

Ab initio Molecular Dynamics and Energy Landscapes

1. The Virial Theorem

In mechanics, the virial theorem provides a general equation relating the average total kinetic energy $2\langle T \rangle$ of a system with its average total potential energy $n\langle V \rangle$, where angle brackets represent the average of the enclosed quantity. Mathematically, the theorem states

$$2\langle T \rangle = \sum_{k=1}^N \mathbf{F}_k \cdot \mathbf{r}_k \quad (1)$$

where \mathbf{F}_k represents the force on the k th particle, which is located at position \mathbf{r}_k . The word "virial" derives from vis, the Latin word for "force" or "energy", and was given its technical definition by Clausius in 1870.

Significance: This allows the average kinetic energy of complicated system to be calculated.

If the force between any two particles of the system results from a potential energy $V(r) = \alpha r^n$ that is proportional to some power n of the inter-particle distance r , the virial theorem adopts a simple form

$$2\langle T \rangle = n\langle V_{TOT} \rangle \quad (2)$$

Let \hat{H} be the time-independent Hamiltonian of a system in the bound stationary state ψ :

$$\hat{H}\psi = E\psi \quad (3)$$

Let \hat{A} be a linear time-independent operator. Then

$$\int \psi^* [\hat{H}, \hat{A}] \psi d\tau = 0 \quad (4)$$

Equation (4) is the hypervirial theorem.

We now choose \hat{A} to be

$$\sum_i \hat{q}_i \hat{p}_i = -i\hbar \sum_i q_i \frac{\partial}{\partial q_i} \quad (5)$$

$$[\hat{A}, \hat{B} + \hat{C}] = [\hat{A}, \hat{B}] + [\hat{A}, \hat{C}], \quad [\hat{A}, \hat{B}\hat{C}] = [\hat{A}, \hat{B}]\hat{C} + \hat{B}[\hat{A}, \hat{C}], \quad [\hat{q}_i, \hat{H}] = \frac{i\hbar}{m} \hat{p}_i$$

$[\hat{H}, \hat{A}]$ now becomes,

$$[\hat{H}, \sum_i \hat{q}_i \hat{p}_i] = \sum_i [\hat{H}, \hat{q}_i \hat{p}_i] = \sum_i \hat{q}_i [\hat{H}, \hat{p}_i] + \sum_i [\hat{H}, \hat{q}_i] \hat{p}_i \quad (6)$$

$$[\hat{H}, \hat{A}] = i\hbar \sum_i q_i \frac{\partial V}{\partial q_i} - i\hbar \sum_i \frac{1}{m_i} \hat{p}_i^2 = i\hbar \sum_i q_i \frac{\partial V}{\partial q_i} - 2i\hbar T \quad (7)$$

For the hypervirial theorem, this yields

$$\int \psi^* i\hbar \sum_i q_i \frac{\partial V}{\partial q_i} \psi d\tau = \int \psi^* (2i\hbar T) \psi d\tau \quad (8)$$

or

$$2\langle T \rangle = \left\langle \sum_i q_i \frac{\partial V}{\partial q_i} \right\rangle \quad (9)$$

Euler's theorem on homogeneous functions states that if $f(x_1, x_2, \dots, x_j)$ is homogeneous function of degree n , then

$$\sum_{k=1}^j x_k \frac{\partial f}{\partial x_k} = n f \quad (10)$$

If V is a homogeneous function of n , the virial theorem simplifies to

$$2\langle T \rangle = n\langle V \rangle \quad (11)$$

(equal-partition theorem)

For a many-electron atom with spin-orbit interaction neglected

$$V = \sum_i^n \frac{Ze^2}{r_i} + \sum_i \sum_{j>i} \frac{e^2}{r_{ij}} \quad (12)$$

V is homogeneous of degree -1. $2\langle T \rangle = -\langle V \rangle$

For many-atom molecules,

$$\sum_i q_i \frac{\partial V_{el}}{\partial q_i} + \sum_\alpha q_\alpha \frac{\partial V_{el}}{\partial q_\alpha} = -V_{el} \quad (13)$$

This produces

$$2\langle T_{el} \rangle = -\langle V_{el} \rangle - \sum_\alpha q_\alpha \frac{\partial E_{el}}{\partial q_\alpha} \quad (14)$$

2. The Hellmann-Feynman Theorem

The Hellmann-Feynman theorem states that once the spatial distribution of the charged particles (usually the electron clouds) has been determined by solving the Schrödinger equation, all the forces in the system can be calculated using the classical electrostatics. It is named for its independent provers Hans Hellmann (1936) and Richard Feynman (1939).

This quantum mechanics theorem relates the energy eigenvalues of a time-independent Hamiltonian operator to the parameters composing it. In general, the theorem states that,

$$\frac{\partial E_n}{\partial \lambda} = \int \psi_n^* \frac{\partial \hat{H}}{\partial \lambda} \psi_n d\tau \quad (15)$$

where \hat{H} is the parameterized Hamiltonian operator,

E_n is the nth Hamiltonian eigenvalue,

λ is a continuous parameter of interest.

3. The Electrostatic Theorem

Hellmann and Feynmann independently applied equation 15 to molecules, taking λ at an atomic coordinate. Using the Born-Oppenheimer approximation, solving the electronic Schrödinger equation for a fixed nuclear configuration

$$\hat{H} \psi_{el} = (\hat{T}_{el} + \hat{V}) \psi_{el} = U \psi_{el} \quad (16)$$

The potential energy U is

$$\hat{V} = \hat{V}_{el} + \hat{V}_{NN} \quad (17)$$

If taking x_δ as the x coordinate of atom δ , the generalized Hellmann-Feynmann theorem gives

$$\frac{\partial U}{\partial x_\delta} = \int \psi_{el}^* \frac{\partial \hat{H}}{\partial x_\delta} \psi_{el} d\tau_{el} \quad (18)$$

...

$$\frac{\partial U}{\partial x_\delta} = -Z_\delta e^2 \int |\psi_{el}|^2 \sum_i \frac{x_i - x_\delta}{r_{i\delta}^3} d\tau_{el} + \sum_{\alpha \neq \delta} Z_\alpha Z_\delta e^2 \frac{x_\alpha - x_\delta}{R_{\alpha\delta}^3} \quad (19)$$

Or

$$\frac{\partial U}{\partial x_\delta} = -Z_\delta e^2 \iiint \rho(x, y, z) \frac{x - x_\delta}{r_\delta^3} dx dy dz + \sum_{\alpha \neq \delta} Z_\alpha Z_\delta e^2 \frac{x_\alpha - x_\delta}{R_{\alpha\delta}^3} \quad (20)$$

This is the Hellmann-Feynmann electrostatic theorem

The effective force acting on a nucleus in a molecule can be calculated by simple electrostatics as the sum of the Coulombic forces exerted by the other nuclei and by a hypothetical electron cloud whose charge density is found by solving the electronic Schrödinger equation.

4. *Ab initio* Molecular Dynamics

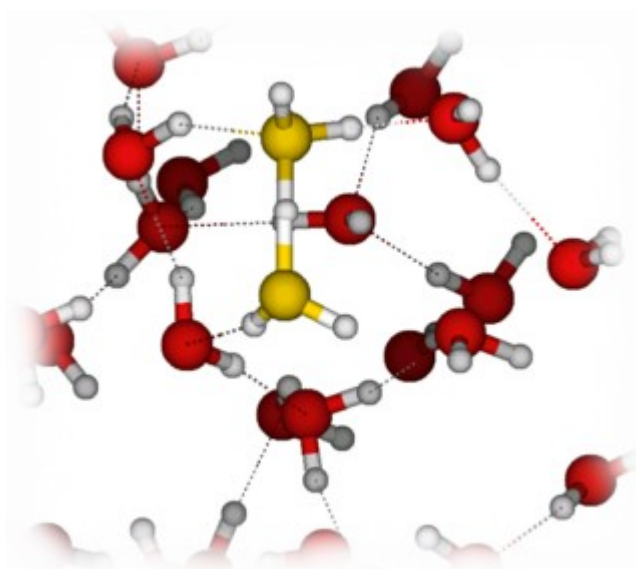
In this lecture, we will be focusing on Born-Oppenheimer Molecular Dynamics.

The aim of molecular dynamics is to model the detailed microscopic dynamical behavior of many

different types of systems in chemistry, physics or biology. The history of MD goes back to the mid 1950's when first computer simulations performed on simple fluids.

Molecular dynamics is a technique to investigate equilibrium and transport properties of many-body systems.

- The nuclear motion of the particles is modeled using the laws of classical mechanics.



4.1 Equation of Motion

The equations of motion are according to Hamilton's equation:

$$\dot{p} = -\frac{\partial H}{\partial q} = -\frac{\partial U}{\partial q} = F \quad (21)$$

$$\dot{q} = \frac{\partial H}{\partial p} = \frac{p}{m} \quad (22)$$

The simplest interpretation of the Hamilton Equations is as follows, applying them to a one-dimensional system consisting of one particle of mass m and exhibiting **conservation of energy**:

Now the time-derivative of the momentum p equals the Newtonian force, and so here the first Hamilton Equation means that the force on the particle equals the rate at which it loses potential energy with respect to changes in x , its location. (Force equals the negative gradient of potential energy.)

The time-derivative of q here means the velocity: the second Hamilton Equation here means that the particle's velocity equals the derivative of its kinetic energy with respect to its momentum.

From which we get Newton's second law

$$M_j R_j = F_j(R^N) \quad (23)$$

4.2 Microcanonical Ensemble

The equations of motion are time reversible (invariant to the transformation $t \rightarrow -t$), and the total energy is a constant of motion.

$$\frac{\partial E}{\partial t} = \frac{\partial H}{\partial t} = 0 \quad (24)$$

These properties are important to establish a link between MD and statistical mechanics.

Statistical ensembles are usually characterized by fixed values of thermodynamic variables such as energy (E), temperature (T); pressure (P); volume (V) or chemical potential (μ).

One fundamental ensemble is called the microcanonical ensemble (NVE).

Other ensembles:

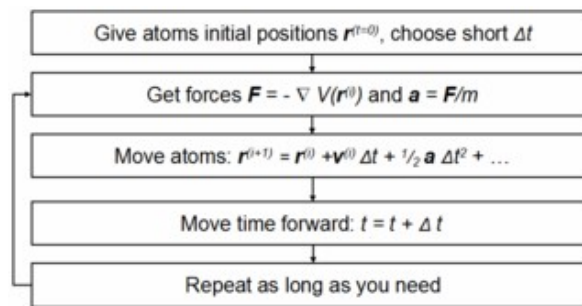
Canonical ensemble NVT

isothermal-isobaric NPT

Grand-canonical μVT

4.3 Numerical Integration

By integration of Hamilton's equation of motion for a number of atoms in a fixed volume, we can create a trajectory; time averages and time correlation functions of the trajectory are directly related to ensemble averages of the microcanonical ensemble.



- In a computer experiment, we will not be able to generate the true trajectory of a system without a given set of initial positions and velocity.
- For all potentials used in real applications, only numerical methods can be used. (based on discretization of time, and repeated calculations of the forces on each particle)

The velocity Verlet algorithm:

$$\mathbf{R}(t + \Delta t) = \mathbf{R}(t) + \mathbf{V}(t) \Delta t + \frac{\mathbf{F}(t)}{2m} \Delta t^2 \quad (25)$$

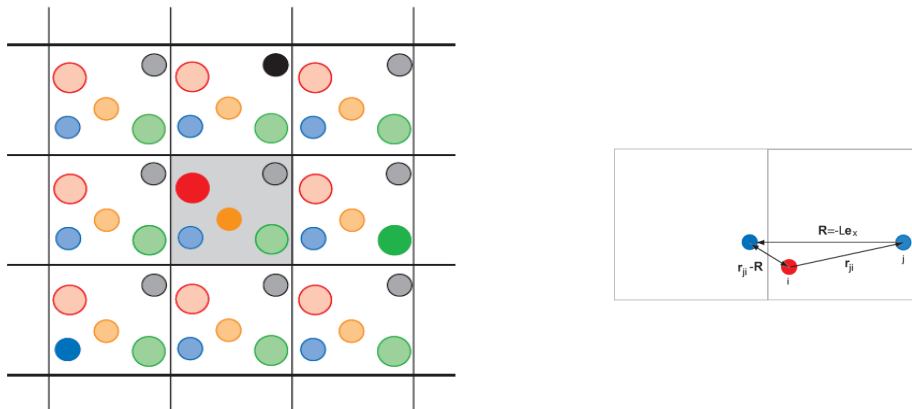
$$V(t+\Delta t) = V(t) \Delta t + \frac{F(t+\Delta t) + F(t)}{2m} \Delta t^2 \tag{26}$$

To perform MD the initial values for positions and velocities have to be chosen together with an appropriate time step Δt . (In the initial stage, strong fluctuations may occur).

- The average temperature $\langle \frac{1}{2} m v^2 \rangle = \frac{1}{2} k_B T$
- Maxwell-Boltzmann velocity distribution: $f_v(v_i) = \sqrt{\frac{m}{2\pi k_B T}} \exp\left[\frac{-mv_i^2}{2k_B T}\right]$.
- The diffusion constant $D = \Delta R^2(\tau) = \langle (R(\tau) - R(0))^2 \rangle$
- The pair correlation function
- The velocity auto-correlation function

4.4 Extended Systems

Minimum Image



Pressure Control

Internal Pressure – It is a quantity independent of container or any external source. It is usually calculated by the Virial Theorem of Clausius

$$PV = N k_B T + \frac{1}{d} \sum_{i < j} F_{ij} \cdot R_{ij} \tag{27}$$

Where d is the dimensionality of the system, P is the internal pressure. Likewise, the stress tensor can be defined $V \pi^{\alpha\beta} = \langle \sum_i m_i v_i^\alpha v_i^\beta + \sum_{i < j} \sum_\alpha \sum_\beta F_{i\alpha j\beta} \cdot R_{i\alpha j\beta} \rangle$.

Keeping the pressure constant is a desirable feature for many applications of molecular dynamics. The concept of constant-pressure molecular dynamics was first introduced by Anderson (H. C. Andersen, Molecular dynamics simulations at constant pressure and/or temperature, J. Chem. Phys. 72, 2384, 1980). The volume of the system becomes a generalized coordinate coupled with the atoms' coordinate in the equation of motion of the whole system.

In the Parrinello-Rahman method the dynamics of the unit cell matrix are governed by the equation

$$W \ddot{h} = (\pi - p) \sigma \quad (28)$$

Where w is a fictitious mass parameter, and $\sigma = V h^{-1}$ and p is the external pressure (stress).

Temperature Control

The common technique of velocity scaling is suitable for use during the equilibration period but does not generate meaningful particle trajectories.

At periodic intervals linear and angular velocities are multiplied by a factor of

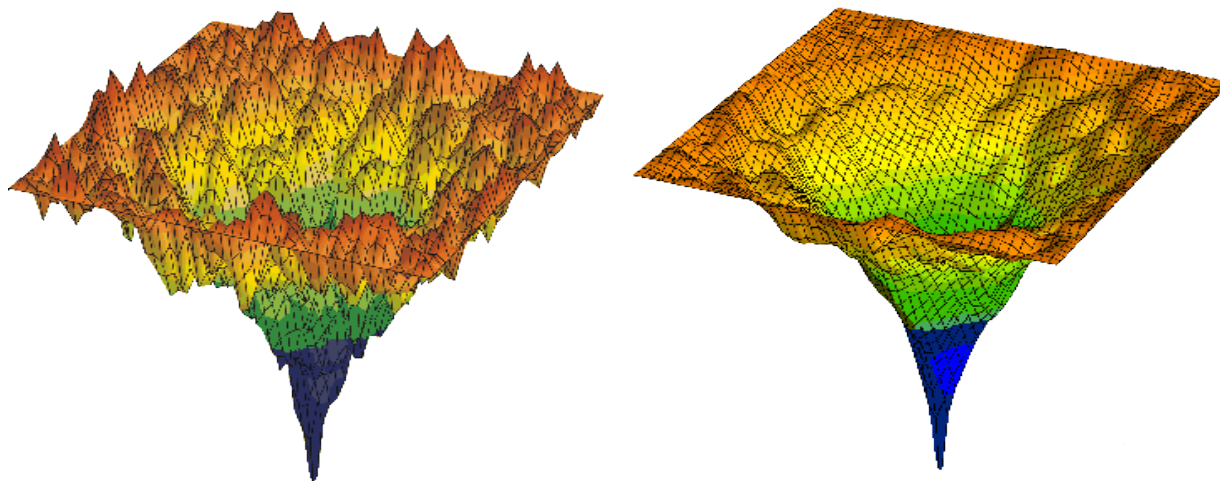
$$s = \sqrt{\frac{g k_B T}{2 K}} \quad (29)$$

where T is the desired temperature. By repeatedly setting the “instantaneous” temperature to the correct value while the system approaches its equilibrium state, the kinetic energy is made to approach its desired value.

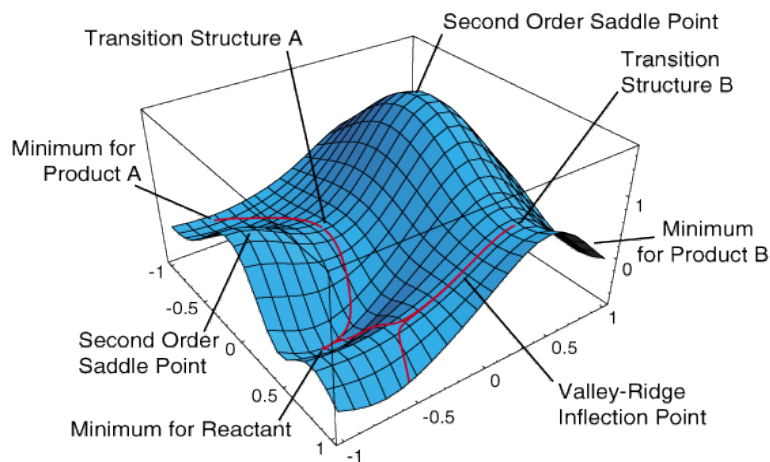
The Nosè-Hoover (chain) method couples the system to a heat bath using a fictional dynamical variable and the Gaussian thermostat replaces the Newton-Euler equations by variants of which the kinetic energy is a conserved quantity.

5. Energy Landscapes

The term “energy landscape” was probably first introduced in the context of potential energy surfaces, which represents the potential energy of a given system as a function of all the relevant atomic or molecular coordinates.



- High dimensional (hyper-surface)
- Manifestations of all chemical reactions, kinetics and structures of complex matter.
- Basic features of PES



Potential, Gradient, and Hessian (eigenvalue and eigenvector)

In mathematics, the Hessian matrix is the square matrix of second-order partial derivatives of a function. Given the real-valued function $f(x_1, x_2, x_3, \dots)$

$$H(f) = \begin{bmatrix} \frac{\partial^2 f}{\partial x_1^2} & \frac{\partial^2 f}{\partial x_1 \partial x_2} & \dots & \frac{\partial^2 f}{\partial x_1 \partial x_n} \\ \frac{\partial^2 f}{\partial x_2 \partial x_1} & \frac{\partial^2 f}{\partial x_2^2} & \dots & \frac{\partial^2 f}{\partial x_2 \partial x_n} \\ \dots & \dots & \dots & \dots \\ \frac{\partial^2 f}{\partial x_n \partial x_1} & \frac{\partial^2 f}{\partial x_n \partial x_2} & \dots & \frac{\partial^2 f}{\partial x_n^2} \end{bmatrix} \quad (30)$$

Mass-weighted force-constants is defined as $H_{ij} = \frac{1}{\sqrt{m_i m_j}} \left(\frac{\partial^2 U}{\partial x_i \partial x_j} \right)$

Normal Modes (explain here)

Harmonica vibration frequency is obtained by diagonalizing H $\det(H_{ij} - \delta_{ij} \lambda_k) = 0$

$$\nu_k = \frac{1}{2\pi} \sqrt{\lambda_k} \quad (31)$$

Vibrational energy $E_{vib} = \sum_{n=1}^{3n-6} \left(\nu_k + \frac{1}{2} \right) h \nu$

Basins (Megabins)
 Stationary points (minima, and saddle points)
 Pathways

5.1 Take a walk on the energy landscape

5.1.1 Finding local minima

The field of geometry optimization involves the location of stationary points on the PES, be they minima, transition states or higher index saddles with more than one negative Hessian eigenvalues.

- Steepest Decent

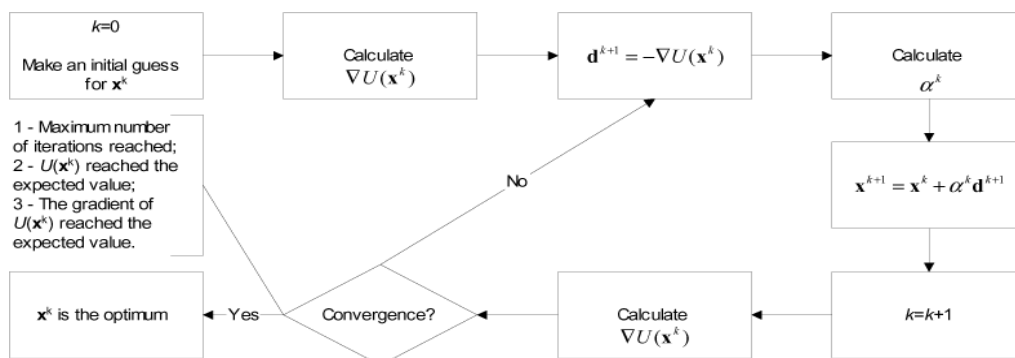
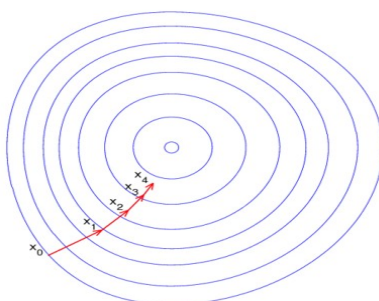
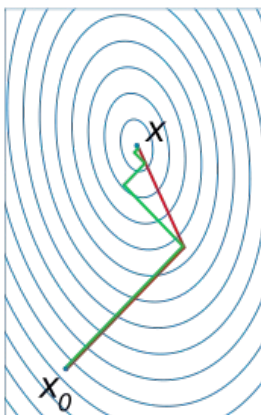


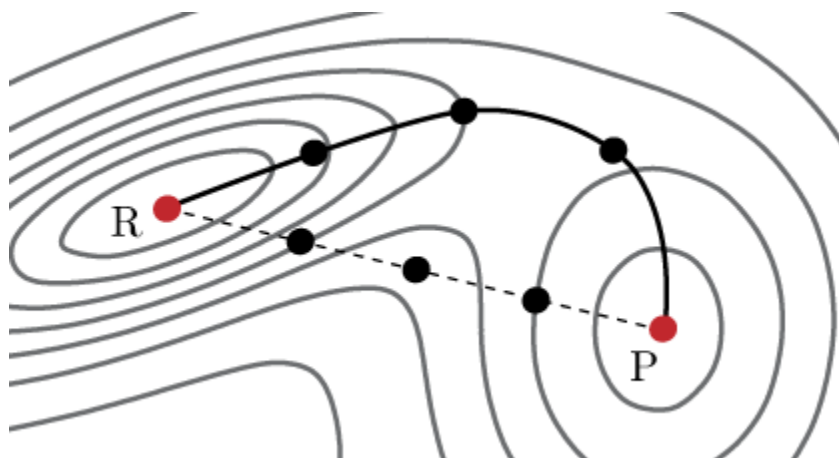
Figure 1. Iterative procedure for the Steepest Descent Method.

- Conjugate Gradient



5.1.2 Finding Transition States

- Eigen-mode following method
- Dimer method
- Nudged elastic band



The Nudged Elastic Band method is to find transition paths (and the corresponding energy barriers) between the given initial and final states of a chemical reaction. Following the Nudged Elastic Band method, a chain of replicas (also called images) of the system is constructed. Then, the chain is deformed in order to minimize the energy barrier for the reaction. The class implements the algorithm described in the references

Calculating reaction pathways

5.2 Global Optimization (conformation search)

- Basin hopping
- Simulated annealing
- Molecular Dynamics (Accelerated Dynamics)
- Various Monte Carlo Methods (Landau-Wang)
- Genetic Algorithms
- Energy Landscape Paving
- Potential Energy Surface Deformation

5.3 Properties of Energy Landscape

ab initio methods are capable of quantifying PES and related properties.

Thermodynamics, Kinetics (Transition State Theory) ... beyond the scope of this course.