4.2.1 The Reversible RESPA Scheme

In many molecular dynamics applications, the system may be decomposed as $H(q,p) = p^T M^{-1} p/2 + U_S(q) + U_F(q)$ where U_S is a "soft" potential, in which the natural motion would be relatively slow, whereas U_F is a much stronger term which would give rise to relatively rapid motion. We further suppose U_S (with its gradient) is expensive to compute, perhaps because it involves many terms, whereas U_F is relatively simple. Because U_F requires small timesteps, we think of separating the calculation of a timestep, typically in a symmetric form. Let $\mathscr{G}_h^F$ denote the map associated to the Verlet method for the system without U_S, using a stepsize h:

$$\mathscr{G}_h^F = e^{\frac{h}{2}\mathcal{L}_{U_F}} e^{h\mathcal{L}_K} e^{\frac{h}{2}\mathcal{L}_{U_F}},$$

where $\mathcal{L}_K$ is the Lie-derivative corresponding to the kinetic energy component of the Hamiltonian ($K = p^T M^{-1} p/2$). Now consider the map constructed by taking r steps using $\mathscr{G}_{F,h/r}$ and composing this with kicks from the soft force:

$$\mathscr{G}_h^{MTS} = e^{\frac{h}{2}\mathcal{L}_{U_S}} [\mathscr{G}_{h/r}^F]^r e^{\frac{h}{2}\mathcal{L}_{U_S}}.$$

One step of the multiple timestepping algorithm is then implemented as follows:

Reversible RESPA Algorithm

$$P := p - (h/2)\nabla U_S(q),$$

$$Q := q,$$

Repeat r times:

$$\left| \begin{array}{l} P := P - (h/2)\nabla U_F(Q)/r, \\ Q := Q + hM^{-1}P/r, \\ P := P - (h/2)\nabla U_F(Q)/r, \end{array} \right. \qquad (4.2)$$

$$P := P - (h/2)\nabla U_S(Q).$$

Multiple timestepping is widely used for efficiency purposes in systems with expensive force computations, but it should be used cautiously. To illustrate the potential dangers of multiple timestepping, one need only consider its application to a linear one-DOF model problem

$$H(q,p) = p^2/2 + U_S(q) + U_F(q), \qquad U_S(q) = q^2/2, \qquad U_F(q) = \Omega^2 q^2/2,$$

where it is assumed that $\Omega \gg 1$. The differential equations describing this system are

$$\dot{q} = p,$$
$$\dot{p} = -(1 + \Omega^2)q.$$

The frequency is therefore $\bar{\Omega} = \sqrt{1 + \Omega^2}$. In the limit of small inner step, we solve the system with Hamiltonian $H_F = p^2/2 + \Omega^2 q^2/2$ *exactly*, meanwhile punctuating with impulses from U_S, thus the MTS flow map approximation, which is linear in this case, can be written in the form of a matrix-vector multiply

$$\begin{bmatrix} Q \\ P \end{bmatrix} = W_h \begin{bmatrix} q \\ p \end{bmatrix},$$

where

$$W_h = S_{h/2} F_h S_{h/2},$$

with

$$S_h = \begin{bmatrix} 1 & 0 \\ -h & 1 \end{bmatrix}, \quad F_h = \begin{bmatrix} \cos(\Omega h) & \Omega^{-1}\sin(\Omega h) \\ -\Omega\sin(\Omega h) & \cos(\Omega h) \end{bmatrix}.$$

Both of these matrices have unit determinant for any h, so the product of the eigenvalues of W_h is 1. On the other hand, a short calculation shows that

$$\lambda_1 + \lambda_2 = \text{Tr}(W_h) = 2\cos(h\Omega) - \frac{h}{\Omega}\sin(h\Omega).$$

For a given h, the eigenvalues of W_h are either complex conjugates or they are real and reciprocal to one another. If they are complex conjugates with nonzero imaginary part, then we have $\lambda_1 \lambda_2 = \lambda_1 \bar{\lambda}_1 = 1$, so $|\lambda_1| = 1$ and the two eigenvalues are clearly distinct and on the unit circle in the complex plane.
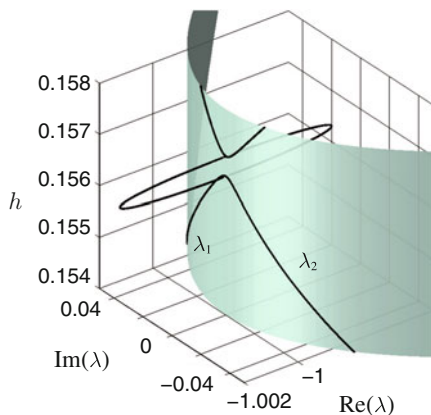
   If we consider a relatively small step of size $h\Omega = k\pi$ we find that the eigenvalues cross, and the system is unstable. For example, at $h = \pi/\Omega$, we have

$$F_h = -I \Rightarrow W_h = -S_{h/2}^2 = -\begin{bmatrix} 1 & 0 \\ -h & 1 \end{bmatrix},$$

so that

$$W_h^n = (-1)^n \begin{bmatrix} 1 & 0 \\ -nh & 1 \end{bmatrix},$$

and the norm of the solution will oscillate and grow linearly with n as $n \to \infty$. This is the simplest type of *linear resonance* present in multiple timestepping. The resonance at $h = \pi/\Omega$ only gives rise to a relatively weak 'linear' instability, but what is more serious is that in the vicinity of $h = \pi/\Omega$ the eigenvalues actually leave the unit circle. We can see this by expanding $\mu(h) = 2\cos(h\Omega) - \frac{h}{\Omega}\sin(h\Omega)$ in a Taylor expansion around $h = \pi/\Omega$:

$$\mu(h) = -2 + \varepsilon, \qquad \varepsilon = \frac{\pi}{\Omega}(h - \pi/\Omega).$$

Both eigenvalues satisfy

$$\lambda + \lambda^{-1} = -2 + \varepsilon + \mathcal{O}(\varepsilon^2).$$

In case $\varepsilon > 0$, i.e. *after* $h = \pi/\Omega$, we have complex eigenvalues and we already know this case to be stable. For $\varepsilon < 0$, however, we have

$$\lambda = -1 \pm (|\varepsilon|/2)^{1/2} + \mathcal{O}(\varepsilon).$$

Here both eigenvalues are real and one is outside the unit circle. There is thus a small interval of *exponential* instability directly below $h = \pi/\Omega$.

We can easily solve for the two eigenvalues as functions of h and graph them as points in three dimensions: $x = \text{Re}(\lambda)$, $y = \text{Im}(\lambda)$, $z = h$ (Fig. 4.3). Such resonances will also occur at integer multiples of π/Ω, and we can therefore expect many small intervals in the stepsize where the multiple timestepping method is unstable. When a large system involves a combination of many different interactions, the intervals of instability would expect to proliferate from all the different natural frequencies.

A linear resonance is a rational relationship between the period of the harmonic oscillator and the timestep used in simulation. If we substitute a nonlinear oscillator

for the harmonic one, then we encounter more complicated *nonlinear resonances*. It is challenging (perhaps impossible) to analyze the destabilizing effect of such resonances in a general molecular dynamics setting, but it is possible to do so in some cases for low-dimensional model problems [247, 329, 339].

In practice the presence of resonances may or may not render the multiple timestepping technique ineffective. One would be concerned if the only gain were from the Verlet stability threshold at $\bar{h}_{\text{Verlet}} = 2/\Omega$ to the location of the first resonance peak at $\bar{h}_{\text{MTS}} = \pi/\Omega$, since the multiple timestepping method introduces additional complexity. However, the picture is complicated by the observation that the strength of the leading resonance is often modest, so the growth observed in practice may be slow and, depending on the nature of the coupling of the variables of the system (which depends on details of the potential energy functions, natural coupling of the modes of the system, and the presence of solvent molecules which may introduce a stochastic effect) the growth of error due to resonance may be masked by other factors of a strongly system-dependent nature. Moreover, molecular systems are often subject to a stochastic thermostat (a topic to be addressed in later chapters) which may further alter the role of the resonances. Thus the study of the effect of linear and nonlinear resonance peaks on the error in molecular dynamics simulation becomes quickly a numerical issue which must be investigated using carefully crafted experiments. The analysis of [245] clearly raises some concerns regarding the use of multiple timestepping in molecular simulation, in particularly they suggest that the usable gain from RESPA simulations in systems with detailed solvent (water) is only around a factor of $\pi/2$ compared what can be achieved using a standard integrator such as Verlet (similar what would be suggested by resonance analysis). Nevertheless there are practical examples where multiple timestepping is used, especially in schemes incorporating stochastic perturbation and with relatively strong scale separation, as when multiple timestepping is combined with the particle-mesh Ewald summation long-ranged force computation technique. In Sect. 7.13 we discuss the use of multiple timestepping in connection with Langevin dynamics. In Sect. 8.6, we describe the combination of multiple timestepping with isokinetic constraints and stochastic perturbation, where very substantial increases in outer timestep are found to be possible.

4.2.2   The Mollified Impulse Method

The onset of instability of multiple timestepping is a consequence of introducing periodic impulses (via slow force updates) in resonance with a natural frequency of the system. As a means of avoiding or at least ameliorating the effect of resonances, it has been proposed to modify the points at which the slow forces in multiple timestepping are evaluated. The *mollified impulse method* (MOLLY) [141] is a form of multiple timestepping in which the potential energy function is modified based on an averaging of the position variable (over fast dynamics) in such a way as to filter out destabilizing excitations. Effectively, one replaces $U_S(\boldsymbol{q})$ wherever it appears