

Exponential Integrators

§1 Evaluating the matrix exponential

In the previous chapter, we were obstructed by the requirement to find *exactly symmetric* approximations to $\exp(-i\tau H/(2\epsilon))$. If we consider as well approximations, which are not precisely symmetric, we are free to take advantage of the superior efficiency of iterative methods for evaluating the matrix exponential. In the following, we will compare three different approaches. Furthermore, these iterative methods will allow for the construction of very elaborated numerical schemes.

Chebyshev approximation The well known expansion of $\exp(-i\tau H/\epsilon)$ into Chebyshev polynomials T_k [111] is one of the most frequently used integration technique in numerical quantum dynamics:

$$\exp(-\frac{i}{\epsilon} H \tau)\psi(t) \approx \sum_{k=1}^N \alpha_k(\rho\tau) T_k(-\frac{i}{\epsilon} H)\psi \quad (7.1)$$

with appropriately chosen coefficients α_k and an estimate ρ for the spectral radius of the Hamiltonian H . Eq. (7.1) can be evaluated with N matrix–vector products, since the T_k are given via the Chebyshev recurrence relation. This technique allows for large stepsizes if the truncation index N is chosen large enough. The degree N necessary for achieving a specific accuracy depends linearly on the stepsize τ and the spectral radius of H . The author and his coworkers analyzed the numerical stability of (7.1) and developed an adaptive stopping criterion for the iteration based on the decay of the coefficients α_k [88, 58, 59].

Krylov approximation of the matrix exponential The iterative approximation of the matrix exponential based on Krylov subspaces (via the Lanczos method) has been studied in different contexts [52, 91, 29]. After the iterative construction of the Krylov basis $\{v_1, \dots, v_n\}$, the matrix exponential is approximated by using the representation A of $H(q)$ in this basis:

$$\exp(-\frac{i\tau}{\epsilon} H(q)) \psi \approx V \exp(-\frac{i\tau}{\epsilon} A) V^* \psi, \quad \text{with } V = [v_1, \dots, v_n].$$

The evaluation of $\exp(-i\tau A/\epsilon)$ is cheap since A is tridiagonal.

In [55], an efficient residual error estimation scheme has been introduced for controlling the quality of the approximation. This gives us a stopping criterion for the iteration guaranteeing that the quality of the approximation fits to the accuracy requirements of the stepsize control.

In most cases, this Lanczos–based technique proves to be superior to the Chebyshev method introduced above. It is the method of choice for application problems with only a few eigenstates of $H(q)$ being occupied. The Chebyshev method is superior only in the case that nearly all eigenstates of the Hamiltonian are substantially occupied.

However, using the Lanczos iteration for evaluating the matrix exponential produces two eventual drawbacks. Firstly, the iteration does not use any of the information gathered in the last step. But if the eigenvectors undergo only minor changes from step to step, some approximate eigenvectors of the last step may be used as good initial choices for the next iteration. This idea can be realized by using Block-Lanczos iteration instead of the pure Lanczos scheme. The second drawback is important if the motion under consideration is nearly adiabatic and only a few, let us say m , eigenstates are occupied. By approximating these eigenstates in a Krylov basis with typically $d > m$ basis vectors, the Lanczos scheme necessarily introduces (small) artificial populations of other than the m states occupied. From time step to time step, this will lead to an artificial and unwanted blow-up of the dimension of the occupied subspace.

Subspace-controlling iteration methods Out of this observation we also have studied some subspace-controlling algorithms. In these approaches, we do *not* try to construct an (eventually large) basis set for transforming the Hamiltonian into a form appropriate for an efficient evaluation of the matrix exponential. Instead of this, we directly approximate a (small) basis set for the relevant (small) subspace. Only then, the matrix exponential is computed using this basis. In the course of the iteration, appropriate error estimates control whether the subspace dimension has to be increased or may be reduced. Mainly two techniques were tested in order to evaluate the basis set: a simultaneous minimization of the Rayleigh quotient in the subspace via an appropriately preconditioned conjugate gradient iteration [26] and a multi grid approach to the eigenvalue problem as introduced in [23]. Both techniques prove to be superior to the Lanczos approach for nearly adiabatic problems with very few eigenstates occupied. But they quickly get inefficient if a non-adiabatic excitation of previously unimportant states is essential.

§2 Exponential schemes for QCMD

In [53, 54], M. HOCHBRUCK and CH. LUBICH have proposed a bunch of integrators, which take the highly oscillatory character of the wave function into account. More precisely, they have focused on methods which do not depend on stepsize restrictions due to large bounds on spatial derivatives of the solution. That means for a spatially discretized system, that the bound on T_N does not influence the error terms of the time discretizations proposed. Understandably, the integration methods have surprisingly complicated convergence properties depending on resonances and spatial regularity of the solution.

In the following, assume, that

(N1) the potential and its derivations are bounded by

$$\|\nabla^j V(q)\| \leq L_j \quad j = 0, 1, 2,$$

(N2) the Hamiltonian is smoothly diagonalizable,

$$H(q) = Q(q)E(q)Q(q)^T, \quad E(q) = \text{diag}(E_\lambda(q)),$$

with $\|\nabla_q Q(q(t))\| \leq L_*$.

§2.1 Pointwise Verlet

First of all, M. HOCHBRUCK and CH. LUBICH have analyzed the global error of the symmetric method (6.7) using the Velocity Verlet and exponential integration methods to solve the quantum propagation. They found that for not sufficiently regular solutions, method (6.7) becomes inefficient for its modest convergence properties:

Theorem 7.1 (Thm. 4.1 of [54]) *Let Assumptions (N1) and (N2) hold and additionally let $H(q(t))$ be positive semidefinite for all t and let there exists $0 < \alpha \leq 2$ such that*

$$\|H(q(t))^\alpha \psi(t)\| \leq C_\alpha, \quad 0 \leq t \leq T.$$

Then, the error of the method (6.7) is bounded by

$$\begin{aligned} \|q^n - q(t_n)\| &\leq C \tau^\alpha \\ \|\psi^n - \psi(t_n)\| &\leq C \tau^\alpha, \end{aligned}$$

for $0 \leq t_n \leq T$. The constant C depends only on C_α , $\|\dot{q}_\|$, L_1 , L_2 , and T .*

Obviously, the error term is influenced by the highest essentially occupied eigenvalue of $H(q)$. If the solution is sufficiently regular, that means, that $\|H(q(t))\psi\|$ is comparably small, this theorem recapitulates an $\mathcal{O}(\tau)$ error estimation.

§2.2 Enhanced integrators

Inspired by the identity

$$\begin{aligned} q_\epsilon(t + \tau) - 2q_\epsilon(t) + q_\epsilon(t - \tau) = \\ - \int_0^\tau (\tau - s) \left(\langle \psi, \nabla_{q_\epsilon} V(q) \psi \rangle \Big|_{(t+s)} + \langle \psi, \nabla_{q_\epsilon} V(q) \psi \rangle \Big|_{(t-s)} \right) ds. \end{aligned}$$

M. HOCHBRUCK and CH. LUBICH suggested an integration scheme for the classical subsystem, which takes advantage of the iterative solvers described above:

$$\begin{aligned} q^{n+1} - 2q^n + q^{n-1} &= - \int_0^\tau (\tau - s) (f^n(s) + f^n(-s)) ds. \\ f^n(s) &= - \langle \phi^n(s) \nabla_q V(q^n) \phi^n(s) \rangle \\ \phi^n(s) &= \exp \left(-i \frac{s}{\epsilon} H(q^n) \right) \psi^n \\ q^1 &= q_* + \tau \dot{q}_* + \int_0^\tau (\tau - s) f^0(s) ds. \end{aligned} \tag{7.2}$$

The integral averages over the approximated quantum evolution $\exp(-i \frac{s}{\epsilon} H(q^n)) \psi^n$ whereas the classical force is evaluated only at q^n . It is an intriguing point, that the integral in (7.2) may be evaluated explicitly and can efficiently be computed via the exponential methods introduced above. For a description of the algorithmic realization, we refer to [54].

In a second step, an elaborated third-order-scheme for the quantum propagation based on the variation-of-constants formula has been derived. We define

$$J_{\pm}^n = \frac{1}{\epsilon} \int_0^{1/2} \exp\left(-\frac{is\tau}{\epsilon} H(q^n)\right) \left(sH'_n \pm \frac{1}{2}s^2\tau H''_n\right) \exp\left(\frac{is\tau}{\epsilon} H(q^n)\right) ds$$

where H'_n and H''_n are finite difference approximations of the first and second time derivatives of H at q^n using the values of $H(q^{n+1})$, $H(q^n)$ and $H(q^{n-1})$, respectively.¹ Now, variation-of-constants leads to

$$\begin{aligned} \psi^n &= (\mathbb{I} + i\tau^2 J_-^n) \exp\left(-\frac{i\tau}{2\epsilon} H(q^n)\right) \psi^{n-1/2} + \mathcal{O}(\tau^4), \\ \psi^n &= (\mathbb{I} + i\tau^2 J_+^{n*}) \exp\left(-\frac{i\tau}{2\epsilon} H(q^n)\right) \psi^{n+1/2} + \mathcal{O}(\tau^4). \end{aligned}$$

A symmetric and norm-conserving scheme for the quantum propagation can be derived by a small modification. Combined with the averaging Verlet scheme (7.2), one obtains a third-order method with very promising convergence results

$$\text{Averaging Verlet} \begin{cases} \psi^{1/2} &= \exp\left(-\frac{i\tau}{2\epsilon} H(q^n)\right) \exp(-i\tau^2 J_+^{n*}) \psi^n \\ p^{n+1/2} &= p^n - \int_0^\tau (\tau-s)(f^n(s) + f^n(-s)) ds \\ q^{n+1} &= q^n + \tau p^{n+1/2} \\ p^{n+1} &= p^{n+1/2} - \int_0^\tau (\tau-s)(f^{n+1}(s) + f^{n+1}(-s)) ds \\ \psi^1 &= \exp(i\tau^2 J_-^{n+1}) \exp\left(-\frac{i\tau}{2\epsilon} H(q^{n+1})\right) \psi^{1/2}. \end{cases} \quad (7.3)$$

Theorem 7.2 (Thm. 4.2 of [54]) *Let Assumptions (N1) and (N2) hold, then method (7.3) satisfies*

$$\begin{aligned} \|q^n - q(t_n)\| &\leq C \tau^2 \\ \|\psi^n - \psi(t_n)\| &\leq C \tau^2, \end{aligned}$$

for $0 \leq t_n \leq T$. The constant C depends only on $\|\dot{q}_*\|$, L_0, L_1, L_2, L_* , and T .

For the proof and hints on a favorable implementation see [54]. Intriguingly, bounds on T_N or on $\|H(q(t))\psi\|$ do not enter the error term. Thus, neither the order of convergence nor the constant in front of the leading error term does depend on the regularity of the solution.

Unfortunately, the use of Krylov subspaces to approximate J_{\pm}^n cannot be recommended since the definition of J_{\pm}^n contains not only $H(q^n)$ but also approximations of $d/dt H(q^n)$ and $d^2/dt^2 H(q^n)$. Generally, these matrices do not commute. Therefore, there is no low-dimensional Krylov subspace in which we can accurately approximate J_{\pm}^n .

Fortunately, there exists an implementation via the Chebyshev approximation to the exponential as described in [54]. However, up to now, the usefulness

¹Apparently, this yields an implicit method. To circumvent this, see the implementation given in [54].

of this method for high-dimensional systems could not be shown for the lack of experience on application problems.

Giving up the requirement of error bounds completely independent of the norm of T_N , one can apply methods based on a truncated Magnus series for the quantum propagation [54]:

$$\begin{aligned}\psi^{n+1/2} &= \exp\left(-\frac{i\tau}{2\epsilon}S_+^n\right)\psi^n \\ \psi^{n+1} &= \exp\left(-\frac{i\tau}{2\epsilon}S_+^{n+1}\right)\psi^{n+1/2}\end{aligned}$$

using the Hermitian matrix

$$S_{\pm}^n = H(q^n) + \frac{1}{2}\tau H'_n + \frac{1}{6}\tau^2 H''_n + \frac{i}{12}\tau^2 (H(q^n)H'_n - H'_n H(q^n))$$

where we have used the previously defined approximations on the time derivatives of H . Again, very promising convergence results for this third-order scheme are presented in [54].

§3 Adaptive Methods

Adaptive Stepsize Control We have to pay a price for the advantages of previously described symplectic and symmetric methods: The stepsize τ has to be constant during the simulation, because, up to now, there is no appropriate strategy for efficiently controlling the stepsize without destroying the “structural stability”. This means, that the overall stepsize has to be reduced until it satisfies the accuracy requirements during the whole integration period. In many real life applications of QCMD, the dynamical behavior of the solution can change dramatically during the course of the simulation (collisions, excitation processes). In principle, one would like to make large time steps where “nothing important happens” and small ones where it is necessary to resolve important processes, i.e., the stepsize should be adapted to the accuracy wanted. The conceptual framework [22, 43] requires the control of the approximation error *in each time step* via choosing the stepsize with respect to a given accuracy requirement. That is, the stepsize is controlled in a way which bounds the local approximation error by a given tolerance TOL.

The local error in the step from time t to $t + \tau$, i.e., the error, which is produced by calculating a discrete solution in this step instead of exactly solving the QCMD equations, is given as follows:

$$\epsilon_{\tau}(t + \tau) = \Phi_p^{\tau} z(t) - \exp(\tau L_{\mathcal{H}}) z(t),$$

where $\exp(\tau L_{\mathcal{H}}) z(t)$ denotes the exact solution of the QCMD model and Φ_p^{τ} the discrete evolution of order p and with stepsize τ , for example the map given by (6.7).

Unfortunately, this local error ϵ_{τ} cannot be calculated, since we do not know the exact solution to the QCMD equations. The clue to this problem is given by the introduction of an approximation to ϵ_{τ} . Let us consider another discrete evolution Φ_q^{τ} with an order $q > p$ and define an error estimation $\hat{\epsilon}_{\tau}$ via $\hat{\epsilon}_{\tau}(t + \tau) = \Phi_p^{\tau} z(t) - \Phi_q^{\tau} z(t)$.

The control scheme tries to choose the stepsize τ so that $\|\hat{e}_\tau\| = \text{TOL}$ in some adequate norm. In case of a tolerance exceeding error, i.e., for $\|\hat{e}_\tau\| > \text{TOL}$, one reduces the stepsize according to

$$\tau_{new} = \rho^{p+1} \sqrt{\rho \text{TOL} / \|\hat{e}_\tau\|} \tau_{old}. \quad (7.4)$$

with an additional safety factor $\rho < 1$. The same formula is used in order to predict a proper stepsize for the next step. Problems can arise, when the error approaches zero. We cope with them by restricting the allowed increase of the stepsize.

For realizing (7.4), we need an adequate norm for measuring the error. It obviously makes no sense to use an Euclidean norm of z indiscriminately of quantum and classical parts. We advocate the use of a scaled norm in the classical subsystem and the usual 2-Norm for the quantum part:

$$\|\hat{e}_\tau(t)\| = \sqrt{\|\psi(t) - \hat{\psi}(t)\|_2^2 + \left| \frac{q(t) - \hat{q}(t)}{\max(q(t), s_{min})} \right|^2 + \left| \frac{p(t) - \hat{p}(t)}{\max(p(t), s_{min})} \right|^2},$$

where ψ, q and p denote the results of Φ_q^τ and $\hat{\psi}, \hat{q}$ and \hat{p} that of Φ_q^τ . A threshold value $s_{min} > 0$ avoids an exploding error for locations or momenta close to zero.

The error estimate approximates the error of the propagation with the less accurate method Φ_p^τ . Nonetheless, the next step is started with the more precise result of Φ_q^τ .

We are now concerned with the selection of two integration methods of different order. A first idea – which we are not advocating – is to use the PICKABACK integrator (6.6) as Φ_q^τ together with a first order scheme based on the Trotter formula (6.4) replacing Φ_p^τ . Recalling that the stepsize of these methods are dominated by the splitting of $\exp(-i\tau H/\epsilon)$, we actually foresee the effect of such an adaptive method. The scheme correctly resolves the dynamical behavior but forces the stepsize to remain restricted to the order of the inverse of the largest eigenvalue of the Hamiltonian.

A more convincing approach leads to an adaptive method based on the symmetric second order scheme (6.7). As a first step, we have to introduce a first order scheme substituting Φ_p^τ of the previous section. In what follows, we use the following pair of schemes:

$$\begin{array}{l} \text{2nd order} \\ \text{symmetric scheme} \\ \text{as } \Phi_q^\tau \end{array} \left\{ \begin{array}{l} \psi_{1/2} = \exp\left(-i\frac{\tau}{2\epsilon}H(q_0)\right) \psi_0 \\ q_{1/2} = q_0 + \frac{\tau}{2}p_0 \\ p_1 = p_0 - \tau \langle \psi_{1/2}, D_q V(q_{1/2}) \psi_{1/2} \rangle \\ q_1 = q_{1/2} + \frac{\tau}{2}p_1 \\ \psi_1 = \exp\left(-i\frac{\tau}{2\epsilon}H(q_1)\right) \psi_{1/2} \end{array} \right. \quad (7.5)$$

$$\begin{array}{l} \text{For comparison:} \\ \text{1st order} \\ \text{Euler scheme} \\ \text{as } \Phi_p^\tau \end{array} \left\{ \begin{array}{l} \hat{\psi}_1 = \exp\left(-i\frac{\tau}{\epsilon}H(q_0)\right) \psi_0 \\ \hat{q}_1 = q_0 + \tau p_0 \\ \hat{p}_1 = p_0 - \tau \langle \psi_{1/2}, D_q V(\hat{q}_1) \psi_{1/2} \rangle \end{array} \right.$$

Since it is known [44], that the usual stepsize control mechanism destroys the reversibility of the discrete solution we may use iterative methods for evaluating the matrix exponential.

Obviously, a combination the enhanced exponential schemes of Sec. §2.2 with the concept of adaptivity is very interesting. However, up to now no simulations have been conducted using such advanced methods.

Illustration To illustrate the presented methods, we have applied them to a photo dissociation process of a collinear ArHCl molecule (see Fig. 7.1). The photo dissociation is modeled via a transition of the bounding Hydrogen-Chlorine ground state into a repulsive excited state. The Hydrogen starts oscillating between Argon and Chlorine transferring more and more kinetic energy to the Argon atom. Using Jacobi coordinates and reduced masses, the

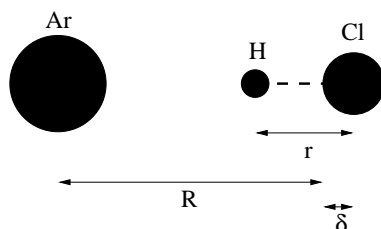


FIGURE 7.1. Collinear ArHCl system with the Jacobi-coordinates used.

Hydrogen-Chlorine interaction is modeled quantum mechanically whereas the Ar-HCl interaction classically. The potentials used, initial data and additional computational parameters are listed in detail in [87].

When analyzing the adaptive Verlet integrator, we observe that the stepsize control just adapts to the dynamical behavior of the classical subsystem. The internal (quantal) dynamics of the Hydrogen-Chlorine subsystem does not lead to stepsize reductions.

As pointed out before, it seems to be unreasonable to equip the Pickaback scheme with a stepsize control, because, as we indeed observe in Fig. 7.2, the stepsize never increases above a given level. This level depends solely on the eigenvalues of the quantum Hamiltonian.

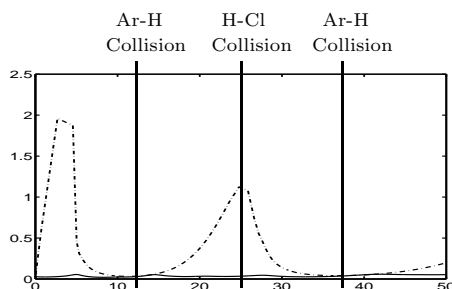


FIGURE 7.2. Stepsize τ used in the simulation of the collinear photo dissociation of ArHCl: the adaptive Verlet-based exponential integrator using the Lanczos iteration (dash-dotted line) for the quantum propagation, and a stepsize controlling scheme based on PICKABACK (solid line). For a better understanding we have added vertical lines marking the collisions (same tolerance TOL). We observe that the quantal H-Cl collision does not lead to any significant stepsize restrictions.