

Questions and Exercises on Classical Mechanics

Molecular Modeling of Nanosystems – CNE Master

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1. Classical mechanics can be formulated in different ways, such as with Newton's law

$$M \frac{d^2 \mathbf{R}}{dt^2} = \mathbf{F}$$

the Lagrange equation

$$\frac{d}{dt} \left(\frac{\partial L}{\partial \dot{\mathbf{q}}_i} \right) - \frac{\partial L}{\partial \mathbf{q}_i} = 0$$

where L is the Lagrangian $L = T - V$, with T the kinetic energy and V the potential energy, and Hamilton's equations

$$\begin{aligned} \frac{d\mathbf{q}}{dt} &= \frac{\partial H}{\partial \mathbf{p}} \\ \frac{d\mathbf{p}}{dt} &= - \frac{\partial H}{\partial \mathbf{q}} \end{aligned}$$

where H is the Hamiltonian $H = T + V$ (for a conservative system).

What are the advantages of each of these formulations? Which type of problems is each one more suited for?

2. Consider a single particle of mass M trapped in an anisotropic material. The particle feels a potential

$$V(x, y, z) = kx^2 \cos(\omega z)$$

what are the components x , y , and z of the force acting on the particle?

3. Consider the table below. If you simulate the molecular dynamics of a molecule containing O-H groups, which integration time step would you adopt? Why?

Table 1 Some typical vibrational modes^a

Vibrational mode	Wavelength of absorption [cm ⁻¹] (1/λ)	Absorption frequency [s ⁻¹] (ν = c/λ)	Period [fs] (1/ν)	Period/π [fs]
O–H stretch	3200–3600	1.0 × 10 ¹⁴	9.8	3.1
N–H stretch				
C–H stretch	3000	9.0 × 10 ¹³	11.1	3.5
O–C–O asymmetric stretch	2400	7.2 × 10 ¹³	13.9	4.5
C≡C, C≡N stretch	2100	6.3 × 10 ¹³	15.9	5.1
C=O (carbonyl) stretch	1700	5.1 × 10 ¹³	19.6	6.2
C=C stretch				
H–O–H bend	1600	4.8 × 10 ¹³	20.8	6.4
C–N–H bend	1500	4.5 × 10 ¹³	22.2	7.1
H–N–H bend				
C=C (aromatic) stretch				
C–N stretch (amines)	1250	3.8 × 10 ¹³	26.2	8.4
Water Libration (rocking)	800	2.4 × 10 ¹³	41.7	13
O–C–O bending	700	2.1 × 10 ¹³	47.6	15
C=C–H bending (alkenes)				
C=C–H bending (aromatic)				

^aAll values are approximate; a range is associated with each motion depending on the system. The value of $c = 3.00 \times 10^{10}$ cm s⁻¹. The last column indicates the timestep limit for leap-frog stability for a harmonic oscillator: $\Delta t < 2/\omega = 2/(2\pi\nu)$.

- Why does the harmonic approximation play a central role in physical and chemical sciences?
- The position of a one-dimensional forced harmonic oscillator is given approximately by

$$x(t) \rightarrow \frac{F_0}{m(\omega_0^2 - \omega_v^2)} \cos(\omega_v t + \varphi)$$

What is the condition for the occurrence of resonance? Explain.

- If we take a general one-dimensional potential energy and expand it in a Taylor series around one of its minima, we get

$$V(x - x_0) = V(x_0) + \frac{dV(x_0)}{dx}(x - x_0) + \frac{1}{2} \frac{d^2V(x_0)}{dx^2}(x - x_0)^2 + O\left[(x - x_0)^3\right]$$

Explain the reason we can simplify this equation to

$$V(x) \approx \frac{1}{2} \frac{d^2V(0)}{dx^2} x^2$$

7. Consider the following output of the normal modes analysis of the CNH_4^+ molecule.

		1			2			3		
		A			A			A		
Frequencies	--	481.8584			507.1950			777.1631		
Red. masses	--	1.2246			1.0492			1.0078		
Frc consts	--	0.1675			0.1590			0.3586		
IR Inten	--	24.7883			13.6434			0.0006		
Atom	AN	X	Y	Z	X	Y	Z	X	Y	Z
1	14	0.08	0.00	0.00	0.00	-0.04	0.00	0.00	0.00	0.00
2	6	-0.08	0.00	0.00	0.00	0.01	0.00	0.00	0.00	0.00
3	1	-0.70	-0.01	0.04	-0.03	0.31	-0.49	0.42	0.00	-0.02
4	1	-0.69	-0.01	0.01	0.00	0.26	0.52	-0.42	0.00	0.01
5	1	0.10	0.00	-0.01	0.01	0.21	0.34	-0.57	0.00	0.02
6	1	0.10	-0.01	0.00	-0.01	0.24	-0.32	0.57	0.00	-0.02
		4			5			6		
		A			A			A		
Frequencies	--	886.6525			907.6044			942.8130		
Red. masses	--	1.2159			1.3458			1.0975		
Frc consts	--	0.5632			0.6532			0.5748		
IR Inten	--	73.3644			85.8594			48.4937		
Atom	AN	X	Y	Z	X	Y	Z	X	Y	Z
1	14	0.00	0.00	0.00	0.00	0.06	0.00	0.00	0.00	0.00
2	6	0.14	0.00	0.00	0.00	-0.15	-0.01	0.00	-0.01	0.09
3	1	-0.18	0.00	0.01	0.01	-0.17	0.31	-0.02	0.38	-0.58
4	1	-0.18	0.00	0.00	-0.01	-0.13	-0.30	-0.02	-0.33	-0.62
5	1	-0.68	0.00	0.03	0.02	0.20	0.57	0.01	0.00	0.10
6	1	-0.68	0.00	0.02	-0.02	0.25	-0.56	0.00	0.00	0.08
		7			8			9		
		A			A			A		
Frequencies	--	1020.1072			1505.1730			2303.2127		
Red. masses	--	3.7635			1.1693			1.0291		
Frc consts	--	2.3075			1.5609			3.2164		
IR Inten	--	11.1673			7.9407			36.1150		
Atom	AN	X	Y	Z	X	Y	Z	X	Y	Z
1	14	0.01	-0.01	0.21	0.00	0.00	-0.01	0.00	0.00	-0.03
2	6	-0.01	0.02	-0.37	0.00	-0.01	0.12	0.00	0.00	0.00
3	1	-0.01	0.31	-0.23	0.00	-0.03	0.01	0.01	0.60	0.40
4	1	-0.01	-0.29	-0.26	0.00	0.03	0.01	0.01	-0.61	0.33
5	1	-0.02	-0.03	-0.51	-0.02	-0.39	-0.58	0.00	-0.01	-0.01
6	1	-0.02	0.08	-0.51	-0.02	0.44	-0.55	0.00	0.01	-0.01
		10			11			12		
		A			A			A		
Frequencies	--	2322.5838			3263.5319			3355.4398		
Red. masses	--	1.0554			1.0550			1.1128		
Frc consts	--	3.3542			6.6205			7.3816		
IR Inten	--	122.3409			0.1788			0.0829		
Atom	AN	X	Y	Z	X	Y	Z	X	Y	Z
1	14	0.00	0.04	0.00	0.00	0.00	0.00	0.00	0.00	0.00
2	6	0.00	0.00	0.00	0.00	0.00	0.07	0.00	0.10	0.00
3	1	-0.01	-0.56	-0.40	0.00	0.00	0.00	0.00	0.00	0.00
4	1	0.02	-0.62	0.37	0.00	0.00	0.00	0.00	0.00	0.00
5	1	0.00	0.00	-0.01	-0.01	0.62	-0.33	0.02	-0.60	0.36
6	1	0.00	0.00	0.01	-0.01	-0.59	-0.39	-0.01	-0.57	-0.41

- How many normal modes does this molecule have?
- What are the lowest and highest harmonic frequencies?
- What is the mode with the highest infrared absorption?

8. When simulating molecular dynamics, we can precompute potential energies before the dynamics or compute the energies on the fly for each point of the dynamics. What are the advantages and disadvantages of these two strategies?

9. A molecule with N nuclei has $3N$ classical degrees of freedom. However, the number of vibrational degrees is only $3N-6$. Why?

10. The potential energy estimated from a general molecular force field is

$$E = \sum_{\text{bonds}} K_b (b - b_{eq})^2 + \sum_{\text{angles}} K_\theta (\theta - \theta_{eq})^2 + \sum_{\text{dihedrals}} \frac{V_n}{2} [1 + \cos(n\phi - \gamma)] + \sum_{i < j} \left[\frac{A_{ij}}{R_{ij}^{12}} - \frac{B_{ij}}{R_{ij}^6} + \frac{q_i q_j}{\epsilon R_{ij}} \right]$$

Explain what each of those terms represent.

11. What is the difference between adiabatic and nonadiabatic dynamics?

12. Surface hopping is one of the most employed approximations to simulate nonadiabatic dynamics. Explain the main features of this method.

13. Suppose you want to simulate 100 molecular dynamics trajectories of 10 ps each. The integration time step is 0.5 fs, and each step takes 0.1 CPU.h (6 min). How many CPU.h will this simulation take?