Other degrees of freedom (internal to molecules)

- orientation
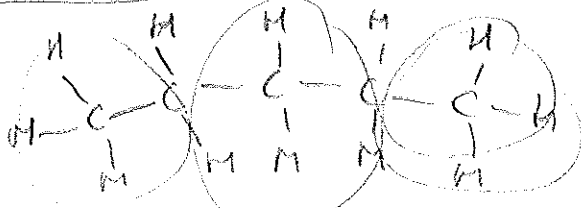 f.e water   +H—O⁻   hydrogen bonds.
  and polar molecules   H₊
      (CO, NO, etc.)
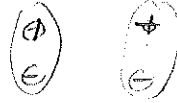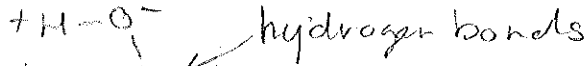
- chain molecules effective treatment

  hydrocarbons, polymers etc.
  chain of
      spherical particles
      with some binding
          interaction
  (can allow
   to dissociate)

  benzene ring ⟶ disc-shaped particles, etc.
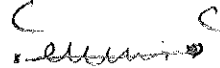 groups of particles ⟶ effective particle.
      complex   (often with LJ interaction)

- actual chemical bonds: effective treatment with Morse, f.e.
      inside molecules, etc...
  stretching

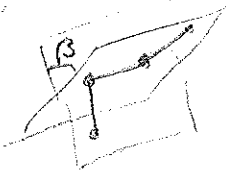$$U_{stretch} = \tfrac{1}{2} k_{stretch} (r-r_0)^2$$

$$U_{bend} = k_{bend}[\cos(\phi-\phi_0) + \cos(\phi+\phi_0)]$$
$$\approx k_{bend}[(\phi-\phi_0)^2 \cancel{+}]$$

$$U_{torsion} = U_{torsion}\{\cos(\beta-\beta_0) + \cos(\beta+\beta_0)\}$$
$$or = U_{torsion}[1 + S/|S| \cos(|S|\beta)]$$

or some other similar expres⁰ ns symmetry

Bond order potentials
effective constants obtained from — vib frequencies — QM calculations
                                   — bond lengths
                                   — configurations
                                   — testing large molecules
                                   — etc.

f.e Tripos 5.2, AMBER
table I lists atom types.   m ≈ 12 m_proton { typical length scale
                                                                    $\omega = \sqrt{k/m}$
stretching table II   O(10³ kcal/mol Å²)   fast   high frequency
                $\sqrt{k/m} \approx \omega \approx O(10^{14})$ → 50 fs r ≈ 1 Å

bending table III   O(10⁻² kcal/mol deg²) = O(10¹ kcal/
                                                 mol rad²)
                $\omega \approx O(10^{12})$ → 500 fs.

torsion table V |S|=3 O(10⁻¹ kcal/mol) ⟹ O(kcal/mol)
                                                slow
                                             low-frequency
fast dynamics might not be relevant.

___ end lecture 4

typical angle scale

Eliminating fast vibrations: constraints

- sometimes explicitly. i.e. rigid molecules, water

  No——N N_2 or   or $-C\langle\bigcirc\rangle C-$ benzene

  H——O——H water   moment of inertia tensor I

  centre of mass (3 d.o.f.) rotation (2 or 3 d.o.f.)

- general constraints: lagrangian multipliers

  $\mathcal{L} = T^{(b)} - V(r)$

  constraints $\sigma_k^u(r_1, \dots r_N) = 0$ $k = 1 \dots \ell$

  typically something like $\mathcal{L} = \sum \frac{1}{2} m \dot{r}_j^2 - V(r_1, \dots r_N)$

  Unconstrained :   constraints $|r_1 - r_2| = R$

  $\frac{d}{dt} \frac{\partial \mathcal{L}}{\partial \dot{r}} - \frac{\partial \mathcal{L}}{\partial r} = 0$

  $m \ddot{r}_j - F_j(r_1, \dots r_N) = 0$ $\Rightarrow$ $\dot{v} = \frac{F}{m} \stackrel{=a}{}$, $\dot{r} = v$

  $\dot{y} = f(y)$

  Constrained :   constraining force

  $\frac{d}{dt} \frac{\partial \mathcal{L}}{\partial \dot{r}_j} - \frac{\partial \mathcal{L}}{\partial r_j} = -\sum_k \lambda_k(t) \frac{\partial \sigma_k}{\partial r_j}$ $+ \ell$ constraints $\Rightarrow$ solution

  ℓ (multipliers)

  problem, new variables, must solve

  $\sigma_k = 0$ force $\perp$ to constraining surface.

  sometimes can be solved analytically   can also be solved systematically

  $\dot{v} = a(t) - \sum_k \lambda_k(t) \frac{\partial \sigma_k}{\partial r_j}$

Implementation in Verlet

- Do normal unconstrained time step

  $r^u(t+h) = 2r(t) - r(t-h) + h^2 a(t)$ (or something)

  This breaks the constraint.

- Try to approximate $\lambda_k(t)$

  $\sigma_k^c(t+h) = \sigma_k^u(t+h) + \sum_j \frac{\partial \sigma_k}{\partial r_j}(t+h) (r_j^c(t+h) - r_j^u(t+h)) + \mathcal{O}(h^4)$

  $\parallel$
  0
  $\underbrace{- \frac{h^2}{m} \sum_k \lambda_k(t) \frac{\partial \sigma_k}{\partial r_j}(t)}_{approximation}$

  $\Rightarrow$ $\sigma_k^u(t+h) = h^2 (\text{big matrix}) \cdot (\lambda_1, \lambda_2 \dots \lambda_\ell)$

- Solve for λ_k by inverting is expensive.

  SHAKE:
  do one constraint at a time, iterate until constraints sufficiently satisfied

  (margin note: watch out with averages, see B.H.)

So far: classical effective descriptions
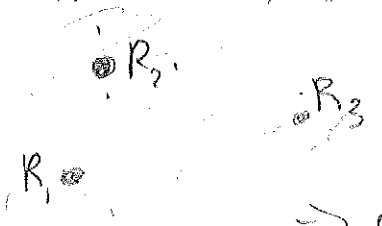
    - molecules interact in pairs (usually)

    - we know roughly what the interactions look like
    - Sometimes obtained from QM
often quite good, but not always

$\Rightarrow$ go back to underlying Quantum Mechanics.

$\Rightarrow$ calculate <u>force</u> from QM or something <u>on the fly</u>

---

bunch of atoms + electrons wave function

    $\bullet R_2$ electronic time scale $<<$
        $\bullet R_3$ atomic motion
            ($m_e << m_p$)

   $R_1 \bullet$

        $\Rightarrow$ adiabatic approximation,
           electrons <u>always in ground state</u>
                or in <u>same excited state</u>

force calculation at every time step   classical QM
                           $r, v \rightarrow \psi(r, v)$

$$F_n = -\nabla_{R_n} E = -\nabla_{R_n} \left[\frac{\langle \psi | H | \psi \rangle}{\langle \psi | \psi \rangle} \right]$$

6-dim ∞-dim.
phase space Hilbert Space
<u>easy</u>   <u>hard</u>

    H is electronic hamiltonian, assuming $R_1, R_2, \ldots$

problem
① There are a lot of electrons, solving Schrödinger Equation
   is too much work: $\Rightarrow$ Quantum Chemistry methods
     $\Rightarrow$ Density Functional Theory (DFT)

② Derivative means $\langle \psi | H | \psi \rangle$ must be calculated
   to high accuracy.

   $\Rightarrow$ very expensive

Speeding things up often means truncating the ∞ dim

   Hilbert space basis functions

   $\psi = \sum\limits_{i=1}^{\infty} c_i \phi_i$ such that c_i will be small if $i >$ some
                                 number
   Lot of effort directed at finding
     nice ways to do this
        $\hookleftarrow$ fast, easy

   Ground state must be found <u>iteratively</u> using this basis set

     $\{c_i\} \rightarrow$ better $\{c_i\}$ $\leftarrow$ can be written as classical
                             eqs of motion for c_i, but
                            solving still requires QM calc