

Lecture 34

Modeling and simulations of materials

Textbooks:

- Computational Materials Science: J. Gunn Lee
- Understanding Molecular Simulations: D. Frenkel and B. Smit
- **Molecular Modelling Principles and Applications: Andrew Leach (Chapter 4)**

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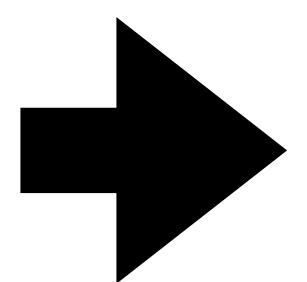
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Recap...

- Computational materials science: Introduction
- Role of simulations
- Modeling in simulations: multi-scale modeling
- Developing a model

How would you create a *model* of water molecules?

The BIG Picture



The Scale

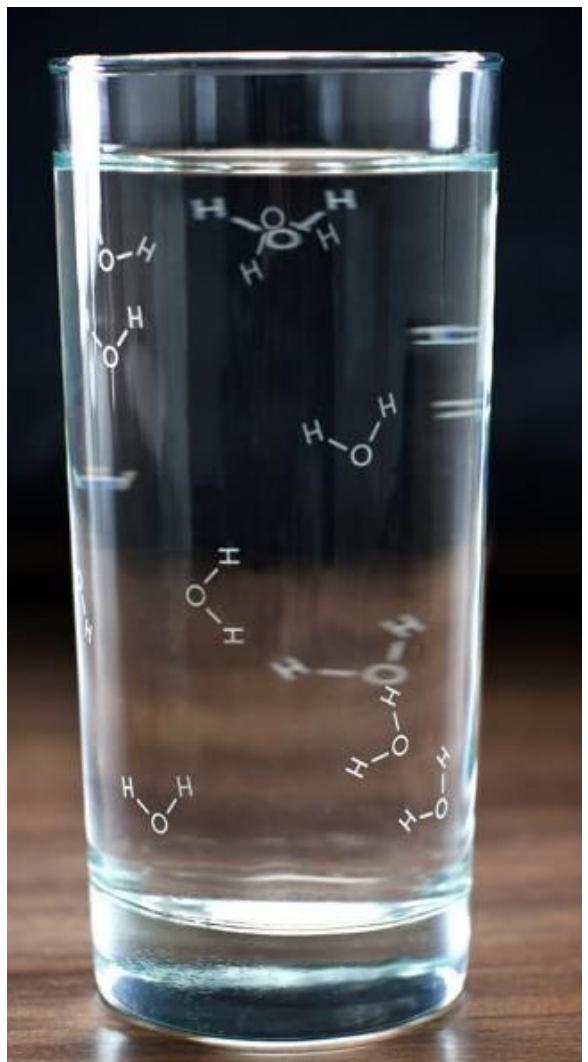
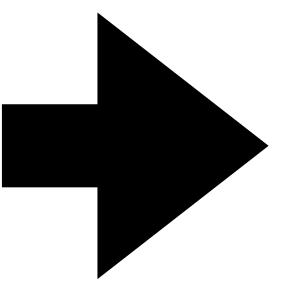


Behaviour of water as a solvent

Water as a solvent

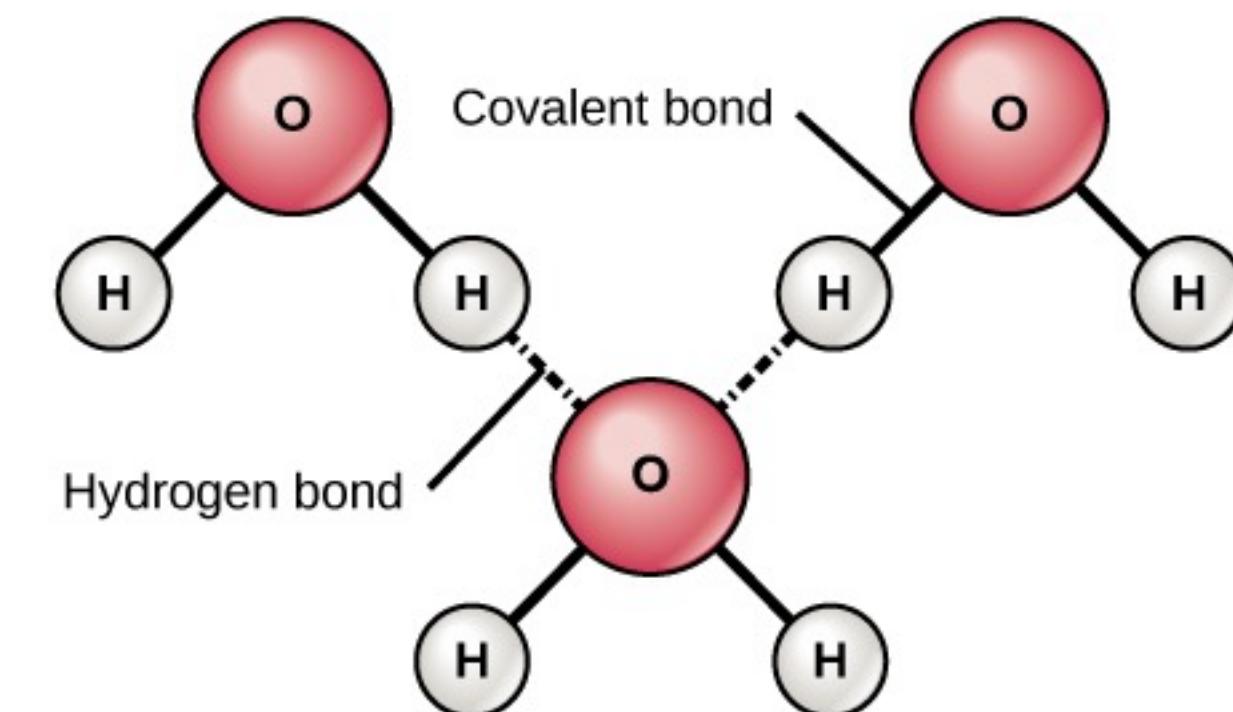
Google images

The Details



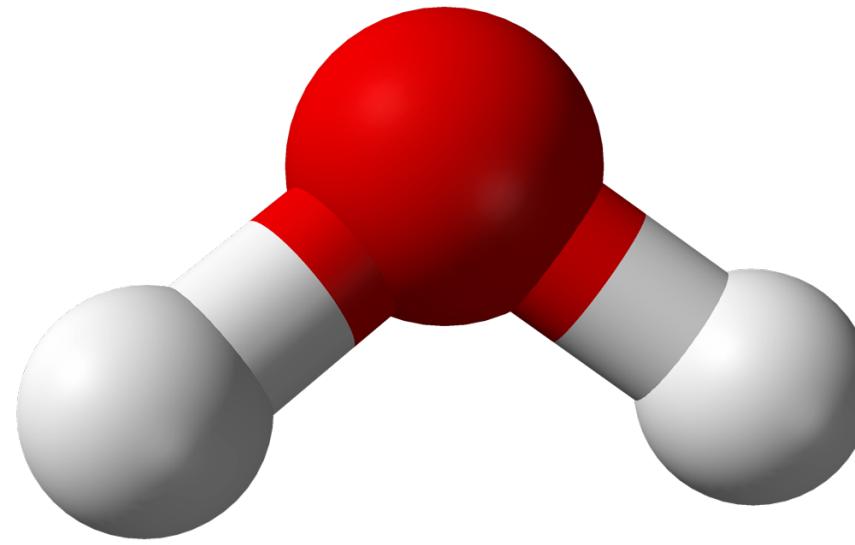
How do water molecules look inside a glass of water? How many molecules: $\sim 10^{25}$

The Connections



How do water molecules interact?

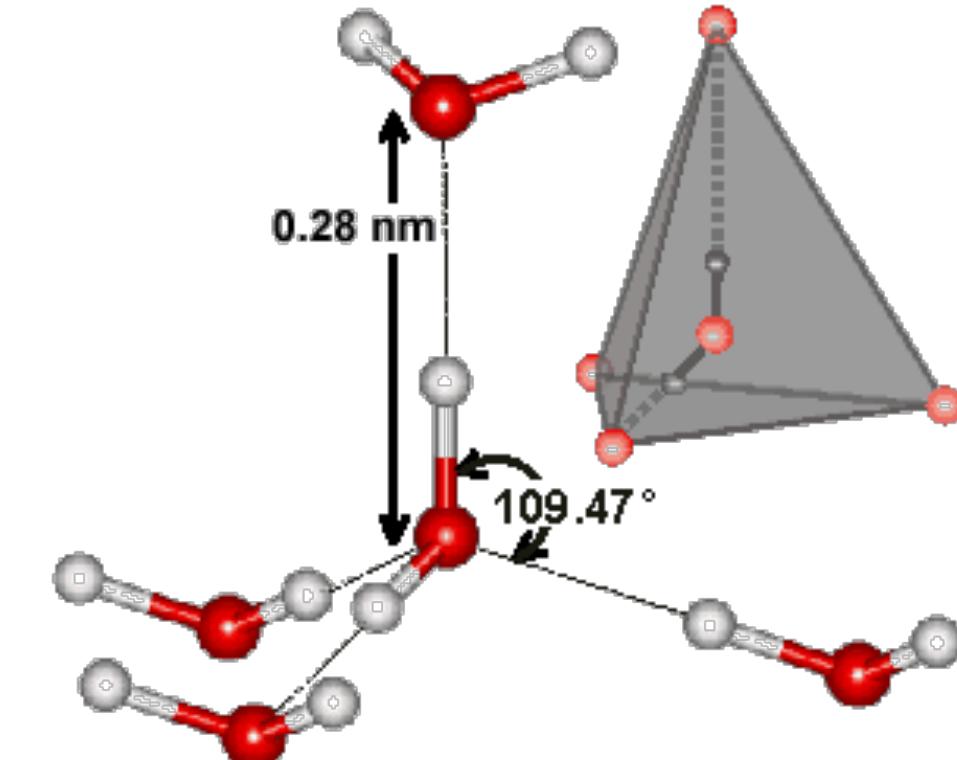
A meaningful model of water



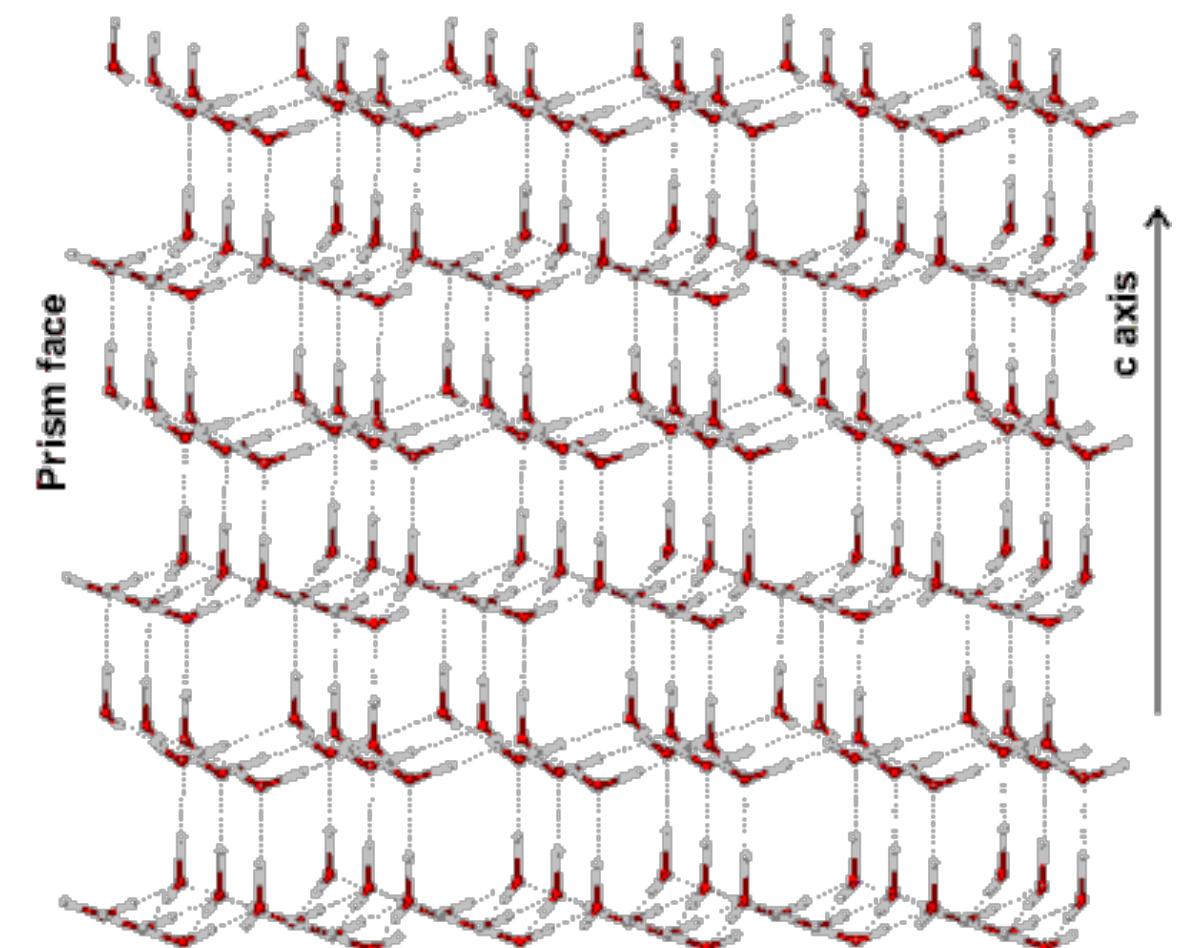
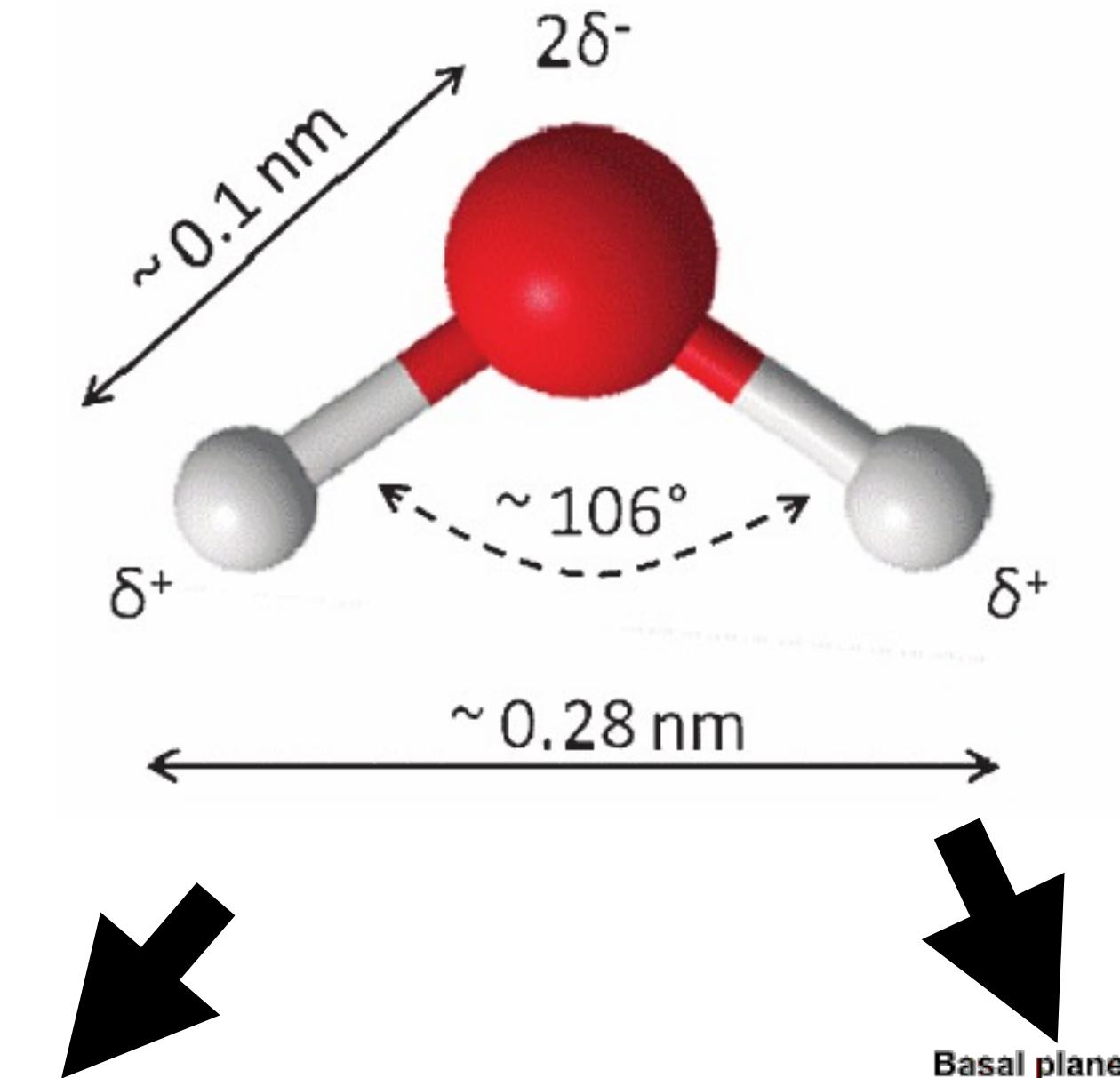
Toy model

Attractions and repulsions:

- Bonded interactions
- Electrostatic Interactions
- Dispersive interactions



Hydrogen bonding in water



Ice

A mathematically meaningful model of water

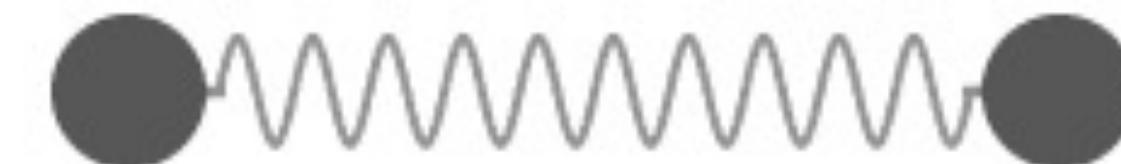
Molecules undergo vibrations at room temperature



A ball free to move around
(Monoatomic gas like
Argon, Neon ..)



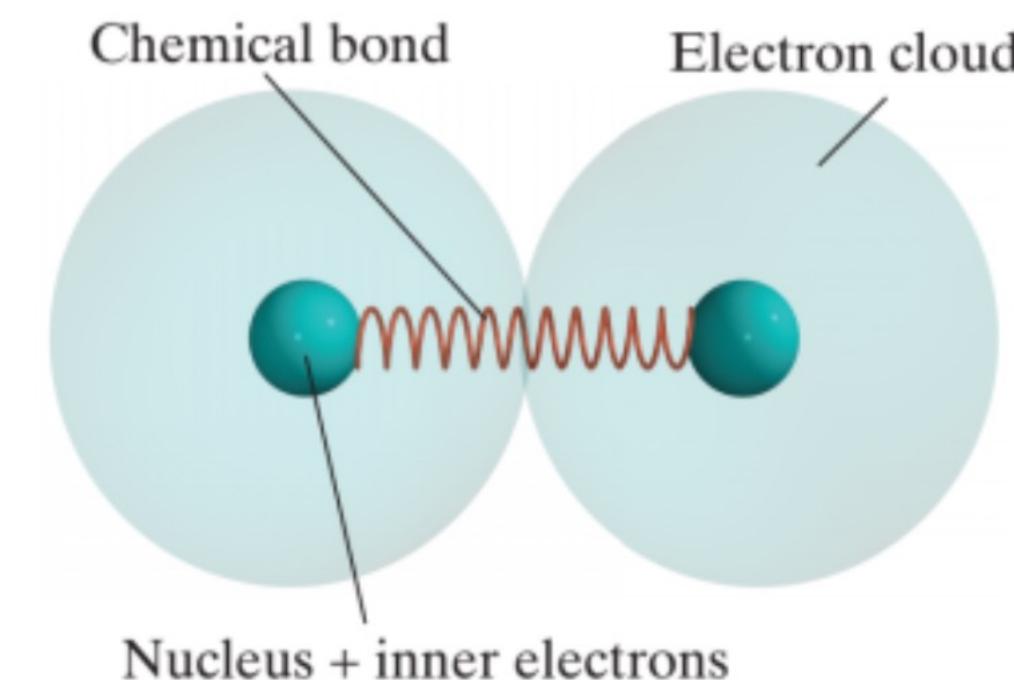
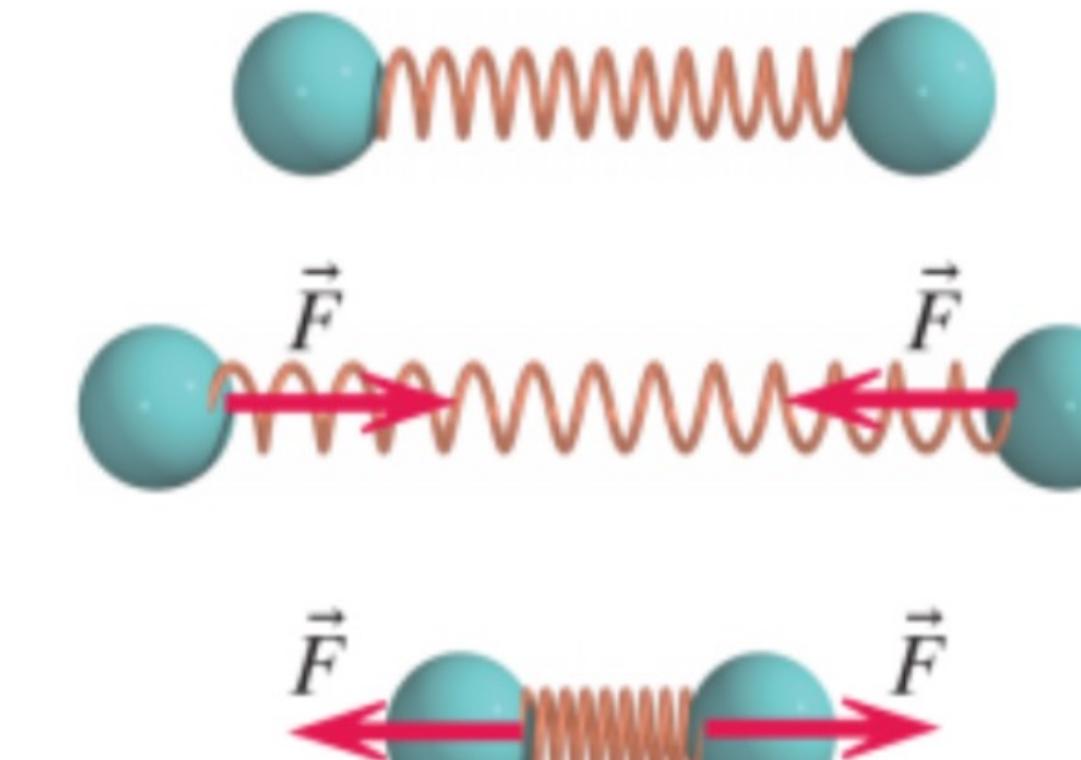
Restricted motion of
the ball



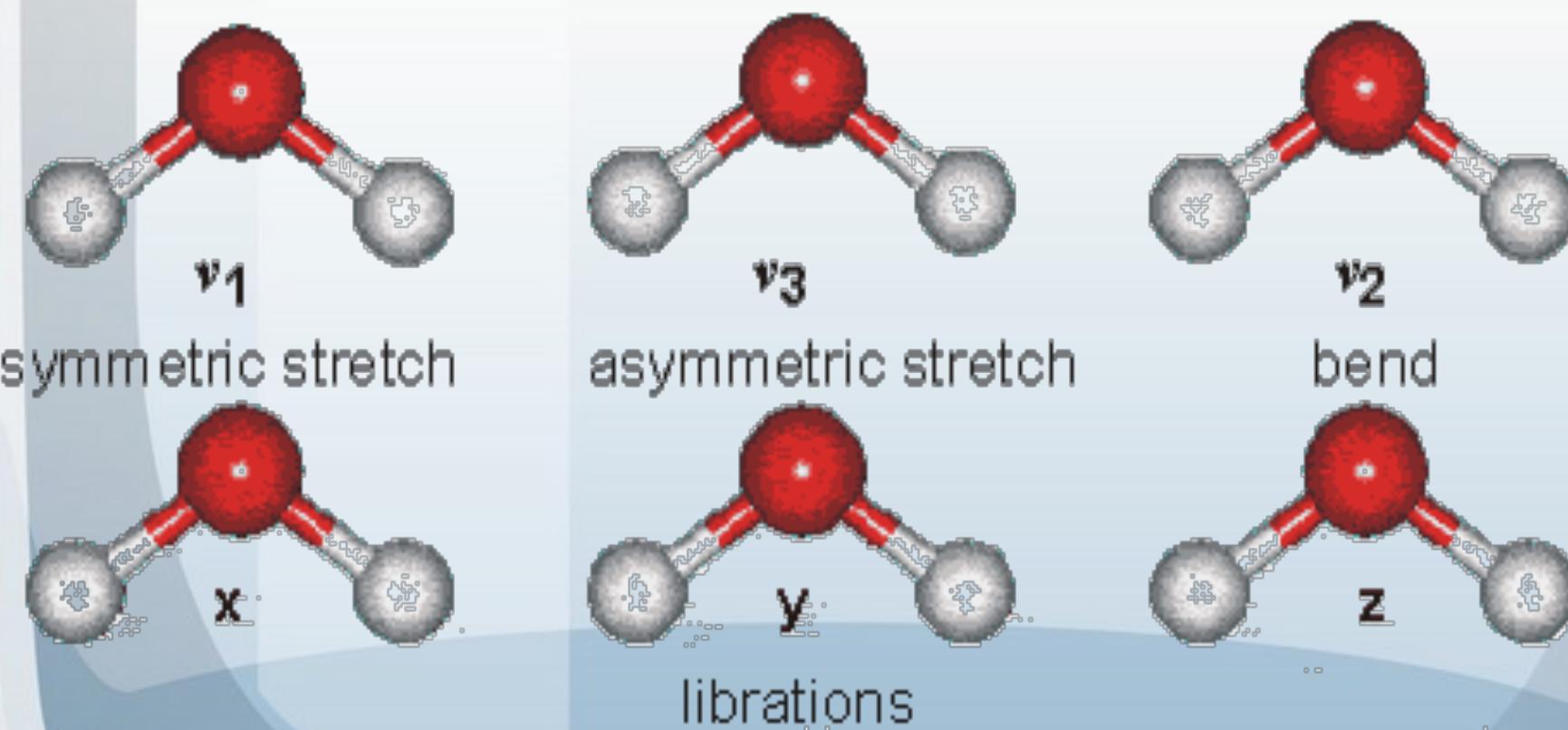
Molecules vibrate, rotate and translate

Hooke's Law

$$F = kx$$



Vibrations in water molecules



Model of a molecule (Force-field)

$$U(r) = U_{bonded}(r) + U_{non-bonded}(r)$$

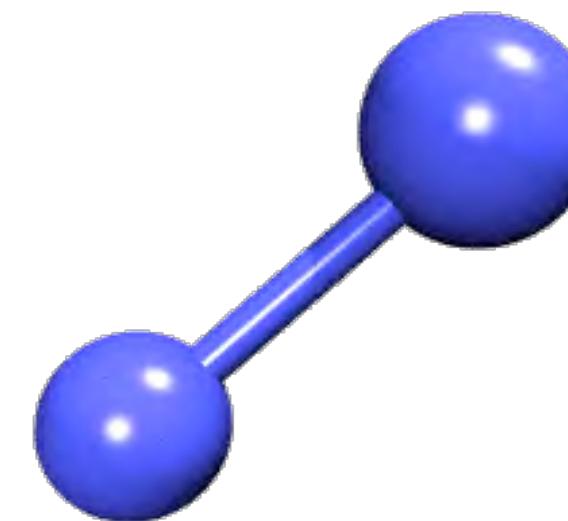
$$U(r) = U_{bond}(r) + U_{angle}(r) + U_{torsions} + U_{dispersion} + U_{electrostatic}$$

Force-field or Potential energy surface: Mathematical function that describes the energy of molecules as a function of the geometry/coordinates of molecules.



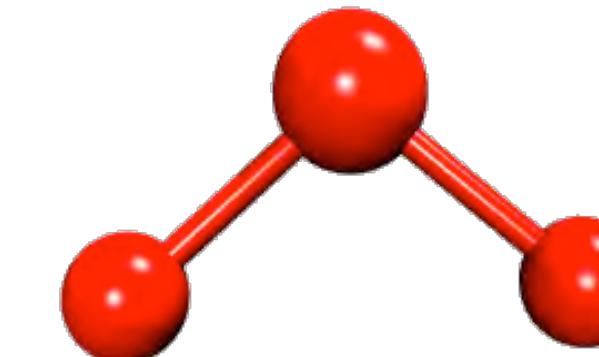
Each vibration (or libration) corresponds to a peak in Infrared spectrum (vibrational spectroscopy)

Types of Bonded interactions



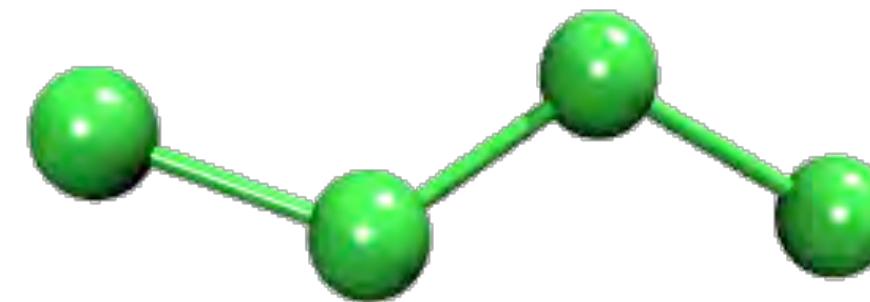
Bond

2-body interaction



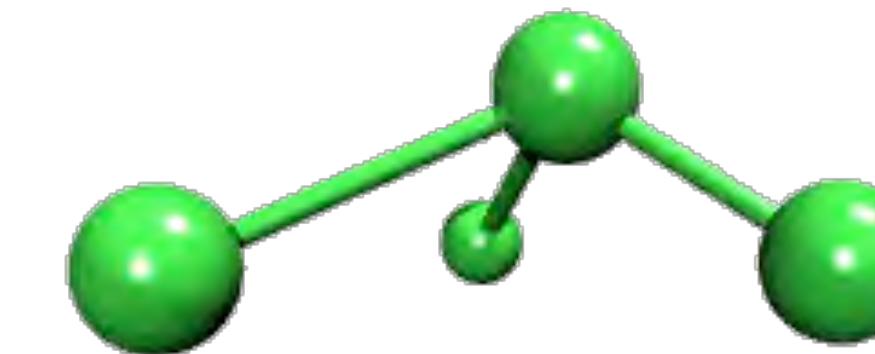
Angle

3-body interaction



Dihedral

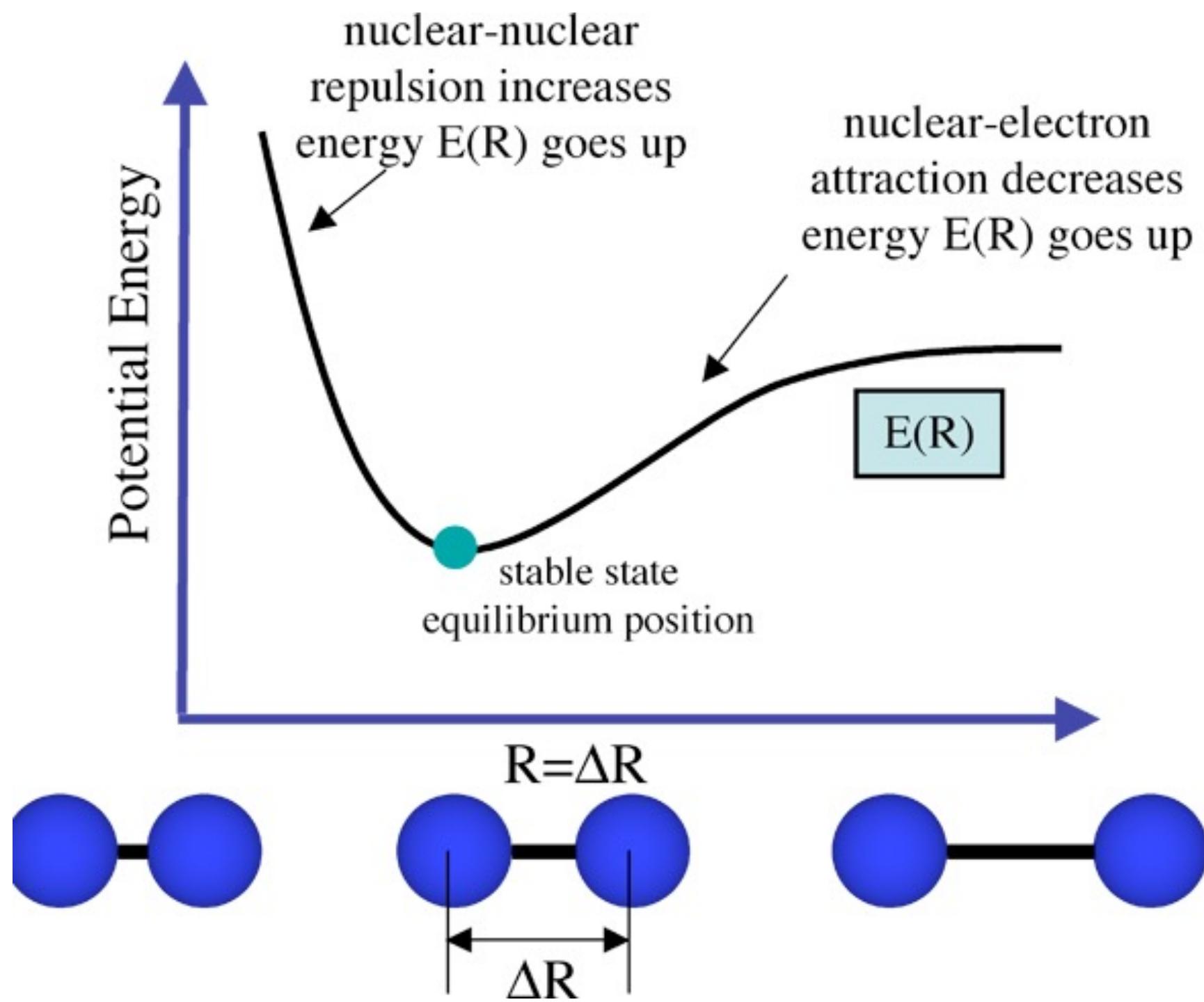
4-body interaction



Improper

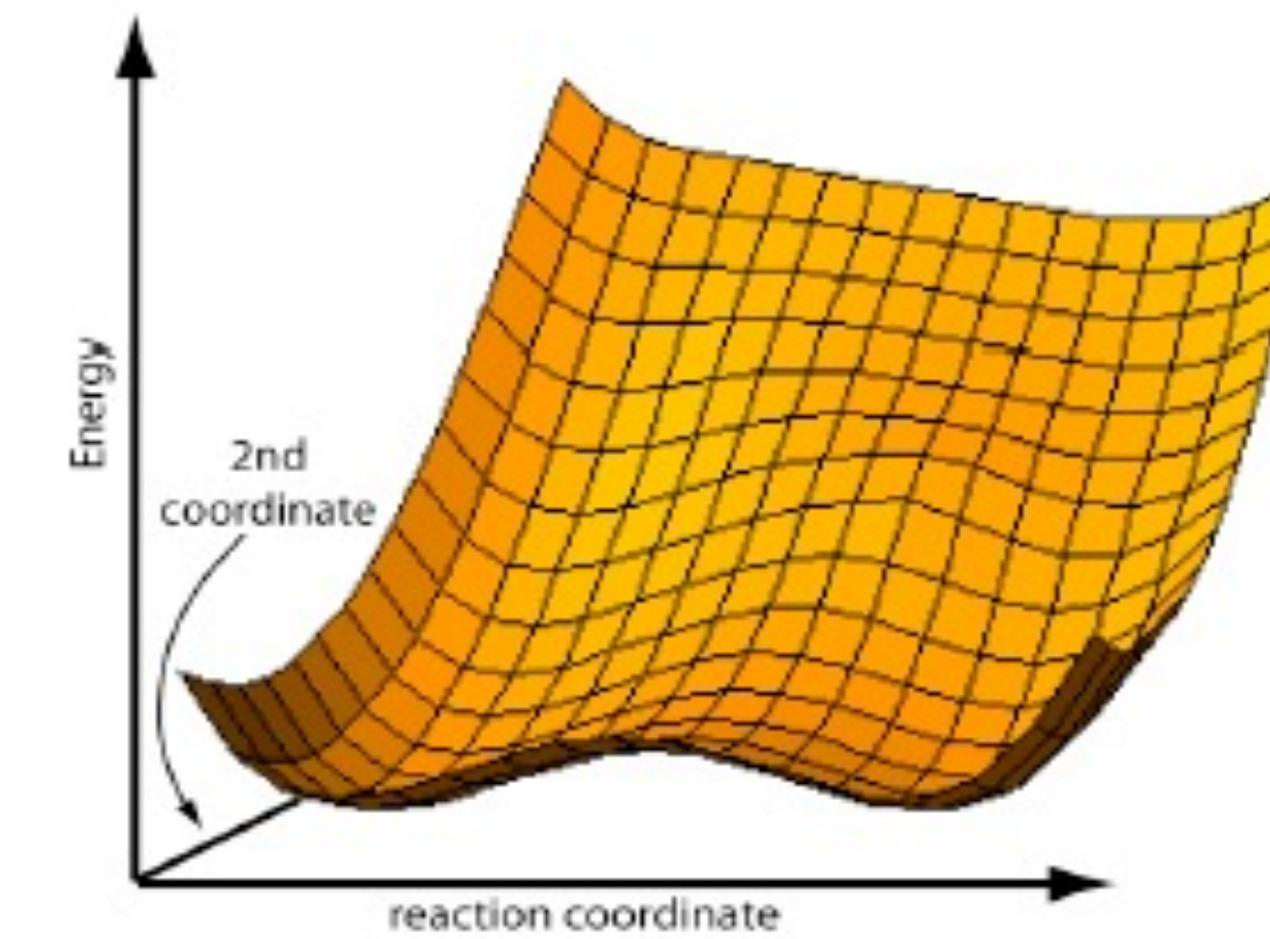
4-body interaction

PES of a diatomic molecule



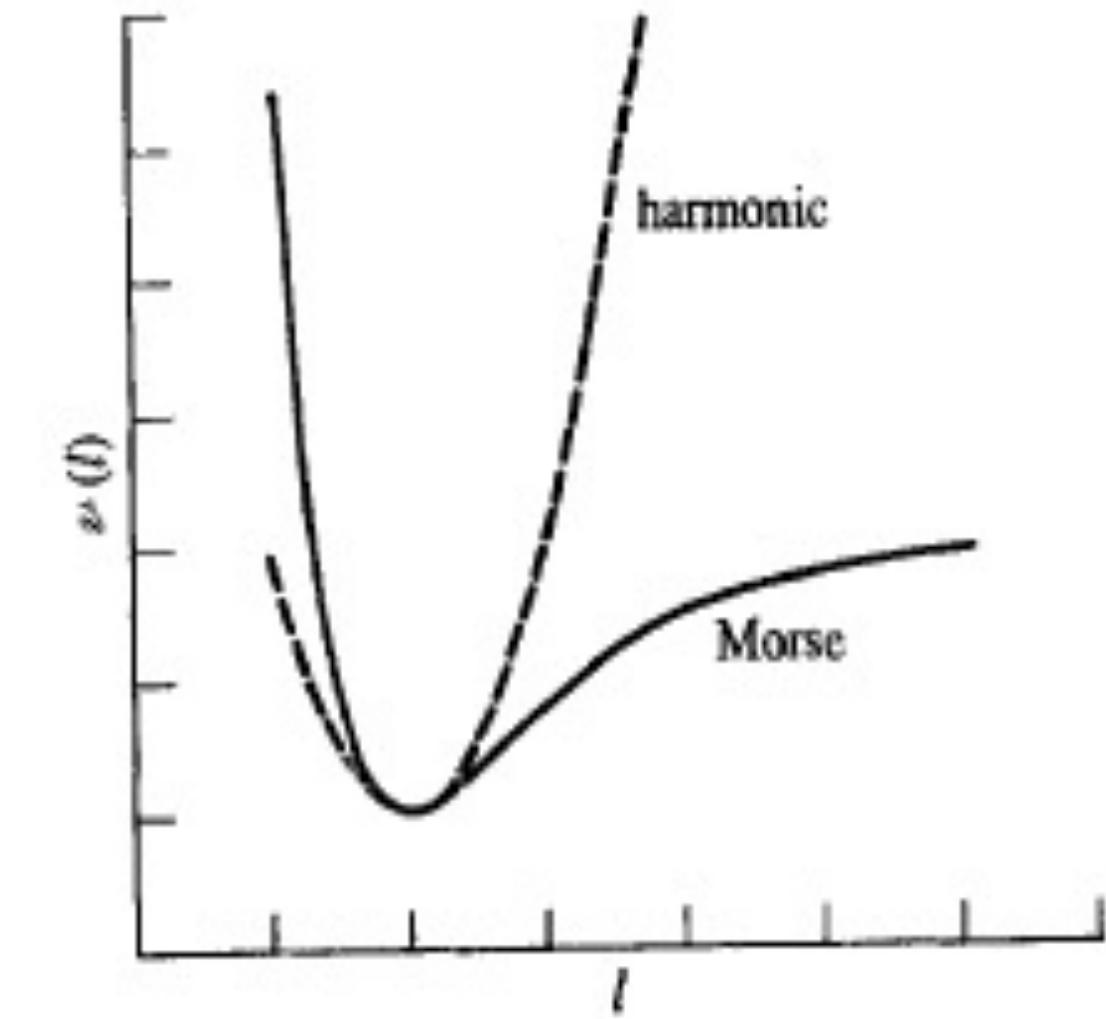
Morse potential

$$V'(r) = D_e (1 - e^{-a(r-r_e)})^2$$



Hooke's law

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

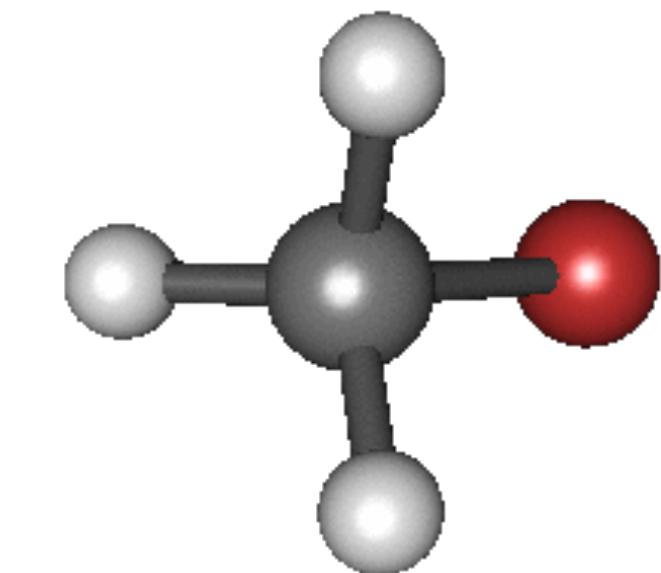


A two-dimensional PES

Modeling the bonded interactions

Bond stretching

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



Hooke's law $v(l) = \frac{k}{2}(l - l_0)^2$

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

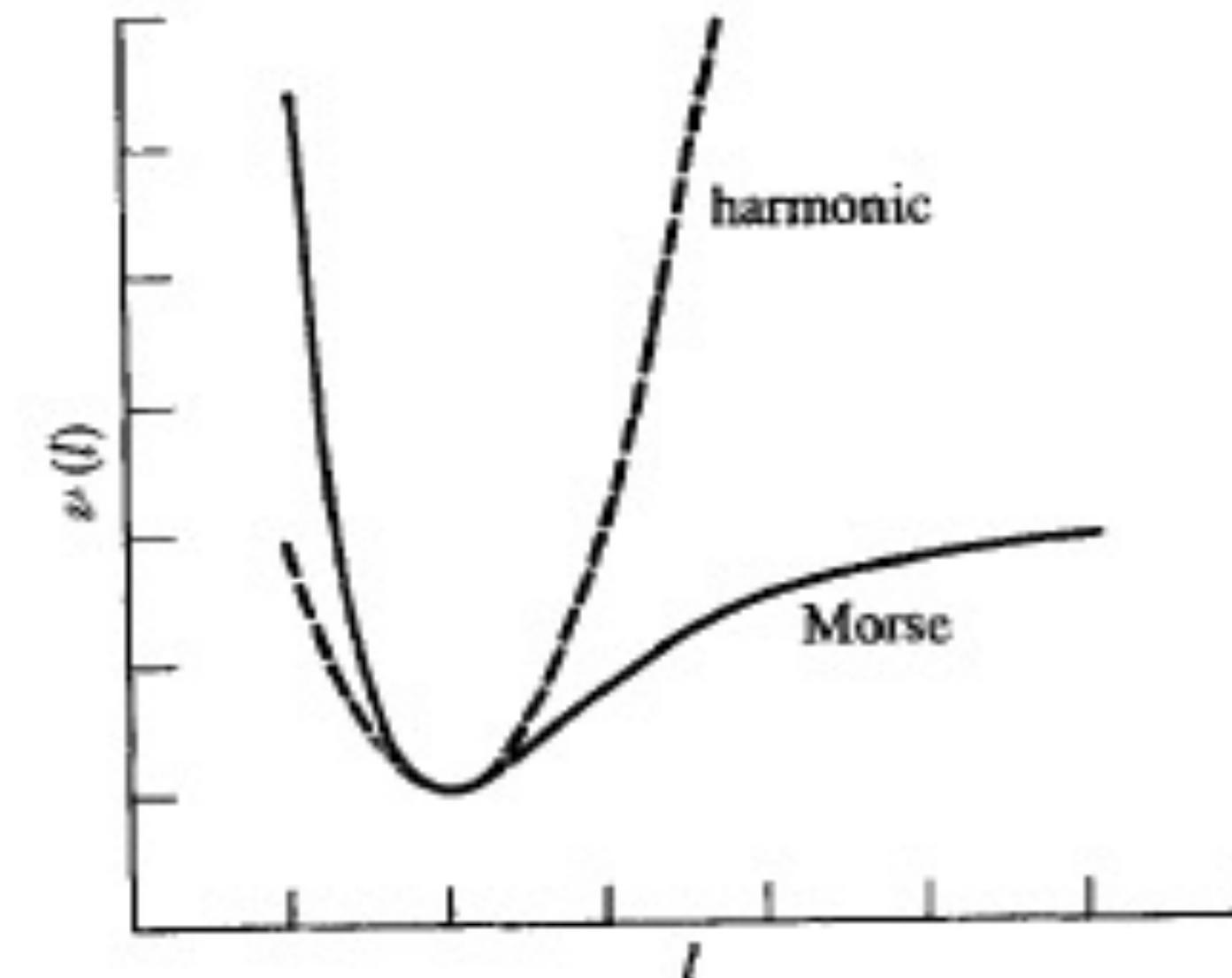


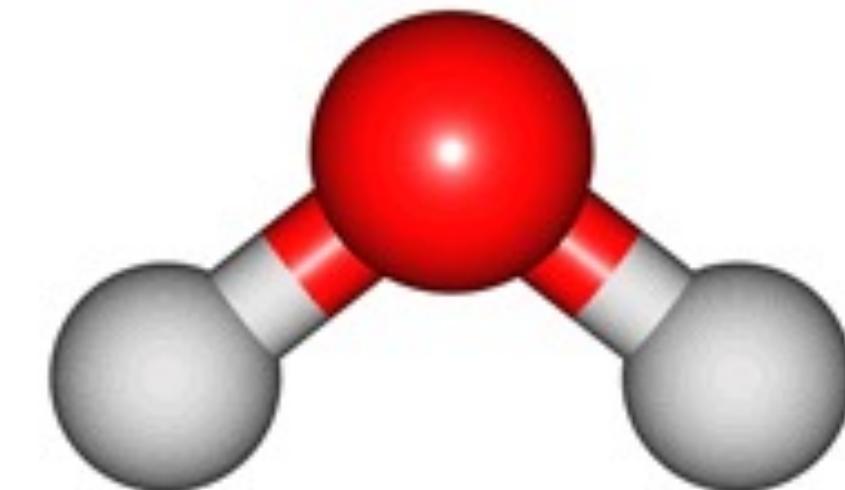
Table 4.1 Force constants and reference bond lengths for selected bonds [Allinger 1977]

Modeling the bonded interactions

Angle bending

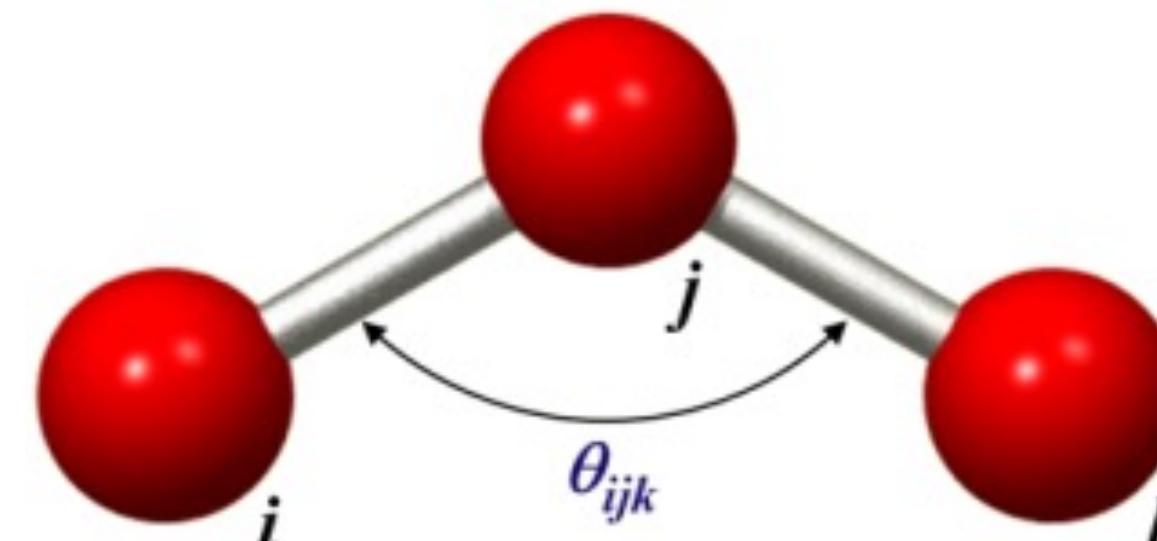
Hooke's law (harmonic potential)

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



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

Table 4.2 Force constants and reference angles for selected angles
[Allinger 1977].

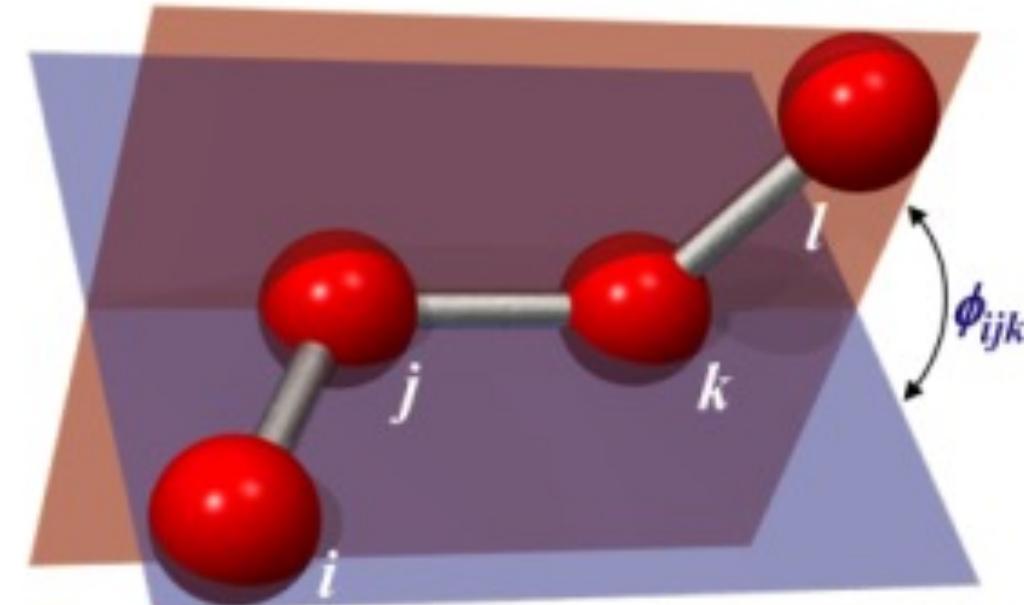


Modeling the bonded interactions

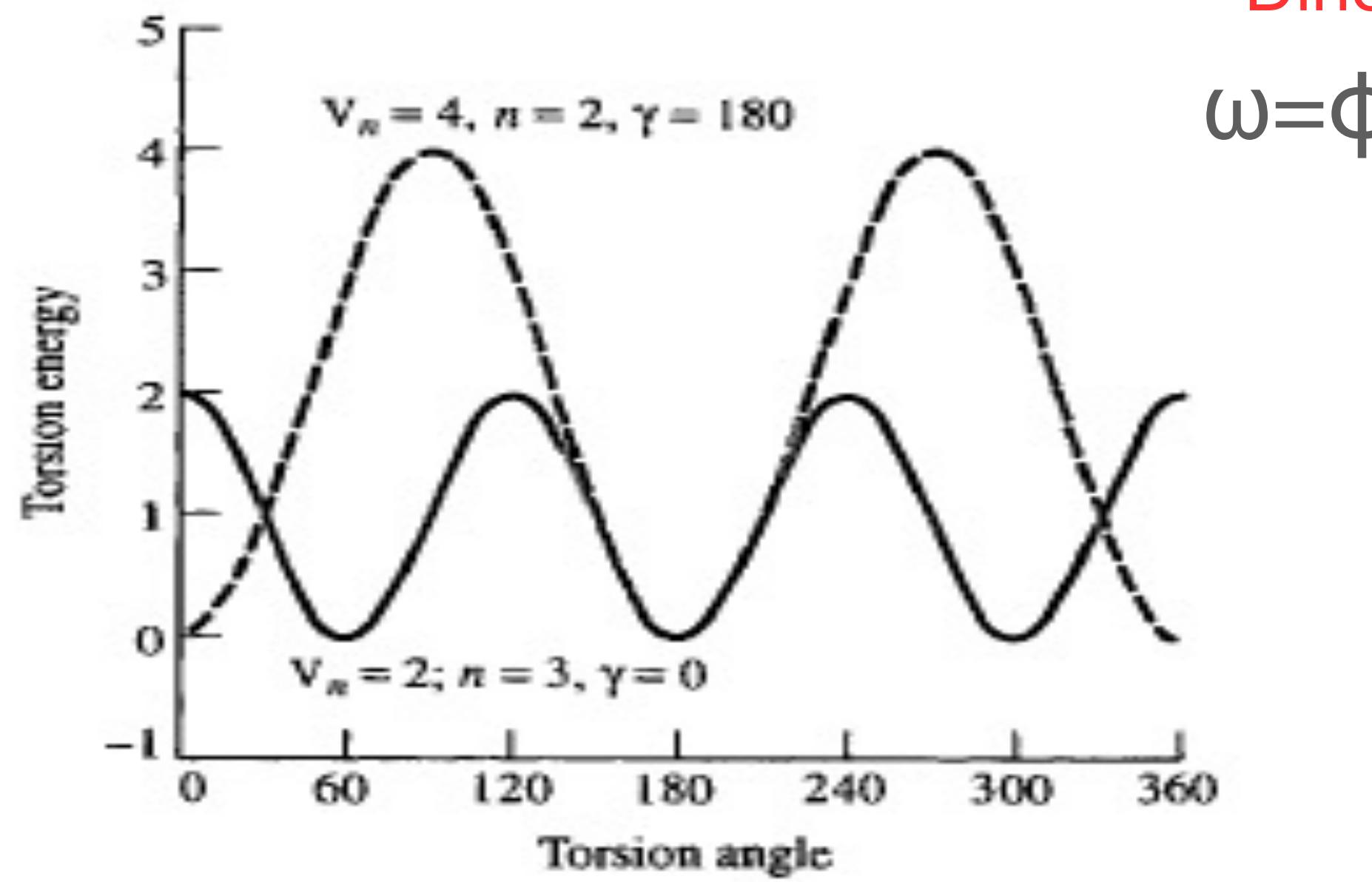
Torsions (1,4- interactions)

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

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



Dihedral (Proper torsion)

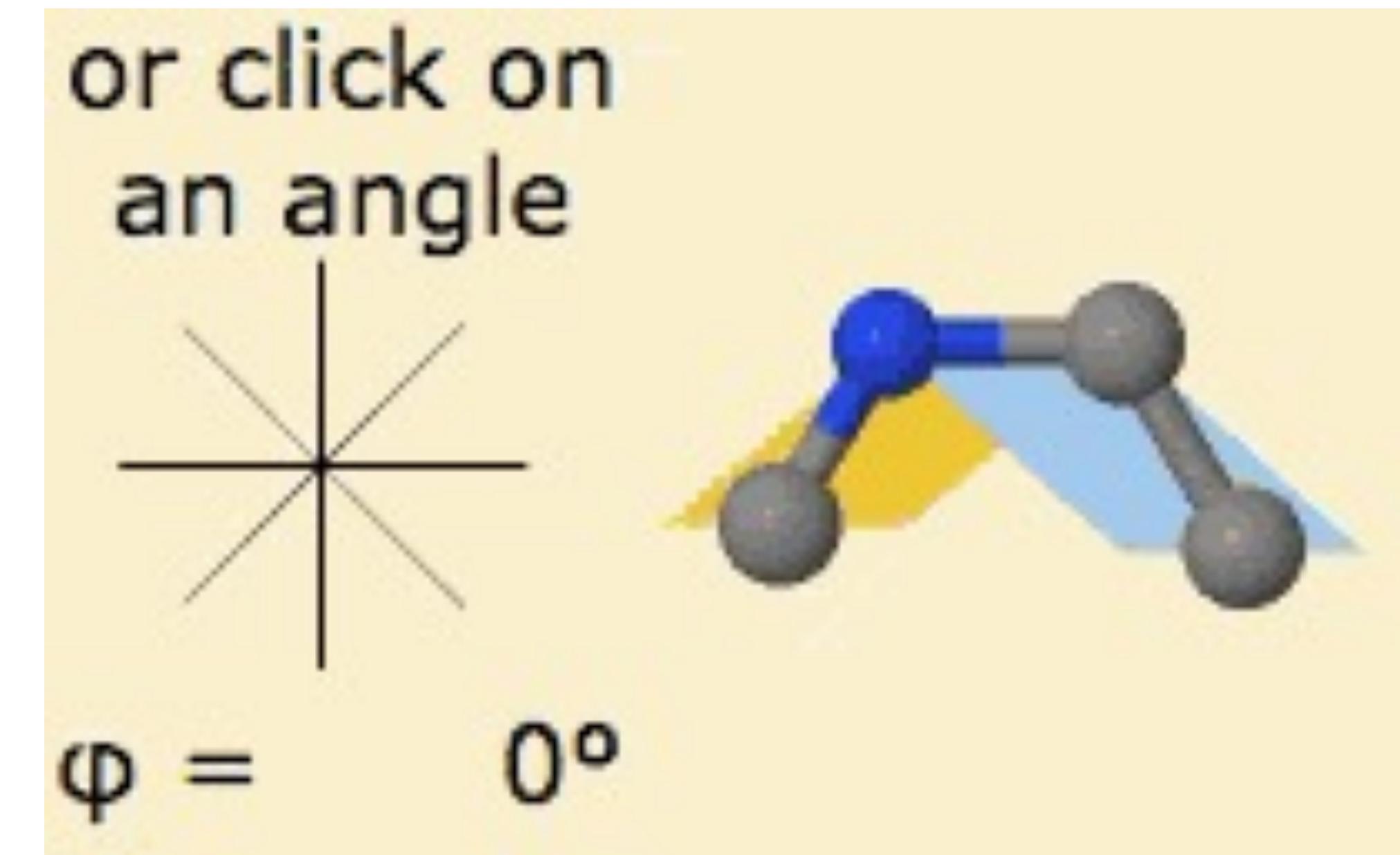


$$\omega = \phi$$

V_n = barrier height

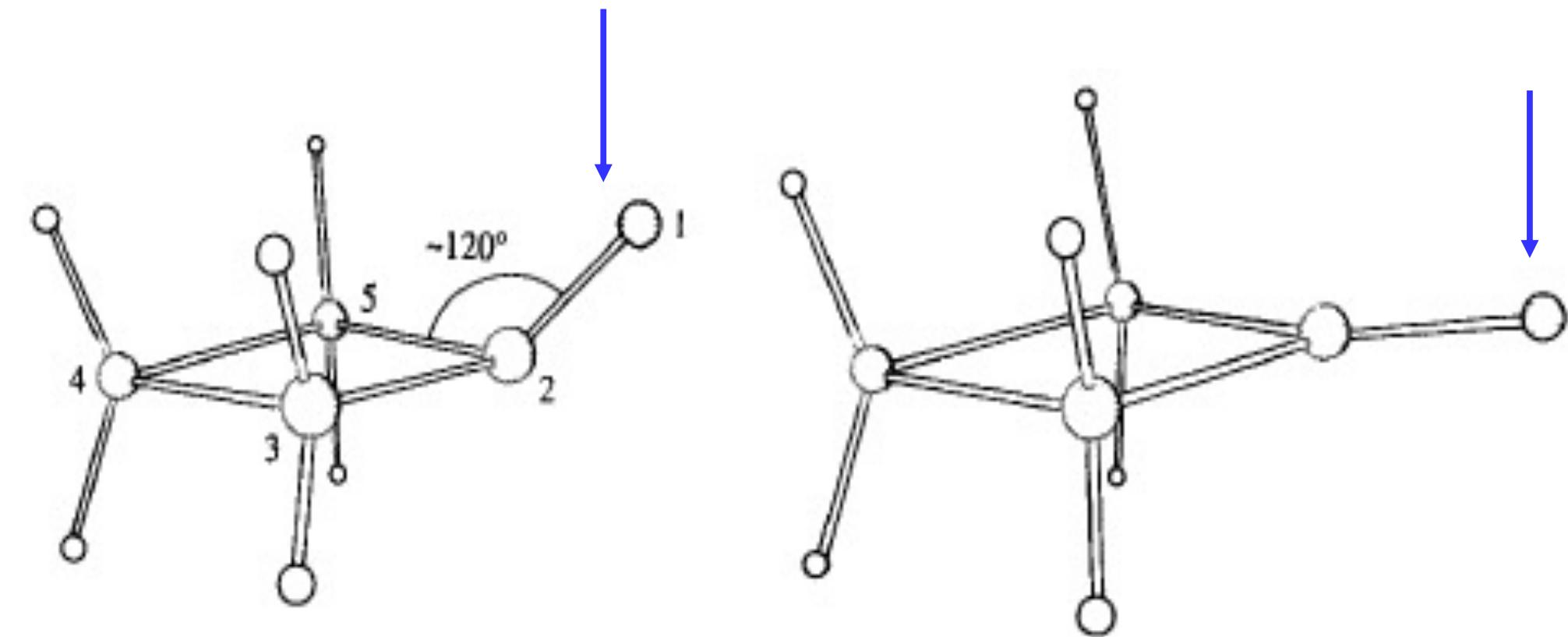
n = multiplicity (the no. of minimum points in the function as the bond is rotated through 360 deg)

γ = phase factor (where the torsion angle passes through minimum)



Modeling the bonded interactions

Improper Torsions (1,4- interactions)

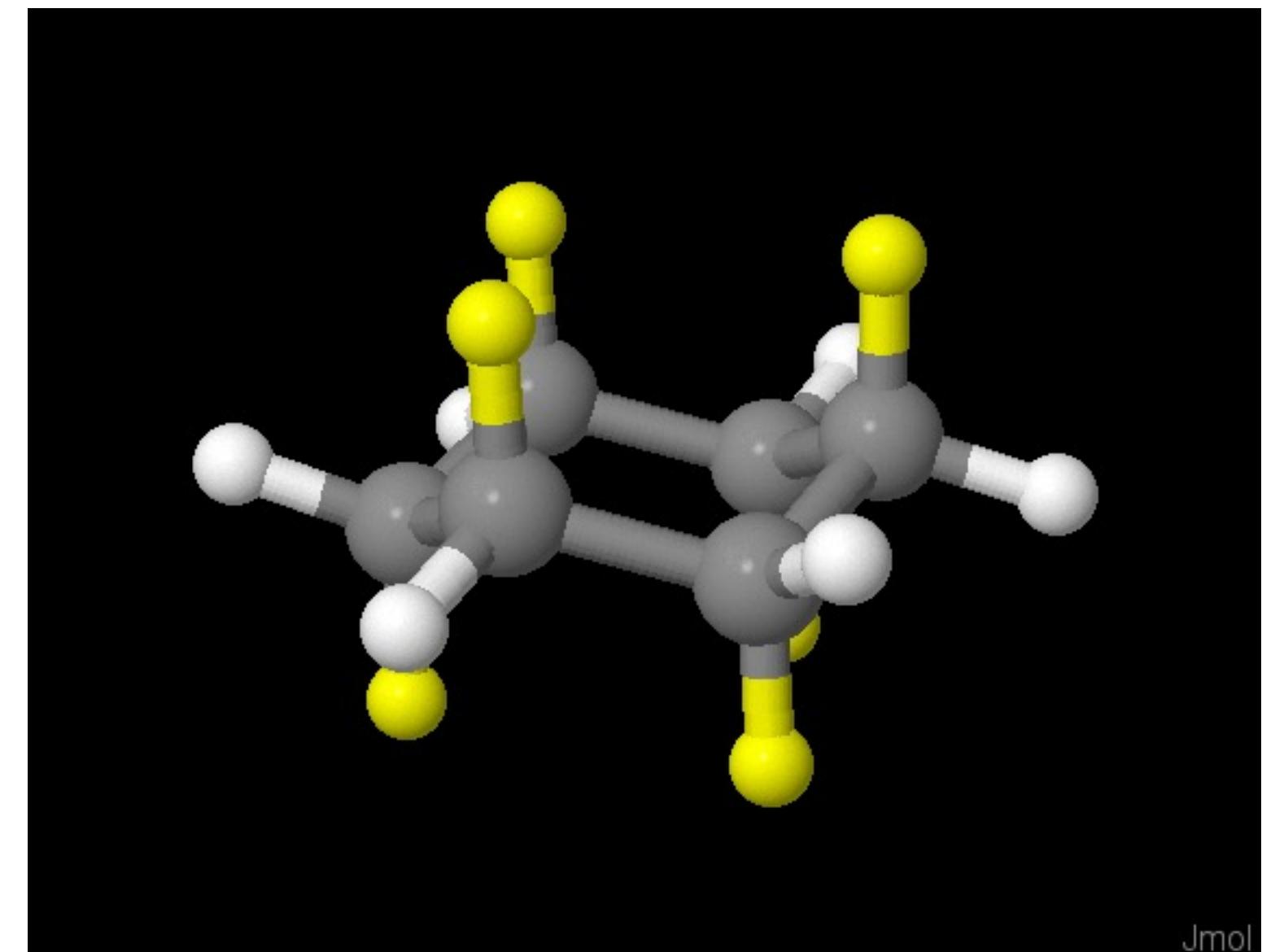
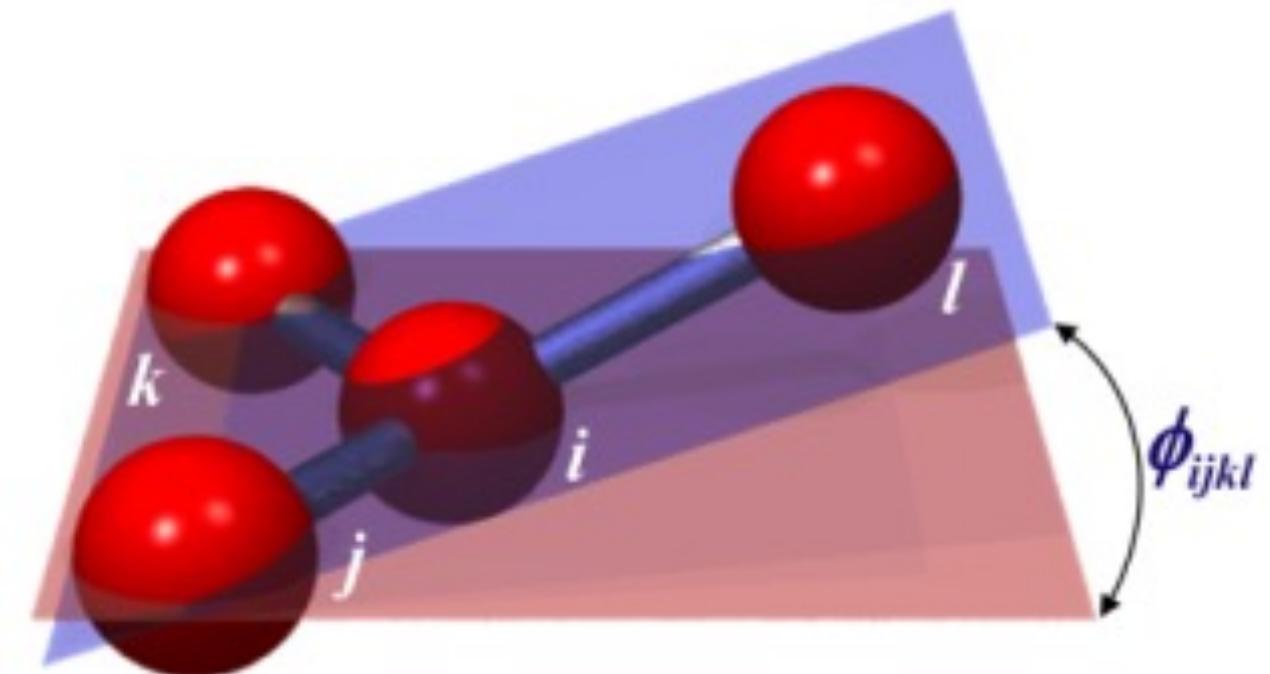


obtained

desired

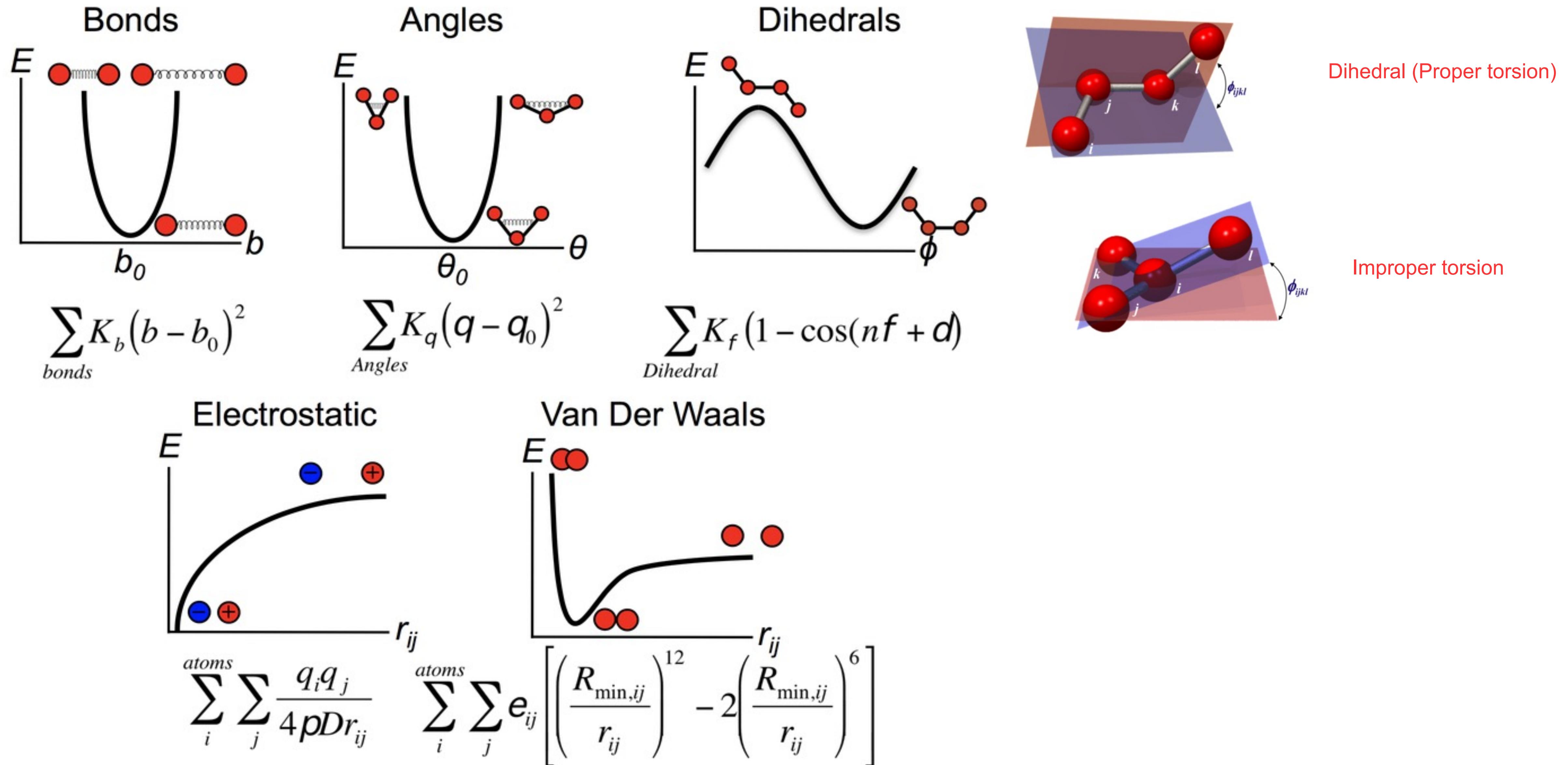
$$v(\omega) = k(1 - \cos 2\omega)$$

(out-of-plane bending term)



Jmol

Models of different interactions: Summary

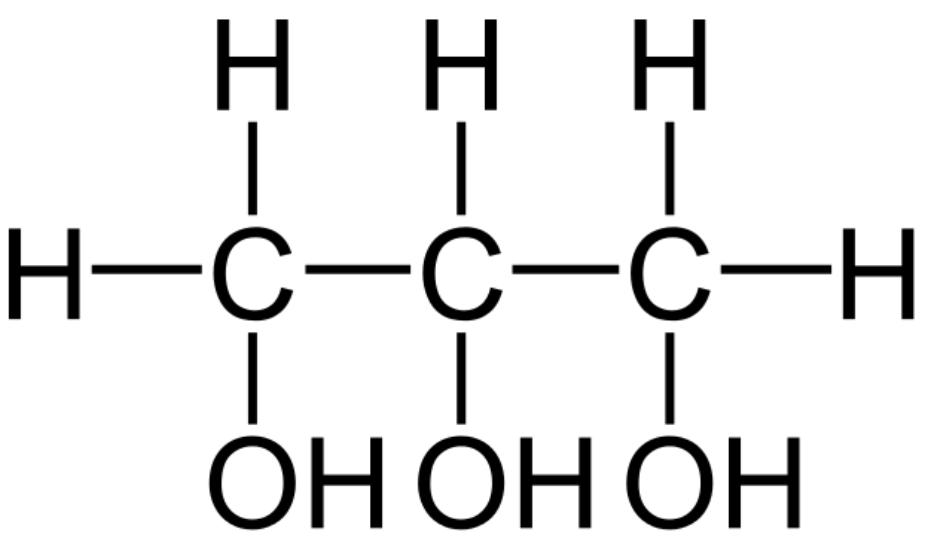


Potential energy surface: Examples

Molecular model

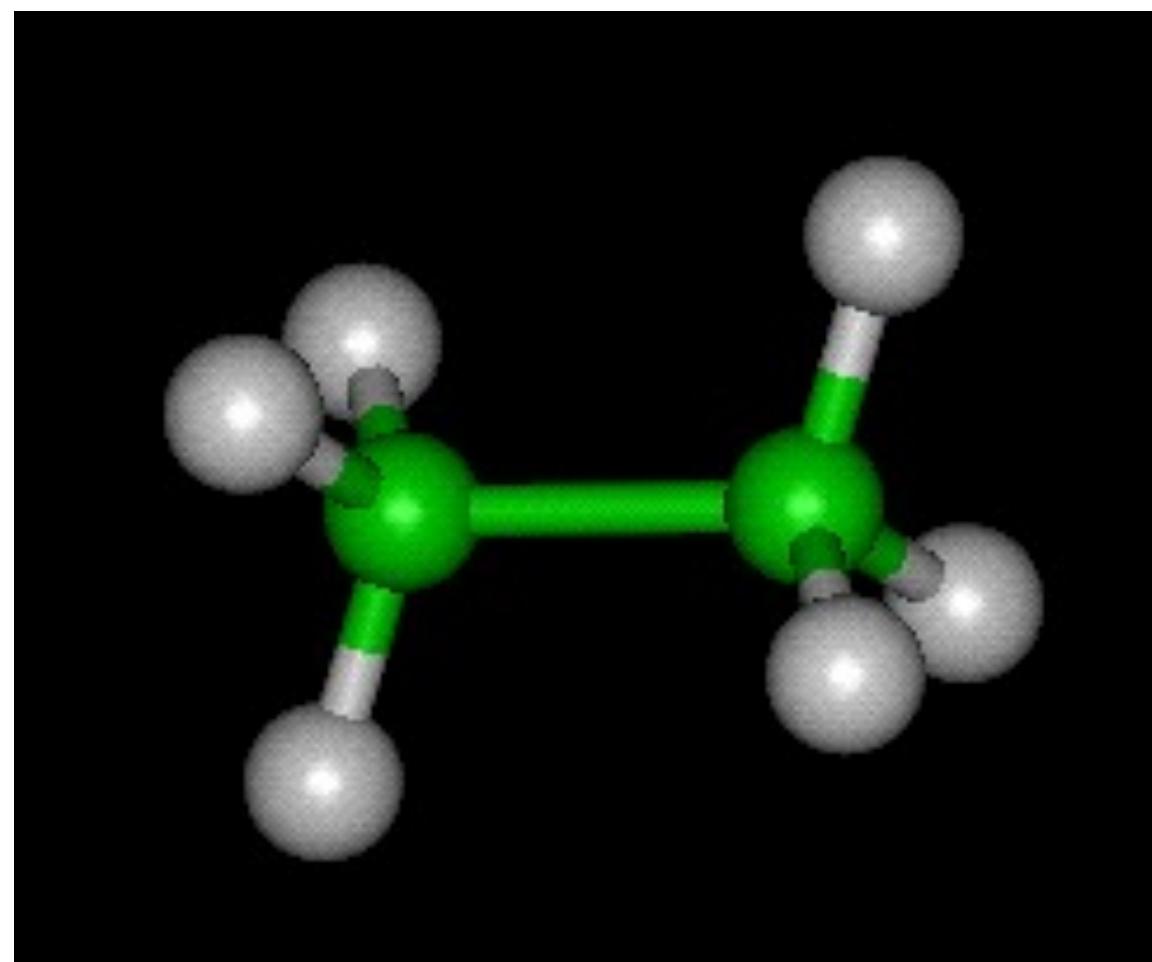


glycerol

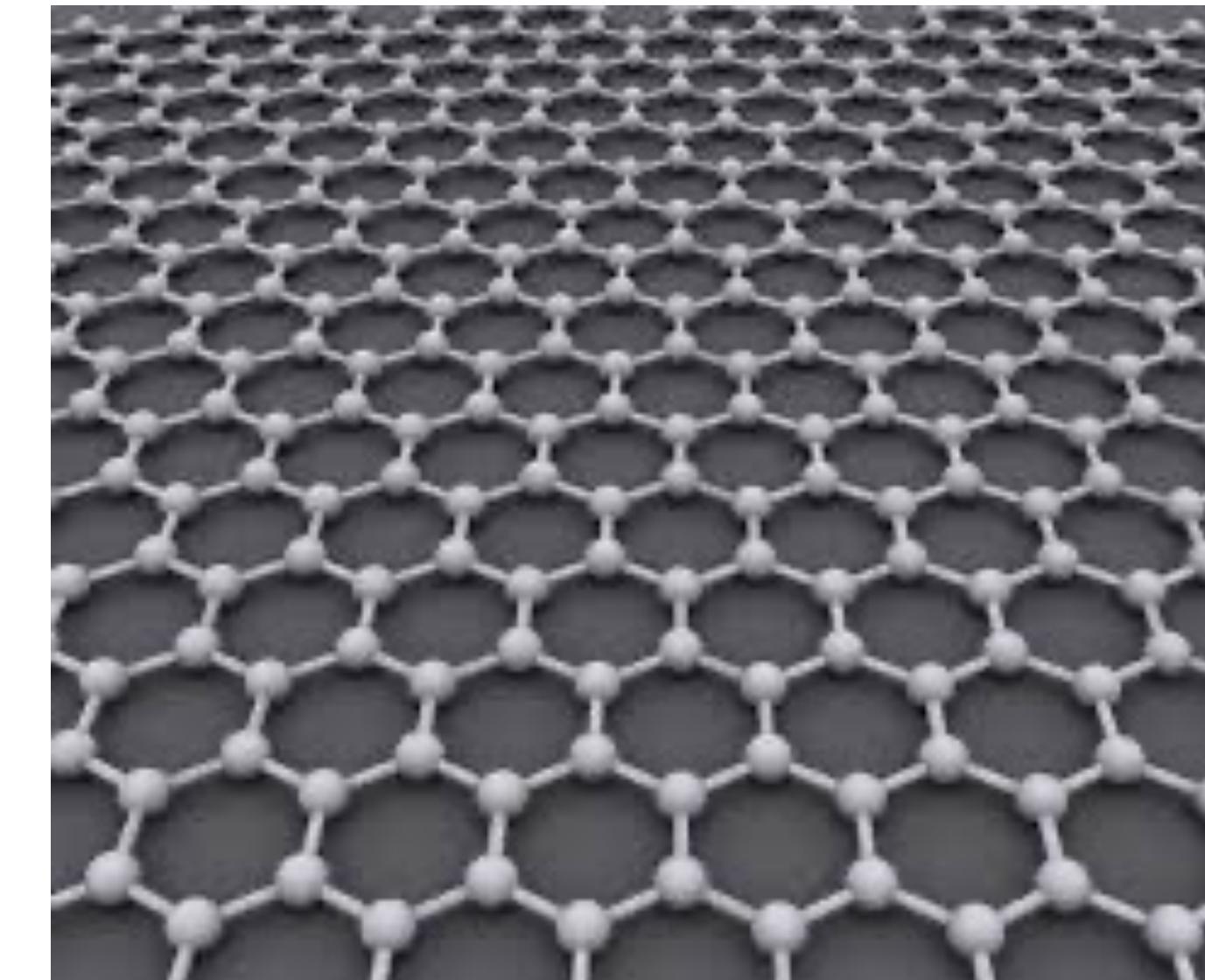


$$U(r) = U_{bonded}(r) + U_{non-bonded}(r)$$

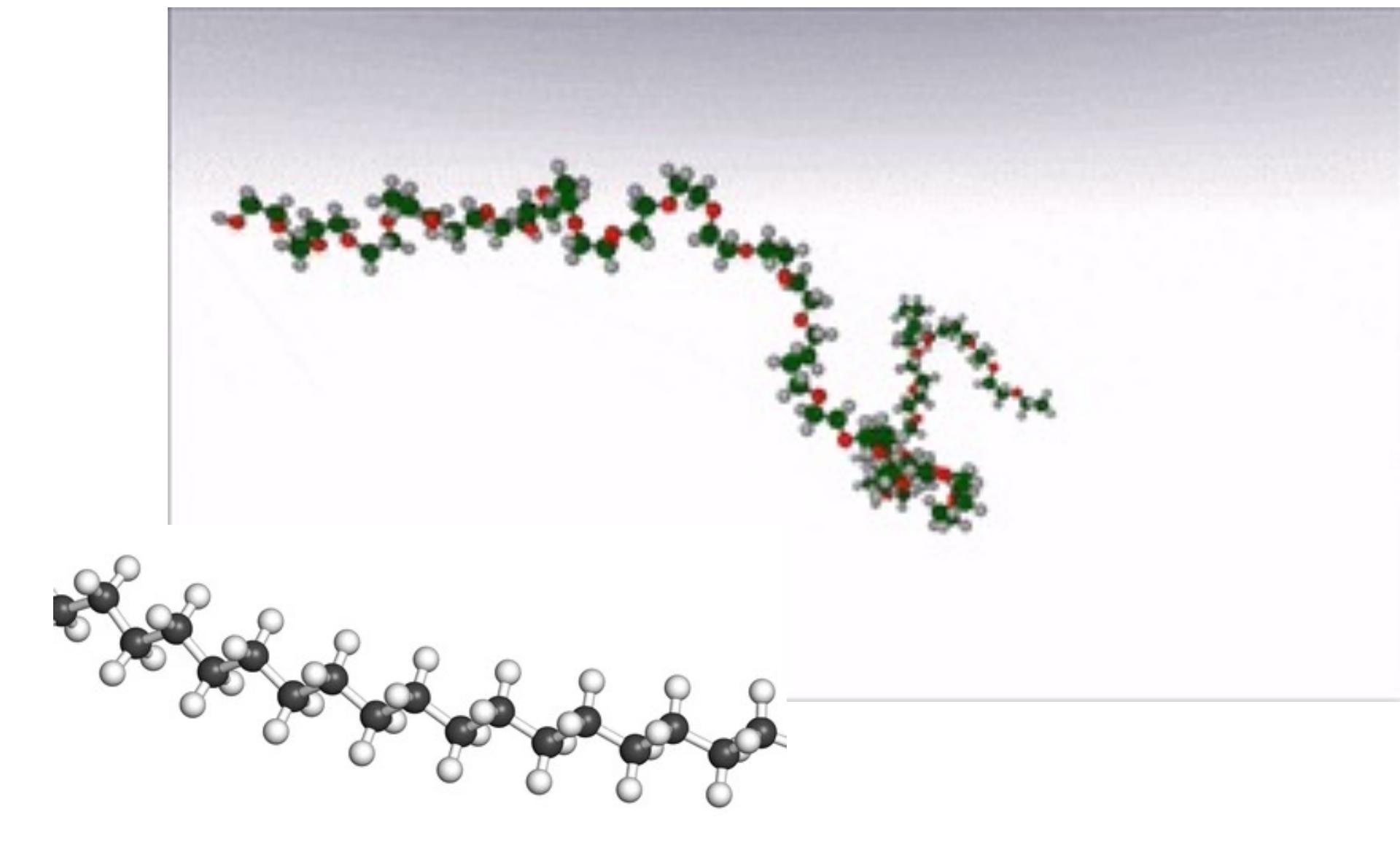
No. of bonds:
No. of angles:
No. of dihedrals:



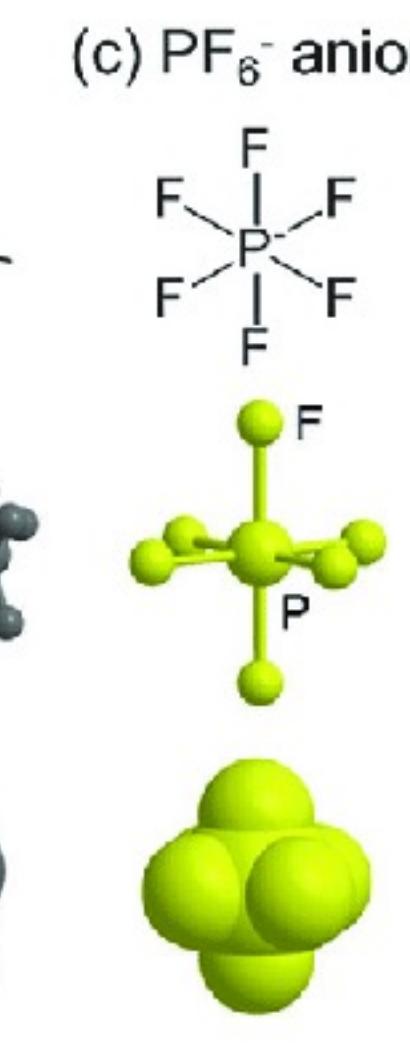
Alkanes



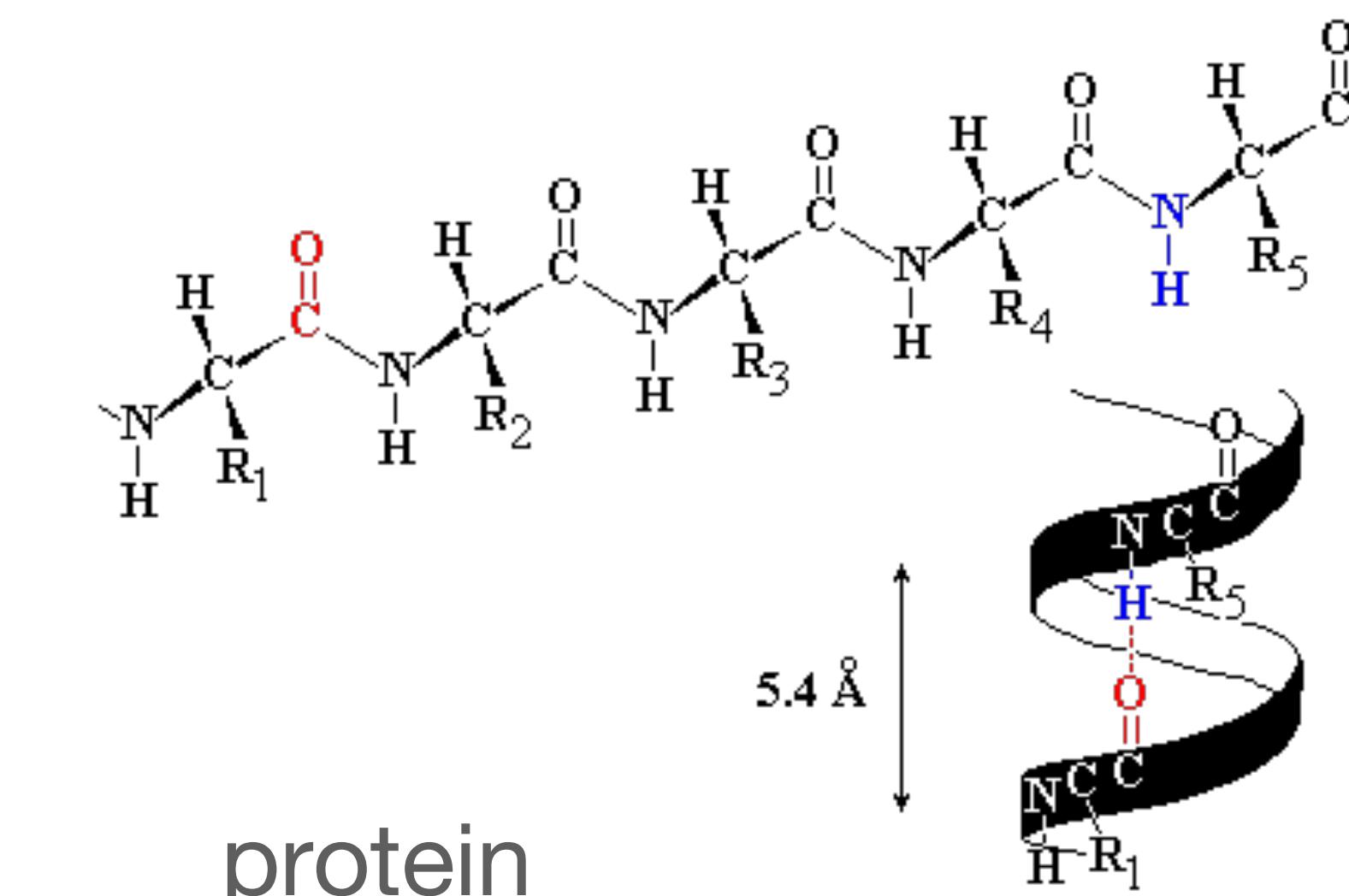
graphene



polymer



Ionic liquid

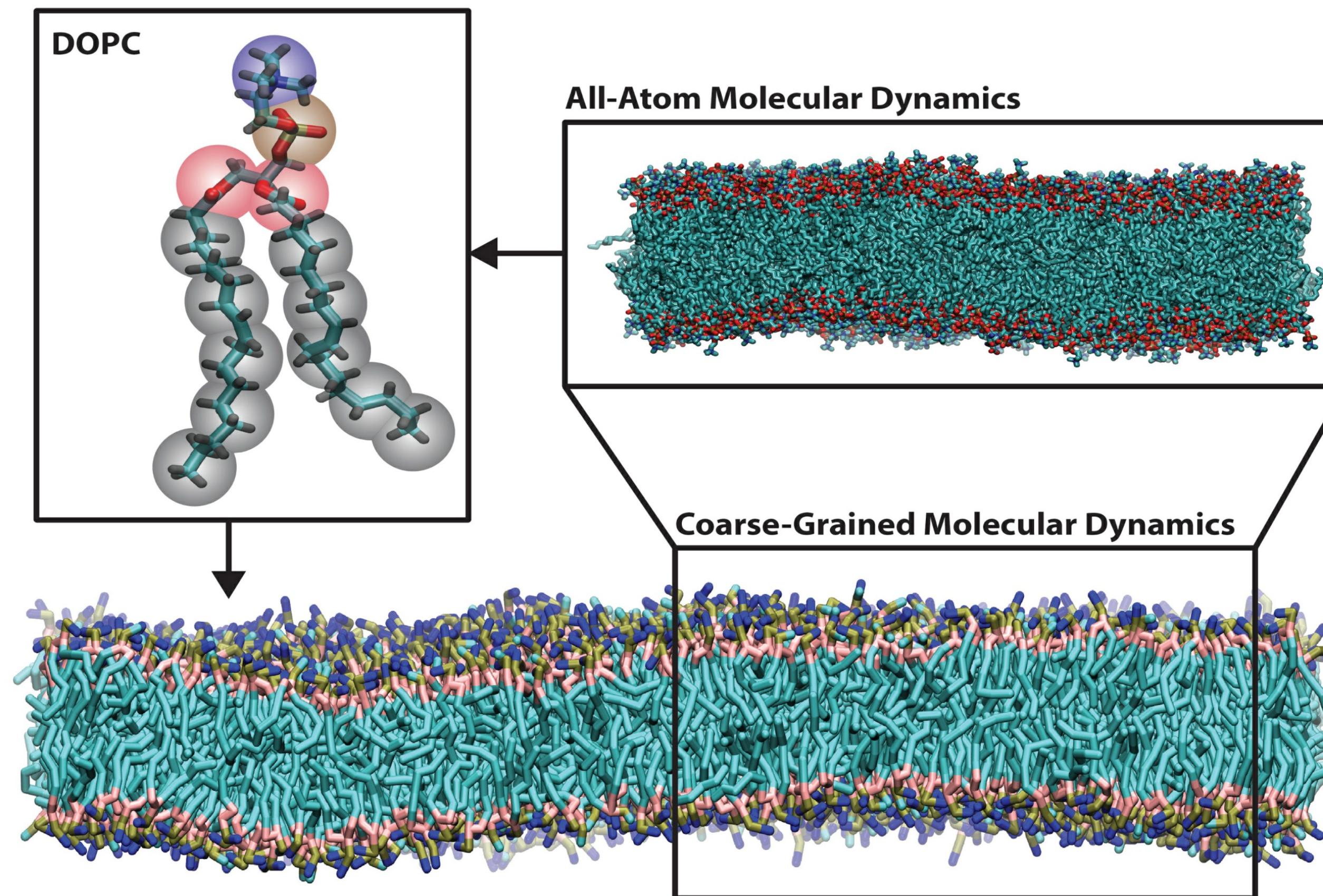


protein

Parameterisation of force-fields

- Non-bonded and torsional terms most sensitive
- Vibrational frequencies
- Atomic coordinates: X-ray diffraction, neutron scattering
- Inter-atomic distance: NMR
- Quantum mechanics calculations provide data for parameterisation

Coarse-grained modeling: Membrane modeling

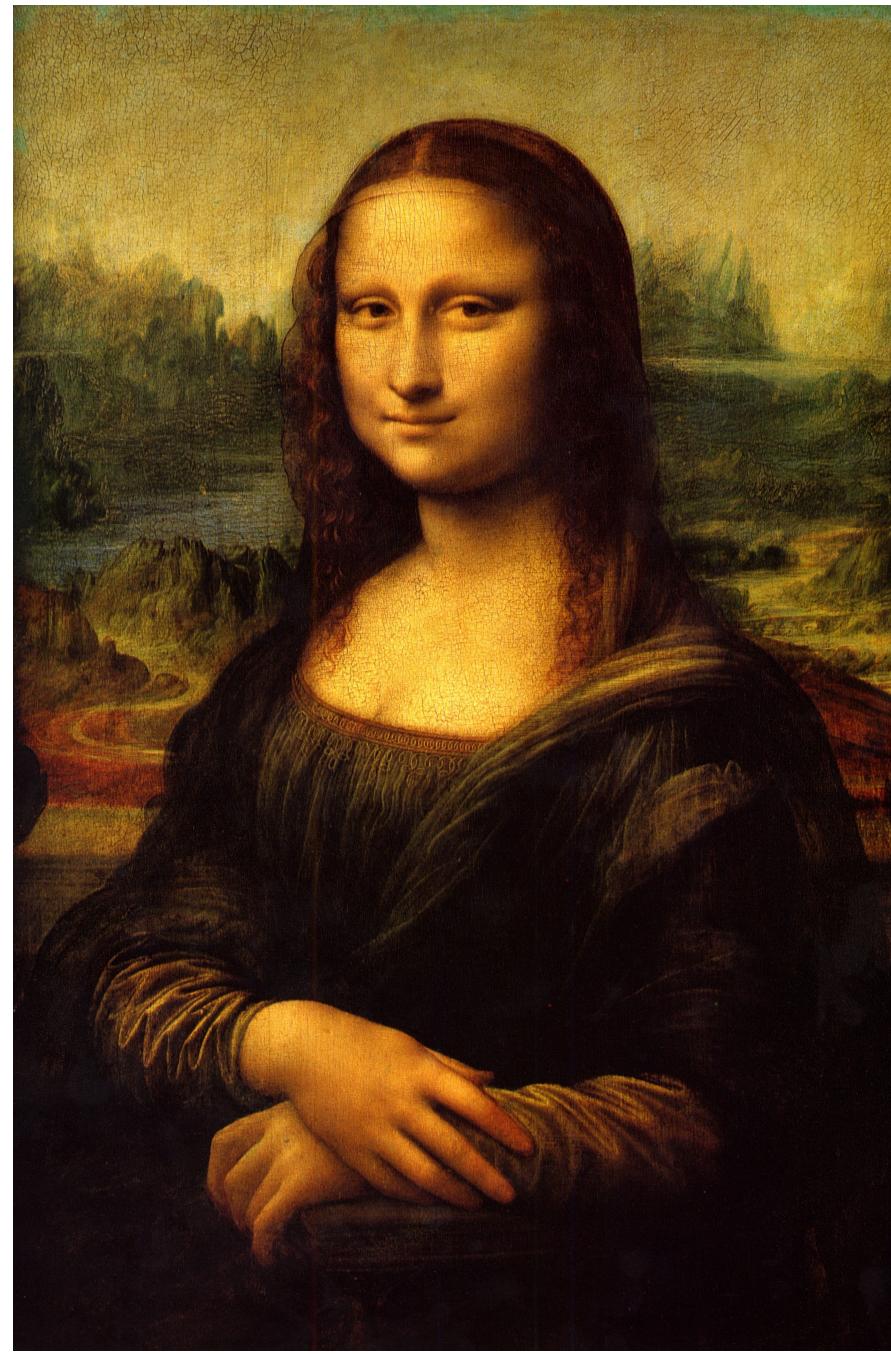


Coarse-graining: Multi-scale models

- Many complex physical phenomena in liquids, soft materials, and biomolecular systems occur over length and time scales that are well beyond the current capabilities of atomic-level simulation.
- Novel approaches are developed that can access longer time and length scale phenomena : Coarse-graining
 - Group of atoms clustered into new “CG” sites.
 - CG sites interact through more computationally efficient effective interactions.
 - **3 goals:**
 - a.) to develop a computationally cheaper CG model
 - b.) to develop a CG model that has a smoother underlying energy landscape:
Faster equilibration, larger time steps
 - c.) to represent correct physical behavior



Louvre Museum, Paris



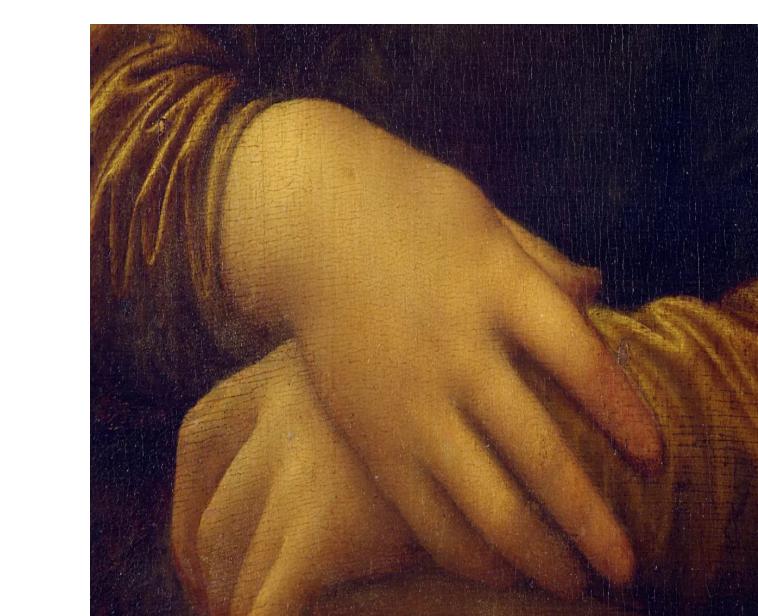
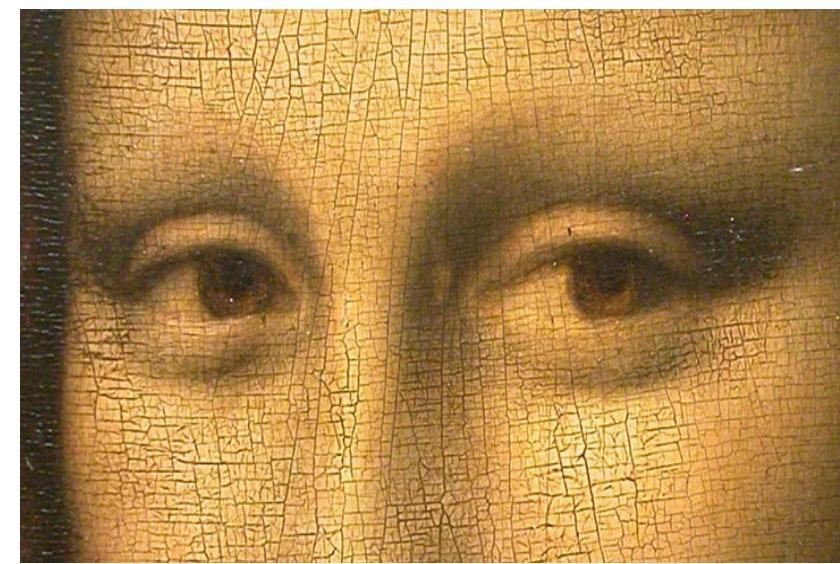
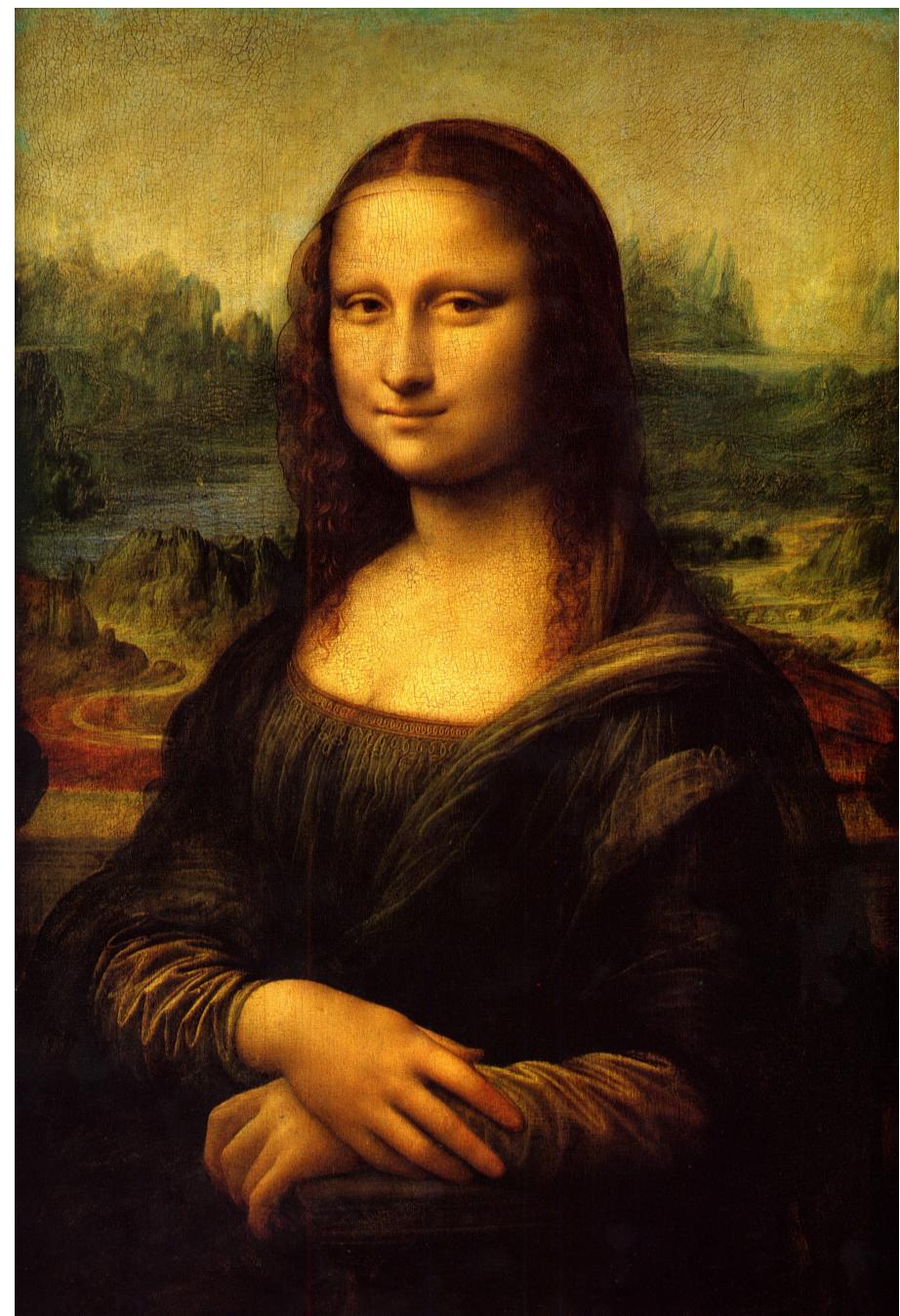
High resolution



Low resolution

“Coarse grained “

Desired properties determine the level of coarse graining or fine-grained details



X



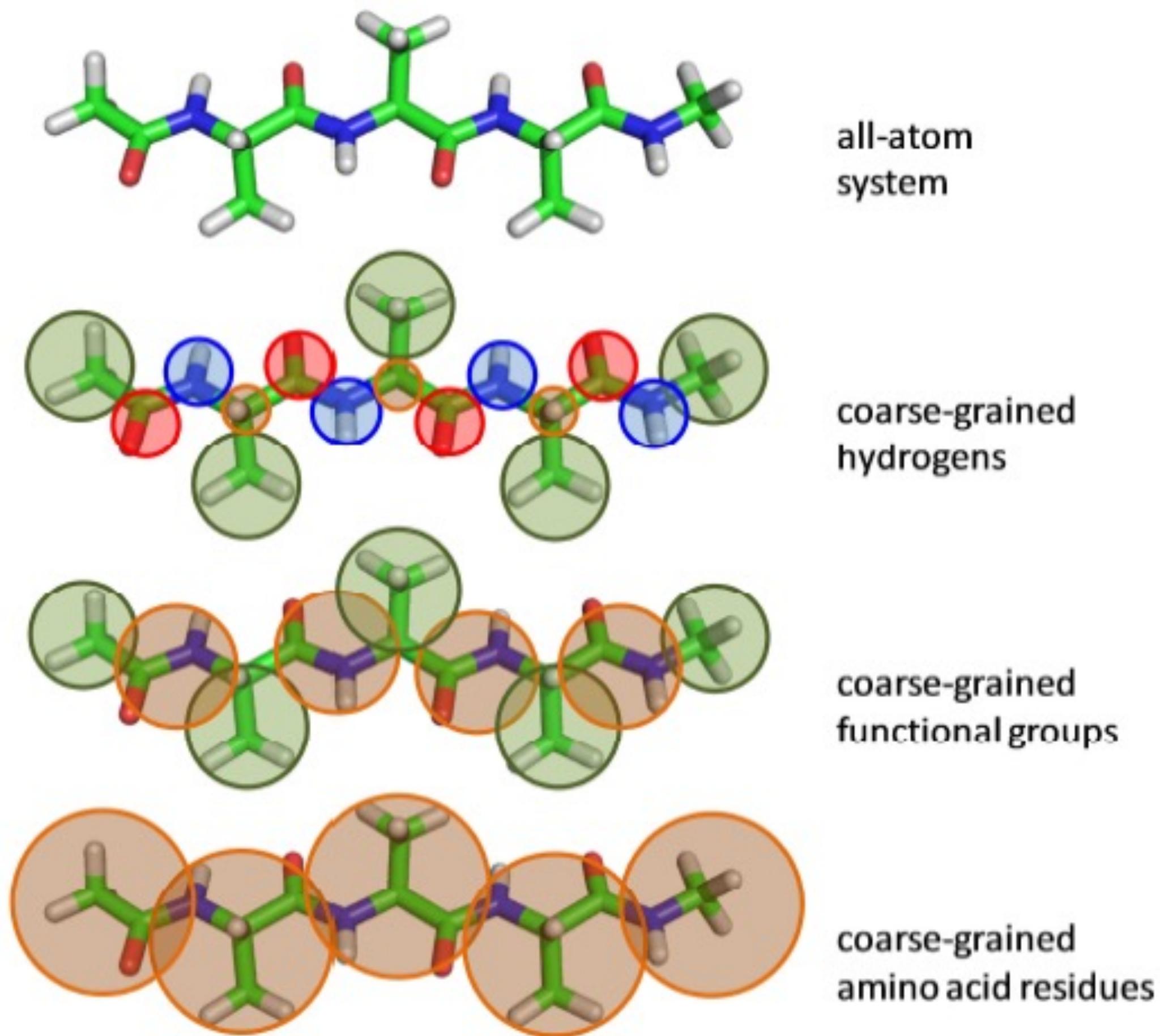
X



The overall properties of the coarse-grained model should remain the same as in fine-grained all-atom model

Procedure of coarse-graining models

Mapping scheme



Fine-grained model

Mapping scheme

- irrelevant degree of freedom can be lost, important ones should be kept
- there is no way to determine an optimal mapping scheme.

Coarse-grained model

