r}, t),$$

$$+2\sum_{j=1}^{N/2} D_{q(t),p(t)} H_{\mathrm{KS}}[q(t), p(t), u, t]\varphi_j(\vec{r}, t) \tag{50}$$

$$\tilde{q}_a(T) = -\frac{\partial F^{\mathrm{term}}}{\partial p_a}[q(T), p(T), \varphi(T)] \tag{51}$$

$$\tilde{p}_a(T) = \frac{\partial F^{\mathrm{term}}}{\partial q_a}[q(T), p(T), \varphi(T)] \tag{52}$$

$$\chi_j(\vec{r}, T) = \frac{\delta F^{\mathrm{term}}}{\delta\varphi^*(\vec{r}, T)}. \tag{53}$$

These equations establish the map $u \to \chi[u]$. This is the ingredient needed to compute the gradient of G, which, in analogy to the equation (30) obtained in the previous section, is given by:

$$\frac{\partial G}{\partial u_m}[u] = \left.\frac{\partial J[q, p, \varphi, \tilde{q}, \tilde{p}, \chi, u]}{\partial u_m}\right|_{q=q[u],p=p[u],\varphi=\varphi[u],\tilde{q}=\tilde{q}[u],\tilde{p}=\tilde{p}[u],\chi=\chi[u]}. \tag{54}$$

4. The H$_2^+$ molecule

We finish by particularizing the previous rather abstract formalism to the case of the simplest of molecules, H$_2^+$, composed of two protons and one electron, in the presence of an electric field. To simplify even further, so that the resulting equations are as clear as possible, we will reduce the number of classical degrees of freedom to only one (the internuclear distance). To achieve this, we will work in the reference frame of the nuclear center of mass, neglect the inertial force due to its acceleration, and assume cylindrical symmetry along the molecular axis.

The quantum-classical Hamiltonian is given by:

$$\hat{H} = \frac{1}{2M}\vec{P}_1^2 + \frac{1}{2M}\vec{P}_2^2 + \frac{1}{2}\hat{\vec{p}}^2 + w(\vec{R}_1 - \vec{R}_2) - w(\hat{\vec{r}} - \vec{R}_1) - w(\hat{\vec{r}} - \vec{R}_2)$$

$$-\varepsilon(u, t)\vec{\pi}\cdot\vec{R}_1 - \varepsilon(u, t)\vec{\pi}\cdot\vec{R}_2 + \varepsilon(u, t)\vec{\pi}\cdot\hat{\vec{r}}. \tag{55}$$

In this equation, $(\vec{R}_1, \vec{P}_1)$ and $(\vec{R}_2, \vec{P}_2)$ are the position and momentum pairs of the two (classical) protons, and $(\hat{\vec{r}}, \hat{\vec{p}})$ is the position and momentum operator pair of the electron. M is the proton mass in atomic units, and w is the particle–particle interaction function (the proton–proton and electron–proton interactions are identical, except for the opposite sign).

The last terms are the interaction of the particles with an electric field $\varepsilon(u, t)\vec{\pi}$ in the dipole approximation.

It is convenient to transform the classical variables into the nuclear center-of-mass and relative particle coordinates:

$$\vec{R} = \vec{R}_1 - \vec{R}_2, \tag{56}$$

$$\vec{R}_{\text{CM}} = \tfrac{1}{2}(\vec{R}_1 + \vec{R}_2). \tag{57}$$

The Hamiltonian changes into:

$$\hat{H} = \frac{1}{2M_{\text{CM}}}\vec{P}_{\text{CM}}^2 + \frac{1}{2\mu}\vec{P}^2 + w(\vec{R}) - \varepsilon(u, t)\vec{\pi} \cdot \vec{R}_{\text{CM}} + \frac{1}{2}\hat{\vec{p}}^2 + \hat{V}(\hat{\vec{r}}; \vec{R}_{\text{CM}}, \vec{R}), \tag{58}$$

where:

$$\hat{V}(\hat{\vec{r}}; \vec{R}_{\text{CM}}, \vec{R}) = -w\left(\hat{\vec{r}} - \vec{R}_{\text{CM}} - \tfrac{1}{2}\vec{R}\right) - w\left(\hat{\vec{r}} - \vec{R}_{\text{CM}} + \tfrac{1}{2}\vec{R}\right) + \varepsilon(u, t)\vec{\pi} \cdot (\hat{\vec{r}} - \vec{R}_{\text{CM}}). \tag{59}$$

The mass of the nuclear center of mass M_{CM} is $2M$, whereas the reduced mass μ is $M/2$. This full Hamiltonian can be conveniently split into a classical and a quantum part as:

$$H_{\text{clas}} = \frac{1}{2M_{\text{CM}}}\vec{P}_{\text{CM}}^2 + \frac{1}{2\mu}\vec{P}^2 + w(\vec{R}) - \varepsilon(u, t)\vec{\pi} \cdot \vec{R}_{\text{CM}}. \tag{60}$$

$$\hat{H}_{\text{quantum}} = \frac{1}{2}\hat{\vec{p}}^2 + \hat{V}(\hat{\vec{r}}; \vec{R}_{\text{CM}}, \vec{R}). \tag{61}$$

By noticing that

$$\hat{V}(\hat{\vec{r}} + \vec{R}_{\text{CM}}; \vec{R}_{\text{CM}}, \vec{R}) = \hat{V}(\hat{\vec{r}}; \vec{0}, \vec{R}), \tag{61}$$

it becomes clear that some simplification is to be expected if we move to the reference system of the center of mass. Schrödinger's equation for the electron is:

$$i\frac{d}{dt}|\psi(t)\rangle = \left[\frac{1}{2}\hat{\vec{p}}^2 + \hat{V}(\hat{\vec{r}}; \vec{R}_{\text{CM}}, \vec{R})\right]|\psi(t)\rangle, \tag{62}$$

but we may instead perform a unitary transformation in the form:

$$|\Psi(t)\rangle = \hat{U}[\vec{R}_{\text{CM}}(t)]|\psi(t)\rangle, \tag{63}$$

where

$$\hat{U}[\vec{R}_{\text{CM}}(t)] = \exp(i\vec{R}_{\text{CM}}(t) \cdot \hat{\vec{p}} - i\dot{\vec{R}}_{\text{CM}}(t) \cdot \hat{\vec{r}} + \frac{i}{2}\int_0^t d\tau \,\dot{\vec{R}}_{\text{CM}}^2(\tau)). \tag{64}$$

This type of gauge transformation is employed to move between different Galilean reference frames [31, 32]. The corresponding Schrödinger's equation for this transformed state is:

$$i\frac{d}{dt}|\Psi(t)\rangle = \left[\frac{1}{2}\hat{\vec{p}}^2 + \hat{V}(\hat{\vec{r}}; \vec{0}, \vec{R})\right]|\Psi(t)\rangle + \ddot{\vec{R}}_{\text{CM}}(t) \cdot \hat{\vec{r}}|\Psi(t)\rangle. \tag{65}$$

Note the presence of an *inertial* term, due to the acceleration of the nuclear center of mass. If we assume this term to be small (an assumption which is based on the heavy weight of the nuclei), the previous equation is completely decoupled from the center of mass variable, and we may write:

$$i\frac{d}{dt}|\Psi(t)\rangle = \left[\frac{1}{2}\hat{\vec{p}}^2 - w\left(\hat{\vec{r}} - \frac{1}{2}\vec{R}\right) - w\left(\hat{\vec{r}} + \frac{1}{2}\vec{R}\right) + \varepsilon(u, t)\vec{\pi} \cdot \hat{\vec{r}}\right]|\Psi(t)\rangle. \tag{66}$$

The equation of motion for the relative particle can then also be exactly written without the presence of the center of mass variables:

$$\frac{\mathrm{d}}{\mathrm{d}t}\vec{P}(t) = -\nabla w(\vec{R}) - \langle\psi(t)|\nabla_{\vec{R}}V(\hat{\vec{r}}(t), \vec{R}_{\mathrm{CM}}(t), \vec{R}(t))|\psi(t)\rangle$$

$$= -\nabla w(\vec{R}) - \langle\Psi(t)|\nabla_{\vec{R}}V(\hat{\vec{r}}(t), \vec{0}, \vec{R}(t))|\Psi(t)\rangle$$

$$= -\nabla w(\vec{R}) - \langle\Psi(t)|\frac{1}{2}\nabla w\left(\hat{\vec{r}} - \frac{1}{2}\vec{R}\right) - \frac{1}{2}\nabla w\left(\hat{\vec{r}} - \frac{1}{2}\vec{R}\right)|\Psi(t)\rangle. \tag{67}$$

The last two equations can be considered to be derived from the following quantum and classical Hamiltonians, that consider the relative particle only:

$$H_{\mathrm{clas}} = \frac{1}{2\mu}\vec{P}^2 + w(\vec{R}), \tag{68}$$

$$\hat{H}_{\mathrm{quantum}} = \frac{1}{2}\hat{\vec{p}}^2 - w\left(\hat{\vec{r}} - \frac{1}{2}\vec{R}\right) - w\left(\hat{\vec{r}} + \frac{1}{2}\vec{R}\right) + \varepsilon(u, t)\vec{\pi}\cdot\hat{\vec{r}}. \tag{69}$$

We may simplify the problem further by considering the existence of cylindrical symmetry around the molecular axis, which requires that the electrical field is directed in that direction: $\vec{\pi} = \vec{z}$, assuming that the molecular axis is the z-direction. If the initial momentum is zero (or is also parallel to the z-axis), and the initial electronic wavefunction is cylindrically symmetric, then this symmetry will be preserved and we need only take care of the z component $q = \vec{R}\cdot\vec{z}$, and its corresponding momentum $p = \vec{P}\cdot\vec{z}$. Therefore, if we define:

$$v(q, \hat{\vec{r}}) = -w\left(\hat{\vec{r}} - \tfrac{1}{2}q\vec{z}\right) - w\left(\hat{\vec{r}} + \tfrac{1}{2}q\vec{z}\right), \tag{70}$$

we may finally describe the system with the following Hamiltonians:

$$H_{\mathrm{clas}} = \frac{1}{2\mu}p^2 + w(q), \tag{71}$$

$$\hat{H}_{\mathrm{quantum}} = \frac{1}{2}\hat{\vec{p}}^2 + v(q, \hat{\vec{r}}) + \varepsilon(u, t)\vec{\pi}\cdot\hat{\vec{r}}. \tag{72}$$

The corresponding equations of motion are:

$$\dot{p}(t) = -w'(q(t)) - \langle\Psi(t)|\frac{\partial v}{\partial q}(q(t), \hat{\vec{r}})|\Psi(t)\rangle, \tag{73}$$

$$\dot{q}(t) = \frac{1}{\mu}p(t), \tag{74}$$

$$\mathrm{i}\frac{\mathrm{d}}{\mathrm{d}t}|\Psi(t)\rangle = \left[\frac{1}{2}\hat{\vec{p}}^2 + v(q(t), \hat{\vec{r}}) + \varepsilon(u, t)\vec{\pi}\cdot\hat{\vec{r}}\right]|\Psi(t)\rangle. \tag{75}$$

Once we have a dynamical system clearly defined, we can proceed to pose and solve optimization problems. For example, one may wish to find a laser pulse that dissociates the molecule. This can be formulated by requiring the maximization of the relative coordinate q at the final time of the propagation. One may therefore define, for example:

$$F^{\mathrm{term}}[q(T), p(T), u] = q^2(T), \tag{76}$$

so that:

$$G[u] = q^2[u](T). \tag{77}$$

We may now directly apply the expressions obtained in section 2. The result is the following: The equation for the gradient of function G is:

$$\frac{\partial G}{\partial u_m}[u] = 2\,\mathrm{Im}\int_0^T \mathrm{d}t\,\langle\chi[u](t)|\,\frac{\partial\varepsilon}{\partial u_m}(u,t)\vec{\pi}\cdot\hat{\vec{r}}\,|\Psi[u](t)\rangle. \tag{78}$$

In order to compute this expression one needs the 'costate' wavefunction χ, which can be obtained by backward propagation of its equation of motion. This equation, along with the also necessary equations for the other auxiliary classical costate variables $\tilde{q}$, $\tilde{p}$, is:

$$\dot{\tilde{q}}(t) = \frac{\tilde{p}(t)}{\mu}$$

$$\dot{\tilde{p}}(t) = -\langle\Psi(t)|\,\tilde{q}(t)\frac{\partial^2 v}{\partial q^2}(q(t),\hat{\vec{r}}) + \tilde{q}(t)w''(q(t))\,|\Psi(t)\rangle + 2\,\mathrm{Re}\,\mathrm{i}\langle\chi(t)|\frac{\partial v}{\partial q}(q(t),\hat{\vec{r}})|\Psi(t)\rangle, \tag{79}$$

$$\dot{\chi}(x,t) = -\mathrm{i}\hat{H}^\dagger_{\mathrm{quantum}}[q(t),p(t),u,t]\chi(x,t)$$
$$\times\left[\tilde{q}(t)\frac{\partial v}{\partial q}(q(t),\hat{\vec{r}}) + \tilde{q}(t)w'(q(t)) + \frac{1}{\mu}\tilde{p}(t)p(t)\right]\Psi(x,t). \tag{80}$$

And, to conclude, the final-time conditions are:

$$\tilde{q}(T) = 0, \tag{81}$$

$$\tilde{p}(T) = 2q(T), \tag{82}$$

$$\chi(x,T) = 0. \tag{83}$$

5. Conclusions

Ehrenfest moleular dynamics (MD) based on TDDFT is a computationally practical model, as demonstrated in the past by numerous studies. The evolution of molecular systems in the presence of laser fields can be simulated in reasonable times, depending, of course, on the size of the molecular system and on the required propagation time. One may then wonder whether it is also possible to perform optimization calculations with this model: this means, in the context of molecules irradiated with laser pulses, the calculation of those pulse shapes that induce an optimal behavior of the system, as defined by a given target functional.

While control theory in the context of engineering problems (obviously addressing classical problems), and QOCT are already mature disciplines, there has been no attempt to extend optimal control theory to quantum-classical models. In this work, we have presented the fundamental equations of an optimal control theory for systems containing both quantum electrons and classical ions. In particular, the model of choice has been Ehrenfest dynamics, a non-adiabatic variant of MD. The general formulation, that needs the fully correlated many-electron wavefunction, can be simplified by making use of TDDFT. In this case, the optimal control equations require some modifications that we have also provided.

The key equations that we have derived are those that permit to compute the gradient of the target function with respect to the optimizing parameters. Armed with this gradient, one can use any of the various nonlinear optimization algorithms available. In essence, the required computations amount to the forwards propagation of the system itself, along with a backward propagation of an auxiliary system. The computational complexity of this backward propagation is similar to the complexity of the forward propagation, and therefore one may conclude that the optimization is feasible as long as the propagation of the initial model is

also feasible. Work toward the numerical implementation of these ideas is in progress. For this purpose we will use the optimal control capabilities already implemented in the octopus code [33, 34], which has been used for electronic-only control problems in various previous works, e.g. [27, 29, 35–38].

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