12 Propagators for the Time-Dependent Kohn-Sham Equations

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12.1 Introduction

The main practical result of the Runge-Gross theorem are the time-dependent Kohn-Sham (TDKS) equations: a set of coupled one-particle Schrödinger-like equations with the form (atomic units are used hereafter)

\[ i \frac{\partial \varphi_i(t)}{\partial t} = [\hat{T} + \hat{V}_{\text{KS}}(t)] \varphi_i(t), \quad (12.1a) \]

\[ v_{\text{KS}}(r, t) = v_{\text{ext}}(r, t) + \int d^3 r' \frac{n(r', t)}{|r - r'|} + v_{\text{xc}}[n](r, t). \quad (12.1b) \]

In these equations, the index \( i \) runs through all the occupied Kohn-Sham states \( \varphi_i \); \( \hat{T} \) is the kinetic operator; \( v_{\text{ext}} \) is any (possibly time-dependent) external potential acting on the electronic system; \( v_{\text{xc}}[n] \) is the exchange and correlation potential – which is a functional of the time-dependent density

\[ n(r, t) = \left< \Phi(t) \right| \sum_i \delta(r - \hat{r}_i) \left| \Phi(t) \right> = \sum_i |\varphi_i(r, t)|^2. \quad (12.2) \]

During the last years, most applications of TDDFT were performed within linear response theory, where the response properties of the system are usually obtained in frequency domain. One may, however, work directly in the time-domain, propagating (12.1a). This has the advantage of allowing the inclusion of intense external perturbations, beyond the linear response regime. Of course, this “real-time” formulation of TDDFT requires the use of an algorithm to propagate Schrödinger-like equations.

Not surprisingly, the study of efficacious algorithms for this purpose has a long history, and multiple answers. We are concerned with a very general problem, yet we must beware of general purpose solutions: one expects that the efficiency depends strongly on the characteristics of the time-independent part of the Hamiltonian, on the time-dependent perturbation, and also on the initial state. From all possible approaches, we focus in this chapter on the ones most relevant to the propagation of the TDKS equations. This case has several important features:
• The Hamiltonian is intrinsically time-dependent, which is obvious since it depends parametrically on the time-dependent density.
• This time dependence is not known a priori, since it is deduced from the solution density itself, $v_{KS} = v_{KS}[^n]$. The problem may then be formulated as follows: given $\varphi(\tau)$ and $\hat{H}(\tau)$ for $\tau \leq t$, calculate $\varphi(t + \Delta t)$ for some $\Delta t$. This unpleasant fact is usually not taken into account in most studies of Schrödinger’s equation, and adds extra difficulties, since all approximators will require the knowledge of the Hamiltonian in the interval $[t, t + \Delta t]$.
• Typically, one works with very large basis sets, where the Hamiltonian is represented as a very large, sparse matrix. This happens for instance in the real-space representations we have used.
• The Hamiltonian is usually Hermitian. Also, it is unbounded – and this fact is one of the roots of the numerical difficulties.

In this chapter, we give a pedagogical introduction to the problem of propagating the Kohn-Sham equations, and to some of its solutions. We have been enlightened by several sources, not all of them focused on TDDFT. Most of the literature refers to nuclear wavepacket propagation, either in quantum, semi-classical, or mixed schemes. The equations are, nevertheless, identical, and experience from this field may be translated to others. We learned from Kosloff’s review [Kosloff 1988], from the work of Lubich and coworkers [Lubich 2002, Hochbruck 1998, Hochbruck 1999], from the comparisons of Truong and others [Truong 1992], and from other references that will be cited when appropriate. For the particular problem of TDDFT, we would like to refer to the work of Sugino and Miyamoto [Sugino 1999]. It is also important to mention here the advances in the simulation of (adiabatic) molecular dynamics using the Car-Parrinello approach [Car 1985]. The time-integration is effectively performed using modified Verlet and Gaussian dynamics including multiple time-scale methodologies [Tuckerman 1994a, Tuckerman 1994b]. However, those works do not address the real electron dynamics of a system but a fictitious one determined by an effective electron mass, and need to impose the orthogonality constraint for the wavefunctions (which is automatically fulfilled in the unitary propagation schemes to be described below). Finally, we also refer the reader to our previous work on the subject [Castro 2004a], where on top of the algorithmic discussion that we present here, a quantitative analysis of some of the possible solutions is also given.

We have implemented some of the most common approaches to the propagation of a quantum wave-packet in our computer code octopus,¹ a general purpose pseudopotential, real-space code.² The routines that implement these

¹ The octopus project is aimed at describing the electron-ion dynamics in finite and extended systems under the influence of time-dependent electromagnetic fields. The program can be freely downloaded from http://www.tddft.org/programs/octopus/. For details see [Marques 2003b].
² By real-space, or direct-space, we mean that all functions are discretized on a grid, and that the Laplacian is approximated by finite differences [Beck 2000].