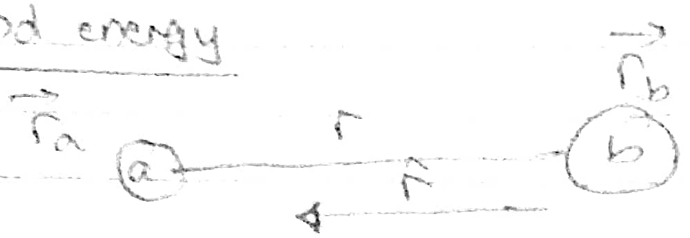
Calculation of derivatives :

1 Bond energy



$$\hat{r} = \frac{(\vec{r}_a - \vec{r}_b)}{|\vec{r}_a - \vec{r}_b|}$$

$$u(r) = k(r - r_0)^2, \quad r = |\vec{r}_a - \vec{r}_b|$$
$$= \sqrt{(\vec{r}_a - \vec{r}_b)\cdot(\vec{r}_a - \vec{r}_b)}$$

$$\frac{\partial u}{\partial r_a} = \frac{\partial u}{\partial r} \cdot \frac{\partial r}{\partial r_a}.$$
$$= 2k(r - r_0) \cdot \frac{\partial r}{\partial r_a}.$$

$$\frac{\partial r}{\partial r_a} = \cancel{2k(r - r_0)} \frac{\partial}{\partial r_a} \sqrt{(\vec{r}_a \cdot \vec{r}_a - 2\vec{r}_a \cdot \vec{r}_b + \vec{r}_b \cdot \vec{r}_b)}$$
$$= \frac{1}{2\sqrt{}\, r} \cdot (2\vec{r}_a - 2\vec{r}_b + 0)$$
$$= \frac{(\vec{r}_a - \vec{r}_b)}{r}$$
$$= \frac{\vec{r}}{r} = \hat{r}.$$

Hence $\quad \dfrac{\partial u}{\partial \vec{r}_a} = +2k(r - r_0) \cdot \hat{r};$

Force on atom a : $f_a = -\dfrac{\partial u}{\partial \vec{r}_a} = -2k(r - r_0) \cdot \hat{r}.$

Similarly,

$$\frac{\partial U}{\partial \vec{r}_b} = 2k(r-r_0)\cdot\left(0 - \frac{2\vec{r}_a + 2\vec{r}_b}{2r}\right)$$

$$= 2k(r-r_0)\cdot(-\hat{r})$$

$$= -2k(r-r_0)\cdot\hat{r}$$

$$f_b = -\frac{\partial U}{\partial r_b} = 2k(r-r_0)\cdot\hat{r}.$$

$\vec{f}_a + \vec{f}_b = 0$, which satisfies equilibrium conditions.

Notes:

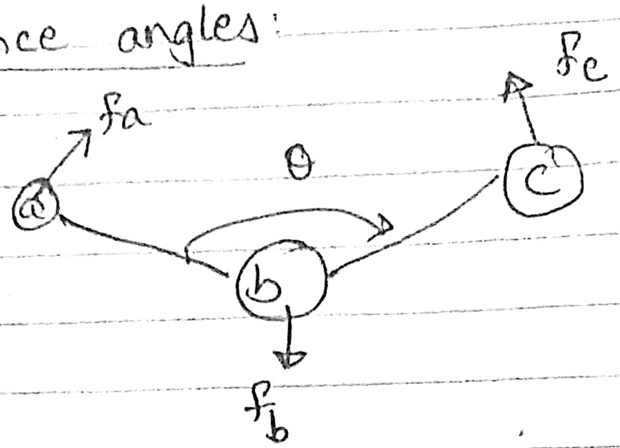
1. when $r > r_0$, $f_a \propto -\hat{r}$, which tends to pull a towards b. Hence pulls them close.
2. Similarly, when $r < r_0$, $f_a \propto \hat{r}$, which tends to repel a and b.

→ Box 1

~~2. Valence~~

$$\boxed{\text{Imp: If } r = |\vec{r}_a - \vec{r}_b|, \text{ then } \frac{\partial r}{\partial r_a} = \hat{r}}$$

2. Valence angles:



· Forces applied to 3 atoms all belong to the abc plane.

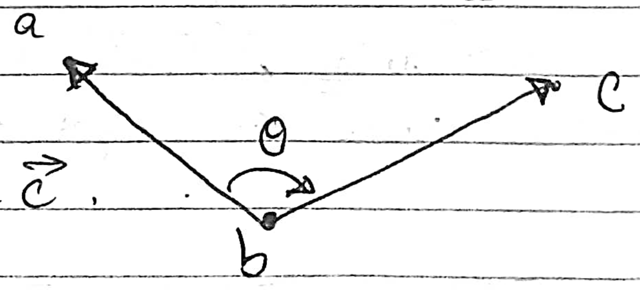
$$u(\theta) = k(\theta - \theta_0)^2.$$

$$\frac{\partial u}{\partial \theta} = 2k(\theta - \theta_0)$$

$$\frac{\partial u}{\partial r_a} = \frac{\partial u}{\partial \theta} \cdot \frac{\partial \theta}{\partial r_a}$$

$$= 2k(\theta - \theta_0) \cdot \frac{\partial \theta}{\partial r_a}.$$

For this section,



~~cos(θ)~~

$\vec{r}_a \equiv \vec{a}$, $\vec{r}_c \equiv \vec{c}$.

$\vec{r}_b \equiv \vec{b}$,

Define $\vec{ab} = \vec{a} - \vec{b}$,

$\vec{cb} = \vec{c} - \vec{b}$, then

$$\cos(\theta) = \frac{(\vec{a} - \vec{b}) \cdot (\vec{c} - \vec{b})}{|(\vec{a} - \vec{b}) \cdot (\vec{c} - \vec{b})|} = x$$

$$\theta = \cos^{-1}(x).$$

$$\frac{\partial \theta}{\partial \vec{a}} = \frac{-1}{\sqrt{1-x^2}} \cdot \frac{\partial x}{\partial \vec{a}}$$

$$= \frac{-1}{\sin\theta} \cdot \frac{\partial x}{\partial \vec{a}}$$

$$\frac{\partial x}{\partial \vec{a}} = \frac{\partial}{\partial \vec{a}} \left[\frac{(\vec{ab}) \cdot (\vec{cb})}{|ab| \cdot |cb|} \right]$$

$$= \left\{ \frac{\partial}{\partial \vec{a}} [|ab| \cdot |cb|] \cdot [(ab) \cdot (cb)] - |ab| \cdot |cb| \cdot \frac{\partial}{\partial \vec{a}} [(\vec{ab}) \cdot (\vec{cb})] \right\} \Big/ (|ab| \cdot |cb|)^2$$

$$= \frac{\cancel{|cb|} \cdot \hat{ab} \cdot (ab) \cdot (cb) - |ab| \, \cancel{|cb|} \, (\vec{cb})}{|ab|^2 |cb|^{\cancel{2}}} \quad \text{[From Box 1]}$$

$$= \frac{1}{|ab|^3 \, |cb|} \cdot \left[(ab \cdot cb) \, \vec{ab} - (\vec{ab} \cdot \vec{ab}) \, cb \right]$$

[Mult & divide by |ab|]

$$= \frac{1}{|ab|^3 |cb|} [\vec{ab} \times (\vec{ab} \times \vec{cb})]$$

$$\boxed{\frac{\partial x}{\partial \vec{a}} = \frac{1}{|ab|^3 \cdot |cb|} [\vec{ab} \times (\vec{ab} \times \vec{cb})]}$$

$$\frac{\partial x}{\partial a} = -\frac{(\vec{ba} \times (\vec{ba} \times \vec{bc}))}{|ba|^3 \, |bc|}$$

$$\frac{\partial \theta}{\partial \vec{a}} = \frac{1}{\sin\theta} \, \frac{[\vec{ba} \times (\vec{ba} \times \vec{bc})]}{|ba|^2 \, |bc|} \, \frac{1}{|ba|}$$

$$= \frac{\hat{p}}{|ba|}, \quad \vec{p} = [\vec{ba} \times (\vec{ba} \times \vec{bc})]$$

Hence $$\frac{\partial U}{\partial \vec{r_a}} = 2k(\theta - \theta_0) \cdot \frac{\hat{p}}{|ba|}$$

$$\vec{f_a} = -2k(\theta - \theta_0) \cdot \frac{\hat{p}_a}{|ba|}$$

$\vec{a}$ & $\vec{c}$ are symmetrical in the expression, so.

$$\vec{f_c} = -2k(\theta - \theta_0) \frac{\hat{p}_c}{|bc|}, \quad \vec{p_c} = [\vec{bc} \times (\vec{bc} \times \vec{ba})]$$

$$\vec{f_b} = -\vec{f_c} - \vec{f_a}$$

Torques:

$$|\vec{ba} \times \vec{P_a}| = 2k(\theta - \theta_0)$$

$$|\vec{bc} \times \vec{P_c}| = \cancel{\beta}\, 2k(\theta - \theta_0)\cancel{\beta}$$

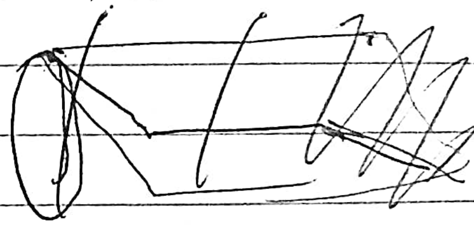
$$\vec{ba} \times \vec{P_a} + \vec{bc} \times \vec{P_c} = 0$$

$\therefore$ No rotation around b.

Dihedral angles:

$$U = \cancel{K}(1 + \cos(n\phi - \text{phase})) K$$

$$\frac{\partial U}{\partial \phi} = -K\sin(n\phi - \text{phase}) \cdot n.$$



$$\frac{\partial \phi}{\partial r_a} = \frac{1}{|ab| \sin(\theta_1)},$$

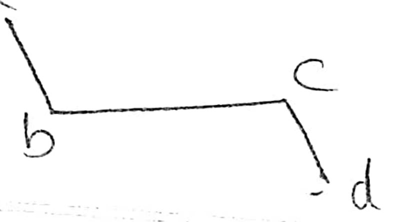
$$\theta_1 = \angle abc.$$

direction of force $= \dfrac{\vec{ba} \times \vec{bc}}{|\vec{ba}| \cdot |\vec{bc}| \sin\theta_1} = \hat{P}_1$

$$\frac{\partial U}{\partial \vec{r_a}} = -K\sin(n\phi - \text{phase}) \cdot n \cdot \frac{1}{|ab|\sin(\theta_1)} \cdot \hat{P}_1$$

Similarly, $\dfrac{\partial U}{\partial \vec{r_c}} = -K\sin(n\phi - \text{phase}) \cdot n \cdot \dfrac{1}{|cd|\sin\theta_2} \cdot \hat{P}_2$

$$\hat{P}_2 = \frac{\vec{cd} \times \vec{cb}}{|\vec{cd} \times \vec{cb}|}$$



Eq: conditions: $\vec{f_a}+\vec{f_b}+\vec{f_c}+\vec{f_d}=0$.

O → centre of bc bond

$$\vec{oa}\times\vec{f_a}+\vec{od}\times\vec{f_d}+\vec{ob}\times\vec{f_b}+\vec{oc}\times\vec{f_c}=0$$

$$\Rightarrow (\vec{ob}+\vec{ba})\times\vec{f_a}+(\vec{oc}+\vec{cd})\times\vec{f_d}+\vec{ob}\times\vec{f_b}+\vec{oc}\times\vec{f_c}=0$$

$$\Rightarrow (-\vec{oc}+\vec{ba})\times\vec{f_a}+(\vec{oc}+\vec{cd})\times\vec{f_d}-\vec{oc}\times\vec{f_b}+\vec{oc}\times\vec{f_c}=0$$

$$\Rightarrow \vec{oc}\times(-\vec{f_a}+\vec{f_d}-\vec{f_b}+\vec{f_c})+\vec{ba}\times\vec{f_a}+\vec{cd}\times\vec{f_a}=0$$

$$\Rightarrow \vec{oc}\times 2(\vec{f_d}+\vec{f_c})+\vec{ba}\times\vec{f_a}+\vec{cd}\times\vec{f_d}=0$$

$$\vec{oc}\times\vec{f_c}=-(\vec{oc}\times\vec{f_d}+0.5\,\vec{cd}\times\vec{f_d}+0.5\,\vec{ba}\times\vec{f_a})=\vec{t_c}$$

$$\vec{f_c}=\left(\frac{1}{|oc|^2}\right)\vec{t_c}\times\vec{oc}$$

$\vec{t_c}=-(\vec{oc}\times\vec{f_d}+0.5\,\vec{cd}\times\vec{f_d}+0.5\,\vec{ba}\times\vec{f_a})$

$\vec{oc}\times\vec{x}=\vec{t_c}$ has ~~one~~ many solutions, one of which is ~~$\perp$ to $\vec{oc}$, and~~

$\vec{f_c}=\frac{1}{|oc|^2}\,\vec{t_c}\times\vec{oc}$ is a solution

$$\vec{f_b} = -\vec{f_a} - \vec{f_c} - \vec{f_d}$$

<u>LJ:</u>

$$U = 4\varepsilon\left[\frac{A}{|r|^{12}} - \frac{B}{|r|^{6}}\right] \qquad \begin{array}{l} A = \sigma^{12} \\ B = \sigma^{6} \end{array}$$

$$\frac{\partial U}{\partial \vec{r}} = 4\varepsilon\left[\frac{-12A}{|r|^{13}} + \frac{6B}{|r|^{7}}\right] \cdot \frac{\partial |r|}{\partial \vec{r}}$$

$$= -\frac{24\varepsilon}{r}\left[2\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^{6}\right] \cdot \hat{r}$$

$$\frac{\partial U}{\partial \vec{r_a}} = \frac{\partial U}{\partial \vec{r}} \cdot \frac{\partial \vec{r}}{\partial \vec{r_a}}$$

since $\vec{r} = \vec{r_a} - \vec{r_b}$, $\frac{\partial \vec{r}}{\partial \vec{r_a}} = 1$,

$$\frac{\partial \vec{r}}{\partial \vec{r_b}} = -1.$$

$$\frac{\partial U}{\partial \vec{r_a}} = -\frac{24\varepsilon}{r}\left[2\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^{6}\right] \cdot \hat{r}$$

$$\vec{f_a} = -\frac{\partial U}{\partial \vec{r_a}}, \quad \vec{f_b} = -\vec{f_a}$$

Improper:

$$\vec{f}_a = -2k(\phi - \phi_0) \cdot \frac{1}{|ab|\sin\theta_1} \cdot \hat{p}_1$$

$$= \frac{\partial U}{\partial \phi} \frac{\partial \phi}{\partial r_a}$$

$$\vec{f}_d = -2k(\phi - \phi_0) \cdot \frac{1}{|cd|\sin\theta_2} \cdot \hat{p}_2$$

$$\vec{f}_c = \left(\frac{1}{|oc|^2}\right) \vec{tc} \times \vec{oc}$$

$$\vec{f}_a = -(\vec{f}_a + \vec{f}_b + \vec{f}_c)$$