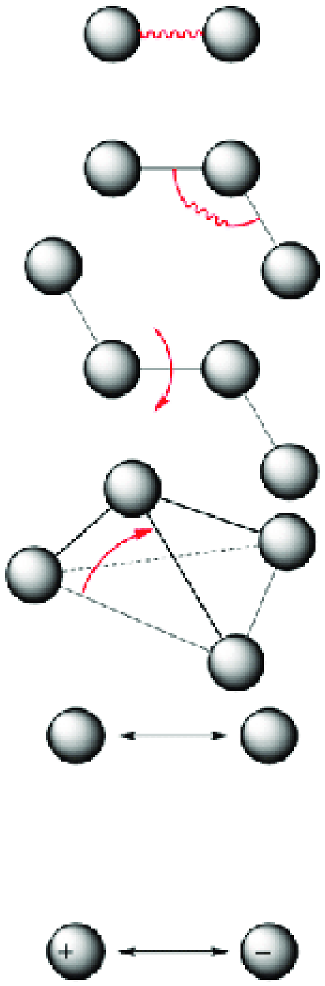
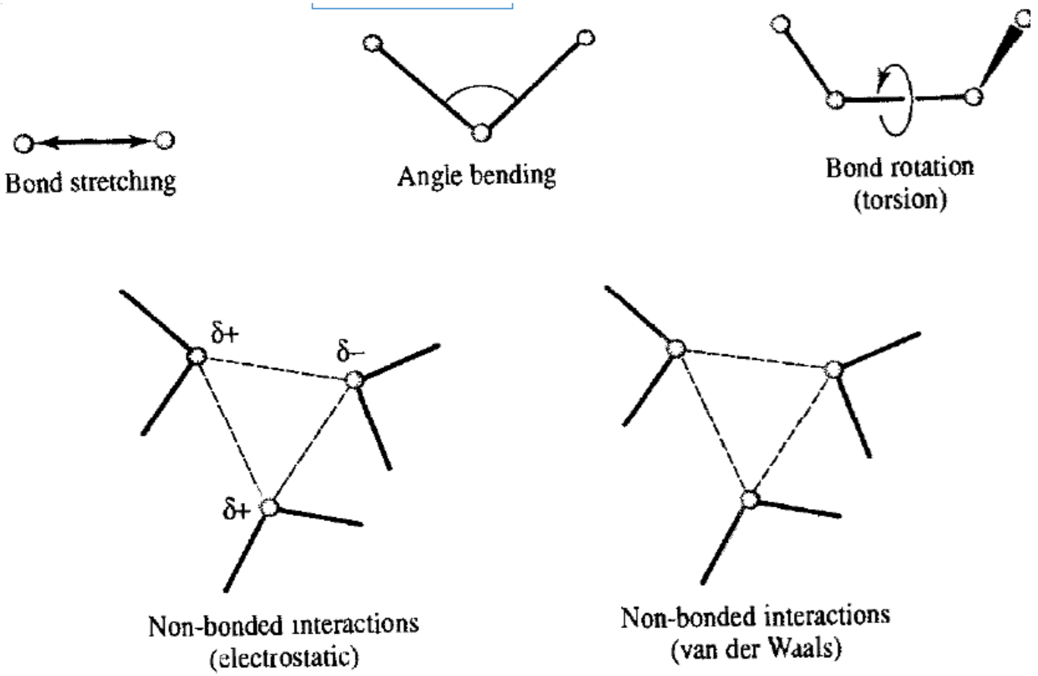
Lecture 6: Empirical Force Field Models

Force Field

$$
\begin{aligned}
U(R) &= \sum_{bonds} k_r \left(r - r_{eq}\right)^2 && \textit{bond} \\
&+ \sum_{angles} k_\theta \left(\theta - \theta_{eq}\right)^2 && \textit{angle} \\
&+ \sum_{dihedrals} k_\phi \left(1 + \cos\left[n\phi - \gamma\right]\right) && \textit{dihedral} \\
&+ \sum_{impropers} k_\omega \left(\omega - \omega_{eq}\right)^2 && \textit{improper} \\
&+ \sum_{i<j}^{atoms} \varepsilon_{ij} \left[\left(\frac{r_m}{r_{ij}}\right)^{12} - 2\left(\frac{r_m}{r_{ij}}\right)^{6} \right] && \textit{van der Waals} \\
&+ \sum_{i<j}^{atoms} \frac{q_i q_j}{4\pi\varepsilon_0 r_{ij}} && \textit{electrostatic}
\end{aligned}
$$

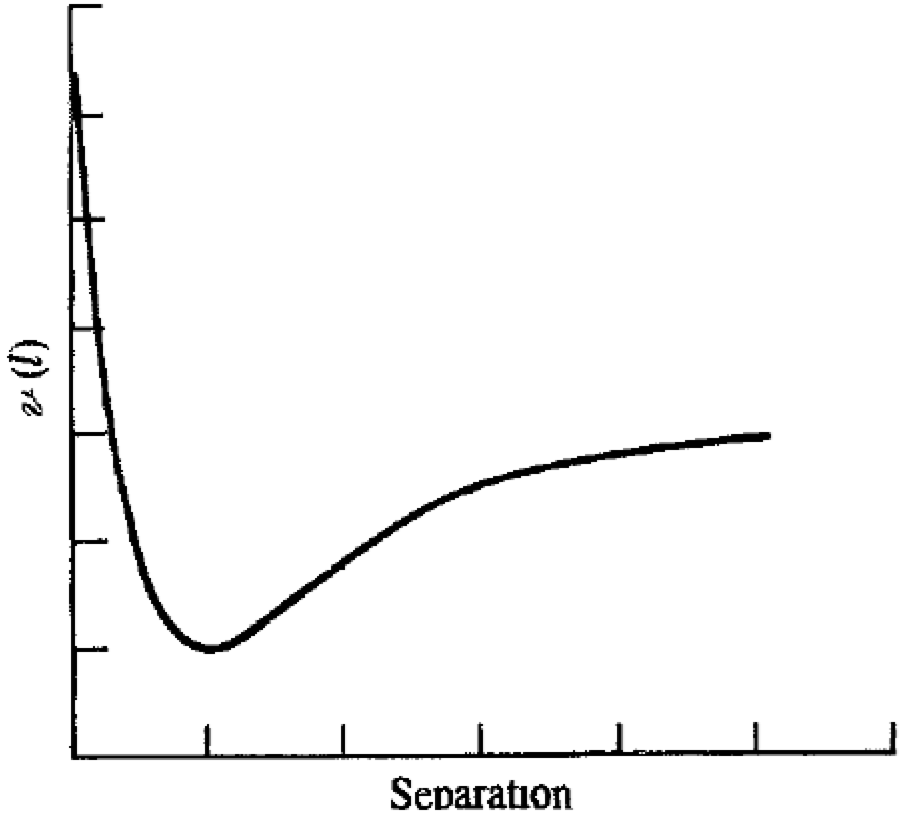


$$\mathscr{V}(\mathbf{r}^N) = \sum_{\text{bonds}} \frac{k_i}{2}(l_i - l_{i,0})^2 + \sum_{\text{angles}} \frac{k_i}{2}(\theta_i - \theta_{i,0})^2 + \sum_{\text{torsions}} \frac{V_n}{2}(1 + \cos(n\omega - \gamma)) + \sum_{i=1}^{N} \sum_{j=i+1}^{N} \left(4\varepsilon_{ij}\left[\left(\frac{\sigma_{ij}}{r_{ij}}\right)^{12} - \left(\frac{\sigma_{ij}}{r_{ij}}\right)^{6}\right] + \frac{q_i q_j}{4\pi\varepsilon_0 r_{ij}} \right)$$



Bond

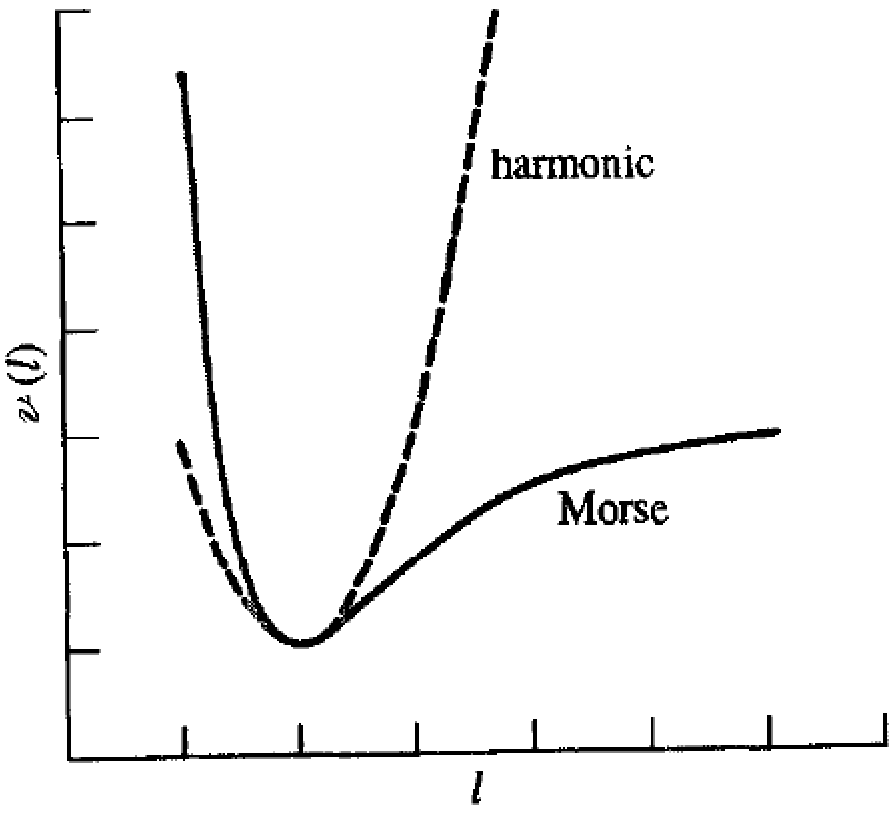
$$v(l) = D_e\{1 - \exp[-a(l - l_0)]\}^2$$



$$v(l) = \frac{k}{2}(l - l_0)^2$$

Bond	l_0 (Å)	k (kcal mol^{-1} $Å^{-2}$)
Csp^3-Csp^3	1.523	317
Csp^3-Csp^2	1.497	317
$Csp^2=Csp^2$	1.337	690
$Csp^2=O$	1.208	777
Csp^3-Nsp^3	1.438	367
C–N (amide)	1 345	719

Bond



Angle

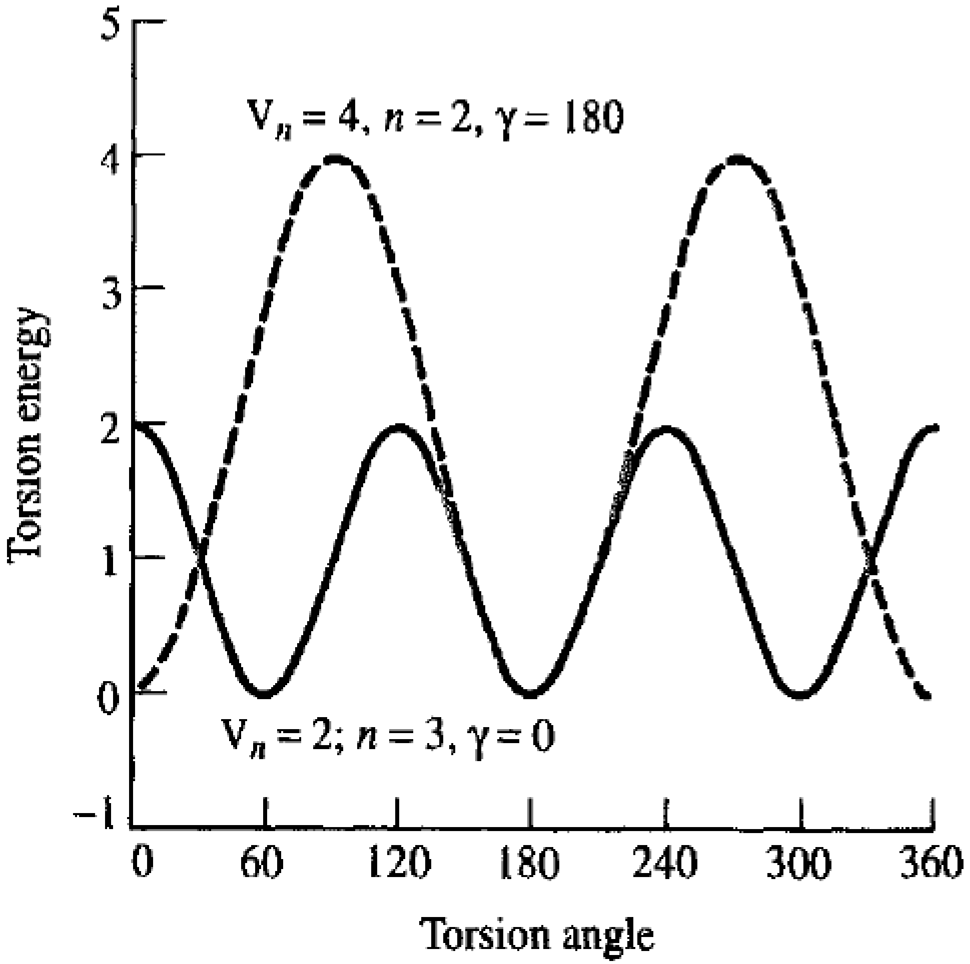
$$\upsilon(\theta) = \frac{k}{2}(\theta - \theta_0)^2$$

Angle	θ_0	k (kcal mol^{-1}deg^{-1})
$Csp^3-Csp^3-Csp^3$	109.47	0.0099
Csp^3-Csp^3-H	109.47	0.0079
$H-Csp^3-H$	109.47	0 0070
$Csp^3-Csp^2-Csp^3$	117.2	0.0099
$Csp^3-Csp^2{=}Csp^2$	121.4	0.0121
$Csp^3-Csp^2{=}O$	122.5	0.0101

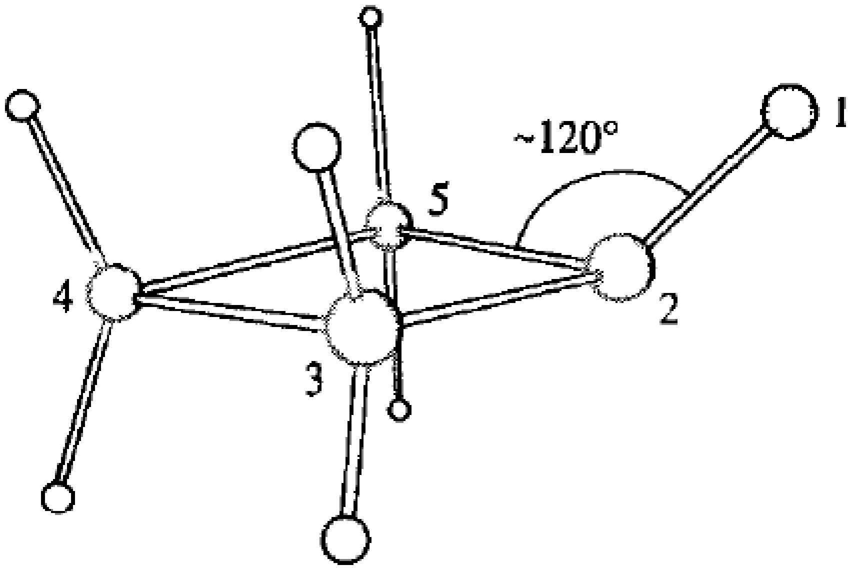
Proper Dihedral Angle

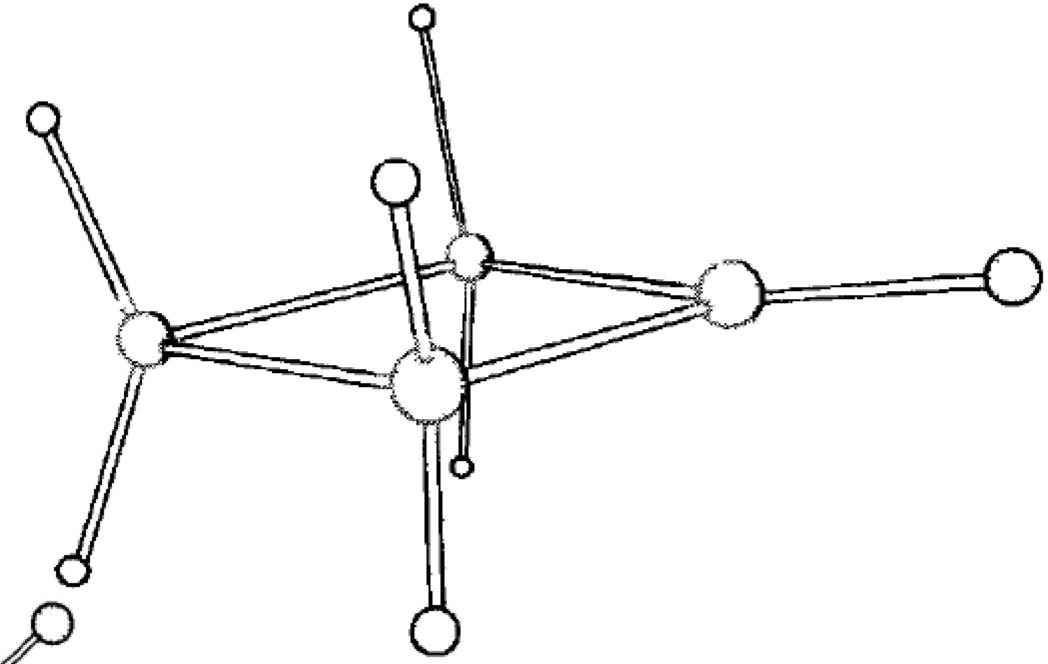
$$v(\omega) = \sum_{n=0}^{N} \frac{V_n}{2}\left[1 + \cos(n\omega - \gamma)\right]$$

$$v(\omega) = \sum_{n=0}^{N} C_n \cos(\omega)^n$$

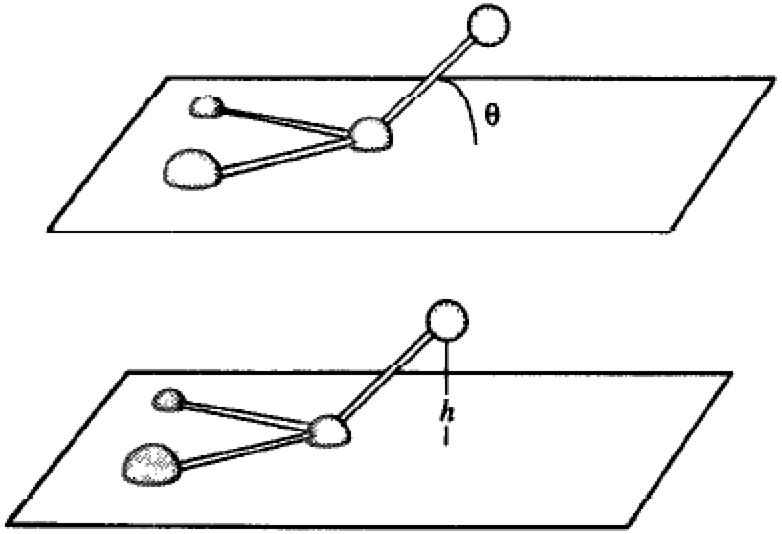


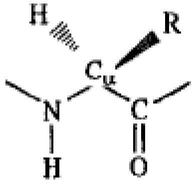
Improper Dihedral Angle and United Atom Approximation



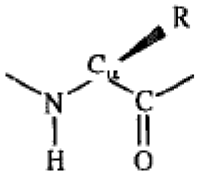


$$v(\theta) = \frac{k}{2}\theta^2; \qquad v(h) = \frac{k}{2}h^2$$





All atom



United atom

$$
\mathscr{V}(\mathbf{r}^N) = \sum_{\text{bonds}} \frac{k_i}{2}(l_i - l_{i,0})^2 + \sum_{\text{angles}} \frac{k_i}{2}(\theta_i - \theta_{i,0})^2 + \sum_{\text{torsions}} \frac{V_n}{2}(1 + \cos(n\omega - \gamma))
$$

$$
+ \sum_{i=1}^{N} \sum_{j=i+1}^{N} \left(4\varepsilon_{ij} \left[\left(\frac{\sigma_{ij}}{r_{ij}} \right)^{12} - \left(\frac{\sigma_{ij}}{r_{ij}} \right)^{6} \right] + \frac{q_i q_j}{4\pi\varepsilon_0 r_{ij}} \right)
$$

Electrostatics

$$\mathscr{V} = \sum_{i=1}^{N_A} \sum_{j=1}^{N_B} \frac{q_i q_j}{4\pi\varepsilon_0 r_{ij}}$$