

B. NUMERICAL ALGORITHMS

The numerical realization of QCMD simulations⁴ requires efficient and reliable numerical integrators adapted to the investigated application problems. The usage of one single numerical algorithm for all different cases of applications would not only be extremely inefficient but could even make the simulation of certain systems impossible.

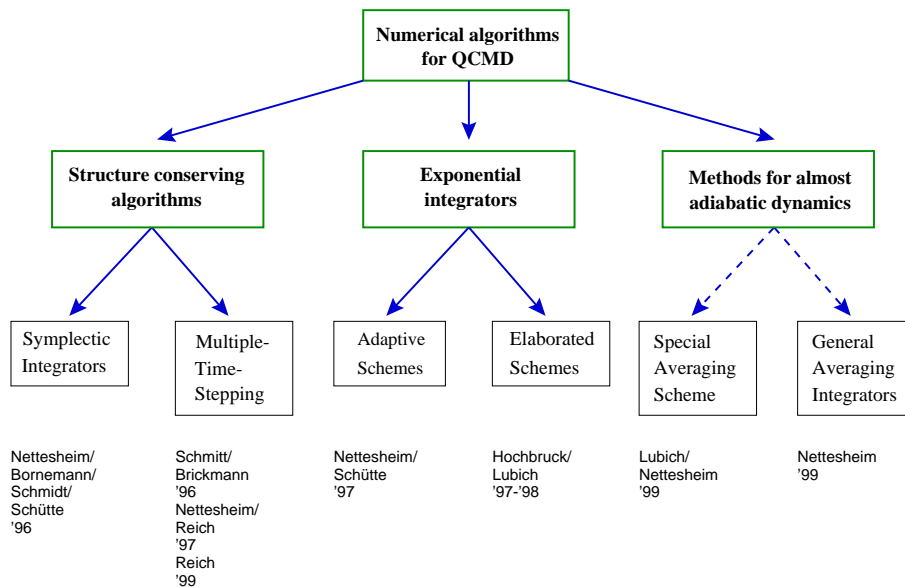


FIGURE 5.9. Classification of numerical integrators for QCMD.

For a precise understanding of the situation, it is therefore necessary to recognize the differences between a wide range of applications, because these differences demand for specific features of the numerical integrators. A suitable classification of the application problems based on the theoretical properties of the QCMD model will help to characterize the appropriate method for every application. Let us remind you that QCMD couples the highly oscillatory dynamics of the quantum state ψ_{QC} — we will throughout this discussion consider the Schrödinger equation to be spatially discretized (cf., Sec. 2.§4) — on a comparably slow classical dynamics. The highest frequencies dominating the quantum dynamics correspond to the largest occupied eigenvalues of the Hermitian Hamiltonian matrix $H(q) = T_N + V(q)$ as well as to the inverse of the smallness parameter ϵ .

In the course of the following discussion, we will introduce three different classes of integration techniques (see Fig. 5.9 and Fig. 5.10):

⁴The particular structure of the QCL equations allows for a reformulation into a stochastic and a deterministic subproblem (see Sec. 5.§5). The latter has the structure of QCMD in the adiabatic case. Thus, the development of QCMD integrators indicates the way in the future construction of QCL integrators.

Smallness parameter	ϵ substantially different from zero	Adaptive/ Elaborated schemes	Structure conserving methods
	$\epsilon \rightarrow 0$	Averaging integrators	?
		short	long
		Simulation time span	

FIGURE 5.10. Appropriate methods for some classes of application problems

In Chapter. 6, some recent developments of “structure conserving” integrators will be reviewed. Such *symplectic* or *symmetric* integrators are built 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 (Chap. 7), we discuss discretization schemes for accurate short-term integration 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 [52]. Exploiting these iterative methods, an intriguing approach has been proposed by M. HOCHBRUCK and CH. LUBICH [54]: they advocate methods, which average over an approximation of the fast quantum dynamics to obtain better convergence properties. In fact, solutions with excited high eigenvalues of T_N (the discretization of the Laplacian) due to either low spatial regularity or unbounded states do no longer lead to inefficient stepsize restrictions. Also, the construction of *adaptive* methods is made possible by iterative techniques to evaluate the matrix exponential. 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 approach was realized in an adaptive *Verlet-based exponential integrator* for QCMD.

A third class of techniques covers the case of an *almost adiabatic dynamics*. Here, the oscillations of the quantum part become highly oscillatory for an almost vanishing ϵ , thus, resulting for common integrators in prohibitively expensive stepsize restrictions. However, the model analysis of the almost adiabatic dynamics indicates that we have to reconsider the purpose of QCMD simulations here. To talk of a quantum wave function in the vicinity of the adiabatic dynamics is misleading: typically the almost adiabatic dynamics is determined by the slower population dynamics and not by the phases as indicated by surface hopping algorithms (cf., Sec. 5.§4). Nevertheless, the phases trigger transitions in the populations. To circumvent an exploding error for large

stepsizes, a new class of integrators has to be created. This topic is addressed in the chapters 8 and 9 where an innovative technique is presented: Averaging integrators are derived from averaging transformations (cf., Chap. 4). In the case of an oscillatory Hamiltonian test system, this approach does not only lead to the scheme presented in [54], one can also understand the characteristic convergence properties of these averaging integrators and systematically construct suitable schemes. In principle, the application of this technique to the QCMD equations is possible, but by far more lengthy. Since furthermore the future of QCMD in the almost adiabatic case will be dominated by the future of the QCL model, an explicit construction of QCMD integrators with this technique is omitted [73].

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.

If not expressed otherwise, we will assume that the QCMD solution is sufficiently smooth to justify our estimates.