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EXPONENTIAL INTEGRATORS FOR QUANTUM-CLASSICAL MOLECULAR DYNAMICS

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Abstract.

We study time integration methods for equations of mixed quantum-classical molecular dynamics in which Newtonian equations of motion and Schrödinger equations are nonlinearly coupled. Such systems exhibit different time scales in the classical and the quantum evolution, and the solutions are typically highly oscillatory. The numerical methods use the exponential of the quantum Hamiltonian whose product with a state vector is approximated using Lanczos' method. This allows time steps that are much larger than the inverse of the highest frequencies. We describe various integration schemes and analyze their error behaviour, without assuming smoothness of the solution. As preparation and as a problem of independent interest, we study also integration methods for Schrödinger equations with time-dependent Hamiltonian.

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1 Introduction.

The inclusion of quantum behaviour in molecular dynamics simulations is a topic of considerable current interest; see the contributions in the recent volume [4]. Since a full quantum simulation of molecules is out of question, mixed quantum-classical models offer feasible alternatives. A widely used model couples Newtonian equations of motion and Schrödinger equations in the following way:

$$\begin{aligned} My'' &= -\nabla_y(\psi^* H(y)\psi) \ , \\ i\psi' &= H(y)\psi \ . \end{aligned} \tag{1.1}$$

Here, y denotes the positions of the classical particles and ψ represents the wave functions. M is the mass matrix and $H(y)$ is the Hamilton operator or – as will be assumed here – its spatial discretization. The typical situation is that $H(y)$ is a sum of a (discretized) negative Laplacian and a position-dependent bounded multiplication operator. We refer to [3] for an in-depth discussion of this quantum-classical molecular dynamics (QCMD) model.

Systems of this form describe largely different physical phenomena, such as electron-ion interactions and proton transfer in biological molecules. Also the

computational treatment encompasses widely different situations, ranging from models with just a few suitably chosen basis functions to represent the wave functions, to systems with many degrees of freedom arising from a pseudospectral space discretization of the Schrödinger equation. A feature in common is the presence of widely different time scales for the quantum and the classical evolution, which leads to particular challenges for the time integration. The different time scales come from two sources: from the high frequencies of the Laplacian, and possibly also from a small parameter multiplying the time derivative of the wave function in (1.1). This parameter is the square root of the ratio of the masses of light (quantum) and heavy (classical) particles. Its presence creates no numerical problems in proton transfer processes, where a typical mass ratio is 1/16, but it does so in electron-ion interactions, with a mass ratio of 1/2000 or less. In the present paper we will not deal with the additional numerical difficulties resulting from a very small mass ratio.

Various time integration schemes for the QCMD equations (1.1) have been proposed in [2, 9, 17, 18, 19, 25]. Starting from the observation that (1.1) is a Hamiltonian system, most of these papers construct symplectic methods for (1.1). This appears promising in view of the known strong results on long-time integration by symplectic methods, which are obtained using a backward error analysis that interprets the numerical solution as the "almost" exact solution of a perturbed Hamiltonian system [1, 7, 24]. However, all these theoretical results break down when the product of the time step with the highest frequencies in the system is not small, which is the computational situation we are interested in. For example, symplecticness then does not guarantee long-time near-conservation of the total energy. To our knowledge, there is no theoretical or numerical evidence that indicates an advantage of symplectic algorithms over non-symplectic, symmetric methods when such large step sizes are used.

For none of the proposed methods, there exists so far an error analysis on finite time intervals which applies to step sizes larger than the inverse of the highest frequencies, and which takes the highly oscillatory behaviour of the wave functions into account and therefore assumes no bounds on their derivatives. Such an error analysis is of interest not only from a purely mathematical point of view but it also gives important insight into relative strengths and weak points of the methods and shows situations where difficulties are likely to appear. For oscillatory second-order differential equations, long-time-step error analyses have been given, for suitable methods that integrate linear systems exactly, in [6] and [10]. The analysis techniques used in the present paper are related to those developed in [10].

Here, we study symmetric exponential integrators of the type proposed in [9] which use, in every time step, the product of the exponential of the quantum Hamiltonian with a vector. This product can be efficiently computed by Krylov subspace methods. As a preparation for the numerical treatment of (1.1), and as a problem of independent interest [23, 27], we begin by analyzing methods for Schrödinger equations with time-dependent Hamiltonian

$$i\psi' = H(t)\psi \ . \tag{1.2}$$

In Section 2 we study a simple exponential scheme, which has surprisingly complicated convergence properties, with a convergence order ranging between 1 and 2 depending on possible resonances and spatial regularity. The convergence analysis does not assume temporal smoothness of the solution which is typically highly oscillatory. More elaborate schemes for (1.2) are studied in Section 3 where we consider an unconditionally third-order scheme and a method based on the Magnus expansion [12, 16]. In Section 4 we study methods for the full QCMD equations (1.1). We discuss a simple and a more elaborate discretization of the first equation in (1.1) which are combined with methods for (1.2).

Summarizing, this paper deals with the first two of the following problems in the numerical analysis of QCMD and related equations:

(i) to derive long-time-step methods for QCMD;
(ii) to give a finite-time error analysis of these methods;
(iii) to compare the variety of proposed methods on realistic examples;
(iv) to develop QCMD integrators that are robust in the adiabatic limit of the mass ratio tending to zero;
(v) to explain the numerically observed satisfactory long-time behaviour, e.g., energy conservation.

Detailed numerical experiments and method comparisons on realistic examples will be reported elsewhere. First preliminary experiments [22] indicate that the methods studied here are highly competitive, in particular when potential evaluations dominate the computational cost. We also refer to [19] for some thoughtful comments on the expected efficiency of different method classes for different problem scenarios in QCMD simulations.

Concerning (iv), we mention that the more elaborate discretization of the classical equations of motion proposed in Section 4 has the desired robustness property, but the discretization of the quantum equations will have to be modified. Nothing appears to be known about (v) when the product of the time step with the highest frequencies is not very small.

2 A simple exponential integrator for Schrödinger equations with time-dependent Hamiltonian.

In this section we study an integration method for (1.2) which uses the exponential of the current Hamiltonian in every time step.

2.1 Assumptions and notation.

We assume that, for every $t \in [0,T]$, $H(t)$ is a real symmetric $N \times N$ matrix which can be split as

$$H(t) = U + V(t) \ ,$$

where the constant symmetric matrix U may have arbitrarily large norm, and where V and its derivatives are assumed to be bounded for $t \in [0,T]$:

$$\|V^{(j)}(t)\| \le M_j \ , \qquad j = 0,1,2 \tag{2.1}$$

and in Section 3 also for $j = 3$. Throughout the paper, $\|\cdot\|$ is the Euclidean norm (possibly scaled) or its induced matrix norm, the spectral norm.

We assume further that $H(t)$ has the eigendecomposition

$$H(t) = Q(t)\Lambda(t)Q(t)^T\ , \qquad \Lambda(t) = \mathrm{diag}(\lambda_k(t)) \tag{2.2}$$

with

$$\|Q'(t)\| \le M_*\ . \tag{2.3}$$

In the following, let μ_k denote the eigenvalues of U, ordered such that $|\mu_k - \lambda_k(t)| \le M_0$. We write

$$\lambda_k(t) = \mu_k + \nu_k(t).$$

For the initial state $\psi(0) = \psi_0$ we assume

$$\|\psi_0\| = 1\ ,$$

which implies $\|\psi(t)\| = 1$ for all t.

2.2 A simple exponential scheme.

We discretize (1.2) using a time step h. For integer n, let $t_n = nh$ and $t_{n+1/2} = t_n + \frac{1}{2}h$. A simple symmetric scheme that uses the exponential of $H_n = H(t_n)$, recursively produces approximations ψ_n to $\psi(t_n)$ via

$$\begin{aligned} \psi_n &= \exp(-\tfrac{i}{2}hH_n)\,\psi_{n-1/2}\ , \\ \psi_{n+1/2} &= \exp(-\tfrac{i}{2}hH_n)\,\psi_n\ . \end{aligned} \tag{2.4}$$

A variant of this scheme, shifted by a half-step, reads $\psi_{n+1} = \exp(-ihH_{n+1/2})\psi_n$. For the extension to the QCMD equations, the formulas (2.4) are, however, more favorable.

We are interested in obtaining error bounds which do not depend on the size of the eigenvalues of $H(t)$ nor require smoothness of the solution ψ, which in general is highly oscillatory. The convergence properties of this scheme turn out to be unexpectedly complex.

THEOREM 2.1. *(i) Under the assumptions of Subsection 2.1, the error of the method* (2.4) *is bounded by*

$$\|\psi_n - \psi(t_n)\| \le C\,h$$

for $0 \le t_n \le T$. *Here,* C *depends only on* M_1 *and* T.

(ii) In addition to the assumptions of Subsection 2.1, assume that

$$|h\mu_k - h\mu_l - 2m\pi| \ge a > 0 \tag{2.5}$$

for all k, l *and for all integers* $m \ne 0$. *Then, the error of the method* (2.4) *is bounded by*

$$\|\psi_n - \psi(t_n)\| \le \frac{C\,h^2}{a}$$

for $0 \le t_n \le T$. *Here,* C *depends only on* M_0, M_1, M_2, M_*, *and* T.

(iii) In addition to the assumptions of Subsection 2.1, assume that $H(t)$ *is positive semi-definite and there exists* $0 < \alpha \le 1$ *such that*

$$\|H(t)^\alpha \psi(t)\| \le C_\alpha \tag{2.6}$$

$$\|H(t)^\alpha H'(t)\psi(t)\| \le C_\alpha \tag{2.7}$$

for $0 \le t \le T$. *Then, the error of the method* (2.4) *is bounded by*

$$\|\psi_n - \psi(t_n)\| \le C\, h^{1+\alpha}$$

for $0 \le t_n \le T$. *Here,* C *depends only on* C_α, M_0, M_1, M_2, *and* T.

In (i) and (iii), the smoothness of the eigendecomposition is not required.

In (ii), the dependence on a in the bound cannot be omitted. The proof shows that, in general, a second order bound does not hold when $h\mu_k - h\mu_l$ is close to a multiple of 2π.

In (iii), for $\alpha = \frac{1}{2}$, the condition (2.6) is just the condition of finite energy,

$$\psi(t)^* H(t)\psi(t) \le \text{Const.}$$

For higher α, in the typical case that U is a (discretized) multiple of the Laplacian, condition (2.6) imposes higher spatial regularity. Condition (2.7) is then satisfied if $V(t)$ is a (discretized) spatially smooth potential.

The assumption of a positive semi-definite $H(t)$ is not essential. If the eigenvalues of $H(t)$ are bounded from below by $-\kappa$, then the result still holds when $H(t)$ is replaced by $H(t) + \kappa I$ in (2.6) and (2.7).

The proof of Theorem 2.1 is given in Subsection 2.4.

2.3 Implementation.

The scheme (2.4) requires the computation of $\exp(-i\tau A)b$ where $A = H_n$ is a real symmetric matrix, b is a vector, and τ is a real scalar. Direct computation of the matrix exponential by diagonalization becomes prohibitively expensive unless the dimension of A is small, in particular so because A changes in each time step.

Fortunately, there are several possibilites to approximate $\exp(-i\tau A)b$ efficiently also for high-dimensional A. Here we discuss in some detail the computation via Lanczos' method, we mention briefly Chebyshev approximation and then turn to multiple time-stepping using Strang splitting.

Lanczos' method. The symmetric Lanczos process [15, 21] generates recursively an orthonormal basis $V_m = [v_1 \cdots v_m]$ of the mth Krylov subspace $\mathcal{K}_m(A, b) = \text{span}\{b, Ab, \ldots, A^{m-1}b\}$ such that

$$AV_m = V_m T_m + \beta_m [0 \cdots 0\, v_{m+1}].$$

The symmetric tridiagonal $m \times m$ matrix $T_m = V_m^T A V_m$ is the orthogonal projection of A onto $\mathcal{K}_m(A, b)$. This yields the approximation [5, 8, 20, 28]

$$\exp(-i\tau A)b \approx V_m \exp(-i\tau T_m) V_m^T b, \tag{2.8}$$

where $V_m^T b = \|b\| [1\,0\,\cdots 0]^T$. The matrix exponential $\exp(-i\tau T_m)$ can be computed from the eigendecomposition $T_m = Q_m D_m Q_m^T$, with diagonal D_m, via

$$\exp(-i\tau T_m) = Q_m \exp(-i\tau D_m) Q_m^T.$$

In [11] we proposed to stop the Lanczos process if

$$\beta_m \, |[\exp(-i\tau T_m)]_{m,m}| \, \|b\| < \texttt{tol},$$

where $[\cdot]_{m,m}$ denotes the (m,m) entry of a matrix. This stopping criterion can be motivated by a generalization of a residual bound which is the most popular stopping criterion for iterative methods for solving linear systems, see [11] for details. In extensive numerical tests, this criterion was found to work reliably. We thus have the following algorithm.

ALGORITHM 2.1. *Implementation of one time step of the scheme* (2.4)*:*

(i) *run the Lanczos process with* $A = H_n$ *and* $b = \psi_{n-1/2}$*, yielding* V_m*,* T_m*, and* β_m *for* $m = 1, 2, \ldots$*;*

(ii) *stop if* $\beta_m |[\exp(-ihT_m)]_{m,m}| < \texttt{tol}$*;*

(iii) *compute*

$$\begin{aligned} \psi_n &= V_m \exp(-\tfrac{i}{2} h T_m) V_m^T \psi_{n-1/2}, \\ \psi_{n+1/2} &= V_m \exp(-\tfrac{i}{2} h T_m) V_m^T \psi_n. \end{aligned}$$

The convergence behaviour of the approximation (2.8) is analyzed in [8, Theorem 4]. According to that result, there is nearly no error reduction for $m \leq \frac{1}{2}\|\tau A\|$, but very rapid, superlinear error decay for $m \geq \frac{1}{2}\|\tau A\|$ (assuming here that A is positive semi-definite). These bounds are almost sharp for the worst possible case that the eigenvalues of A are densely distributed in $[0, \|A\|]$ and that the vector b has no prefered eigendirections, but else the convergence may be considerably faster. If the number m of Lanczos steps is not allowed to exceed a given bound, say $m \leq 64$, then this bound may entail a mild step size restriction $\|hA\| \lesssim 100$.

The Algorithm 2.1 is clearly norm-preserving. Since V_m depends on $\psi_{n-1/2}$, time reversibility is lost although we have $\psi_n = V_m \exp(\frac{i}{2} h T_m) V_m^T \psi_{n+1/2}$. If maintaining strict time reversibility is considered important, then the tolerance for the Lanczos process should be chosen rather tight. Because of the superlinear convergence behaviour, this usually requires only few more Lanczos steps than for a moderate tolerance.

Chebyshev approximation to the exponential provides a popular alternative to Lanczos' method; see, e.g., [14, 26]. Here, one uses a truncated Chebyshev series expansion of $\exp(ix)$ on the interval $[0, \|\tau A\|]$. The dependence of the error on the truncation order m is exactly as described above for the worst case in Lanczos' method. In our numerical experiments, we generally found Algorithm 2.1 more efficient.

Multiple time stepping in method (2.4) is obtained by applying a time-stepping procedure to $i\psi' = A\psi$, $\psi(0) = b$ to approximate $\exp(-i\tau A)b$. In particular, when $A = U + V$ where U results from a pseudospectral discretization of the negative Laplacian (and hence is diagonalized by fast Fourier transforms) and V is a diagonal matrix carrying the grid values of a smooth potential, then an attractive scheme is the *Strang splitting*

$$\exp(-i\tau A)b \approx S_{\tau/m}^m b \ ,$$

where, for $\theta = \tau/m$,

$$S_\theta = \exp(-\tfrac{i}{2}\theta V)\exp(-i\theta U)\exp(-\tfrac{i}{2}\theta V) \ .$$

Multiple time stepping with Strang splitting has been advocated in the QCMD context in [18]. Its accuracy, or the required step number m, depends strongly on the spatial regularity of the data b. It is very efficient for smooth data, but becomes inaccurate for rough data. It is shown in [13] that, for arbitrary $\alpha \in [0,2]$,

$$\|\exp(-i\tau A)b - S_{\tau/m}^m b\| \le C\tau\left(\frac{\tau}{m}\right)^\alpha \|A^\alpha b\| \ ,$$

when A is positive definite (as can be assumed without loss of generality).

2.4 Proof of Theorem 2.1.

The proof makes repeated use of the variation-of-constants formula applied to the differential equation for ψ rewritten, for fixed t and τ and variable s between 0 and τ, as

$$i\psi'(t-\tau+s) = H(t)\psi(t-\tau+s) + \Big(H(t-\tau+s) - H(t)\Big)\psi(t-\tau+s) \ .$$

This yields

$$\begin{aligned}\psi(t) = {} & \exp(-i\tau H(t))\,\psi(t-\tau) \ - \\ & i\int_0^\tau \exp(-i(\tau-s)\,H(t))\Big(H(t-\tau+s) - H(t)\Big)\psi(t-\tau+s)\,ds \ .\end{aligned} \tag{2.9}$$

It is convenient to prove the error bounds for the half-step errors

$$\varepsilon_{n+1/2} = \psi_{n+1/2} - \psi(t_{n+1/2}) \ .$$

The result for $\psi_n - \psi(t_n)$ then follows immediately from (2.9). By formula (2.9) with $t = t_n$ and $\tau = \pm\frac{1}{2}h$, we obtain

$$\exp(\tfrac{i}{2}hH_n)\,\varepsilon_{n+1/2} = \exp(-\tfrac{i}{2}hH_n)\,\varepsilon_{n-1/2} + \vartheta_n \ , \tag{2.10}$$

where

$$\begin{aligned}\vartheta_n \ &= \ -i\int_{-h/2}^{h/2} \exp(isH_n)\Big(H(t_n+s) - H(t_n)\Big)\psi(t_n+s)\,ds \\ &= \ -\,i\int_{-h/2}^{h/2} \exp(isH_n)\,sH'(t_n)\,\exp(-isH_n)\,ds\cdot\psi(t_n) + O(h^3) \ .\end{aligned}$$

We now prove the stated error bounds in the sequence (i), (iii), (ii).

(i) Since $\|\vartheta_n\| \le \frac{1}{2} M_1 h^2$, (2.10) yields the stated error bound with $C = \frac{1}{2} M_1 T$.

(iii) In the defect ϑ_n, we write $\psi(t_n) = H_n^{-\alpha} H_n^{\alpha} \psi(t_n)$. Since

$$\|(\exp(-isH_n) - I) H_n^{-\alpha}\| \le \max_{x>0} |(e^{-isx} - 1)/x^{\alpha}| \le C\,|s|^{\alpha} \ ,$$

we have by condition (2.6)

$$\int_{-h/2}^{h/2} \exp(isH_n)\, sH'(t_n) \big(\exp(-isH_n) - I\big) H_n^{-\alpha}\, ds \cdot H_n^{\alpha} \psi(t_n) = O(h^{2+\alpha}) \ ,$$

and therefore

$$\vartheta_n = -i \int_{-h/2}^{h/2} \exp(isH_n) s\, ds \cdot H'(t_n) \psi(t_n) + O(h^{2+\alpha}) \ .$$

Using condition (2.7) and once more the same argument to get rid of the remaining factor $\exp(isH_n)$, we obtain

$$\vartheta_n = -i \int_{-h/2}^{h/2} s\, ds \cdot H'(t_n) \psi(t_n) + O(h^{2+\alpha}) = O(h^{2+\alpha}) \ ,$$

because the integral vanishes. The bound (iii) then follows from (2.10).

(ii) (a) With the orthogonal matrix $Q_n = Q(t_n)$ that diagonalizes H_n, we transform to

$$\widetilde{\varepsilon}_{n+1/2} = Q_n^T \varepsilon_{n+1/2} \ , \qquad \widetilde{\vartheta}_n = Q_n^T \exp(-\tfrac{i}{2} h H_n)\, \vartheta_n \ .$$

We then obtain

$$\widetilde{\varepsilon}_{n+1/2} = \exp(-ih\Lambda(t_n))\, \widetilde{\varepsilon}_{n-1/2} + hS_n \widetilde{\varepsilon}_{n-1/2} + \widetilde{\vartheta}_n \ ,$$

where the matrix S_n is bounded by $\|S_n\| \le \|Q_n - Q_{n-1}\|/h \le M_*$. With $D = \operatorname{diag}(\mu_k)$, we then have

$$\widetilde{\varepsilon}_{n+1/2} = \exp(-ihD)\, \widetilde{\varepsilon}_{n-1/2} + hR_n \widetilde{\varepsilon}_{n-1/2} + \widetilde{\vartheta}_n \ ,$$

where $\|R_n\| \le M_0 + M_*$, and consequently

$$\widetilde{\varepsilon}_{n+1/2} = h \sum_{j=0}^{n-1} \exp(-i(n-j)hD)\, R_{j+1}\, \widetilde{\varepsilon}_{j+1/2} + \sum_{j=1}^{n} \exp(-i(n-j)hD)\, \widetilde{\vartheta}_j \ .$$

Via a discrete Gronwall inequality, the stated error bound follows if we show that

$$\Big\| \sum_{j=1}^{n} \exp(-i(n-j)hD)\, \widetilde{\vartheta}_j \Big\| \le \frac{C\, h^2}{a} \ .$$

(b) This bound will be proved in the sequel. We have

$$\widetilde{\vartheta}_n = h^2 B(t_n)\, Q_n^T \psi(t_n) + O(h^3) \ ,$$

where, with $G(t) = Q(t)^T H'(t) Q(t)$, we write

$$B(t) = -i \exp(-\tfrac{i}{2} hD) \int_{-1/2}^{1/2} \exp(i\theta hD)\, \theta G(t)\ \exp(-i\theta hD)\, d\theta \ .$$

The (k,l) entry of this matrix is

$$b_{kl}(t) = -ie^{-\frac{i}{2}h\mu_k} \delta(h\mu_k - h\mu_l)\, g_{kl}(t) \ ,$$

where

$$\delta(x) = \int_{-1/2}^{1/2} \theta\, e^{i\theta x} d\theta \ .$$

Using the variation-of-constants formula (2.9) with $\tau = t$, we write

$$\psi(t) = \exp(-itH(t))\, \rho(t) \ ,$$

where

$$\rho(t) = \psi_0 - i \int_0^t \exp(isH(t)) \Big(H(s) - H(t) \Big) \psi(s)\, ds \tag{2.11}$$

has a derivative bounded by $(2M_0 T + 1) M_1 T$. We then have

$$Q(t)^T \psi(t) = \exp(-itD) \eta(t) \ ,$$

where

$$\eta(t) = \exp\big((-it(\Lambda(t) - D) \big)\, Q(t)^T \rho(t) \tag{2.12}$$

satisfies

$$\|\eta(t)\| \le 1 \ , \quad \|\eta'(t)\| \le C \ ,$$

with a constant C which depends only on M_0, M_1, M_*, and T. Putting all this together, we obtain

$$\widetilde{\vartheta}_n = -h^2 i \exp(-\tfrac{i}{2} hD)\, \gamma(t_n) + O(h^3)$$

where the kth component of $\gamma(t)$ is given as

$$\gamma_k(t) = \sum_l \delta(h\mu_k - h\mu_l)\, g_{kl}(t)\, e^{-it\mu_l} \eta_l(t) \ ,$$

or equivalently, setting $\Delta = (\delta(h\mu_k - h\mu_l))_{k,l=1}^N$ and denoting by $\bullet$ the entrywise product of matrices,

$$\gamma(t) = (\Delta \bullet G(t))\ \exp(-itD)\, \eta(t) \ .$$

(c) It remains to be shown that

$$\Big\| \sum_{j=1}^{n} \exp(-i(n-j)hD)\, \gamma(t_j) \Big\| \le \frac{C}{a} \ .$$

By partial summation we have, with $G_j = G(t_j)$,

$$\sum_{j=1}^{n} \exp(ijhD)\, \gamma(t_j) = (E_n \bullet G_{n+1})\, \eta(t_{n+1})$$
$$- \sum_{j=1}^{n} \big(E_j \bullet G_j\big) \big(\eta(t_{j+1}) - \eta(t_j)\big) - \sum_{j=1}^{n} \big(E_j \bullet (G_{j+1} - G_j)\big)\, \eta(t_{j+1}) \ ,$$

where $E_n = (\epsilon_n(h\mu_k - h\mu_l))_{k,l=1}^N$ is defined by the function

$$\epsilon_n(x) = \sum_{j=1}^{n} e^{ijx}\, \delta(x) = (1 - e^{inx})\, \varphi(x)$$

with $\varphi(x) = \delta(x)\, e^{ix}/(1 - e^{ix})$. For an arbitrary matrix G, we can write

$$E_n \bullet G = F \bullet G - \exp(inhD)\, (F \bullet G)\, \exp(-inhD)$$

with $F = (\varphi(h\mu_k - h\mu_l))_{k,l=1}^N$. Since $\delta(2m\pi) \neq 0$ for integer $m \neq 0$, the function φ becomes unbounded at nonzero integer multiples of 2π. Because of condition (2.5), we may, however, replace φ in the definition of F by the function f defined as the continuous function on $\mathbf{R}$ which equals φ outside a-neighbourhoods of nonzero integer multiples of 2π, and which is linear within such a-neighbourhoods. Lemma 2.2 and the bound (2.13) below then yield

$$\|F \bullet G\| \le \frac{c}{a}\, \|G\| \ ,$$

and hence the desired bound (ii) follows from the above identities. □

In the proof we used the following lemma.

LEMMA 2.2. *Let $f : \mathbf{R} \to \mathbf{C}$ have a Fourier transform $\widehat{f} \in L^1(\mathbf{R})$. Let $x_1, \ldots, x_N$ be arbitrary real numbers, and let $F = (f(x_k - x_l))_{k,l=1}^N$. In the matrix norm induced by the Euclidean norm, the entrywise product of F with an arbitrary $N \times N$ matrix G is then bounded by*

$$\|F \bullet G\| \le \|\widehat{f}\|_{L^1} \cdot \|G\| \ .$$

PROOF. We have

$$f(x) = \int_{\mathbf{R}} e^{i\xi x}\, \widehat{f}(\xi)\, d\xi \ ,$$

and consequently, with $D = \operatorname{diag}(x_k)$,

$$F \bullet G = \int_{\mathbf{R}} \exp(i\xi D)\, G\, \exp(-i\xi D)\, \widehat{f}(\xi)\, d\xi \ ,$$

which yields the stated bound. □

We note that the L^1 norm of $\widehat{f}$ can be bounded in terms of the L^2 norms of f and its derivative by

$$\|\widehat{f}\|_{L^1}^2 \le \pi \left(a^{-1}\|f\|_{L^2}^2 + a\,\|f'\|_{L^2}^2\right) \ , \tag{2.13}$$

for arbitrary $a > 0$. This follows readily by applying the Cauchy-Schwarz inequality to the integral over $(1+a^2\xi^2)^{-1/2}\cdot(1+a^2\xi^2)^{1/2}|\widehat{f}(\xi)|$ and using Parseval's formula.

3 More elaborate exponential integrators for Schrödinger equations with time-dependent Hamiltonian.

In this section we describe integration methods which give higher accuracy, at the price of more costly numerical linear algebra.

3.1 A third-order scheme.

A method of order 3 can be constructed by starting from the variation-of-constants formula (2.9). For small τ, that formula gives

$$\psi(t) = \Bigg(I - i\int_0^\tau \exp(-i(\tau-s)H(t))\Big(H(t-\tau+s) - H(t)\Big)\cdot \\ \exp(+i(\tau-s)H(t))\,ds\Bigg)\exp(-i\tau H(t))\psi(t-\tau) + O(\tau^4) \ .$$

We use this with $t = t_n$, $\tau = \pm\frac{1}{2}h$. We let $H_n = H(t_n)$ and set $H_n' = H'(t_n)$ and $H_n'' = H''(t_n)$, or the corresponding difference quotients $H_n' = (H_{n+1} - H_{n-1})/(2h)$ and $H_n'' = (H_{n+1} - 2H_n + H_{n-1})/h^2$. We define

$$J_n^\pm = \int_0^{1/2} \exp(-i\theta h H_n)\,(\theta H_n' \pm \tfrac{1}{2}\theta^2 h H_n'')\,\exp(i\theta h H_n)\,d\theta \ . \tag{3.1}$$

We note that $J_n^\pm$ is a Hermitian matrix, and

$$\psi(t_n) = (I + ih^2 J_n^-)\,\exp(-\tfrac{i}{2}hH_n)\,\psi(t_{n-1/2}) + O(h^4) \ , \\ \psi(t_n) = (I + ih^2 \overline{J}_n^+)\,\exp(\tfrac{i}{2}hH_n)\,\psi(t_{n+1/2}) + O(h^4) \ .$$

Hence, the following symmetric and norm-preserving scheme has a local error of size $O(h^4)$:

$$\psi_n = \exp(ih^2 J_n^-)\,\exp(-\tfrac{i}{2}hH_n)\,\psi_{n-1/2} \ , \\ \psi_{n+1/2} = \exp(-\tfrac{i}{2}hH_n)\,\exp(-ih^2\overline{J}_n^+)\,\psi_n \ . \tag{3.2}$$

This yields immediately the first of the following error bounds.

THEOREM 3.1. *(i) Under the assumptions of Subsection 2.1, the error of the method* (3.2) *is bounded by*

$$\|\psi_n - \psi(t_n)\| \le C\,h^3$$

for $0 \le t_n \le T$. *The constant* C *depends only on* M_1, M_2, M_3, *and* T.

(ii) Consider the method (3.2) *where* H_n *is replaced by* U *in the definition* (3.1) *of* $J_n^{\pm}$. *In addition to the assumptions of Subsection 2.1, assume that conditions* (2.6), (2.7), *and further* $\|H(t)^\alpha H''(t)\psi(t)\| \le C_\alpha$ *hold for some* $0 \le \alpha \le 1$. *Then, the error is bounded by*

$$\|\psi_n - \psi(t_n)\| \le C\,h^{2+\alpha}$$

for $0 \le t_n \le T$. *The constant* C *depends only on* C_α, M_1, M_2, M_3, *and* T.

The proof of (ii) is obtained with the arguments of the proof of Theorem 2.1 (iii).

3.2 Implementation.

When the dimension is sufficiently small to compute the eigendecomposition of H_n, the scheme can be implemented as follows. Diagonalize $H_n = Q_n \Lambda_n Q_n^T$ and let $G_n' = Q_n^T H_n' Q_n$ and $G_n'' = Q_n^T H_n'' Q_n$. Then,

$$J_n^{\pm} = Q_n \int_0^{1/2} \exp(-i\theta h\Lambda_n)(\theta G_n' \pm \tfrac{1}{2}\theta^2 h G_n'') \exp(i\theta h\Lambda_n)\, d\theta\; Q_n^T = Q_n Z_n^{\pm} Q_n^T$$

with

$$Z_n^{\pm} = A_n \bullet G_n' \pm h B_n \bullet G_n'' \,,$$

where $\bullet$ denotes the entrywise product of matrices, and

$$\begin{aligned} [A_n]_{k,l} &= \int_0^{1/2} \exp(-i\theta h(\lambda_k(t_n) - \lambda_l(t_n)))\,\theta\, d\theta \,, \\ [B_n]_{k,l} &= \tfrac{1}{2}\int_0^{1/2} \exp(-i\theta h(\lambda_k(t_n) - \lambda_l(t_n)))\,\theta^2\, d\theta \,. \end{aligned}$$

The integrals are computed explicitly. Then, (3.2) becomes

$$\begin{aligned} \psi_n &= Q_n \exp(ih^2 Z_n^-)\, \exp(-\tfrac{i}{2}h\Lambda_n)\, Q_n^T \psi_{n-1/2} \,, \\ \psi_{n+1/2} &= Q_n \exp(-\tfrac{i}{2}h\Lambda_n)\, \exp(-ih^2 \overline{Z}_n^+)\, Q_n^T \psi_n \,. \end{aligned} \tag{3.3}$$

For large dimensions, we cannot use Krylov subspaces to approximate $J_n^{\pm}$. The difficulty is that the integral (3.1) defining $J_n^{\pm}$ contains not only the matrix H_n but also H_n' and H_n''. If these matrices do not commute, then it does not appear possible to approximate $J_n^{\pm}$ accurately in a low-dimensional Krylov subspace.

However, the scheme (3.2) can be implemented using Chebyshev approximations to the exponential. We consider the case that U is a spectrally discretized

Laplacian, and we take U instead of H_n in the definition of $J_n^{\pm}$ (see Theorem 3.1 (ii)). Here we have $U = F^{-1}DF$, where F is the N-dimensional Fourier transform matrix and $D = \mathrm{diag}(\mu_1, \ldots, \mu_N)$. For $0 \le \theta \le \frac{1}{2}$, we approximate

$$\exp(i\theta hU) \approx \sum_{k=0}^{m-1} c_k(\theta)\, p_k(hU),$$

where p_k are shifted and scaled Chebyshev polynomials. This will require $m > \frac{1}{4}\|hU\|$. With $P_k = \mathrm{diag}(p_k(h\mu_j))$, we have $p_k(hU) = F^{-1}P_kF$. Inserting this approximation in (3.1) yields

$$J_n^{\pm} \approx F^{-1}\Big(\sum_k P_k F\Big(H_n' F^{-1}\sum_l a_{kl}P_l \pm hH_n'' F^{-1}\sum_l b_{kl}P_l\Big)\Big)F \ , \tag{3.4}$$

where, for $k, l = 0, \ldots, m-1$,

$$a_{kl} = \int_0^{1/2} \overline{c_k(\theta)}\, c_l(\theta)\, \theta\, d\theta \ , \qquad b_{kl} = \tfrac{1}{2}\int_0^{1/2} \overline{c_k(\theta)}\, c_l(\theta)\, \theta^2\, d\theta \ .$$

This permits to compute matrix-vector products $J_n^-\psi$ or $\overline{J}_n^+\psi$ in a number of $(3m+2)N\log N + 2m^2N + O(mN)$ operations, assuming that $H'\psi$ and $H''\psi$ are computed in $O(N)$ operations. Since $h^2J_n^{\pm}$ is of small norm, $\exp(ih^2J_n^-)\psi$ and $\exp(-ih^2\overline{J}_n^+)\psi$ can be approximated using just a few matrix-vector multiplications with J_n^- and $\overline{J}_n^+$, respectively.

We have included the scheme (3.2) mainly to show what a method looks like which achieves higher order with error bounds that are entirely independent of the norm of U and of the smoothness of the solution. We are not sure about its practical usefulness for high-dimensional systems in the implementation (3.4).

3.3 A scheme based on the Magnus expansion.

If we give up the requirement that the error bounds should be completely independent of the norm of U, then it appears attractive to use a truncated Magnus series [12, 16, 27]. Here, the solution operator of a non-autonomous linear system of differential equations is expressed as the exponential of a power series in the time step, whose coefficients consist of repeated integrals of commutators of the system matrices. Let again $H_n = H(t_n)$, $H_n' = H'(t_n)$ or $H_n' = (H_{n+1} - H_{n-1})/(2h)$, and $H_n'' = H''(t_n)$ or $H_n'' = (H_{n+1} - 2H_n + H_{n-1})/h^2$. Using the Taylor series expansion of $H(t_n + \tau)$ at t_n, truncating the Magnus series after the first commutator and dropping terms of formal order 3, we obtain the approximation

$$\psi(t_n + \tau) \approx \exp\big(-i\tau S_n(\tau)\big)\psi(t_n)$$

with the Hermitian matrix

$$S_n(\tau) = H_n + \tfrac{1}{2}\tau H_n' + \tfrac{1}{6}\tau^2 H_n'' + \tfrac{i}{12}\tau^2(H_nH_n' - H_n'H_n) \ .$$

This suggests the following symmetric and norm-preserving scheme, where we set $H_n^{\pm} = S_n(\pm\frac{1}{2}h)$:

$$\begin{aligned} \psi_n &= \exp\bigl(-\tfrac{i}{2}hH_n^-\bigr)\psi_{n-1/2} \ , \\ \psi_{n+1/2} &= \exp\bigl(-\tfrac{i}{2}hH_n^+\bigr)\psi_n \ . \end{aligned} \tag{3.5}$$

This scheme can be implemented similarly to the simple scheme (2.4). We now need to apply the Lanczos process twice in each time step and moreover, each matrix-vector multiplication with $H_n^{\pm}$ requires two multiplications with H_n, two with H_n', and one with H_n''.

To understand the approximation properties of this method, we consider the case of particular interest where $H(t) = U + V(t)$ is obtained from a pseudospectral space discretization of the Schrödinger equation

$$i\frac{\partial \Psi}{\partial t} = -\tfrac{1}{2}\Delta\Psi + a(x,t)\Psi \ , \tag{3.6}$$

posed on $[0,1]^d$ with periodic boundary conditions. Here $a(x,t)$ is a continuous space-periodic scalar function of which we assume that, for every t, it is real-analytic in x and uniformly bounded in a fixed complex neighbourhood of $[0,1]^d$, of radius larger than $\rho > 0$. In this situation, we take U as the spectrally discretized negative Laplacian, and $V(t)$ as the diagonal matrix containing the values of $a(x,t)$ on the equidistant space grid.

THEOREM 3.2. *In the above situation, if $h^2\|U\| \le c$, where c is a sufficiently small constant, the error of the method* (3.5) *is bounded by*

$$\|\psi_n - \psi(t_n)\| \le C\, h^3\, \|U\|$$

for $0 \le t_n \le T$. Here, C is independent of the smoothness of the solution.

PROOF. The proof rests on the observation that the commutator of the Laplacian with a multiplication operator is a *first-order* differential operator. In the discretization, we obtain analogously for the commutators of $A(\tau) = H(t_n + \tau)$, by tedious calculations with trigonometric series which we omit,

$$\|\,[A(\tau), A(\sigma)]\,\| \le Ch\|U\|^{1/2} \ , \qquad |\tau - \sigma| \le h \ ,$$

and more generally, for $|\tau_j| \le h$,

$$\|\,[A(\tau_k), [A(\tau_{k-1}), [\ldots, [A(\tau_1), A(\tau_0)]\ldots]]]\,\| \le k!\, C\rho^{-k}\, \|U\|^{k/2} h \ .$$

If $h\|U\|^{1/2}$ is sufficiently small, this yields that the Magnus series is convergent for $|\tau| \le h$, see [12, Section 2], and the error resulting from the truncation of this series becomes

$$\exp\bigl(-i\tau S_n(\tau)\bigr)\psi(t_n) = \psi(t_n + \tau) + O(\tau^4\|U\|) \ .$$

Therefore, the local error of the scheme (3.5) is $O(h^4\|U\|)$, and the result follows. □

REMARK 3.1. For the pth order Magnus series methods of [12], the same proof gives the error bound

$$\|\psi_n - \psi(t_n)\| \leq C\, h^p\, \|U\|^{(p-1)/2} \ .$$

3.4 Numerical experiments.

To illustrate the behaviour of the different methods, we consider the simple example

$$i\psi' = \left(\begin{bmatrix} 0 & 0 \\ 0 & \mu \end{bmatrix} + \sin(t) \begin{bmatrix} 2 & 1 \\ 1 & 1 \end{bmatrix} \right) \psi \ , \qquad \psi(0) = \frac{1}{\sqrt{1+\mu^{-1}}} \begin{bmatrix} 1 \\ \mu^{-1/2} \end{bmatrix} \ .$$

In Figure 3.1 we plot errors at $t = 1$ versus step sizes for $\mu = 1, 10^2, 10^4, 10^6$ for the simple method (2.4), the elaborate scheme (3.2) implemented via (3.3), and the Magnus-type scheme (3.5). While the error curves of the simple and the elaborate scheme are nearly independent of μ, the errors of the Magnus-type scheme deteriorate with increasing μ.

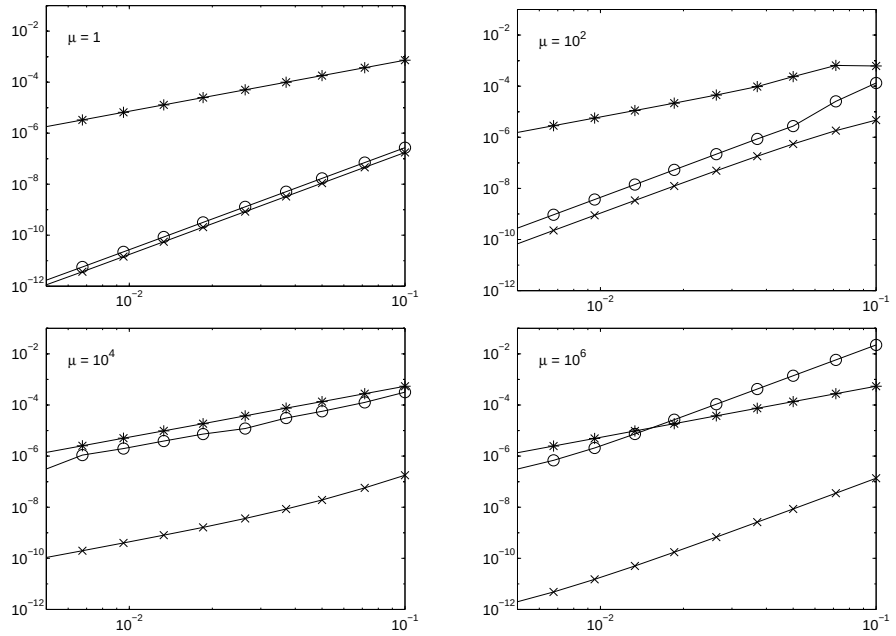

Figure 3.1: Error versus step sizes for the small example: simple scheme $*$, third-order scheme $\times$, Magnus-type scheme $\circ$.

As a second example we consider a one-dimensional Schrödinger equation (3.6) with the data taken from [23]:

$$a(x,t) = \tfrac{1}{2}x^2 + \sin^2(t)x \ .$$

This models an atom/molecule interacting with a high intensity CW laser. Semi-discretization in space is done by a pseudospectral method with $N = 256$ Fourier modes on the space interval $x \in [-\ell, \ell]$ for $\ell = 10$ with periodic boundary conditions. This leads to the non-autonomous linear system of differential equations for $\psi = (\psi_1, \ldots, \psi_N)^T$

$$i\psi' = \left(-\tfrac{1}{2}F^{-1}D^2F + \tfrac{1}{2}X^2 + \sin^2(t)X\right)\psi,$$

Here, $\psi_j(t)$ is an approximation to $\Psi(x_j,t)$ at $x_j = -\ell + j\frac{2\ell}{N}$, $X = \mathrm{diag}(x_j)$, F is the discrete Fourier-transform operator, and

$$D = i\tfrac{\pi}{\ell}\,\mathrm{diag}(0, 1, \ldots, \tfrac{N}{2}-1, -\tfrac{N}{2}, -\tfrac{N}{2}+1, \ldots, -1) \ .$$

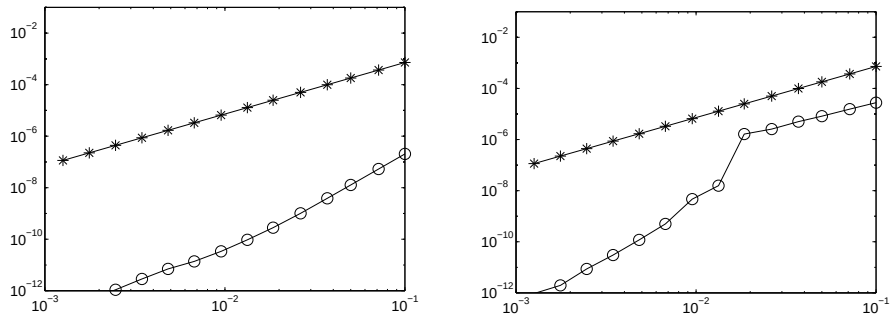

Figure 3.2: Error versus step sizes for the laser example: simple scheme $*$, Magnus-type scheme $\circ$. Smooth and nonsmooth initial data.

In Figure 3.2 we give precision–step size diagrams at $t = 1$ for two different initial values. For the first picture we have chosen $\Psi(x,0) = e^{-x^2/2}$, which corresponds to the eigenstate of the unforced harmonic oscillator to the lowest energy level. The second picture corresponds to nonsmooth initial data of finite energy chosen as $\psi_0 = F^{-1}(I - iD)^{-1}v/\rho$, where v is a vector of normally distributed random numbers, and ρ is chosen such that $\|\psi_0\| = 1$. We implemented the simple scheme (2.4) and the Magnus-type scheme (3.5), using Algorithm 2.1 in both cases. Note that both methods use the same number of potential evaluations for the same step size. This is not the dominant computational cost in the present example, but it is in more complicated problems. We did not implement the elaborate scheme (3.2) via the Chebyshev approximation (3.4), because it is considerably more expensive than the Magnus scheme and cannot be expected to show a much better error behaviour in this example.

4 Integration methods for the QCMD equations.

In this section we extend the integration schemes of Sections 2 and 3 to the coupled equations (1.1) of the QCMD model.

4.1 Assumptions and notation.

We assume that (2.2) and (2.3) hold for $H(t) = H(y(t))$, and that

$$\|\nabla H(y)\| \le L_1, \qquad \|\nabla^2 H(y)\| \le L_2, \qquad \text{for all} \quad y. \tag{4.1}$$

We assume that M is symmetric positive definite, with $\|M^{-1}\| \le 1$ for simplicity. We introduce the tensor (pile of matrices)

$$K(y) := \nabla H(y)$$

and define

$$f(t) = -\nabla_y \Big(\psi(t)^*\, H(y(t))\, \psi(t)\Big) = -\psi(t)^*\, K(y(t))\, \psi(t),$$

so that $y''(t) = M^{-1} f(t)$.

4.2 A simple scheme.

Arguably the simplest method for (1.1) consists of taking

$$M(y_{n+1} - 2y_n + y_{n-1}) = -h^2 \psi_n^* K(y_n)\psi_n \tag{4.2}$$

and propagating ψ_n by (2.4) with $H_n = H(y_n)$. An appropriate starting step would then be

$$y_1 = y_0 + hy_0' - \tfrac{1}{2}h^2 M^{-1}\psi_0^* K(y_0)\psi_0 \ . \tag{4.3}$$

Unless the solution of (1.1) has high regularity, the convergence properties of this scheme are modest.

THEOREM 4.1. *Let the assumptions of Section 4.1 hold, and assume in addition that $H(t) = H(y(t))$ is positive semidefinite for all t and there exists $0 < \alpha \le 2$ such that*

$$\|H(t)^\alpha \psi(t)\| \le C_\alpha \ , \qquad 0 \le t \le T \ . \tag{4.4}$$

Then, the error of the method (4.2), (4.3), (2.4) *is bounded by*

$$\begin{aligned} \|y_n - y(t_n)\| &\le C\, h^\alpha, \\ \|\psi_n - \psi(t_n)\| &\le C\, h^\alpha, \end{aligned}$$

for $0 \le t_n \le T$. The constant C depends only on C_α, $\|y'(0)\|$, L_1, L_2, and T.

Concerning condition (4.4), we refer to the remarks after Theorem 2.1.

The proof, which is deferred to the end of this section, gives strong indication that the stated order of convergence cannot be improved without assuming more regularity of the solution.

4.3 A more elaborate scheme.

To derive a more accurate method, we note that the exact solution of (1.1) satisfies

$$\begin{aligned} y(t+h) - 2y(t) + y(t-h) &= \int_0^h (h-\tau)\,(y''(t+\tau) + y''(t-\tau))\;d\tau \\ &= M^{-1} \int_0^h (h-\tau)\,(f(t+\tau) + f(t-\tau))\;d\tau\;. \end{aligned}$$

This motivates the following symmetric integration scheme:

$$\begin{aligned} y_{n+1} - 2y_n + y_{n-1} &= M^{-1} \int_0^h (h-\tau)\,(f_n(\tau) + f_n(-\tau))\;d\tau \\ f_n(\tau) &= -\phi_n(\tau)^*\, K_n\, \phi_n(\tau) \\ \phi_n(\tau) &= \exp\left(-i\tau H_n\right) \psi_n\;, \end{aligned} \tag{4.5}$$

where $H_n = H(y_n)$, $K_n = K(y_n)$, and ψ_n is defined via (2.4) or (3.2) or (3.5). A suitable starting value is given by

$$y_1 = y_0 + h y_0' + M^{-1} \int_0^h (h-\tau) f_0(\tau)\,d\tau\;. \tag{4.6}$$

THEOREM 4.2. *Under the assumptions of Section 4.1, the method* (4.5), (4.6), *and* (3.2) *satisfies*

$$\begin{aligned} \|y_n - y(t_n)\| &\le C\,h^2, \\ \|\psi_n - \psi(t_n)\| &\le C\,h^2, \end{aligned}$$

for $0 \le t_n \le T$. *The constant* C *depends only on* $\|y'(0)\|$, L_1, L_2, M_*, *and* T.

The proof is given in Subsection 4.5.

REMARK 4.1. *If, instead of* (3.2), *the simpler method* (2.4) *is taken for the quantum propagation, then the error bound is* $O(h)$, $O(h^2/a)$, *or* $O(h^{1+\alpha})$ *in the situations (i), (ii), (iii) of Theorem* 2.1, *respectively.*

This follows without new difficulty by combining the proofs of Theorems 2.1 and 4.2.

In the combination of (4.5) with the methods (3.2) and (3.5), the symmetric finite difference approximations of the time derivatives of H using the values H_{n+1}, H_n, H_{n-1} give a symmetric method that is implicit in y_{n+1}. A way to avoid this implicitness and nevertheless to preserve the symmetry, is to use the first formula of (4.5) in addition with $\frac{1}{2}h$ instead of h to generate half-step approximations $y_{n+1/2}$. With the help of these intermediate values, we can obtain difference approximations to H_n' and H_n'' that use only known y-values. We explain this in more detail for the Magnus series method (3.5): Given y_n, $y_{n-1/2}$, y_{n-1}, and $\psi_{n-1/2}$, we first compute ψ_n by the first formula of (3.5), where we use, for $\tau = -\frac{1}{2}h$,

$$H_n^- = H_n + \tfrac{1}{2}\tau (H_n')^- + \tfrac{1}{6}\tau^2 (H_n'')^- + \tfrac{i}{12}\tau^2 \Big(H_n (H_n')^- - (H_n')^- H_n \Big)$$

with

$$\begin{aligned}(H_n')^- &= -\big(\tfrac{3}{2}H_n - 2H_{n-1/2} + \tfrac{1}{2}H_{n-1}\big)/\tau \\ (H_n'')^- &= \big(H_n - 2H_{n-1/2} + H_{n-1}\big)/\tau^2 \ .\end{aligned}$$

We then compute y_{n+1} by (4.5) and $y_{n+1/2}$ by the same formula with $\frac{1}{2}h$ instead of h and $y_{n-1/2}$ instead of y_{n-1}. Finally we compute $\psi_{n+1/2}$ by the second formula of (3.5), where H_n^+ is defined like H_n^-, but with $\tau = \frac{1}{2}h$ and $n - \frac{1}{2}$, $n-1$ replaced by $n + \frac{1}{2}$, $n+1$, respectively. This gives a symmetric method which requires two evaluations of H and one evaluation of K per time step. The error is bounded by $O(h^2 + h^3\|U\|)$ in the combined situation of Theorems 3.2 and 4.2.

4.4 Implementation using Lanczos' method.

The implementation of the simple scheme (4.2) combined with (2.4) is straightforward, using Algorithm 2.1. We just remark that it is favorable to use the one-step velocity formulation of the scheme:

$$v_{n+1/2} = v_n + \tfrac{1}{2}ha_n \ , \quad y_{n+1} = y_n + hv_{n+1/2} \ , \quad v_{n+1} = v_{n+1/2} + \tfrac{1}{2}ha_{n+1}$$

with $a_n = -M^{-1}\psi_n^* K(y_n)\psi_n$.

We now discuss the combination of the schemes (4.5) and (2.4). Using the notation of Section 2.3, we approximate the function $\phi_n(\tau)$ in the Krylov subspace created for approximating ψ_n and $\psi_{n+1/2}$, hence

$$\phi_n(\tau) \approx V_m Q_m \exp(-i\tau D_m) Q_m^T V_m^T \psi_n$$

with the diagonal matrix $D_m = \operatorname{diag}(\omega_1, \ldots, \omega_m)$. We insert this approximation in (4.5). With the projected tensor

$$G_m = Q_m^T V_m^T K(y_n) V_m Q_m \ , \tag{4.7}$$

whose computation requires $O(m^2 N)$ operations in the typical case that the y–dependent part of $H(y)$ is a diagonal $N \times N$ matrix, we obtain

$$f_n(\tau) \approx -\psi_n^* V_m Q_m \exp(i\tau D_m) G_m \exp(-i\tau D_m) Q_m^T V_m^T \psi_n \ .$$

Defining

$$[F_m]_{k,l} = 2\,\mathrm{Re} \int_0^1 (1-\theta)\exp\big(i\theta h(\omega_k - \omega_l)\big)\,d\theta \tag{4.8}$$

finally yields

$$\int_0^h (h-\tau)\,\big(f_n(\tau) + f_n(-\tau)\big)\,d\tau \approx -h^2 \psi_n^* V_m Q_m \big(F_m \bullet G_m\big) Q_m^T V_m^T \psi_n \ .$$

The only approximation is for $\phi_n(\tau)$. The accuracy of this approximation can be controlled via the stopping criterion of the Lanczos process.

ALGORITHM 4.1. *Implementation of one time step of the scheme* (4.5) *with* (2.4)*, starting from* y_{n-1}*,* y_n*, and* $\psi_{n-1/2}$*:*

(i) *run the Lanczos process with* $A = H(y_n)$ *and* $b = \psi_{n-1/2}$ *providing* V_m*,* T_m*, and* β_m *for* $m = 1, 2, \ldots$*;*

(ii) *stop if* $\beta_m |[\exp(-\frac{3}{2} i h T_m)]_{m,m}| <$ `tol`*;*

(iii) *diagonalize* T_m*:* $T_m = Q_m D_m Q_m^T$*;*

(iv) *compute the tensor* G_m *defined in* (4.7) *and the matrix* F_m *from* (4.8)*;*

(v) *compute* ψ_n *and* $\psi_{n+1/2}$ *via Step (iii) of Algorithm* 2.1*;*

(vi) *compute* y_{n+1} *from*

$$M\,(y_{n+1} - 2y_n + y_{n-1}) = -h^2 \psi_n^* V_m Q_m (F_m \bullet G_m) Q_m^T V_m^T \psi_n \ .$$

In Step (ii), the stopping criterion taken over $\frac{3}{2}h$ ensures that $\phi_n(\tau)$ is approximated accurately enough for all $0 < \tau < h$ involved in the integral in (4.5).

In Step (vi), it is again preferable to work with the one-step formulation of the scheme. We omit the obvious modification.

Alternatively, the method (4.5) could be implemented using Chebyshev approximations to the exponential similarly to Section 3.2.

4.5 Proof of Theorem 4.2.

For simplicity, we write

$$H(t) := H(y(t)) \qquad \text{and} \qquad K(t) := K(y(t)) \ ,$$

and similarly for $V(t)$ and $Q(t)$. Using this notation, by (4.1) we have the bounds (2.1) and

$$\|K(t)\| \le M_0', \qquad \|K'(t)\| \le M_1', \qquad \|K''(t)\| \le M_2'$$

where M_j and M_j' depend only on $\|y'(0)\|$, L_1, L_2, because a bound of y'' is available from the differential equation (1.1). Let us denote those quantities in (4.5) which are computed from exact solutions $\psi(t_n)$, $H(t_n)$, and $K(t_n)$, by $\widetilde{\phi}_n$, $\widetilde{f}_n$, i.e.,

$$\widetilde{f}_n(\tau) \ = \ -\widetilde{\phi}_n(\tau)^* \, K(t_n) \, \widetilde{\phi}_n(\tau) \ , \tag{4.9}$$

$$\widetilde{\phi}_n(\tau) \ = \ \exp\left(-i\tau H(t_n)\right) \psi(t_n) \ . \tag{4.10}$$

LEMMA 4.3. *The defect* d_n *defined by*

$$d_n = \int_0^h (h - \tau) \left(\widetilde{f}_n(\tau) - f(t_n + \tau) + \widetilde{f}_n(-\tau) - f(t_n - \tau) \right) d\tau$$

is of the form

$$d_n = h^3\,\xi(t_n)^*\big(\Delta \bullet G(t_n)\big)\xi(t_n) + r_n,$$

where $\xi(t) = Q(t)^T\psi(t)$, $G(t) = Q(t)^T K'(t)Q(t)$, *and* $\Delta = (\delta(h\mu_k - h\mu_l))_{k,l=1}^N$ *with*

$$\delta(x) = \int_0^1 (1-\theta)\theta(e^{i\theta x} - e^{-i\theta x})\,d\theta.$$

The remainder term is bounded by $\|r_n\| \le Ch^4$.

Proof. We begin by noting that

$$\psi(t_n+\tau) = \widetilde{\phi}_n(\tau) + \vartheta_n(\tau) \quad \text{with} \quad \|\vartheta_n(\tau)\| \le M_1\tau^2\ , \tag{4.11}$$

which follows from the variation-of-constants formula (2.9). Next we show

$$\begin{aligned} \widetilde{f}_n(\tau) - f(t_n+\tau) &= \tau\widetilde{\phi}_n^*(\tau)K'(t_n)\widetilde{\phi}_n(\tau) + s_n(\tau) \\ &\text{with} \quad \|s_n(\tau)\| \le C\tau^2\ . \end{aligned} \tag{4.12}$$

From (4.11) we obtain immediately

$$\begin{aligned} \|\widetilde{f}_n(\tau) - f(t_n+\tau) &- \widetilde{\phi}_n^*(\tau)[K(t_n+\tau) - K(t_n)]\widetilde{\phi}_n(\tau)\| \\ &\le (2\|\vartheta_n(\tau)\| + \|\vartheta_n(\tau)\|^2)M_0' \\ &\le \tau^2(2 + M_1\tau^2)M_1M_0'. \end{aligned}$$

Since $\|K(t_n+\tau) - K(t_n) - \tau K'(t_n)\| \le \frac{1}{2}\tau^2 M_2'$, we obtain (4.12).
Now, by (4.12) we have

$$\begin{aligned} d_n = -\int_0^h (h-\tau)\tau\ [&\widetilde{\phi}_n(\tau)^*K'(t_n)\widetilde{\phi}_n(\tau) \\ &-\widetilde{\phi}_n(-\tau)^*K'(t_n)\widetilde{\phi}_n(-\tau)]\,d\tau + q_n\ , \end{aligned}$$

where

$$\|q_n\| \le \int_0^h (h-\tau)\big(\|s_n(\tau)\| + \|s_n(-\tau)\|\big)\,d\tau \le Ch^4\ .$$

Inserting

$$\widetilde{\phi}_n(\tau) = Q(t_n)\exp\big(-i\tau\Lambda(t_n)\big)\,\xi(t_n) = Q(t_n)\exp(-i\tau D)\,\xi(t_n) + O(h)$$

with $D = \operatorname{diag}(\mu_k)$ completes the proof. □

We have the following error recursions.

Lemma 4.4. *For* $n \ge 1$, *the errors* $e_n = y_n - y(t_n)$ *and* $\varepsilon_n = \psi_n - \psi(t_n)$ *satisfy*

$$\begin{aligned} \|\varepsilon_n\| &\le \|\varepsilon_{n-1/2}\| + ch\|e_n\| + Ch^3 \\ \|\varepsilon_{n+1/2}\| &\le \|\varepsilon_n\| + ch\|e_n\| + Ch^3 \\ \|e_{n+1}\| &\le n\|e_1 - e_0\| + \|e_1\| + ch^2\sum_{j=1}^n (n-j+1)(\|e_j\| + \|\varepsilon_j\|) \\ &\qquad + \Big\|\sum_{j=1}^n (n-j+1)d_j\Big\|\ . \end{aligned}$$

PROOF. The first two inequalities follow immediately from (3.2) and the Lipschitz constants (4.1). To prove the last inequality, similar to Lemma 4.3 we define

$$c_n = \int_0^h (h-\tau)\,(f_n(\tau) - f(t_n+\tau) + f_n(-\tau) - f(t_n-\tau))\,d\tau \ ,$$

so that the error satisfies $e_{n+1} - 2e_n + e_{n-1} = M^{-1}c_n$. Hence, for $n \geq 1$

$$\begin{aligned} e_{n+1} \quad = \quad & n(e_1 - e_0) + e_1 - M^{-1}\sum_{j=1}^{n}(n-j+1)d_j \\ & - M^{-1}\sum_{j=1}^{n}(n-j+1)(c_j - d_j) \ . \end{aligned}$$

It remains to bound $\|c_n - d_n\|$. From $\|\psi(t_n)\| = 1$ and the Lipschitz bound (4.1) we obtain

$$\begin{aligned} &\|\phi_n(\tau) - \widetilde{\phi}_n(\tau)\| = \|e^{-i\tau H(t_n)}\psi(t_n) - e^{-i\tau H_n}\psi_n\| \\ &\leq \|e^{-i\tau H(t_n)}\psi(t_n) - e^{-i\tau H_n}\psi(t_n)\| + \|e^{-i\tau H_n}\psi(t_n) - e^{-i\tau H_n}\psi_n\| \\ &\leq \tau L_1\|e_n\| + \|\varepsilon_n\| \ , \end{aligned}$$

using the variation-of-constants formula

$$\left(e^{-i\tau H(t_n)} - e^{-i\tau H_n}\right)\psi(t_n) = -i\int_0^\tau e^{-i(\tau-\sigma)H_n}\,(H(t_n) - H_n)e^{-i\sigma H(t_n)}\psi(t_n)\,d\sigma.$$

Finally,

$$\begin{aligned} \|f_n(\tau) - \widetilde{f}_n(\tau)\| &= \|\phi_n(\tau)K_n\phi_n(\tau) - \widetilde{\phi}_n(\tau)K(t_n)\widetilde{\phi}_n(\tau)\| \\ &= \|\phi_n(\tau)K_n\phi_n(\tau) - \widetilde{\phi}_n(\tau)K_n\widetilde{\phi}_n(\tau) + \\ &\qquad \widetilde{\phi}_n(\tau)K_n\widetilde{\phi}_n(\tau) - \widetilde{\phi}_n(\tau)K(t_n)\widetilde{\phi}_n(\tau)\| \\ &\leq L_2\|e_n\| + 2L_1\|\phi_n(\tau) - \widetilde{\phi}_n(\tau)\| \\ &\leq (2\tau L_1^2 + L_2)\|e_n\| + 2L_1\|\varepsilon_n\| \end{aligned}$$

yields

$$\|c_n - d_n\| \leq Ch^2(\|e_n\| + \|\varepsilon_n\|) \ ,$$

where C depends only on L_1, L_2, and T. □

It remains to show that the last sum in Lemma 4.4 does not exceed Ch^2.

LEMMA 4.5. *For $0 \leq t_n \leq T$ we have*

$$\Big\|\sum_{j=1}^{n}(n-j+1)\,d_j\Big\| \leq Ch^2 \ .$$

PROOF. The proof is similar to parts (b) and (c) of the proof of Theorem 2.1 (ii). As in that proof, we have

$$\xi(t) = Q(t)^T \psi(t) = \exp(-itD)\,\eta(t) \ ,$$

where $\eta(t)$ defined by (2.12) and (2.11) satisfies

$$\|\eta(t)\| \le 1 \ , \quad \|\eta'(t)\| \le C \ .$$

We write

$$\sum_{j=1}^{n} (n-j+1)\, d_j = \sum_{m=1}^{n} \sum_{j=1}^{m} d_j \ ,$$

and from Lemma 4.3 we know

$$d_j = h^3 \eta(t_j)^* e^{it_j D} \big(\Delta \bullet G(t_j)\big) e^{-it_j D} \eta(t_j) + r_j$$

with $\sum_{j=1}^{n} (n-j+1)\|r_j\| \le Ch^2$. We introduce the matrix

$$E_n = (\epsilon_n(h\mu_k - h\mu_l))_{k,l=1}^{N} \ , \tag{4.13}$$

$$\text{with} \ \ \epsilon_n(x) = \sum_{j=1}^{n} e^{ijx} \delta(x) = (1 - e^{inx})\varphi(x) \ ,$$

where $\varphi(x) = \delta(x) e^{ix}/(1-e^{ix})$. Partial summation yields, with $\eta_j = \eta(t_j)$ and $G_j = G(t_j)$,

$$\begin{aligned} &\sum_{j=1}^{m} \eta_j^* e^{it_j D} \big(\Delta \bullet G_j\big) e^{-it_j D} \eta_j \\ &= \eta_m^* (E_m \bullet G_m) \eta_m - \sum_{j=1}^{m-1} \Big(\eta_{j+1}^* (E_j \bullet G_{j+1}) \eta_{j+1} - \eta_j^* (E_j \bullet G_j) \eta_j \Big) \ . \end{aligned}$$

By Lemma 4.6 we have $\|E_m \bullet G_m\| \le C$ and

$$\begin{aligned} &\|\eta_{j+1}^* (E_j \bullet G_{j+1}) \eta_{j+1} - \eta_j^* (E_j \bullet G_j) \eta_j\| \\ &\qquad \le \ \|(\eta_{j+1} - \eta_j)^* (E_j \bullet G_{j+1}) \eta_{j+1}\| \\ &\qquad\quad + \|\eta_j^* (E_j \bullet (G_{j+1} - G_j)) \eta_{j+1}\| \\ &\qquad\quad + \|\eta_j^* (E_j \bullet G_j)(\eta_{j+1} - \eta_j)\| \\ &\qquad \le \ Ch \ . \end{aligned}$$

Combining these estimates completes the proof of the lemma. □

LEMMA 4.6. *There is a constant C such that the entrywise product of E_n, defined by* (4.13)*, with an arbitrary complex $N \times N$ matrix G is bounded by*

$$\|E_n \bullet G\| \le C\|G\| \ .$$

PROOF. We introduce the matrix $F = (\varphi(h\mu_k - h\mu_l))_{k,l=1}^n$ and note that

$$E_n \bullet G = F \bullet G - \exp(inhD)(F \bullet G)\exp(-inhD) \ .$$

Since $\delta(2m\pi) = 0$ for all integers m, the function φ and its derivative are square integrable over $\mathbf{R}$. Thus it follows from Lemma 2.2 and (2.13) (with $a = 1$) that $\|F \bullet G\| \le C\|G\|$. □

The error bound of Theorem 4.2 now follows from Lemmas 4.4 and 4.5 via a discrete Gronwall inequality.

4.6 Proof of Theorem 4.1.

We consider the method (4.2) as a perturbation of (4.5). We begin with an analogue of Lemma 4.3.

LEMMA 4.7. *The defect b_n defined by*

$$b_n = h^2 f(t_n) - \int_0^h (h-\tau)\left(\widetilde{f}_n(\tau) + \widetilde{f}_n(-\tau)\right) d\tau \ ,$$

with $\widetilde{f}_n(\tau)$ defined by (4.9), is of the form

$$b_n = h^2\, \xi(t_n)^* \big(\Delta(t_n) \bullet G(t_n)\big)\xi(t_n) \ ,$$

where $\xi(t) = Q(t)^T\psi(t)$, $G(t) = Q(t)^T K(t) Q(t)$, and $\Delta(t) = (\delta(h\lambda_k(t) - h\lambda_l(t)))_{k,l=1}^N$ with

$$\delta(x) = 1 - \int_0^1 (1-\theta)(e^{i\theta x} + e^{-i\theta x})\, d\theta \ .$$

Under condition (4.4), with $0 \le \alpha \le 2$, we have

$$\|b_n\| \le Ch^{2+\alpha} \ .$$

We remark that $\delta(x) = O(x^2)$ as $x \to 0$, but $\delta(2m\pi) \ne 0$ for integer $m \ne 0$, in contrast to Lemma 4.3.

PROOF. The formula for b_n follows directly from the definitions of the quantities involved. To prove the bound, we begin by noting that $H(t)^\alpha \psi(t) = Q(t)\Lambda(t)^\alpha \xi(t)$. Let first $0 \le \alpha \le 1$. As in the proof of Theorem 2.1 (iii), we use

$$\|\exp(i\tau\Lambda)\xi - \xi\| \le C\,|\tau|^\alpha\, \|\Lambda^\alpha \xi\| \ ,$$

which gives, for Λ, ξ and G evaluated at t_n,

$$\begin{aligned} b_n &= h^2\xi^* G\xi - h^2 \int_0^1 (1-\theta)\Big(\big(\exp(i\theta h\Lambda)\xi\big)^* G \exp(i\theta h\Lambda)\xi \ + \\ &\qquad\qquad \big(\exp(-i\theta h\Lambda)\xi\big)^* G \exp(-i\theta h\Lambda)\xi\Big)\, d\theta \\ &= h^2\Big(1 - 2\int_0^1 (1-\theta)\, d\theta\Big)\cdot \xi^* G\xi + O\,(h^{2+\alpha}) \\ &= O(h^{2+\alpha}) \ . \end{aligned}$$

Let now $1 \le \alpha \le 2$. Here we use

$$\| \exp(i\tau\Lambda)\xi - (I + i\tau\Lambda)\xi \| \le C\,|\tau|^\alpha\, \|\Lambda^\alpha \xi\|$$

to obtain

$$\begin{aligned} b_n &= h^2 \xi^* G \xi - h^2 \int_0^1 (1-\theta) \Big(\big((I + i\theta h\Lambda)\xi\big)^* G (I + i\theta h\Lambda)\xi + \\ &\qquad \big((I - i\theta h\Lambda)\xi\big)^* G (I - i\theta h\Lambda)\xi \Big)\, d\theta + O(h^{2+\alpha}) \\ &= O(h^{2+\alpha}) \ , \end{aligned}$$

where the last bound follows by multiplying out. □

To complete the proof of Theorem 4.1, we recall that the local error of (2.4) is $O(h^2)$, and the truncation error of (4.2) is $b_n + d_n = O(h^{2+\alpha})$, since d_n of Lemma 4.3 is bounded by $d_n = O(h^{3+\alpha} + h^4)$ under condition (4.4), as is shown in the same way as for b_n above. The error propagation is still as in Lemma 4.4, with $b_n + d_n$ in place of d_n. A Gronwall-type inequality then gives the error bound stated in Theorem 4.1.

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