

A. MODELLING

Typical simulations of biomolecular systems are based on classical molecular dynamics (MD) assuming that the system of interest obeys a classical Hamiltonian equation of motion. In this case quantum theory is only used in order to construct the atom-to-atom interaction potentials in the context of Born-Oppenheimer approximation.

In many situations classical MD allows a sufficiently accurate description of complex realistic molecular systems. But it simply cannot be valid if the nature of the process under consideration is “deeply quantum mechanically”, e.g., proton transfer processes in solution [115, 47, 107, 46, 38, 113, 10, 8] or in the active site of a protein [3, 95], electron diffusion in molten salts [106], or photo-induced excitations in molecular systems [81, 98, 65, 119, 27]. In those cases a quantum dynamical description is unavoidable. However, since a full quantum description of, e.g., a complete enzyme, is not feasible, there is a growing interest in including specific quantum dynamical effects into the otherwise classical description of some large molecular system.

The so-called QCMD model on which we will focus throughout this work, consists of a *singularly perturbed* Schrödinger equation nonlinearly coupled to classical Newtonian equations, see Sec. 2.§2.

We will carefully review the assumptions under which this QCMD model is known to approximate the full quantum dynamical (QD) evolution of the system (Chap. 3). Subsequently, we will correlate the model to other approaches in the literature. They are all based on a separation of the full quantum system via some tensor product ansatz into several parts with a coupled quantum description. Then, the evolution of *each* part is modeled on different levels: quantally, semi-classically, or (purely) classically. Some of the proposed models can be classified via the different description levels they are mixing: some remain on the quantum level for all parts and are well-known as *time-dependent self-consistent field* (TDSCF)-methods (cf. [36][32] in our context; a lot of references in nuclear physics use the notion of *time-dependent Hartree approximation* or *time-dependent mean-field approximation*); other methods combine semi-classical models for most of the parts with a quantum description for the particularly interesting part, usually called *quantum-semi-classical* (QSCMD)-models (see [31] and the references cited therein). However, we are particularly interested in *quantum-classical molecular dynamics* (QCMD)-models, which use Hamiltonian equations for space and momentum of the “classical” atoms (for biomolecular systems see [6][7][3]; more references may be found in studies for van der Waals molecules, e.g., [33][48]).

One important insight is that both, the QCMD model and the full QD evolution, in fact have the same *adiabatic limit system*, the well-known time-dependent Born-Oppenheimer (BO) model, see Chap. 4. The adiabatic limit of a model equation can be derived in various different ways relying on different assumptions: in a weak* topology, via averaging transformations and via a transformation into a rotating axes frame. Since these techniques may be used in the following construction of integrators, we will specify all of them in detail and exemplify their application.

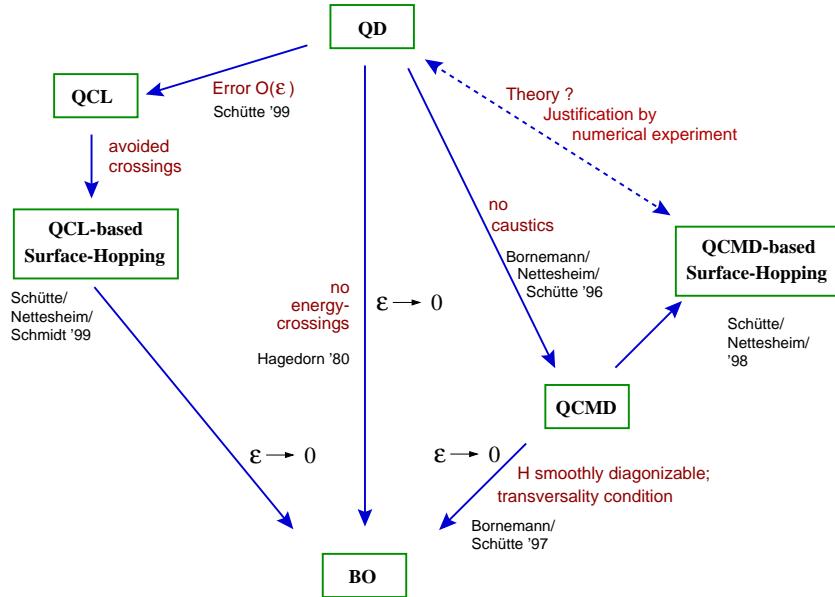


FIGURE 1.2. Approximation properties of some quantum classical models.

It is well-known that BO simulations are sufficient approximations of the full QD evolution in many important situations but lead to entirely wrong descriptions in as many other “non-adiabatic” cases. In contrast to the BO model, the QCMB model includes non-adiabatic processes, e.g., transitions between the energy levels of the quantum system or resonance effects near level crossings, see Chap. 5. The literature on this topic contains a significant number of specific examples in which QCMB simulations yield better approximations of QD than the simple BO approximation. We will analyze in Sec. 5.§3 the “non-adiabatic” effects in QCMB.

Unfortunately, the literature also contains important examples in which QCMB fails entirely because it is a single-trajectory model while the full QD solution develops *multi-configuration* character [69]. In the present article, these observations will be illustrated by means of a certain simple example, see Sec. 5.§2.

Subsequently, a heuristic *surface hopping* extension of QCMB [104] will be introduced and compared with similar approaches [72, 117, 114, 115, 116], Sec. 5.§4. The insights gained in the example will then allow to understand the algorithmic strategy of such QCMB-based surface hopping algorithms: to exploit the advantages of the non-adiabatic effects in QCMB while preventing the algorithm from behaving like QCMB in situations where multiply-branched classical paths are required for an accurate description. However, a rigorous mathematical justification of the surface hopping techniques does not exist.

Recently, a considerably new approach to an approximation of the quantum dynamics was almost simultaneously presented by C. MARTENS et al. [75, 61] and CH. SCHÜTTE [103]. Applying a partial Wigner transform to the full quantum dynamical description — that is, a Wigner transform [118] on the

classical degrees of freedom only — they derive the *quantum-classical Liouville equation* (QCL). The mathematical justification given in [103] allow for an interpretation of the QCL solutions as classical phase space densities, at least near the adiabatic limit. Moreover, the QCL gives a suitable starting point for the construction of trajectory bundle based algorithms [105].