

§2 Forces and interactions

Solving the Hamiltonian Eq. requires, as we have seen, specification of initial conditions and then, formally, the system described by them is determined for all t .

At least two more details are needed to do anything "practical":

- 1) What are the forces acting on the particles?
- 2) How to numerically solve the Hamiltonian Eqs.? $\hookrightarrow \S 3$

2.1 The quantum-mechanical "reality"

What is a molecule?

Collection of N nuclei and N_e electrons

heavy $\xrightarrow{\text{classical}}$ quantum

Potential acting on the nuclei for a given \mathbf{q}

$$V(q_1, \dots, q_N) = \sum_{i,j}^N \frac{z_i z_j}{|q_i - q_j|} + V_{\text{elec}}(q_1, \dots, q_N)$$

z_i, z_j
nuclear charge

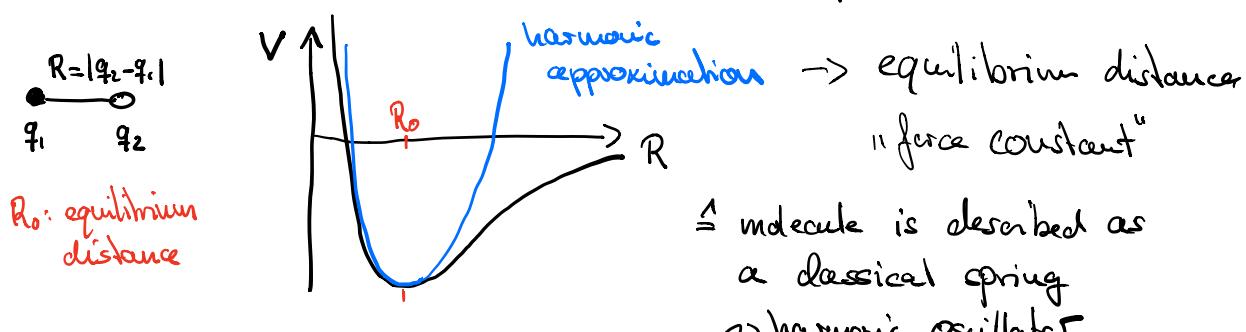
electrostatic repulsion
of the nuclei

contains also electrostatic
repulsion of the electrons
BUT importantly also
nuclei-electron
attraction

V_{elec} is a quantum-mechanical object \rightarrow not part of the course

but it sets some reference for the following discussion.

Example: Diatomic molecule ($\text{O}_2, \text{H}_2, \dots$)



2.2 Empirical potentials - Force Fields

In practice, many of such 1D "projections" of a high-dimensional potential $V(q_1, \dots, q_N)$ are represented by relatively easy to compute formulas, like the harmonic potential.

Force field: collection of functional forms of interactions
plus parameters

fit to some high-quality reference potential

microscopic bottom-up

matching thermodynamic properties

macroscopic top-down

In general: splitting of the N -body potential $V(q_1, \dots, q_N)$ into contributions from 2, 3, 4 body interactions.

2 - body:



, electrostatic, L_f
(pairwise)

3 - body:



(pariwise) $\frac{1}{R}$

4 - body :



bond
angle
dihedral

• periodic

\Rightarrow harmonic potential of the bonds are typically the strongest \rightarrow vibrational frequencies \rightarrow numerics

§3 Numerical Integration Schemes

In all practical computer simulations the evolution of the dynamical variables of the system must be performed using numerical schemes.

Let's consider "simple" algorithms using Taylor expansions for positions and momenta:

$$q_i(t + \Delta t) = q_i(t) + \Delta t \dot{q}_i(t) + \frac{\Delta t^2}{2} \ddot{q}_i(t) + \frac{\Delta t^3}{3!} \dddot{q}_i(t) + \dots$$

$$p_i(t + \Delta t) = p_i(t) + \Delta t \dot{p}_i(t) + \frac{\Delta t^2}{2} \ddot{p}_i(t) + \frac{\Delta t^3}{3!} \dddot{p}_i(t) + \dots$$

or - in practice often - for the velocities:

$$\underline{v}_i(t + \Delta t) = \underline{v}_i(t) + \Delta t \dot{\underline{v}}_i(t) + \frac{\Delta t^2}{2} \ddot{\underline{v}}_i(t) + \dots$$

with the Newtonian dynamics encoded via

$$\ddot{q}_i(t) = \frac{\underline{F}_i(t)}{m_i} = \dot{\underline{v}}_i(t)$$

The obvious question now is, how far to go in these expansions and how to combine them into reliable algorithms.

\Rightarrow "integrators"

2.1 Euler algorithm

Expansion of \underline{q} to second and \underline{v} to first order.

$$q_i(t + \Delta t) = q_i(t) + \Delta t \dot{q}_i(t) + \frac{\Delta t^2}{2} \ddot{q}_i(t)$$

$$\underline{v}_i(t + \Delta t) = \underline{v}_i(t) + \Delta t \dot{\underline{v}}_i(t)$$

$$= \underline{v}_i(t) + \Delta t \frac{\underline{F}_i(t)}{m_i}$$

BAD integrator:

- no time-reversibility
- no phase-space conservation
↳ soon...

2.2 Verlet algorithm

The algorithm starts again from second order expansion of \dot{q}_i :

$$\dot{q}_i(t + \Delta t) = \dot{q}_i(t) + \Delta t \ddot{q}_i(t) + \frac{\Delta t^2}{2} \ddot{\ddot{q}}_i(t)$$

and also for $-\Delta t$:

$$\dot{q}_i(t - \Delta t) = \dot{q}_i(t) - \Delta t \ddot{q}_i(t) + \frac{\Delta t^2}{2} \ddot{\ddot{q}}_i(t)$$

Add both:

$$\begin{aligned} \dot{q}_i(t + \Delta t) + \dot{q}_i(t - \Delta t) &= 2\dot{q}_i(t) + \Delta t^2 \ddot{\ddot{q}}_i(t) \\ &= 2\dot{q}_i(t) + \Delta t^2 \frac{\underline{F}_i(t)}{m_i} \end{aligned}$$

Rearrange to form position update:

$$\dot{q}_i(t + \Delta t) = 2\dot{q}_i(t) - \dot{q}_i(t - \Delta t) + \frac{\Delta t^2}{m_i} \underline{F}_i(t)$$

Subtract both:

$$\dot{q}_i(t + \Delta t) - \dot{q}_i(t - \Delta t) = 2\Delta t \dot{\dot{q}}_i(t) = 2\Delta t \underline{v}_i(t)$$

$$\underline{v}_i(t) = \frac{\dot{q}_i(t + \Delta t) - \dot{q}_i(t - \Delta t)}{2\Delta t}$$

Taken together, these two updates are known as Verlet algorithm.

A few noteworthy points:

- velocities are not needed to update positions
- however \underline{v}_i are needed to calculate observables, e.g. the kinetic energy
- problem: velocities are only available after $\dot{q}_i(t + \Delta t)$ has been computed
- numerical problems can arise $\rightarrow \Delta t^2$
(what Δt is needed? in what units?)
- start of the integration? Needs info about two previous time steps...

\Rightarrow do a single Euler step, then Verlet

3.3 Leapfrog

3.4 Velocity Verlet

This is a modification of the standard Verlet algorithm to avoid/reduce the problems identified above. For this, we consider Taylor expansions of q_i and \underline{v}_i to second order:

$$q_i(t + \Delta t) = q_i(t) + \Delta t \dot{q}_i(t) + \frac{\Delta t^2}{2m_i} \ddot{F}_i(q(t))$$

$$\underline{v}_i(t + \Delta t) = \underline{v}_i(t) + \Delta t \frac{\underline{F}_i(q(t))}{m_i} + \frac{\Delta t^2}{2} \ddot{\underline{v}}_i(t)$$

where we have already made use of $\dot{\underline{v}} = \ddot{q} = \frac{\underline{F}}{m}$.

The occurrence of the second derivative $\ddot{\underline{v}}(t)$ is a problem.

The idea to tackle this problem is to also write the first time derivative of \underline{v} to first order in Taylor:

$$\dot{\underline{v}}_i(t + \Delta t) = \dot{\underline{v}}_i(t) + \Delta t \ddot{\underline{v}}_i(t)$$

Now multiply this by $\frac{\Delta t}{2}$ and isolate the term with $\ddot{\underline{v}}$:

$$\begin{aligned} \frac{\Delta t^2}{2} \ddot{\underline{v}}_i(t) &= \frac{\Delta t}{2} (\dot{\underline{v}}_i(t + \Delta t) - \dot{\underline{v}}_i(t)) \\ &= \frac{\Delta t}{2m_i} (\underline{F}_i(q(t + \Delta t)) - \underline{F}_i(q(t))) \end{aligned}$$

Enter this into the velocity update:

$$\begin{aligned} \underline{v}_i(t + \Delta t) &= \underline{v}_i(t) + \Delta t \frac{\underline{F}_i(q(t))}{m_i} + \frac{\Delta t}{2m_i} (\underline{F}_i(q(t + \Delta t)) - \underline{F}_i(q(t))) \\ &= \underline{v}_i(t) + \frac{\Delta t}{2m_i} (\underline{F}_i(q(t + \Delta t)) + \underline{F}_i(q(t))) \end{aligned}$$

- gives positions and velocities at the same time step
- retains the numerically problematic Δt^2 term in the position update.

Remark: diatomic molecule \rightarrow harmonic potential

$$\sigma = \frac{1}{2\pi} \sqrt{\frac{k}{\mu}} \quad \begin{array}{l} k: \text{force constant} \\ \mu: \text{reduced mass} \end{array}$$

$$CO \quad \sigma \approx 6.5 \cdot 10^{13} \text{ s}^{-1}$$

$$T \approx 1.5 \cdot 10^{-14} \text{ s} = 15 \text{ fs}$$

\Rightarrow numerical simulations need to be able to
resolve such fast oscillations

$$\Delta t \ll T \Rightarrow 10^{-15} \text{ s}$$