Symplectic Multiple-Time-Stepping Integrators for Quantum-Classical Molecular Dynamics

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Abstract. The overall Hamiltonian structure of the Quantum-Classical Molecular Dynamics model makes – analogously to classical molecular dynamics – symplectic integration schemes the methods of choice for long-term simulations. This has already been demonstrated by the symplectic PICKABACK method [12]. However, this method requires a relatively small step-size due to the high-frequency quantum modes. Therefore, following related ideas from classical molecular dynamics, we investigate symplectic multiple-time-stepping methods and indicate various possibilities to overcome the step-size limitation of PICKABACK.

1 Introduction

In this paper, we consider the symplectic integration of the so-called Quantum-Classical Molecular Dynamics (QCMD) model. In the QCMD model (see [8,7,3,5,6] and references therein), most atoms are described by classical mechanics, but an important small portion of the system by quantum mechanics. This leads to a coupled system of Newtonian and Schrödinger equations.

We focus on so-called symplectic methods [18] for the following reason: It has been shown that the preservation of the symplectic structure of phase space under a numerical integration scheme implies a number of very desirable properties. Namely,

- symplectic methods preserve the total energy over very (exponentially) long periods of time up to small fluctuations [2,11,14] and
- symplectic methods also conserve the adiabatic invariants of the problem under consideration [15].

Note that the same results have not been shown for symmetric (time-reversible) integration methods, although symmetric methods seem to perform quite well in practice. For a discussion of symmetric methods in the context of the QCMD model see [16,17,13].

For ease of presentation, we consider the case of just one quantum degree of freedom with spatial coordinate x and mass m and N classical particles with coordinates $\boldsymbol{q} \in \mathcal{R}^{3N}$ and diagonal mass matrix $\boldsymbol{M} \in \mathcal{R}^{3N\times 3N}$. Upon denoting the interaction potential by $V(x,\boldsymbol{q})$, we obtain the following equations of motion for the QCMD model:

$$\begin{aligned} i\hbar\frac{\partial}{\partial t}\psi &= H(\boldsymbol{q})\,\psi\,, \\ \frac{\partial}{\partial t}\boldsymbol{q} &= \boldsymbol{M}^{-1}\boldsymbol{p}\,, \\ \frac{\partial}{\partial t}\boldsymbol{p} &= -\langle\psi,\nabla_{\boldsymbol{q}}V(\boldsymbol{q})\psi\rangle - \nabla_{\boldsymbol{q}}U_{cl}(\boldsymbol{q}) \end{aligned}$$

with U_{cl} a purely classical potential energy function and with $H(\boldsymbol{q})$ the quantum Hamiltonian operator given by

$$H(\boldsymbol{q}) = T + V(x,\boldsymbol{q}), \qquad T = -\frac{\hbar^2}{2m}\Delta_x.$$

In the sequel, we assume that the quantum subsystem has been truncated to a finite-dimensional system by an appropriate spatial discretization and a corresponding representation of the wave function ψ by a complex-valued vector $\boldsymbol{\psi} \in \mathcal{C}^d$. The discretized quantum operators T, V and H are denoted by $\boldsymbol{T} \in \mathcal{C}^{d\times d}$, $\boldsymbol{V}(\boldsymbol{q}) \in \mathcal{C}^{d\times d}$ and $\boldsymbol{H}(\boldsymbol{q}) \in \mathcal{C}^{d\times d}$, respectively. In the following construction of the time-propagators, we will exploit special matrix structures of some spatial discretizations:

a) $\boldsymbol{V}(\boldsymbol{q})$ is diagonal,
b) $\boldsymbol{H}(\boldsymbol{q})$ is real-valued, and
c) all other cases.

2 Conservation Properties of the QCMD model

For long-term simulations, it generally proves advantageous to consider numerical integrators which pass the structural properties of the model onto the calculated solutions. Hence, a careful analysis of the conservation properties of QCMD model is required. A particularly relevant constant of motion of the QCMD model is the total energy of the system

$$\mathcal{H} = \frac{\boldsymbol{p}^T \boldsymbol{M}^{-1} \boldsymbol{p}}{2} + \boldsymbol{\psi}^* \boldsymbol{H}(\boldsymbol{q}) \boldsymbol{\psi} + U_{cl}(\boldsymbol{q}). \tag{1}$$

Here $\boldsymbol{\psi}^*$ denotes the conjugate transpose of $\boldsymbol{\psi}$. Another conserved quantity is the norm of the vector $\boldsymbol{\psi}$, i.e., $\boldsymbol{\psi}^* \boldsymbol{\psi} = const.$ due to the unitary propagation of the quantum part.

In the context of this paper, the most important conservation property of QCMD is related to its canonical Hamiltonian structure which implies the symplecticness of the solution operator [1]. There are different ways to consider the QCMD model as a canonical Hamiltonian system with Hamiltonian (1). Here we follow the presentation given in [5,16]: We decompose the complex-valued vector $\boldsymbol{\psi}$ into its real and imaginary part, i.e.,

$$\boldsymbol{\psi} = \frac{1}{\sqrt{2\hbar}} (\boldsymbol{q}_\psi + i \boldsymbol{p}_\psi) \,.$$

Then, after introducing generalized positions $\boldsymbol{Q} = (\boldsymbol{q}_\psi^T, \boldsymbol{q}^T)^T \in \mathcal{R}^{d+3N}$ and generalized momenta $\boldsymbol{P} = (\boldsymbol{p}_\psi^T, \boldsymbol{p}^T)^T \in \mathcal{R}^{d+3N}$, the equations of motion can be written as

$$\begin{aligned} \frac{d}{dt} \boldsymbol{Q} &= +\nabla_{\boldsymbol{P}} \mathcal{H}(\boldsymbol{Q}, \boldsymbol{P}) \,, \\ \frac{d}{dt} \boldsymbol{P} &= -\nabla_{\boldsymbol{Q}} \mathcal{H}(\boldsymbol{Q}, \boldsymbol{P}) \,. \end{aligned}$$

These equations of motion are also time-reversible [13].

Finally, we like to mention that the QCMD model reduces to the Born-Oppenheimer approximation in case the ratio of the mass m of the quantum particles to the masses of the classical particles vanishes [6]. This implies that the populations $|\theta_i(t)|^2$, $i = 1, \ldots, k$, corresponding to the eigenvalues $E_i(\boldsymbol{q}(t)))$ of the operator $\boldsymbol{H}(\boldsymbol{q})$ become adiabatic invariants.

Note that the conservation of total energy and the conservation of the adiabatic invariants associated to the Born-Oppenheimer limit of the QCMD model provide a simple test for the behavior of a numerical integrator.

3 Construction of Symplectic Integrators

Our aim is the construction of numerical integrators which reproduce the conserved quantities in long-term simulations. To this end, we focus on symplectic methods, i.e., methods that conserve the

canonical structure of phase space [18]. A convenient way to derive symplectic methods for general Hamiltonian systems is based on an appropriate splitting of the Hamiltonian $\mathcal{H}$ into a sum of sub-Hamiltonians, e.g., the two-term decomposition $\mathcal{H}_1 + \mathcal{H}_2$, each of which corresponds either to an explicitly solvable system or has a given symplectic integrator [18]. This procedure can be illustrated using a phase space representation of the Hamiltonian flow. The time-evolution over Δt units of time is then given by $\exp(\Delta t L_{\mathcal{H}})$ where $L_{\mathcal{H}}$ is the Liouville operator of the whole system [18,12]. The Liouville operator $\exp(\Delta t L_{\mathcal{H}})$ can be approximated via the second order Strang splitting [18]:

$$\exp(\Delta t L_{\mathcal{H}}) \;=\; \exp(\frac{\Delta t}{2} L_{\mathcal{H}_1})\, \exp(\Delta t L_{\mathcal{H}_2})\, \exp(\frac{\Delta t}{2} L_{\mathcal{H}_1}) \;\; + \mathcal{O}(\Delta t^3). \tag{2}$$

The resulting numerical method is obviously symplectic since $\exp(\frac{\Delta t}{2} L_{\mathcal{H}_1})$ and $\exp(\Delta t L_{\mathcal{H}_2})$ are symplectic maps and the composition of symplectic maps yields a symplectic map.

The symplectic PICKABACK method [12], for instance, uses the following selection:

$$\mathcal{H}_1 = \frac{\boldsymbol{p}^T \boldsymbol{M}^{-1} \boldsymbol{p}}{2} + \boldsymbol{\psi}^* \boldsymbol{T} \boldsymbol{\psi} \qquad \text{and} \qquad \mathcal{H}_2 = \boldsymbol{\psi}^* \boldsymbol{V}(\boldsymbol{q}) \boldsymbol{\psi} + U_{cl}(\boldsymbol{q})\,.$$

The corresponding differential equations can be solved explicitly provided the operator $\boldsymbol{V}(\boldsymbol{q})$ is diagonal.

PICKABACK conserves total energy up to small fluctuations and the norm of the vector $\boldsymbol{\psi}$ exactly. Its main drawback is the step-size restriction which is of the order of the inverse of the largest eigenvalue of the quantum operator $\boldsymbol{H}(\boldsymbol{q})$. Thus, if the evaluation of the operator $\boldsymbol{V}(\boldsymbol{q})$ and the gradients $\nabla_{\boldsymbol{q}} \boldsymbol{V}(\boldsymbol{q})$ and $\nabla_{\boldsymbol{q}} U_{cl}(\boldsymbol{q})$ are expensive due to long-range interactions, then the PICKABACK scheme can become inefficient, i.e., the permitted step-size might be much smaller than required by the pure classical dynamics. To overcome this problem, symmetric integration schemes are considered in [16,17] and [13].

4 Symplectic Multiple-Time-Stepping Methods

Here we suggest a different approach that propagates the system using multiple step-sizes, i.e., few steps with step-size Δt are taken in the "slow" classical part whereas many smaller steps with step-size δt are taken in the highly oscillatory quantum subsystem (see, for example, [4] for symplectic multiple-time-stepping methods in the context of classical molecular dynamics). Therefore, we consider a splitting of the Hamiltonian $\mathcal{H} = \mathcal{H}_1 + \mathcal{H}_2$ in the following way:

$$\mathcal{H}_1 = \frac{\boldsymbol{p}^T \boldsymbol{M}^{-1} \boldsymbol{p}}{2} \qquad \text{and} \qquad \mathcal{H}_2 = \boldsymbol{\psi}^* \boldsymbol{H}(\boldsymbol{q}) \boldsymbol{\psi} + U_{cl}(\boldsymbol{q})\,.$$

Let us write down the corresponding differential equations. First for $\mathcal{H}_1$:

$$\begin{aligned} i\hbar \frac{d}{dt} \boldsymbol{\psi} &= \boldsymbol{0}\,, \\ \frac{d}{dt} \boldsymbol{q} &= \boldsymbol{M}^{-1} \boldsymbol{p}\,, \\ \frac{d}{dt} \boldsymbol{p} &= \boldsymbol{0}\,, \end{aligned}$$

next for $\mathcal{H}_2$:

$$i\hbar \frac{d}{dt} \boldsymbol{\psi} = \boldsymbol{H}(\boldsymbol{q}) \boldsymbol{\psi}\,, \tag{3}$$

$$\frac{d}{dt} \boldsymbol{q} = \boldsymbol{0}\,, \tag{4}$$

$$\frac{d}{dt} \boldsymbol{p} = -\boldsymbol{\psi}^* \nabla_{\boldsymbol{q}} \boldsymbol{V}(\boldsymbol{q}) \boldsymbol{\psi} - \nabla_{\boldsymbol{q}} U_{cl}(\boldsymbol{q})\,. \tag{5}$$

The solution to $\mathcal{H}_1$ is just a translation of classical particles with constant momentum $\boldsymbol{p}$.

The intriguing point about the second set of equations is that $\boldsymbol{q}$ is now kept constant. Thus the vector $\boldsymbol{\psi}$ evolves according to a time-independent Schrödinger equation and the update of the classical momentum $\boldsymbol{p}$ is obtained by integrating the Hellmann-Feynman forces [5] acting on the classical particles along the computed $\boldsymbol{\psi}(t)$ (plus a constant update due to the purely classical force field).

Upon computing the eigenvalues of the operator $\boldsymbol{H}(\boldsymbol{q})$, the equations (3)-(5) can be solved exactly. However, this is, in general, an expensive undertaken. Therefore we proceed with the following multiple-time-stepping approach: The first step is to consider the identity

$$\exp(\Delta t L_{\mathcal{H}_2}) = \underbrace{\exp(\delta t L_{\hat{\mathcal{H}}_2}) \cdots \exp(\delta t L_{\hat{\mathcal{H}}_2})}_{j\ times} \exp(\Delta t L_{U_{cl}})\,,$$

where $\delta t = \Delta t/j$, j even, and

$$\hat{\mathcal{H}}_2 = \boldsymbol{\psi}^* \boldsymbol{H}(\boldsymbol{q}) \boldsymbol{\psi}\,.$$

The second step is to use this identity in (2) which yields

$$\exp\left(\Delta t L_{\mathcal{H}}\right) = \exp(\frac{\Delta t}{2} L_{\mathcal{H}_1}) \underbrace{\exp(\delta t L_{\hat{\mathcal{H}}_2}) \cdots \exp(\delta t L_{\mathcal{H}_2})}_{j\,times} \exp(\Delta t L_{U_{cl}})\ \exp(\frac{\Delta t}{2} L_{\mathcal{H}_1}) + \\ + \mathcal{O}(\Delta t^3)\,.$$

The last step is to find a symplectic, second order approximation $\Phi_{\delta t}$ to $\exp(\delta t L_{\hat{\mathcal{H}}_2})$. In principle, we can use any symplectic integrator suitable for time-dependent Schrödinger equations (see, for example, [9]). Here we focus on the following three different possibilities corresponding to special properties of the spatially truncated operators $\boldsymbol{H}(\boldsymbol{q})$ and $\boldsymbol{V}(\boldsymbol{q})$.

a) Provided that $\boldsymbol{V}(\boldsymbol{q})$ *is diagonal*, an efficient method $\Phi_{\delta t}$ is obtained by exploiting the natural splitting of the quantum operator $\boldsymbol{H}(\boldsymbol{q}) = \boldsymbol{T} + \boldsymbol{V}(\boldsymbol{q})$ in a procedure similar to the one used in PICKABACK. This yields two exactly solvable subsystems [12]

$$\hat{\mathcal{H}}_{2,1} = \boldsymbol{\psi}^* \boldsymbol{T} \boldsymbol{\psi} \qquad \text{and} \qquad \hat{\mathcal{H}}_{2,2} = \boldsymbol{\psi}^* \boldsymbol{V}(\boldsymbol{q}) \boldsymbol{\psi}\,.$$

Again, we use (2) to construct a symplectic, second order approximation $\Phi_{\delta t}$ to $\exp(\delta t\, L_{\hat{\mathcal{H}}_2})$. The resulting integrator for QCMD is of second order, explicit, symplectic, and conserves the norm of the wave-function:

$$\begin{aligned}
\boldsymbol{q}_{1/2} &= \boldsymbol{q}_0 + \frac{\Delta t}{2} \boldsymbol{M}^{-1} \boldsymbol{p}_0\,, \\
\hat{\boldsymbol{p}}_0 &= \boldsymbol{p}_0 - \Delta t \nabla_{\boldsymbol{q}} V_{cl}(\boldsymbol{q}_{1/2})\,, \\
j \text{ times the} \\ \text{application of } \Phi_{\delta t}; \\ k = 1 \ldots j
&\left\{ \begin{aligned}
\hat{\boldsymbol{\psi}}_{k/j} &= \exp\left(-\tfrac{i}{\hbar}\tfrac{\delta t}{2} \boldsymbol{T}\right)\ \boldsymbol{\psi}_{(k-1)/j} \\
\hat{\boldsymbol{p}}_{k/j} &= \hat{\boldsymbol{p}}_{(k-1)/j} \ - \ \delta t\ \hat{\boldsymbol{\psi}}^*_{k/j} \nabla_{\boldsymbol{q}} \boldsymbol{V}(\boldsymbol{q}_{1/2}) \hat{\boldsymbol{\psi}}_{k/j} \\
\boldsymbol{\psi}_{k/j} &= \exp\left(-\tfrac{i}{\hbar}\tfrac{\delta t}{2} \boldsymbol{T}\right)\ \exp\left(-\tfrac{i}{\hbar} \delta t\, \boldsymbol{V}(\boldsymbol{q}_{1/2})\right)\ \hat{\boldsymbol{\psi}}_{k/j}
\end{aligned} \right. \\
\boldsymbol{p}_1 &= \hat{\boldsymbol{p}}_1\,, \\
\boldsymbol{q}_1 &= \boldsymbol{q}_{1/2} + \frac{\Delta t}{2} \boldsymbol{M}^{-1} \boldsymbol{p}_1\,.
\end{aligned}$$

b) If the spatially discretized quantum Hamiltonian operator $\boldsymbol{H}(\boldsymbol{q})$ is *real-valued*, i.e.,

$$\mathcal{H} = \frac{1}{2\hbar}\boldsymbol{q}_\psi^T H(\boldsymbol{q})\boldsymbol{q}_\psi + \frac{1}{2\hbar}\boldsymbol{p}_\psi^T \boldsymbol{H}(\boldsymbol{q})\boldsymbol{p}_\psi + \frac{1}{2}\boldsymbol{p}^T \boldsymbol{M}^{-1}\boldsymbol{p} + U_{cl}(\boldsymbol{q})\,,$$

then the Hamiltonian $\hat{\mathcal{H}}_2$ can be written as

$$\hat{\mathcal{H}}_2 = \underbrace{\frac{1}{2\hbar}\boldsymbol{q}_\psi^T \boldsymbol{H}(\boldsymbol{q})\boldsymbol{q}_\psi}_{\hat{\mathcal{H}}_{2,1}} + \underbrace{\frac{1}{2\hbar}\boldsymbol{p}_\psi^T \boldsymbol{H}(\boldsymbol{q})\boldsymbol{p}_\psi}_{\hat{\mathcal{H}}_{2,2}}$$

and the equations of motion corresponding to each of the two terms in the Hamiltonian $\hat{\mathcal{H}}_2$, namely

$$\begin{aligned}
\hbar\frac{d}{dt}\boldsymbol{q}_\psi &= \boldsymbol{0}\,,\\
\hbar\frac{d}{dt}\boldsymbol{p}_\psi &= -\boldsymbol{H}(\boldsymbol{q})\boldsymbol{q}_\psi\,,\\
\frac{d}{dt}\boldsymbol{q} &= \boldsymbol{0}\,,\\
\frac{d}{dt}\boldsymbol{p} &= -\frac{1}{2\hbar}\boldsymbol{q}_\psi^T\nabla_{\boldsymbol{q}}\boldsymbol{V}(\boldsymbol{q})\boldsymbol{q}_\psi\,,
\end{aligned}$$

and

$$\begin{aligned}
\hbar\frac{d}{dt}\boldsymbol{q}_\psi &= \boldsymbol{H}(\boldsymbol{q})\boldsymbol{p}_\psi\,,\\
\hbar\frac{d}{dt}\boldsymbol{p}_\psi &= \boldsymbol{0}\,,\\
\frac{d}{dt}\boldsymbol{q} &= \boldsymbol{0}\,,\\
\frac{d}{dt}\boldsymbol{p} &= -\frac{1}{2\hbar}\boldsymbol{p}_\psi^T\nabla_{\boldsymbol{q}}\boldsymbol{V}(\boldsymbol{q})\boldsymbol{p}_\psi\,,
\end{aligned}$$

can be solved analytically. Thus we define

$$\Phi_{\delta t} = \exp\left(\frac{\delta t}{2}L_{\hat{\mathcal{H}}_{2,1}}\right)\,\exp(\delta t L_{\hat{\mathcal{H}}_{2,2}})\,\exp\left(\frac{\delta t}{2}L_{\hat{\mathcal{H}}_{2,1}}\right)\,.$$

For stability reasons, the micro-step-size δt has to be chosen smaller than the inverse of the largest eigenvalue of the (scaled) truncated quantum operator $\hbar^{-1}\boldsymbol{H}(\boldsymbol{q})$. This can imply a very small value of δt compared to the macro-step-size Δt.

c) The most straightforward but also an expensive $\Phi_{\delta t}$ is obtained by discretizing the equations of motion corresponding to $\hat{\mathcal{H}}_2$ by the (symplectic) implicit midpoint rule which results in

$$\begin{aligned}
\boldsymbol{\psi}_{k/j} &= \boldsymbol{\psi}_{(k-1)/j} + \delta t\,\boldsymbol{H}(\boldsymbol{q_{1/2}})\boldsymbol{\psi}_{(k-1/2)/j}\,,\\
\hat{\boldsymbol{p}}_{k/j} &= \hat{\boldsymbol{p}}_{(k-1)/j} - \delta t\,\boldsymbol{\psi}^*_{(k-1/2)/j}\nabla_{\boldsymbol{q}}\boldsymbol{V}(\boldsymbol{q_{1/2}})\boldsymbol{\psi}_{(k-1/2)/j}\,,
\end{aligned}$$

$k = 1, \ldots, j$, with $\boldsymbol{\psi}_{(k-1/2)/j} = (\boldsymbol{\psi}_{k/j} + \boldsymbol{\psi}_{(k-1)/j})/2$. Note that each integration step requires the solution of a d-dimensional linear system of equations in the unknown $\boldsymbol{\psi}_{k/j}$.

Our multiple-time-stepping methods are close to methods suggested in [16,17]. The method considered in [16] is time-reversible but not symplectic. More importantly, the method updates the

momenta $\boldsymbol{p}$ of all classical particles only once per macro-time-step Δt. As indicated in [10,13], this might lead to a substantial phase drift in the discrete solution. In [10], an averaging procedure of the quantum-classical Hellmann-Feynman force field along $\boldsymbol{\psi}(t)$ is suggested to overcome this problem. Note that, for the multiple-time-stepping schemes suggested here, this averaging is carried out automatically and is a direct consequence of proposed splitting of the Hamiltonian equations of motion. We finally like to mention that symplectic methods are also discussed in [17]. In particular, the suggested methods are symplectic in the quantum part and the classical part if considered separately. However, this does not imply that the overall method is symplectic.

5 Conclusions

We have derived time-reversible, symplectic, and second-order multiple-time-stepping methods for the finite-dimensional QCMD model. Theoretical results for general symplectic methods imply that the methods conserve energy over exponentially long periods of time up to small fluctuations. Furthermore, in the limit $m \to 0$, the adiabatic invariants corresponding to the underlying Born-Oppenheimer approximation will be preserved as well. Finally, the phase shift observed for symmetric methods with a single update of the classical momenta $\boldsymbol{p}$ per macro-time-step Δt should be avoided by the suggested methods. The additional costs for this frequent update per micro-time-step δt are relatively low. Note that the update only requires taking the inner product $\boldsymbol{\psi}^* \nabla_{\boldsymbol{q}} \boldsymbol{V}(\boldsymbol{q}) \boldsymbol{\psi}$ with respect to a constant gradient $\nabla_{\boldsymbol{q}} \boldsymbol{V}(\boldsymbol{q})$ and only with respect to those classical particles that interact with the quantum degree of motion.

Acknowledgement. It is a pleasure to thank Christof Schütte for discussions on the subject of this paper.

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