Journal of Computational Mathematics
Vol.41, No.5, 2023, 933–955.

http://www.global-sci.org/jcm
doi:10.4208/jcm.2207-m2020-0302

GRADIENT FLOW FINITE ELEMENT DISCRETISATIONS WITH ENERGY-BASED ADAPTIVITY FOR EXCITED STATES OF SCHRÖDINGER'S EQUATION*

Pascal Heid
Mathematical Institute, University of Oxford, Woodstock Road, Oxford OX2 6GG, UK
Email: pascal.heid@maths.ox.ac.uk

Abstract

The purpose of this paper is to verify that the computational scheme from [Heid et al., *Gradient flow finite element discretizations with energy-based adaptivity for the Gross–Pitaevskii equation*, J. Comput. Phys. **436** (2021)] for the numerical approximation of the ground state of the Gross–Pitaevskii equation can equally be applied for the effective approximation of excited states of Schrödinger's equation. That procedure employs an adaptive interplay of a Sobolev gradient flow iteration and a novel local mesh refinement strategy, and yields a guaranteed energy decay in each step of the algorithm. The computational tests in the present work highlight that this strategy is indeed able to approximate excited states, with (almost) optimal convergence rate with respect to the number of degrees of freedom.

Mathematics subject classification: 35Q40, 81Q05, 65N25, 65N30, 65N50.
Key words: Schrödinger's equation, Excited states, Gradient flows, Adaptive finite element methods.

1. Introduction

Schrödinger's equation is the fundamental equation of physics for describing quantum mechanical behaviour, see, e.g., [37, Ch. 1] or [31, Ch. 1] for an introduction to its basic theory. The time-dependent dimensionless Schrödinger equation reads as

$$\mathrm{i}\partial_t\psi(\boldsymbol{x},t) = -\frac{1}{2}\Delta_{\boldsymbol{x}}\psi(\boldsymbol{x},t) + V(\boldsymbol{x})\psi(\boldsymbol{x},t); \tag{1.1}$$

here, $\boldsymbol{x}$ and t denote the spatial and time variables, respectively, $\Delta_{\boldsymbol{x}}$ is the Laplacian in the spatial coordinates, and ψ is a normalized time-dependent single-particle wavefunction. The stationary state solution of Schrödinger's equation (1.1) can be found by solving the *linear* eigenvalue problem (EVP)

$$-\frac{1}{2}\Delta_{\boldsymbol{x}}\psi(\boldsymbol{x}) + V(\boldsymbol{x})\psi(\boldsymbol{x}) = E\psi(\boldsymbol{x}), \tag{1.2}$$

which is called the time-independent Schrödinger equation. Any (normalized) eigenfunction of the EVP (1.2) is a quantum state of the underlying quantum mechanical system, and the corresponding eigenvalue E is the total energy. Moreover, the stationary Schrödinger equation (1.2) coincides with the time-independent Gross–Pitaevskii equation (GPE) for non-interacting

* Received December 7, 2020 / Revised version received October 29, 2021 / Accepted July 12, 2022 / Published online December 22, 2022 /

bosons, see, e.g., [4] for a profound mathematical treatment of Bose–Einstein condensates and, in turn, of the GPE.

In this work, we restrict our focus to the following weak formulation of the time-independent Schrödinger equation (1.2): Find $E \in \mathbb{R}$ and $\psi \in \mathrm{H}^1_0(\Omega)$ such that

$$\int_\Omega \left(\frac{1}{2} \nabla_{\boldsymbol{x}} \psi \cdot \nabla_{\boldsymbol{x}} \varphi + V(\boldsymbol{x}) \psi \varphi \right) \mathrm{d}\boldsymbol{x} = E(\psi, \varphi)_{\mathrm{L}^2(\Omega)} \qquad \forall \varphi \in \mathrm{H}^1_0(\Omega), \tag{1.3}$$

where $\Omega \subset \mathbb{R}^d$, $d = \{1, 2, 3\}$, is a bounded, connected, and open set with Lipschitz boundary, $V \in \mathrm{L}^\infty(\Omega)$ is a potential function with $V \geq 0$ almost everywhere, and $(\cdot, \cdot)_{\mathrm{L}^2(\Omega)}$ denotes the standard $\mathrm{L}^2(\Omega)$-inner product. We further note that, upon defining the functional

$$\mathsf{E}(\psi) := \int_\Omega \left(\frac{1}{2} |\nabla_{\boldsymbol{x}} \psi|^2 + V(\boldsymbol{x}) |\psi|^2 \right) \mathrm{d}\boldsymbol{x}, \tag{1.4}$$

the weak Schrödinger equation (1.3) is the Euler–Lagrange formulation of the constrained minimisation problem

$$\operatorname*{arg\,min}_{\psi \in S_{\mathbb{H}}} \mathsf{E}(\psi), \tag{1.5}$$

with $S_{\mathbb{H}} := \{\psi \in \mathrm{H}^1_0(\Omega) : \|\psi\|_{\mathrm{L}^2(\Omega)} = 1\}$ signifying the $\mathrm{L}^2(\Omega)$-unit sphere in $\mathrm{H}^1_0(\Omega)$. In particular, the weak Schrödinger equation (1.3) can equivalently be written as

$$\frac{1}{2} \langle \mathsf{E}'(\psi), \varphi \rangle = E(\psi, \varphi)_{\mathrm{L}^2(\Omega)} \qquad \forall \varphi \in \mathrm{H}^1_0(\Omega), \tag{1.6}$$

with E' denoting the Fréchet derivative and $\langle \cdot, \cdot \rangle$ the duality pairing in $\mathrm{H}^{-1}(\Omega) \times \mathrm{H}^1_0(\Omega)$. Moreover, any solution of the local minimisation problem (1.5) is an $\mathrm{L}^2(\Omega)$-normalized eigenfunction of Schrödinger's equation (1.3). We further note that if $\psi \in S_{\mathbb{H}}$ is an eigenfunction of (1.3) with associated eigenvalue E, then

$$E = \mathsf{E}(\psi),$$

i.e., $\mathsf{E}(\psi)$ is the energy of the quantum state ψ.

Given that $V \geq 0$ (almost everywhere in Ω), the stationary Schrödinger equation (1.3) has a unique ($\mathrm{L}^2(\Omega)$-normalized) positive eigenfunction $\psi_{\mathrm{GS}} > 0$, which is called the *ground state*, see, e.g., [27, Lem. 5.4]. Moreover, ψ_{GS} is an eigenfunction to the minimal (and simple) eigenvalue, denoted by E_{GS}, of (1.3), see [11].

Eigenfunctions of Schrödinger's equation (1.3) of higher (corresponding) energy are called *excited states*. We emphasise that every excited state is orthogonal to the ground state, since the eigenvalue problem is linear. Indeed, it holds the following orthogonality property, which will be crucial in the analysis below.

Proposition 1.1. *If ψ_1 and ψ_2 are two eigenfunctions of Schrödinger's equation* (1.3) *to distinct eigenvalues E_1 and E_2, respectively, then ψ_1 and ψ_2 are orthogonal with respect to the* $\mathrm{L}^2(\Omega)$*-inner product, i.e. $(\psi_1, \psi_2)_{\mathrm{L}^2(\Omega)} = 0$.*

Proof. First, we note that

$$\langle \mathsf{E}'(\psi_1), \psi_2 \rangle = \int_\Omega (\nabla_{\boldsymbol{x}} \psi_1 \cdot \nabla_{\boldsymbol{x}} \psi_2 + 2V(\boldsymbol{x}) \psi_1 \psi_2) \, \mathrm{d}\boldsymbol{x} = \langle \mathsf{E}'(\psi_2), \psi_1 \rangle.$$