FIFTH LECTURE

CONTENTS

I. SUMMARY PREVIOUS LECTURE

A. Hamiltonian function

$$\mathcal{H}(x,p) \;=\; \frac{p^2}{2m} + V(x)\,, \tag{1}$$

B. Equations of motion

$$\begin{cases} \dot{x} &= \dfrac{\partial \mathcal{H}}{\partial p} = \dfrac{p(t)}{m} \\ \dot{p} &= -\dfrac{\partial \mathcal{H}}{\partial x} = F(t) = -\dfrac{d}{dx}V(x(t)) \end{cases} . \tag{2}$$

C. Semi-implicit Euler integrator

Consider a discretization of the time interval $[0,\tau]$ in timesteps $t_0, t_1, t_2, ..., t_{N_\tau}$, with $t_0 = 0$, $t_{N_\tau} = \tau$, and $t_{k+1} - t_k = \Delta t$.

$$\begin{cases} F(t_k) = -\dfrac{d}{dx}V(x(t_k)) \\ x(t_{k+1}) = x(t_k) + \dfrac{p(t_k)}{m}\Delta t + \dfrac{F(t_k)}{m}\Delta t^2 \\ p(t_{k+1}) = p(t_k) + F(t_k)\Delta t \end{cases} . \tag{3}$$

D. Velocity Verlet integrator

$$\begin{cases} F(t_k) = -\dfrac{d}{dx}V(x(t_k)) \\ x(t_{k+1}) = x(t_k) + \dfrac{p(t_k)}{m}\Delta t + \dfrac{F(t_k)}{m}\Delta t^2 \\ F(t_{k+1}) = -\dfrac{d}{dx}V(x(t_{k+1})) \\ p(t_{k+1}) = p(t_k) + \dfrac{1}{2}\left[F(t_k) + F(t_{k+1})\right]\Delta t \end{cases}, \tag{4}$$

E. Taylor expansion

The Taylor expansion of a function $f(x)$ at $x + \Delta x$, where Δx is a small interval, is

$$\begin{aligned} f(x+\Delta x) &= \sum_{n=0}^{\infty} \frac{f^{(n)}(x)}{n!}\Delta x^n \\ &= f(x) + \frac{f'(x)}{1!}\Delta x + \frac{f''(x)}{2!}\Delta x^2 + \frac{f'''(x)}{3!}\Delta x^3 + \cdots . \end{aligned} \tag{5}$$

F. Comments

- Hamiltonian dynamics is a mathematical framework that describes the evolution of physical systems by considering their energy, expressed through a function called the Hamiltonian, and the associated equations of motion.

- Solving the equations of motion means finding an $x(t)$ function for position and a $p(t)$ function for momentum that describes the time evolution of the system's physical state. The function $x(t)$ is also called the trajectory of the system.

- The equations of motion are ordinary differential equations, but only in a few fortunate cases is it possible to find an analytical solution (i.e. an exact solution), for example the harmonic oscillator. In most cases, we can only find numerical solutions (i.e. approximate solutions) by applying an integrator scheme.

- There are different integrator schemes, each with advantages and disadvantages. Integrator schemes are constructed by applying the Taylor expansion to the functions $x(t)$ and $p(t)$. The Euler scheme is very simple, it is based on the Taylor expansion truncated at the second term, but the approximate solution diverges from the exact solution in the short term. To improve the accuracy, it is necessary to use a very small integrator step Δt, but this requires an increase in the number of timesteps.

- Verlet's scheme is more precise, since it is based on Taylor's expansion truncated at the third term. However, the greater precision requires greater computational calculation, as it is necessary to calculate the force twice, at time t_k and time t_{k+1}.

II. SIMULATION OF A DIATOMIC MOLECULE

A. The system

Consider two atom nuclei in two-dimensional space. The atoms are represented by two two-dimensional vectors:

$$\mathbf{r}_1 = \begin{pmatrix} x_1 \\ y_1 \end{pmatrix} \; ; \quad \mathbf{r}_2 = \begin{pmatrix} x_2 \\ y_2 \end{pmatrix} . \tag{6}$$

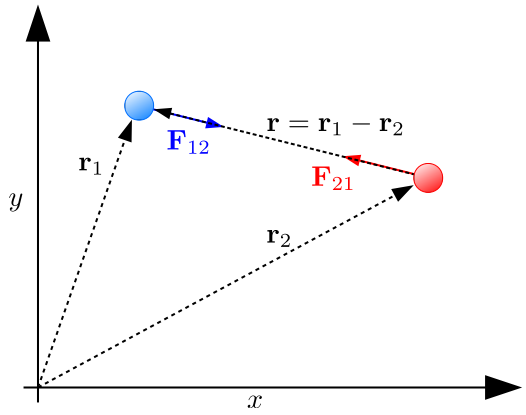
The difference vector that connects the two atoms is

$$\mathbf{r} = \mathbf{r}_1 - \mathbf{r}_2 = \begin{pmatrix} x_1 - x_2 \\ y_1 - y_2 \end{pmatrix} . \tag{7}$$

The Euclidean distance between the two atoms is

$$r = \|\mathbf{r}\| = \|\mathbf{r}_1 - \mathbf{r}_2\| = \sqrt{(x_1 - x_2)^2 + (y_1 - y_2)^2} , \tag{8}$$

where the notation $\| \cdot \|$ denotes the Euclidean norm.



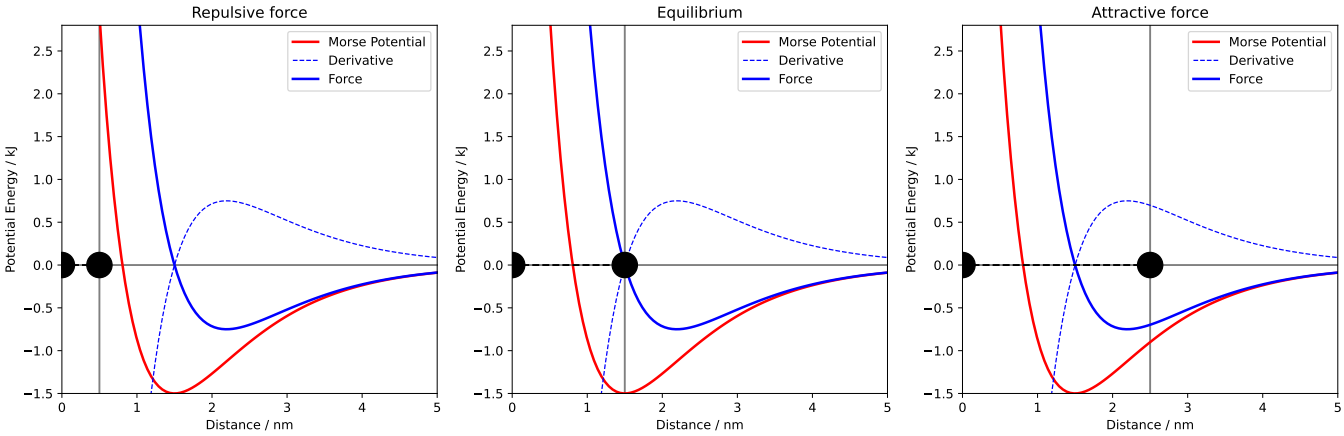
B. The Morse potential

The system is governed by a potential energy function $V(r)$, where r is the Euclidean distance. Being the Euclidean distance a function of all the coordinates of the atoms, the potential can be written also as a function of the coordinates $V(x_1, y_1, x_2, y_2)$, or of the two vectors denoting the position of the atoms in space $V(\mathbf{r}_1, \mathbf{r}_2)$. Several potentials can be used to model the interaction between two atoms, here we consider the Morse potential

$$V(r) = V(x_1, y_1, x_2, y_2) = V(\mathbf{r}_1, \mathbf{r}_2) = D \left(1 - e^{-\alpha(r - r_e)}\right)^2 , \tag{9}$$

where:

- r is the Euclidean distance as defined in eq. 8,
- r_e is the equilibrium bond length,
- D is the dissociation energy (depth of the potential well),
- α is the parameter determining the width of the well.



C. The interatomic force between atoms

The potential generates a pair of forces $\mathbf{F}_{12}$ and $\mathbf{F}_{21}$ that can be attractive or repulsive depending on the Euclidean distance between the two atoms. $\mathbf{F}_{12}$ is the force exerted on atom 1, and it is defined by the gradient of the potential:

$$\mathbf{F}_{12} = -\nabla_{\mathbf{r}_1} V(r) = \begin{pmatrix} F_{12,x_1} \\ \\ F_{12,y_1} \end{pmatrix} = \begin{pmatrix} -\dfrac{dV(r)}{dx_1} \\ -\dfrac{dV(r)}{dy_1} \end{pmatrix} . \tag{10}$$

1. Gradient of a function

In eq. 10, we used the gradient of a function: Consider a two-dimensional arbitrary function $f(x, y) : \mathbb{R}^2 \to \mathbb{R}$, the gradient of the function is the vector which contains the derivatives in both directions:

$$\nabla f = \begin{pmatrix} \dfrac{df}{dx} \\ \dfrac{df}{dy} \end{pmatrix} . \tag{11}$$

In eq. 10, the notation $\nabla_{\mathbf{r}_1} V(r)$ denotes the gradient with respect to the coordinates x_1 and y_1 of the vector $\mathbf{r}_1$.

2. Chain rule

To calculate the derivative of $V(r)$ with respect to x_1, we use the chain rule. Consider two arbitrary functions $f(x), g(x) : \mathbb{R} \to \mathbb{R}$ and the composite function

$$y = f(g(x)) , \tag{12}$$

then the derivative of y with respect to x is

$$\frac{dy}{dx} = \frac{d\, f(g(x))}{dx} = \frac{df}{dg}\frac{dg}{dx} . \tag{13}$$

The Euclidean distance r is a function of all coordinates x_1, y_1, x_2, y_2, then we can apply the chain rule:

$$F_{12,x_1} = -\frac{dV(r)}{dx_1} = -\frac{dV(r)}{dr}\frac{dr}{dx_1} , \tag{14}$$

and

$$F_{12,y_1} = -\frac{dV(r)}{dy_1} = -\frac{dV(r)}{dr}\frac{dr}{dy_1} . \tag{15}$$

D. The law of action and reaction

To find the components of the force $\mathbf{F}_{21}$ acting on atom 2, we apply the law of action and reaction:
For every action, there is an equal and opposite reaction. This means that when one particle at $\mathbf{r}_1$ exerts a force $\mathbf{F}_{21}$ on another particle $\mathbf{r}_2$, the second particle exerts an equal and opposite force $\mathbf{F}_{12}$ back on the first particle:

$$\mathbf{F}_{21} = -\mathbf{F}_{12} . \tag{16}$$

Then the components of $\mathbf{F}_{21}$ are

$$\begin{pmatrix} F_{21,x_2} &=& -F_{12,x_1} \\ \\ F_{21,y_2} &=& -F_{12,y_1} \end{pmatrix} \tag{17}$$

E. Derivative of the Morse potential and Euclidean distance

Finally, to calculate the force components defined in eq. 14, 15, we need the derivative of the potential $V(r)$ with respect to the Euclidean distance r:

$$\frac{dV(r)}{dr} = 2D\alpha e^{-\alpha(r-r_e)}\left(1 - e^{-\alpha(r-r_e)}\right), \tag{18}$$

and the derivatives of the Euclidean distance r with respect to the coordinates x_1, y_1, x_2, y_2:

$$\frac{dr}{dx_1} = \frac{(x_1 - x_2)}{\sqrt{(x_1 - x_2)^2 + (y_1 - y_2)^2}} = \frac{(x_1 - x_2)}{r}; \tag{19}$$

$$\frac{dr}{dy_1} = \frac{(y_1 - y_2)}{r}; \tag{20}$$

$$\frac{dr}{dx_2} = -\frac{(x_1 - x_2)}{r}; \tag{21}$$

$$\frac{dr}{dy_2} = -\frac{(y_1 - y_2)}{r}. \tag{22}$$

F. The Hamiltonian of a diatomic molecule

The kinetic energy of the full system is the sum of the kinetic energy of each particle:

$$\begin{aligned} E_k &= \sum_{i=1}^{2} \frac{1}{2} m_i \mathbf{v}_i^2 = \frac{1}{2} m_1 \mathbf{v}_1^2 + \frac{1}{2} m_2 \mathbf{v}_2^2 \\ &= \sum_{i=1}^{2} \frac{\mathbf{p}_i^2}{2m_i} = \frac{\mathbf{p}_1^2}{2m_1} + \frac{\mathbf{p}_2^2}{2m_2} \\ &= \frac{p_{x_1}^2}{2m_1} + \frac{p_{y_1}^2}{2m_1} + \frac{p_{x_2}^2}{2m_2} + \frac{p_{y_2}^2}{2m_2} \end{aligned} \tag{23}$$

The Hamiltonian function of a system with N particles moving in Euclidean space is

$$\mathcal{H}(\mathbf{r}_1, \mathbf{r}_2, \mathbf{p}_1, \mathbf{p}_2) = \sum_{i=1}^{2} \frac{\mathbf{p}_i^2}{2m_i} + V(\mathbf{r}_1, \mathbf{r}_2), \tag{24}$$

The equations of motion are

$$\begin{cases} \dot{\mathbf{r}_1} &= \dfrac{\partial \mathcal{H}}{\partial \mathbf{p}_1} = \dfrac{\mathbf{p}_1(t)}{m_1} \\ \dot{\mathbf{r}_2} &= \dfrac{\partial \mathcal{H}}{\partial \mathbf{p}_2} = \dfrac{\mathbf{p}_2(t)}{m_2} \\ \dot{\mathbf{p}_1} &= -\dfrac{\partial \mathcal{H}}{\partial \mathbf{r}_1} = -\nabla_{\mathbf{r}_1} V(\mathbf{r}_1(t), \mathbf{r}_2(t)) = \mathbf{F}_{12}(t) \\ \dot{\mathbf{p}_2} &= -\dfrac{\partial \mathcal{H}}{\partial \mathbf{r}_2} = -\nabla_{\mathbf{r}_2} V(\mathbf{r}_1(t), \mathbf{r}_2(t)) = \mathbf{F}_{21}(t) \end{cases}. \tag{25}$$

The equations of motion for each coordinate are written as

$$\begin{cases} \dot{x_1} &= \dfrac{\partial \mathcal{H}}{\partial p_{x_1}} = \dfrac{p_{x_1}(t)}{m_1} \\ \dot{y_1} &= \dfrac{\partial \mathcal{H}}{\partial p_{y_1}} = \dfrac{p_{y_1}(t)}{m_1} \\ \dot{x_2} &= \dfrac{\partial \mathcal{H}}{\partial p_{x_2}} = \dfrac{p_{x_2}(t)}{m_2} \\ \dot{y_2} &= \dfrac{\partial \mathcal{H}}{\partial p_{y_2}} = \dfrac{p_{y_2}(t)}{m_2} \\ \dot{p_{x_1}} &= -\dfrac{\partial \mathcal{H}}{\partial x_1} = -\dfrac{dV}{dx_1} = F_{12,x_1}(t) \\ \dot{p_{y_1}} &= -\dfrac{\partial \mathcal{H}}{\partial y_1} = -\dfrac{dV}{dy_1} = F_{12,y_1}(t) \\ \dot{p_{x_2}} &= -\dfrac{\partial \mathcal{H}}{\partial x_2} = -\dfrac{dV}{dx_2} = F_{21,x_2}(t) \\ \dot{p_{y_2}} &= -\dfrac{\partial \mathcal{H}}{\partial y_2} = -\dfrac{dV}{dy_2} = F_{21,y_2}(t) \end{cases} . \tag{26}$$