Chapter 6

Structure Conserving Integration Schemes

§1 The structure of QCMD

In this section, we will review the properties of the QCMD solution with the aim, to pass as many as possible of these properties to the numerical approximation.

§1.1 Conservation of Energy

The total energy of the full quantum system (2.8) in the state Ψ is given by

$$\mathcal{H}_{\text{QD}}(\Psi) = -\frac{1}{2}\langle\Psi, \Delta_x\Psi\rangle - \frac{\epsilon^2}{2}\langle\Psi, \Delta_q\Psi\rangle + \langle\Psi, V\Psi\rangle.$$

Inserting the two approximation steps leading to QCMD (separation and WKB limit), we get

$$\begin{aligned}\mathcal{H}_{\text{QD}}(\Psi) &= \mathcal{H}_{\text{QD}}(\Psi_\otimes) + \mathcal{O}(\delta) \\ &= \langle\psi_{\text{QC}}, H(t)\psi_{\text{QC}}\rangle - \frac{\epsilon^2}{2}\langle\phi_S, \Delta_q\phi_S\rangle + \mathcal{O}(\delta+\epsilon)\end{aligned}$$

with the time-dependent Hamilton operator $H = -\frac{1}{2}\Delta_x + V(\cdot, q(t))$ and the semi-classical wave function $\phi_S(q,t) = a(q,t)\exp\left(\frac{iS(q,t)}{\epsilon}\right)$. Remember, that $a^2(\cdot,t)$ is an approximate δ-function at position $q(t)$ and that the relation (3.8) gives us $\nabla_q S(q(t),t) = p(t)$. This allows to derive (see [14] for details)

$$\mathcal{H}_{\text{QD}}(\Psi) = \langle\psi_{\text{QC}}, H(t)\psi_{\text{QC}}\rangle + \frac{1}{2}|p(t)|^2 + \Delta\mathcal{H}_{\text{QD}}(t) + \mathcal{O}(\delta+\epsilon), \tag{6.1}$$

where the term

$$\Delta\mathcal{H}_{\text{QD}}(t) = \frac{\epsilon^2}{2}\langle\nabla_q a(\cdot,t), \nabla_q a(\cdot,t)\rangle$$

represents the *zero-point energy* or *self energy* of the heavy "classical" particle. This self energy remains nearly constant in time. Since $\Delta\mathcal{H}_{\text{QD}}$ is part of the quantum mechanical description of the "classical" particle, it is reasonable to view the function

$$\mathcal{H}_{\text{QC}}(t) = \langle\psi_{\text{QC}}, H(t)\psi_{\text{QC}}\rangle + \frac{1}{2}|p(t)|^2$$

as the natural total energy for the QCMD system (2.9). This energy is easily seen to be a *conserved* quantity:

$$\begin{aligned}\frac{d\mathcal{H}_{\text{QC}}}{dt} &= \langle\psi_{\text{QC}}, \dot{H}\psi_{\text{QC}}\rangle + p\dot{p} + \underbrace{\langle\dot{\psi}_{\text{QC}}, H\psi_{\text{QC}}\rangle + \langle\psi_{\text{QC}}, H\dot{\psi}_{\text{QC}}\rangle}_{=0} \\ &= \langle\psi_{\text{QC}}, \nabla_q V\psi_{\text{QC}}\rangle\dot{q} + \dot{q}\dot{p} \\ &= 0.\end{aligned}$$

Thus, the quantum mechanical energy decomposes up to small terms into the energy $\mathcal{H}_{\mathrm{QC}}$ of the QCMD model and the *initial* self energy of the "classical" particle. Since $\mathcal{H}_{\mathrm{QC}}$ is conserved the numerical simulation of the QCMD model should reproduce this conservation property.

§1.2 Canonical Hamiltonian Structure

For the purpose of QCMD simulations, it is extremely helpful to note that the QCMD system (2.9) constitutes a canonical system with respect to the energy $\mathcal{H}_{\mathrm{QC}}$, i.e., that the evolution of (2.9) is *symplectic*. To this end we decompose the Hamilton operator

$$H = H_s + iH_a$$

into the selfadjoint and skew adjoint part and the wave function

$$\psi_{\mathrm{QC}} = \frac{1}{\sqrt{2\epsilon}}(q_\psi + ip_\psi) \tag{6.2}$$

into a scaled real and imaginary part. Now, introducing the generalized position $\mathcal{Q}_N = (q_\psi, q)^T$ and generalized momentum $\mathcal{P}_N = (p_\psi, p)^T$ the energy reads as

$$\mathcal{H}_{\mathrm{QC}} = \mathcal{H}_{\mathrm{QC}}(\mathcal{Q}_N, \mathcal{P}_N) = \frac{1}{2\epsilon}\left(\langle q_\psi, H_s q_\psi\rangle + \langle p_\psi, H_s p_\psi\rangle + 2\langle p_\psi, H_a q_\psi\rangle\right) + \frac{1}{2}|p|^2.$$

A simple *formal* calculation shows, that the corresponding canonical equations

$$\dot{\mathcal{Q}}_N = \frac{\partial}{\partial \mathcal{P}_N}\mathcal{H}_{\mathrm{QC}}, \qquad \dot{\mathcal{P}}_N = -\frac{\partial}{\partial \mathcal{Q}_N}\mathcal{H}_{\mathrm{QC}}$$

are just another form of writing the QCMD system (2.9).

§2 Liouville formalism

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 (2.9) into the Liouville formalism. To this end, we introduce a new state z in the phase space, $z = (\mathcal{Q}_N, \mathcal{P}_N)^T$, and define the nonlinear Liouville operator $L_{\mathcal{H}_{\mathrm{QC}}} z_i = \{z_i, \mathcal{H}_{\mathrm{QC}}\}$, using the common Poisson brackets $\{\ ,\ \}$. This permits us to denote the QCMD equations (2.9) in the form $\dot{z} = L_{\mathcal{H}_{\mathrm{QC}}} z$. The formal solution can now be written as

$$z(\tau) \quad = \quad e^{\tau L_{\mathcal{H}_{\mathrm{QC}}}} z(0). \tag{6.3}$$

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

$$L_{\mathcal{H}_{\mathrm{QC}}} = L_{\mathcal{H}_1} + L_{\mathcal{H}_2} + \ldots.$$

Using splitting schemes of the exponential function allows for a generation of numerical integrators. For example [112, 108]:

$$e^{\tau(L_{\mathcal{H}_1}+L_{\mathcal{H}_2})} \quad = \quad e^{\tau L_{\mathcal{H}_1}}\, e^{\tau L_{\mathcal{H}_2}} + \mathcal{O}\left(\tau^2\right) \tag{6.4}$$

$$e^{\tau(L_{\mathcal{H}_1}+L_{\mathcal{H}_2})} \quad = \quad e^{\frac{\tau}{2} L_{\mathcal{H}_1}}\, e^{\tau L_{\mathcal{H}_2}}\, e^{\frac{\tau}{2} L_{\mathcal{H}_1}} + \mathcal{O}\left(\tau^3\right), \tag{6.5}$$

which can easily be extended to higher orders [120].

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

§3 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 [42]. 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. 6.1). This "structural stability" makes symplectic integrators superior for long term simulations.

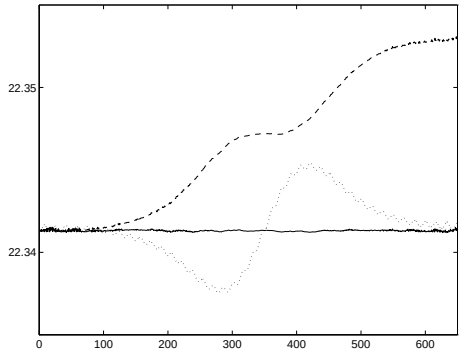

Figure 6.1. Total energy (in kJ/mol) versus time (in fs) for different integrators for a collinear collision of a classical particle with a harmonic quantum oscillator (for details see Sec. 3.§3). Dashed line: Nonsymplectic scheme. Dotted: Symplectic integrator of first order. Solid: Pickaback (symplectic, 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 (6.4) and (6.5) 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 (6.4) and (6.5) 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.

§3.1 An explicit and symmetric scheme

We decompose $\mathcal{H}_{\mathrm{QC}}$ into a kinetic and a potential term:

$$\mathcal{H}_{\mathrm{QC}} = \mathcal{H}_1 + \mathcal{H}_2 \quad \text{with} \quad \mathcal{H}_1 = \frac{|p|^2}{2} + \langle \psi, T_N\, \psi \rangle \quad \text{and} \quad \mathcal{H}_2 = \langle \psi, V(q)\, \psi \rangle.$$

As shown in [87], 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 (6.5),

we derive an integration scheme which is explicit, symplectic and symmetric. This scheme was denoted Pickaback emphasizing the interwoven structure of the partial steps.

$$\begin{aligned} q^{n+1/2} &= q^n + \frac{\tau}{2} p^n \\ \psi^{n+1/2} &= \exp\Big(- i \frac{\tau}{2\epsilon} T_N \Big)\, \psi^n \\ p^{n+1} &= p^n - \tau \left\langle \psi^{n+1/2},\, D_q V(q^{n+1/2}) \psi^{n+1/2} \right\rangle \\ \psi^{n+1} &= \exp\Big(- i \frac{\tau}{2\epsilon} T_N \Big)\, \exp\Big(- i \frac{\tau}{\epsilon} V_N(q^{n+1/2}) \Big)\, \psi^{n+1/2} \\ q^{n+1} &= q^{n+1/2} + \frac{\tau}{2} p^{n+1}. \end{aligned} \tag{6.6}$$

A main advantage of Pickaback is its reliability. But the reader might notice, that the splitting of the quantum propagator $\exp(-i\frac{\tau}{2\epsilon}H)$ 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 consider multiple time stepping methods.

§3.2 Symplectic multiple time stepping

An intriguingly simple idea for reducing the number of pure classical force evaluations is given by multiple time stepping methods [89]. (A symmetric multiple time stepping scheme is given in [101]). It copes with the different time scales of classical and quantum degrees of freedom by splitting the quantum propagation in some small "substeps". Therefore, consider the following decomposition of $\mathcal{H}_{\mathrm{QC}}$

$$\mathcal{H}_{\mathrm{QC}} = \mathcal{H}_1 + \mathcal{H}_2 \quad \text{with} \quad \mathcal{H}_1 = \frac{p^2}{2} \quad \text{and} \quad \mathcal{H}_2 = \langle \psi, H(q)\, \psi \rangle.$$

Now, subdivide $\exp(\tau L_{\mathcal{H}_2})$ instead of making one single step:

$$\exp\left(\tau L_{\mathcal{H}_{\mathrm{QC}}}\right) = \exp\left(\frac{\tau}{2} L_{\mathcal{H}_1}\right) \underbrace{\exp\left(\frac{\tau}{m} L_{\mathcal{H}_2}\right) \cdots \exp\left(\frac{\tau}{m} L_{\mathcal{H}_2}\right)}_{m \text{ times}} \exp\left(\frac{\tau}{2} L_{\mathcal{H}_1}\right) + \\ + \mathcal{O}\left(\tau^3\right).$$

Unfortunately, there is no analytical solution to the equations corresponding to $\mathcal{H}_2$. Thus, we have to find a symplectic, second order approximation $\exp(\tau\, L_{\mathcal{H}_2}/m)$. Two major possibilities have been discussed in [89]: The further application of a splitting scheme and a discretization via the implicit midpoint rule. Using the

first approach yields

$$\begin{array}{rcl} q^{n+1/2} & = & q^n + \frac{\tau}{2} p^n \,, \\ m \text{ times} \\ k = 1 \dots m & \left\{ \begin{array}{ll} \hat{\psi}^{k/j} & = \exp\left(-\frac{i}{\epsilon}\frac{\tau}{2m} T_N\right) \psi^{(k-1)/j} \\ p^{k/j} & = p^{(k-1)/j} - \frac{\tau}{m} \left\langle \hat{\psi}^{k/j}, D_q V(q^{n+1/2}) \hat{\psi}^{k/j} \right\rangle \\ \psi^{k/j} & = \exp\left(-\frac{i}{\epsilon}\frac{\tau}{2m} T_N\right) \exp\left(-\frac{i}{\epsilon}\frac{\tau}{m} V(q^{n+1/2})\right) \hat{\psi}^{(k-1)/j} \end{array} \right. \\ q^1 & = & q^{n+1/2} + \frac{\tau}{2} p^1 \,. \end{array}$$

The splitting of the quantum propagator in $\exp(\tau L_{\mathcal{H}_2})$ negatively effects the efficiency of the scheme especially if ϵ is small, i.e., if the quantum oscillation are much faster than the classical motion and the number m of substeps is becoming inefficiently large. Moreover, the efficiency depends strongly on the regularity of the wave function ψ. Data with large norms of $\|H^\alpha \psi\|$ yield a loss of accuracy as can be seen from [60, 54]:

$$\begin{array}{rcl} \left\| \exp(-i\tau H)\psi - \left(\exp\left(-\frac{i\tau}{2m} T\right) \exp\left(-\frac{i\tau}{m} V\right) \exp\left(-\frac{i\tau}{2m} T\right) \right)^m \psi \right\| \\ \leq C\tau \left(\frac{\tau}{m}\right)^\alpha \|H^\alpha \psi\| \end{array}$$

for $\alpha \in [0, 2]$ and a positive definite $H = T + V$.

§4 Symmetric Integration Schemes

In addition to the conservation properties of QCMD its equations of motion possess another important geometric structure by being time reversible. As shown in [44], 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 $e^{\tau L_{\mathcal{H}_{\mathrm{QD}}}}$ symmetrically. To this end, let us consider the Liouville generator for the Hamiltonian $\mathcal{H}$ from above:

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

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

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

Using the symmetric Velocity Verlet algorithm for integrating $\exp(\tau L^{cl}_{\mathcal{H}})$ yields:

$$\begin{array}{rcl} \psi^{n+1/2} & = & \exp\Big(-i\frac{\tau}{2\epsilon}H(q^n)\Big)\,\psi^n \\ \text{Velocity Verlet} \left\{ \begin{array}{rcl} p^{n+1/2} & = & p^n - \frac{\tau}{2}\left\langle \psi^n,\, D_q V(q^n)\psi^n \right\rangle \\ q^{n+1} & = & q^n + \tau p^{n+1/2} \\ p^{n+1} & = & p^{n+1/2} - \frac{\tau}{2}\left\langle \psi^{n+1}\, D_q V(q^{n+1})\psi^{n+1} \right\rangle \end{array} \right. \\ \psi^{n+1} & = & \exp\Big(-i\frac{\tau}{2\epsilon}H(q^{n+1})\Big)\,\psi^{n+1/2}. \end{array} \tag{6.7}$$

The question remains how to evaluate $\exp(-i\tau H(q^n)/(2\epsilon))\psi$ while retaining the symmetric structure. In the next chapter we will introduce some iterative techniques for evaluating the matrix exponential but the approximative character of these techniques will in principle destroy the symmetry. However, these techniques allow for the construction of very efficient and quasi–symmetric integrators for the QCMD equations.