Chapter 8

Algorithms for almost adiabatic dynamics

This chapter deals with the case, that the smallness parameter ϵ becomes very small but does not vanish. The asymptotical effects of $\epsilon \to 0$ on the QCMD model have been discussed previously in Chapters 4 and 5. We saw that under some assumptions on the spectral decomposition of the Hamiltonian $H(q)$ in (2.9) (Assumption (E3) on page 39) the solution of the QCMD model converges to a solution of the Born-Oppenheimer model.

In approaching the limit $\epsilon \to 0$, the dynamics becomes adiabatic. In the limit solution the highly oscillatory character of the QCMD solution vanishes: the classical motion is only determined by the eigenvalues of $H(q)$ and by the initial populations.

To illustrate this, let us recapitulate the asymptotic properties of QCMD under Assumption (E3). The quantum wave function ψ_ϵ is only weak* convergent[1] for $\epsilon \to 0$:

$$\psi_\epsilon \overset{*}{\rightharpoonup} 0 \qquad \text{in} \quad L^\infty([t_0,T])$$

whereas the classical location q_ϵ and momentum p_ϵ converge strongly:

$$q_\epsilon \to q_0 \qquad \text{in} \quad L^\infty([t_0,T]); \qquad p_\epsilon \to p_0 \qquad \text{in} \quad L^\infty([t_0,T]).$$

However, the forces $\ddot{q}_\epsilon$ converge as well only in a weak* sense

$$\ddot{q}_\epsilon \overset{*}{\rightharpoonup} \ddot{q}_0 \qquad \text{in} \quad L^\infty([t_0,T]).$$

Nevertheless, for ϵ small but finite, the phase of the quantum wave function ψ_ϵ oscillates with very high frequencies — the frequencies correspond to ϵ^{-1}. Most common integrators are restricted to the region of linear stability, that is, they resolve every oscillation, thus requiring a stepsize adapted to the highest frequency of the system.

§1 Approximating highly oscillatory phases

Let us be more precise on the stepsize restriction due to the high–frequency oscillation: Let us assume for a moment, that the *exact* classical location q_0 of the Born–Oppenheimer model is given.

In Sec. 5.§3, the wave function ψ_ϵ of the quantum subsystem is under the exclusion of energy level crossings (Assumption (E4) on page 44) expanded as

$$\psi(t) = \sum_\lambda \sqrt{\theta_*^\lambda} \exp\big(-i\epsilon^{-1}\,\phi_0^\lambda(t)\big) e_\lambda(q_0(t)) + \mathcal{O}(\epsilon).$$

[1] see Thm. III.1 in [13]

where ϕ_0^λ denotes the Born–Oppenheimer phase function,

$$\phi_0^\lambda(t) = \int_0^t E_\lambda(q_0(s))ds,$$

and θ_*^λ the initial population of energy level E_λ.

Hence, for computing the leading order in ϵ of the wave function ψ_ϵ, we just have to deal with the integration error when approximating the phase function ϕ_0^λ. Let $\tilde{\phi}_0^\lambda(\tau)$ denote an approximation of order β_{int} to the integral

$$\tilde{\phi}_0^\lambda(t) - \int_0^t E_\lambda(q_0(s))ds = \mathcal{O}(\tau^{\beta_{\text{int}}}), \quad \beta_{\text{int}} \geq 0$$

where $1 > \tau > 0$ denotes some stepsize.

Now, the approximation of the Born-Oppenheimer phases $\exp(-i\epsilon^{-1}\,\phi_0^\lambda)$ results in the following error

$$\left\|\exp\left(-i\epsilon^{-1}\,\phi_\lambda(t)\right) - \exp(-i\epsilon^{-1}\,\tilde{\phi}_\lambda(t)\right\| = \begin{cases} \mathcal{O}\left(\frac{\tau^{\beta_{\text{int}}}}{\epsilon}\right) & \text{for} \quad \tau^{\beta_{\text{int}}} \leq \epsilon, \\ \mathcal{O}\left(1\right) & \text{for} \quad \tau^{\beta_{\text{int}}} > \epsilon. \end{cases}$$

where we have used, that the LHS is, in fact, bounded by 2 as well. To get an error which vanishes with $\epsilon \to 0$, we have to satisfy the following condition

$$\tau^{\beta_{\text{int}}} \leq \epsilon.$$

That is, the higher the order of the integration, the larger the stepsize allowed. But note, an ϵ–independent stepsize, that is an $\mathcal{O}(1)$–stepsize, is —whatever β_{int} we choose— not permitted without risking an uncontrolled error for $\epsilon \to 0$.

We have learned from this example that a possible concept in the construction of long–stepsize methods is the use of high–order approximations of the phase functions. Unfortunately, this can be very costly itself for in a realistic situation also the location q_0 is only approximatively given.

The question arises whether there are other methods allowing for stepsizes much larger than the smallness parameter ϵ:

$$\tau \gg \epsilon.$$

Obviously, the problems in approximating the wave function originate from the weak* convergence of ψ_ϵ.

We can obtain strongly convergent variables in the quantum subsystem if we consider the populations θ_ϵ^λ and the corresponding phase functions ϕ_ϵ^λ,

$$\theta_\epsilon^\lambda \to \theta_*^\lambda \quad \text{in} \quad L^\infty([t_0,T]), \qquad \phi_\epsilon^\lambda \to \phi_0^\lambda \quad \text{in} \quad L^\infty([t_0,T]),$$

for $\epsilon \to 0$. Therefore, a derivation of large–stepsize integrators based on q_ϵ, p_ϵ, θ_ϵ^λ and ϕ_ϵ^λ seems to be possible. Such a restriction onto q_ϵ, p_ϵ, θ_ϵ^λ and ϕ_ϵ^λ might be justified because many reduced models describing almost adiabatic dynamics — cf., surface hopping algorithms as in Sec. 5.§4 — just do rely on the population dynamics and not on the phase of the wave function. The following section will reveal, what concept we have in mind in the construction of appropriate large–stepsize integrators.

§2 Inheriting asymptotic dynamics

In the construction of large–stepsize methods for almost adiabatic dynamics, we are guided by the following idea: our knowledge of the asymptotic behavior of the model should allow for the creation of integrators, which inherit exactly this asymptotic behavior of the model.

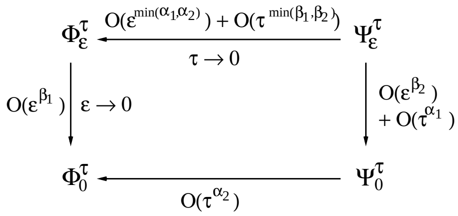
Let us illustrate this idea for a simplified model. Consider a family of dynamical systems with strongly converging solution $u_\epsilon : \mathbb{R} \to \mathbb{R}^d$ for $\epsilon \to 0$:

$$u_\epsilon \to u_0 \quad \text{for} \qquad \epsilon \to 0 \quad \text{in} \quad L^\infty([t_0, T]); \qquad u_\epsilon(t_0) = u_*.$$

Denote the analytic flow of the dynamical systems for a step with stepsize τ by Φ_ϵ^τ. The limit system is given by $u_0 : \mathbb{R} \to \mathbb{R}^d$, $u_0(t_0) = u_*$ and its flow Φ_0^τ. Now, let us abstractly consider an integration method Ψ_ϵ^τ approximating the analytic flow Φ_ϵ^τ, and assume that the former obeys the same asymptotic behavior as the model,

$$\begin{aligned}
\Phi_\epsilon^\tau\, u_* - \Phi_0^\tau\, u_* &= \mathcal{O}(\epsilon^{\beta_1}) && \text{with} \quad \beta_1 > 0\\
\Psi_\epsilon^\tau\, u_* - \Psi_0^\tau\, u_* &= \mathcal{O}(\tau^{\alpha_1}) + \mathcal{O}(\epsilon^{\beta_2}) && \text{with} \quad \alpha_1 > 0\\
\Psi_0^\tau\, u_* - \Phi_0^\tau\, u_* &= \mathcal{O}(\epsilon^{\alpha_2}) && \text{with} \quad \alpha_2 > 0
\end{aligned}$$

where Ψ_0^τ denotes the numerical approximation of the flow of the limit system. This means, for fixed stepsize τ and $\epsilon \to 0$ the propagator Ψ_ϵ^τ becomes an integration scheme Ψ_0^τ of the limit flow Φ_0^τ. A diagram showing the convergence properties might then look like



The local error of the method Ψ_ϵ^τ with respect to Φ_ϵ^τ can be derived via the asymptotic limit using a triangle inequality. This yields

$$\Psi_\epsilon^\tau\, u_* - \Phi_\epsilon^\tau\, u_* = \mathcal{O}\left(\tau^{\min\{\alpha_1,\alpha_2\}}\right) + \mathcal{O}\left(\epsilon^{\min\{\beta_1,\beta_2\}}\right).$$

or, with the stepsize τ coupled to ϵ by

$$\tau = \epsilon^\gamma, \qquad \gamma > 1,$$

one obtains for the local error

$$\Psi_\epsilon^\tau\, u_* - \Phi_\epsilon^\tau\, u_* = \mathcal{O}\left(\epsilon^{\min\left\{\gamma \min\{\alpha_1,\alpha_2\},\min\{\beta_1,\beta_2\}\right\}}\right).$$

It becomes evident that a method Ψ_ϵ^τ with $\beta_2 > 0$ converges for $\epsilon \to 0$ to an integration scheme Ψ_0^τ of the limit dynamics. Moreover, the method allows for stepsizes $\tau \gg \epsilon$ without exploding error.

This example illustrates that the construction of integrators in the case of very small ϵ should be guided by the intrinsic asymptotic behavior of the model equations.

Remark. Clearly, this example draws a simplified picture. Not only it requires a strongly converging solution but assumes furthermore $\Psi_\epsilon^\tau u_* - \Psi_0^\tau u_* = \mathcal{O}(\tau^{\alpha_1}) + \mathcal{O}(\epsilon^{\beta_2})$ which might not be possible to satisfy. Still, it gives a good impression of our motives in the development of techniques for $\epsilon \to 0$.

Remark. The reader might note, that only a strongly converging solution was required. No assumption on the convergence of the time derivatives of the solution have been made.

However, this example does not only present the idea of inheriting the asymptotic dynamics. Additionally, it outlines the construction of those methods in three steps:

1. First, the limit dynamics of the model has to be discovered. This can be done by the methods described in Chap. 4. In the case of our example above: one analyzes $\Phi_\epsilon^\tau\, u_* - \Phi_0^\tau\, u_*$.
2. In a second step, an appropriate numerical integrator Ψ_0^τ for the limit dynamics Φ_0^τ must be selected.
3. By transforming the limit system back, using the transformation technique used in 1., one obtains higher order correction terms in ϵ to the limit solution. The discretization of those is added to the discretization of the limit system.

Finally, one obtains a method which might have the promising properties of the integrator Ψ_ϵ^τ of our illustrative example.

This approach governs, essentially, the construction of averaging integrators in the next chapter.