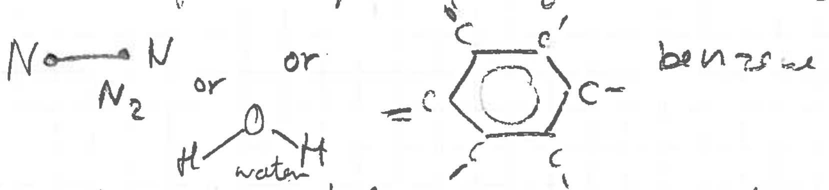
Eliminating fast vibrations: constraints

- sometimes explicitly i.e rigid molecules, water



moment of inertia tensor I

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

- general constraints: Lagrangian multipliers

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

constraints $\sigma_k(r_1, \dots r_N) = 0$ $k = 1 \dots l$

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

constraints $|r_1 - r_2| = R$

Unconstrained:

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

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

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

Constrained:

$$\frac{d}{dt}\frac{\partial \mathcal{L}}{\partial \dot{r}_j} - \frac{\partial \mathcal{L}}{\partial r_j} = \overbrace{-\sum_k \lambda_k(t) \underbrace{\frac{\partial \sigma_k}{\partial r_j}}}^{\text{constraining force}}$$

+ l constraints ⇒ solution

$\sigma_k = 0$

problem, new variables (multipliers), must solve

→ force ⊥ 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 $\lambda_k(t)$

$$\underset{\underset{0}{\parallel}}{\sigma_k^c(t+h)} = \sigma_k^u(t+h) + \sum_j \frac{\partial \sigma_k}{\partial r_j}(t+h)\Big(\underbrace{r_j^c(t+h) - r_j^u(t+h)}_{\text{approximation}}\Big) + \mathcal{O}(h^4)$$

$$r_j^c(t+h) - r_j^u(t+h) \approx -\frac{h^2}{m_k} \sum \lambda_k(t) \frac{\partial \sigma_k}{\partial r_j}(t)$$

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

watch out with averages [illegible]

- Solve for λ_k by inverting is expensive,

SHAKE:

- Go one constraint at a time, iterate untill constraints sufficiently satisfied

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⑲

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>

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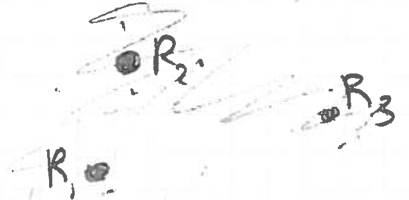
bunch of atoms + electrons wave function



electronic time scale << atomic motion ($m_e << m_p$)

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

force calculation at every time step

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

classical QM
$r, v \rightarrow \psi(r,v)$
6-dim phasespace <u>easy</u>
∞ dim. Hilbert Spa <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

$\psi = \sum_{i=1}^{\infty} c_i \phi_i$ such that c_i will be small if $i >$ some number

Lot of effort directed at finding nice ways to do this
↳ fast, easy

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

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

Car-Parrinello

replace iteration steps by time in fictitious additional fast dynamics.

- quantum case: coordinates c_i. $\Rightarrow$ Classical MD with c_i & R_j, V_j
  still QM to be done, but elegant way to speed it up & cope
  inverse adiabatic approximation! (with friction)

Example in classical system (see Frenkel & Smit)

Polarizable molecules. (dipoles)

$$U = U_0 + U_{pol} \longleftarrow \text{electrostatic due to dipoles}$$

U_0 ← other interaction

$$U_{pol} = -\sum_i E_i \mu_i + \underbrace{\frac{1}{2\alpha} \sum (\mu_i)^2}_{}$$ polarizability.

μ_i ← induced dipole in i

E_i ← field at particle i, depends on all charges

local field depends on all dipoles

$$E_i = T_{ij} (\mu_j + \mu_{0,j})$$

E_i ↑

μ_j ← induced

$\mu_{0,j}$ ← permanent.

Assumption: induced dipoles adiabatic, i.e. Upol always minim

$$\frac{\partial U_{pol}}{\partial \mu_i} = 0 = -E_i + \frac{1}{\alpha} \mu_i \quad \Rightarrow \quad \mu_i = \alpha E_i$$

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$\Rightarrow$ 3N coupled linear equations, could be solved iteratively, but expensive.

same sort of problem as in QMD before.

Car-Parrinello say:

treat μ_i as dynamical variables and find an effective treatment

Dipoles should go to minimum of Upol

But have "kinetic energy" $T_{pol} = \frac{1}{2} \sum_i M \dot{\mu}_i^2$

M ← effective mass

eqs of motion
$$M \ddot{\mu}_i = \underbrace{-\frac{\mu_i}{\alpha} + E_i}_{\text{effective force}}.$$

adaptation to E should be fast, so M small.

$\Rightarrow$ energy still conserved.

If Tpol is low, dipoles stay close to ground state

$$T_{pol} \ll T \quad \& \quad M \ll m$$

↑ problem with equipartition, heat exchange

for this, we need thermostats.

iteration replaced by smaller time steps, which is less bad.

— end lecture 5