

Theoretical Methods and Techniques

To obtain the potential energy surface (PES) of a molecule, one needs to solve the electronic Schrödinger equation for all possible (fixed) nuclear coordinates. PES helps us to understand the energetics of a reaction. However, the issue is the dimensionality of the PES. A molecule containing N number of atoms has 3N nuclear coordinates. Subtracting the translational and rotational degrees of freedom, a non-linear molecule has 3N-6 and a linear molecule has 3N-5 vibrational degrees of freedom. PES of a molecule containing 10 atoms is 24 dimensional which is very hard to visualize. Solving the electronic Schrödinger equation for a medium sized molecule is achievable easily today due to the developments in computational techniques. In this thesis, PES were computed from quantum mechanics by solving the electronic Schrödinger equation.

2.1 GEOMETRY OPTIMIZATION

A **single point energy calculation** is solving the electronic Schrödinger equation at a fixed nuclear geometry. Stationary points on a PES such as a minimum or a saddle point can be found by performing a **geometry optimization**. To begin the process of optimizations, a guess geometry that resembles the desired stationary point is required. Then using a suitable algorithm [Baker, 1987; Deaven and Ho, 1995; Schlegel, 1982] such as a Newton based method [Schlegel, 2011], the stationary point is found. It is desirable to assess once geometry optimization has found a point that whether it is a transition state or a minimum. The stationary point is found using first and second-order derivatives, where the first derivatives confirm the stationary points and second-order derivatives confirm the nature of the stationary points. The second order derivative provides the normal-mode frequencies of a molecule. The matrix of the second order derivatives of the PES with respect to geometry is termed a Hessian (or force constant) matrix. A transition state will have (3N-5) real and one imaginary normal-mode frequency (corresponding to reaction coordinate) and for minima all (3N-6) frequencies are real and positive. Mathematically, a stationary point is the one on a multidimensional PES where the first derivative of potential energy with respect to each geometrical coordinate becomes zero.

$$\frac{dU}{dq_1} = \frac{dU}{dq_2} = \dots = 0 \quad (2.1)$$

Here, q_1, q_2, \dots are the normal coordinates. To decide the nature of a stationary point, the sign of the second order derivative of potential energy with respect to the coordinates is checked. For a minimum,

$$\frac{d^2U}{dq_i^2} > 0 \quad (2.2)$$

for all q_i , whereas, a saddle point is one where

$$\frac{d^2U}{dq_i^2} > 0 \quad (2.3)$$

for all q_i except the reaction coordinate q_{rc} , for which

$$\frac{d^2U}{dq_{rc}^2} < 0 \quad (2.4)$$

So, a stationary point is known as minima if all the eigenvalues of hessian matrix are positive, and if this minima is lowest on whole PES, than it is called global minima. The number of hessian evaluations depends on the order of integrator (described in the next section). A transition state (first order saddle point) is maximum in the direction of reaction coordinate but along all other directions, it is a minimum. The above description is for a first order saddle point. For a second order saddle point, two imaginary frequencies are obtained, i.e., it is a maximum along two pathways connecting stationary points. Zero-point energy (ZPE) is the energy which a molecule has even at absolute zero temperature. Energies $U(\vec{R})$ obtained as described above are classical energies without ZPE corrections. The vibrational frequency data can be used to calculate ZPE which can be added to the classical energies to obtain the zero point corrected energies. The ZPE of a molecule is not often small but it tends to cancel out for the whole reaction energy profile when ZPE is added to all the reactant, transition states, and products. To compare with experimental data, ZPE corrected energies are used. The computer program which was used for the electronic structure calculations reported in this thesis is the NorthWest computational chemistry (NWChem) program, an open-source computational chemistry package[Valiev *et al.*, 2010; Kendall *et al.*, 2000].

2.2 TRAJECTORY INTEGRATION

To perform a classical trajectory simulation, either Hamilton's or Newton's equation of motions are numerically integrated. A flowchart describing the steps involved in a classical trajectory simulation is shown in Figure 2.1. A number of different integration algorithms such as Gear, Gauss-Radau, AdamsMoulton, Runge-kutta and Bulirsch-Stoer[Press *et al.*, 1992; Stoer and Bulirsch, 2013; Bolton and Nordholm, 1994] algorithms are available. These algorithms are commonly used for smaller systems and accuracy order of these algorithms lies either at or higher than fourth order. These algorithms allow a maximum possible integration time-step, thus reducing the number of quantum chemistry single point calculations. Another class of integration method is, symplectic integrator scheme[Gray *et al.*, 1994; Janezic and Merzel, 1995] used for integrating the classical equations of motion. Symplectic integrators are better than the non-symplectic methods in various aspects. Symplectic integrators provide good energy conservation for longtime trajectories of large systems. The Verlet[Verlet, 1967] algorithm is an example of symplectic integrator which is generally used to integrate Newton's equation of motion. Symplectic integration scheme is favorable to study large systems for longer times but they are slow in comparison to non-symplectic methods. Further study about higher order integrators can be found in the literature[Schlier and Seiter, 1998, 2000]. In this thesis, two different symplectic integration schemes were used. One is Velocity Verlet and other is 6th order symplectic integrator. Symplectic integrators are used to solve explicitly single-step ordinary differential equation. These are based on Runge-Kutta methods[Sanz-Serna and Calvo, 2018]. Consider a differential equation of the form

$$\ddot{q}(t) = f[q] \quad (2.5)$$

The Verlet algorithm[Verlet, 1967] to solve the above equation is

$$q(t + \delta t) = 2q_i(t) - q_i(t - \delta t) - \delta t^2 f[q(t)] \quad (2.6)$$

To solve the differential equation, one needs to start with the value of $q(0)$ and $q(\delta t)$ and calculate consecutive values of q from above mentioned equation. To calculate the velocity in the verlet algorithm following approximation is used

$$\dot{q}(t) = \frac{q(t + \delta t) - q(t - \delta t)}{2\delta t} \quad (2.7)$$

By using the above expression, error after the iterative procedure to integrate the equation of motion for finite time interval is the order of δt^2 [Andersen, 1983]. The velocity and position both give the error of order δt^2 . The magnitude of error varies with the size of $q_{\delta t}$ and precision of the computer. This problem can be avoided by using velocity version of Verlet algorithm[Swope *et al.*, 1982].

$$q(t + \delta t) = q(t) + \delta t \dot{q}(t) + \frac{\delta t^2 f[q(t)]}{2} \quad (2.8)$$

$$\dot{q}(t + \delta t) = \dot{q}(t) + \frac{\delta t [f[q(t)] + f[q(t + \delta t)]]}{2} \quad (2.9)$$

These equations are equivalent to verlet algorithm. Above mentioned both equations allow one to calculate position and velocities at time $t + \delta t$ when the starting time is t . Also this procedure solves the differential equation with more accuracy on computers of fixed precision.

Integrators which belong to type S, compose of single symplectic steps[McLachlan, 1995]. These can be used to integrate any Hamiltonian system which can be written in partitioned form i.e. total energy is sum of kinetic and potential energy $H = T(p) + V(q)$. One complete step of S6 is given by

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do i = 0, 2, 4, ....., 14, 16
  q = q + delta t a(i) dot q
  p = p + delta t a(i + 1) dot p
end do
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$$q = q + \delta t a(18) \dot{q}$$

The vector components which are defined in the right-hand sides of the differential equations $\dot{p}_i = -\frac{\partial H}{\partial q_i}$, $\dot{q}_i = \frac{\partial H}{\partial p_i}$ and δt is the (full) time step. Further information about coefficients $a(i)$ and integrator can be found in literature [Schlier and Seiter, 1998].

2.2.1 Integration Timestep

The selection of an appropriate integration timestep for numerically integrating the classical equations of motions is very important as it plays an essential role in the formation of products and energy conservation of the trajectories. The value of integration timestep varies with systems due to their different vibrational frequency values. To select an appropriate timestep, one needs to take the largest vibrational frequency among all possible vibrational modes of the system and divide the corresponding *period* ($T = \frac{1}{\nu}$) by 10. The chosen timestep should not be as large, so the solution get altered and not too small as it increases the computational time of a trajectory.

2.3 TRAJECTORY INITIAL CONDITIONS

Selecting suitable initial conditions i.e., positions and momenta of all the atoms of a system at time $t = 0$ is a crucial step for a successful classical trajectory simulation. Initial conditions are selected to mimic experimental conditions. Various initial condition selection schemes are available. For example, classical and quantum micro-canonical sampling (fixed total energies) and thermal sampling (fixed temperature sampling) can be used for unimolecular reactions. A few barrier sampling schemes are also available. Review articles [Peslherbe *et al.*, 1999; Cho *et al.*, 1992] discussing these different sampling schemes are present in the literature. In the present work, classical micro-canonical sampling technique was used primarily. This scheme is used for mimicking gas phase experimental conditions. A description of this method is given below.

Classical Micro-canonical Sampling

One of the widely used scheme for initial condition selection is micro-canonical sampling where total energy available in the molecule is uniformly distributed over the entire classical phase space of the molecule [Ben-Naim, 2013]. For uniform distribution of total energy in the classical phase space energy shell $H(p,q)$, position q_i and momenta p_i are selected randomly. There are two ways to do this, classical and quantum micro-canonical sampling. The classical sampling randomly distributes the energy among the normal modes of the molecule without considering quantization and zero point energy restrictions. In the quantum algorithm, energy quanta are distributed among the modes considering zero point energy restrictions. Classical micro-canonical sampling technique is used in the present dynamics calculations.

In the normal-mode micro-canonical sampling, random values are chosen for the mode energies E_i , which are then used to select random values of position and momenta coordinates. The total energy of a molecule containing s harmonic oscillators is $E = \sum_{i=1}^s E_i$ where E_i is the energy associated with individual modes. Probability $P(E_1)dE_1$ for oscillator 1 having energy between E_1 to $E_1 + dE_1$ is proportional to the density of states of all the remaining oscillators [Hase and Buckowski, 1980]. The probability can be written as

$$P(E_i) = \frac{[E - \sum_{j=1}^{i-1} E_j - E_i]^{s-1-i}}{\int [E - \sum_{j=1}^{i-1} E_j - E_i']^{s-1-i} dE_i'} \quad (2.10)$$

where the integral is solved between the limit 0 to $\sum_{j=1}^{i-1} E_j$. The von Neumann rejection method or cumulative distribution function [Hammersley and Handscomb, 1964] can be used to calculate $P(E)$. The randomly selected energy values are then used to get the values of position and conjugate momenta, which are then used in classical trajectory simulations. Since constant energy is involved in micro-canonical sampling technique, this method is useful for studying intrinsic RRKM (Rice-Ramsperger-Kassel-Marcus) behavior of molecules [Baer *et al.*, 1996].

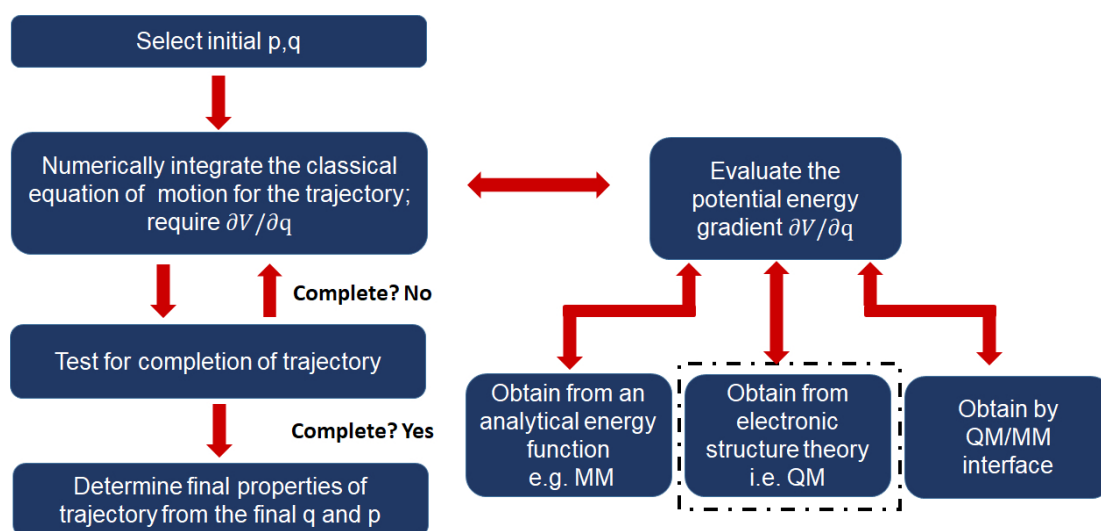


Figure 2.1 : Flowchart of a classical trajectory simulation.

2.4 RRKM RATE CONSTANT CALCULATIONS

This thesis is focused on studying the unimolecular dynamics of reactions in the gas phase. Initial conditions mimicking experiments are time propagated and the trajectory results are analyzed for different reaction pathways, mechanisms, and product energy distributions. The trajectory results are compared with experimental data or a statistical reaction rate theory predictions. Comparing the trajectory results with rate theory predictions provide information about the nature of the intra-molecular dynamics. One of the most celebrated unimolecular reaction rate theories is Rice-Ramsperger-Kassel-Marcus (RRKM) theory. RRKM theory is based on the assumption of (a) equal probability of distribution of internal energy in all the modes of an energized molecule and (b) steady state approximation [Levine, 2009; Di Giacomo, 2015]. A molecule is assumed as a collection of coupled harmonic oscillators and each state of the molecule is equally probable. An ensemble of molecules are activated to a state possessing a certain amount of total energy E out of which E_{rot}^* exists as rotational energy and remaining as internal vibrational energy. Activation of molecule (A^*) can be done via thermal, collisional or photochemical methods. These activated molecules have energy $E - E_{rot}^*$ distributed randomly among the vibrational degree of freedom [Callear, 1983; Berne *et al.*, 1988]. RRKM theory further assumes that intra-molecular vibrational energy redistribution (IVR) is spontaneous and fast and occurs well before the molecule undergoes dissociation. The RRKM rate constant is

$$k(E, E_{rot}) = \frac{G(E^\ddagger)}{N(E - E_{rot})h} \quad (2.11)$$

Here, $G(E^\ddagger)$ is the sum of states for the active degrees of freedom in the transition state and $N(E - E_{rot})$ is the density of states for the active degrees of freedom in the reactant. RRKM rate constants were calculated using the computer program developed by William Hase and co-workers[Zhu and Hase, 1994].

2.5 SOFTWARE

Electronic structure calculations reported in the present work were carried out using the electronic structure theory package NWChem[Valiev *et al.*, 2010]. The dynamics calculations were performed using the general chemical dynamics program VENUS[Hase *et al.*, 1996; Hu *et al.*, 1991]. The two programs were compiled together using a tight coupling algorithm[Lourderaj *et al.*, 2014]. Classical trajectories were integrated by VENUS with potentials and gradients computed on-the-fly using the NWChem program.

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