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

$$\frac{d\mathbf{q}}{dt}=\frac{\partial H}{\partial \mathbf{p}}$$
$$\frac{d\mathbf{p}}{dt}=-\frac{\partial H}{\partial \mathbf{q}}$$

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}] ($1/\lambda$)	Absorption frequency [s^{-1}] ($\nu = c/\lambda$)	Period [fs] ($1/\nu$)	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)				

[a]All 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: $\Delta t < 2/\omega = 2/(2\pi\nu)$.

4. Why does the harmonic approximation play a central role in physical and chemical sciences?

5. The position of a one-dimensional forced harmonic oscillator is given approximately by

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

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

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

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

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.

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                     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
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a) How many normal modes does this molecule have?
b) What are the lowest and highest harmonic frequencies?
c) 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

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

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?