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Introduction to algorithms for molecular simulations

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INTRODUCTION TO ALGORITHMS
FOR MOLECULAR SIMULATIONS

Martin Kramář

Abstract

In the first part of the paper we survey some algorithms which describe time evolution of interacting particles in a bounded domain. Applications to macroscale as well as microscale are presented on two examples: motion of planets and collision of two bodies. In the second part of the paper we present solution to stationary Schrödinger equation for simple molecular models.

1 Algorithm for dynamic simulation

We consider a system of n particles, which are determined by their weights $\{m_1, \ldots, m_n\}$, positions $\{\mathbf{x}_1, \ldots, \mathbf{x}_n\}$ and velocities $\{\mathbf{v}_1, \ldots, \mathbf{v}_n\}$. We assume the following computational domain: $\Omega = [0, L_1] \times [0, L_2]$ or $\Omega = [0, L_1] \times [0, L_2] \times [0, L_3]$ in two or three dimensions, respectively. Further we assume that particles that left Ω do not interact any longer with those in Ω. The time evolution is described by Newton's equation of motion $m_i \dot{\mathbf{v}}_i = \mathbf{F}_i$ or $m_i \ddot{\mathbf{x}}_i = \mathbf{F}_i, i = 1, \ldots, n$ [1].

1.1 Velocity-Störmer-Verlet method

We consider the time interval $[0, t_{end}]$ to be discretized into subintervals with the step δt so that Newton's equation of motion are replaced with an algebraic system at $n \cdot \delta t$ where $n = 1, \cdots, n_{t_{end}}$, while using the second central difference $\left[\frac{d^2 x}{dt^2}\right]_n = \frac{1}{\delta t^2}(x(t_{n+1}) - 2x(t_n) + x(t_{n-1}))$. This leads to the so-called velocity Störmer-Verlet method
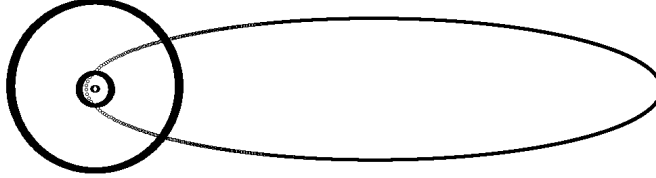
$$\mathbf{x}_i^{n+1} = \mathbf{x}_i^n + \delta t \mathbf{v}_i^n + \mathbf{F}_i^n \cdot \delta t^2/(2m_i), \tag{1}$$

$$\mathbf{v}_i^{n+1} = \mathbf{v}_i^n + (\mathbf{F}_i^n + \mathbf{F}_i^{n+1})\delta t/(2m_i). \tag{2}$$

where we denote the positions by $\mathbf{x}_i^n = \mathbf{x}_i(t_n)$ and analogously $\mathbf{F}_i^n$ and $\mathbf{v}_i^n$ stand for forces and velocities, respectively.

We consider the gravitational force $\mathbf{F}_i = \sum_{j=1, j \neq i}^{n} \mathbf{F}_{ij}$ where $\mathbf{F}_{ij} = \frac{m_i m_j}{r_{ij}^3} \mathbf{r}_{ij}$. The method is demonstrated on a simplified 2-dimensional model, which consists of the Sun, the Earth, the Jupiter, and Halley's Comet. Figure 1 shows the resulting orbits and initial data.

$$
\begin{array}{lll}
m_{sun} = 1 & \mathbf{x}^0_{sun} = (0,0) & \mathbf{v}^0_{sun} = (0,0) \\
m_{Earth} = 3 \cdot 10^{-6} & \mathbf{x}^0_{Earth} = (0,1) & \mathbf{v}^0_{Earth} = (-1,0) \\
m_{Jupiter} = 9.55 \cdot 10^{-4} & \mathbf{x}^0_{Jupiter} = (0,5.36) & \mathbf{v}^0_{Jupiter} = (-0.425,0) \\
m_{Halley} = 1 \cdot 10^{-14} & \mathbf{x}^0_{Halley} = (34.75,0) & \mathbf{v}^0_{Halley} = (0,0.0296) \\
\delta t = 0.015 & t_{end} = 468.5 &
\end{array}
$$

Fig. 1: *Trajectories of Halley's Comet, the Sun, the Earth and Jupiter. In this model are all masses divided by the mass of the Sun, all distances are divided by the d_{ES} (distance from the Earth to the Sun) and all velocities are divided by the v_E (velocity of the Earth). It means that the time is divided by d_{ES}/v_E.*

1.2 Cutoff radius

Calculation of forces is very time consuming for system with thousands and more mutually interacting particles. We shall accelerate the computation by considering only interactions of particles in a given neighbourhood by which we reduce the complexity from $\mathcal{O}(n^2)$ to $\mathcal{O}(n)$.

As a model, we choose the Lennard-Jones potential [1]

$$
U(r_{ij}) = 4 \cdot \varepsilon \left(\frac{\sigma}{r_{ij}}\right)^6 \cdot \left(\left(\frac{\sigma}{r_{ij}}\right)^6 - 1\right), \tag{3}
$$

where $\sigma > 0$ is the distance, at which the force switches between repulsive and attractive and ε is depth of the potential.

The approximation of the potential function for n particles is truncated double sum

$$
V(\mathbf{x}_1, \ldots, \mathbf{v}_n) = \sum_{i=1}^{n} \sum_{j:0<r_{ij}\leq r_{cut}}^{n} U(r_{ij}), \tag{4}
$$

and the approximation of the corresponding force $\mathbf{F}_i$ on the particle i is given by

$$
\mathbf{F}_i = -\nabla_{x_i} V(\mathbf{x}_1, \ldots, \mathbf{x}_n) = 24 \cdot \varepsilon \cdot \sum_{0<r_{ij}\leq r_{cut}}^{n} \frac{1}{r_{ij}^2} \left(\frac{\sigma}{r_{ij}}\right)^6 \cdot \left(1 - 2 \cdot \left(\frac{\sigma}{r_{ij}}\right)^6\right) \mathbf{r}_{ij}. \tag{5}
$$

where r_{cut} is chosen $2.5 \cdot \sigma$ typically [1].

The algorithm was applied to a problem of collision of two bodies which are created from 10×10 and 30×10 particles of equal mass, respectively, arranged on a lattice of mesh size $2^{1/6} \cdot \sigma$. For the initial data and numerical simulation we refer to Figure 2.

$$L_1 = 50 \quad \varepsilon = 5 \quad \mathbf{v} = (0, -10) \quad N_1 = 100 \quad r_{cut} = 2.5\sigma$$
$$L_2 = 50 \quad \sigma = 1 \quad m = 1 \qquad\qquad N_2 = 300 \quad \delta t = 0.00005$$
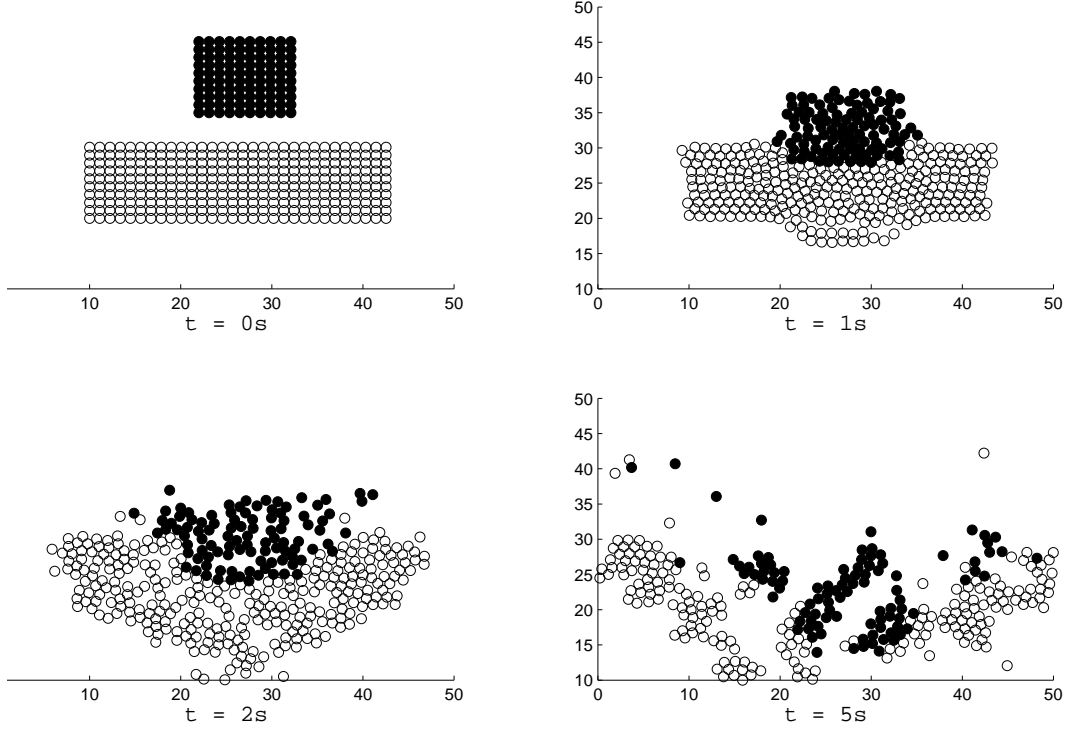
Fig. 2: *Collision of two bodies. Time evolution of the distribution of the particles.*

2 Time indenpendent Schrödinger equation

Consider a single particle. Schrödinger wave function $\Psi(x, y, z)$ is quantity which describes state of the particle. It is related to the probability $\rho(x, y, z)$ that a particle is at a given position by $\rho = \Psi^* \cdot \Psi$ where Ψ^* is complex conjugate to function Ψ. The Schrödinger equation reads as follows: $\mathcal{H}\Psi = E\Psi$ with the Hamilton operator

$$\mathcal{H} = -\frac{h^2}{8\pi^2 m}\frac{\mathrm{d}^2}{\mathrm{d}x^2} + \mathcal{V}(x), \tag{6}$$

where $\mathcal{V}(x)$ is operator of the potential energy, m is mass of the particle and h is the Planck constant. After adjustment we can write the Schrödinger wave equation in the form

$$\frac{\mathrm{d}^2\Psi}{\mathrm{d}x^2} + \frac{8\pi^2 m}{h^2}(E - \mathcal{V})\Psi = 0. \tag{7}$$

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2.1 Particle in the potential well

We consider a particle moving inside one-dimensional potential well in the direction of the x-axis. We assume that the particle has the same potential energy at any point of the well. It is useful to put the potential energy equal to zero in the well and equal to infinity elsewhere. Schrödinger wave equation for the particle in the potential well is written in the form (because $\mathcal{V} = 0$)
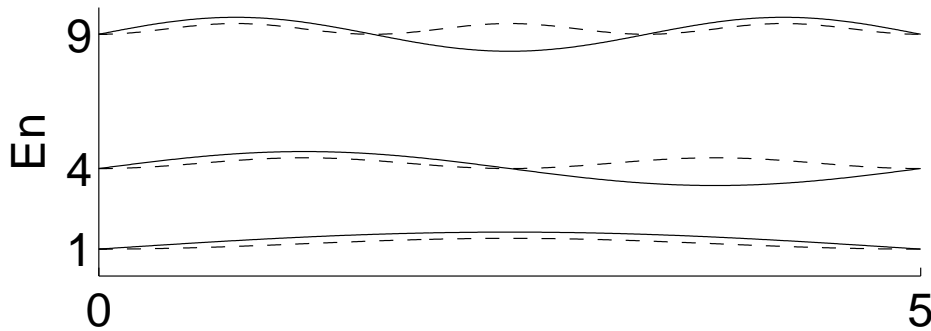
$$\frac{\mathrm{d}^2\Psi(x)}{\mathrm{d}x^2} + \frac{8\pi^2 m}{h^2} E\Psi(x) = 0, \tag{8}$$

$$\Psi(0) = \Psi(a) = 0. \tag{9}$$

The solution to (8) and (9) reads as follows:

$$\Psi_n(x) = \sqrt{2/a}\sin(n\pi x/a), \quad E_n = (nh)^2/(8ma^2), \quad n = 1, 2, 3, \ldots, \tag{10}$$

where normalization factor $\sqrt{2/a}$ results from $\int_0^a \Psi^2(x)\mathrm{d}x = 1$ and a is the width of the well. The analytical solution is shown in Figure 3.
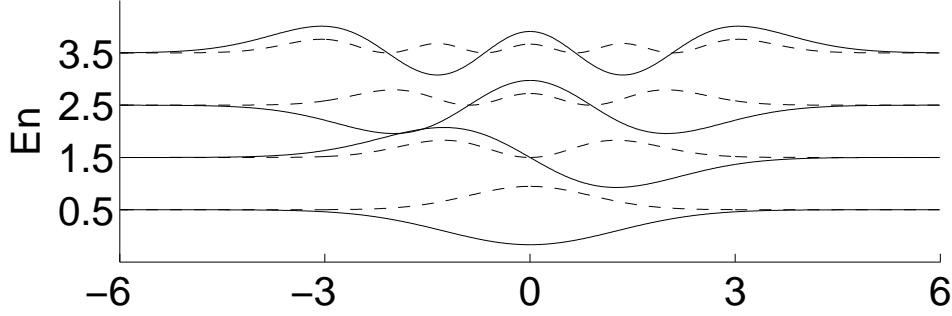

Fig. 3: *Potential well. Wave functions Ψ_i (solid line) and the probability functions $\Psi_i^*\Psi_i$ (dashed line) shifted vertically by the related energies E_i for $i = 1, 2, 3$.*

2.2 Harmonic oscillator

Another simple system of quantum mechanics is a harmonic motion of a particle. This system is interesting for us because it plays important role in the reasoning in molecular spectroscopy.

We consider a particle of the mass m which is moving along the x-axis alternately in positive and negative direction so that point $x = 0$ is the equilibrium. The acting force is given by $F = -kx$ with $k > 0$, which results in the potential energy $V = -\int_0^x(-kx)\mathrm{d}x = \frac{1}{2}kx^2$ and the following Schrödinger equation

$$\frac{\mathrm{d}^2\Psi(x)}{\mathrm{d}x^2} + \frac{8\pi^2 m}{h^2}\left(E - \frac{1}{2}kx^2\right)\Psi(x) = 0. \tag{11}$$

Fig. 4: *Harmonic oscillator. Wave functions Ψ_i (solid line) and the probability functions $\Psi_i^*\Psi_i$ (dashed line) shifted vertically by the related energies E_i for $i = 1, 2, 3, 4$.*

The solution can be found by cutting off infinite power series and total energy can be computed as [2]

$$E_n = h/(2\pi) \cdot \sqrt{k/m} \cdot (n + 1/2), \quad n = 0, 1, 2, \ldots. \tag{12}$$

The solution can be found also by using numerical solvers. We solve problem (11), after adjustment we obtain

$$\frac{\mathrm{d}^2\Psi(x)}{\mathrm{d}x^2} + (\lambda - b^2 x^2)\Psi(x) = 0, \quad \lambda = \frac{8\pi^2 m E}{h^2} \quad b = \frac{2\pi\sqrt{mk}}{h} \tag{13}$$

$$\Psi(x) = 0, \quad \text{for } |x| \to \infty. \tag{14}$$

We assume that the wave function is close to zero at distance l. We can write variational formulation of problem (13) and (14) and look for $\lambda > 0$ and $\Psi(x) \in H_0^1(-l, l)$ such that

$$\int_{-l}^{l} \Psi'(x)v'(x)\mathrm{d}x + b^2 \int_{-l}^{l} x^2\Psi(x)v(x)\mathrm{d}x = \lambda \int_{-l}^{l} \Psi(x)v(x)\mathrm{d}x, \quad \forall v \in H_0^1(-l, l).$$

We employ a finite element discretization to the latter formulation which leads to an approximate solution $\Psi_h(x) = \sum_{i=1}^{n} \psi_i\varphi_i(x)$ with continuous piecewise linear basis function $\varphi_i(x)$. The coefficients vector $\bar{\Psi}$ and energies λ solve the following eigenvalue problem

$$A\bar{\Psi} = \lambda B\bar{\Psi},$$

$$[A]_{ij} = \int_{-l}^{l} \varphi_i'(x)\varphi_j'(x)\mathrm{d}x + b^2 \int_{-l}^{l} x^2\varphi_i(x)\varphi_j(x)\mathrm{d}x,$$

$$[B]_{ij} = \int_{-l}^{l} \varphi_i(x)\varphi_j(x)\mathrm{d}x.$$

The Matlab software was use to solve the eigenvalue problem. Figure 4 shows the solution.

Conclusion

In this paper we have presented some methods for dynamic simulation of particle effects. In the second part we showed analytical solution of the simple problems in quantum mechanics and numerical approach using the finite element method.

References

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[2] Polák, R. and Zahradník, R.: *Kvantová chemie: Základy teorie a aplikace.* SNTL, Praha, 1985.