Numerical Integrators for Quantum-Classical Molecular Dynamics

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Abstract. It was revealed that the QCMD model is of canonical Hamiltonian form with symplectic structure, which implies the conservation of energy. An efficient and reliable integrator for transfering these properties to the discrete solution is the symplectic and explicit PICKABACK algorithm. The only drawback of this kind of integrator is the small stepsize in time induced by the splitting techniques used to discretize the quantum evolution operator. Recent investigations concerning Krylov iteration techniques result in alternative approaches which overcome this difficulty for a wide range of problems. By using iterative methods in the evaluation of the quantum time propagator, these techniques allow for the stepsize to adapt to the classical motion and the coupling between the classical and the quantum mechanical subsystem. This yields a drastic reduction of the numerical effort. The pros and cons of both approaches as well as the suitable applications are discussed in the last part.

1 Introduction

Various kinds of *mixed quantum-classical* models have been introduced in the literature. We will concentrate on the so-called quantum-classical molecular dynamics (QCMD) model, which consists of a Schrödinger equation coupled to classical Newtonian equations (cf. Sec. 2).

In this paper, we focus on numerical techniques for integrating the QCMD equations of motion. The aim of the paper is to systematize the discussion concerning numerical integrators for QCMD by:

- giving a derivation of the different techniques based on a common construction principle,
- classifying the application problems in order to link together the properties of the integrators and the structure of the problem under consideration.

For this purpose, a short overview will be given concerning some *theoretical* properties of the QCMD model (Sec. 2). This will allow for a suitable classification of the application problems. In the course of the following discussion, we will introduce two different classes of integration techniques:

In Sec. 3, some recent developments of "structure conserving" integrators will be reviewed. Such *symplectic* or *symmetric* integrators are build to preserve certain geometric properties of the exact QCMD solution like energy conservation or reversibility. They are preferable for applications to long-term simulations, but turn out to have some crucial disadvantages when short-term simulations up to a given precision are wanted.

Hence, as the second class of techniques, we discuss *adaptive* methods for accurate short-term integration (Sec. 4). For this class, it is the major requirement that the discretization allows for the stepsize to adapt to the classical motion and the coupling between the classical and the quantum mechanical subsystem. This means, that we are interested in discretization schemes which avoid stepsize restrictions due to the fast oscillations in the quantum part. We can meet this requirement by applying techniques recently developed for evaluating matrix exponentials iteratively [12]. This approach yields an adaptive *Verlet-based exponential integrator* for QCMD.

Finally, in Sec. 5, the theoretical results are illustrated by applying two adaptive schemes to the collinear photo dissociation of ArHCl.

2 The QCMD Model

There are various approaches to the problem of coupling quantum degrees of freedom to classical degrees of freedom. The QCMD model is given by the following equations of motion:

$$\begin{aligned}
i\,\hbar\,\dot{\psi} &= \Big(\underbrace{T + V(x,q)}_{H}\Big)\,\psi, \qquad T = -\frac{\hbar^2}{2m}\Delta_x \qquad && \psi|_{t=0} = \psi_0 \\
M\dot{q} &= p, && q(0) = q_0, \\
\dot{p} &= -\langle \psi, \nabla_q V \psi \rangle, && p(0) = p_0
\end{aligned} \tag{1}$$

The quantum degrees of freedom are described by a wave function $\psi = \psi(x,t)$. It obeys Schrödinger's equation with a parameterized coupling potential V which depends on the location $q = q(t)$ of the classical particles. This location $q(t)$ is the solution of a classical Hamiltonian equation of motion in which the time–dependent potential arises from the expectation value of V with regard to ψ. For simplicity of notation, we herein restrict the discussion to the case of only two interacting particles. Nevertheless, all the following considerations can be extended to arbitrary many particles or degrees of freedom.

2.1 Conservation Properties of the QCMD Model

In a first discretization step, we apply a suitable spatial discretization to Schrödinger's equation, e.g., based on pseudospectral collocation [15] or finite element schemes. From now on, we consider ψ, T, V and H as denoting the corresponding vector and matrix representations, respectively. The total energy expectation value of the system

$$\mathcal{H} = \psi^* H(q)\psi + \frac{1}{2M}|p|^2, \tag{2}$$

to which we will simply refer as "energy", is a constant of motion [2]. Another conserved quantity is the norm of the wave function, due to the unitary propagator in the quantum part. We are interested in constructing numerical integrators which reproduce these conservation properties. To this end, it is enormously helpful to observe that the QCMD equations are of canonical Hamiltonian form with respect to $\mathcal{H}$. In order to illustrate this fact, we decompose the wave function into a scaled real and imaginary part $\psi = (q_\psi + ip_\psi)/\sqrt{2\hbar}$ and introduce generalized positions $Q = (q_\psi, q)^T$ and momenta $P = (p_\psi, p)^T$. This allows for denoting the whole system (1) in canonical Hamiltonian form:

$$\dot{Q} = \frac{\partial}{\partial P}\mathcal{H}, \qquad \dot{P} = -\frac{\partial}{\partial Q}\mathcal{H}, \tag{3}$$

with the usual symplectic structure (cf. [16]).

2.2 Adiabatic Limit of QCMD

QCMD describes a coupling of the "fast" motions of a quantum particle to the "slow" motions of a classical particle. In order to classify the types of coupled motion we eventually have to deal with, we first analyze the case of an extremely heavy classical particle, i.e., the limit $M \to \infty$ or, better, $m/M \to 0$. In this "adiabatic limit", the classical motion is so slow in comparison with the quantal motion that it cannot induce an excitation of the quantum system. That means, that the populations $\theta_k(t) = |\langle\psi(t), \Phi_k(q(t))\rangle|$ of the eigenstates $\Phi_k(q)$ of the Hamiltonian $H(q)$ remain *constant* along the classical path $q = q_{\mathrm{BO}}$. Hence, the limit populations $\theta_k(t) = \theta_k(0)$ may be computed from the initial conditions. The classical limit path is given by the time–dependent Born–Oppenheimer model:

$$M\,\ddot{q}_{\mathrm{BO}} = -\sum_k \theta_k(0)^2\,(\mathrm{grad}_q E_k)(q_{\mathrm{BO}}), \quad q_{\mathrm{BO}}(0) = q_0,\ \dot{q}_{\mathrm{BO}}(0) = p_0/M,$$

where the $E_k(q)$ are the eigenenergies of $H(q)$ (for details concerning the adiabatic limit see [20] in this collection, or [3,1]). The associated asymptotic expression for the wave function

$$\psi(t) = \sum_k \theta_k(0)\,\exp\left(-\frac{i}{\hbar}\int_0^t E_k(q_{\mathrm{BO}}(s))ds\right)\Phi_k(q_{\mathrm{BO}}(t)) + \underbrace{\mathcal{O}(\sqrt{m/M})}_{\text{nonadiabaticity}} \tag{4}$$

deserves our attention because it uncovers some essential features of QCMD motion:

1. The quantal motion is highly oscillatory with frequencies given by the eigenvalues of the Hamiltonian H.

2. For m/M small enough, the populations of the eigenstates Φ_k are nearly constant and the quantal motion is given in terms of the evolution of the eigenstates and eigenenergies E_k along q_{BO}.
3. For larger values of m/M, we have to expect *nonadiabatic* redistribution of the populations induced by the classical motion.

2.3 Classification of Application Problems

It is the aim of this paper to take into account a wide range of systems to which QCMD is applied. For a precise understanding of the situation, it is necessary to recognize the differences between these applications, because these differences demand for specific features of the numerical integrator. In the following, we will describe a suitable classification of the application problems.

1. For *long term simulations*, it turns out that the reproduction of the conservation properties is most important in order to ensure reliable results.
2. For *short term simulations*, accuracy requirements on the discrete solution make sense and we advocate error controlling adaptive integrators. Moreover, we have to further subdivide our classification due to the observations in Sec. 2.2:
   (a) Problems with (nearly) adiabatic motion.
   (b) Problems with essentially nonadiabatic motion.

In most real life applications, the evaluation of the forces acting on the classical particles (i.e., the evaluation of the gradient of the interaction potential) is by far the most expensive operation due to the large number of classical degrees of freedom. Therefore we will concentrate on numerical techniques which try to minimize the number of force evaluations.

3 Structure Conserving Integration Schemes

Since we have discovered the underlying Hamiltonian structure of the QCMD model we are able to apply methods commonly used to construct suitable numerical integrators for Hamiltonian systems. Therefore we transform the QCMD equations (1) into the Liouville formalism. To this end, we introduce a new state z in the phase space, $z = (\mathcal{Q}_{\mathcal{N}}, \mathcal{P}_{\mathcal{N}})^T$, and define the nonlinear Liouville operator $L_{\mathcal{H}}\, z_i \;=\; \{z_i, \mathcal{H}\}$, using the common Poisson brackets $\{\ ,\ \}$. This permits us to denote the QCMD equations (1) in the form $\dot{z} = L_{\mathcal{H}} z$. The formal solution can now be written as

$$z(\tau) \;=\; e^{\tau L_{\mathcal{H}}} z(0). \tag{5}$$

At this point we may apply well-known approximation techniques. For each decomposition of $\mathcal{H}$, i.e., $\mathcal{H} \;=\; \mathcal{H}_1 + \mathcal{H}_2 + \ldots$, the corresponding Lie-generator decomposes accordingly

$$L_{\mathcal{H}} \;=\; L_{\mathcal{H}_1} + L_{\mathcal{H}_2} + \ldots.$$

Using splitting schemes of the exponential function allows for a generation of numerical integrators. For example [23,21]:

$$e^{\tau(L_{\mathcal{H}_1}+L_{\mathcal{H}_2})} = e^{\tau L_{\mathcal{H}_1}} e^{\tau L_{\mathcal{H}_2}} + \mathcal{O}\left(\tau^2\right) \tag{6}$$

$$e^{\tau(L_{\mathcal{H}_1}+L_{\mathcal{H}_2})} = e^{\frac{\tau}{2} L_{\mathcal{H}_1}} e^{\tau L_{\mathcal{H}_2}} e^{\frac{\tau}{2} L_{\mathcal{H}_1}} + \mathcal{O}\left(\tau^3\right), \tag{7}$$

which can easily be extended to higher orders [24].

Note, that the choice of the $\mathcal{H}_k$ crucially influences the properties of the resulting integrator.

3.1 Symplectic Integrators

A well-known property of symplectic integrators is the conservation of the total energy within a very accurate deviation range even for long term simulations. It can be shown that symplectic integrators in application to Hamiltonian systems solve a system corresponding to a modified Hamiltonian with a small stepsize-dependent perturbation [8]. This leads to a "quasi conservation" of some first integrals, so that, for example, the total energy of the discrete solution oscillates around its initial value with a small amplitude that decreases with the stepsize used (cf. Fig. 1). This "structural stability" makes symplectic integrators superior for long term simulations.

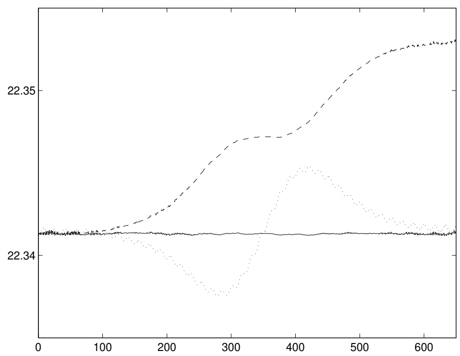

Fig. 1. Total energy (in kJ/mol) versus time (in fs) for different integrators for a collinear collision of a classical particle with a harmonic quantum oscillator (for details see [2]). Dashed line: Nonsymplectic scheme. Dotted: Symplectic integrator of first order. Solid: PICKABACK (symplectic, second order).

A convenient and constructive approach to attain symplectic maps is given by the composition of symplectic maps, which yields again a symplectic map. For appropriate $\mathcal{H}_k$, the splittings (6) and (7) are exactly of this form: If the $\mathcal{H}_k$ are Hamiltonians with respect to the whole system, then the $\exp(\tau L_{\mathcal{H}_k})$

define the phase flow generated by these $\mathcal{H}_k$. Thus, the $\exp(\tau L_{\mathcal{H}_k})$ are symplectic maps on the whole phase space and the compositions in (6) and (7) are symplectic maps, too. Moreover, in order to allow for a direct numerical realization, we have to find some $\mathcal{H}_k$ for which either $\exp(\tau L_{\mathcal{H}_k})$ has an analytic solution or a given symplectic integrator. We herein consider the first case only:

Pickaback We decompose $\mathcal{H}$ into a kinetic and a potential term:

$$\mathcal{H} = \mathcal{H}_1 + \mathcal{H}_2 \quad \text{with} \quad \mathcal{H}_1 = \frac{p^2}{2\,M} + \psi^* T\,\psi \quad \text{and} \quad \mathcal{H}_2 = \psi^* V(q)\,\psi.$$

As shown in [16], the two corresponding flow maps, $\exp(\tau L_{\mathcal{H}_1})$ and $\exp(\tau L_{\mathcal{H}_2})$, can be represented analytically. Using the second order Strang splitting (7), we derive an integration scheme which is explicit, symplectic and symmetric. This scheme was denoted Pickaback emphasizing the interwoven structure of the partial steps.

$$\begin{aligned}
q_{1/2} &= q_0 + \frac{\tau}{2}\frac{p_0}{M} \\
\psi_{1/2} &= \exp\Big(- i\frac{\tau}{2}T_N\Big)\,\psi_0 \\
p_1 &= p_0 - \tau\,\psi^*_{1/2}\,D_q V(q_{1/2})\psi_{1/2} \\
\psi_1 &= \exp\Big(- i\frac{\tau}{2}T_N\Big)\,\exp\Big(- i\tau V_N(q_{1/2})\Big)\,\psi_{1/2} \\
q_1 &= q_{1/2} + \frac{\tau}{2}\frac{p_1}{M}.
\end{aligned} \tag{8}$$

A main advantage of Pickaback is its reliability. But the reader might notice, that the splitting of the quantum propagator $\exp(-i\frac{\tau}{2}H)$ restricts the stepsize to the order of the inverse of the largest eigenvalue of H. Thus, the overall time steps are connected to the shortest significant period of phase oscillation in the quantum subsystem – demanding more evaluations of the pure classical forces than required by the classical motion itself. In order to circumvent the problem we switch to symmetric but no longer symplectic methods.

3.2 Symmetric Integration Schemes

Beneath the conservation properties of QCMD its equations of motion possess another important geometric structure by being time reversible. As shown in [10], the application of symmetric integrators to reversible problems yields the solution of a perturbed but again reversible problem. Hence, all the characteristics which are connected to reversibility are structurally inherited if the discretization scheme is symmetric.

The splitting technique, introduced above for the construction of symplectic schemes, is also adequate for symmetric ones. Now, the only condition is that we have to split $e^{\tau L_{\mathcal{H}}}$ symmetrically. To this end, let us consider the Liouville generator for the Hamiltonian $\mathcal{H}$ from above:

$$L_{\mathcal{H}} = \underbrace{(\nabla_q \mathcal{H})^T \nabla_p - (\nabla_p \mathcal{H})^T \nabla_q}_{L_{\mathcal{H}}^{cl}} + \underbrace{(\nabla_{q_\psi} \mathcal{H})^T \nabla_{p_\psi} - (\nabla_{p_\psi} \mathcal{H})^T \nabla_{q_\psi}}_{L_{\mathcal{H}}^{qm}}$$

decomposing as $L_{\mathcal{H}} = L_{\mathcal{H}}^{cl} + L_{\mathcal{H}}^{qm}$, with $L_{\mathcal{H}}^{cl}$ acting on the classical coordinates and $L_{\mathcal{H}}^{qm}$ acting on the quantum subsystem only. This permits to produce symmetric schemes via, for example, the second order Strang splitting:

$$e^{\tau L_{\mathcal{H}}} = e^{\frac{\tau}{2} L_{\mathcal{H}}^{qm}} \, e^{\tau L_{\mathcal{H}}^{cl}} \, e^{\frac{\tau}{2} L_{\mathcal{H}}^{qm}} + \mathcal{O}\left(\tau^3\right)$$

Using the symmetric Verlet algorithm for integrating $\exp(\tau L_{\mathcal{H}}^{cl})$ yields the following scheme (which formally is of second order):

$$\begin{array}{rrcl}
 & \psi_{1/2} & = & \exp\Big(-i\dfrac{\tau}{2\hbar} H(q_0)\Big)\, \psi_0 \\
\text{Leapfrog} \left\{ \begin{array}{l} \\ \\ \\ \end{array} \right. \!\!\!\!\!\! & \begin{array}{r} q_{1/2} \\ p_1 \\ q_1 \end{array} & \begin{array}{c} = \\ = \\ = \end{array} & \begin{array}{l} q_0 + \frac{\tau}{2} \frac{p_0}{M} \\ p_0 - \tau\, \psi_{1/2}^* D_q V(q_{1/2}) \psi_{1/2} \\ q_{1/2} + \frac{\tau}{2} \frac{p_1}{M} \end{array} \\
 & \psi_1 & = & \exp\Big(-i\dfrac{\tau}{2\hbar} H(q_1)\Big)\, \psi_{1/2}.
\end{array} \tag{9}$$

The question remains how to evaluate $\exp(-i\tau H(q_0)/(2\hbar))\psi_i$ while retaining the symmetric structure. In Sec. 4.2 we will introduce some iterative techniques for evaluating the matrix exponential but the approximative character of these techniques will in principle destroy the symmetry.

Symmetric multiple time stepping An intriguingly simple idea for realizing a symmetric approximation of the matrix exponential is presented in [19]. It copes with the different time scales of classical and quantum degrees of freedom by splitting the quantum propagation in some small "substeps". The resulting scheme is a variant of (9) with its quantum steps replaced by

$$\psi_{1/2} = \left(e^{-i\frac{\tau}{2\hbar n} H(q_0)}\right)^n \psi_0 = \left(e^{-i\frac{\tau}{4\hbar n} T}\, e^{-i\frac{\tau}{2\hbar n} V(q_0)}\, e^{-i\frac{\tau}{4\hbar n} T}\right)^n \psi_0 + \mathcal{O}\left(\frac{\tau^3}{n^2}\right)$$

The splitting of the quantum propagator negatively effects the efficiency of the scheme especially if m/M is small, i.e., if the quantum oscillation are much faster than the classical motion and the number n of substeps is becoming inefficiently large.

4 Adaptive Methods

4.1 Adaptive Stepsize Control

We have to pay a price for the advantages of 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 fulfills 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. In Numerical Analysis, such stepsize control strategies have extensively been discussed. In the following, we will give a brief overview on the usual strategy (for details cf. [4,9]). The conceptual framework 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 (9).

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 $||\hat{\epsilon}_\tau|| = \mathrm{TOL}$ in some adequate norm. In case of a tolerance exceeding error, i.e., for $||\hat{\epsilon}_\tau|| >$ TOL, one reduces the stepsize according to

$$\tau_{new} \;=\; \sqrt[p+1]{\frac{\rho\ \mathrm{TOL}}{||\hat{\epsilon}_\tau||}}\; \tau_{old}. \tag{10}$$

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 (10), we need an adequate norm for measuring the error. It obviously makes no sense to use an Euclidian 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:

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

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 (8) as Φ_q^τ together with a first order scheme based on the Trotter formula (6) replacing Φ_p^τ. Recalling that the stepsize of these methods are dominated by the splitting of $\exp(-i\tau H/\hbar)$, 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. An illustrative example of these drawbacks is given in Sec. 5.

4.2 A Verlet-based Adaptive Integrator

A more convincing approach leads to an adaptive method based on the symmetric second order scheme (9). 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:

2nd order symmetric scheme as Φ_q^τ

$$\left\{\begin{array}{rcl} \psi_{1/2} &=& \exp\left(-i\frac{\tau}{2\hbar}H(q_0)\right)\,\psi_0 \\ q_{1/2} &=& q_0 + \frac{\tau}{2}\frac{p_0}{M} \\ p_1 &=& p_0 - \tau\,\psi_{1/2}^*\,D_qV(q_{1/2})\psi_{1/2} \\ q_1 &=& q_{1/2} + \frac{\tau}{2}\frac{p_1}{M} \\ \psi_1 &=& \exp\left(-i\frac{\tau}{2\hbar}H(q_1)\right)\,\psi_{1/2} \end{array}\right. \tag{11}$$

For comparison: 1st order Euler scheme as Φ_p^τ

$$\left\{\begin{array}{rcl} \hat{\psi}_1 &=& \exp\left(-i\frac{\tau}{\hbar}H(q_0)\right)\,\psi_0 \\ \hat{q}_1 &=& q_0 + \tau\frac{p_0}{M} \\ \hat{p}_1 &=& p_0 - \tau\,\psi_{1/2}^*\,D_qV(\hat{q}_1)\psi_{1/2} \end{array}\right.$$

When considering the construction of *exactly* symmetric schemes, we are obstructed by the requirement to find *exactly* symmetric approximations to $\exp(-i\tau H/(2\hbar))$. But it is known [10], that the usual stepsize control mechanism destroys the reversibility of the discrete solution. Since we are applying this mechanism, we now may use approximations to $\exp(-i\tau H/(2\hbar))$ which are not precisely symmetric, i.e., 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.

Chebyshev approximation The well known expansion of $\exp(-i\tau H/\hbar)$ into Chebyshev polynomials T_k [22] is one of the most frequently used integration technique in numerical quantum dynamics:

$$\exp(-\tfrac{i}{\hbar}\,H\,\tau)\psi(t) \approx \textstyle\sum_{k=1}^{N} \alpha_k(\rho\tau)\,T_k(-\tfrac{i}{\hbar}H)\psi$$

with appropriately chosen coefficients α_k and an estimate ρ for the spectral radius of the Hamiltonian H. This technique allows for large stepsizes if the truncation index N is chosen large enough. The N necessary for achieving a specific accuary depends linearly on the stepsize τ and the spectral radius of H. We use an adaptive stopping criterion for the iteration based on the decay of the coefficients α_k [14].

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 [12,18,7]. After the iterative construction of the Krylov basis $\{v_1, \ldots, v_n\}$, the matrix exponential is approximated by using the representation A of $H(q)$ in this basis:

$$\exp\left(-\tfrac{i\tau}{\hbar}H(q)\right)\psi \;\approx\; V\,\exp\left(-\tfrac{i\tau}{\hbar}A\right)\,V^*\psi, \quad \text{with } V = [v_1, \ldots, v_n].$$

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

In [13], 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 the application problems of class 2b of Sec. 2. 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 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 [6] and a multi grid approach to the eigenvalue problem as introduced in [5]. Both techniques prove to be superior to the Lanczos approach for nearly adiabatic problems with very few eigenstates occupied (class 2a). But they quickly get inefficient if a nonadiabatic excitation of previously unimportant states is essential.

5 An Illustrative Example

In this section, the theoretical results are checked and illustrated by numerical simulations. Therefore we consider a well-known test problem which is of class 2b in our classification from page 4: a photo dissociation process of a collinear ArHCl molecule (see Fig. 2). 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 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 [16].

Obviously, one test example is not enough to illuminate all the effects pointed out previously. Thus, we have to concentrate herein on some main ideas. An extensively example-based comparison is in preparation [17].

The stepsize controlling adaptive QCMD integrators presented in the previous section differ only with respect to the approximation of the quantum propagation. We herein compare three of these integrators, all of them

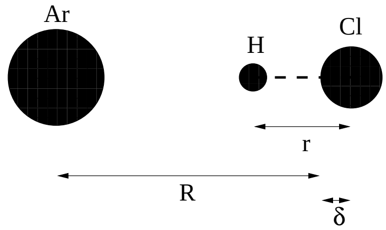

Fig. 2. Collinear ArHCl-system with the Jacobi-coordinates used.

equipped with the stepsize control mechanism (10): two integrators based on the pair of discretization schemes from page 9, with on one hand a Chebyshev approximation and on the other hand a Krylov approximation of the matrix exponential, and – just to show the stepsize restriction due to the splitting of the quantum propagator – a stepsize controlled Pickaback scheme.

To begin with, we compare the stepsizes used in the simulations (Fig. 3). 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. 3, the stepsize never increases above a given level. This level depends solely on the eigenvalues of the quantum Hamiltonian. When analyzing the other integrators, 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.

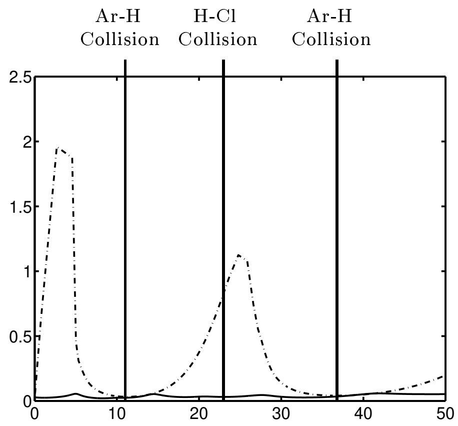

Fig. 3. Stepsize τ used in the simulation of the collinear photo dissociation of ArHCl: the adaptive Verlet-based exponential integrator using the Lanczos iteration (dash-dotted line) for the quantum propagation, and a stepsize controlling scheme based on PICKABACK (solid line). For a better understanding we have added horizontal lines marking the collisions (same tolerance TOL). We observe that the quantal H-Cl collision does not lead to any significant stepsize restrictions.

Large stepsizes result in a strong reduction of the number of force field evaluations per unit time (see left hand side of Fig. 4). This represents the major advantage of the adaptive schemes in comparison to structure conserving methods. On the right hand side of Fig. 4 we see the number of FFTs (i.e., matrix-vector multiplication) per unit time. As expected, we observe that the Chebyshev iteration requires about double as much FFTs than the Krylov techniques. This is due to the fact that only about half of the eigenstates of the Hamiltonian are essentially occupied during the process. This effect occurs even more drastically in cases with less states occupied.

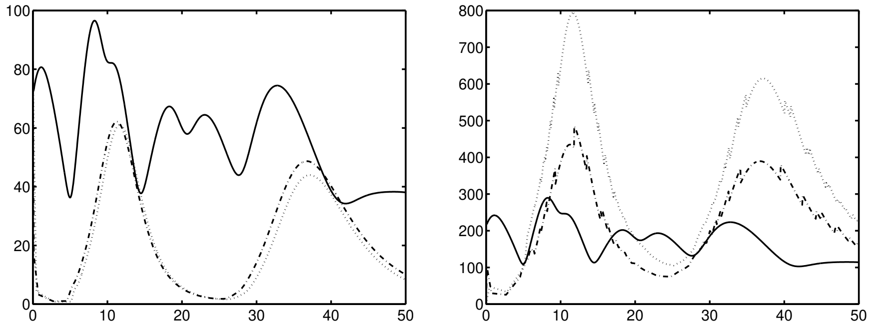

Fig. 4. Photo dissociation of ArHCl. Left hand side: the number of force field evaluations per unit time. Right hand side: the number of Fast-Fourier-transforms per unit time. Dotted line: adaptive Verlet with the Chebyshev approximation for the quantum propagation. Dash-dotted line: with the Lanczos iteration. Solid line: stepsize controlling scheme based on Pickaback. If the FFTs are the most expensive operations, Pickaback-like schemes are competitive, and the Lanczos iteration is significantly cheaper than the Chebyshev approximation.

Everything seems to be in favor of the stepsize controlling schemes, but the reader might notice, that there are —up to now— some drawbacks. When computing the autocorrelation function, e.g., the complex valued function $\psi(0)^*\psi(t)$, used for instance in the calculation of absorption spectra, we find a substantial phase shift in the discrete solution. This results from the fact that the error control mechanism is not adapted to detect phase errors because both schemes from page 9 depend on *pointwise* updates of the Hamiltonian only. It should be possible to overcome this problem by applying alternative Verlet-based schemes using *averaged* updates and forces. Promising candidates for these schemes were recently introduced by Hochbruck and Lubich (see [11] in this collection). Extensive numerical experiments using such schemes in the adaptive context introduced herein will be presented in a forthcoming paper [17].

6 Conclusions

We discussed numerical integration techniques for different classes of applications of QCMD. We mainly distinguished between *long* and *short term* simulations. Short term simulations are characterized by the fact that specific (global) accuracy requirements for the numerical solution make sense. For long term simulations one is more interested in certain stability and conservation properties of the solution, despite the fact that its global accuracy might be spoiled by the amplification of numerical error. Consequently, the advocated numerical techniques should be divided into two categories:

Long term simulations require "structurally stable" integrators. *Symplectic* and *symmetric* methods nearly perfectly reproduce structural properties of the QCMD equations, as, for example, the conservation of the total energy. We introduced an explicit symplectic method for the QCMD model — the PICKABACK scheme— and a symmetric method based on multiple time stepping.

For short-term simulations we advocate the use of *stepsize controlling* integrators which gain efficiency by adapting the stepsize to the dynamics of the system. We presented an adaptive Verlet-based exponential integrator for QCMD with iterative evaluation of the quantum propagation. It permits us to use stepsizes which are not restricted by the fast phase oscillations in the quantum part. For the iterative realization of the quantum propagation steps, we analyzed three different approaches: the Chebyshev approximation, the Lanczos iteration and a subspace controlling method. For the application problems with a (nearly) adiabatic behavior (class 2a from page 4), the subspace controlling method appeared to be best suited, because it does not artificially blow up the excited subspace. For all other cases of short-term simulation (class 2b), we advocate the Lanczos iteration scheme owing to its efficient adaption of the basis set to the dynamical behavior.

References

1. Bornemann, F. A.: Homogenization in time of singularly perturbed conservative mechanical systems. Manuscript (1997) 146pp
2. Bornemann, F. A., Nettesheim, P., Schütte, Ch.: Quantum-classical molecular dynamics as an approximation to full quantum dynamics. J. Chem. Phys., **105** (1996) 1074-1083
3. Bornemann, F. A., Schütte, Ch.: On the singular limit of the quantum-classical molecular dynamics model. Preprint SC 97-07 (1997) Konrad-Zuse-Zentrum Berlin. SIAM J. Appl. Math. (submitted)
4. P. Deuflhard and F. Bornemann: Numerische Mathematik II — Integration gewöhnlicher Differentialgleichungen. Walter de Gruyter, Berlin, New York (1994)
5. P. Deuflhard, T. Friese, F. Schmidt, R. März, and H.-P. Nolting: Effiziente Eigenmodenberechnung für den Entwurf integriert–optischer Chips.

In W. Jäger, Th. Lohmann, and H. Schunck, editors, Mathematik – Schlüsseltechnologie für die Zukunft. Springer Verlag.

6. B. Dietrich: Numerische Behandlung der zeitabhängigen Schrödingergleichung mit iterativen Unterraummethoden. Master's thesis, Freie Universität Berlin (1997)
7. V.L. Druskin and L.A. Knizhnerman: Krylov subspace approximation of eigenpairs and matrix functions in exact and computer arithmetics. *Num. Lin. Alg. Appl.*, **2** (1995) 205-217
8. E. Hairer and Ch. Lubich: The life-span of backward error analysis for numerical integrators. Numer. Math. **76** (1997) 441–462
9. E. Hairer, S.P. Nørsett, and G. Wanner: Solving Ordinary Differential Equations I, Nonstiff Problems. Springer Verlag, Berlin, Heidelberg, New York, Tokyo, 2nd edition (1993)
10. E. Hairer and D. Stoffer: Reversible long–term integration with variable step sizes. Report (1995)
11. M. Hochbruck and Ch. Lubich: A bunch of time integrators for quantum/classical molecular dynamics. (1997) (submitted to proceedings of MacroMM97)
12. M. Hochbruck and Ch. Lubich: On Krylov subspace approximations to the matrix exponential operator. SIAM J. Numer. Anal. **34** (1997) (to appear)
13. M. Hochbruck, Ch. Lubich, and H. Selhofer: Exponential integrators for large systems of differential equations. SIAM J. Sci. Comp. (1998) (to appear)
14. W. Huisinga: Faber-, Newton- und Krylov-Approximation zur Integration großer Differentialgleichungssysteme aus der Quantendynamik. Master's thesis, Freie Universität Berlin (1997)
15. Ronnie Kosloff: Quantum molecular dynamics on grids. In R. E. Wyatt and J. Z. Zhang, editors, Dynamics of Molecules and Chemical Reactions, pages 185–230. Marcel Dekker, New York (1996)
16. P. Nettesheim, F. A. Bornemann, B. Schmidt, and Ch. Schütte: An explicit and symplectic integrator for quantum-classical molecular dynamics. Chem. Phys. Lett. **256** (1996) 581–588
17. P. Nettesheim, Ch. Schütte, M. Hochbruck, and Ch. Lubich. (work in preparation)
18. T.J. Park and J.C. Light: Unitary quantum time evolution by iterative Lanczos reduction. J. Chem. Phys. **85** (1986) 5870–5876
19. U. Schmitt and J. Brickmann: Chem. Phys. **208(45)** (1996)
20. Schütte, Ch., Bornemann, F. A.: Approximation Properties and Limits of the Quantum-Classical Molecular Dynamics Model. Preprint SC 97-41 (1997) Konrad-Zuse-Zentrum Berlin (submitted to proceedings of MacroMM97)
21. G. Strang: On the construction and comparison of difference schemes. SIAM J. Numer. Anal. **5** (1968) 506–517
22. H. Tal-Ezer and R. Kosloff: An accurate and efficient scheme for propagating the time dependent Schrödinger equation. J. Chem. Phys. **81(9)** (1984) 3967–3971
23. H.F. Trotter: On the product of semi-groups of operators. Proc. Am. Math. Soc. **10** (1959) 545–551
24. H. Yoshida: Construction of higher order symplectic integrators. Physics Letters A **150** (1990) 262–268