Gas-Surface Dynamics

In the preceding chapters we have been concerned with the solution of the electronic Schrödinger equation for fixed nuclear coordinates. By performing total-energy calculations for many different nuclear configurations, energy minima and whole potential energy surfaces for chemical reactions at surfaces can be determined. However, this static information is often not sufficient to really understand how a reaction proceeds. Furthermore, in the experiment the potential energy surface (PES) is never directly measured but just reaction rates and probabilities. For a real understanding of a reaction mechanism a dynamical simulation has to be performed. This also allows a true comparison between theory and experiment and thus provides a reliable check of the accuracy of the calculated PES on which the dynamics simulation is based.

In this chapter methods to perform dynamical simulations will be introduced. In principle the atomic motion should be described by a quantum mechanical treatment, but often classical mechanics is sufficient. I will therefore first present classical methods and then review quantum mechanical methods.

7.1 Classical Dynamics

One can perform classical molecular dynamics studies by integrating the classical equations of motion, either Newton’s equation of motion

\[
M_i \frac{\partial^2}{\partial t^2} \mathbf{R}_i = -\frac{\partial}{\partial \mathbf{R}_i} V(\{\mathbf{R}_j\}),
\] (7.1)

or Hamilton’s equation of motion

\[
\dot{q} = \frac{\partial H}{\partial p} \quad \dot{p} = -\frac{\partial H}{\partial q}.
\] (7.2)

The solution of the equations of motion can be obtained by standard numerical integration schemes like Runge–Kutta, Bulirsch–Stoer or predictor-corrector
methods (see, e.g., [17]). Very often the rather simple Verlet algorithm [290, 291] is used which is easily derived from a Taylor expansion of the trajectory.

\[ \mathbf{r}_i(t + h) = \mathbf{r}_i(t) + h \frac{d\mathbf{r}_i}{dt} \bigg|_{h=0} \right. \left. + \frac{h^2}{2} \frac{d^2\mathbf{r}_i}{dt^2} \bigg|_{h=0} \right. \left. + \frac{h^3}{6} \frac{d^3\mathbf{r}_i}{dt^3} \bigg|_{h=0} + \ldots \right] 

Here we have introduced the velocity \( \mathbf{v}_i = \frac{d\mathbf{r}_i}{dt} \). Furthermore, we have used Newton’s equation of motion to include the force \( \mathbf{F}_i = m \frac{d^2\mathbf{r}_i}{dt^2} \) acting on the \( i \)-th particle. Analogously we can derive

\[ \mathbf{r}_i(t-h) = \mathbf{r}_i(t) - h \mathbf{v}_i(t) + \frac{h^2}{2} \frac{\mathbf{F}_i(t)}{m} - \frac{h^3}{6} \frac{d^3\mathbf{r}_i}{dt^3} \bigg|_{h=0} + \ldots \]  

(7.3)

Adding (7.3) and (7.4) yields the Verlet algorithm [290]

\[ \mathbf{r}_i(t + h) = 2\mathbf{r}_i(t) - \mathbf{r}_i(t-h) + h^2 \frac{\mathbf{F}_i(t)}{m} + O(h^4). \]  

(7.5)

There is a simple test whether the numerical integration of the equations of motion is accurate and reliable: the total energy, i.e., the sum of the kinetic energy and potential energy, should be conserved along the trajectory. In order to evaluate the kinetic energies, the velocities at time \( t \) are needed. Note that they do not explicitly appear in (7.5). They can be estimated by

\[ \mathbf{v}_i(t) = \frac{\mathbf{r}_i(t+h) - \mathbf{r}_i(t-h)}{2h}. \]  

(7.6)

However, the kinetic energy evaluated with (7.6) belongs to the time step prior to the one used for the positions (7.5) which enter the evaluation of the potential energy. This problem can be avoided in the so-called velocity Verlet algorithm [291]

\[ \mathbf{r}_i(t + h) = \mathbf{r}_i(t) + h \mathbf{v}_i(t) + \frac{h^2}{2} \frac{\mathbf{F}_i(t)}{m} \]  

\[ \mathbf{v}_i(t + h) = \mathbf{v}_i(t) + h \frac{\mathbf{F}_i(t + h) + \mathbf{F}_i(t)}{2m}, \]  

(7.7)

which is mathematically equivalent to the Verlet algorithm (Problem 7.1).

In order to perform molecular dynamics simulations with the Verlet algorithm, a specific time step has to be chosen. Of course, the error associated with each time step is the smaller, the shorter the time step. On the other hand, a shorter time step means more iterations for a given trajectory or simulation time which increases the computational cost. Furthermore, the error of each time step may accumulate. Hence the chosen time step will represent a compromise. The change in the total energy during one molecular run should