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An explicit and symplectic integrator for quantum–classical molecular dynamics

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Abstract

An explicit and symplectic integrator called PICKABACK for quantum–classical molecular dynamics is presented. The 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 is split by the Strang splitting yielding the symplectic discretization PICKABACK. Finally the new method is compared with a widely used hybrid method in two examples: a collinear collision of a particle with a quantum oscillator and, additionally, a photodissociation process of an ArHCl molecule. It is shown that the PICKABACK algorithm is more stable and accurate at no additional numerical effort.

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 or pure classical calculations. Quantum models show far too large a complexity to be practically solved for the larger molecules whereas classical models do not describe “deeply” quantum mechanical processes, for example, tunneling processes or proton-transfer reactions. There are a variety of quantum–semiclassical (QSCMD) [1] and quantum–classical (QCMD) models [2–5] in use. The present authors consider a QCMD model that is mathematically derivable from full quantum dynamics [6]. It was revealed that this model has a canonical Hamiltonian structure [6], which implies symplecticity and the conservation of energy. This Letter presents the construction of an efficient integrator, which passes these properties to the discrete solution.

The energy exchange between the quantum and the classical part of the molecular system is of 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 purposes it is sufficient to use so-called symplectic discretizations, which conserve the energy within an accurate deviation range even for long time simulations [7]. In contrast to this, ad hoc schemes typically cause an energy drift which increases in time – thus being inappropriate to our problem.

In Section 2, our discussion starts with the analysis of the structure of the QCMD model used. In Section 3, we use the Lie formalism [8,7] 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 produc-

ing the same numerical effort as a widely used hybrid method [9] which is composed of a leapfrog (Verlet) scheme for the classical part [10] and a split operator technique for the quantum part [11]. The two discretizations only differ in the updates of the potential energy evaluation but PICKABACK achieves one additional order of accuracy. Moreover, our integration scheme is time reversible and unitary, thus conserving the norm of the wavefunction of the quantum part. Finally, in Section 4, we wish 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 of a particle 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 arbitrarily 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 ψ ,

$$i\hbar \frac{\partial}{\partial t} \psi = \left(\underbrace{-\frac{\hbar^2}{2m} \frac{\partial^2}{\partial x^2}}_{=T} + V(x, q(t)) \right) \psi,$$

$$\frac{\partial}{\partial t} q = \frac{p}{M},$$

$$\frac{\partial}{\partial t} p = -\langle \psi(t) | \frac{\partial}{\partial q} V(x, q) \psi(t) \rangle_x. \quad (1)$$

The total energy expectation value of the system, to which we will simply refer as "energy" in the following, reads [6]

$$\mathcal{H}(\psi; q, p) = \langle \psi | T(x) \psi \rangle_x + \langle \psi | V(x, q) \psi \rangle_x + \frac{p^2}{2M}. \quad (2)$$

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., it can be described formally in terms of classical mechanics. To illustrate this, we decompose the wavefunction into a scaled real and imaginary part:

$$\psi = \frac{1}{\sqrt{2\hbar}} (q_\psi + ip_\psi). \quad (3)$$

Now, after introducing a generalized position and momentum,

$$Q = (q_\psi, q)^\top, \quad P = (p_\psi, p)^\top, \quad (4)$$

and some formal calculations (using functional derivatives $\partial/\partial P$ and $\partial/\partial Q$, note that q_ψ and p_ψ still are functions) the system (1) can be written as

$$\frac{\partial}{\partial t} Q = \frac{\partial}{\partial P} \mathcal{H}, \quad \frac{\partial}{\partial t} P = -\frac{\partial}{\partial Q} \mathcal{H}. \quad (5)$$

The theory of classical mechanics [12] asserts for every phase flow corresponding to a Hamilton function there is not only the conservation of energy but also 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 to a system of ordinary differential equations (ODE). Therefore we must carry out two discretization steps: time and space discretization. The first step is a spatial discretization of the PDE by applying Fourier collocation methods [13].

Representing the state ψ by the values of the wavefunction at N equidistant grid points x_k ,

$$\psi_N(t) = (\psi(x_1, t), \dots, \psi(x_N, t))^\top, \quad (6)$$

we consider the vector ψ_N and the matrices T_N, V_N as discretizations of the state ψ and the operators T, V with respect to the mesh points (x_k) .

Note that one may alternatively use a Fourier–Galerkin approach [14] for the spatial discretization. Then ψ_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 an ODE system corresponding to (1) 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 like Eq. (5) for the discretized Hamilton function,

$$\mathcal{H}_N = \frac{p^2}{2M} + \psi_N^* T_N \psi_N + \psi_N^* V_N(q) \psi_N. \quad (7)$$

3.1. The symplectic PICKABACK integration scheme

In a second step we introduce the time discretization scheme called PICKABACK. Using Poisson brackets, well-known from classical mechanics [12,15], helps us to write the Hamilton equations of motion (5) as [8,7]

$$\frac{\partial}{\partial t} z = L_{\mathcal{H}_N} z, \quad (8)$$

where $L_{\mathcal{H}_N} z_i = \{z_i, \mathcal{H}_N\}$ and $z = (Q_N, P_N)^T$ with Q_N and P_N as discretizations of Q and P with respect to the quantum part q_ψ and p_ψ of (4).

It should be noted that the 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 a Lie generator of the flow connected to \mathcal{H}_N , so that we obtain the formal solution to (8) as

$$z(t) = \exp(tL_{\mathcal{H}_N})z(0). \quad (9)$$

The Hamilton function (7) can be decomposed as

$$\begin{aligned} \mathcal{H}_N &= \mathcal{H}_1 + \mathcal{H}_2, \\ \mathcal{H}_1 &= \frac{p^2}{2M} + \psi_N^* T_N \psi_N, \\ \mathcal{H}_2 &= \psi_N^* V_N(q) \psi_N. \end{aligned} \quad (10)$$

In this case we may 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 (9) for a short time step Δt with either the Trotter formula or with the Strang splitting. The Trotter formula [16] yields an $\mathcal{O}(\Delta t^2)$ approximation:

$$\begin{aligned} \exp(\Delta t L_{\mathcal{H}_N}) &= \exp(\Delta t L_{\mathcal{H}_1}) \exp(\Delta t L_{\mathcal{H}_2}) + \mathcal{O}(\Delta t^2), \end{aligned} \quad (11)$$

whereas Strang splitting [17] results in an $\mathcal{O}(\Delta t^3)$ approximation:

$$\begin{aligned} \exp(\Delta t L_{\mathcal{H}_N}) &= \exp\left(\frac{\Delta t}{2} L_{\mathcal{H}_1}\right) \exp(\Delta t L_{\mathcal{H}_2}) \exp\left(\frac{\Delta t}{2} L_{\mathcal{H}_1}\right) \\ &+ \mathcal{O}(\Delta t^3). \end{aligned} \quad (12)$$

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 the split operator technique [11]. However, one should note, that a splitting of higher order is possible as well but, unfortunately, results in negative time steps which may be numerically unstable [18]. Each $e^{\Delta t L_{\mathcal{H}_i}}$ is a symplectic map because it consists of an exact propagator to the phase flows of the altered Hamiltonian function \mathcal{H}_i . Thus, (11) and (12) are a composition of symplectic maps and are symplectic, too.

Now, the individual propagators of (12) deserve our 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 order $\mathcal{O}(\Delta t^3)$ for each of them. Fortunately, the present 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 (12), we obtain the integration scheme PICKABACK which is explicit and symplectic as well as time reversible and (in the quantum part) unitary.

$$q_{1/2} = q_0 + \frac{\Delta t}{2} \frac{p_0}{M},$$

$$\begin{aligned}
\psi_{N,1/2} &= \exp\left(-i\frac{\Delta t}{2}T_N\right)\psi_{N,0}, \\
p_1 &= p_0 - \Delta t \psi_{N,1/2}^* \frac{\partial}{\partial q} V(q_{1/2}) \psi_{N,1/2}, \\
\psi_{N,1} &= \exp\left(-i\frac{\Delta t}{2}T_N\right) \exp\left(-i\Delta t V_N(q_{1/2})\right) \psi_{N,1/2}, \\
q_1 &= q_{1/2} + \frac{\Delta t}{2} \frac{p_1}{M}. \quad (13)
\end{aligned}$$

Remark. The reader should note that the same construction starting with the Trotter formula (11) results in a symplectic but not time reversible scheme causing almost as much computational effort as PICKABACK but being $\mathcal{O}(\Delta t^2)$ accurate only.

3.2. An uncoupled hybrid method for comparison

For comparison with the integration scheme PICKABACK (13) we make use of another hybrid method, which is actually often used in applications [9], but is 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 simply call such an approach a “hybrid method” discussing it in contrast to PICKABACK.

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

$$i\hbar \frac{\partial}{\partial t} \psi_N = (T_N + V_N(q_0)) \psi_N, \quad (14)$$

where q_0 is constant. The integrator of the classical subsystem propagates,

$$\begin{aligned}
\frac{\partial}{\partial t} q &= \frac{p}{M}, \\
\frac{\partial}{\partial t} p &= -\psi_N^* \frac{\partial}{\partial q} V_N(q) \psi_N, \quad (15)
\end{aligned}$$

with a constant parameter ψ_N . Such a hybrid method can be understood as dimensional splitting [19] 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 approximation order $\mathcal{O}(\Delta t^2)$.

The reader should note that the Trotter formula arranges the two integrators one after the other, whereas in the literature [9] 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 observe that independently of the order of the subsystem-integrators we get a method of order $\mathcal{O}(\Delta t^2)$. The realizations of a hybrid method use, for example, a leapfrog (Verlet) [10] integrator for the classical subsystem together with a split operator scheme [11] for the quantum part. If one compares PICKABACK with the hybrid method one discovers that they differ only in the update of q and ψ_N in the potential evaluations as shown in Table 1. 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 (13) with the hybrid method described above in application to two model problems. Our first example is an inelastic collinear collision of a heavy particle with a harmonic oscillator being a simple model for an atom–molecule collision. The other one is a collinear model for the photodissociation of an Ar–HCl molecule similar to the studies of Xe–HI [20]. In the following we will compare the results evaluated with the PICKABACK scheme or the hybrid method with the “exact” solution of the QCMD equations for the model problems introduced. In all cases these “exact” solutions were obtained by calculations with extremely high precision, i.e. using a hundred times smaller stepsize. For this stepsize the

Table 1
Comparison of the hybrid and the PICKABACK scheme for QCMD simulations

	Hybrid method	PICKABACK
$q_{1/2} =$		$q_0 + \frac{\Delta t}{2} \frac{p_0}{M}$
$p_1 =$	$p_0 - \Delta t \psi_{N,0}^* \frac{\partial}{\partial q} V(q_{1/2}) \psi_{N,0}$	$p_0 - \Delta t \psi_{N,1/2}^* \frac{\partial}{\partial q} V(q_{1/2}) \psi_{N,1/2}$
$q_1 =$		$q_{1/2} + \frac{\Delta t}{2} \frac{p_1}{M}$
$\psi_{N,1/2} =$		$\exp\left(-i\frac{\Delta t}{2} T_N\right) \psi_{N,0}$
$\psi_{N,1} =$	$\exp\left(-i\frac{\Delta t}{2} T_N\right) \exp\left(-i\Delta t V_N(q_0)\right) \psi_{N,1/2}$	$\exp\left(-i\frac{\Delta t}{2} T_N\right) \exp\left(-i\Delta t V_N(q_{1/2})\right) \psi_{N,1/2}$

solution is converged, i.e. additional reduction of the stepsize does not change the solution within machine precision.

4.1. An inelastic collinear atom–molecule collision

Let us first have a look at a simple collinear collision of a heavy “classical” particle (with mass $M = 40u$) with a harmonic quantum oscillator (mass $m = 1u$), a model problem which has been treated extensively in the literature [6,21,3]. 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:

$$V_{\text{osc}}(x) = \frac{m}{2} \omega^2 x^2,$$

$$V_{\text{coupling}}(x, q) = a \exp(-b|x - q|), \quad (16)$$

with the parameters

$$\hbar\omega = 11.97 \text{ kJ/mol},$$

$$a = 6.920 \times 10^2 \text{ kJ/mol}, \quad b = 24.38 \text{ nm}^{-1}. \quad (17)$$

The initial wavepacket is constructed using the ground state of the undisturbed oscillator, while the classical particle has the initial location $q(0) = 0.5 \text{ nm}$ and an initial momentum directed towards the oscillator. The initial energy of the full system is 22.34 kJ/mol. We have performed QCMD-calculations applying uniform time steps $\Delta t = 0.05 \text{ fs}$ over a total time interval $t \text{ (fs)} \in [0, 650]$ and in the quantum part a spatial computation domain $x \text{ (pm)} \in [-100, 50]$ with 256 mesh

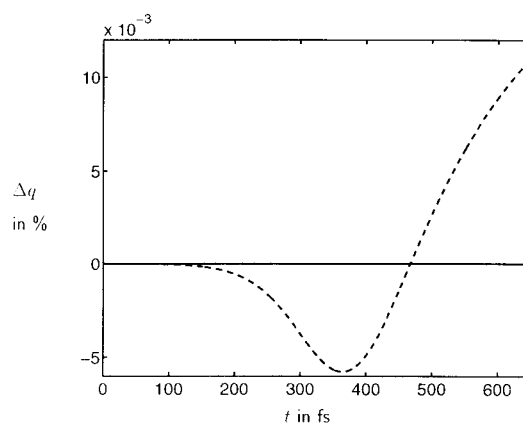


Fig. 1. Error Δq in the classical coordinate in percent of an exact solution of example 1. Results of an integration with PICKABACK (solid line) and the hybrid method (dashed line).

points. The reliability of the QCMD-model in comparison with a full quantum description for this model problem was carefully established [6]. Fig. 1 presents the position error Δq 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. Fig. 2 shows the energy E of the whole system computed via the PICKABACK integration scheme, the hybrid method and a symplectic $\mathcal{O}(\Delta t^2)$ scheme based on the Trotter formula (see remark on page 584, dotted line), respectively. The result corresponds to our prediction that the PICKABACK scheme preserves the energy well, while the energy of the symplectic $\mathcal{O}(\Delta t^2)$ method oscillates around the initial energy value. In compari-

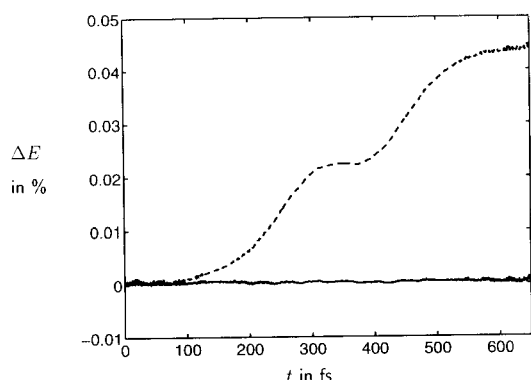


Fig. 2. Conservation of energy in the QCMD-simulation of example 1 with PICKABACK (solid line), the hybrid method (dashed line).

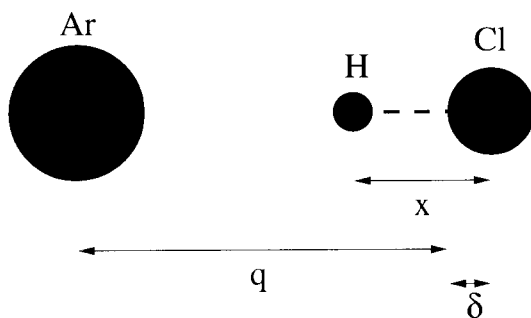


Fig. 3. Collinear Ar-HCl-system with Jacobi-coordinates used. For a more comprehensive description of the Jacobi coordinates q , x and δ see the similar studies of Xe-HI [20].

son to this the hybrid method suffers from an energy drift. Hence, this calculation shows the advantage of symplectic integrators in application to QCMD models: no energy drift impairs long-term simulations.

4.2. A collinear photodissociation

Our second example is the photodissociation process of a collinear ArHCl molecule (see Fig. 3). Upon excitation of the HCl molecule into the repulsive Π state, the van der Waals bond is broken by electronic predissociation. 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 [22] as reported in the literature [23-25]. The potentials used are listed in detail in Table 2.

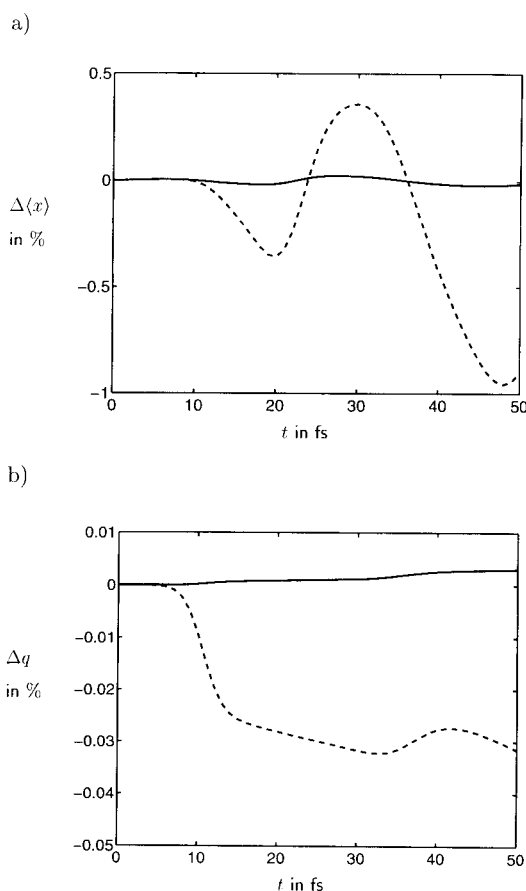


Fig. 4. (a) The error $\Delta\langle x \rangle$ and (b) the error Δq in percent of the expectation value of the quantum and in the classical coordinate, respectively. ArHCl model problem simulated with PICKABACK (solid line) and the hybrid method (dashed line).

Our initial state is based on the ground state of ArHCl corresponding to the attractive HCl $^1\Sigma$ state in the two-dimensional quantum model. The corresponding total energy is $E_{\text{tot}} = 315$ kJ/mol. 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 (pm) $\in [53, 582]$ with 256 mesh points and uniform time steps of 0.1 fs in a total time interval t (fs) $\in [0, 50]$. We again used the same step-sizes for both methods, because this choice results in an equal computational effort.

Fig. 4 presents, in percent, the error $\Delta\langle x \rangle$ and Δq in the expectation value of the quantum and classical

Table 2

Potentials used in the simulation of a photodissociation process of a collinear ArHCl molecule. Note that for HCl only the repulsive ${}^1\Pi$ potential is given

Interaction	Potential	a (kJ/mol)	b (nm $^{-1}$)	c (kJ/mol nm 6)
Ar-Cl [24]	$V_{\text{ArCl}}(r) = ae^{-br} - c/r^6$	8.14×10^5	36.01	6.99×10^{-3}
Ar-H [25]	$V_{\text{ArH}}(r) = ae^{-br} - c/r^6$	1.59×10^5	36.81	1.48×10^{-3}
H-Cl [23]	$V_{\text{HCl}}(r) = ae^{-br}$	6.90×10^4	24.40	–

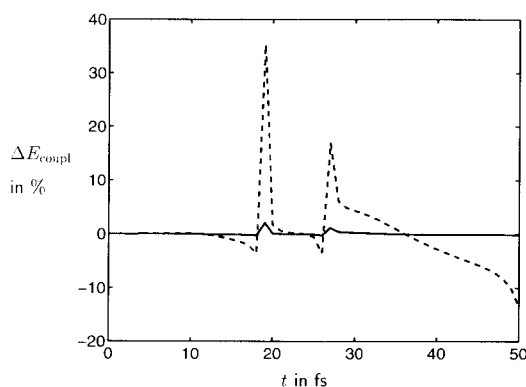


Fig. 5. Relative error ΔE_{couppl} of the coupling energy for the ArHCl model problem. Comparison between PICKABACK (solid line) and the hybrid method (dashed line).

coordinates respectively. Just as in the former example the spatial coordinates are increasingly miscalculated in the simulation using the hybrid method. Interestingly enough, the error in the quantum coordinate oscillates with a rapidly increasing amplitude.

Analogously to the former model problem only the symplectic PICKABACK scheme conserves the energy reliably. The calculation of the coupling energy is more interesting: Hence, Fig. 5 displays the deviation ΔE_{couppl} of the coupling energy E_{couppl} as calculated in the numerical simulations from the exact value

$$E_{\text{couppl}}^{\text{ex}} = \langle \psi | V_{\text{couppl}} | \psi \rangle,$$

$$V_{\text{couppl}}(x, q) = V_{\text{ArCl}}(q + \epsilon x) + V_{\text{ArH}}(q + (\epsilon - 1)x),$$

$$\epsilon = \frac{m_{\text{H}}}{m_{\text{H}} + m_{\text{Cl}}}, \quad (18)$$

evaluated using the exact solution of the QCMD-model. We observe that the nonsymplectic integrator extremely miscalculates the coupling energy at some critical points, thus leading to wrong trajectories as shown in Fig. 5. It is noted that these critical points

do not coincide with the collisions but rather with the points of inflection of quantum motion where the absolute value of the coupling energy is small.

Appendix

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

(i) 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:

$$\frac{\partial}{\partial t} q = \frac{p}{M}, \quad (19)$$

$$\frac{\partial}{\partial t} p = 0, \quad (20)$$

$$\frac{\partial}{\partial t} \psi_N = -iT\psi_N. \quad (21)$$

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

$$(20) \Rightarrow p(t) = p_0, \quad (22)$$

$$(19) \text{ and } (22) \Rightarrow q(t) = q_0 + t \frac{p_0}{M}, \quad (23)$$

$$(21) \Rightarrow \psi_N(t) = e^{-iTt} \psi_{N,0}. \quad (24)$$

(ii) In the second step we examine the Hamiltonian system corresponding to \mathcal{H}_2 . This requires us to consider the following system:

$$\frac{\partial}{\partial t} q = 0, \quad (25)$$

$$\frac{\partial}{\partial t} p = -\psi_N^* \frac{\partial}{\partial q} V(q) \psi_N, \quad (26)$$

$$\frac{\partial}{\partial t}\psi_N = -iV(q)\psi_N. \quad (27)$$

Again, this initial value problem can be solved directly, if the potential matrices $V(q)$ and $s\partial V(q)/\partial q$ commute,

$$[V(q), \frac{\partial}{\partial q}V(q)] = 0, \quad (28)$$

which is the case for collocation methods.

$$(25) \Rightarrow q(t) = q_0, \quad (29)$$

$$(27) \text{ and } (29) \Rightarrow \psi_N(t) = e^{-irV(q_0)}\psi_{N,0}, \quad (30)$$

(26), (29) and (30)

$$\begin{aligned} \Rightarrow \frac{\partial}{\partial t}p(t) &= -\psi_N(t)^* \frac{\partial}{\partial q}V(q) \Big|_{q(t)} \psi_N(t) \\ &= -\psi_{N,0}^* e^{+irV(q_0)} D_q V(q) \Big|_{q_0} e^{-irV(q_0)} \psi_{N,0} \\ &= -\psi_{N,0}^* \frac{\partial}{\partial q}V(q) \Big|_{q_0} \psi_{N,0} \\ \Rightarrow p(t) &= p_0 - t\psi_{N,0}^* \frac{\partial}{\partial q}V \Big|_{q_0} \psi_{N,0}. \end{aligned} \quad (31)$$

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

Remark. At this point we have to emphasize that we could also have used the implicit midpoint rule to solve the system corresponding to \mathcal{H}_2 . In this case we would have replaced the exact $\exp(tL_{\mathcal{H}_2})$ propagator with a symplectic $\mathcal{O}(t^3)$ 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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