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**An**  
**Explicit and Symplectic Integrator**  
**for**  
**Quantum–Classical**  
**Molecular Dynamics**

# An Explicit and Symplectic Integrator for Quantum-Classical Molecular Dynamics

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## Abstract

This paper presents an explicit and symplectic integrator called PICK-ABACK for quantum-classical molecular dynamics. This integration scheme is time reversible and unitary in the quantum part. We use the Lie formalism in order to construct a formal evolution operator which then is split using the Strang splitting yielding the symplectic discretization PICKABACK. Finally the new method is compared with a hybrid method in application to two examples: a collinear collision with a quantum oscillator and additionally a photodissociation process of a collinear ArHCl-molecule.

**Keywords:** quantum-classical molecular dynamics, mixed quantum-classical models, symplecticity, symplectic integration, explicit integrators, Lie formalism, Trotter formula, Strang splitting, photodissociation of collinear ArHCl.

**AMS classification:** 65L20, 81V55, 92C40

# 1 Introduction

Mixed quantum classical models have attracted much interest in molecular dynamics (MD). This is due to the obstacles of either full quantum mechanical and pure classical calculations. Quantum models show a far too large complexity to be practically solved for the interesting molecules whereas classical models do not describe "deeply" quantum mechanical processes, for example proton-transfer reactions.

There is a great variety of quantum-semiclassical (QSCMD) [14] and quantum-classical (QCMD) models [8][9][15][16] in use. We consider a QCMD model that is mathematically derivable from full quantum dynamics [11].

It was revealed that this model has got a canonical Hamiltonian structure [11], which implies symplecticity and the conservation of energy. This paper presents the construction of an efficient integrator, which passes these properties to the discrete solution.

Obviously, the *energy exchange* between the quantum and the classical part of the molecular system is of main importance for the dynamical process. Hence, an accurate reproduction of the energies in the system is an urgent requirement for all discretization schemes. However, there are no efficient schemes which conserve the energy *exactly*. For all practical reasons it is sufficient to use so called *symplectic* discretizations, which conserve the energy within a *very accurate* deviation range even for *long time simulations*, cf. [19]. In contrast to this, ad hoc schemes typically cause an *energy drift* which increases in time — thus being not appropriate for our problem.

In §2, our discussion starts with the analysis of the structure of the QCMD model used.

On the way to an explicit and symplectic integration scheme it follows the red thread of an approach proposed by, e.g, [23] [19]: in §3, we use the Lie formalism to construct a formal evolution operator for the full system and to split it into symplectic parts. By deriving analytically a representation for these parts, we obtain an explicit and symplectic method called PICKABACK producing the same numerical effort as an often used hybrid method. More than that, our integration scheme is time reversible and unitary, thus conserving the norm of the wave function of the quantum part.

Finally, in §4, we want to present the advantages of our integration method by comparing it with the method mentioned above in application to two illustrative examples: a collinear collision with a quantum oscillator and additionally a photodissociation process of a collinear ArHCl-molecule. The integration scheme PICKABACK leads to a significantly smaller error transport in these comparisons.

## 2 The QCMD-Model

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.

Let  $q \in \mathbf{R}^d$  and  $x \in \mathbf{R}^d$  be the space coordinates and  $m$  and  $M$  be the masses of the quantum particle and the classical particle respectively. Moreover, let the interaction potential between them be  $V = V(x, q)$ . The quantum particle is described by the wavefunction  $\psi = \psi(x, t)$  and obeys Schrödinger's equation with a parameterized potential which depends on the position  $q = q(t)$  of the classical particle. 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  $\psi$ .

$$\begin{aligned} i\dot{\psi} &= H_{QM}(t) \psi \quad \text{with} \quad H_{QM}(t) = \underbrace{-\frac{\hbar^2}{2m} \Delta_x + V(x, q(t))}_T \\ \dot{q} &= D_p H_C(t) \\ \dot{p} &= -D_q H_C(t) \quad \text{with} \quad H_C(t) = \frac{p^2}{2M} + \langle \psi(t), V(\cdot, q) \psi(t) \rangle. \end{aligned} \quad (1)$$

The total energy expectation value of the system, to which we will simply refer as "energy" in the following, reads as (cf., [11]):

$$\mathcal{H} = \langle \psi, T \psi \rangle + \langle \psi, V(\cdot, q) \psi \rangle + \frac{p^2}{2M}. \quad (2)$$

For the purpose of finding an integrator that fits into the mathematical structure of this system, it is helpful to note that this QCMD system constitutes a canonical system with respect to the Hamilton function  $\mathcal{H}$ , i.e., can be described formally in terms of classical mechanics. To illustrate this, we decompose the wavefunction into a scaled real and imaginary part:

$$\psi = \frac{1}{\sqrt{2\hbar}}(q_\psi + i p_\psi).$$

Now, after introducing a generalized position and momentum

$$Q = (q_\psi, q)^T \quad P = (p_\psi, p)^T$$

and some formal calculations (using functional derivatives) the system (1) can be written as

$$\dot{Q} = \frac{\partial}{\partial P} \mathcal{H} \quad \dot{P} = -\frac{\partial}{\partial Q} \mathcal{H}.$$

The theory of classical mechanics [4] asserts for every phase flow corresponding to a Hamilton function not only the conservation of energy but also of the symplectic structure. The latter implies volume conservation in phase space (Liouville's theorem), but is more general.

### 3 Discretizations for the QCMD model

The QCMD model consists of a partial differential equation (PDE) coupled with a system of ordinary differential equations (ODE). Therefore we have to carry out two discretization steps. The first step is a spatial discretization of the PDE by applying Fourier-collocation methods [18]. In a second step, then, we introduce the time discretization PICKABACK.

As a result of the spatial discretization we obtain the following system:

$$\begin{aligned} i\dot{\psi}_N &= (T_N + V_N(q))\psi_N \\ \dot{q} &= D_p\left(\frac{p^2}{2M} + \psi_N^* V_N(q) \psi_N\right) = \frac{p}{M} \\ \dot{p} &= -D_q\left(\frac{p^2}{2M} + \psi_N^* V_N(q) \psi_N\right). \end{aligned} \quad (3)$$

In the case of Fourier-collocation we consider the vector  $\psi_N$  and the matrices  $T_N, V_N$  as discretizations of the state  $\psi$  and the operators  $T, V$  with respect to the meshpoints chosen.

Note the possibility to use a Fourier-Galerkin approach [13] for the spatial discretization. Then  $\psi_N$  is a vector of the expansion coefficients and  $T_N$  and  $V_N$  are the matrix representations of the operators  $T$  and  $V$ , respectively.

Formally, both spatial discretizations lead to the same system (3), but Fourier-collocation results in a diagonal matrix  $V_N$  whereas Fourier-Galerkin does not. The diagonal structure of  $V_N$  will be an advantage later on.

Now one can easily show that this semidiscrete system also corresponds to a set of canonical equations

$$\begin{aligned} \dot{Q}_N &= \frac{\partial}{\partial P_N} \mathcal{H}_N \\ \dot{P}_N &= -\frac{\partial}{\partial Q_N} \mathcal{H}_N \end{aligned} \quad (4)$$

using  $\psi_N = \frac{1}{\sqrt{2}}(x_N + iy_N)$ ,  $\mathcal{Q}_N = (x_N, q)^T$  and  $\mathcal{P}_N = (y_N, p)^T$  together with the Hamilton function

$$\mathcal{H}_N = \frac{p^2}{2M} + \psi_N^* T_N \psi_N + \psi_N^* V_N(q) \psi_N. \quad (5)$$

### 3.1 The symplectic PICKABACK integration scheme

Introducing the Poisson brackets [4] helps us to write the Hamilton equations of motion (4) as (cf. [23][19]):

$$\dot{z} = L_{\mathcal{H}_N} z \quad (6)$$

where  $z = (Q_N, P_N)^T$  and  $L_{\mathcal{H}_N} z_i = \{z_i, \mathcal{H}_N\}$ .

It should be noted, that the kind of coupling between the quantum and the classical degrees of freedom in QCMD causes the operator  $L_{\mathcal{H}_N}$  to be nonlinear with respect to  $z$ .

$L_{\mathcal{H}_N}$  can be understood as Lie generator of the flow connected to  $\mathcal{H}_N$ , so that we obtain the formal solution to (6) as

$$z(\tau) = e^{\tau L_{\mathcal{H}_N}} z(0). \quad (7)$$

The Hamilton function (5) decomposes as:

$$\begin{aligned} \mathcal{H}_N &= \mathcal{H}_1 + \mathcal{H}_2 \\ \mathcal{H}_1 &= \frac{p^2}{2M} + \psi_N^* T_N \psi_N \\ \mathcal{H}_2 &= \psi_N^* V_N(q) \psi_N. \end{aligned}$$

In this case we might also write  $L_{\mathcal{H}} z = (L_{\mathcal{H}_1} + L_{\mathcal{H}_2})z$  where every  $L_{\mathcal{H}_i}$  is again a Lie generator of the flow to the altered Hamilton function  $\mathcal{H}_i$ . This allows us to approximate the formal solution (7) with either the Trotter formula or with the Strang splitting.

The Trotter formula [22] yields an  $\mathcal{O}(\tau^2)$  approximation:

$$e^{\tau L_{\mathcal{H}_N}} = e^{\tau(L_{\mathcal{H}_1} + L_{\mathcal{H}_2})} = e^{\tau L_{\mathcal{H}_1}} e^{\tau L_{\mathcal{H}_2}} + \mathcal{O}(\tau^2), \quad (8)$$

whereas Strang splitting [21] results in an  $\mathcal{O}(\tau^3)$  approximation:

$$\begin{aligned} e^{\tau L_{\mathcal{H}_N}} &= e^{\tau(L_{\mathcal{H}_1} + L_{\mathcal{H}_2})} \\ &= e^{\frac{\tau}{2} L_{\mathcal{H}_1}} e^{\tau L_{\mathcal{H}_2}} e^{\frac{\tau}{2} L_{\mathcal{H}_1}} + \mathcal{O}(\tau^3). \end{aligned} \quad (9)$$

This decomposition is quite similar to the Baker-Campbell-Hausdorff-formula which holds for the case of linear operators — in application to quantum-mechanical systems it is also known as split operator technique [5]. However, one should note, that a splitting of higher order is possible as well but, unfortunately, results in *negative* time steps which might be numerically *not stable* [12].

Obviously, each  $e^{\tau L_{\mathcal{H}_i}}$  is a symplectic map because it consists of an exact propagator to the phase flows of the altered Hamiltonian function  $\mathcal{H}_i$ . Thus, (8) and (9) are a composition of symplectic maps and are symplectic, too.

Now, the individual propagators of (9) deserve our full attention. For the purpose of constructing an overall symplectic integration scheme we are obliged to find an exact realization or at least a symplectic approximation of the order  $\mathcal{O}(\tau^3)$  for each of them. Fortunately, this kind of decomposition of the Hamilton function allows the former way. The calculation of the exact solution to the Hamilton functions  $\mathcal{H}_1$  and  $\mathcal{H}_2$  is presented in the appendix.

If we use the results of the appendix and arrange them in the way of (9), we obtain the integration scheme PICKABACK which is *explicit* and *symplectic* as well as *time reversible* and (in the quantum part) *unitary*.

$$\begin{aligned}
q_{1/2} &= q_0 + \frac{\tau p_0}{2M} \\
(\psi_N)_{1/2} &= \exp\left(-i\frac{\tau}{2}T_N\right)(\psi_N)_0 \\
p_1 &= p_0 - \tau(\psi_N)_{1/2}^* D_q V(q_{1/2})(\psi_N)_{1/2} \\
(\psi_N)_1 &= \exp\left(-i\frac{\tau}{2}T_N\right) \exp\left(-i\tau V_N(q_{1/2})\right)(\psi_N)_{1/2} \\
q_1 &= q_{1/2} + \frac{\tau p_1}{2M}.
\end{aligned} \tag{10}$$

**Remark.** The reader should note, that the same construction starting with the Trotter formula (8) results in a symplectic but not time reversible scheme causing almost as much computational effort as PICKABACK but being  $\mathcal{O}(\tau^2)$  accurate only.

### 3.2 A hybrid method for comparison

For comparison with the integration scheme PICKABACK (10) we make use of an often applied method (cf., [6]) constructed out of two uncoupled integration schemes, i.e., one integrator is applied to the quantum subsystem keeping the classical degrees of freedom unchanged whereas the other one acts on the classical subsystem. In our further investigation we will call such an approach a hybrid method.

Now, we analyze the approximation order of a hybrid method. *In every time step*, the integrator of the quantum subsystem solves:

$$i\dot{\psi}_N = (T_N + V_N(q_0))\psi_N \quad \text{where } q_0 \text{ is constant.}$$

The integrator of the classical subsystem propagates:

$$\begin{aligned} \dot{q} &= \frac{p}{M} \\ \dot{p} &= -D_q \psi_N^* V_N(q) \psi_N \quad \text{with a constant parameter } \psi_N. \end{aligned}$$

Such a hybrid method can be understood as *dimensional splitting* [20] of the state space in two separately solved subspaces. This approach allows us to compose the two subsystem-integrators via the Trotter formula or the Strang splitting. Hence, a method which propagates first the quantum part and then the classical — or vice versa — results analogously to the Trotter formula in a scheme of the approximation order  $\mathcal{O}(\tau^2)$ .

The reader should note that the Trotter formula arranges the two integrators one after the other — whereas in the literature [6] both are based on the same initial values per step. However, this has no effect on the approximation order. In the following, we apply this latter *parallel* composition to the model problems.

It is *not* possible to write the individual subsystem-propagators as evolutions of a flow of any Hamilton function which acts on the *full* system. *Thus, the resulting propagators are only symplectic in the corresponding subsystem and not in the total system, i.e., the method is not symplectic with respect to the full system.* One could say that both integrators try to keep the energy of their subsystem unchanged — not taking notice of the coupling energy.

We see, that independently of the order of the subsystem-integrators we get a method of the order  $\mathcal{O}(\tau^2)$ . Realizations of a hybrid method use, for example, a Leapfrog (Verlet) [2] integrator for the classical subsystem together with a split operator scheme [5] for the quantum part.

Hybrid method		PICKABACK
$q_{1/2} =$	$q_0 + \frac{\tau}{2} \frac{p_0}{M}$	
$p_1 =$	$p_0 - \tau (\psi_N)_0^* D_q V(q_{1/2}) (\psi_N)_0$	$p_0 - \tau (\psi_N)_{1/2}^* D_q V(q_{1/2}) (\psi_N)_{1/2}$
$q_1 =$	$q_{1/2} + \frac{\tau}{2} \frac{p_1}{M}$	
$(\psi_N)_{1/2} =$	$e^{-i\frac{\tau}{2} T_N} (\psi_N)_0$	
$(\psi_N)_1 =$	$e^{-i\frac{\tau}{2} T_N} e^{-i\tau V_N(q_0)} (\psi_N)_{1/2}$	$e^{-i\frac{\tau}{2} T_N} e^{-i\tau V_N(q_{1/2})} (\psi_N)_{1/2}$



If one compares PICKABACK with the hybrid method one discovers that they differ only in the update of  $q$  and  $\psi_N$  in the potential evaluations. Thus, both methods require the same computational effort.

## 4 Numerical Results

We shall now illustrate the advantages of our integration scheme PICKABACK by numerical simulations. Therefore we have compared our symplectic integration scheme (10) with the hybrid method described above in application to two essentially different model problems.

The first example models a collinear collision of a heavy particle with a harmonic oscillator deserving a long-term simulation caused by the slow dynamics of the system.

The other one is a collinear model for the photodissociation of an Ar-HCl molecule similar to the studies of XeHI in [1]. In the following a comparison with an "exact" solution means a comparison with a solution calculated with extremely high precision.

### 4.1 Collinear collision with a quantum oscillator

Let us first have a look at a simple collinear collision of a heavy "classical" particle (with mass  $M = 40\text{u}$ ) with a harmonic quantum oscillator (mass  $m = 1\text{u}$ ), a model problem which has been treated extensively in the literature [7][9][11]. Using the notation of Section 2, the potential  $V(x, q) = V_{\text{osc}}(x) + V_{\text{coupling}}(x, q)$  is composed of a potential for the quantum part and the coupling potential:

$$V_{\text{osc}}(x) = \frac{m}{2}\omega^2 x^2; \quad V_{\text{coupling}}(x, q) = a \exp(-b|x - q|);$$

with the parameters:

$$\hbar\omega = 2.86 \frac{\text{kcal}}{\text{mol}}; \quad a = 1.654 \cdot 10^2 \frac{\text{kcal}}{\text{mol}} \quad \text{and} \quad b = 2.438 \text{\AA}^{-1}.$$

The initial wavepacket is constructed using the ground state of the undisturbed oscillator, while the classical particle has the initial location  $q(0) = 5 \text{\AA}$  and an initial momentum directed towards the oscillator. However, the initial energy of the full system is 5.34 kcal/mol. We have performed QCMD-calculations applying uniform time steps  $\tau = 0.05$  fs over a total time interval  $t/\text{fs} \in [0, 650]$  and in the quantum part a spatial computation

domain  $x/\text{\AA} \in [-1, 0.5]$  with 256 meshpoints. For a further study of the reliability of the QCMD-model in comparison with a full quantum model for this model problem see [11].

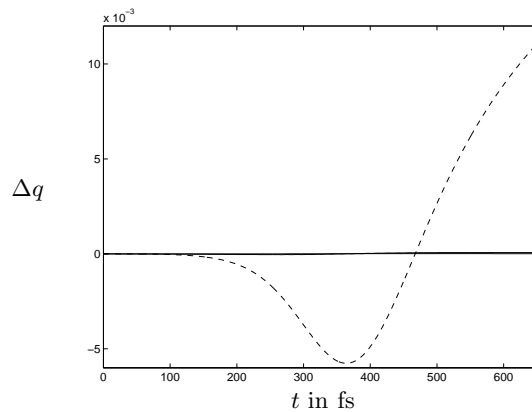


Figure 1: Error  $\Delta q$  in classical coordinate in percentages of an exact solution of example 1. Results of an integration with PICKABACK (solid line) and the hybrid method (dashed line). The result of the symplectic Trotter scheme (see remark on page 5) is almost totally covered by the solid line. Thus we see, the error of the symplectic methods vanishes compared with the error of the hybrid method.

Figure 1 presents the position error  $\Delta q$  of the classical coordinate in percent of an exact solution. Obviously we miscalculate the spatial coordinates if the integrator does not inherit the symplecticity of the exact propagator.

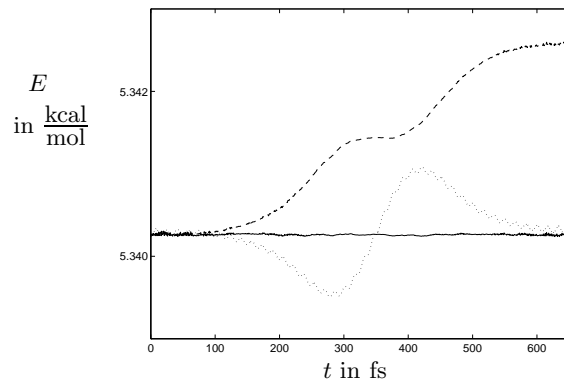


Figure 2: Conservation of energy in the QCMD-simulation of example 1 with PICKABACK (solid line), the hybrid method (dashed line) and the symplectic Trotter scheme (dotted line).

Figure 2 shows the energy  $E$  of the whole system computed via the PICKABACK integration scheme (solid line), the hybrid method (dashed line) and a symplectic  $\mathcal{O}(\tau^2)$  scheme based on the Trotter formula (see remark on page 5, dotted line), respectively. The result corresponds to our prediction that the PICKABACK scheme preserves the energy very well, while the energy of the symplectic  $\mathcal{O}(\tau^2)$  method oscillates around the initial energy value. In comparison to this the hybrid method suffers from an energy drift. Hence, this calculation shows exemplary the advantage of symplectic integrators in application to QCMD models: no energy drift impairs long-term simulations.

## 4.2 A collinear ArHCl-molecule

Our second example again is a well-known test problem (see figure 3). We considered a photodissociation process of a collinear ArHCl molecule.

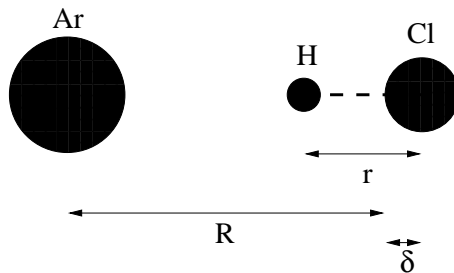


Figure 3: Collinear ArHCl-system with the Jacobi-coordinates used. For a more comprehensive description of the used Jacobi coordinates  $R$ ,  $r$  and  $\delta$  see the similar studies of XeHI in [1].

Calculating in Jacobi coordinates and with reduced masses, the H-Cl interaction is modeled quantum mechanically and the Ar-HCl interaction classically. The interactions are realized by fits of the potentials as reported in [17] [3] [10]. The potentials used are listed in detail in figure 4.

Our initial state is based on the ground state of ArHCl corresponding to the attractive HCl  $^1\Sigma$  state in a full quantum model. Thus, we determined the classical parts of the initial state of the QCMD-model via the computation of expectation values. Both propagations (i.e., with PICKABACK as well as the hybrid method) were carried out with a spatial domain  $x/\text{\AA} \in [0.53, 5.82]$  with 256 meshpoints and uniform time steps of 0.1

Interaction	Potential	$a$ [ $\frac{\text{kcal}}{\text{Mol}}$ ];	$b$ [ $\text{\AA}^{-1}$ ];	$c$ [ $\frac{\text{kcal}}{\text{Mol}} \text{\AA}^6$ ]
Ar-Cl [3]	$V_{\text{ArCl}}(x) = ae^{-bx} - \frac{c}{x^6}$	$1.94 \cdot 10^5$	3.60	$1.67 \cdot 10^3$
Ar-H [10]	$V_{\text{ArH}}(x) = ae^{-bx} - \frac{c}{x^6}$	$3.80 \cdot 10^4$	3.68	$3.54 \cdot 10^2$
H-Cl [17]	$V_{\text{HCl}}(x) = ae^{-bx}$	$1.65 \cdot 10^4$	2.44	

Figure 4: Potentials used in the simulation of a photodissociation process of a collinear ArHCl molecule. Note that the excitation of the HCl results in the HCl<sup>1</sup> $\Pi$  potential.

fs in a total time interval  $t/\text{fs} \in [0, 50]$ .

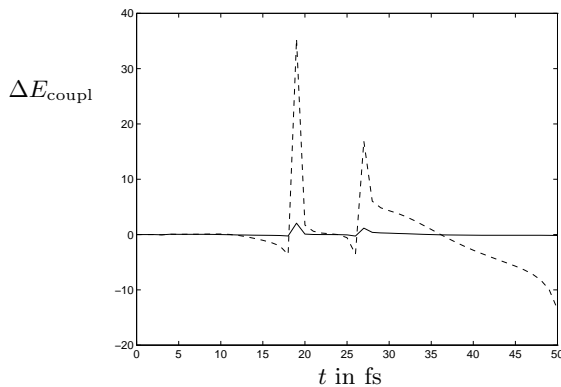


Figure 5: Error  $\Delta E_{\text{coupl}}$  of the coupling energy in percent of an exact solution of the ArHCl model problem. PICKABACK (solid line) and the hybrid method (dashed line).

Analogously to the former model problem only the symplectic PICK-ABACK scheme conserves the energy quite well in spite of the same stepsize in time. We again used the same stepsizes for both methods, because this choice results in an equal computational effort. The calculation of the coupling energy is more interesting: Hence, figure 5 displays the error  $\Delta E_{\text{coupl}}$  in the calculation of the coupling energy. We see that the nonsymplectic integrator extremely miscalculates the coupling energy, thus leading to wrong trajectories as shown in figure 6.

Figure 6 presents in percent the error  $\Delta\langle x \rangle$  and  $\Delta q$  in the expectation value of the quantum and in the classical coordinate respectively. Just as in the former example the spatial coordinates are to an increasing degree miscalculated in the simulation with the hybrid method. Interestingly enough, the error in the quantum coordinate oscillates with an increasing amplitude

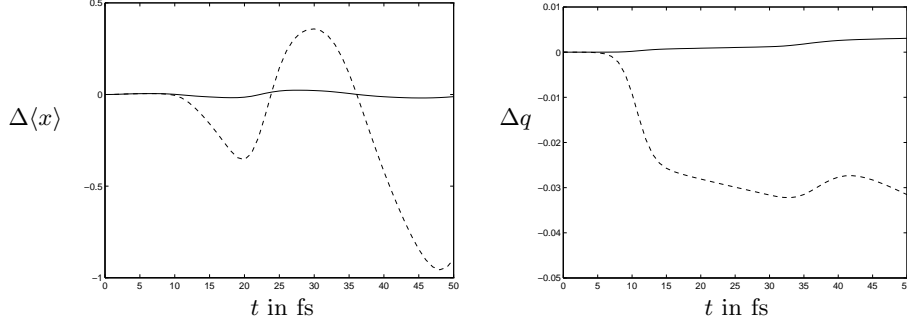


Figure 6: The error  $\Delta\langle x \rangle$  and  $\Delta q$  in percent of the expectation value of the quantum and in the classical coordinate, respectively. ArHCl model problem simulated with PICKABACK (solid line) and the hybrid method (dashed line). Again, the PICKABACK error is extremely smaller than that of the hybrid method.

up to 1%.

## Appendix

Herein it is our aim to present the exact solutions to the Hamiltonian functions  $\mathcal{H}_1$  and  $\mathcal{H}_2$ .

1. If we have a look at the propagator which is associated with the Hamilton function  $\mathcal{H}_1$ , we are looking for the solution to the following canonical equations:

$$\dot{q} = \frac{p}{M} \quad (11)$$

$$\dot{p} = 0 \quad (12)$$

$$\dot{\psi}_N = -iT\psi_N, \quad (13)$$

This initial value problem ( $q(0) = q_0, p(0) = p_0, \psi_N(0) = (\psi_N)_0$ ) can be solved analytically:

$$(12) \quad \Rightarrow \quad p(\tau) = p_0 \quad (14)$$

$$(11) \text{ u. } (14) \quad \Rightarrow \quad q(\tau) = q_0 + \tau \frac{p}{M}$$

$$(13) \quad \Rightarrow \quad \psi_N(\tau) = e^{-i\tau T} (\psi_N)_0$$

2. In the second step we examine the Hamiltonian system corresponding to  $\mathcal{H}_2$ . This requires to consider the following system:

$$\dot{q} = 0 \quad (15)$$

$$\dot{p} = -\psi_N^* D_q V(q) \psi_N \quad (16)$$

$$\dot{\psi}_N = -iV(q)\psi_N, \quad (17)$$

Again, this initial value problem can be solved directly, if the potential matrices  $V(q)$  and  $D_{q_k}V(q)$  commute ( $[V(q), D_{q_k}V(q)] = 0$ ) which is the case for collocation methods.

$$\begin{aligned}
(15) & \Rightarrow q(\tau) = q_0 & (18) \\
(17) \text{ u. } (18) & \Rightarrow \psi_N(\tau) = e^{-i\tau V(q_0)} (\psi_N)_0 & (19) \\
(16), (18) \text{ u. } (19) & \Rightarrow \dot{p}(\tau) = -\psi_N(\tau)^* D_q V(q) \Big|_{q(\tau)} \psi_N(\tau) \\
& = -(\psi_N)_0^* e^{+i\tau V(q_0)} D_q V(q) \Big|_{q_0} e^{-i\tau V(q_0)} (\psi_N)_0 \\
& = -(\psi_N)_0^* D_q V(q) \Big|_{q_0} (\psi_N)_0 \\
& \Rightarrow p(\tau) = p_0 - \tau (\psi_N)_0^* (D_q V) \Big|_{q_0} (\psi_N)_0
\end{aligned}$$

However, one should note, that only this part of the full PICKABACK integration scheme demands a collocation method.

**Remark.** At that point we have to emphasize that we could also have used the implicit midpoint rule to solve the system corresponding to  $\mathcal{H}_L$ . In this case we would have replaced the exact  $\exp(\tau L_{\mathcal{H}_2})$  propagator with a symplectic  $\mathcal{O}(\tau^3)$ -approximation. The original implicit structure of the method would become explicit, i.e., the scheme would be similar to Cayley's, caused by the kind of decomposition of  $\mathcal{H}$ . Unfortunately the appearance of the inverse of the potential does not allow us to circumvent the collocation methods. Moreover, such a method would not be unitary in the quantum part — thus miscalculating the expectation values of the coupling potentials.

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