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A Time-Space Adaptive Method for the Schrödinger Equation

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Abstract. In this paper, we present a discretization of the time-dependent Schrödinger equation based on a Magnus-Lanczos time integrator and high-order Gauss-Lobatto finite elements in space. A truncated Galerkin orthogonality is used to obtain duality-based a posteriori error estimates that address the temporal and the spatial error separately. Based on this theory, a space-time adaptive solver for the Schrödinger equation is devised. An efficient matrix-free implementation of the differential operator, suited for spectral elements, is used to enable computations for realistic configurations. We demonstrate the performance of the algorithm for the example of matter-field interaction.

AMS subject classifications: 65M50, 65M60, 65Z05, 81-08

Key words: a posteriori error estimate, adaptive mesh refinement, finite/spectral elements, time-dependent Schrödinger equation

1 Introduction

With the emergence of femtosecond laser pulses and the seminal experiments by Zewail [58], it became possible to experimentally study molecular processes and chemical reactions. The time-dependent Schrödinger equation (TDSE) gives a theoretical description of the dynamics within molecules,

$$\begin{aligned} &\mathrm{i}\hbar\frac{\partial}{\partial t}\psi(x,t)=\hat{H}(t)\psi(x,t),\quad x\in\mathbb{R}^d,\quad 0<t<t_f<\infty,\\ &\psi(x,0)=\psi_0. \end{aligned} \tag{1.1}$$

The differential operator $\hat{H}(t)=\hat{T}(\frac{\partial^2}{\partial x_1^2},\cdots,\frac{\partial^2}{\partial x_d^2})+\hat{V}(x,t)$ comprises the kinetic ($\hat{T}$) and the potential ($\hat{V}$) energy of the system. Since close analytical expressions for the wave function are only known for very simple configurations, numerical simulations are essential

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for the understanding of the outcome of experimental studies. The major challenge in simulations is the curse of dimensionality: The spatial variables in the model describe the degrees of freedom in the molecule, i.e., the coordinates of each particle, and the dimension of the underlying partial differential equation grows therefore linearly with the number of particles.

Various semiclassical methods have been developed that combat the course of dimensionality by employing some type of classical modeling (see e.g. [10, 20, 30, 45, 46, 57]). These techniques are very powerful but they have difficulties in covering the full quantum dynamical nature of the underlying system like energy transfer via laser fields or tunneling effects. The goal of this work is to solve the TDSE for as large systems as possible without any (semi-)classical approximation. Our focus is on the simulation of the interaction of molecules with time-dependent fields.

For small molecules, it is very common to use pseudospectral methods [12, 19, 22, 40, 56] to solve the full TDSE. Because the solutions are smooth, high accuracy can be obtained with a relatively small number of grid points. However, the method is generalized to higher dimensions by tensor products and a flexible adaption of the mesh to the solution is not possible. An approach for improving the efficiency of the Fourier method is the so-called mapped Fourier method where the coordinates are transformed according to the properties of the Hamiltonian [21, 35]. Also, a sparse grid algorithm for the Fourier method was devised by Hallatschek [28] and later employed for the Schrödinger equation [24, 25]. Still these improvements do not enable solution- or residual-based mesh adaption. Moreover, the one-dimensional stencil couples all the grid points and there is no locality in the method which makes parallelization rather difficult.

On the other hand, much research has been done on error estimation and mesh adaptation for finite element discretizations. A posteriori error theory, based on a global energy norm, was initiated by Babuška and Rheinboldt [3, 4]. The work by Babuška and Miller [2] introduced duality arguments. Later Becker and Rannacher [8, 9] designed the dual-weighted residual (DWR) method for error control. This method allows to design adaptive meshes for more general functionals of the error and in this way the error in some physically meaningful function of the solution can be controlled. For the TDSE, it is common that one is interested in the value of some physical observable that can be expressed as a functional of the solution rather than the full distribution function. Duality-based adaptivity is a means to concentrate the computational effort to regions that are most relevant for simulating this observable instead of on minimizing the global L_2 error. Such an observable could be the crosscorrelation, i.e., the overlap of the solution with a predefined state. While DWR is well-established for elliptic differential equations, the temporal dimension poses additional difficulties. Therefore, most work on a posteriori error estimation for parabolic problems do not directly rely on the solution of the dual problem (see e.g. [18, 48]). Schmich and Vexler [52] have extended the DWR theory to parabolic problems in a setting with a discontinuous Galerkin formulation in time. They separate temporal and spatial error estimation and treat the temporal dimension in a time-stepping approach. Still the fact that the primal and the dual problem are solved