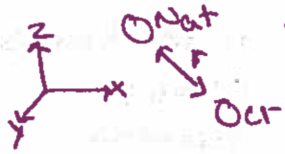
Chem 442 Lecture 2

How to calculate atoms in classical mechanics

1) Potential energy $V(x_1, x_2 \ldots)$ two particles will attract as they get closer, etc.

2) A formula to get $x_j(t+\Delta t)$ from $x_j(t)$

1(a)



make a vector: $\vec{x}_{Na} = \begin{pmatrix} x_{Na} \\ y_{Na} \\ z_{Na} \end{pmatrix} = \begin{pmatrix} x_1 \\ x_2 \\ x_3 \end{pmatrix}$

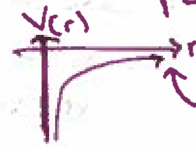
$\vec{x}_{Cl} = \begin{pmatrix} x_{Cl} \\ y_{Cl} \\ z_{Cl} \end{pmatrix} = \begin{pmatrix} x_4 \\ x_5 \\ x_6 \end{pmatrix}$

distance between them

$r = \sqrt{(x_1-x_4)^2 + (x_2-x_5)^2 + \ldots}$

$= \left[\sum_{j=1}^{3} (x_j - x_{j+3})^2\right]^{-1/2}$

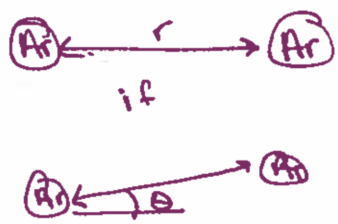
Coulomb potential $\leftarrow V(r) = \dfrac{\overset{Na}{e}\,\overset{Cl}{(-e)}}{4\pi\varepsilon_0 r}$



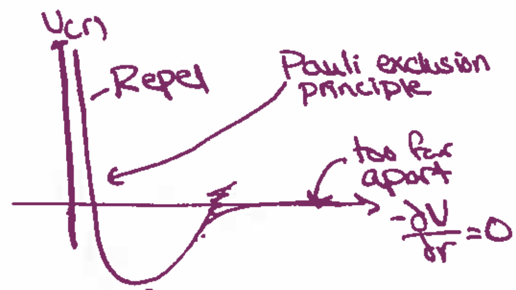
Energy of interaction is negligible

$= \dfrac{-e^2}{4\pi\varepsilon_0} \cdot \dfrac{1}{|x_1|}$ If both atoms lie on x-axis and Cl at origin

1b) How about two Ar atoms ← 1% of atmosphere



- no difference, bc spherically symmetric
- Only distance is important



weak attraction $\sim \frac{1}{r^6}$

Can't rationalize using classical mechanics

$V(r) = 4\varepsilon\left[\left(\frac{r_0}{r}\right)^{12} - \left(\frac{r_0}{r}\right)^6\right]$

at short distances $(\,)^{12}$ takes over and U increases

$\varepsilon = 1.6 \times 10^{-21}$ Joules

$r_0 = 3.4 \times 10^{-10}\,m = 0.34\,N$

2) What about $x_j(t+\Delta t)$ [one atom for simplicity]

$$F = m\frac{\partial^2 x}{\partial t^2} = m\frac{\partial}{\partial t}\left(\frac{\partial x}{\partial t}\right) \approx m\,\frac{\frac{x(t+\Delta t) - x(t)}{\Delta t} - \frac{x(t) - x(t-\Delta t)}{\Delta t}}{\Delta t}$$

$$-\frac{\partial U}{\partial x} \rightarrow -\frac{U(x+\Delta x) - U(x(t)-\Delta x)}{2\Delta x} \approx \frac{m}{\Delta t^2}\left\{x(t+\Delta t) - 2x(t) + x(t-\Delta t)\right\}$$

$$= x(t+\Delta t) = x(t) + [x(t) - x(t-\Delta t)] - \frac{U(x(t)+\Delta x) - U(x(t)-\Delta x)\,\Delta t^2}{2m\Delta x}$$

↓

or $x(t+\Delta t) = x(t) + v(t)\cdot\Delta t + \frac{F(x,t)}{m}\cdot\Delta t^2$ Verlet's formula

Formula used in a computer program to track movement of particles

Computer recipe:

0) pick Δx and Δt
   small = accurate
   ~~large = wrong~~ too small = round-off errors
1) Pick $x_j(t=0)$ and $v_j(t=0)$
   possible in classical mechanics
2) Calculate force for each particle
3) use Verlets formula to determine how far the particle has moved