

Chapter 13

Quantum Optimal Control

Alberto Castro and Eberhard K. U. Gross

13.1 Introduction

All applications of time-dependent density-functional theory (TDDFT) until now have attempted to describe the response of many-electron systems to external fields. Given its success in this task, it seems timely, therefore, to address the inverse problem: given a prescribed goal (e.g., the transfer of electronic charge to a given region in space, or the population of a given excited state), what is the external perturbation that achieves this goal in an optimal way? This is the problem studied by quantum optimal control theory (QOCT). The essentials of this theory make no assumption on the nature of the quantum system whose behaviour is being engineered, or on the particular methodology used to model the system. It must, therefore, be complemented with a suitable model for describing the dynamics of the quantum system. In this chapter, we describe how this model can be TDDFT.

QOCT (Shapiro and Brumer 2003; Rice and Zhao 2000; Werschnik and Gross 2007; Werschnik 2006; Brif et al. 2010; Rabitz 2009) provides the necessary tools to theoretically design driving fields capable of controlling a quantum system towards a given state or along a prescribed path in Hilbert space. This discipline has grown steadily in the last two decades. The reason is that it is the most powerful theoretical counterpart to the exponentially growing field of experimental quantum coherent control. The key aspect for the success of this area is that the laser pulse creation and

A. Castro (✉)

Instituto de Biocomputación y Física de Sistemas Complejos,
Universidad of Zaragoza, Mariano Esquillor s/n, Edificio I+D,
50018 Zaragoza, Spain
e-mail: acastro@bifi.es

E. K. U. Gross

Max-Planck Institut für Mikrostrukturphysik, Weinberg 2,
06120 Halle, Germany
e-mail: hardy@mpi-halle.mpg.de

shaping techniques have improved impressively over the last decades (Weiner 2000), and thus the area of experimental optimal control has become a well established field. An outstanding number of possible technological applications are to be expected: the quest for systems able to perform quantum computing (Tesch et al. 2001; Palao and Kosoff 2002), the synthesis of design-molecules by laser-induced chemical reactions (Laarmann et al. 2007), or the control of electron currents in molecular switches using light (Geppert et al. 2004), to name a few examples, may benefit from these recent advances.

The essential concepts of QOCT can be formulated for arbitrary quantum systems, that are to be described either via the wave function, the density matrix, or in some cases the propagator of the process. Since the full quantum dynamics of interacting particles cannot be treated exactly for more than a few degrees of freedom, the application of QOCT, therefore, relies on the previous existence of a methodology capable of constructing a sufficiently good model for the relevant process. In fact, the solution of the necessary equations typically requires multiple propagations, both forwards and backwards, for the system under study. We know that this is especially challenging if this is a many-electron system. In fact, in most applications, few-level simplifications and models are typically postulated when handling the QOCT equations. Unfortunately, these simplifications are not always accurate enough: strong pulses naturally involve many electronic levels, and normally perturbative treatments are not useful. Non-linear laser-matter interaction must sometimes be described *ab initio*.

As it is shown elsewhere in this book, TDDFT is a viable alternative to computationally more expensive approaches based on the wave function for the description of this type of processes. We are referring to many-electron systems irradiated with femtosecond pulses, with intensities typically ranging from 10^{11} to 10^{15} Wcm⁻², a non-linear regime that nevertheless allows for a non-relativistic treatment. This may lead to a number of interesting phenomena, e.g. above-threshold or tunnel ionization, bond hardening or softening, high harmonic generation, photo-isomerization, photo-fragmentation, Coulomb explosion, etc (Protopapas et al. 1997; Brabec and Krausz 2000; Scrinzi et al. 2006).

It is therefore necessary to inscribe TDDFT into the general QOCT framework. In this chapter, we describe the manner in which this inscription can be done. We present here generalized equations, valid for non-collinear spin configurations as well as providing detailed derivations of the key equations.

13.2 The Essential QOCT Equations

For the sake of completeness, we start by recalling the essential QOCT equations (by which we mean those that provide the gradient or numerical derivative of the target functional with respect to the control function). We do so for a generic quantum system, before establishing the results for TDDFT in the next section. For alternative

presentations of the following results, we refer the reader, for example, to (Peirce et al. 1988; Tersigni et al. 1990; Serban et al. 2005).

We depart from a generic Schrödinger equation in the form:

$$\dot{\varphi}(t) = -i\hat{H}[u, t]\varphi(t), \quad (13.1a)$$

$$\varphi(t_0) = \varphi_0, \quad (13.1b)$$

where $\varphi(t)$ is the state of the system at time t (that lives in the Hilbert space \mathcal{H}), and $\hat{H}[u, t]$ is the Hamiltonian, that depends on some parameter u (or perhaps a set of parameters) that we will call hereafter *control*. We wish to find the control u that makes the evolution optimal in some manner. The goodness of the process is encoded into a functional that depends on how the system evolves:

$$F : \overline{\mathcal{H}}^0 \times \mathcal{P} \rightarrow \mathbb{R} \quad (13.2a)$$

$$(\varphi, u) \rightarrow \mathbb{R}, \quad (13.2b)$$

The set $\overline{\mathcal{H}}^0$ is defined in the following way: if we consider that the process occurs in the time interval $[0, T]$, the possible evolutions of the system can be contained in the space $\overline{\mathcal{H}} = \mathcal{H} \times [0, T]$. However, we restrict the domain of F to those evolutions whose initial condition is consistent with Eq. 13.1b:

$$\overline{\mathcal{H}}^0 = \{\varphi \in \overline{\mathcal{H}} \text{ such that } \varphi(t_0) = \varphi_0\}. \quad (13.3)$$

The set \mathcal{P} contains the allowed control parameters u . The explicit dependence of F on the control u is typically due to the presence of a *penalty* function, whose role is to avoid undesirable regions of the control search space (e.g., too high frequency components of a laser pulse, unrealistic intensities, etc.). In many cases, the functional F is split as:

$$F[\varphi, u] = J_1[\varphi] + J_2[u], \quad (13.4)$$

where J_1 is the real objective, and J_2 is the penalty function. The objective may depend on the full evolution of the system during the time interval $[0, T]$, and/or on the state of the system at the final time T :

$$J_1[\varphi] = J_1^i[\varphi] + J_1^f[\varphi(T)], \quad (13.5)$$

where the functional J_1^i depends on the full evolution of the system, whereas J_1^f is a functional of the final state. In most cases, these functionals are expectation values of some observable:

$$J_1^i[\varphi] = \int dt \langle \varphi(t) | \hat{O}^i(t) | \varphi(t) \rangle, \quad (13.6a)$$

$$J_1^f[\varphi] = \int dt \langle \varphi(T) | \hat{O}^f | \varphi(T) \rangle. \quad (13.6b)$$

The specification of a particular control u determines the evolution of the system; in mathematical terms, we have a mapping:

$$\varphi : \mathcal{P} \rightarrow \overline{\mathcal{H}}^0 \tag{13.7a}$$

$$u \rightarrow \varphi[u]. \tag{13.7b}$$

Therefore, the optimization problem can be formulated as the problem of finding the extrema of the function G :

$$G[u] = F[\varphi[u], u]. \tag{13.8}$$

There are many optimization algorithms capable of maximizing functions utilizing solely the knowledge of the function values (“gradient-free algorithms”). We have recently employed one of them in this context (Castro et al. 2009). However, QOCT provides the solution to the problem of computing the gradient of G —or, properly speaking, the functional derivative if u is a function.

The equations that we are seeking, therefore, are those that provide the gradient of G , that will permit us to efficiently perform its optimization. We start by noting that not all the elements of the domain $\overline{\mathcal{H}}^0$ are possible evolution of the system: the search for maxima of F must be constrained to the subset of solutions of Schrödinger’s equation. This is achieved by introducing a Lagrangian functional in the form:

$$L[\varphi, \lambda, u] = -2\Re \int_0^T dt \langle \lambda(t) | \dot{\varphi}(t) + i\hat{H}[u, t]\varphi(t) \rangle, \tag{13.9}$$

and defining a new “total” functional as the sum of F and this new Lagrangian term:

$$J[\varphi, \lambda, u] = F[\varphi, u] + L[\varphi, \lambda, u]. \tag{13.10}$$

Note that, for a possible evolution of the system $\varphi[u]$, the Lagrangian function is zero, and therefore $J[\varphi[u], \lambda, u] = F[\varphi[u], u] = G[u]$. And note that setting to zero the functional derivative of J with respect to λ gives precisely Schrödinger’s equation:

$$\frac{\delta J[\varphi, \lambda, u]}{\delta \lambda^*(x, t)} = -\dot{\varphi}(x, t) - i\hat{H}[u, t]\varphi(x, t) = 0. \tag{13.11}$$

In other words, nullifying this functional derivative is equivalent to establishing the map $u \rightarrow \varphi[u]$. Analogously, a $u \rightarrow \lambda[u]$ mapping can be established by nullifying the functional derivative of J with respect to φ :

$$\begin{aligned} \frac{\delta J[\varphi, \lambda, u]}{\delta \varphi^*(x, t)} &= \dot{\lambda}(x, t) + i\hat{H}[u, t]\lambda(x, t) - \delta(t - T)\lambda(x, t) + \frac{\delta J_1^i}{\delta \varphi^*(x, t)} \\ &+ \delta(t - T) \frac{\delta J_1^f}{\delta \varphi^*(x, T)}. \end{aligned} \tag{13.12}$$

The $u \rightarrow \lambda[u]$ mapping is thus established by prescribing the following equations of motion:

$$\dot{\lambda}(x, t) = -i\hat{H}[u, t]\lambda(x, t) + \frac{\delta J_1^i}{\delta \varphi^*(x, t)}, \quad (13.13a)$$

$$\lambda(x, T) = \frac{\delta J_1^f}{\delta \varphi^*(x, T)}. \quad (13.13b)$$

Note that (i) if J_1^i is not zero (i.e. the target functional depends on the evolution of the system during the time interval $[0, T]$, or as it is sometimes put, there is a *time dependent target*), the equation of motion is an inhomogeneous Schrödinger equation. If J_1^i is zero, λ follows the same Schrödinger equation as y ; (ii) the boundary condition given by Eq. 13.13b is given at time T . Therefore, Eq. 13.13a must be propagated *backwards*.

Once we have prepared these ingredients, we may compute the gradient of $G[u]$ by utilizing the chain rule in the identity:

$$G[u] = J[\varphi[u], \lambda[u], u]. \quad (13.14)$$

Since the functional derivatives of J with respect to φ and λ , applied at $\varphi[u]$ and $\lambda[u]$ are zero, we are left with the expression:

$$\nabla_u G[u] = \nabla_u J_2[u] + 2\Im \int_0^T dt \langle \lambda[u](t) | \nabla_u H[u, t] | \varphi[u](t) \rangle. \quad (13.15)$$

Often, the controlling field is not specified by a discrete set of parameters, but rather by a real function $\varepsilon(t)$. For example, the Hamiltonian may be:

$$\hat{H}[\varepsilon, t] = \hat{H}_0 + \varepsilon(t)\hat{V}. \quad (13.16)$$

The search space, in this case, is the space of real continuous functions in $[0, T]$. The function G is then a functional $G = G[\varepsilon]$, and consequently the gradient of Eq. 13.15 must then be replaced by a functional derivative with respect to ε , and the result is:

$$\frac{\delta G}{\delta \varepsilon(t)} = \frac{\delta J_2}{\delta \varepsilon(t)} + 2\Im \langle \lambda[\varepsilon](t) | \hat{V} | \varphi[\varepsilon](t) \rangle. \quad (13.17)$$

Finally, let us give an example of a very common choice of penalty function: let the Hamiltonian given by Eq. 13.16 be the one that describes an atom or molecule irradiated by a laser pulse, whose temporal shape is determined by $\varepsilon(t)$. The total irradiated energy or *fluence* will be proportional to $\int_0^T dt \varepsilon^2(t)$, and it is usually considered an undesired feature to require very high fluences. A natural choice for the penalty functional is therefore:

$$J_2[\varepsilon] = -\alpha \int_0^T dt \varepsilon^2(t), \quad (13.18)$$

for α some positive weighting constant. The critical points of G in this case can then easily be found by substituting this expression in Eq. 13.17, and equating the functional derivative to zero:

$$\varepsilon(t) = \frac{1}{\alpha} \Im \langle \lambda[\varepsilon](t) | \hat{V} | \varphi[\varepsilon](t) \rangle. \quad (13.19)$$

In this case, the simplest algorithm to find the optimum consists of the following steps: (i) Propagate the Schrödinger equation 13.11 forward in time with some given initial condition; (ii) Propagate the Schrödinger equation (13.13a) with the initial condition (13.13b); (iii) From the solutions $\varphi(t)$ and $\lambda(t)$ of steps (i) and (ii), calculate a new control field from Eq. 13.19 and then perform again steps (i) and (ii) using the new control field, etc. This algorithm has been shown to be monotonically convergent (Zhu et al. 1998; Ohtsuki et al. 2004; Serban et al. 2005).

13.3 Optimization for the TDKS System

In the previous section, we have summarized some of the fundamental aspects of QOCT for a generic quantum system. Equation 13.15, or alternatively, Eq. 13.17, permits to utilize some optimization algorithm that may lead to a satisfactory maximum. The use of those equations, however, requires the solution of Eqs. 13.1a and 13.1b, and Eqs. 13.13a and 13.13b which are forwards and backwards propagation of Schrödinger's equation for the process being studied. Depending on the nature of the process and on the complexity of the model used to describe it, this task may be anywhere from trivial to unfeasible. In particular, for many-electron systems, an exact numerical solution is not possible, and thus TDDFT may be used to tackle the problem.

At this point, let us recall that TDDFT is not a scheme that permits to solve the Schrödinger equation in some approximate manner, but rather a methodology aimed at *bypassing* the use of the many-electron wave function, and avoiding the Schrödinger equation fulfilled by this wave function. The theory provides us with a method to obtain the time-dependent electron density (by means of solving the equations of the associated Kohn–Sham system), but the many electron wave function is not available. However, the previous description of the QOCT methodology works directly with the wave function, and, in particular, it is assumed that the target functional is defined in terms of this object, i.e. the objective is to find the control u that maximizes a functional of the many-electron wave function,

$$F_{\text{int}} = F_{\text{int}}[\Psi, u]. \quad (13.20)$$

As usual, we allow for the possibility of an explicit dependence of the functional on the control u in order to include, if necessary, a penalty function. The label “int” means that this functional is defined in terms of the wave function of the interacting system of electrons. Every observable, however, is known to be a functional of the time-dependent density by virtue of the fundamental one-to-one correspondence of TDDFT, and therefore, in principle it should be possible to find a functional of the density \tilde{F} , such that:

$$F_{\text{int}}[\Psi, u] = \tilde{F}[n[\Psi], u], \quad (13.21)$$

where $n[\Psi]$ is the electronic density corresponding to the many-electron wave function Ψ (we consider hereafter a system of N electrons):

$$n[\Psi](\mathbf{r}, t) = \langle \Psi(t) | \sum_{i=1}^N \delta(\mathbf{r} - \hat{\mathbf{r}}_i) | \Psi(t) \rangle, \quad (13.22)$$

This is the object provided by TDDFT, and so we may substitute the problem of formulating QOCT in terms of the real interacting system, by the formulation of the optimization problem for the non-interacting system of electrons. The equations of motion for the single-particle orbitals of this system, also known as time-dependent Kohn–Sham equations, are:

$$i \frac{\partial}{\partial t} \varphi_i(\mathbf{r}\sigma, t) = \left[-\frac{\nabla^2}{2} + \hat{V}_0 + v_{\text{H}}[n(t)](\mathbf{r}) + \hat{V}_{\text{xc}}[n_{\sigma\sigma'}(t)] + \hat{V}_{\text{ext}}[u] \right] \varphi_i(\mathbf{r}\sigma, t) \quad (13.23)$$

with the (spin-) densities

$$n_{\sigma\sigma'}(\mathbf{r}, t) = \sum_{i=1}^N \varphi_i^*(\mathbf{r}\sigma, t) \varphi_i(\mathbf{r}\sigma', t), \quad (13.24)$$

and

$$n(\mathbf{r}, t) = \sum_{\sigma} n_{\sigma\sigma}(\mathbf{r}, t), \quad (13.25)$$

for $i = 1, \dots, N$ orbitals. The greek indexes σ, σ' run over the two spin configurations, up and down. The densities are, by construction, equal to that of the *real*, interacting system of electrons. \hat{V}_0 represents the internal, time independent fields—usually a nuclear Coulomb potential $V_{\text{n}}(\mathbf{r})$, and may include as well a spin-orbit coupling term of the form $\boldsymbol{\sigma} \cdot \nabla V_{\text{n}} \times \hat{\boldsymbol{a}}$ (where $\boldsymbol{\sigma}$ is the vector of Pauli matrices). The term

$$v_{\text{H}}[n(t)](\mathbf{r}) = \int d^3 r' \frac{n(\mathbf{r}', t)}{|\mathbf{r} - \mathbf{r}'|} \quad (13.26)$$

is the Hartree potential, and $\hat{V}_{\text{xc}}[n_{\sigma\sigma'}]$ is the exchange and correlation potential operator, whose action is given by:

$$\hat{V}_{\text{xc}}[n_{\sigma\sigma'}(t)]\varphi_i(\mathbf{r}\sigma, t) = \sum_{\sigma'} v_{\text{xc}}^{\sigma\sigma'}[n_{\sigma\sigma'}(t)](\mathbf{r})\varphi_i(\mathbf{r}\sigma', t). \quad (13.27)$$

Note that, for the sake of generality, we allow a spin-resolved exchange and correlation potential, that depends on the four spin components $n_{\sigma\sigma'}$ (in many situations more restricted dependences are assumed). However, we do assume here an *adiabatic* approximation, i.e. v_{xc} at each time t is a functional of the densities at that time, $n_{\sigma\sigma'}(t)$. This restriction is non-essential for the derivations that follow, but the availability of non-adiabatic functionals is very scarce, and adiabatic approximations will result in simpler equations.

The last potential term, \hat{V}_{ext} , is the external time-dependent potential, which is determined by the “control” u . In a typical case, this external potential is the electric pulse created by a laser source in the dipole approximation, and u is the real time-dependent function that determines its temporal shape (in this case, $\hat{V}_{\text{ext}}[u]\varphi_i(\mathbf{r}\sigma, t) = u(t)\mathbf{r} \cdot \boldsymbol{\alpha} \varphi_i(\mathbf{r}\sigma, t)$, where $\boldsymbol{\alpha}$ is the polarization vector of the pulse). We write it however in general operator form, since it can be a 2×2 matrix which may include both a time-dependent electric field as well as a Zeeman-coupled magnetic field.

If we group the N single particle states into a vector $\underline{\varphi}(t)$, we can rewrite the time-dependent Kohn–Sham equations in a matrix form:

$$i\underline{\dot{\varphi}}(t) = \underline{\hat{H}}[n_{\sigma\sigma'}(t), u, t]\underline{\varphi}(t), \quad (13.28)$$

where $\underline{\hat{H}}[n_{\sigma\sigma'}(t), u, t] = \hat{H}_{\text{KS}}[n_{\sigma\sigma'}(t), u, t]I_{\underline{N}}$ and $I_{\underline{N}}$ is the N -dimensional unit matrix. With this notation we stress the fact that we have only *one* dynamical system—and not N independent ones, since all φ_i are coupled. This coupling, however, comes solely through the density, since the Hamilton matrix is diagonal.

The structure of these equations is slightly different from that of the generic case presented in the previous section, and in consequence we cannot directly apply the final results obtained there. First, note that now the system is not described by one single wave function, but rather by the full group of Kohn–Sham orbitals. This does not add a fundamental complication (in fact, the system may be regarded as described by a single wave function—the Slater determinant composed of the N orbitals). But more importantly, the TDKS equations are *non-linear*, since the Hamiltonian depends on the density, which is computed from the wave functions that are to be propagated. In consequence, we must follow carefully the derivation presented in the previous section, modifying the steps that used the linearity of the usual Hamiltonians. This is what we will do in the following.

The specification of the value of the control u , together with the initial conditions, determines the solution orbitals: $u \rightarrow \underline{\varphi}[u]$. Our task is now the following: we wish to find an external field—in the language of OCT, a control u —that induces some given behaviour of the system, which can be mathematically formulated by stating

that the induced dynamics maximizes some target functional F . Since we are using TDDFT, this functional will be defined in terms of the Kohn–Sham orbitals, and will possibly depend explicitly on the control u :

$$F = F[\underline{\varphi}, u]. \quad (13.29)$$

And since the orbitals depend on u as well, the goal of QOCT can be formulated as finding the maximum of the function:

$$G[u] = F[\underline{\varphi}[u], u]. \quad (13.30)$$

As we have mentioned in the beginning of the section, the optimization of this function will be equivalent to that of the initial, real problem posed in terms of the interacting many electron system, if the functional F_{int} that constitutes the true optimization target is in fact equal to a functional of the density alone:

$$F_{\text{int}}[\Psi, u] = \tilde{F}[n[\Psi], u], \quad (13.31)$$

and thus we may define our “Kohn–Sham” target as:

$$F[\underline{\varphi}, u] = \tilde{F}[n[\underline{\varphi}], u], \quad (13.32)$$

thanks to the fundamental TDDFT identity $n[\underline{\varphi}] = n[\Psi]$.

In the most general case, the functional F depends on $\underline{\varphi}$ at all times during the process (we have a “time-dependent target”). In many cases, however, the goal is the achievement of some target at a given time T that determines the end of the propagation interval (we then have a “static target”). In both cases, the determination of the value of the function G is obtained by performing the propagation of the system with the field determined by the control u .

As it happened in the generic case, first we must note that searching for a maximum of G is equivalent to a constrained search for F —constrained by the fact that the $\underline{\varphi}$ orbitals must fulfill the time-dependent Kohn–Sham equations. In order to do so, we introduce a new set of orbitals $\underline{\chi}$ that act as Lagrange multipliers, and define a new functional J by adding a Lagrangian term L to F :

$$J[\underline{\varphi}, \underline{\chi}, u] = F[\underline{\varphi}, u] + L[\underline{\varphi}, \underline{\chi}, u], \quad (13.33)$$

of the form

$$L[\underline{\varphi}, \underline{\chi}, u] = -2 \sum_{j=1}^N \Re \left[\int_0^T dt \langle \chi_j(t) | i \frac{d}{dt} + \hat{H}_{\text{KS}}[n_{\sigma\sigma'}(t), u, t] | \varphi_j(t) \rangle \right]. \quad (13.34)$$

Setting the functional derivatives of J with respect to the χ orbitals to zero, we retrieve the time-dependent Kohn–Sham equations. In an analogous manner, we obtain a set of solution $\underline{\chi}[u]$ orbitals by taking functional derivatives with respect to $\underline{\varphi}$ —remembering that the KS Hamiltonian depends on these orbitals, and in consequence,

one must consider its functional derivatives. From the condition $\delta J / \delta \underline{\varphi}^* = 0$, we obtain

$$i \dot{\underline{\chi}}(t) = \left[\hat{H}_{\text{KS}}[n_{\sigma\sigma'}[u](t), u, t] + \hat{K}[\underline{\varphi}[u](t)] \right] \underline{\chi}(t) - i \frac{\delta F}{\delta \underline{\varphi}^*}, \quad (13.35a)$$

$$\underline{\chi}(T) = \underline{0}. \quad (13.35b)$$

The presence of the non-diagonal operator matrix $\hat{K}[\underline{\varphi}[u](t)]$ is the main difference with respect to the normal QOCT equations for a linear quantum system. Its origin is the non-linear dependence of the Kohn–Sham Hamiltonian with respect to the propagating orbitals. It is defined by:

$$\begin{aligned} \hat{K}_{ij}[\underline{\varphi}[u](t)]\psi(\mathbf{r}\sigma) &= -2i \sum_{\sigma'} \varphi_i[u](\mathbf{r}\sigma', t) \times \Im m \\ &\times \left[\sum_{\alpha\beta} \int d^3r' \psi^*(\mathbf{r}'\alpha) f_{\text{Hxc}}^{\alpha\beta, \sigma\sigma'}[n_{\sigma\sigma'}[u](t)](\mathbf{r}, \mathbf{r}') \varphi_j[u](\mathbf{r}'\beta, t) \right], \end{aligned} \quad (13.36)$$

where $f_{\text{Hxc}}^{\alpha\beta, \sigma\sigma'}$ is the *kernel* of the Kohn–Sham Hamiltonian, defined as:

$$f_{\text{Hxc}}^{\alpha\beta, \sigma\sigma'}[n_{\sigma\sigma'}](\mathbf{r}, \mathbf{r}') = \frac{\delta_{\alpha\beta} \delta_{\sigma\sigma'}}{|\mathbf{r} - \mathbf{r}'|} + \frac{\delta v_{\text{xc}}^{\alpha\beta}[n_{\sigma\sigma'}](\mathbf{r})}{\delta n_{\sigma\sigma'}(\mathbf{r}')}. \quad (13.37)$$

If we now note that $G[u] = J[\underline{\varphi}[u], \underline{\varphi}[u], u]$, we arrive to:

$$\nabla_u G[u] = \nabla_u F[\underline{\varphi}, u] \Big|_{\underline{\varphi}=\underline{\varphi}[u]} + 2\Im m \left[\sum_{j=1}^N \int_0^T dt \langle \chi_j[u](t) | \nabla_u \hat{V}_{\text{ext}}[u](t) | \varphi_j[u](t) \rangle \right]. \quad (13.38)$$

Several aspects deserve further discussion:

- (i) Equation 13.35a represents a set of first-order differential equations, whose solution, as it happened in the generic case, must be obtained by *backwards* propagation, since the boundary condition, Eq. 13.35b is given at the end of the propagation interval, T . Note that this propagation depends on the Kohn–Sham orbitals $\underline{\varphi}[u]$. Therefore, the numerical procedure consists of a forward propagation to obtain $\underline{\varphi}[u]$, followed by a backwards propagation to obtain $\underline{\chi}[u]$.
- (ii) These backwards equations are inhomogeneous, due to the presence of the last term in Eq. 13.35a, the functional derivative of F with respect to $\underline{\varphi}$. The reason is that the previous Eqs 13.35a and 13.35b refer to a general “time-dependet target” case, i.e. the target functional depends on the full evolution of the system. In many cases of interest, however, the target functional F takes a “static” form, which can be expressed as:

$$J_1[\underline{\varphi}, u] = O[\underline{\varphi}(T), u], \quad (13.39)$$

for some functional O whose argument is not the full evolution of the Kohn–Sham system, but only its value at the end of the propagation. In this case, the inhomogeneity in Eq. 13.35a vanishes, and instead we obtain a different final-value condition:

$$\chi_i[u](\mathbf{r}\sigma, T) = \frac{\delta O[\underline{\varphi}[u], u]}{\delta \varphi_i^*(\mathbf{r}\sigma)}. \quad (13.40)$$

- (iii) The previous Eq. 13.38 assumes that u is a set of N parameters, $u \in \mathbb{R}^N$ that determines the control function. As we discussed in the previous section, if the control is in fact a time-dependent function $\varepsilon(t)$, the gradient has to be substituted by a functional derivative, and the result is:

$$\frac{\delta G}{\delta \varepsilon(t)} = \left. \frac{\delta F[\underline{\varphi}, \varepsilon]}{\delta \varepsilon(t)} \right|_{\underline{\varphi}=\underline{\varphi}[\varepsilon]} + 2\Im \left[\sum_{j=1}^N \langle \chi_j[\varepsilon](t) | \hat{D} | \varphi_j[\varepsilon](t) \rangle \right]. \quad (13.41)$$

We have assumed here that the external potential \hat{V}_{ext} is determined by the function u by a linear relationship:

$$\hat{V}_{\text{ext}}[\varepsilon](t) = \varepsilon(t) \hat{D}. \quad (13.42)$$

This is the most usual case (\hat{D} would be the dipole operator, and $\varepsilon(t)$ the amplitude of an electric field), but of course it would be trivial to generalize this to other possibilities.

The previous scheme permits therefore to control the Kohn–Sham system. It is important to reflect on the original assumption given by Eq. 13.21, which permits to identify this control with that of the real system of interest. Although the existence of a density functional equivalent to the wave function functional is known to exist *in principle*, we will not always have explicit knowledge of this density functional. We do have this knowledge immediately, for example, if the target functional F_{int} is given by the expectation value of some one-body local operator \hat{A} :

$$F_{\text{int}}[\Psi] = \langle \Psi(T) | \hat{A} | \Psi(T) \rangle = \int d^3r n(\mathbf{r}, T) a(\mathbf{r}), \quad (13.43)$$

where $\hat{A} = \sum_{i=1}^N a(\hat{\mathbf{r}}_i)$. In this case, Eq. 13.40 is simply:

$$\chi_i[u](\mathbf{r}\sigma, T) = a(\mathbf{r}) \varphi_i[u](\mathbf{r}\sigma, T). \quad (13.44)$$

Unfortunately, in some cases the situation is not that favourable. For example, a very common control goal is the transition from an initial state to a target state. In other words, the control operator \hat{A} is the projection operator onto the target state $\hat{A} = |\Psi_{\text{target}}\rangle \langle \Psi_{\text{target}}|$. We have no exact manner to substitute, in this case, the F_{int}

functional by a functional \tilde{F} defined in terms of the density, and afterwards in terms of the KS determinant. It can be approximated, however, by an expression in the form:

$$F[\underline{\varphi}] = |\langle \underline{\varphi}(T) | \sum_I c_I |\varphi^I \rangle|^2, \quad (13.45)$$

where $\varphi(T)$ is the TDKS determinant at time T , and we compute its overlap with a linear combination of Slater determinants φ^I , weighted with some coefficients c_I . These Slater determinants would be composed of occupied and unoccupied ground state KS orbitals, $\varphi^I = \det[\varphi_1^I, \dots, \varphi_N^I]$. In this case, Eq. 13.40 takes the form:

$$\chi_i[u](\mathbf{r}\sigma, T) = \sum_{IJ} \lambda_{IJ}(\mathbf{r}\sigma) \langle \underline{\varphi}(T) | \varphi^I \rangle \langle \varphi^J | \underline{\varphi}(T) \rangle, \quad (13.46a)$$

$$\lambda_{IJ}(\mathbf{r}\sigma) = c_I c_J^* \text{Tr}\{(\mathbf{M}^I)^{-1} \mathbf{A}_I^i(\mathbf{r}\sigma)\}, \quad (13.46b)$$

where $\mathbf{M}_{mn}^I = \langle \varphi_m | \varphi_n^I \rangle$ and $\mathbf{A}_I^i(\mathbf{r}\sigma)_{mn} = \delta_{mi} \varphi_n^I(\mathbf{r}\sigma)$.

In conclusion, we have shown how TDDFT can be combined with QOCT, and we have demonstrated how the resulting equations are numerically tractable. This provides a scheme to perform QOCT calculations from first principles, in order to obtain tailored function-specific laser pulses capable of controlling the electronic state of atoms, molecules, or quantum dots. Most of the previous applications of QOCT were targeted to control, with femto-second pulses, the motion of the nuclear wave packet on one or few potential energy surfaces, which typically happens on a time scale of hundreds of femtoseconds or picoseconds. The approach shown here, on the other hand, is particularly suited to control the motion of the electronic degrees of freedom which is governed by the sub-femto-second time scale. The possibilities that are open thanks to this technique are numerous: shaping of the high harmonic generation spectrum (i.e. quenching or increasing given harmonic orders), selective excitation of electronic excited states that are otherwise difficult to reach with conventional pulses, control of the electronic current in molecular junctions, and many more.