

Force Field (Part 01)

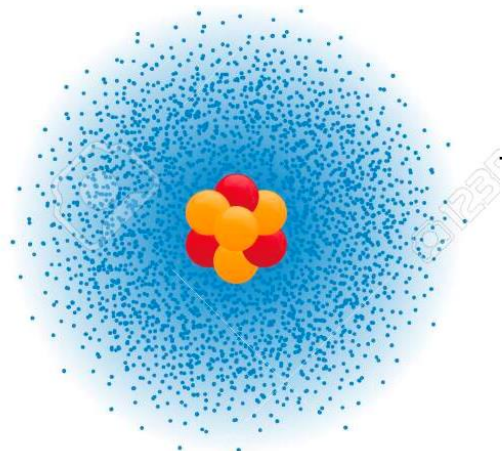
- *How to describe a molecules ?*

P. SATPATI

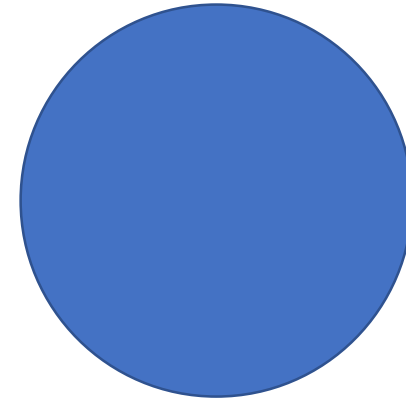
Classical description of atom

Assumption:

- Smallest unit is “atom” (**NO INTERNAL STRUCTURE**)
- Atoms are spheres of various “mass, charge, and size”



Quantum Mechanical Model
Electron Clouds (Orbitals)



Classical description of atom

Mass = XX
Charge = YY
Size = ZZ

Essential features of interactions between simple neutral atoms (Say, Argon atoms)

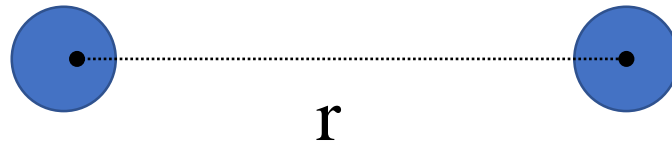


Argon (Ar)

Atomic mass = **39.95 u**

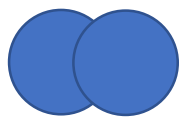
Argon is neutral but it is possible to liquify argon.

- Argon must attract each other.
- How to mimic interaction between two argon atoms ?

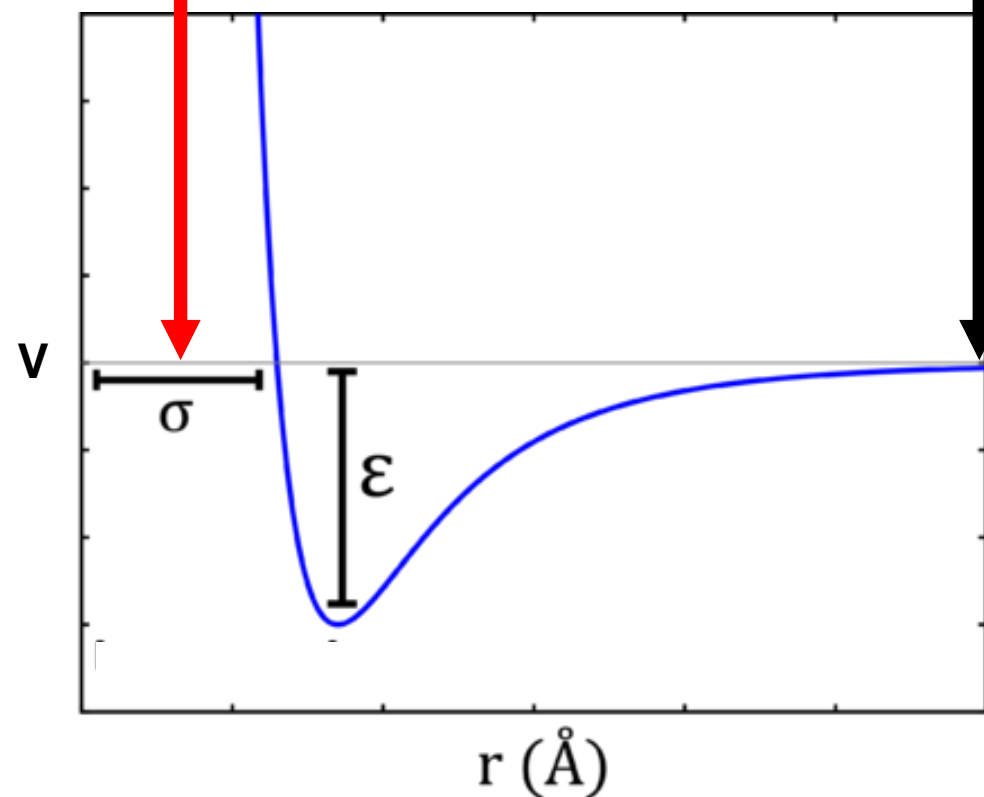
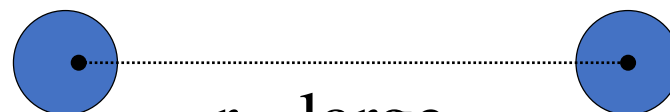


$r = \text{Interatomic distance (nm, \AA)}$

$$r < \sigma$$



$$r = \text{large}$$

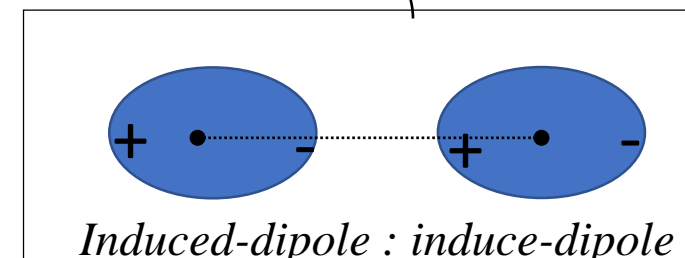


Origin ?

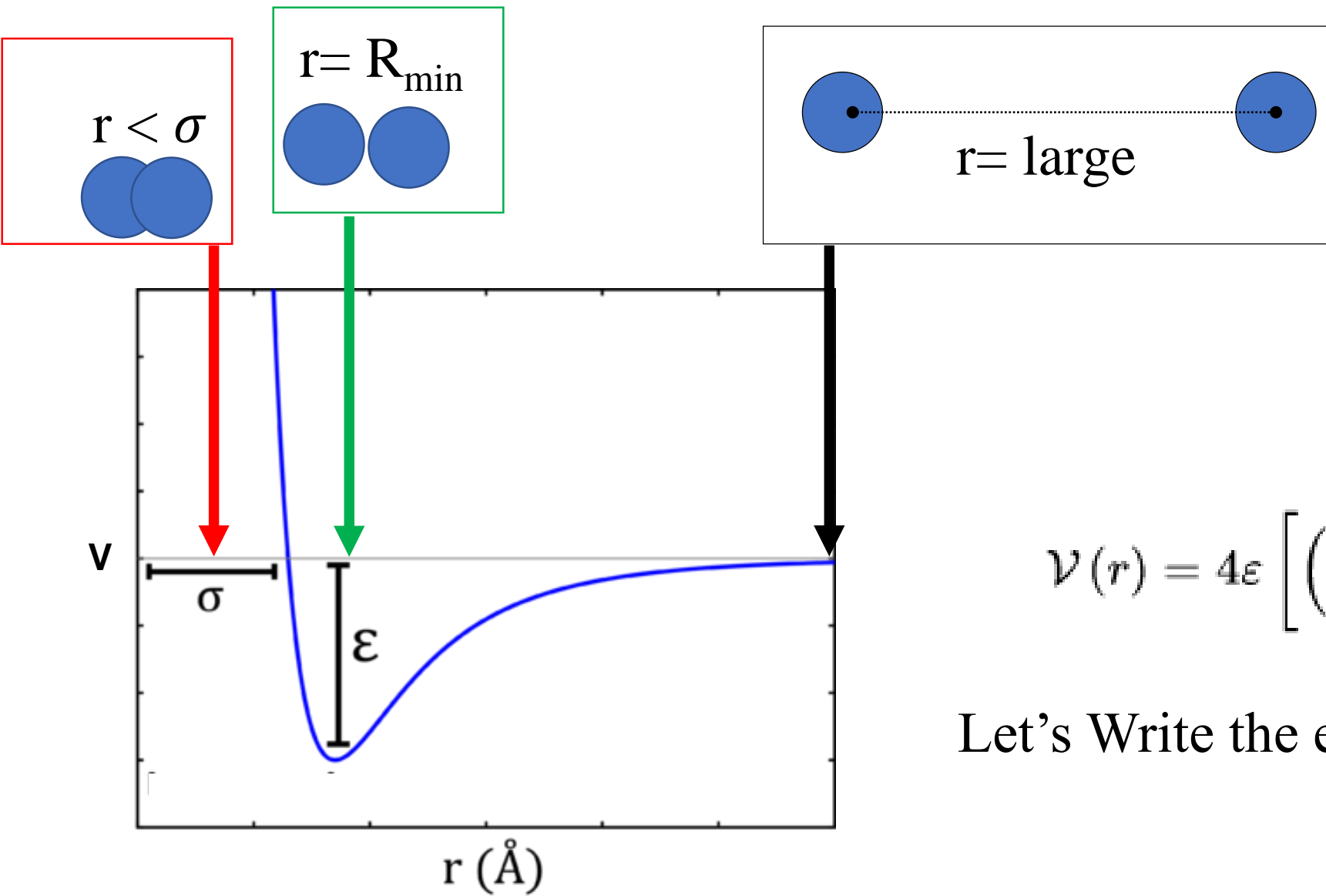
$$V(r) = 4\epsilon \left[\left(\frac{\sigma}{r} \right)^{12} - \left(\frac{\sigma}{r} \right)^6 \right]$$

Lennard-Jones potential

*Pauli's exclusion (electron overlap). **Repulsive**
Actually $V \sim \exp(-r)$.
 r^{12} has no physical basis.*

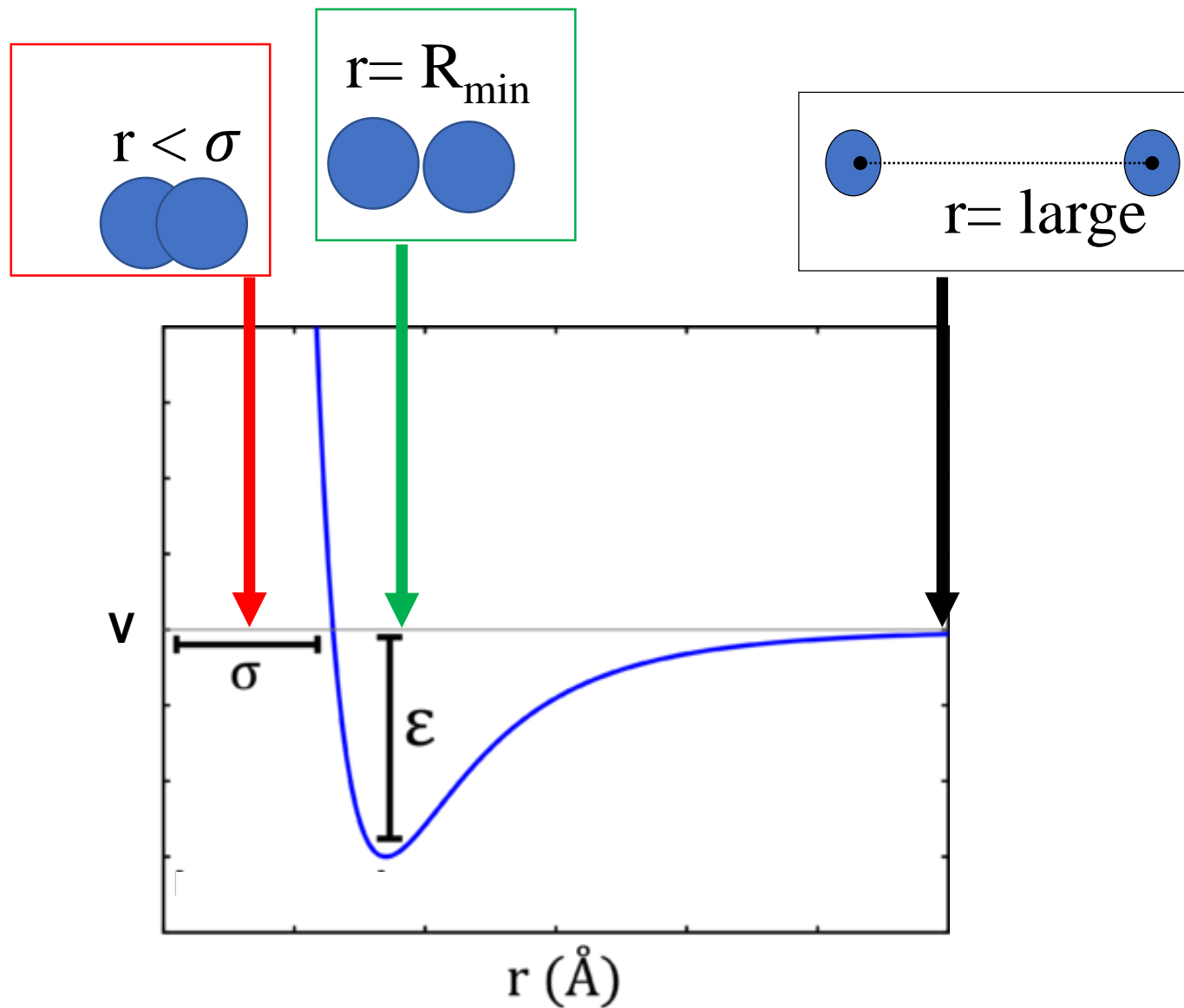


*Induced-dipole : induce-dipole
Attractive
Van der Waals term*



$$V(r) = 4\epsilon \left[\left(\frac{\sigma}{r} \right)^{12} - \left(\frac{\sigma}{r} \right)^6 \right] :$$

Let's Write the equation in terms of R_{\min}



Look at the curve $V(r)|_{r=R_{\min}} = \text{Minimum} \Rightarrow \left(\frac{dV}{dr}\right)_{r=R_{\min}} = 0$

eqn ①

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

$$\Rightarrow \left(\frac{dV}{dr}\right)_{r=R_{\min}} = \left(4\epsilon \left[-\frac{12\sigma^{12}}{r^{13}} + \frac{6\sigma^6}{r^7} \right] \right)_{r=R_{\min}}$$

$$\Rightarrow 0 = 4\epsilon \left[-\frac{12\sigma^{12}}{R_{\min}^{13}} + \frac{6\sigma^6}{R_{\min}^7} \right]$$

$$\Rightarrow \frac{12\sigma^{12}}{R_{\min}^{13}} = \frac{6\sigma^6}{R_{\min}^7}$$

$$\Rightarrow \frac{2\sigma^6}{R_{\min}^6} = 1$$

$$\Rightarrow R_{\min}^6 = 2\sigma^6$$

$$\Rightarrow R_{\min} = (2\sigma^6)^{1/6} = 2^{1/6}\sigma$$

$$\Rightarrow \boxed{R_{\min} = 2^{1/6}\sigma} \text{ --- ②}$$

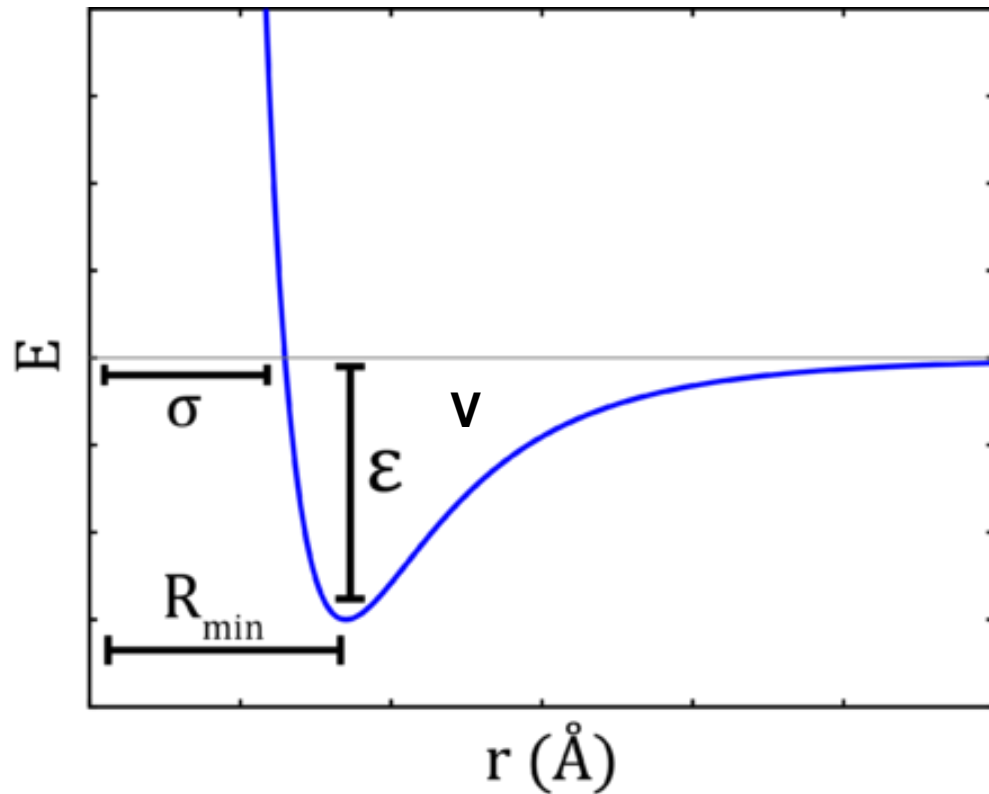
Substituting ② into ①

$$V(r) = 4\epsilon \left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^6 \right] = \epsilon \left[\left(\frac{2\sigma}{\sigma}\right)^{12} - 2\left(\frac{2\sigma}{\sigma}\right)^6 \right]$$

$$V(r) = \epsilon \left[\left(\frac{R_{\min}}{\sigma}\right)^{12} - 2\left(\frac{R_{\min}}{\sigma}\right)^6 \right]$$

$$\mathcal{V}(r) = 4\epsilon \left[\left(\frac{\sigma}{r} \right)^{12} - \left(\frac{\sigma}{r} \right)^6 \right] = \epsilon \left[\left(\frac{R_{min}}{r} \right)^{12} - 2 \left(\frac{R_{min}}{r} \right)^6 \right]$$

$$R_{min} = \sqrt[6]{2}\sigma$$



Unit:

ϵ : Energy (kcal/mole, kJ/mol)

R_{min} : Distance (\AA , nm)

Interesting Facts about LJ-potential

$$\mathcal{V}(r) = 4\epsilon \left[\left(\frac{\sigma}{r} \right)^{12} - \left(\frac{\sigma}{r} \right)^6 \right] = \epsilon \left[\left(\frac{R_{min}}{r} \right)^{12} - 2 \left(\frac{R_{min}}{r} \right)^6 \right]$$

- Always attractive at large distances (**Independent of the nature of the atom**).
- $(1/r^6)$ has strong physical basis (Induce-dipole : Induced-dipole interaction)
- $(1/r^{12})$ has NO STRONG THEORETICAL BASIS. Reality exponential.
Fitting repulsion as $(1/r^6)^2 = (1/r^{12})$ has computational advantage.
- **Short Range**

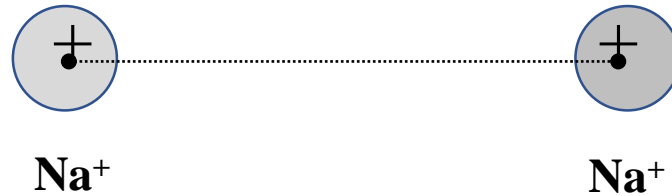
Given (**ϵ and R_{min}**) \rightarrow Possible to reproduce **Argon...Argon interaction**

* Choose (**ϵ and R_{min}**) to reproduce experiment

Parameters

Essential features of interactions between Charged atoms (Say, Na⁺)

Atoms has charges.



Coulomb's Law
Electrostatic energy

$$U_e = k \frac{q_1 q_2}{r}$$

Facts Coulomb potential

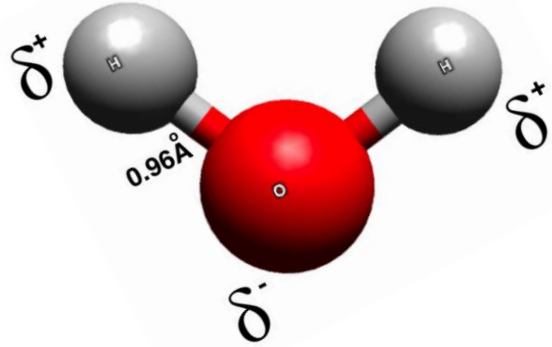
- Long-Range
- Attractive or repulsion (Sign of q₁, q₂)
- Not valid at r = 0 (LJ will take care).

q₁, q₂

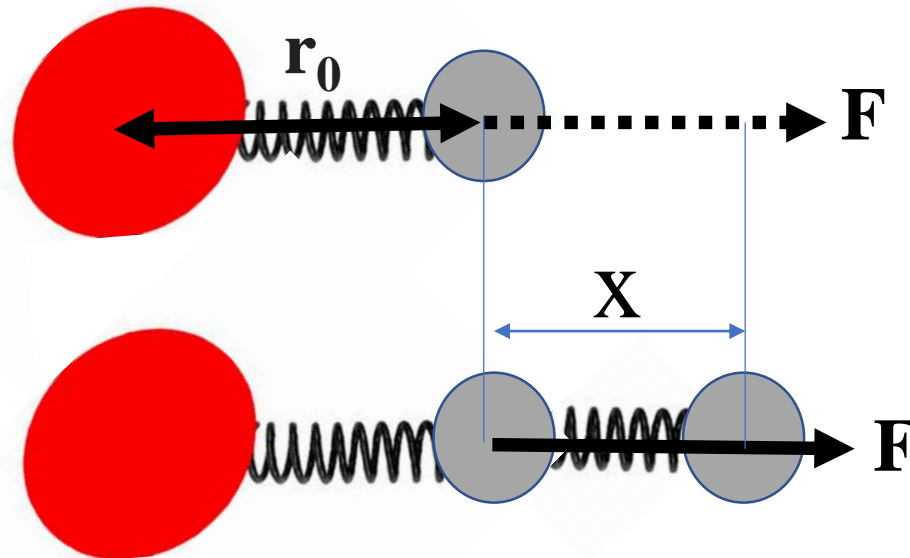
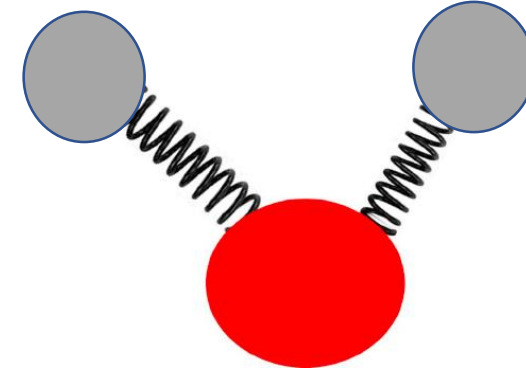
Parameters

Non-bonded energy terms (electrostatics and Lenard-Jones)

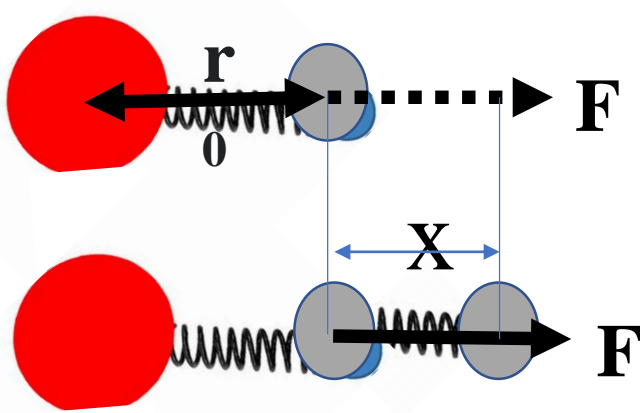
A molecule (internal structure) – Energy Function ?



Bonds \Rightarrow Spring



$X = \text{displacement}$
 $= (r - r_0)$



$$F \propto -x$$

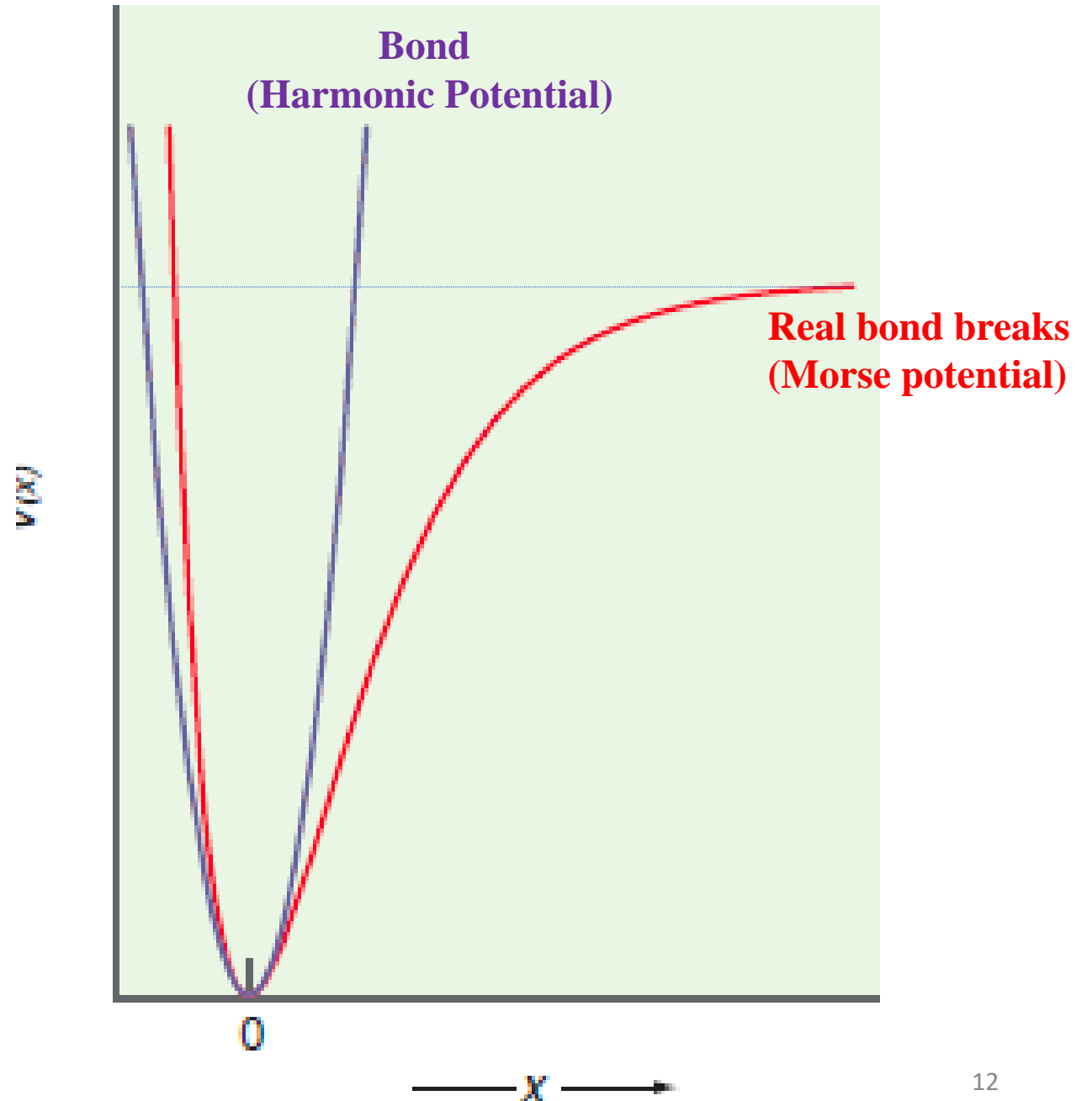
$$\Rightarrow F = -k_b x$$

$$\Rightarrow -\left(\frac{dV}{dx}\right) = -k_b x$$

$$\Rightarrow \int_0^x dV = \int_0^x k_b x dx$$

$$\Rightarrow V(x) - V(0) = \frac{1}{2} k_b x^2$$

$$\Rightarrow V(x) = \cancel{V(0)}^0 + \frac{1}{2} k_b x^2$$



$$X = (r - r_0)$$

$$V(x) = \frac{1}{2} k_b x^2$$

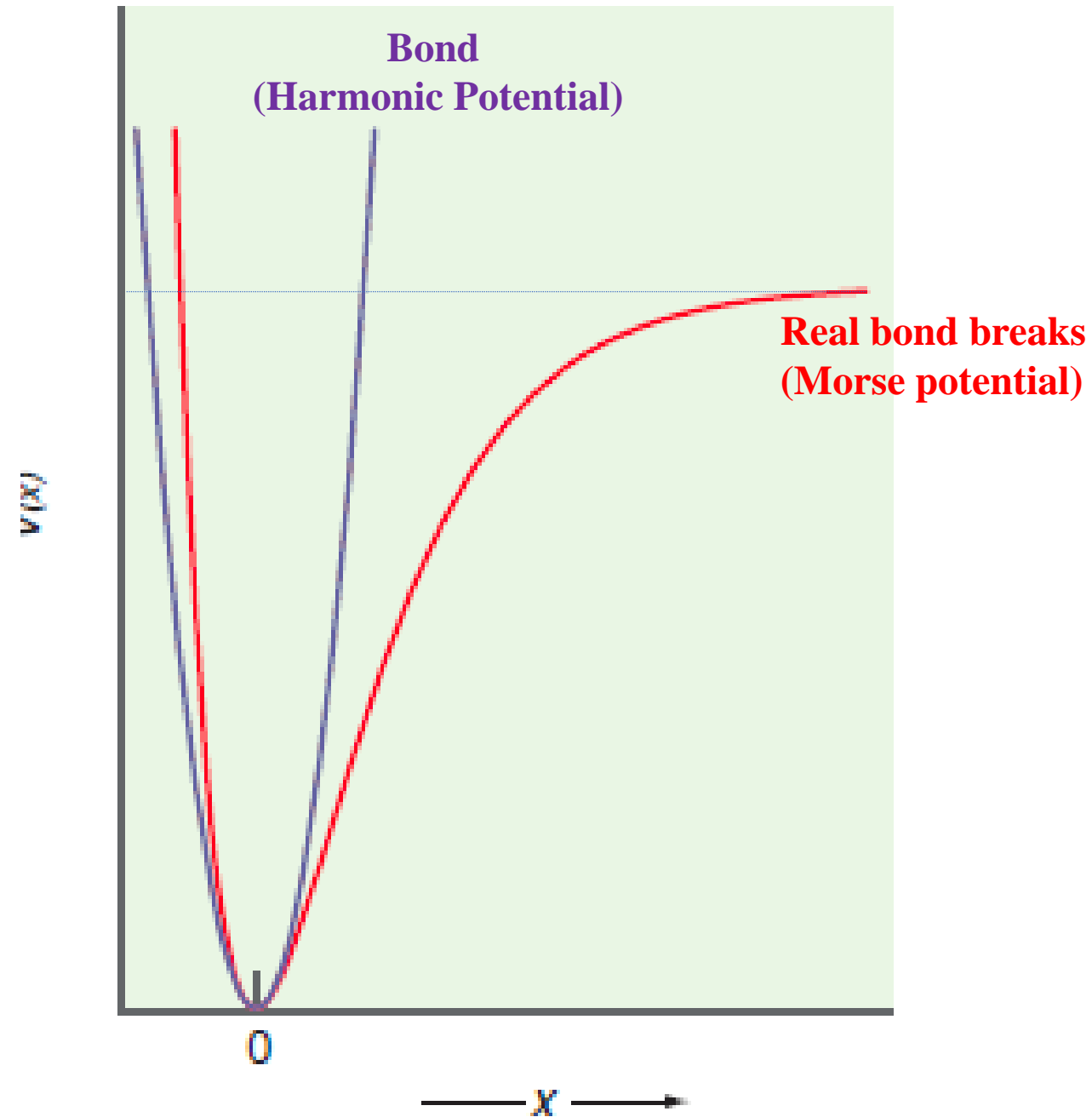
$$\Rightarrow V(r - r_0) = \frac{1}{2} k_b (r - r_0)^2$$

r_0, k_b

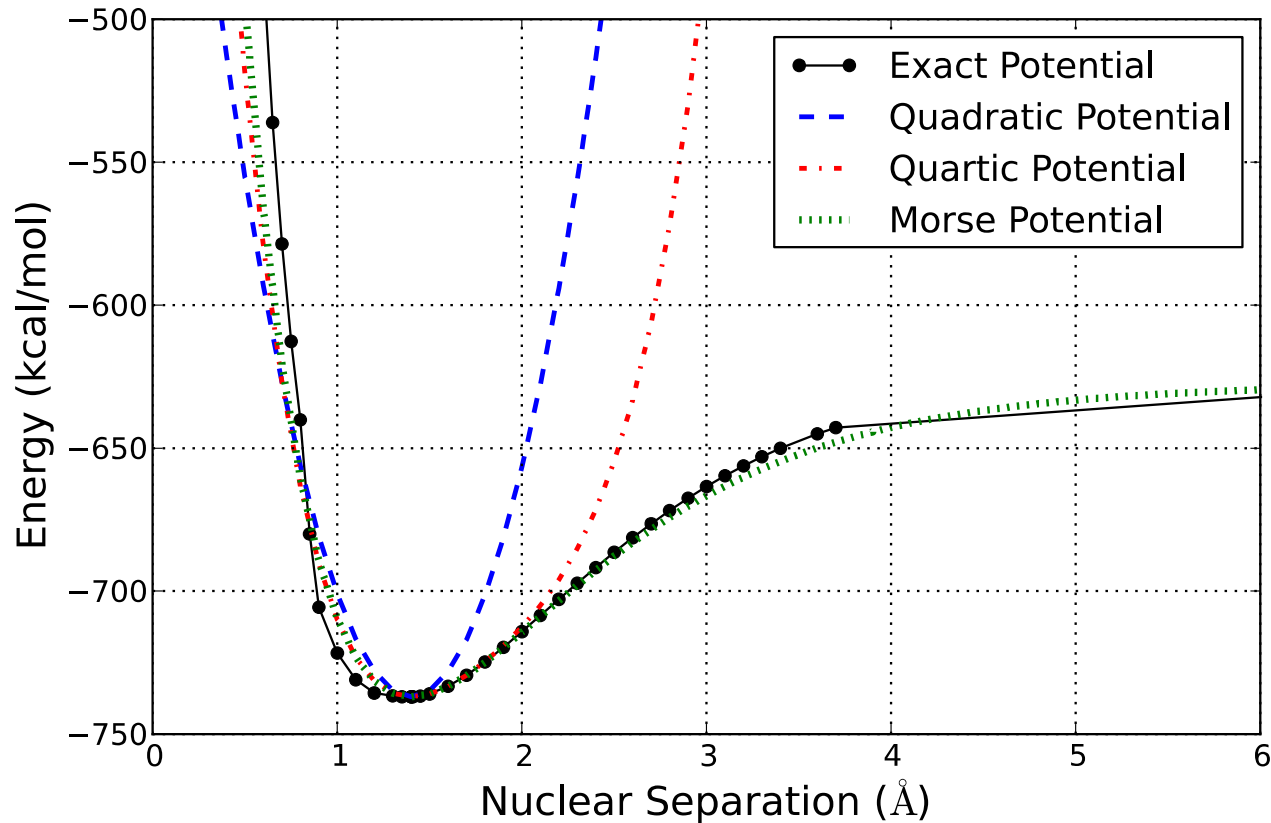
Parameters

Interesting Facts about Harmonic potential

- Good model only around $r = r_0$
- No bond breaking (No chemistry)



Can we do better ?



Ofcourse

1. Quartic potential (x^4 , x^3 , x^2)
2. Morse potential

$$U(x) = D [1 - \exp(\alpha (x - x_0))]^2$$

https://www.researchgate.net/publication/264913317_Free_Energy_Simulations_of_Complex_Biological_Systems_at_Constant_pH

$$V = \frac{1}{2} k_b (r - r_0)^2$$

$$K_b = 2 V / (r - r_0)^2$$

$$= \text{Energy} / (\text{distance})^2$$

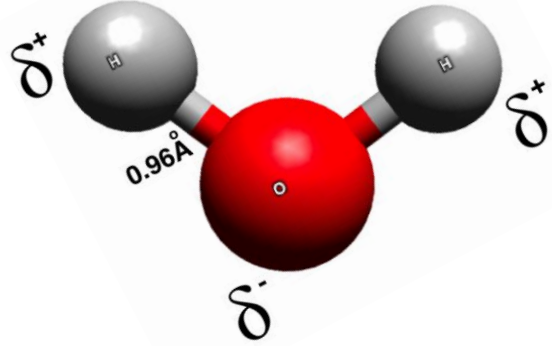
Unit:

$$k_b : (\text{kcal/mole}) / (\text{\AA}^2)$$

or

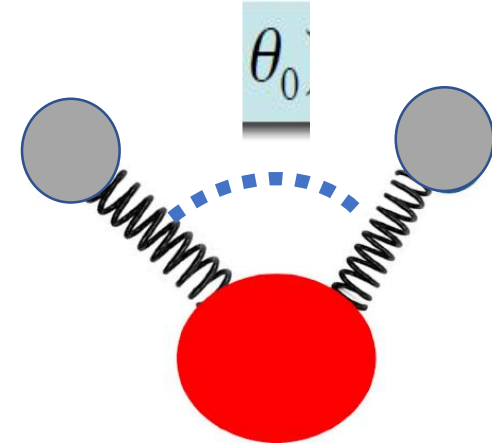
$$(\text{kJ/mole}) / (\text{nm}^2)$$

A molecule (internal structure) – Energy Function ?



Angle ?

$$v_{\text{angle}} = K_{\theta} (\theta - \theta_0)^2$$



Unit ?

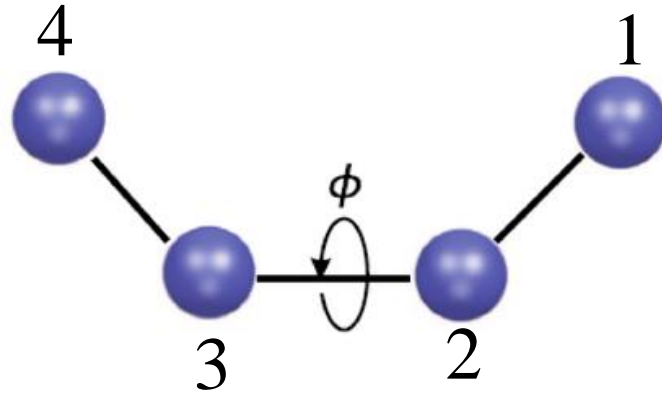
k_{θ}

θ_0, k_{θ}

Parameters ?

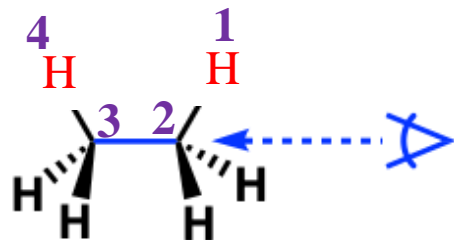
A molecule (internal structure) – Energy Function ?

Consecutive four atoms connection with rotatable bonds ($1 \rightarrow 2 \rightarrow 3 \rightarrow 4$).



- Rotation around 2__3 single bond possible
- Multiple possible conformation (relative orientation of 1 & 4)
- How the energy varies ?

Ethane (C_2H_6)

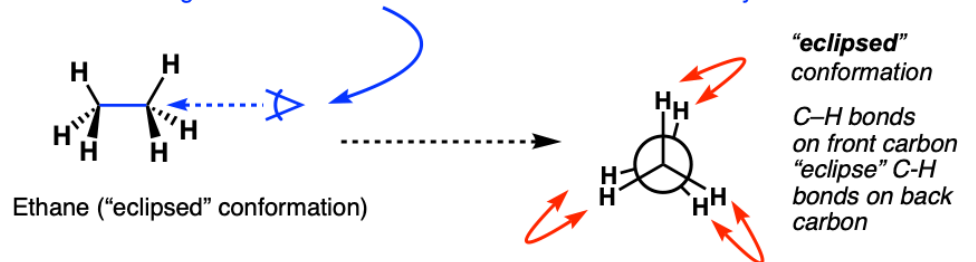


Dihedral Angle (Φ)

Angle between (1,2,3) & (2,3,4)

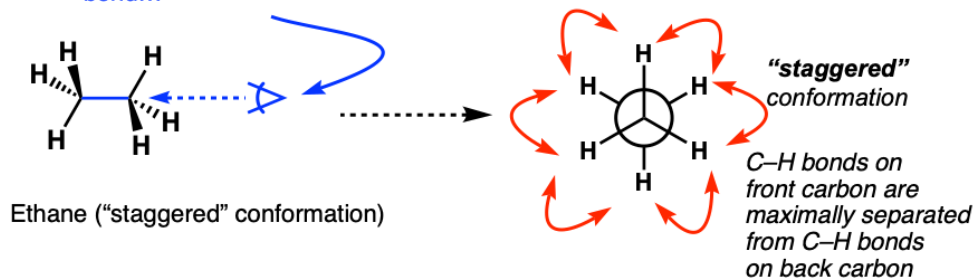
The Newman Projection of Ethane

this symbol says:
"Look along this carbon-carbon bond... ... and this is what you see"



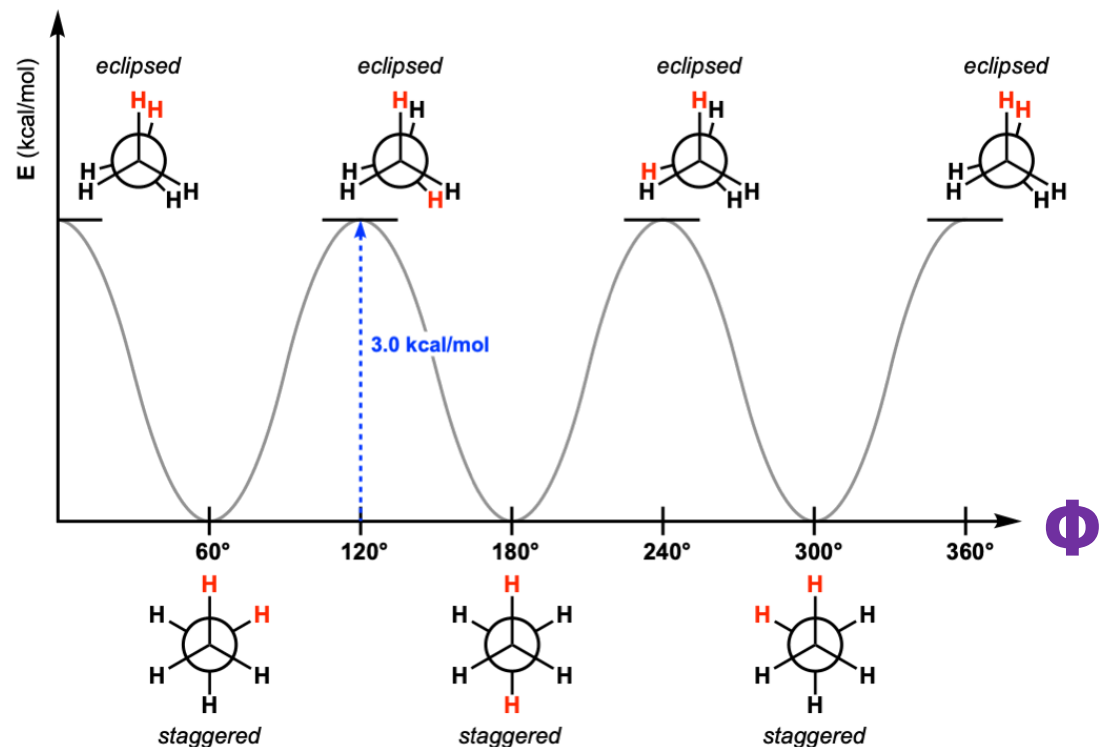
Look along this carbon-carbon bond...

... and this is what you see



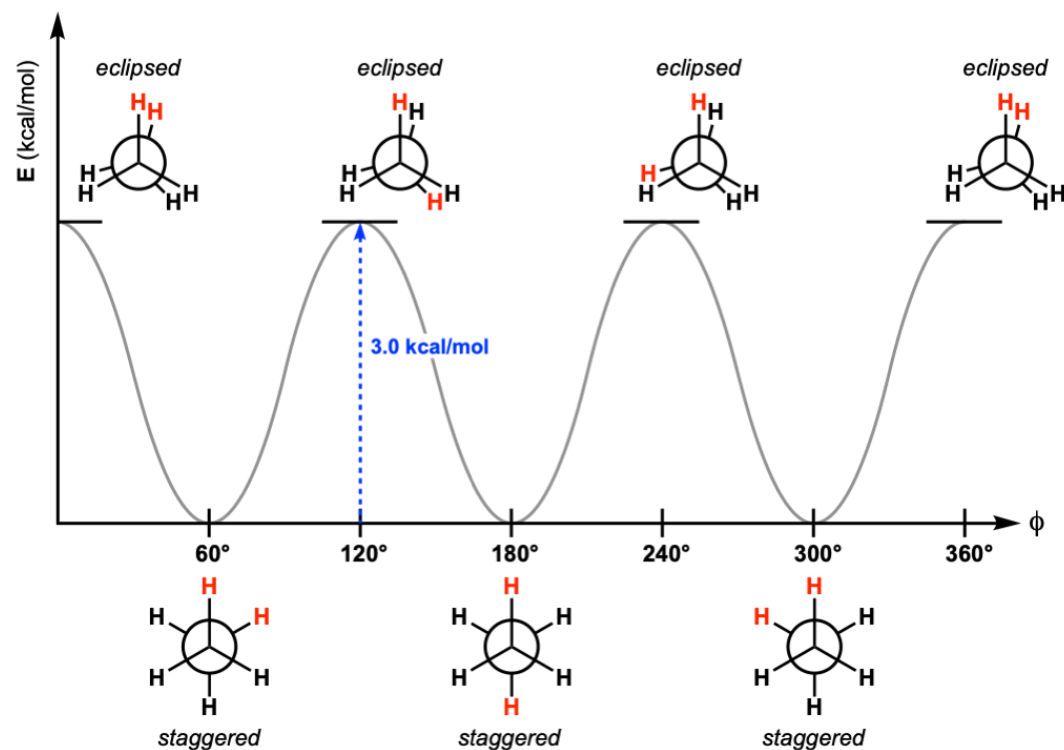
Graphing the rotational barrier in ethane (C_2H_6) as a function of dihedral angle

The barrier to rotation in ethane is about 3.0 kcal/mol.



Graphing the rotational barrier in ethane (C₂H₆) as a function of dihedral angle

The barrier to rotation in ethane is about 3.0 kcal/mol.



Dihedral/Torsional Angle (ϕ)

$$E_{\text{dihedral}} = K_{\phi} [1 + \cos(n\phi - \delta)]$$

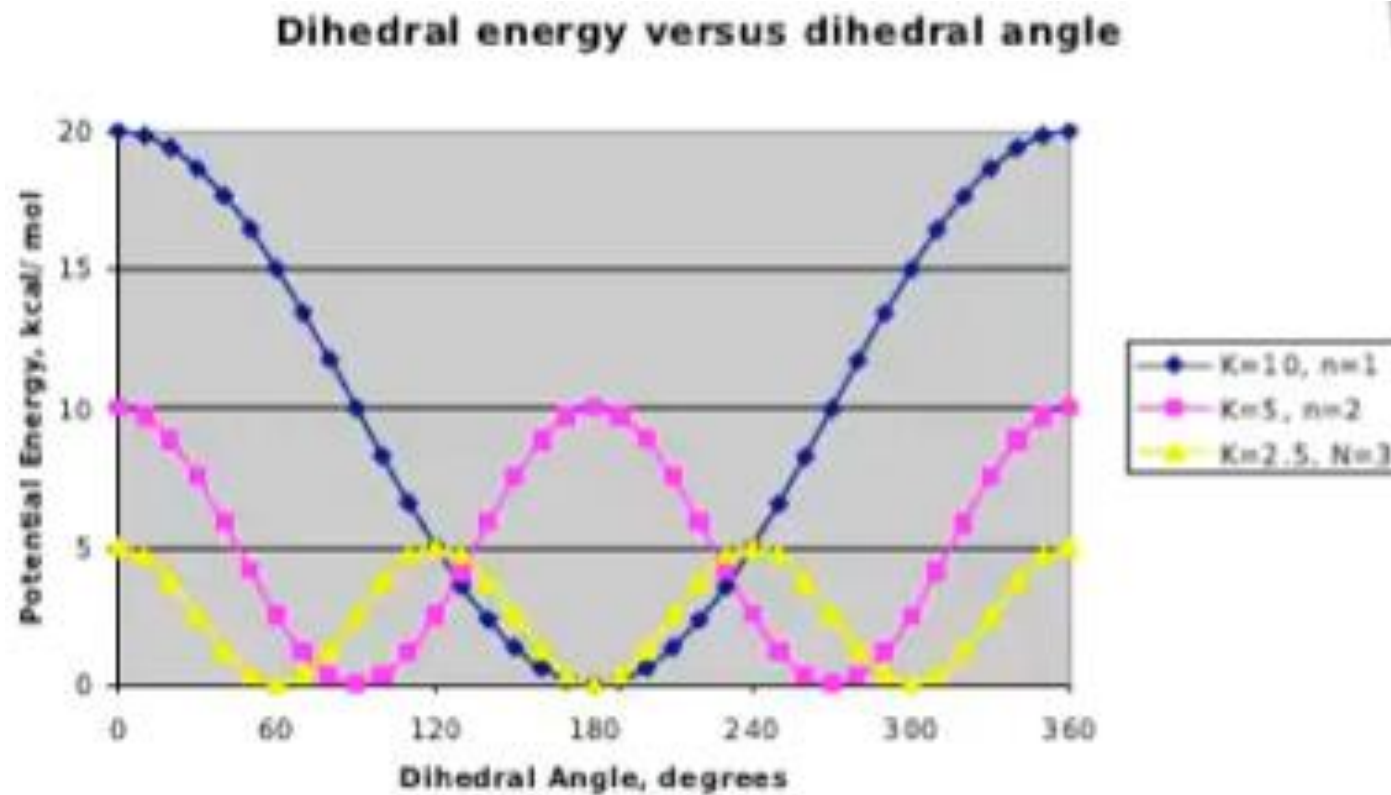
Barrier Height

Multiplicity

= No. of minimum points as the torsional angle Rotated by 360°

Phase-factor
= determine the torsion angles where E will be minimum

$$E_{\text{dihedral}} = K_{\phi} [1 + \cos(n\phi - \delta)]$$

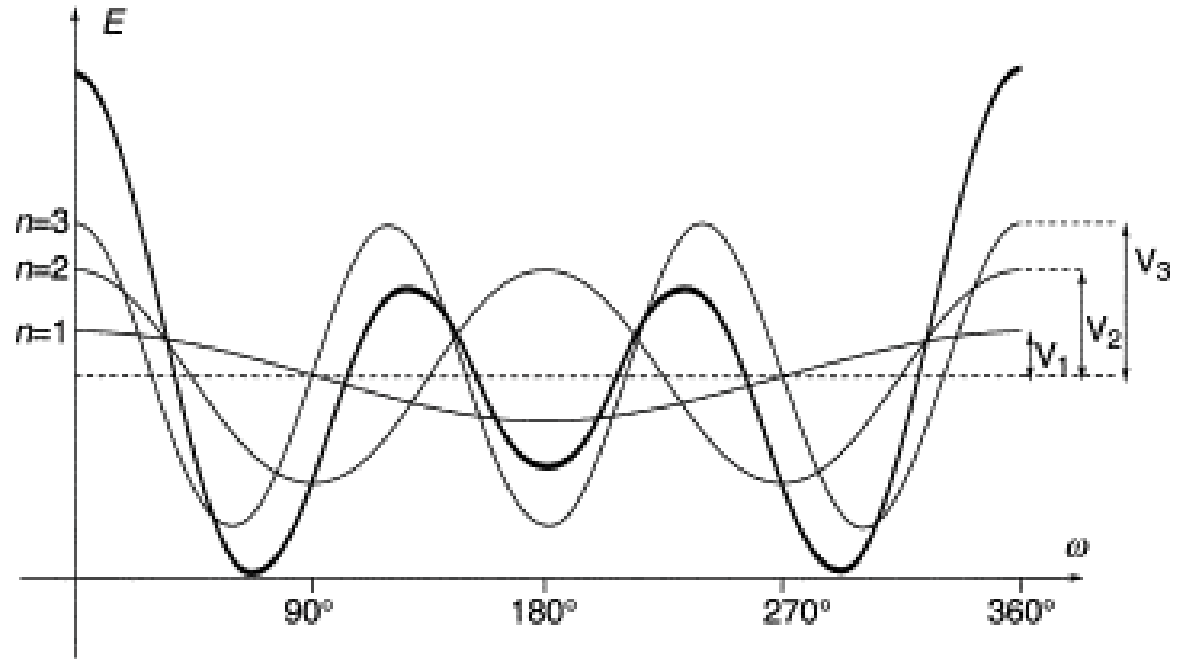
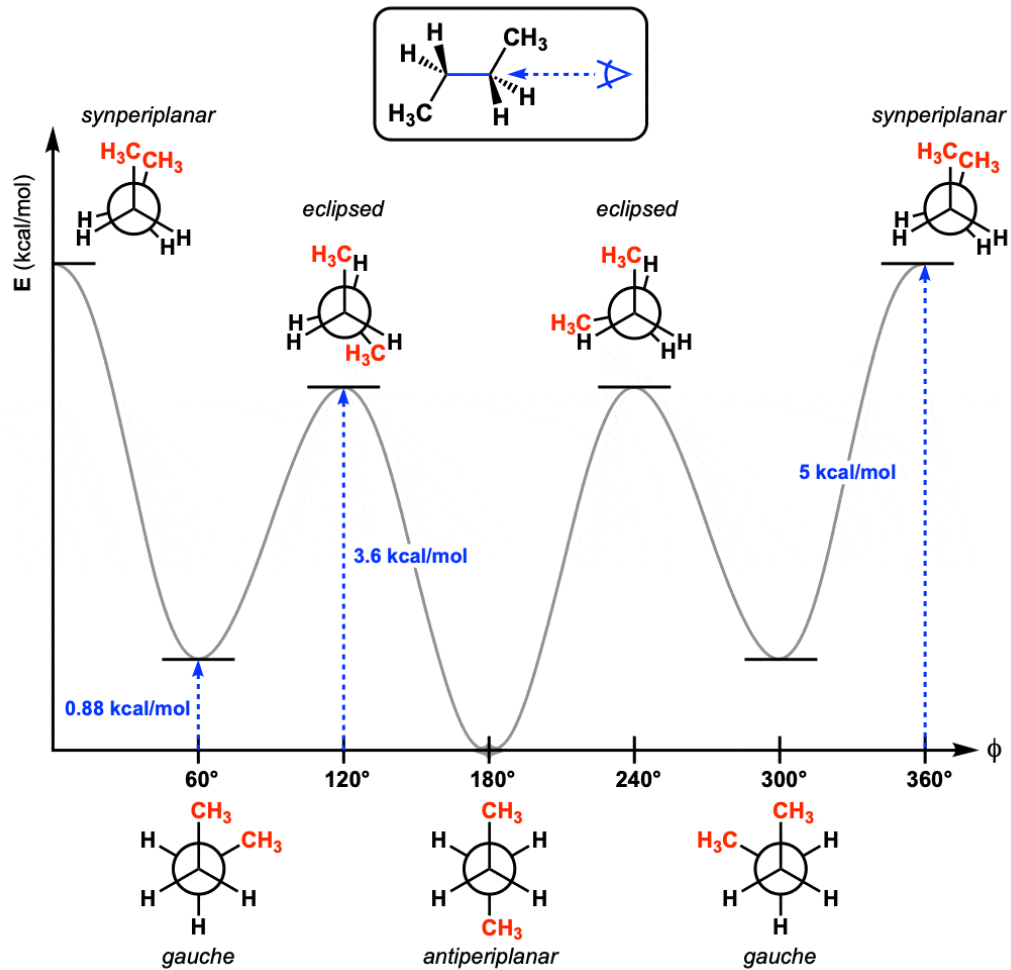


K_{ϕ}, n, δ

Parameters

Complicated potential Energy curve ?

Use combination of cosine function.



<https://www.sciencedirect.com/topics/chemistry/torsional-potential>

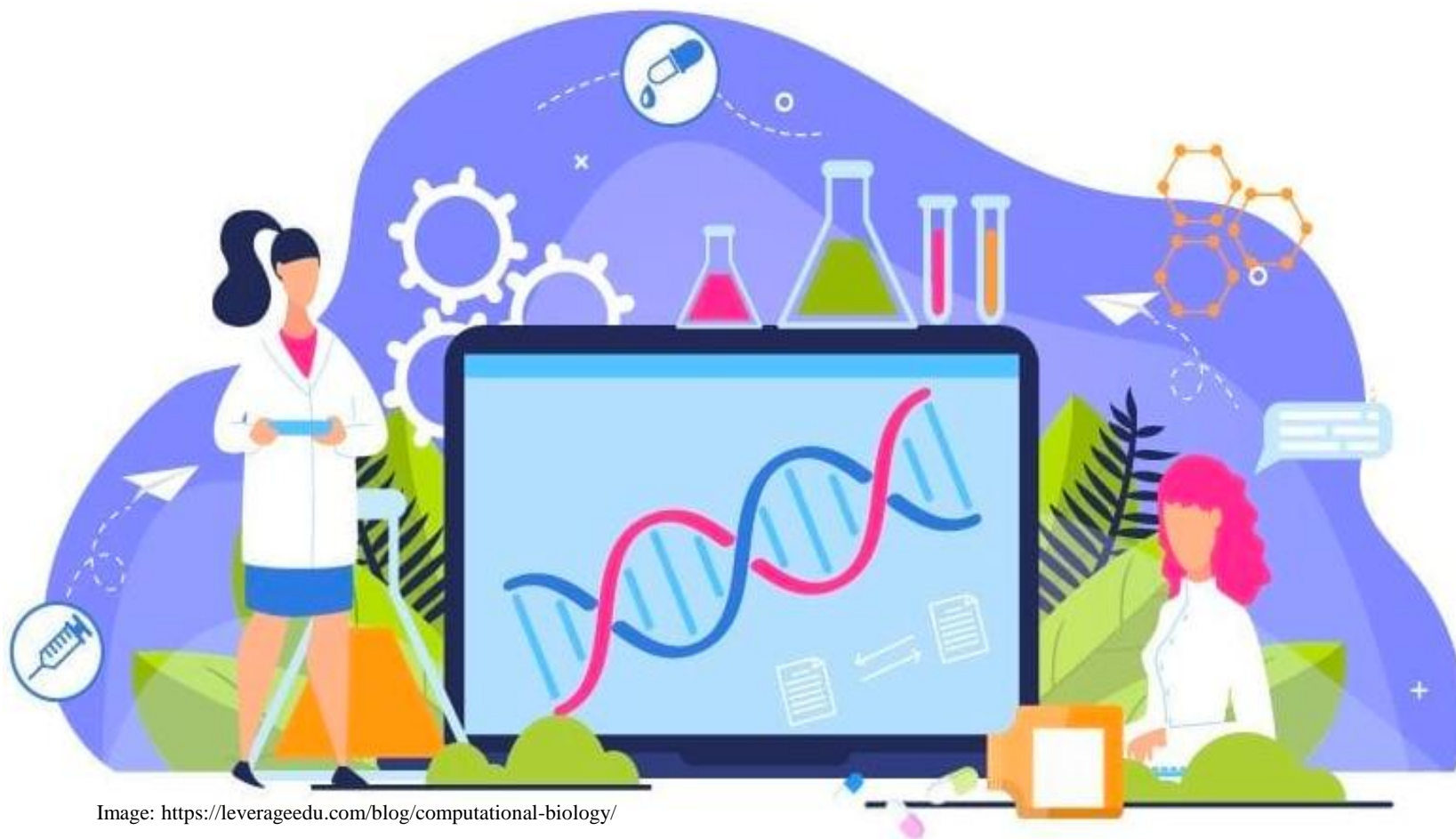


Image: <https://leverageedu.com/blog/computational-biology/>

Next : *How to describe a molecules ? ... continue*