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Efficient Splitting Methods Based on Modified Potentials: Numerical Integration of Linear Parabolic Problems and Imaginary Time Propagation of the Schrödinger Equation

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Abstract. We present a new family of fourth-order splitting methods with positive coefficients especially tailored for the time integration of linear parabolic problems and, in particular, for the time dependent Schrödinger equation, both in real and imaginary time. They are based on the use of a double commutator and a modified processor, and are more efficient than other widely used schemes found in the literature. Moreover, for certain potentials, they achieve order six. Several examples in one, two and three dimensions clearly illustrate the computational advantages of the new schemes.

AMS subject classifications: 65L05, 65M12, 65J10

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1 Introduction

The eigenvalue problem for the stationary Schrödinger equation constitutes an important part in the understanding of basic atomic and molecular phenomena. It is defined by

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($\hbar = m = 1$)

$$\begin{aligned} &\hat{H}\phi_j(x) = E_j\phi_j(x), \qquad j = 0,1,2,\cdots, \\ &\hat{H} = \hat{T} + \hat{V}(x) = -\frac{1}{2}\Delta + \hat{V}(x), \end{aligned} \tag{1.1}$$

where $\hat{V}$ is the potential energy operator and Δ is the Laplacian, an unbounded differential operator. Since the Hamiltonian $\hat{H}$ is Hermitian, then its eigenvalues E_j are real, and the corresponding eigenfunctions ϕ_j can be chosen to form a real orthonormal basis on their domain. By an appropriate election of the origin of the potential we can guarantee that $\hat{V}(x) \geq 0$ in the region of interest, so that $0 \leq E_0 \leq E_1 \leq \cdots$. Given the time-dependent Schrödinger equation

$$i\frac{\partial}{\partial t}\psi(x,t) = \hat{H}\psi(x,t), \quad \psi_0(x) = \psi(x,0), \tag{1.2}$$

if the initial wave function $\psi_0(x)$ is expanded in the orthonormal basis of eigenfunctions ϕ_j,

$$\psi_0(x) = \sum_{j\geq 0} c_j\phi_j(x), \quad c_j = \langle \phi_j(x) \,|\, \psi(x,0)\rangle,$$

where $\langle \cdot | \cdot \rangle$ is the usual L^2-scalar product, then the solution is given by [22]

$$\psi(x,t) = \mathrm{e}^{-it\hat{H}}\psi(x,0) = \sum_{j\geq 0} \mathrm{e}^{-itE_j} c_j\phi_j(x) \tag{1.3}$$

and, in particular, the norm of the solution is preserved for any value of t.

Very often, the so-called imaginary time propagation (ITP) method is the preferred option for solving the eigenvalue problem (1.1) [3, 5, 19] as well as for carrying out path integral simulations in condensed phase quantum systems [16]. By considering the time transformation $t = -i\tau$, Eq. (1.2) is transformed into

$$\frac{\partial}{\partial \tau}\psi(x,\tau) = -\hat{H}\psi(x,\tau), \quad \psi_0(x) = \psi(x,0). \tag{1.4}$$

In this case the solution reads

$$\psi(x,\tau) = \mathrm{e}^{-\tau\hat{H}}\psi(x,0) = \sum_{j\geq 0} \mathrm{e}^{-\tau E_j} c_j\phi_j(x). \tag{1.5}$$

Notice that, in contrast with (1.3), for sufficiently large τ one gets $\psi(x,\tau) \to \mathrm{e}^{-\tau E_0} c_0\phi_0$, since the other exponentials decay more rapidly. In other words, any given wave function at $\tau = 0$ in which $c_0 \neq 0$ converges towards the ground state solution when $\tau \to \infty$. Once an accurate approximation to ϕ_0 is obtained, the associated eigenvalue E_0 can be easily obtained by computing $E_0 = \langle \phi_0(x) | \hat{H} | \phi_0(x) \rangle$. Other functions ϕ_j can also be approximated, e.g., by propagating different wave functions simultaneously in time [2].