Chemie: elektromagnetické síly

Coulombův zákon:

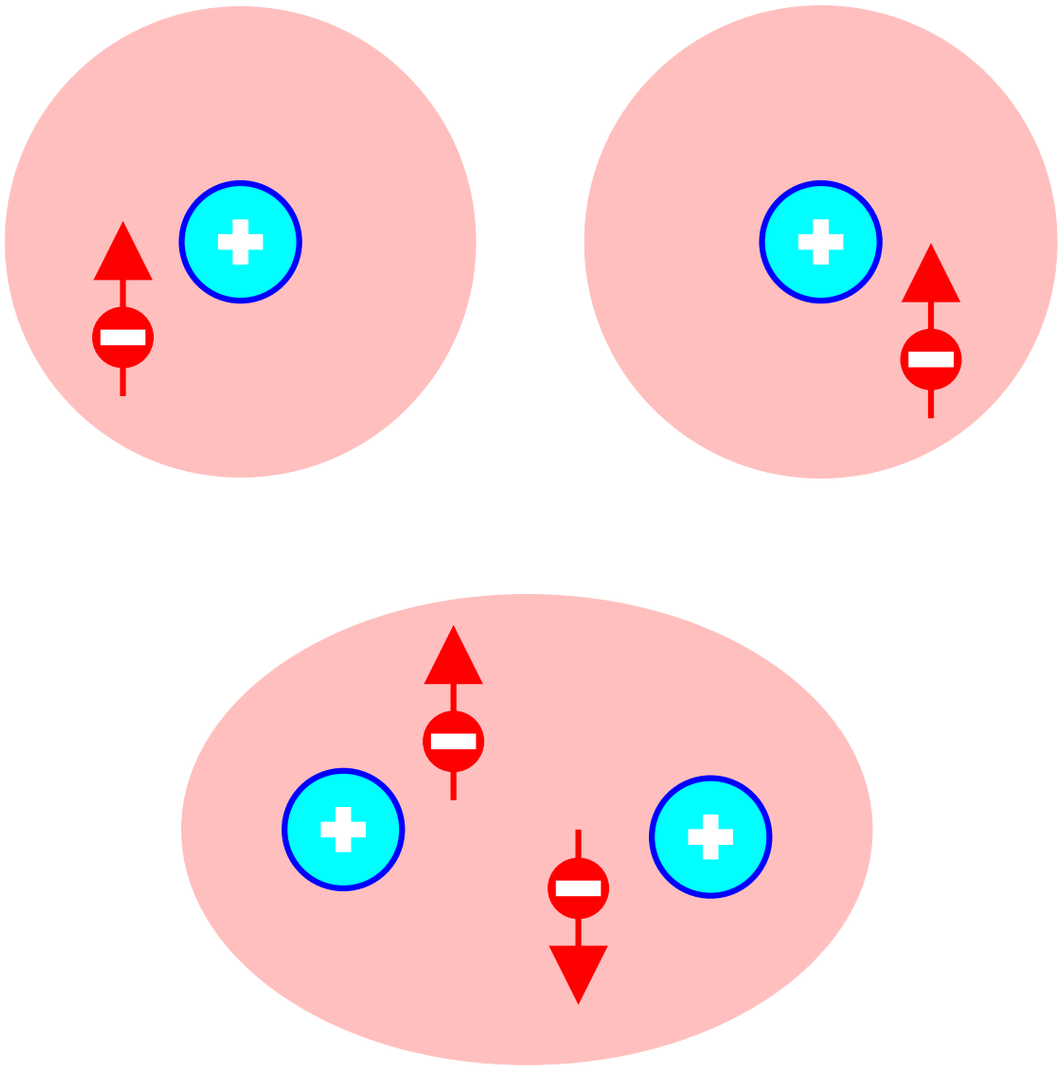
$$F = \frac{1}{4\pi\epsilon_0}\frac{Q_1 Q_2}{r^2}$$

- Síla je vektor: $\vec{F} = \frac{1}{4\pi\epsilon_0}\frac{Q_1 Q_2}{r^2} \cdot \frac{\vec{r}}{r}$ jedn. vektor

- Elektrická intenzita: $\vec{E} = \frac{1}{4\pi\epsilon_0}\frac{Q}{r^2} \cdot \frac{\vec{r}}{r}$

- Energie $U = \frac{N_\mathrm{A}}{4\pi\epsilon_0}\frac{Q_1 Q_2}{r}$ v kJ/mol

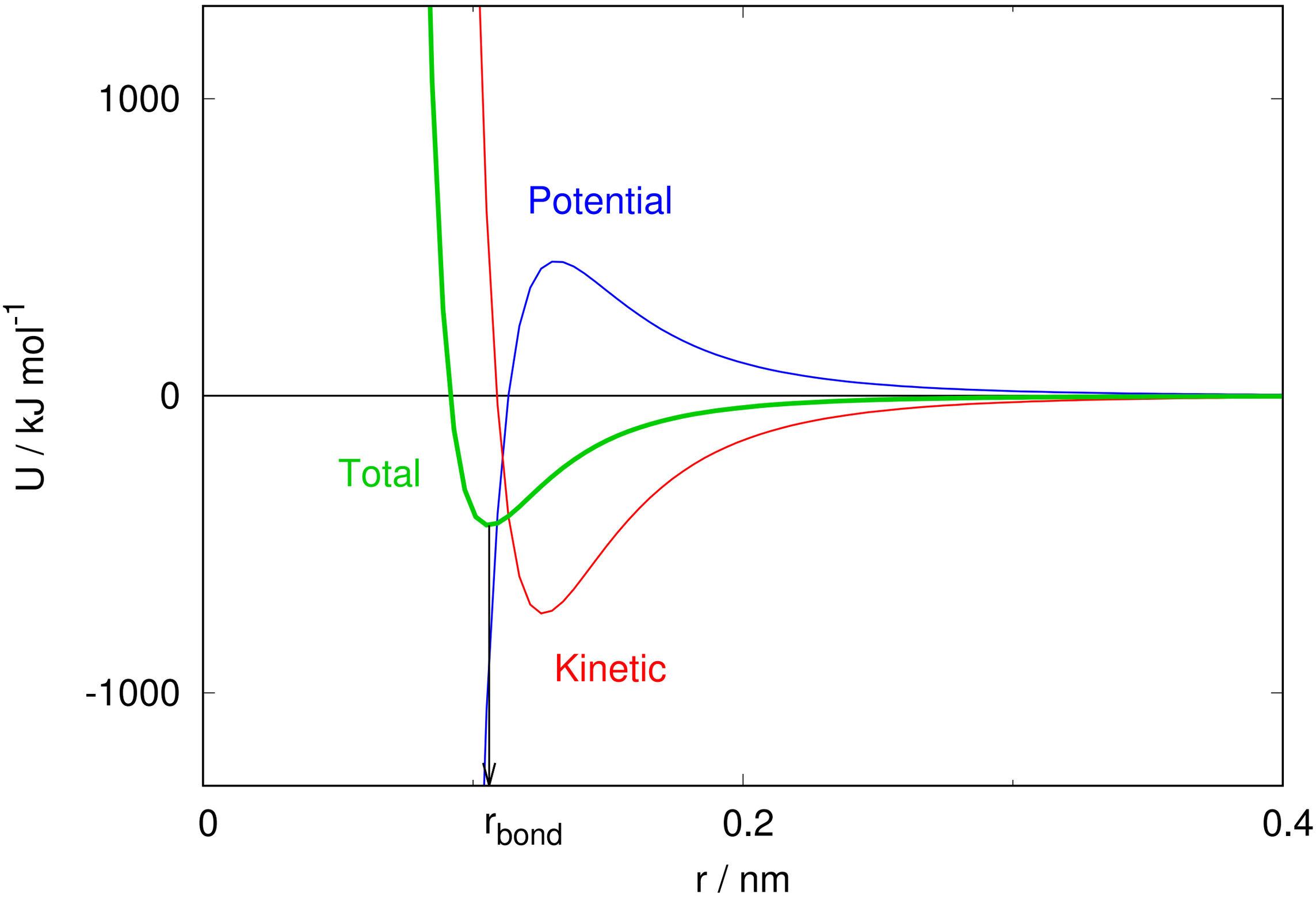
Kovalentní vazba



reference energy

lower energy

higher energy

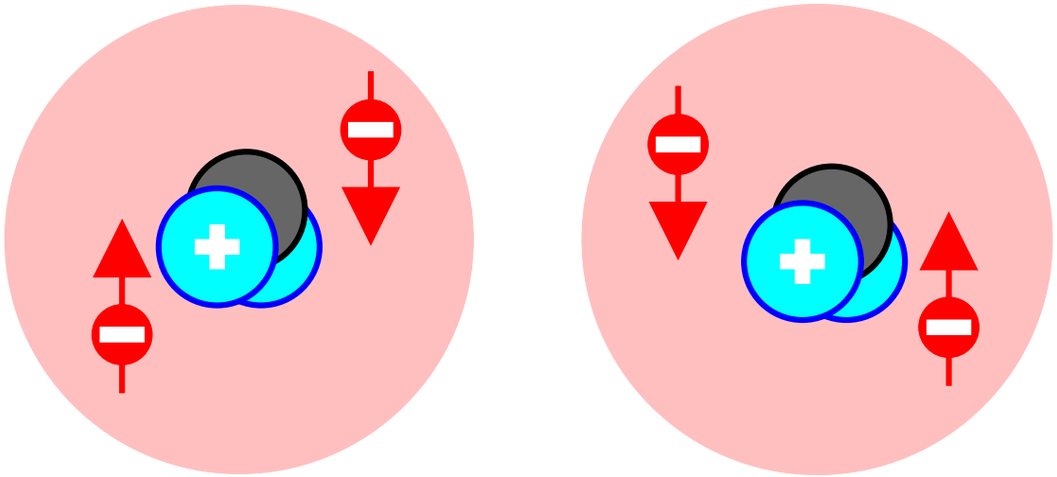

1000
0
-1000
U / kJ mol-1
Potential
Total
Kinetic
0
rbond
0.2
0.4
r / nm

- Primární struktura

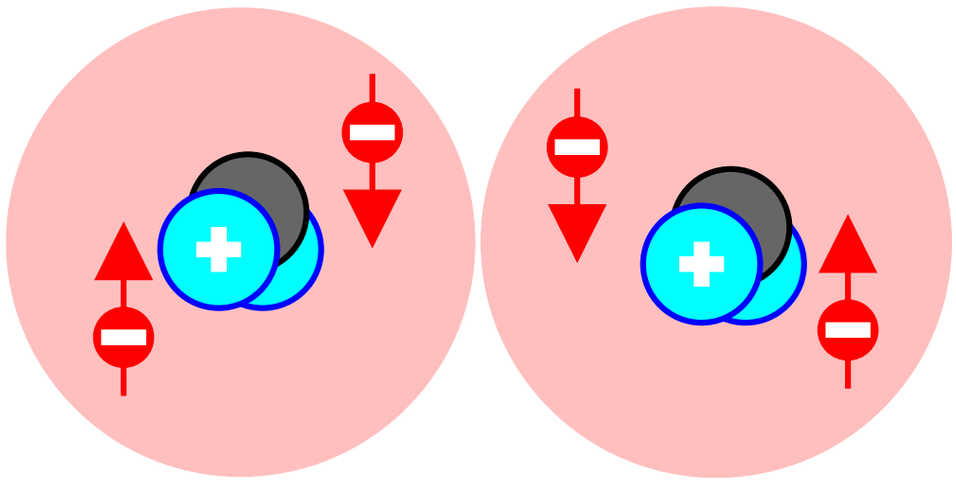
- Disulfidové můstky v extracelulárních proteinech

$$\underbrace{\text{Cys–S–S–Cys}}_{\text{protein}} + 2\ \begin{matrix}\gamma\text{Glu}\\ \text{Cys–SH}\\ \text{Gly}\end{matrix} = \underbrace{\begin{matrix}\gamma\text{Glu}\\ \text{Cys–SH}\end{matrix}\quad\begin{matrix}\gamma\text{Glu}\\ \text{HS–Cys}\end{matrix}}_{\text{protein}} + \begin{matrix}\gamma\text{Glu}\\ \text{Cys–S–S–Cys}\\ \text{Gly}\end{matrix}\quad\begin{matrix}\gamma\text{Glu}\\ \\ \text{Gly}\end{matrix}$$

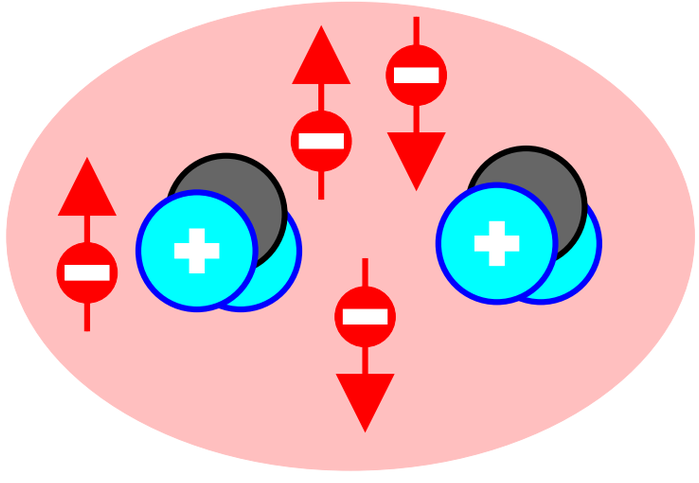
van der Waalsovy síly



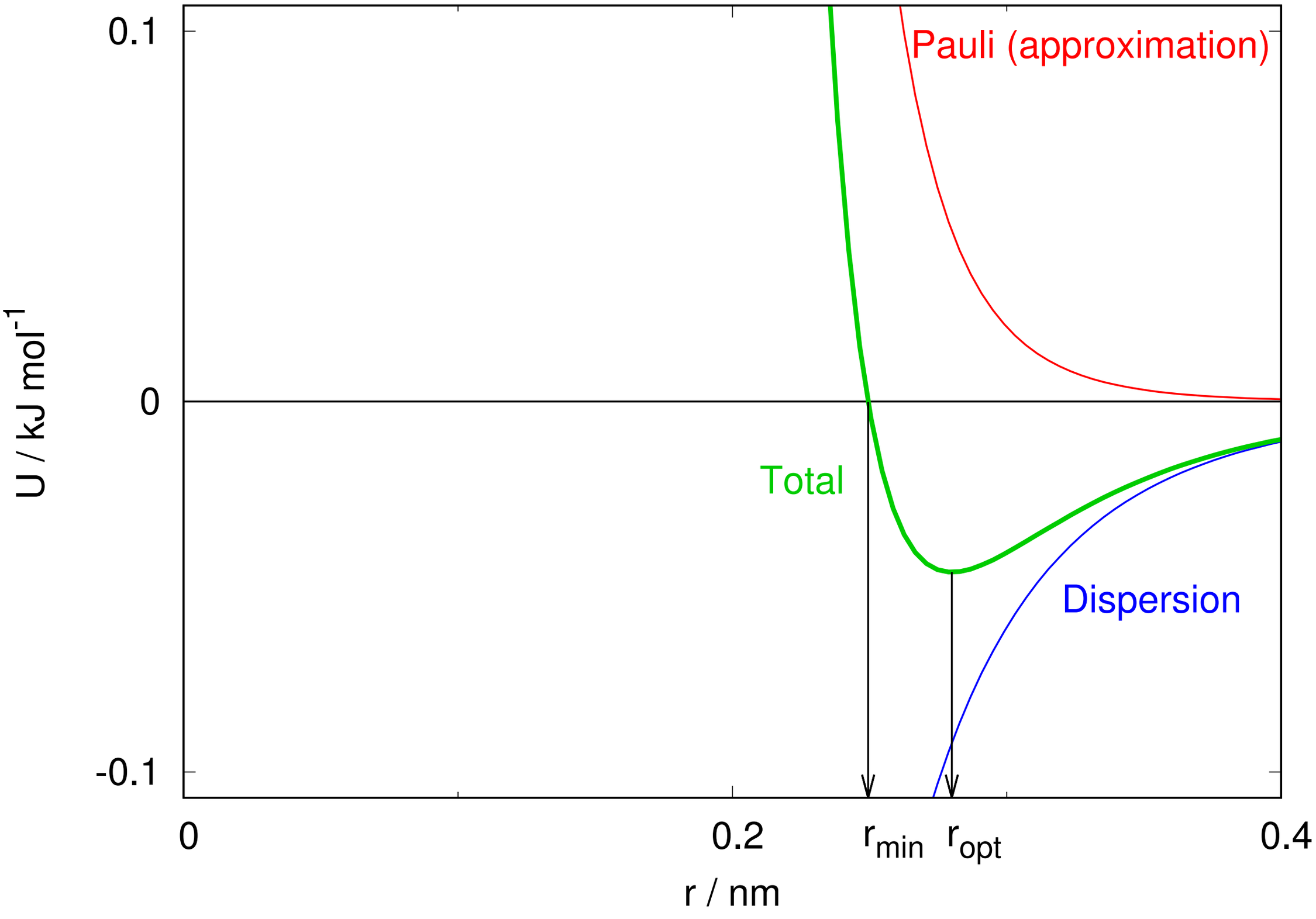
reference energy



lower energy



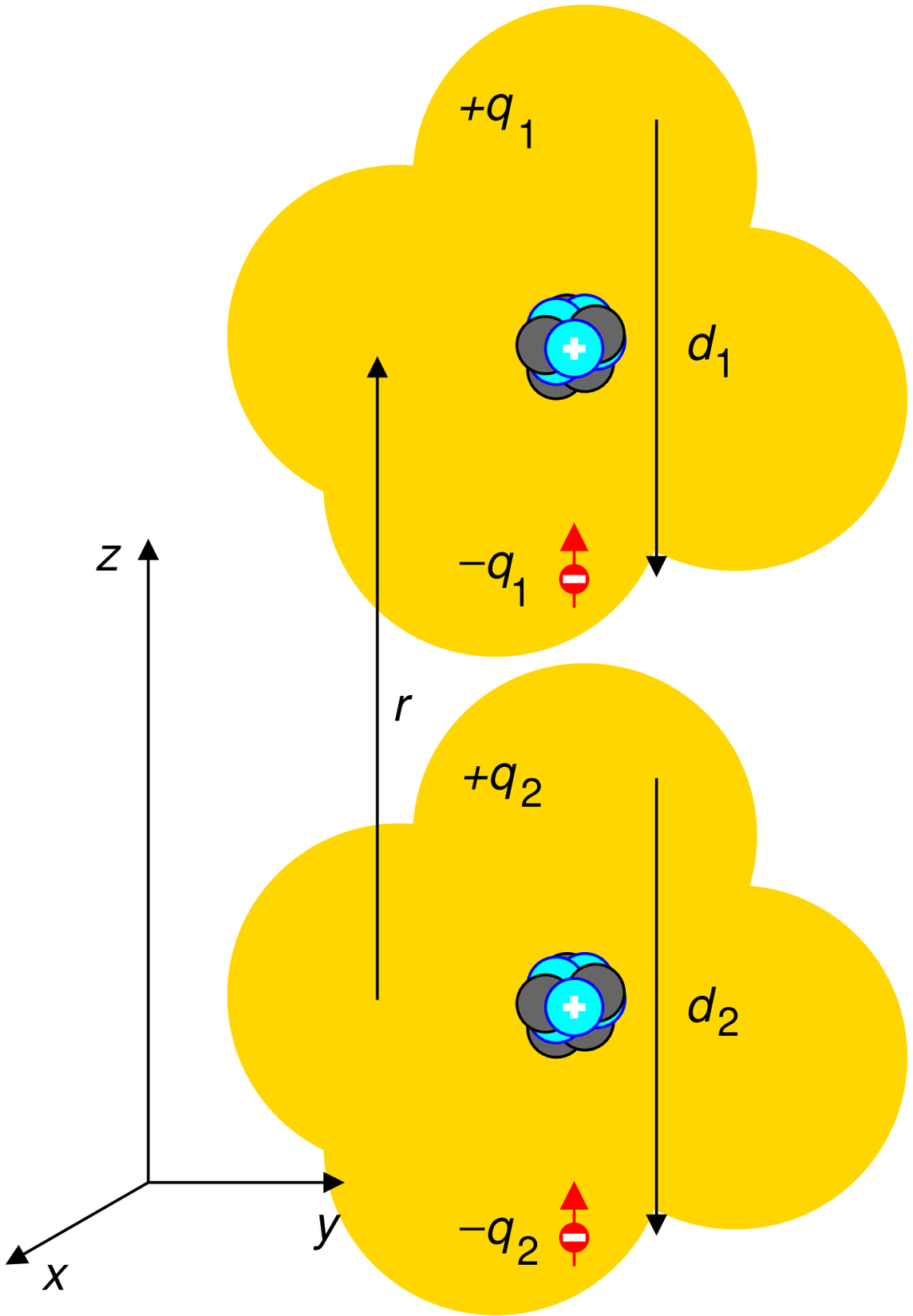
IMPOSSIBLE !

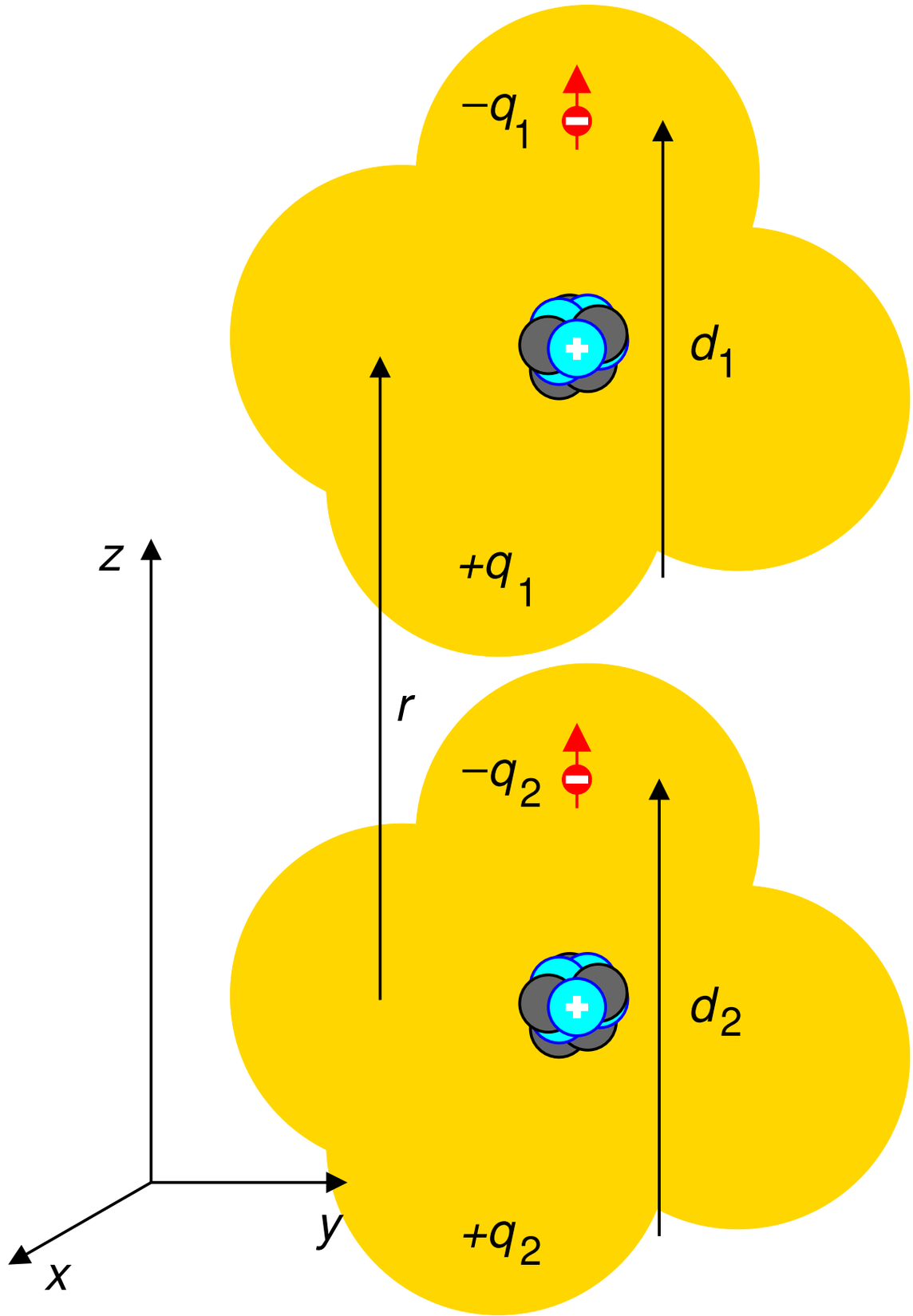

0.1
0
-0.1
U / kJ mol-1
Pauli (approximation)
Total
Dispersion
0
0.2
0.4
rmin
ropt
r / nm

Atom···atom	U_{opt} / kJ mol^{-1}	r_{opt} / nm	r_{min} / nm
He···He	0.05	0.28	0.25
–H···H–	0.50	0.24	0.20
–C···C–	0.50	0.34	0.30
–N···N–	0.85	0.31	0.27
–O···O–	0.95	0.30	0.27

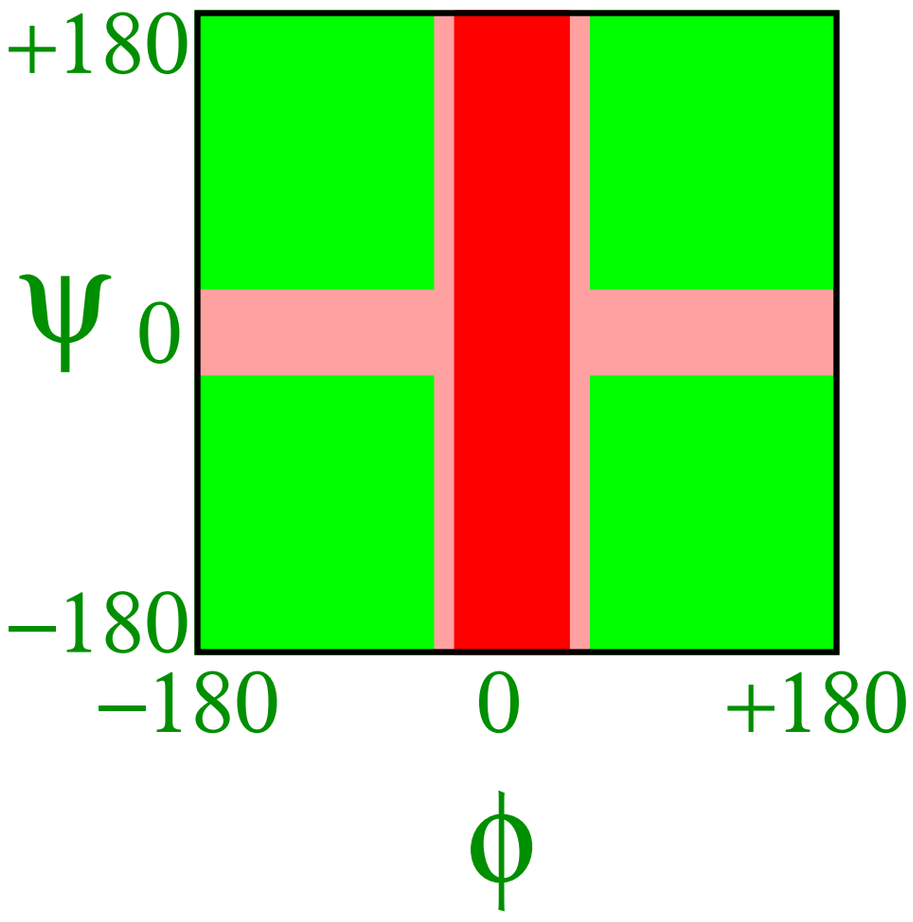
$$U = U_{\mathrm{opt}} \left(\left(\frac{r_{\mathrm{opt}}}{r} \right)^{12} - 2 \left(\frac{r_{\mathrm{opt}}}{r} \right)^{6} \right)$$

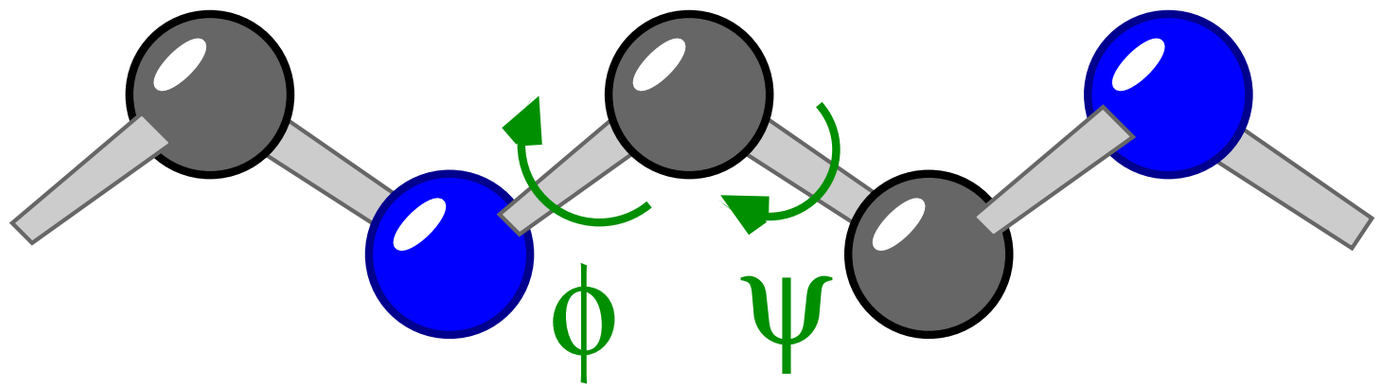
Disperzní síly



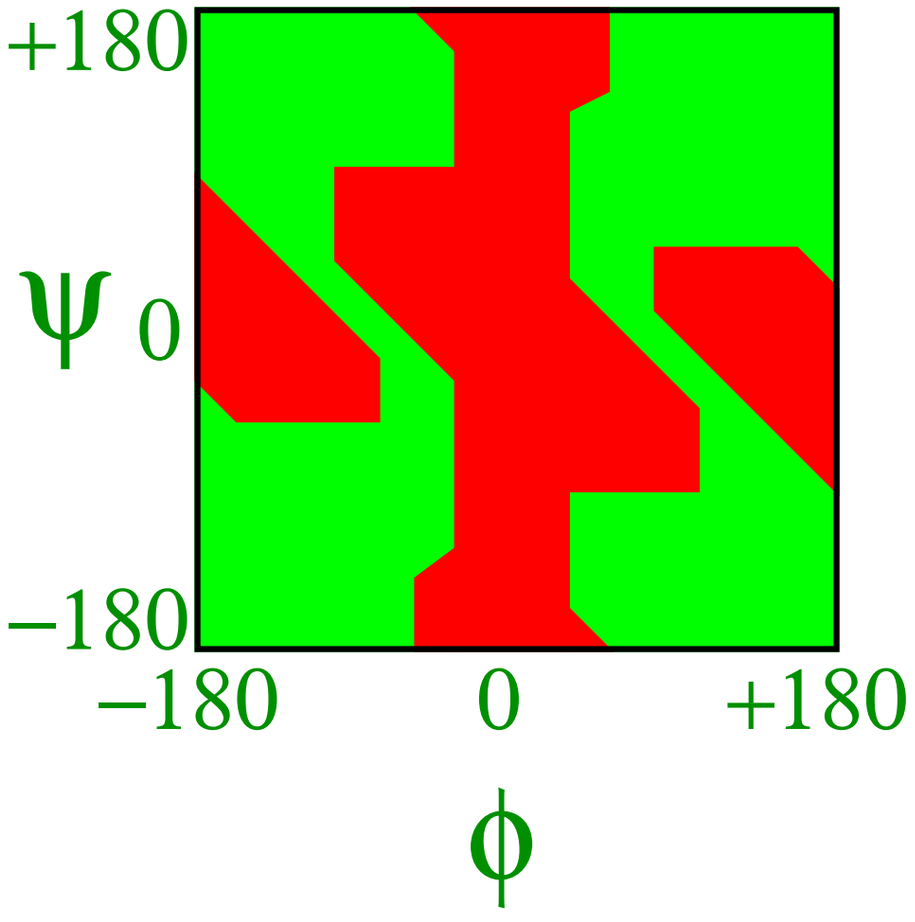


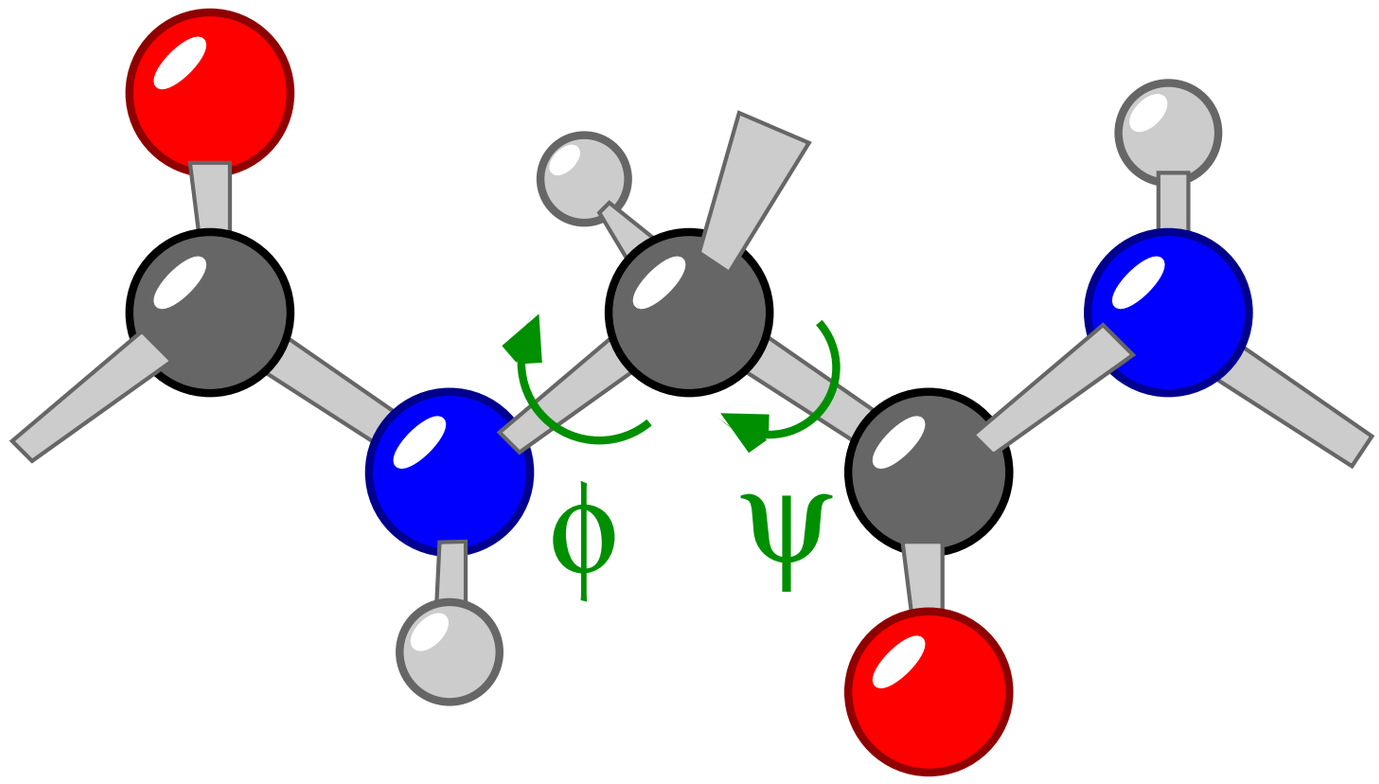
Pauliho repulze



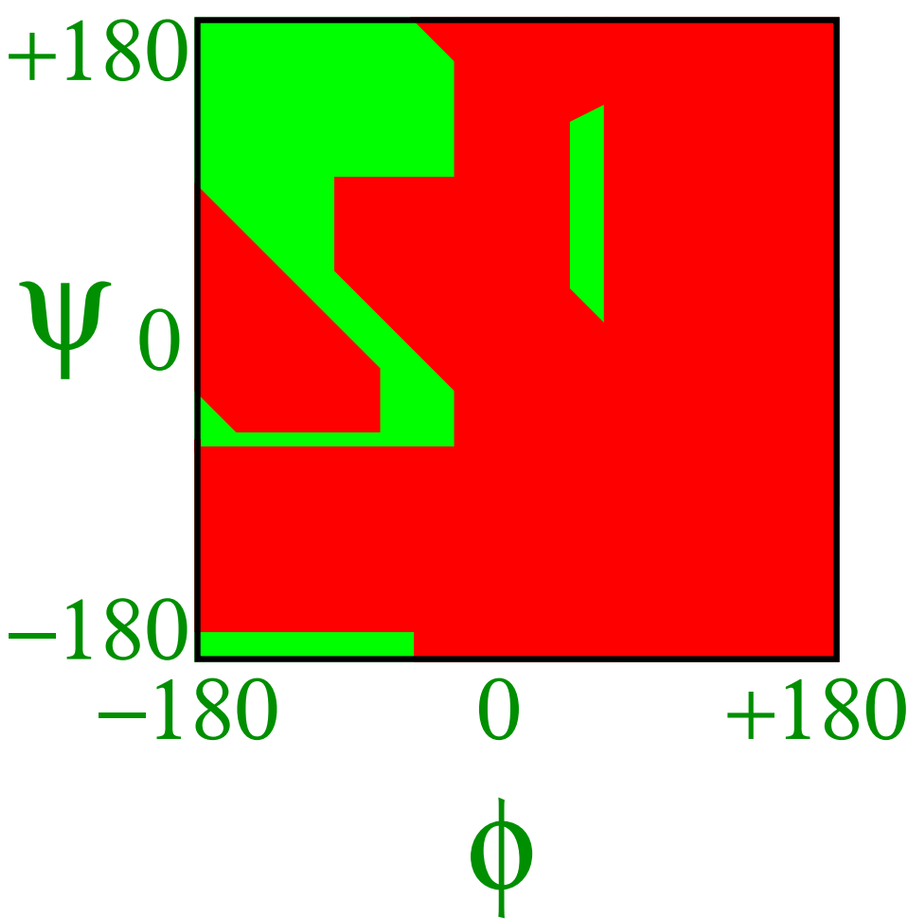


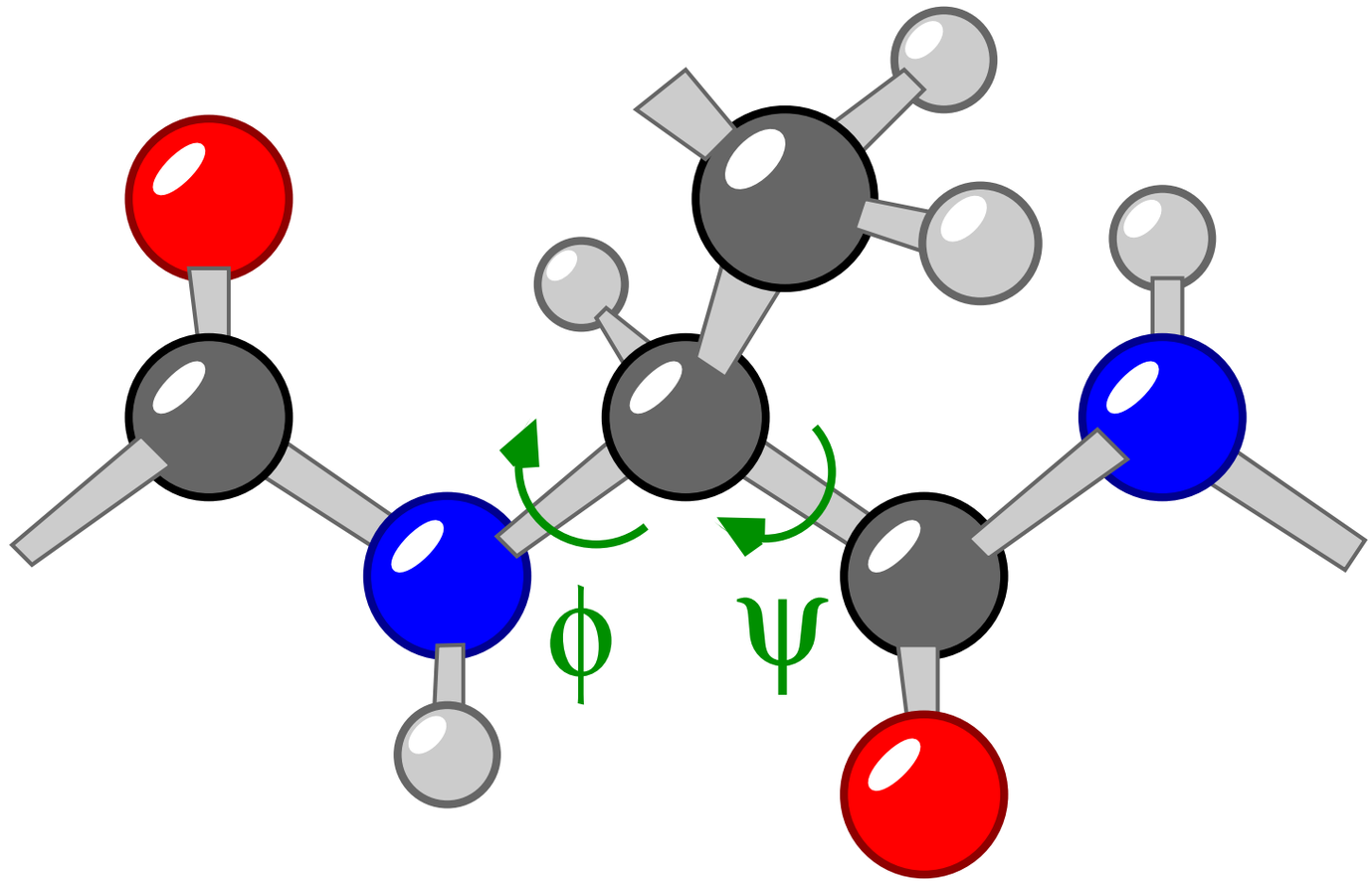
Pauliho repulze



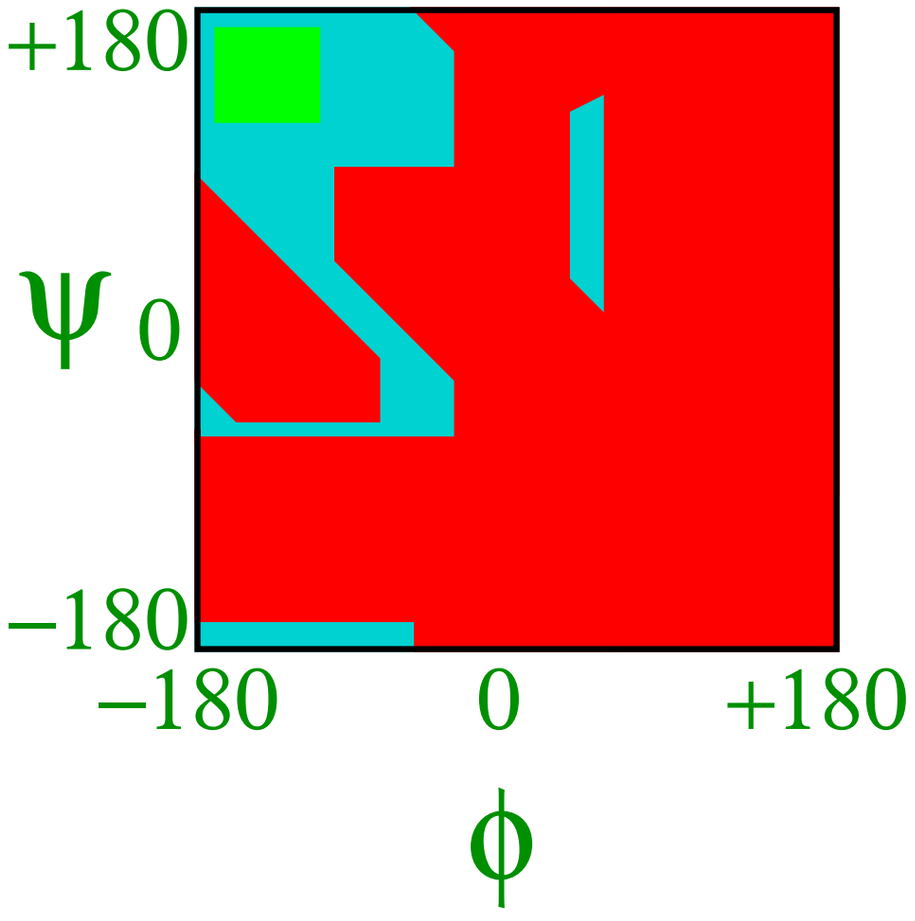


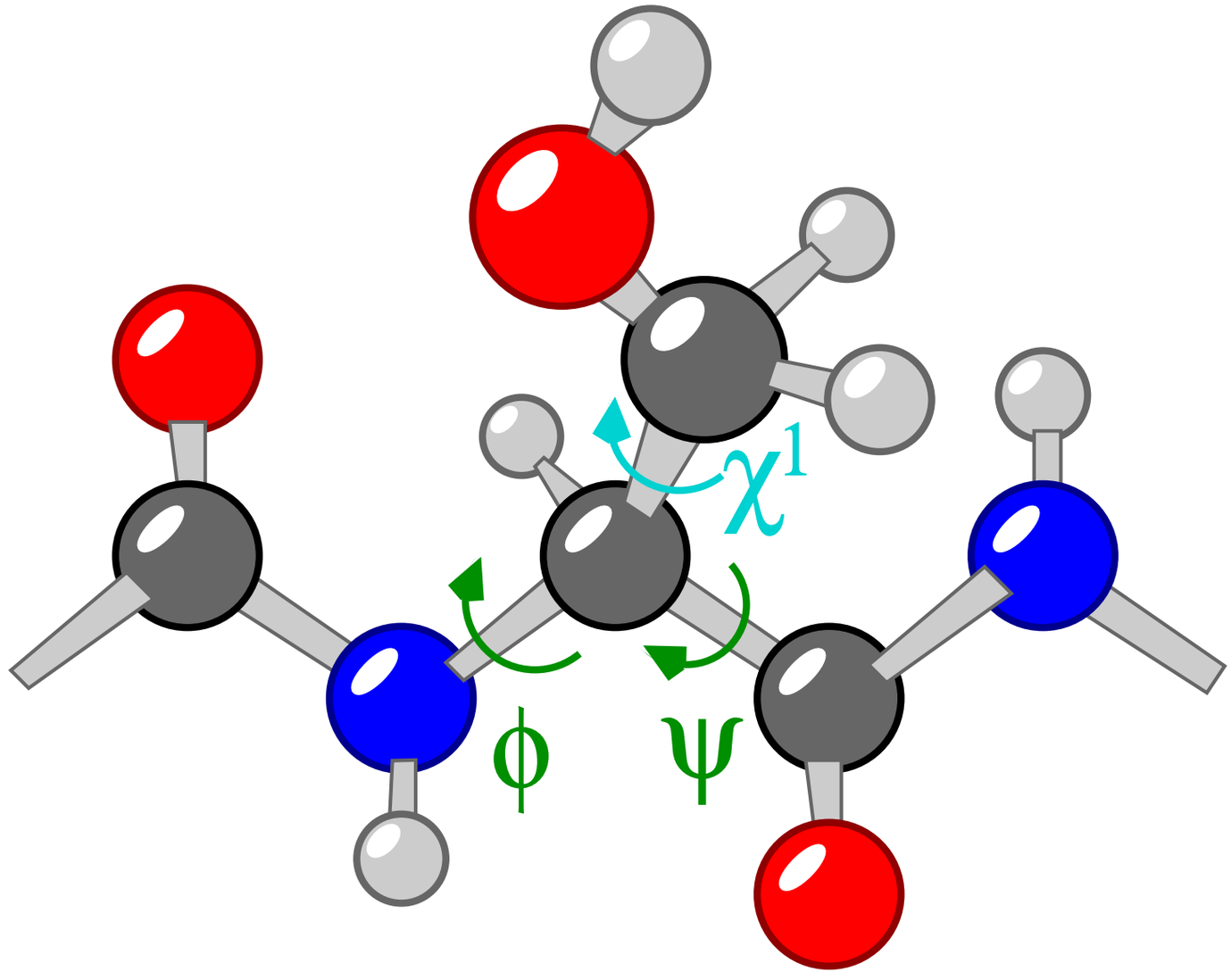
Pauliho repulze





Pauliho repulze



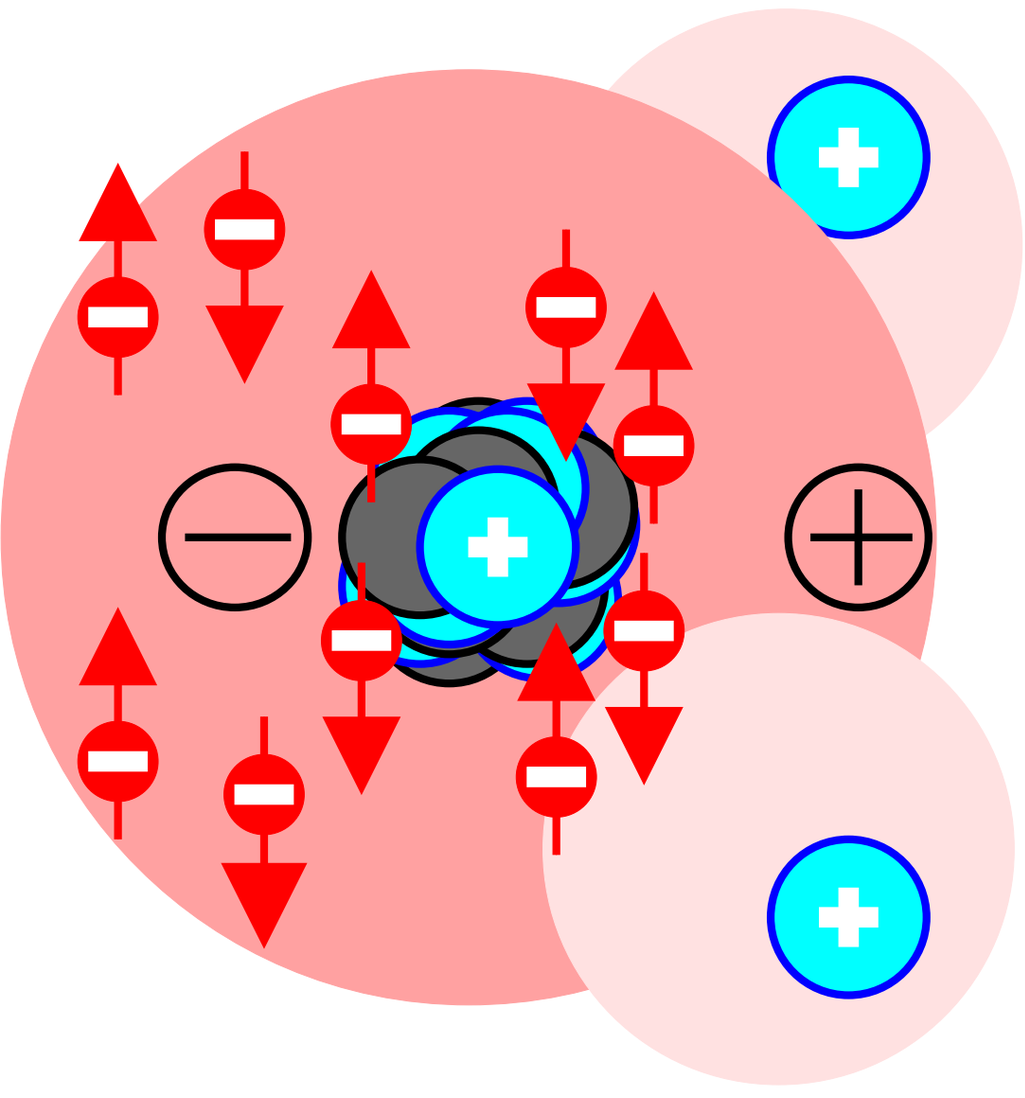


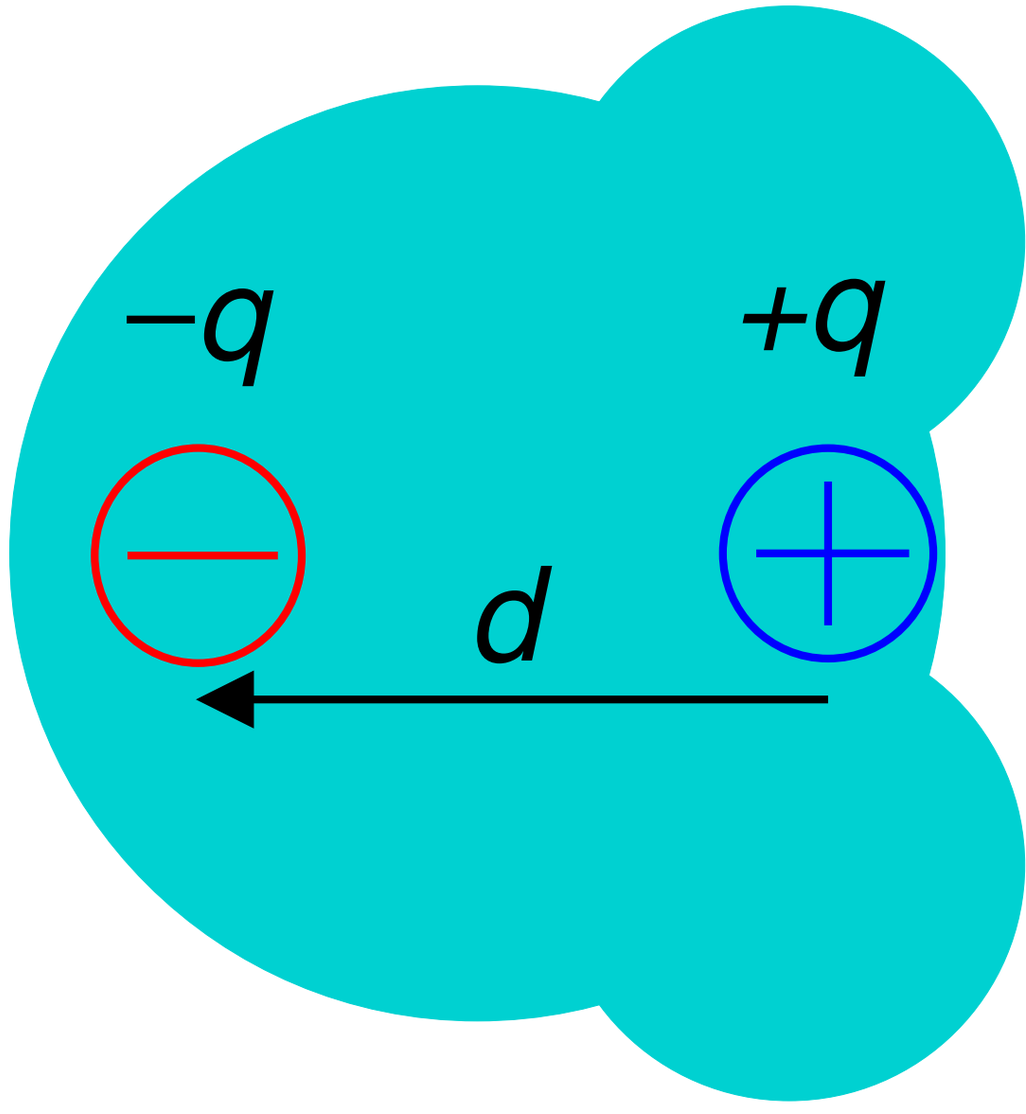
Iontová vazba

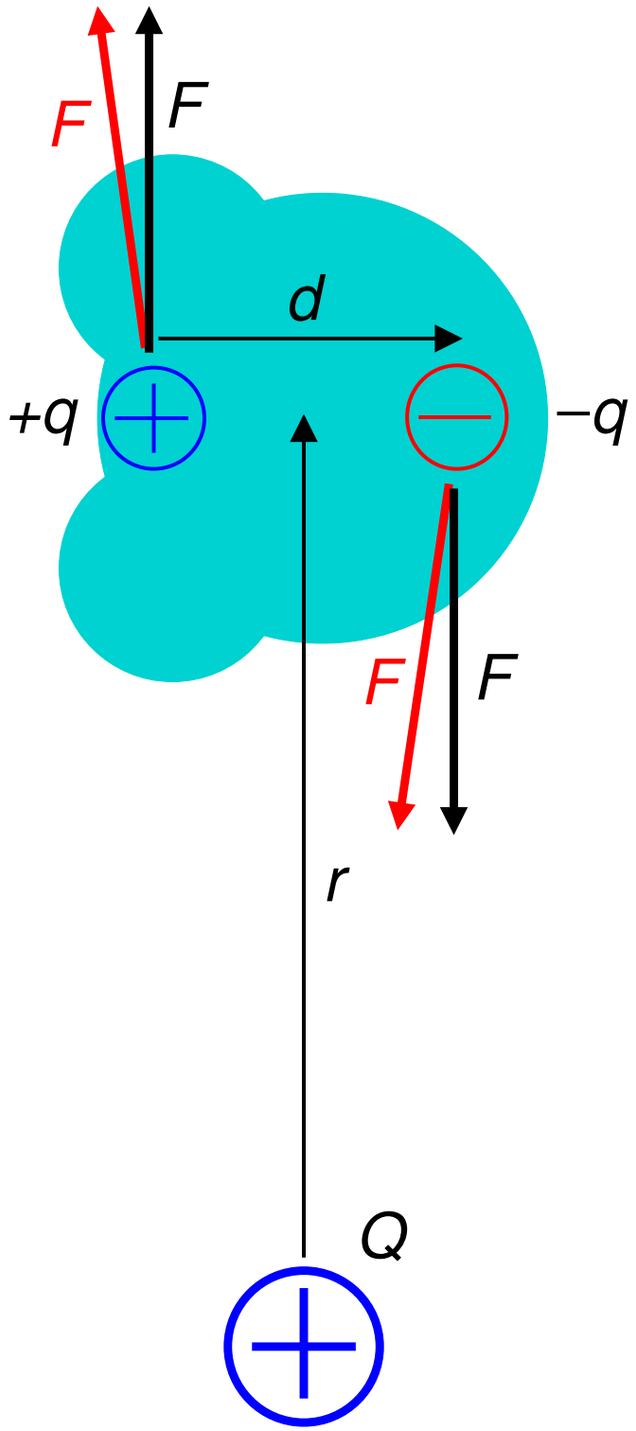
$$F = \frac{N_\mathrm{A}}{4\pi\epsilon_0}\frac{Q_1 Q_2}{r^2}$$

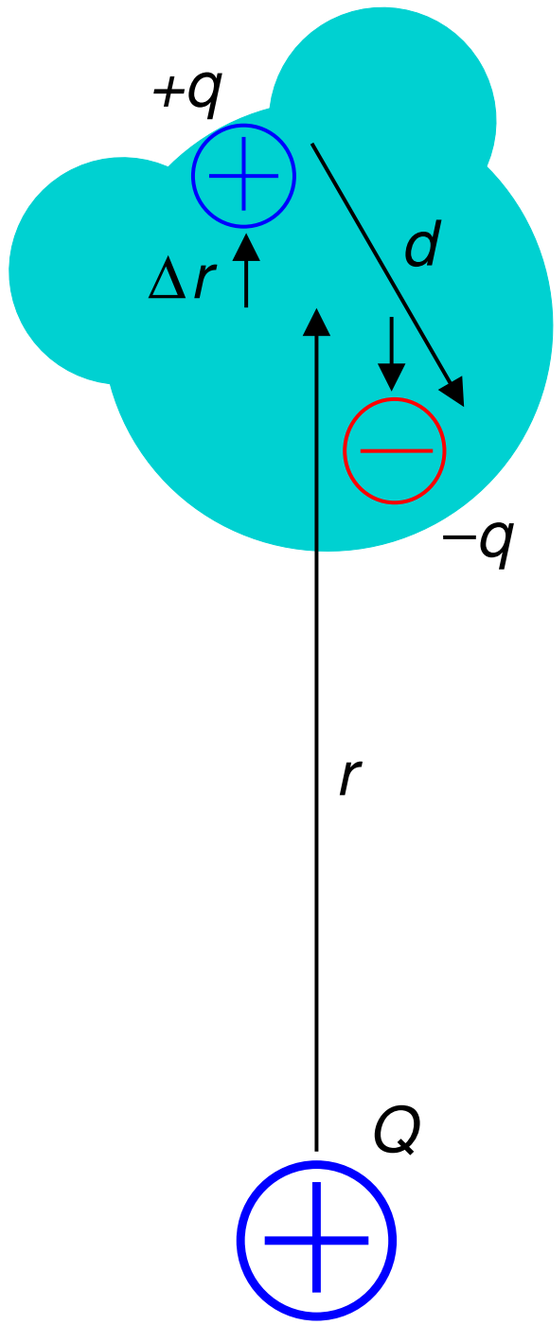
$$U = \frac{N_\mathrm{A}}{4\pi\epsilon_0}\frac{Q_1 Q_2}{r}$$

Polární molekuly

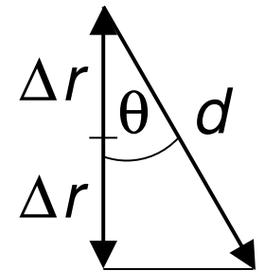








if $d \ll r$



$2\,\Delta r = d\cos\theta$

$F = F$

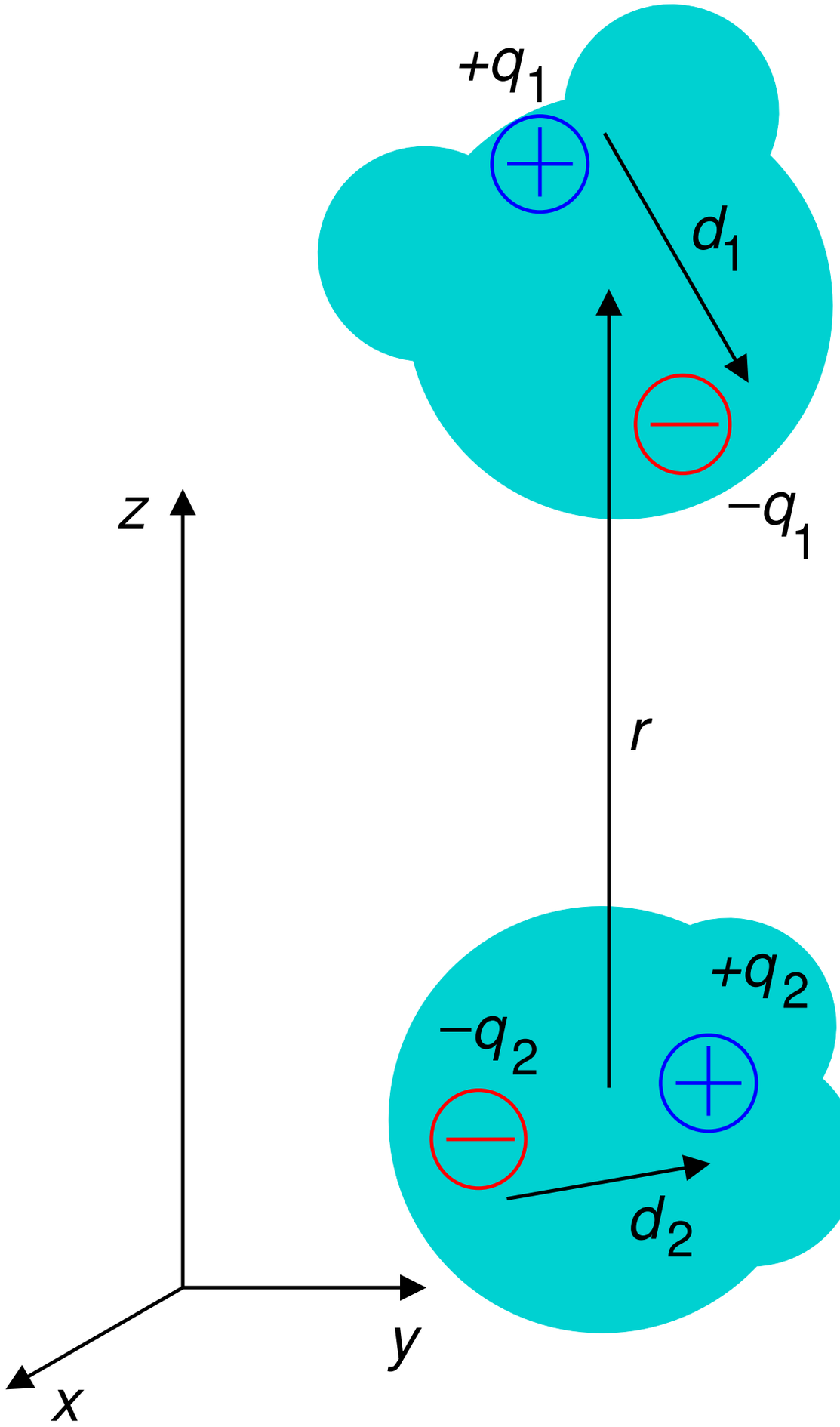
Interakce ion-dipól

ve stejné molekule:

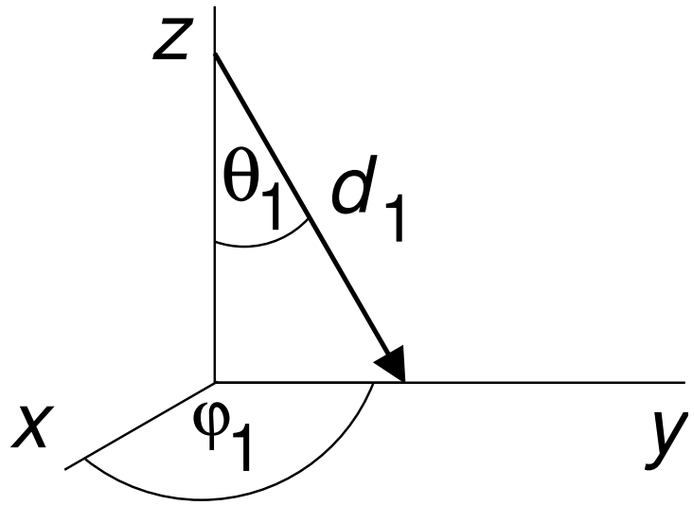
$$U = \int_{r_{\mathrm{ref}}}^{r} F \mathrm{d}r' = 2 \int_{0}^{\Delta r} F \mathrm{d}r' = -\frac{1}{4\pi\epsilon_0} \frac{qQ}{r} \frac{d}{r} \cos\theta$$

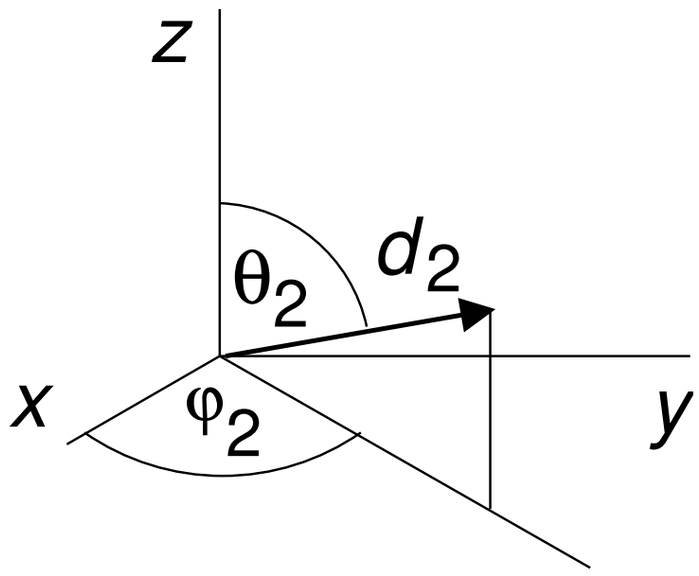
mezi dvěma molekulami

$$\langle U \rangle = -\frac{1}{3RT} \left(\frac{1}{4\pi\epsilon_0} \frac{qQ}{r} \frac{d}{r} \right)^2$$



$d_1 << r \quad d_2 << r$





Interakce dipól-dipól

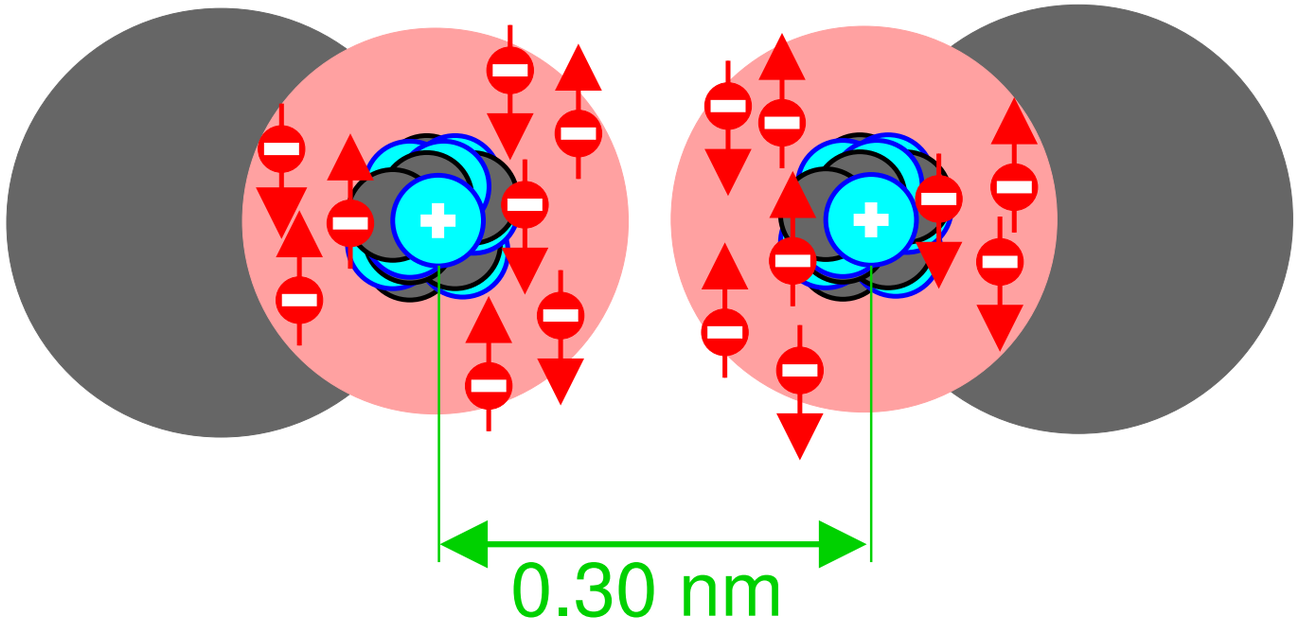
ve stejné molekule:

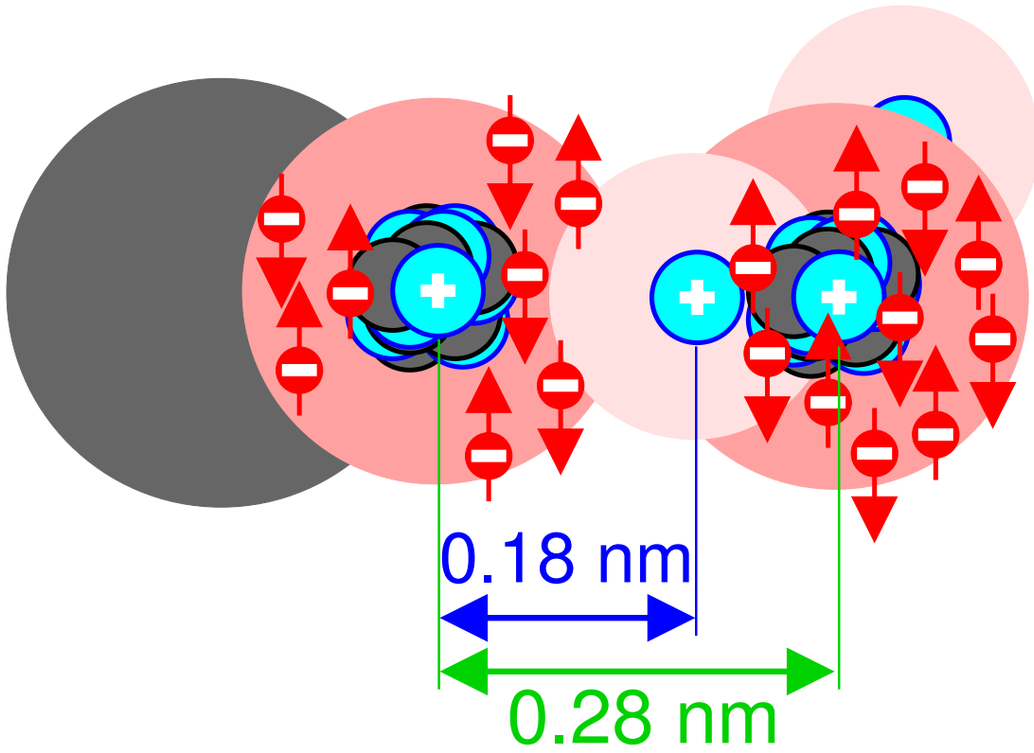
$$U = \frac{1}{4\pi\epsilon_0}\frac{q_1 q_2}{r}\frac{\vec{d_1}}{r}\frac{\vec{d_2}}{r}\left(\sin\theta_1 \sin\theta_2 \cos(\phi_1 - \phi_2) - 2\cos\theta_1 \cos\theta_2\right)$$

mezi dvěma molekulami

$$\langle U \rangle = -\frac{2}{3RT}\left(\frac{1}{4\pi\epsilon_0}\frac{q_1 q_2}{r}\frac{d_1}{r}\frac{d_2}{r}\right)^2$$

Vodíkové vazby



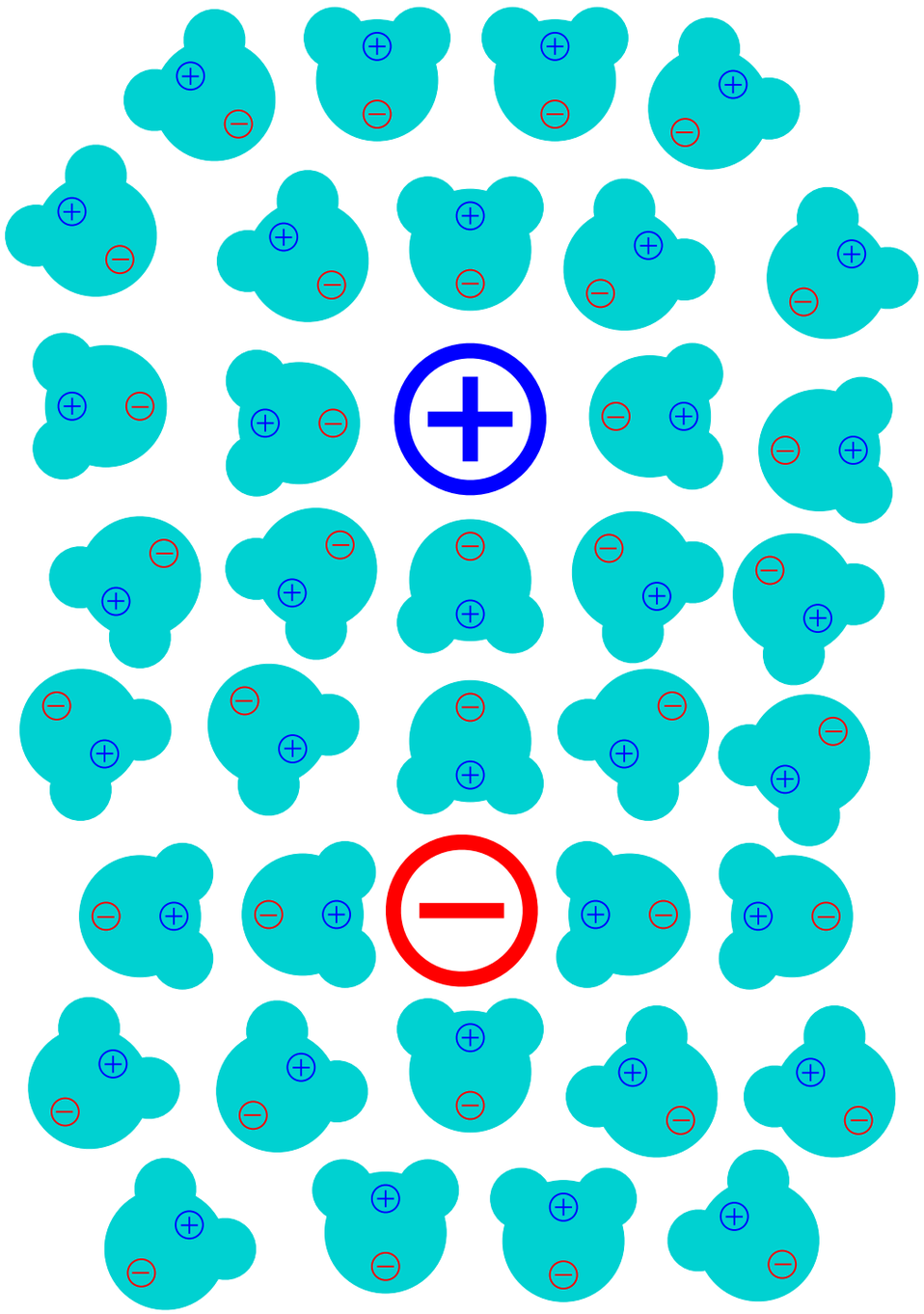


Vodíkové vazby

Atom···atom	U_{opt} / kJ mol^{-1}	r_{opt} / nm	r_{min} / nm
He···He	0.05	0.28	0.25
–H···H–	0.50	0.24	0.20
–C···C–	0.50	0.34	0.30
–N···N–	0.85	0.31	0.27
–NH···N–		0.31	
–O···O–	0.95	0.30	0.27
–OH···O–		0.28	

U(H-bond)= 20 kJ/mol

Vliv solventu (vody)



- polarizace/orientace atomů/skupin v molekule

- orientace molekul solventu

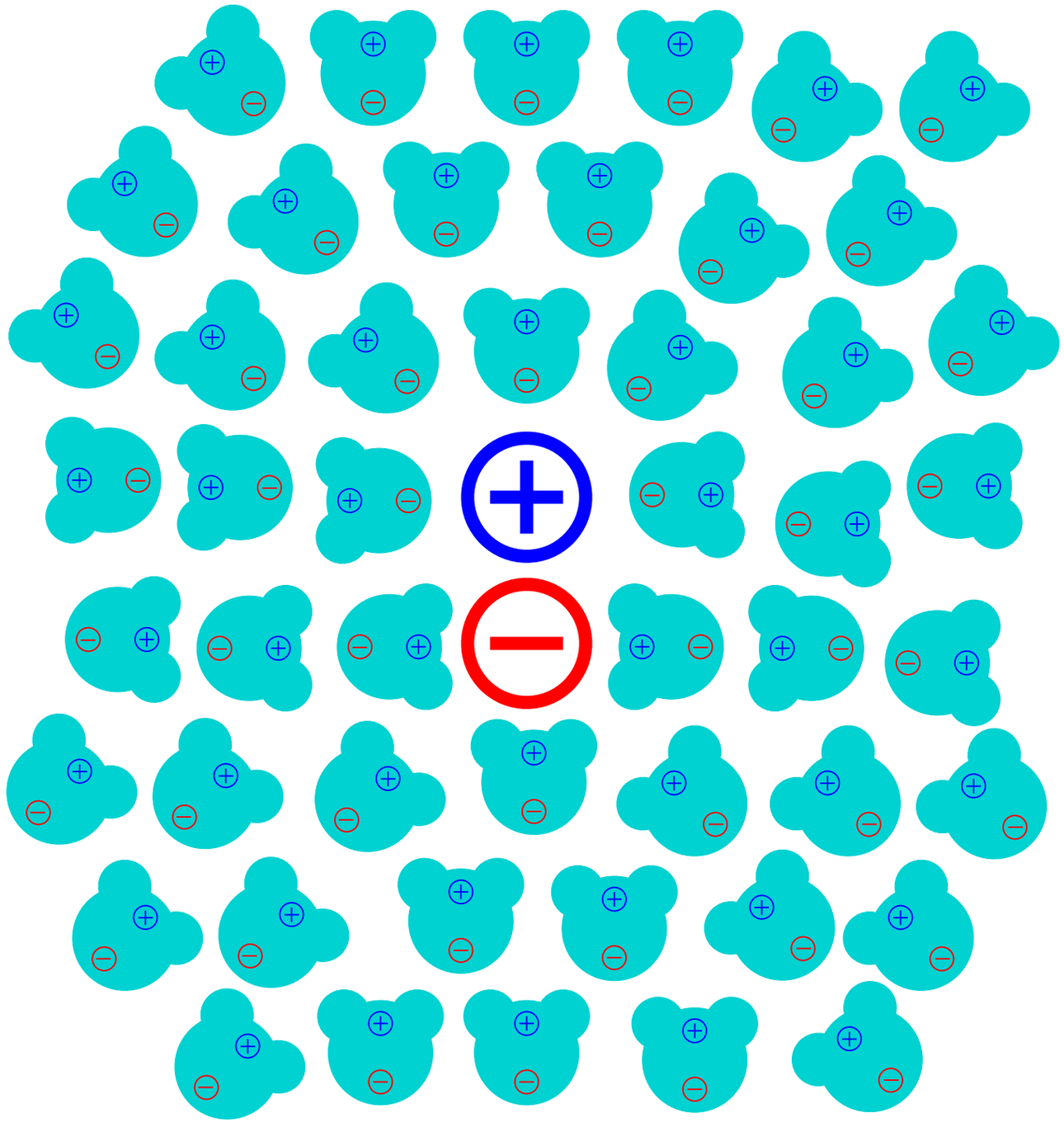
- maximální energie (entalpie) elektrostatických interakcí za cenu sníže entropie

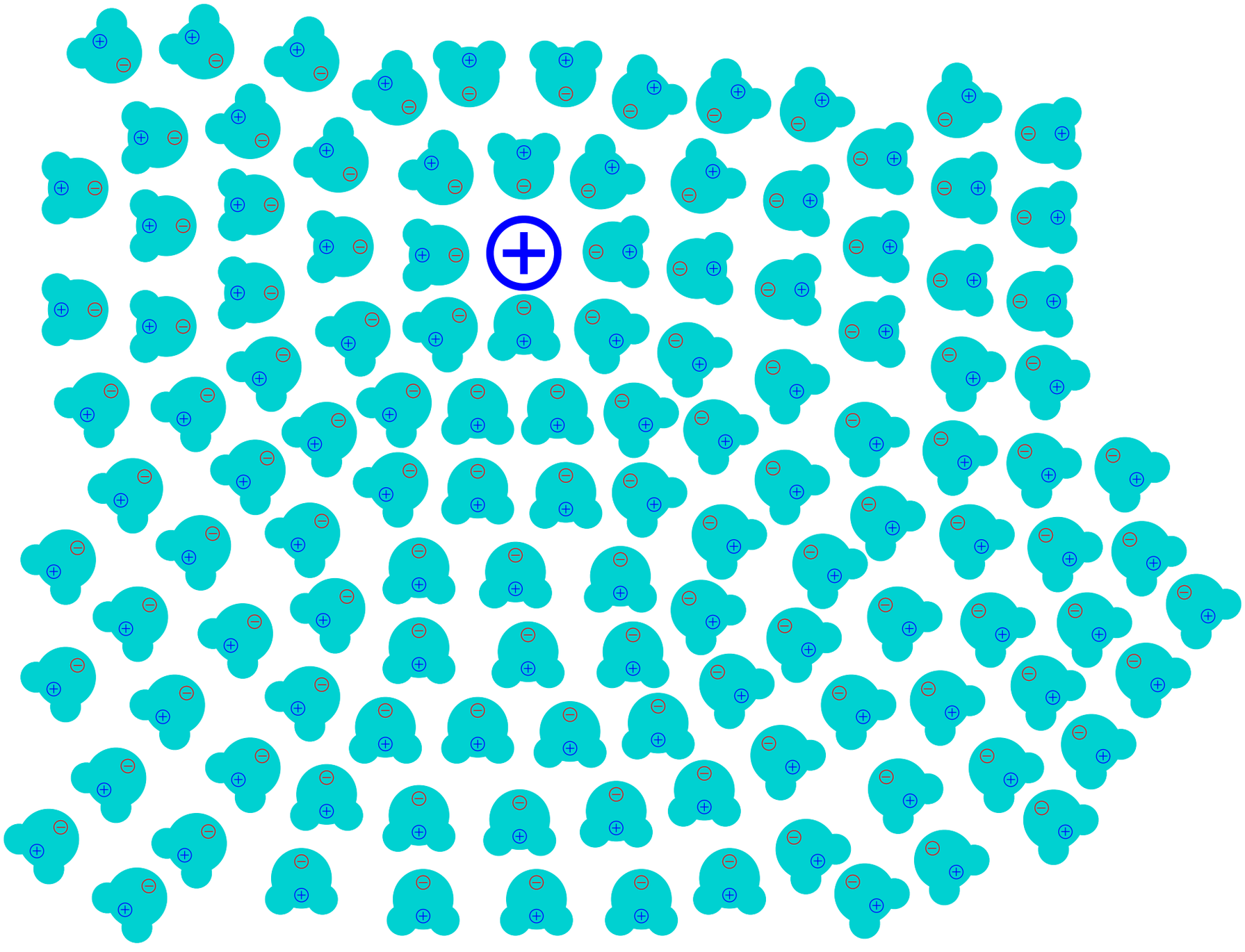
- voda netvoří electrostatickou ”bariéru”

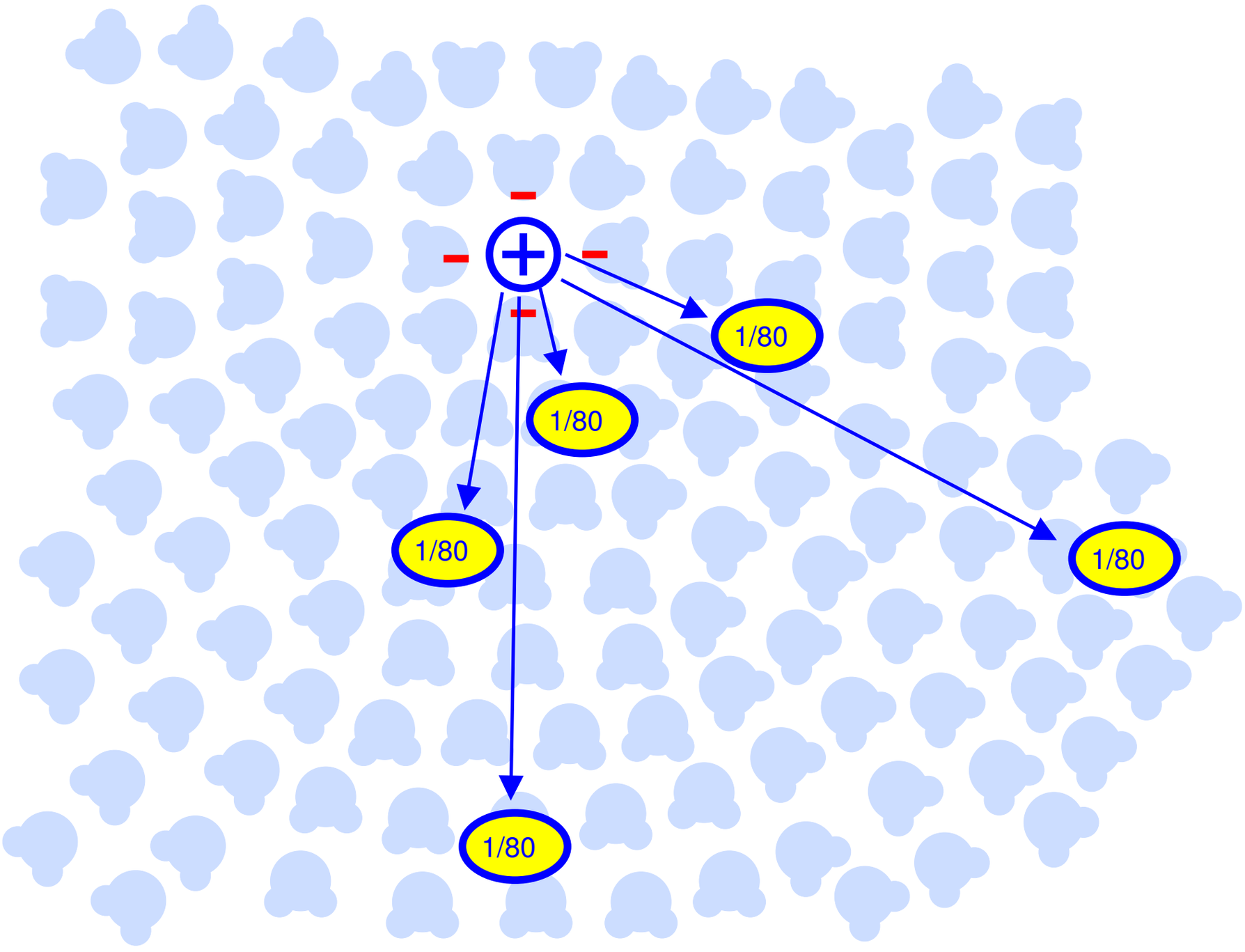
- formálně snižuje ϵ

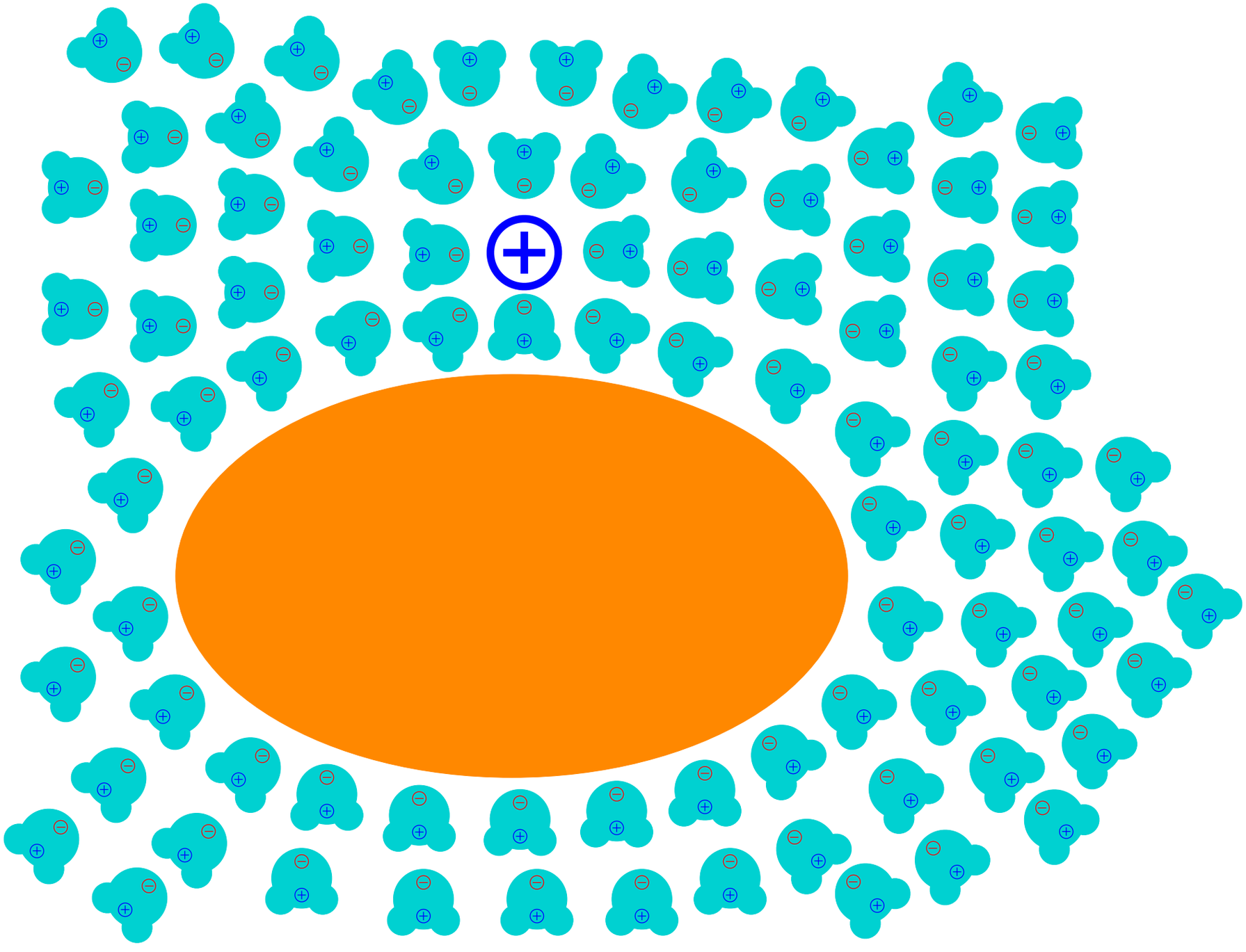
  $\Rightarrow$ increases $\epsilon_0 \rightarrow \epsilon_r\epsilon_0$

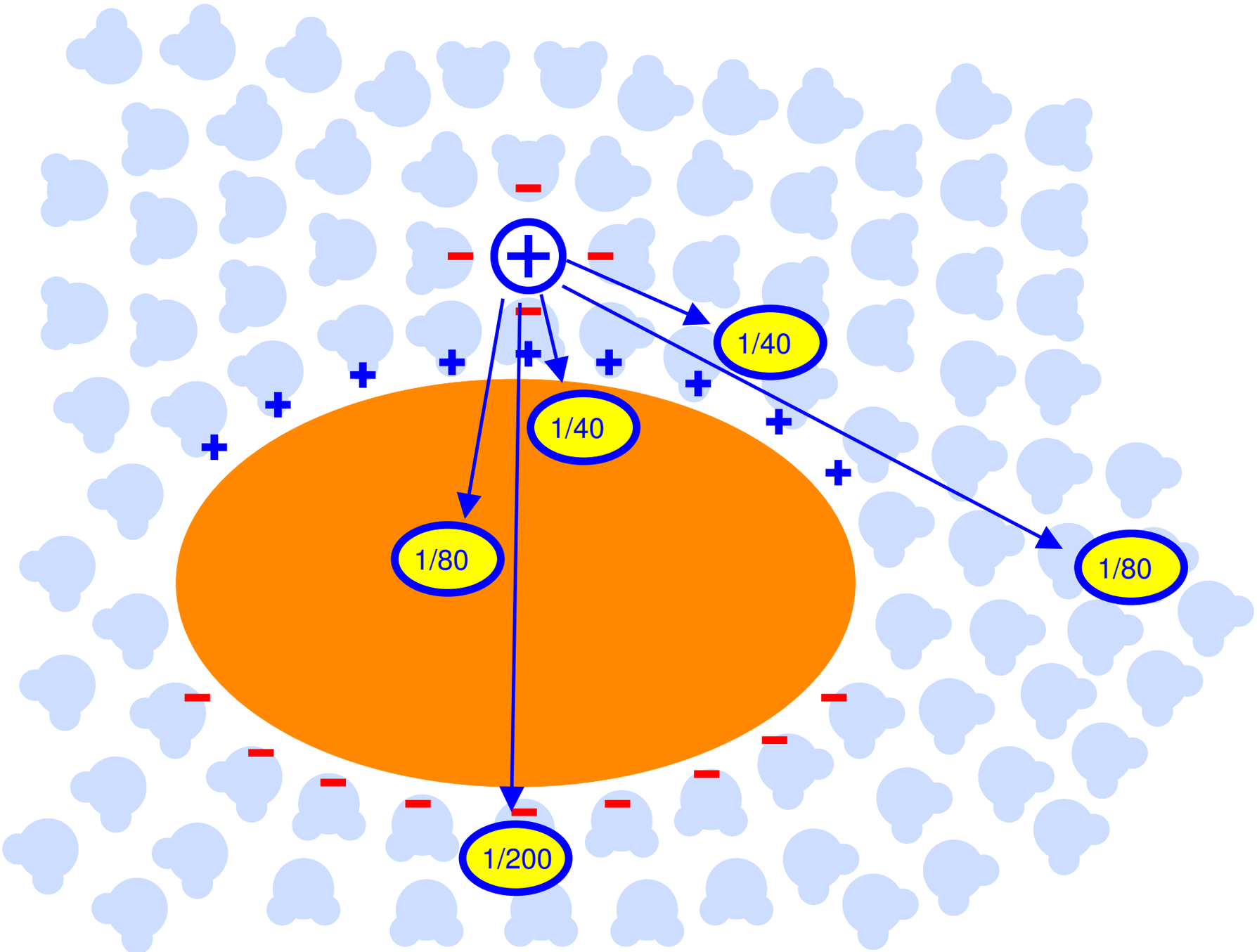
$$F = \frac{1}{4\pi\epsilon_r\epsilon_0}\frac{Q_1Q_2}{r^2}$$

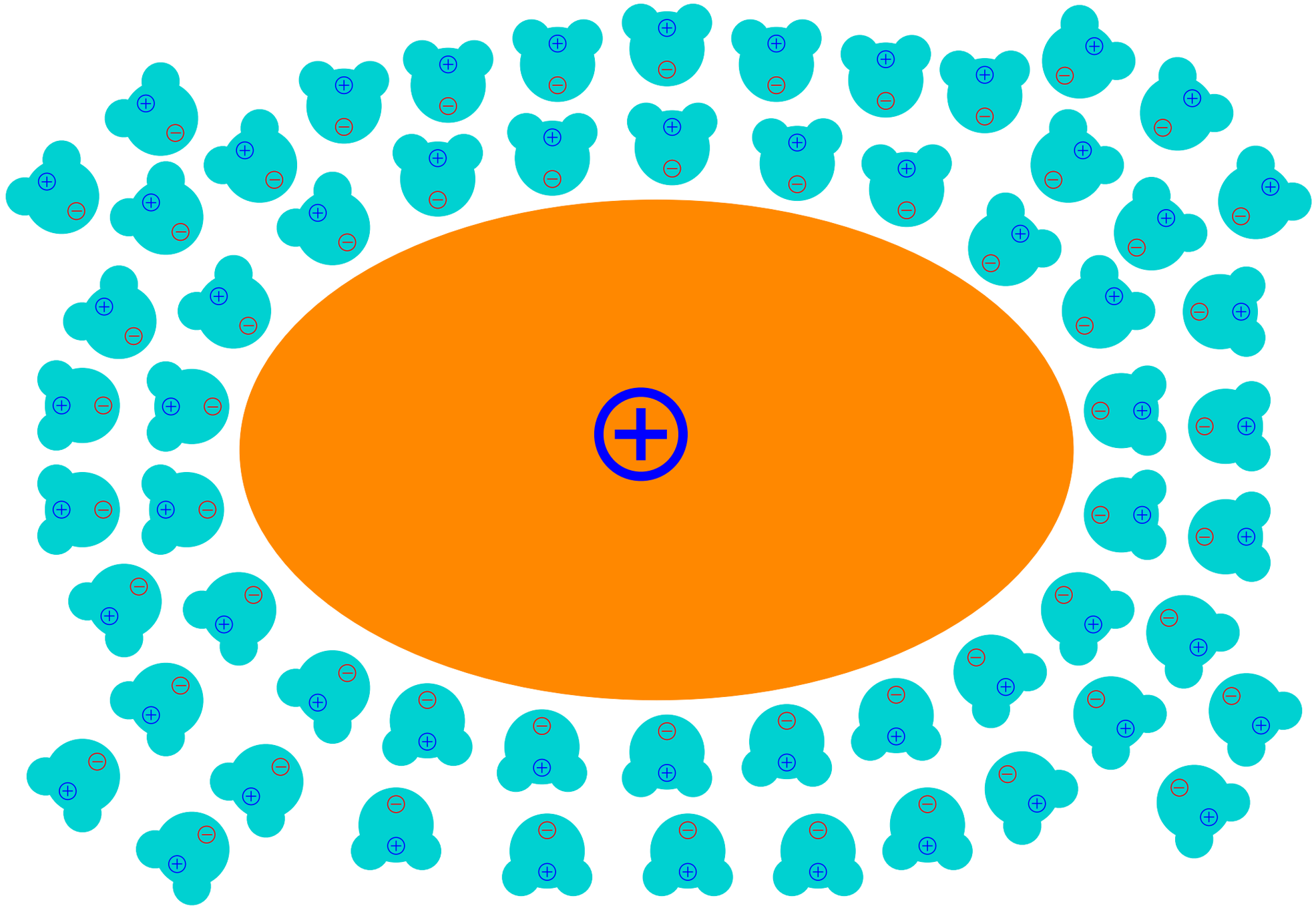


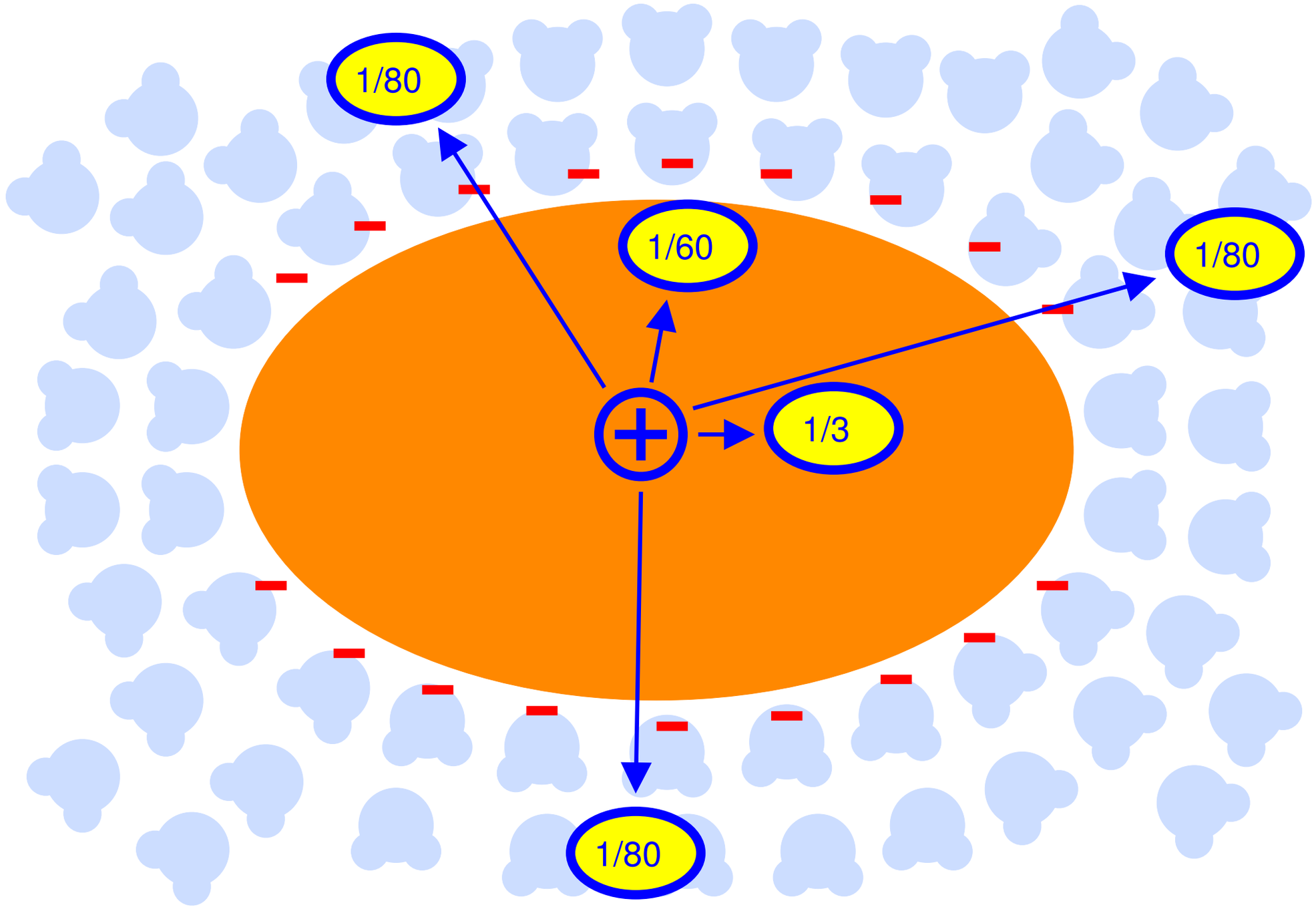


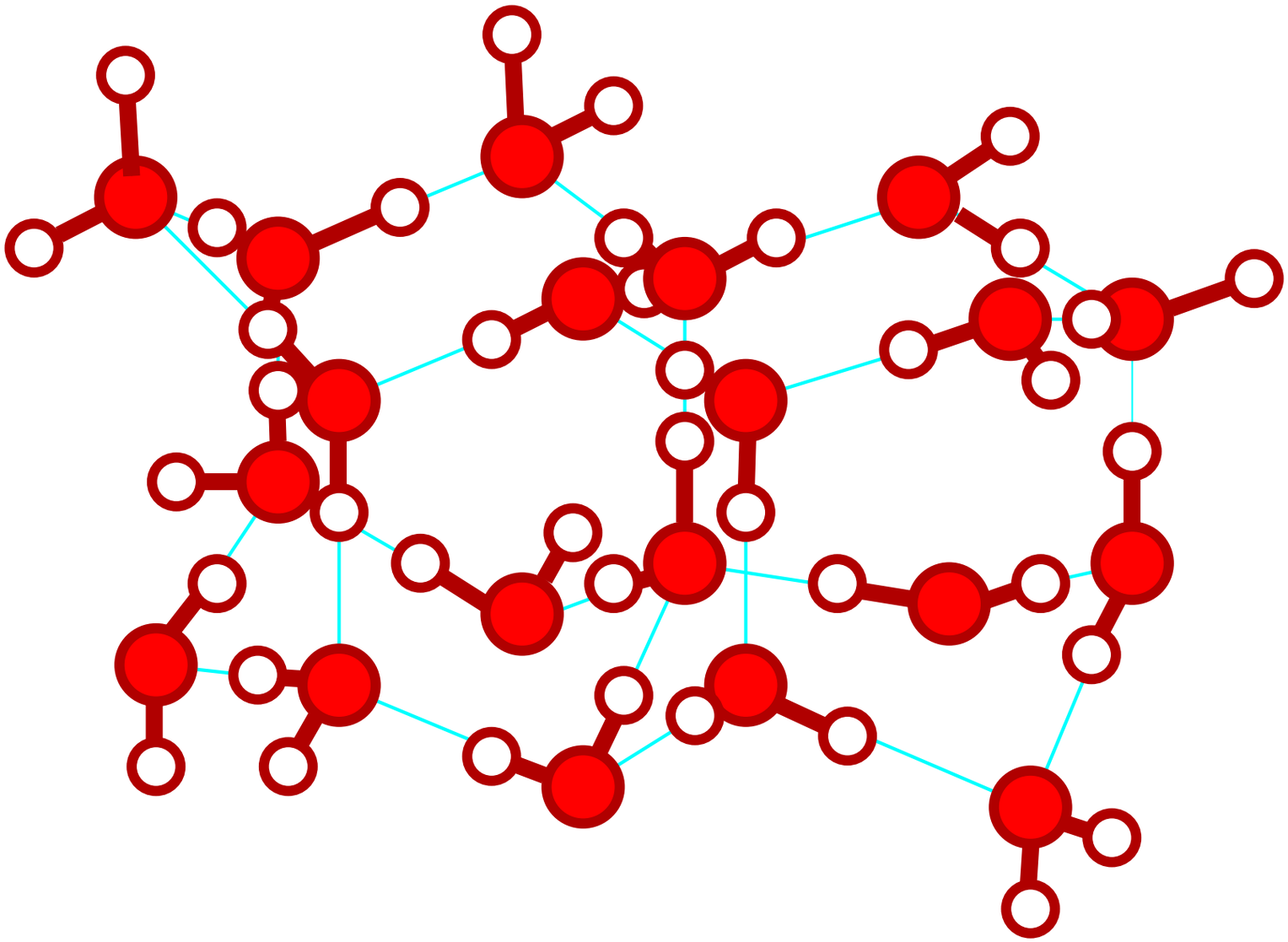

1/80
1/80
1/80
1/80
1/80



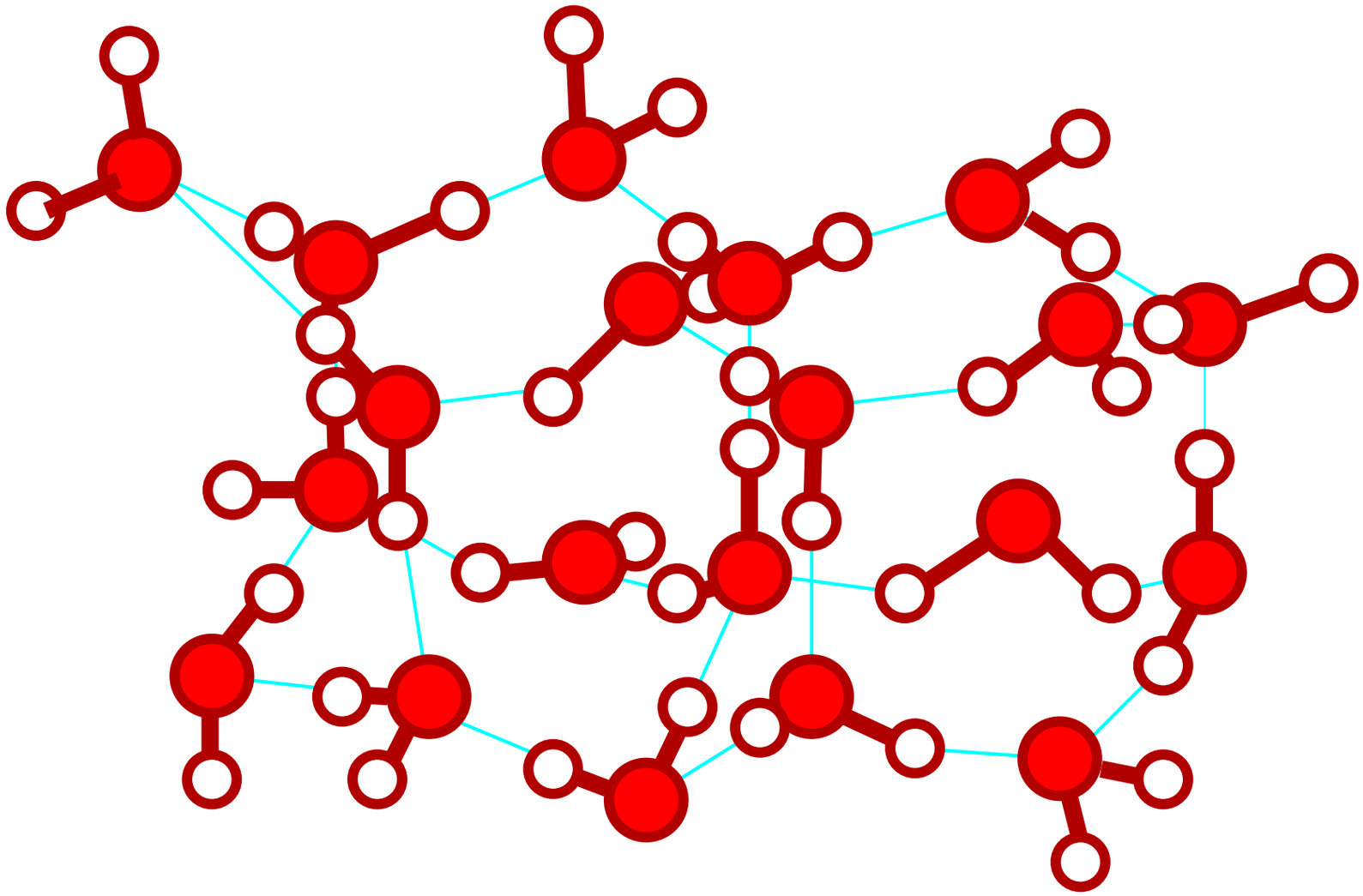

1/40
1/40
1/80
1/80
1/200



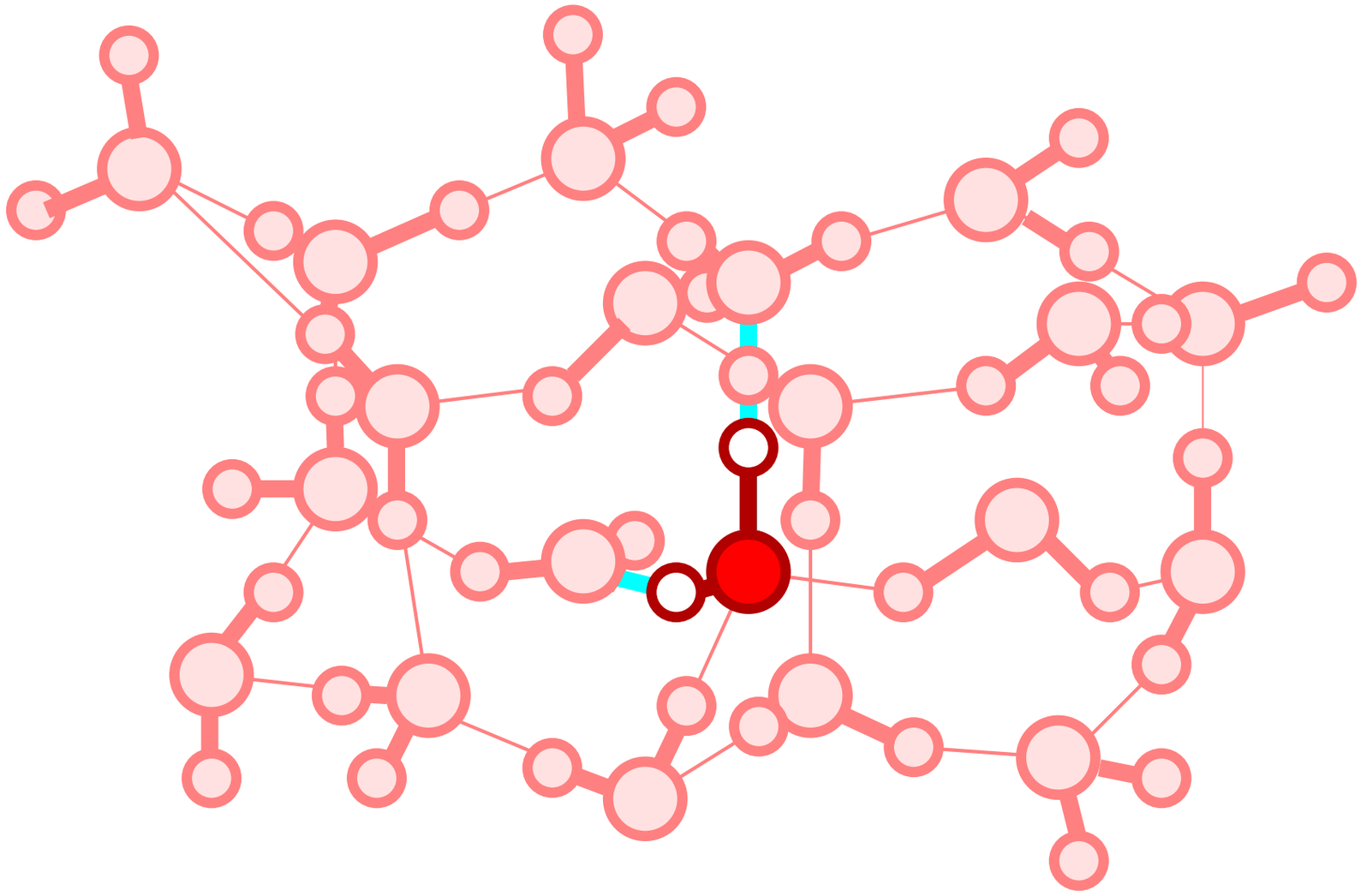

1/80
1/60
1/80
1/3
1/80



H-vazby: 50 kJ/mol



H-vazby: 40 kJ/mol



$\Delta G = 0$

cyklohexan:

0.1 MPa plyn

ΔH = – 30 kJ/mol
$T\Delta S$ = – 12 kJ/mol
ΔG = – 18 kJ/mol

entalpie

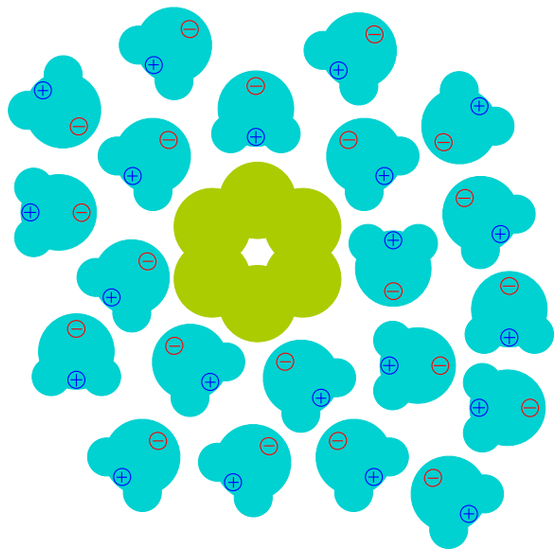
entropie

ΔH = – 30 kJ/mol
$T\Delta S$ = – 40 kJ/mol
ΔG = + 10 kJ/mol

kapalina

ΔH = 0 kJ/mol
$T\Delta S$ = – 28 kJ/mol
ΔG = + 28 kJ/mol

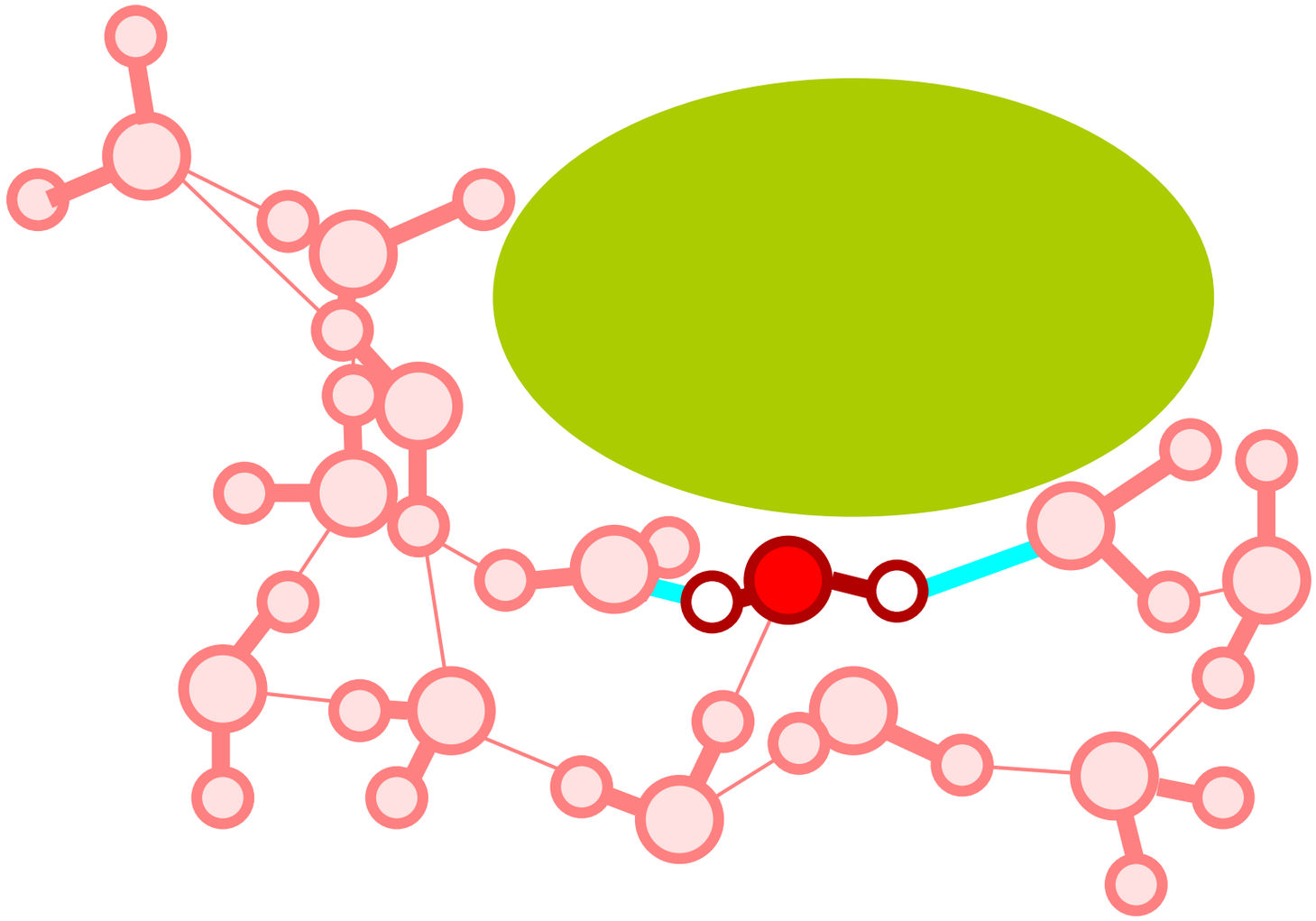
entropie



1M roztok

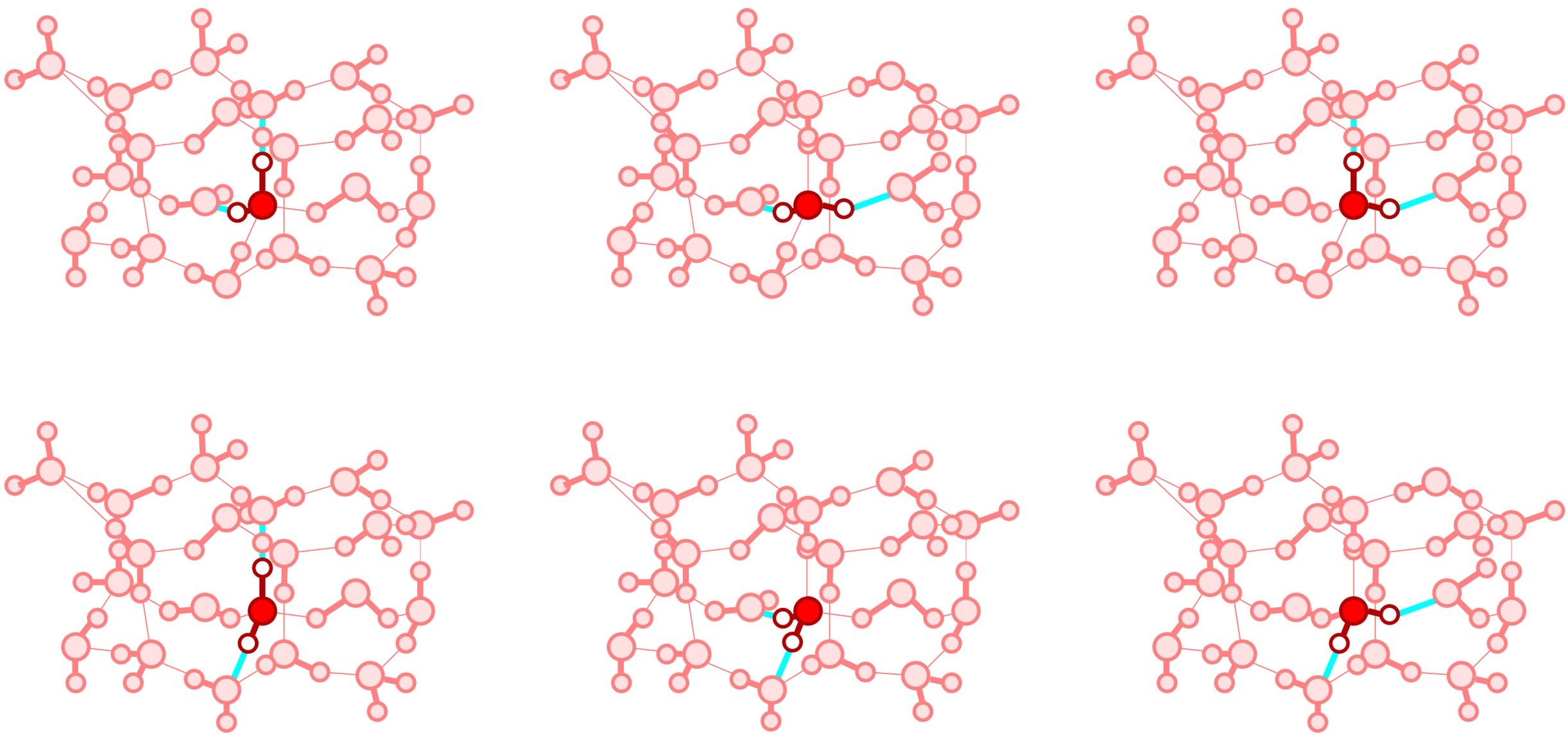
- orientace molekul solventu (vody)

- maximální energie (entalpie) H-vazeb za cenu snížení entropie



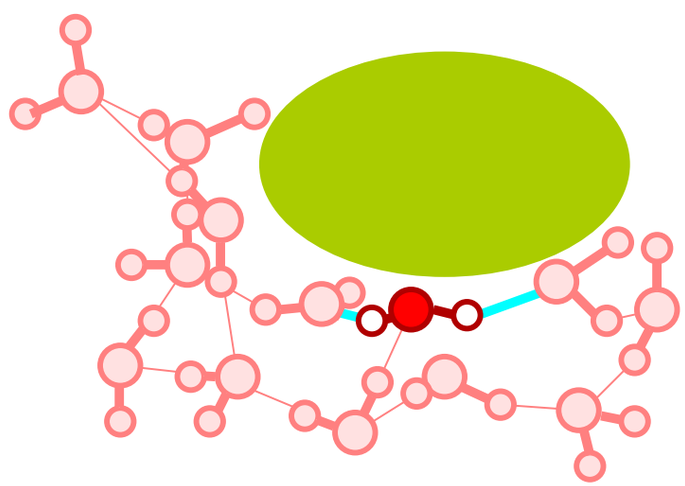
6 možných orientací

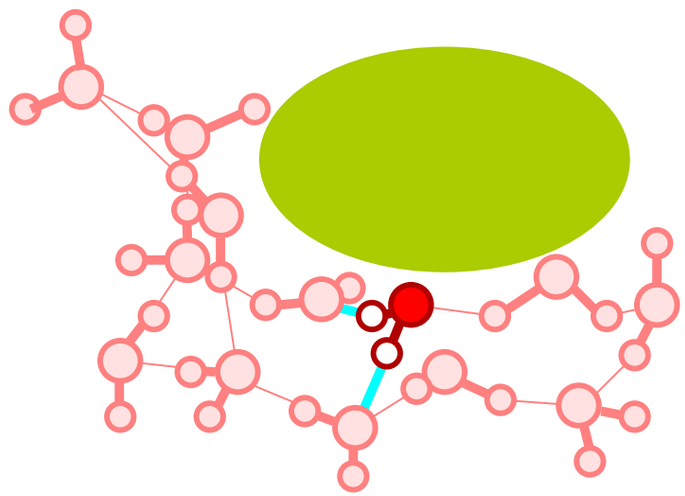
entropický příspěvek $-RT \ln 6 = -15\,\mathrm{kJ/mol}$

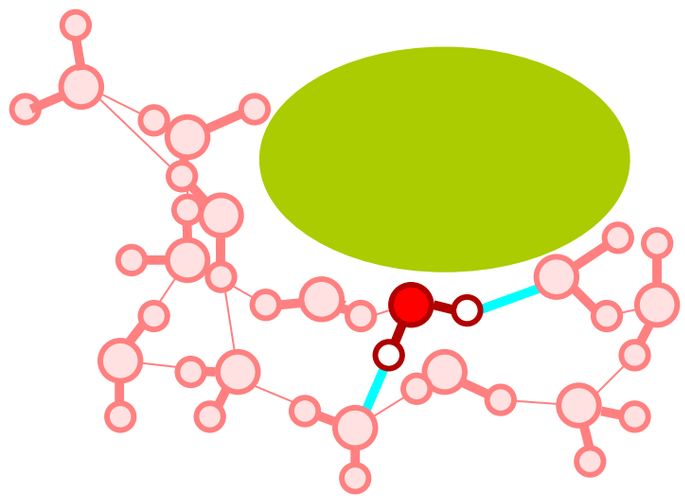


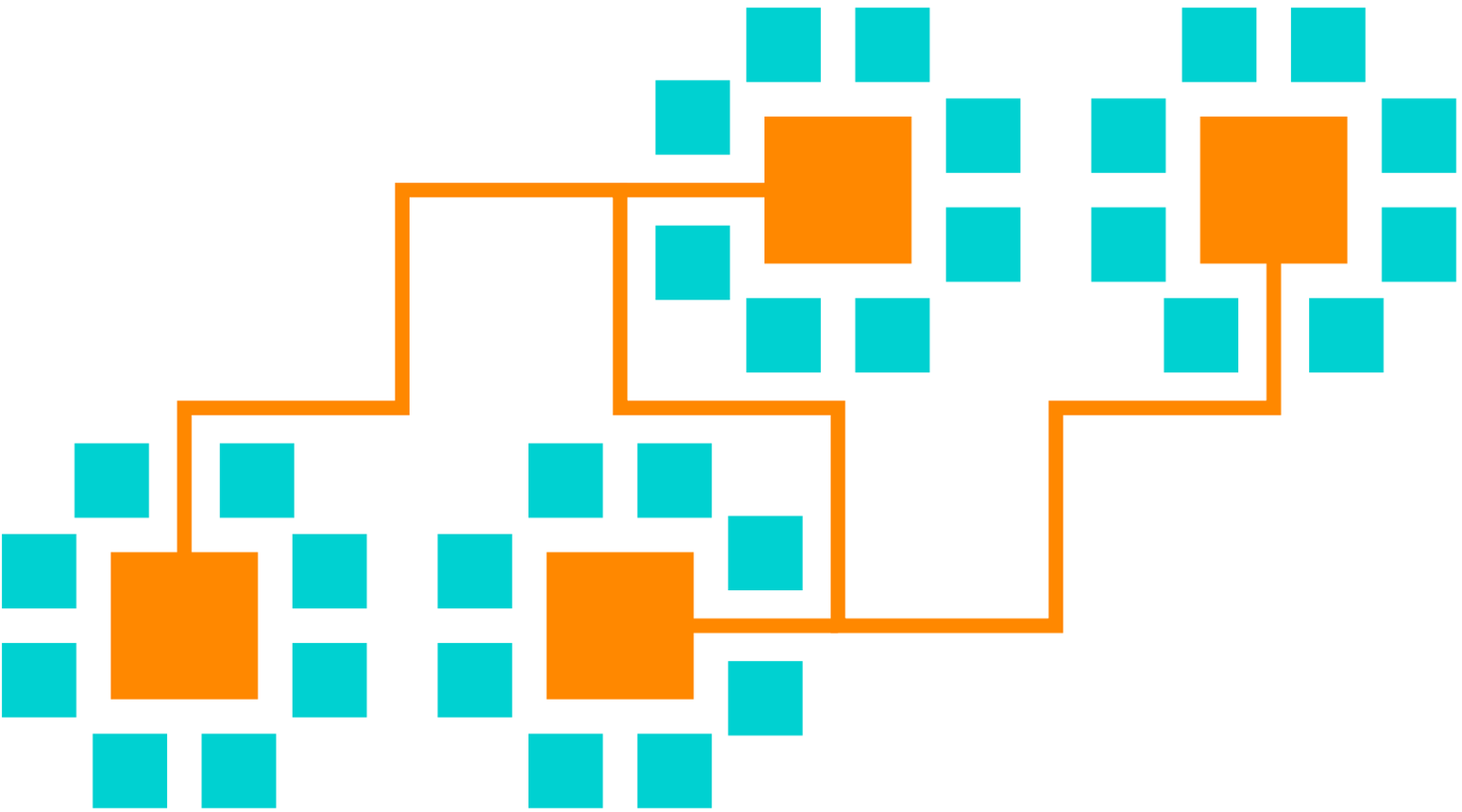
3 možné orientace

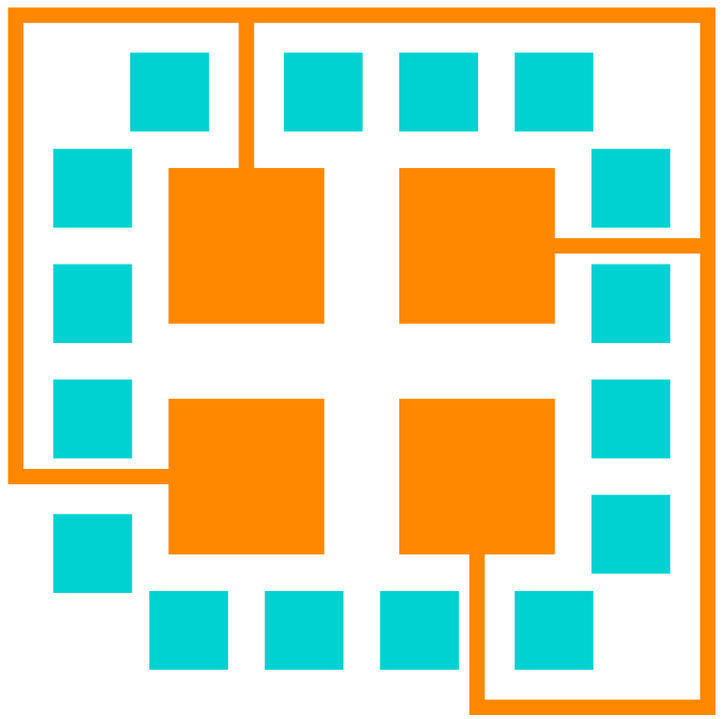
entropický příspěvek $-RT \ln 3 = -7{,}5\,\mathrm{kJ/mol}$











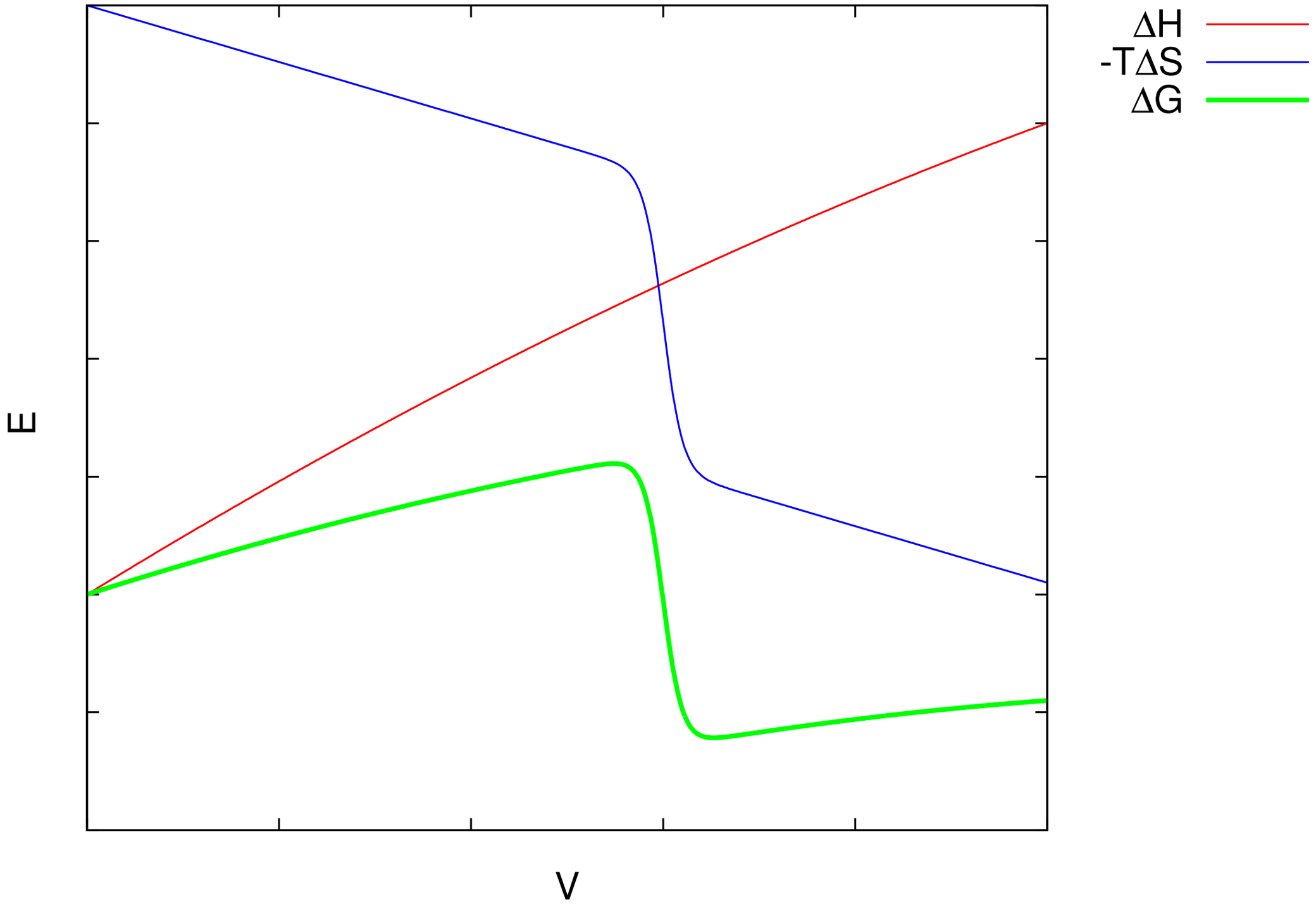
shluknutí nepolárních postranních řetězců snižuje entropii

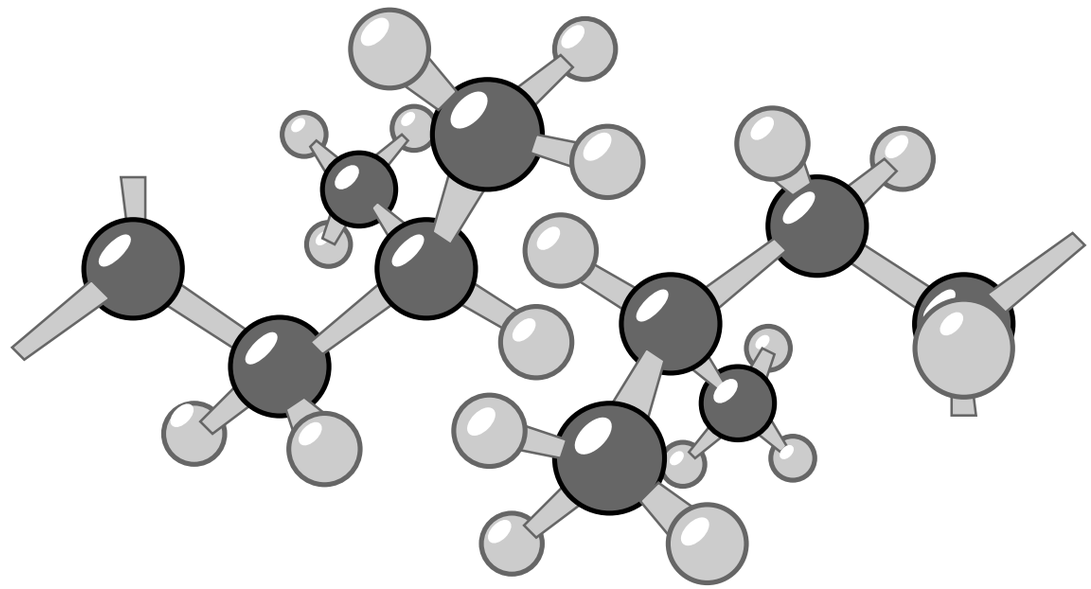
(méně molekul vody s omezenou orientací)

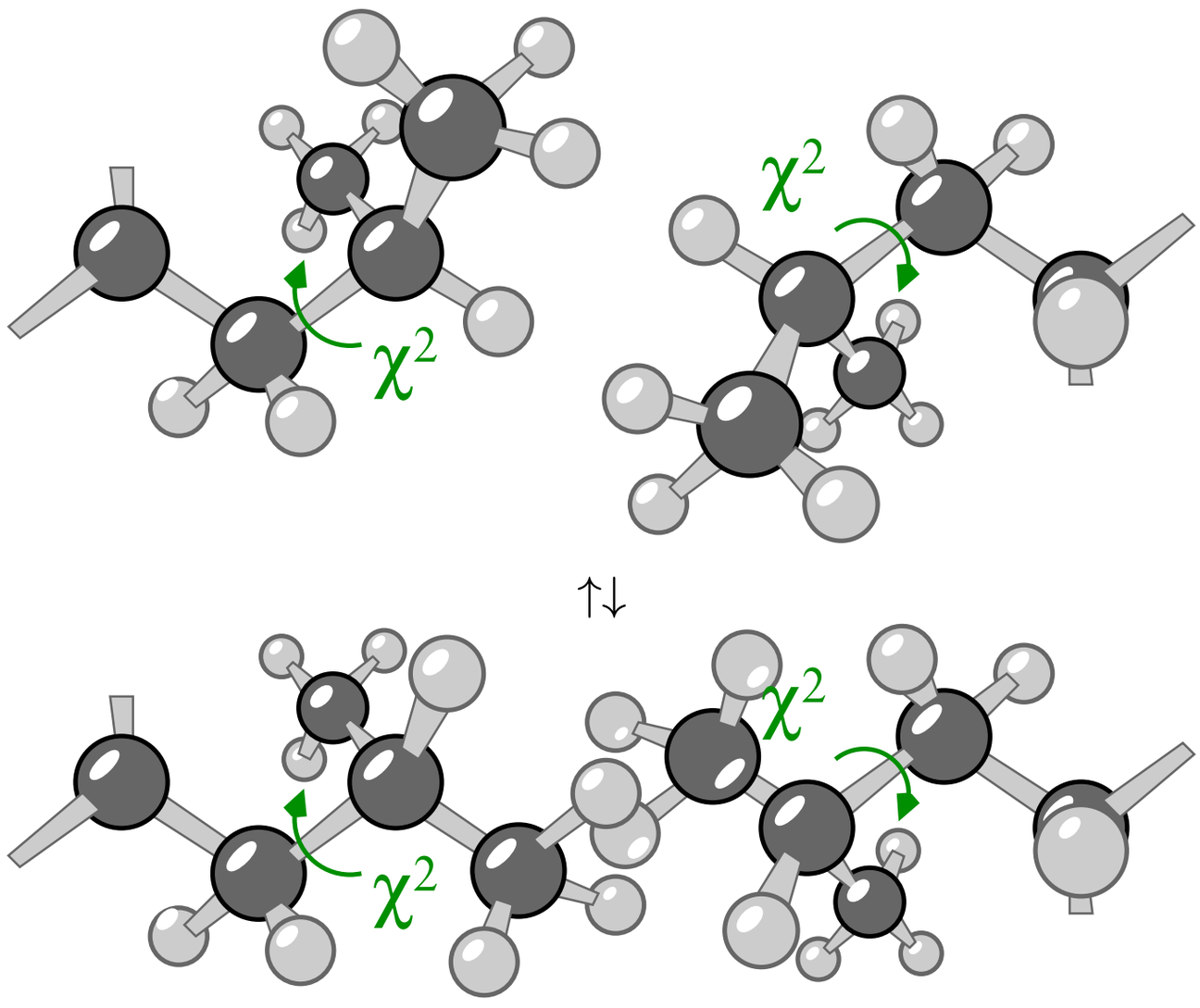
nejdůležitější příspěvek k $-\Delta G$

Ala: 2.5 kJ/mol, Leu: 8 kJ/mol, Phe: 12 kJ/mol

nespecificiký


ΔH
-TΔS
ΔG
E
V




χ2
χ2
↑↓
χ2
χ2

Typ	kJ/mol	podmínky
RT	2,5	at 300 K (27 °C)
kovalentní vazba	350	C–C
ion-ion	460	vzdáleny 0,3 nm ve vakuu
ion-ion	150	vzdáleny 0,3 nm uvnitř proteinu
ion-ion	12	vzdáleny 0,3 nm na povrchu proteinu
dipol-dipol	30	vzdáleny 0,3 nm ve vakuu
dipol-dipol	10	vzdáleny 0,3 nm uvnitř proteinu
ion-dipol	41	vzdáleny 0,5 nm ve vakuu
ion-dipol	14	vzdáleny 0,5 nm uvnitř proteinu
H-vazba	20	ve vakuu ($\Delta G \approx \Delta H$)
H-vazba	6	ve vodě ($\Delta G \approx -T\Delta S$)
hydrofobní efekt	8	na Leu
hydrofobní efekt	12	na Phe