Week 1-2

Establishing Common Language
Crystal Structure and Binding

Chapter 1.4, 2.1-2.4

Objectives: Structure of Organic Solids

- Introduce basic terminology of organic materials
- Discuss relationship of crystal structure to properties
- Introduce the basic terminology and concepts of crystals and crystal lattices
  - Fill in the gaps
- Discuss crystal binding
  - Physical properties and constants
- Learn about organic lattices and their equilibrium structures
  - Energy minimization
- Growth and epitaxy
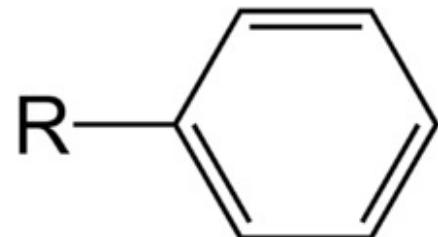
First: Establishing a vocabulary

(Without a common language, there can be no common understanding)
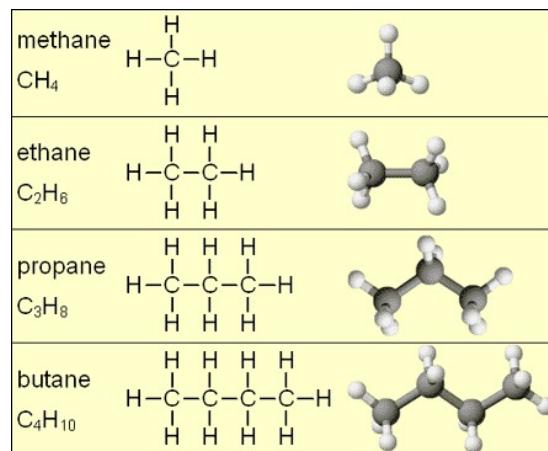
- Illustration of molecular structure
- Basic molecular units and structures
- Standard terminologies

Organic Electronics
Stephen R. Forrest

Benzene, phenyl, aryl
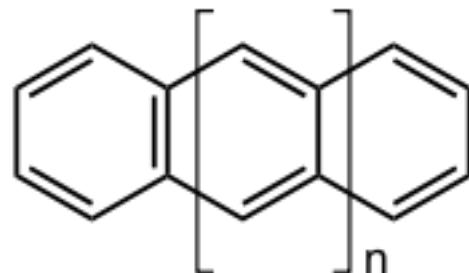
- **Benzene**: C_6H_6

- **Phenyl**: the phenyl group or phenyl ring is a cyclic group of atoms with the formula **C_6H_5**. Phenyl groups are closely related to benzene.

- **Aryl**: A functional group of the form C_6H_5 attached to a molecule

- **Alkanes** are the simplest organic molecules, consisting of only carbon and hydrogen and with <u>only single bonds</u> between carbon atoms. **Alkanes** are the basis for naming the majority of organic compounds (their nomenclature). **Alkanes** have the general formula C_nH_{2n+2}.
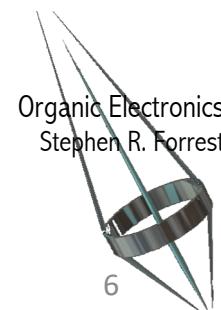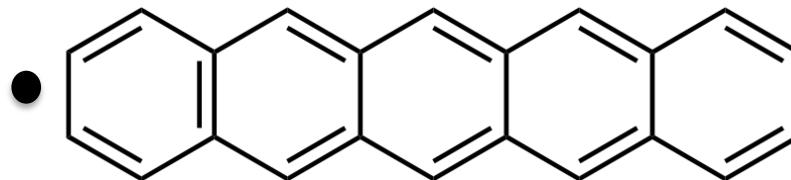

- **Polyacenes**: The acenes or polyacenes are a class of organic compounds, and <u>polycyclic aromatic hydrocarbons</u> made up of linearly fused benzene rings.

Aromatics and Radicals
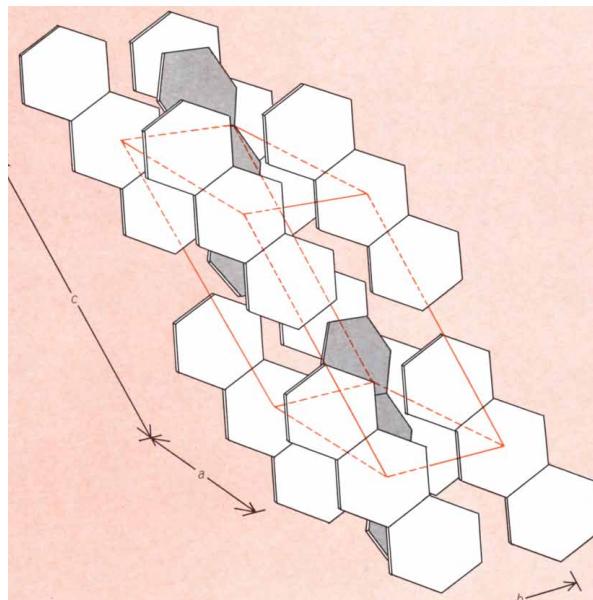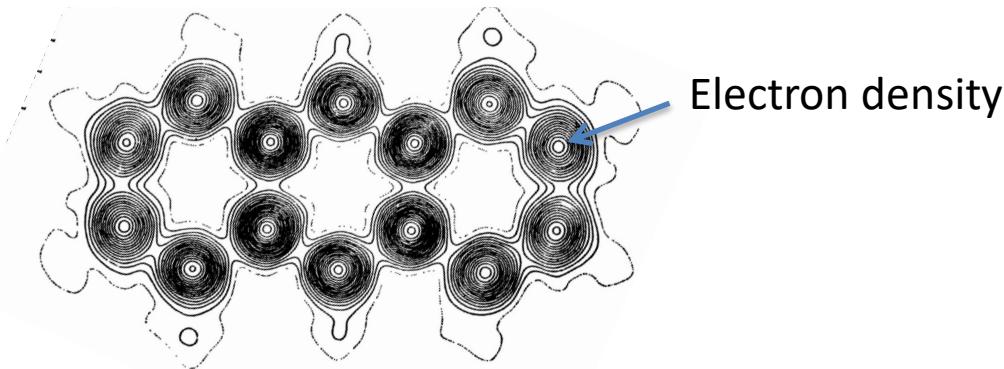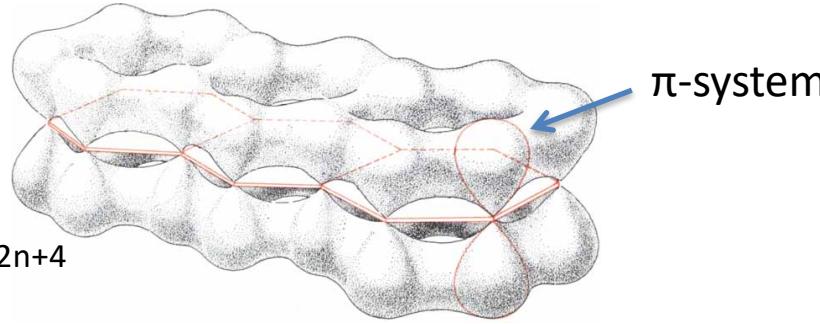
- **Aromaticity**: materials consisting of <u>closed carbon rings </u>where the C bonds are in <u>resonance</u>.

    - Double-single bond structure of the molecule allows the bond arrangement to alternate between C atom pairs in the ring.

    - To be aromatic the molecule must be <u>planar</u> and have <u>an ODD number of π electron pairs</u>. (see anaromatic)

- **Polycyclic Aromatic Hydrocarbon (PAH)**: organic compounds containing only carbon and hydrogen—that are composed of multiple aromatic rings (organic rings in which the electrons are delocalized)

- **Radical**: A charged molecule that is either anionic or cationic. A cation is a <u>positively charged </u>molecule, and an anion is <u>negatively charged</u>. An excess electron is typically denoted by a solid dot.

Pentacene anion

Anthracene: A classic aromatic molecule

- $C_{14}H_{10}$
- It is a PAH with form $C_{4n+2}H_{2n+4}$
- n=number of rings

π-system

Electron density
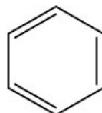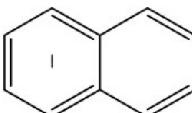
Conjugation

- a **conjugated system** is a system of connected p-orbitals with delocalized electrons in a molecule

- Conjugation lowers the overall energy of the molecule and increases stability.

- Conjugation is conventionally represented as having alternating single and multiple bonds.

A Few Polyacenes
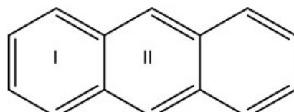
Benzene
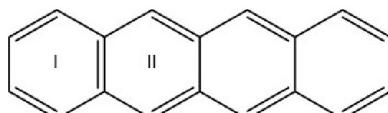
Naphthalene
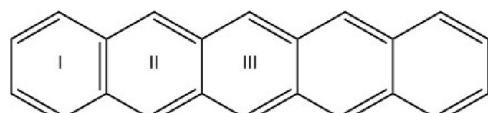
Anthracene
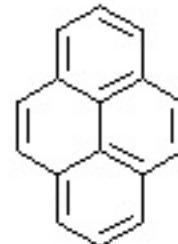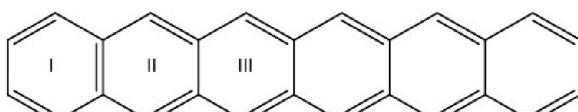
Tetracene
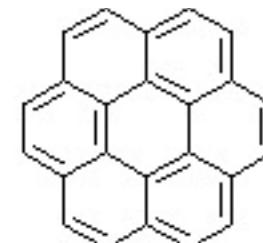
Pentacene
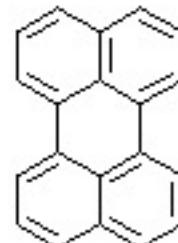
Hexacene
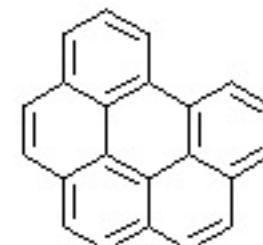
Pyrene
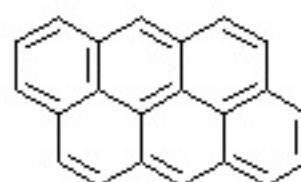
Coronene
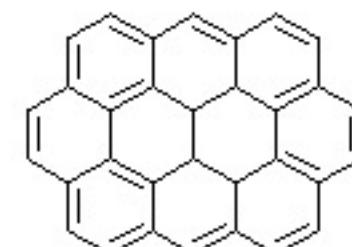
Perylene

Benzoperylene
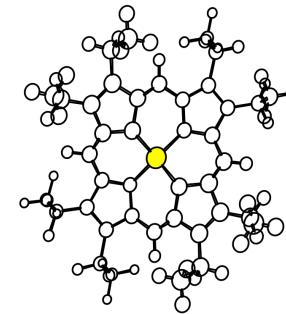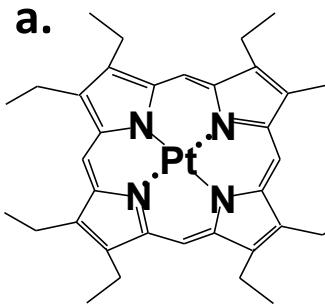
Anthanthrene

Ovalene
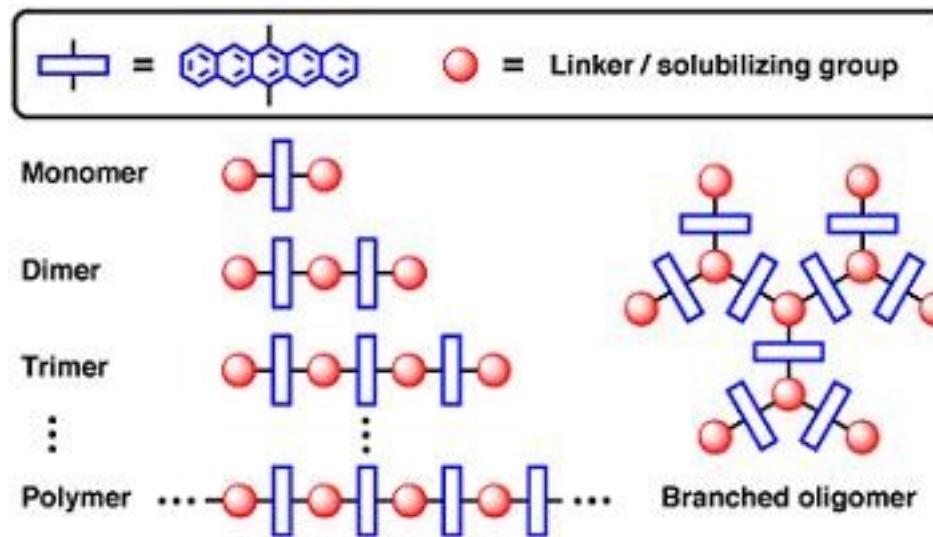
Monomer, Oligomer

- **Monomer:** a molecular complex with a well-defined molecular weight that consists of a single irreducible unit

a.
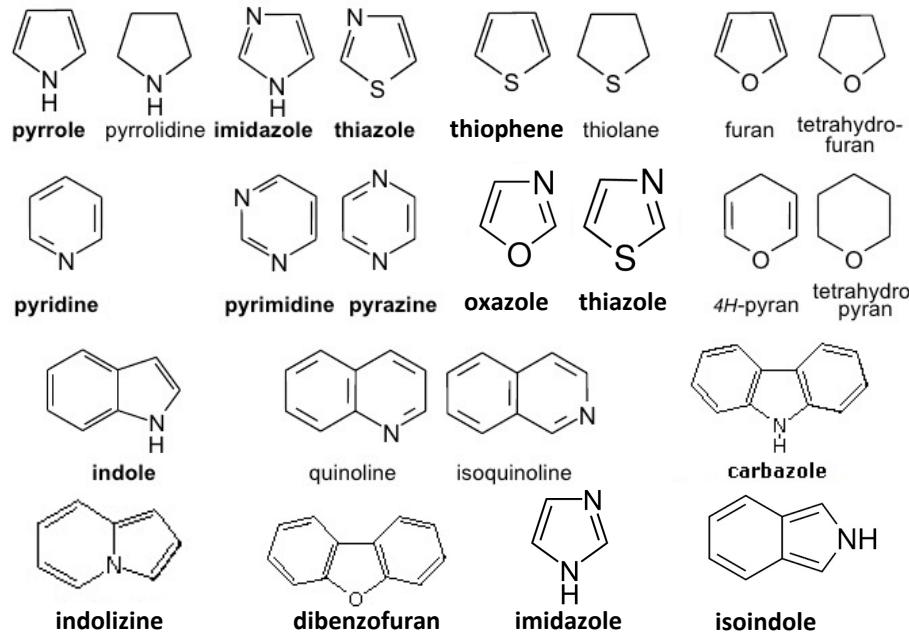
mer (Greek: meros)-part

- **Oligomer:** a molecu... ...onsists of a few monomer unit... the number of mon... ...le, not limited but is always w... defined. (e.g. dimer... ...etc.)

| | = CCCC | ⬤ = Linker / solubilizing group |

Monomer

Dimer

Trimer

⋮ ⋮

Polymer ··· — — ··· Branched oligomer

10

Heterocycles

pyrrole pyrrolidine **imidazole** **thiazole** **thiophene** thiolane furan tetrahydro-furan

pyridine **pyrimidine** **pyrazine** **oxazole** **thiazole** 4H-pyran tetrahydro-pyran

indole quinoline isoquinoline **carbazole**

indolizine **dibenzofuran** **imidazole** **isoindole**
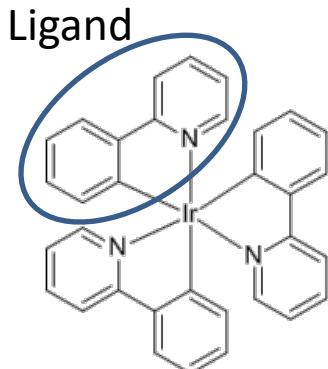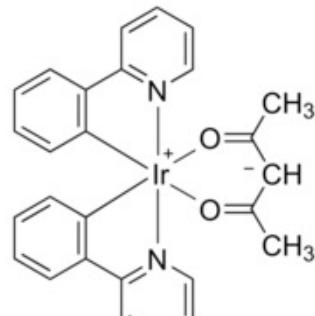
ligand: Latin: can be tied

Metalorganics

Ligand
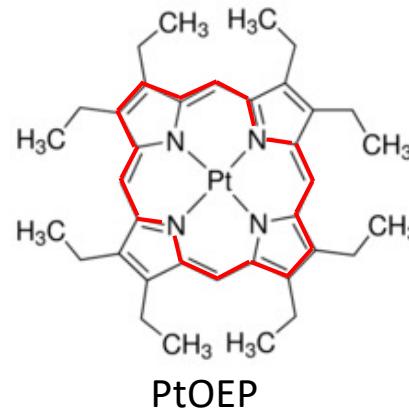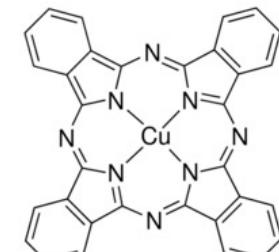
$Ir(ppy)_3$

$Ir(ppy)_2acac$

Porphyrins

PtOEP
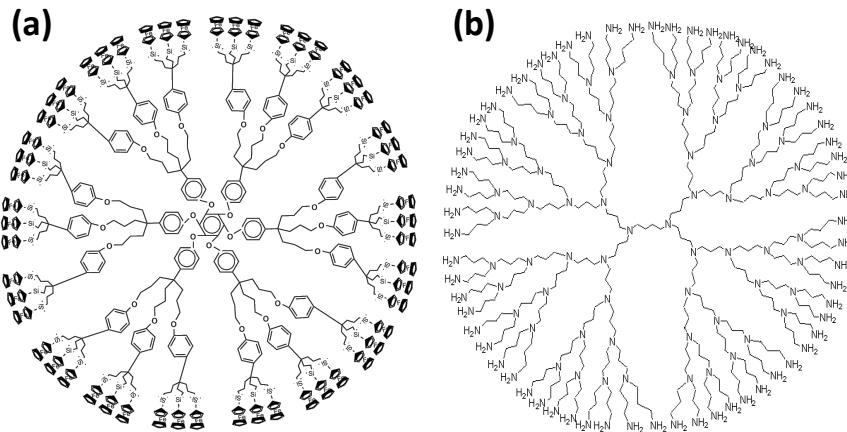
Phthalocyanines
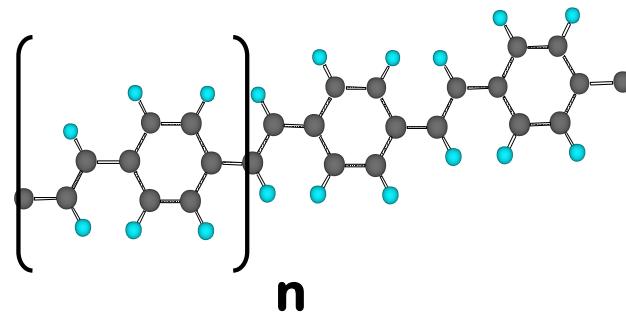
CuPc

Dendrimer, Polymer
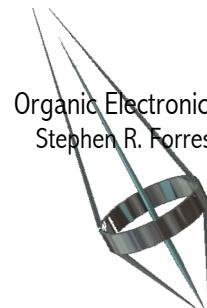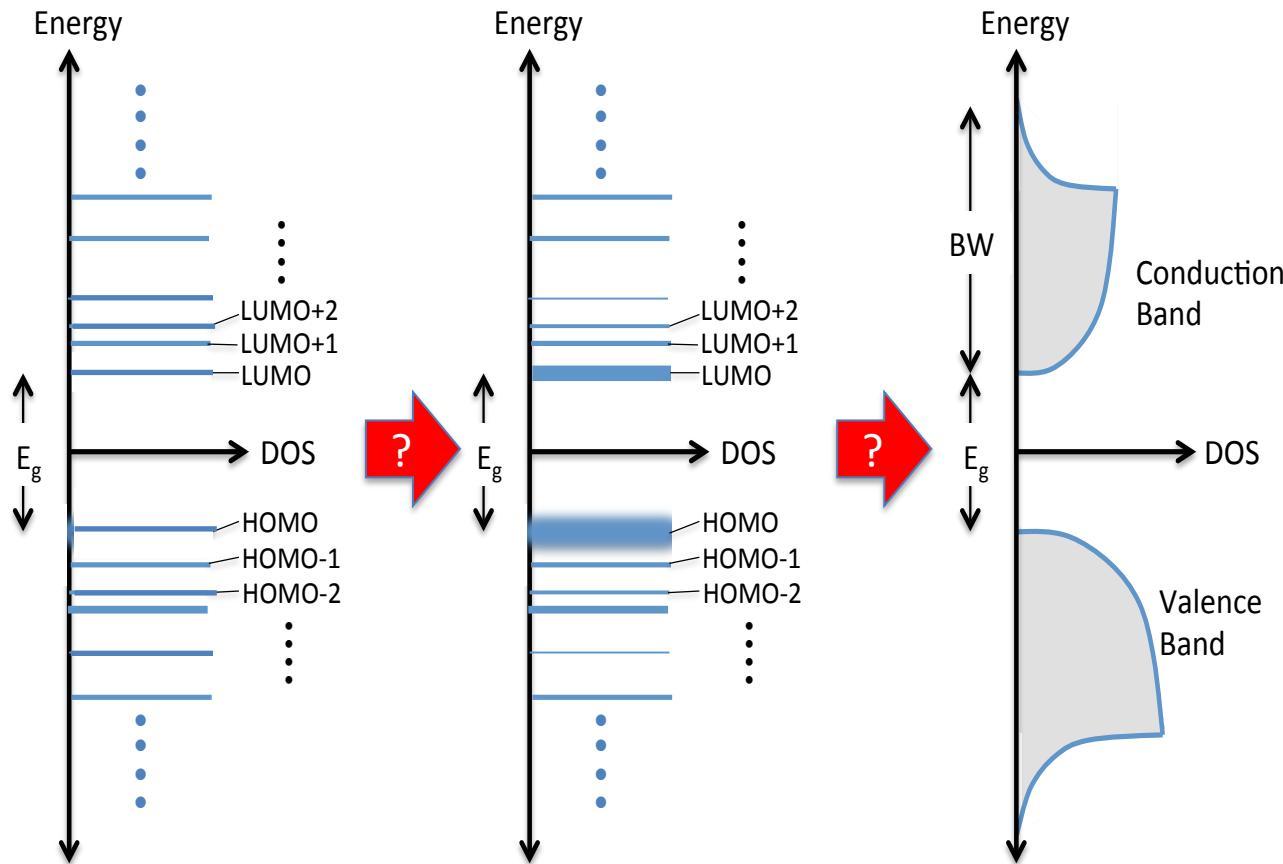
- **Dendrimer**: An oligomer that is built with repeat units radiating (like dendrites) from a central core. Each concentric repeat unit is a *generation*. (a) 54 ferrocene (so named due to the 54 ferrocene groups on its periphery), and (b) a 4th generation dendrimer.

(a) **(b)**

- **Polymer**: a molecular complex consisting of an undefined number of monomeric repeat units and hence undefined molecular weight.

n

At what point does the molecular picture give way to the solid?
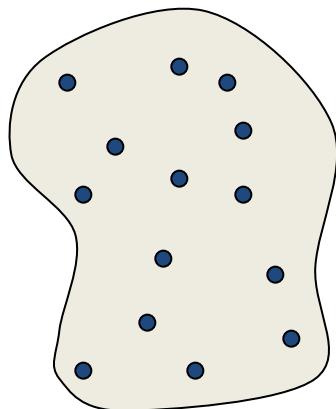
Crystal Morphologies
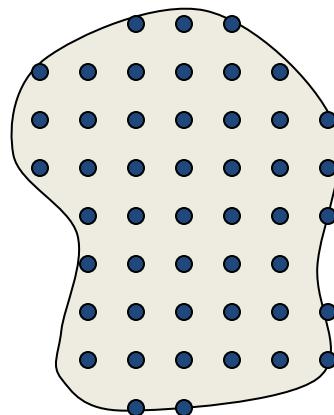
Structure determines electronic properties

- Electrical conduction
    - Range from conducting to insulating
- Solid state: not liquids or gases
- Organics found and exploited in all morphological types
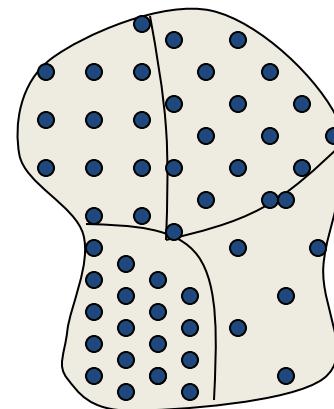
Types of solids

Amorphous   Crystalline   Polycrystalline
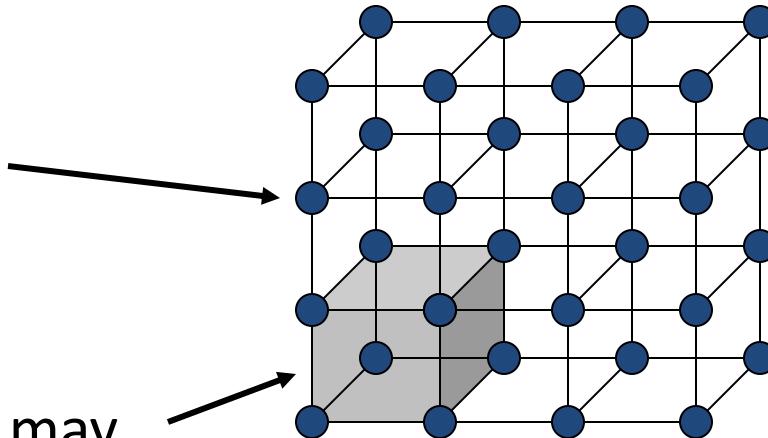
Crystal Structure

Simple cubic

Lattice

Periodic arrangement of atoms in a crystal
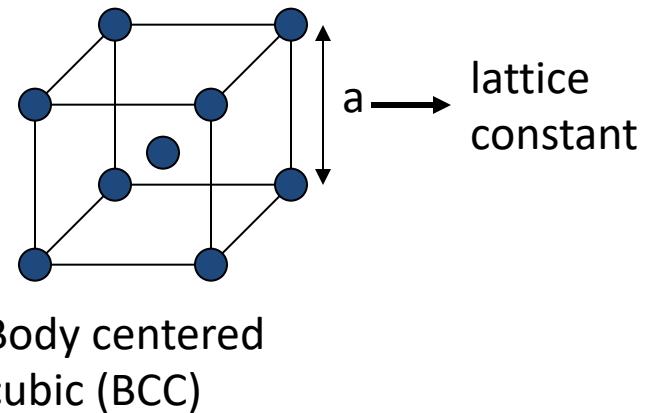
Unit cell

Small volume of crystal that may be used to reproduce the entire crystal—**space filling**
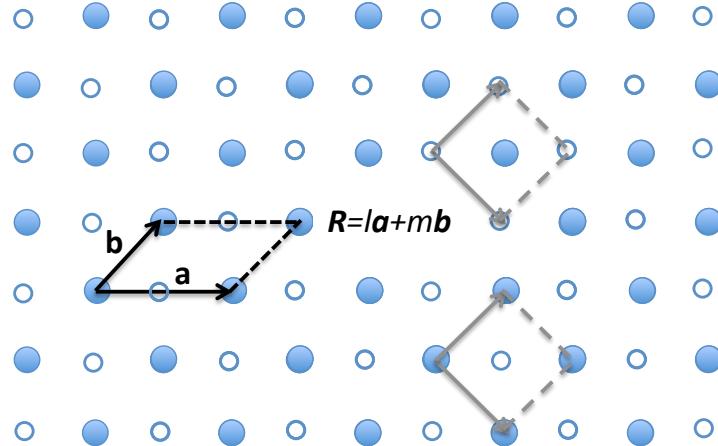
Primitive unit cell

Smallest unit cell that describes the crystal

Lattice constant is a *material parameter*

a — lattice constant

Body centered cubic (BCC)
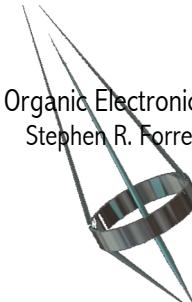
Lattices

$R=l\boldsymbol{a}+m\boldsymbol{b}$

Translation vector: R=la+mb+nc

A translation vector moves a **R** point to an equivalent point in the lattice
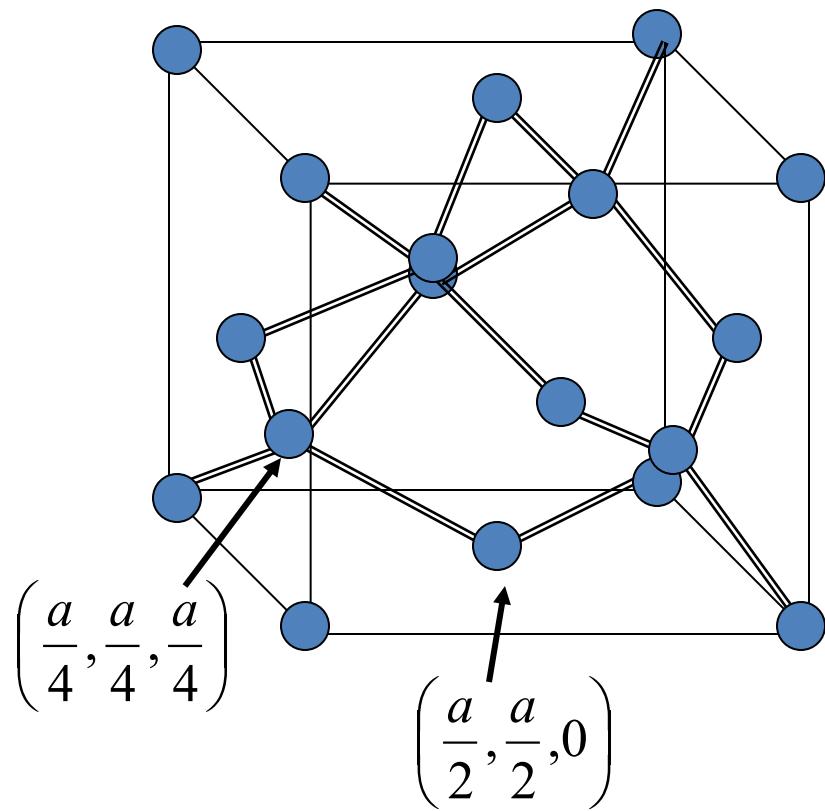
Volume: $V_{Cell} = \mathbf{a} \bullet (\mathbf{b} \times \mathbf{c})$

Common Semiconductor Crystal Structures

Diamond

(Si, Ge)

$$\left(\frac{a}{4}, \frac{a}{4}, \frac{a}{4}\right)$$

$$\left(\frac{a}{2}, \frac{a}{2}, 0\right)$$
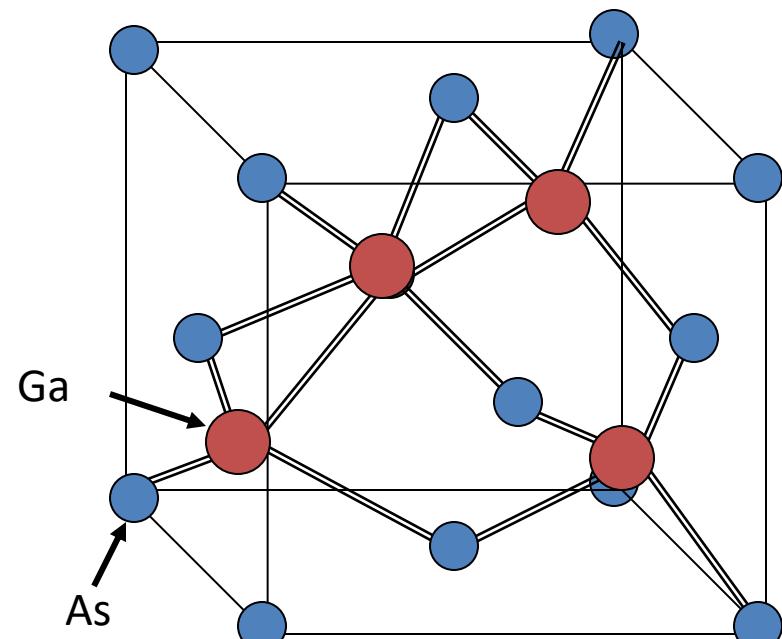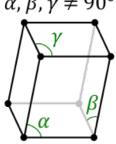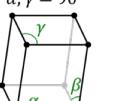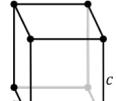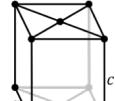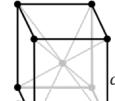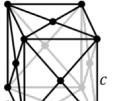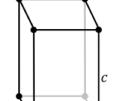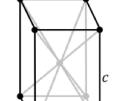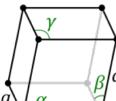
Zinc Blende

(GaAs, InP, AlSb, ...)

Ga

As

Bravais Lattices

- These lattices define the crystal structure

Almost all organics fall
Into these lattice types
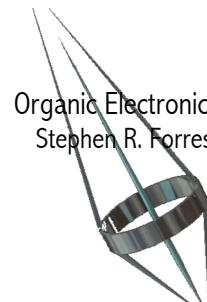
Can you think of a molecule
That fits this structure?

coordination #=12 (fcc)
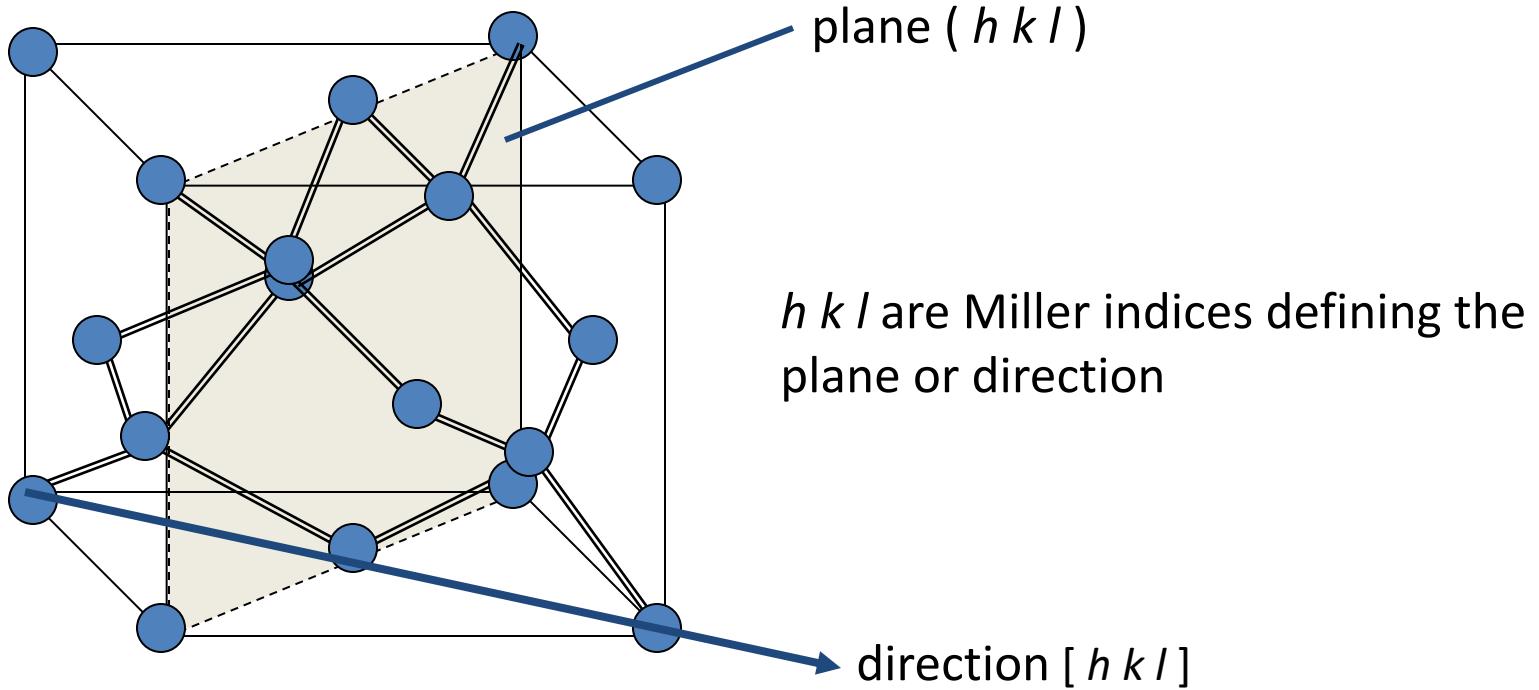
Reciprocal Lattice

- Condition of self transformation: $\psi(\mathbf{r})=\psi(\mathbf{r+R}) \sim e^{i\mathbf{G}\cdot\mathbf{r}} = e^{i\mathbf{G}\cdot(\mathbf{R+r})}$

- Then **G** is the reciprocal lattice vector: $\mathbf{G}\cdot\mathbf{R} = 2\pi$

- The reciprocal lattice defined by **G**, has an <u>identical symmetry to the physical lattice</u> defined by **R**.

- It is then straightforward to show that the primitive reciprocal lattice vectors are defined by the following relationships:

$$\mathbf{\bar{a}} = 2\pi\frac{\mathbf{b}\times\mathbf{c}}{V_{Cell}} \quad \mathbf{\bar{b}} = 2\pi\frac{\mathbf{c}\times\mathbf{a}}{V_{Cell}} \quad \mathbf{\bar{c}} = 2\pi\frac{\mathbf{a}\times\mathbf{b}}{V_{Cell}}$$

- What is the relationship between the unit cell volume in reciprocal to real space?
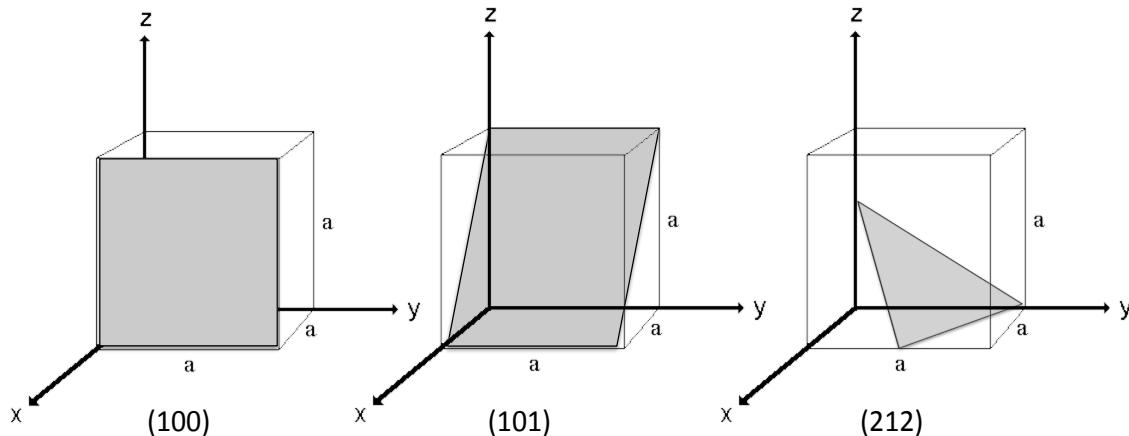
Miller Indices

Need a method to describe crystalline direction/planes

plane (*h k l*)

h k l are Miller indices defining the plane or direction

direction [*h k l*]

Defining Crystal Directions and Planes

- ## Miller indicies

(100) (101) (212)
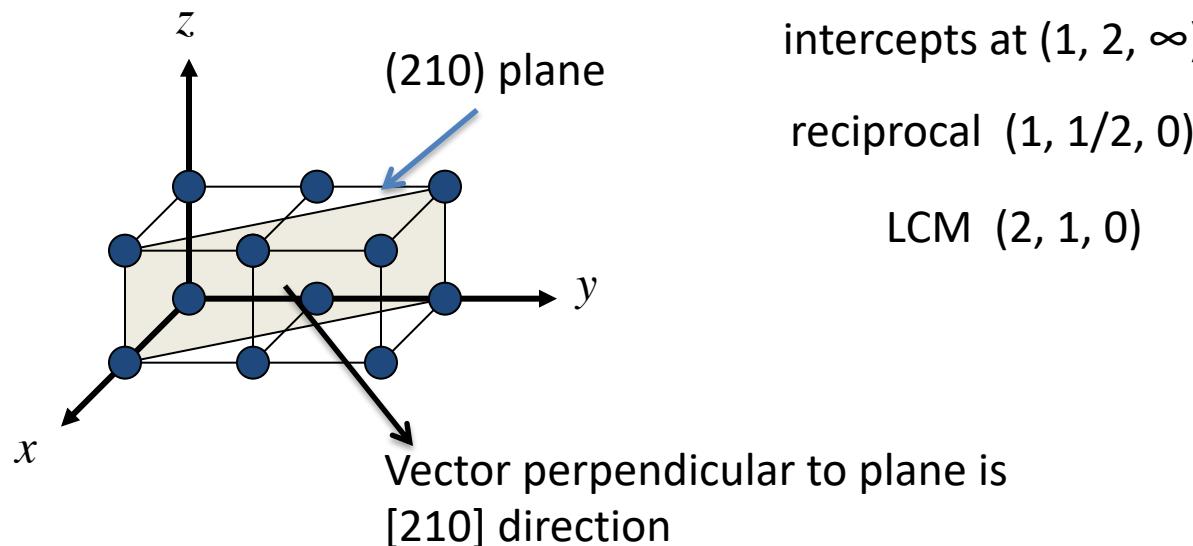
- Miller indices: *h, k, l*, are the <u>lowest integers</u> that are the <u>inverse of the intercepts</u> <u>between the plane and the axes</u>
- (a,b,c) define plane
- {a,b,c} define set of equivalent planes (e.g. (100), (010), (001), etc. for cubic lattice)
- [a,b,c] for lattice direction
- <a,b,c> for set of equivalent lattice directions

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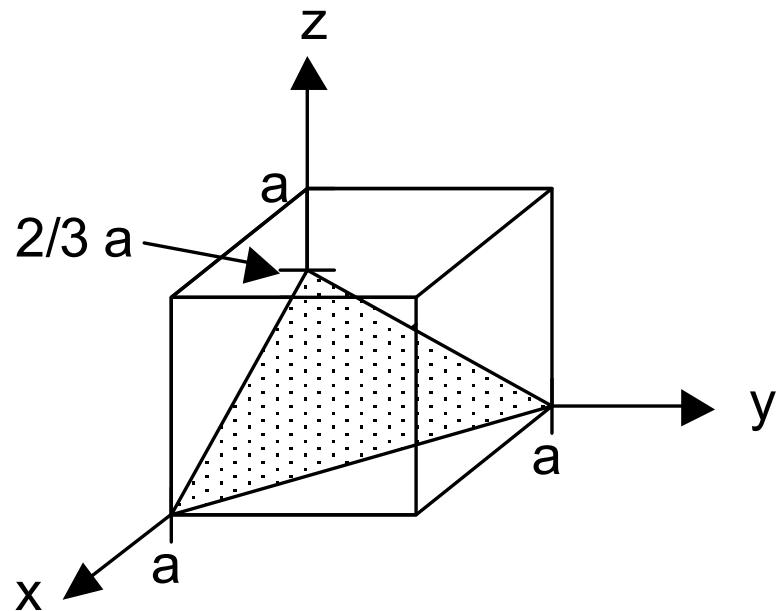
Determining Miller Indices

1. Find intercepts (as multiple of a lattice constant)

2. Take reciprocal

3. Multiply by lowest common denominator

intercepts at (1, 2, ∞)

reciprocal (1, 1/2, 0)

LCM (2, 1, 0)

(210) plane

Vector perpendicular to plane is
[210] direction

Example: Miller Index

Determine the representation of the plane below
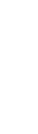
Ionic Bonds

$$U_{ij}(\mathbf{r}) = \pm \frac{q^2}{4\pi\varepsilon_0 |\mathbf{r}_i - \mathbf{r}_j|}$$
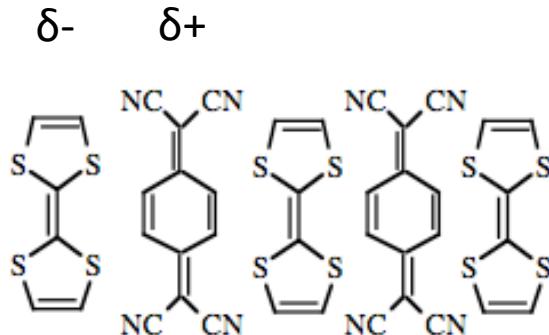
For a solid, pairwise ionic interactions must be summed over all *N* ions, which leads to a net attractive energy of:

$$U_{attract} = \frac{q^2}{4\pi\varepsilon_0} \sum_{i,j}^{N} \left(\frac{1}{\mathbf{R}_{ij}} - \frac{1}{|\mathbf{R}_{ij} - \mathbf{a}|} \right)$$

Similar atoms
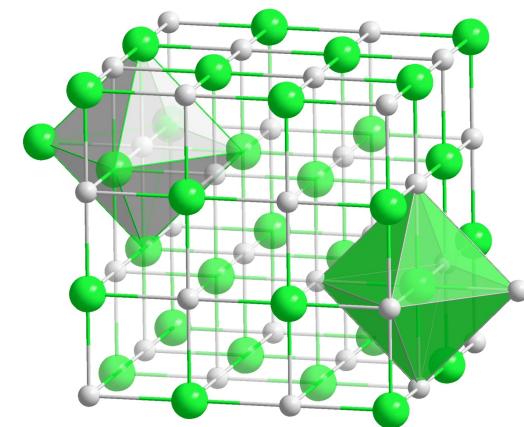
Oppositely charged atoms

δ-   δ+

NaCl (fcc)
TTF-TCNQ: charge transfer complex

$$U_{tot}(r) = \frac{\sigma}{r^m} - \frac{\alpha q^2}{4\pi\varepsilon_0} \frac{1}{r}$$

Madelung Constant $\Rightarrow \alpha_{fcc} = \left(6 - \frac{12}{\sqrt{2}} + \frac{8}{\sqrt{3}} - \frac{6}{2} + ... \right) = 1.7476$

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Equilibrium Crystal Structure
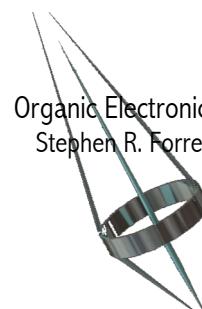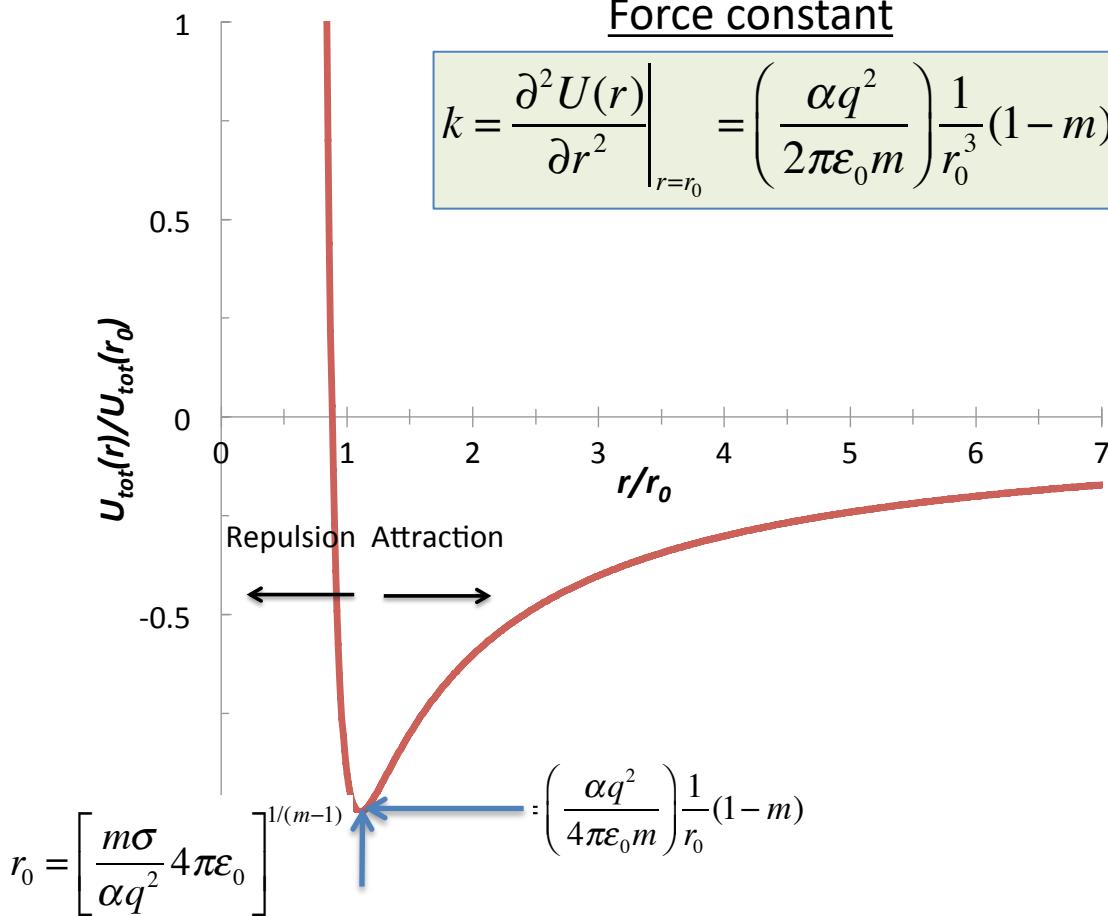
$$U_{tot}(r) = \frac{\sigma}{r^m} - \frac{\alpha q^2}{4\pi\varepsilon_0}\frac{1}{r}$$

$$\left.\frac{\partial U_{tot}}{\partial r}\right|_{r=r_0} = 0$$

Equilibrium condition
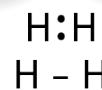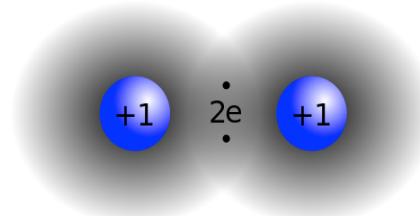
Force constant

$$k = \left.\frac{\partial^2 U(r)}{\partial r^2}\right|_{r=r_0} = \left(\frac{\alpha q^2}{2\pi\varepsilon_0 m}\right)\frac{1}{r_0^3}(1-m)$$

$$r_0 = \left[\frac{m\sigma}{\alpha q^2}4\pi\varepsilon_0\right]^{1/(m-1)}$$

$$= \left(\frac{\alpha q^2}{4\pi\varepsilon_0 m}\right)\frac{1}{r_0}(1-m)$$

Covalent Bonding

Shared electron systems between ionic cores

H:H
H – H

H_2, Si, Ge, C....
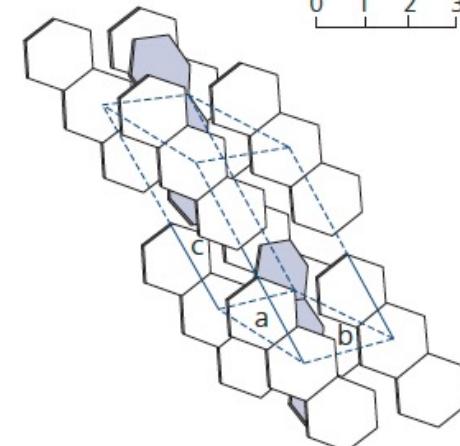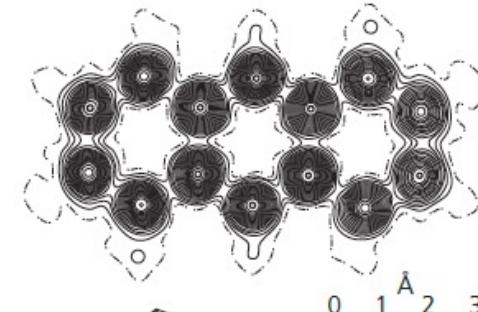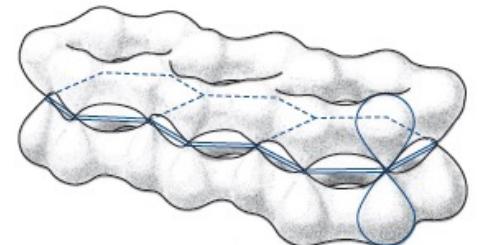
H_2^+

$$H\Psi(\mathbf{r},\mathbf{R}) = E\Psi(\mathbf{r},\mathbf{R})$$

$$H = -\frac{\hbar^2}{2m}\nabla_\mathbf{r}^2 - \sum_i \frac{\hbar^2}{2M_i}\nabla_{\mathbf{R}_i}^2 + V(\mathbf{r},\mathbf{R}_i)$$

$$V(\mathbf{r},\mathbf{R}_1,\mathbf{R}_2) = -\frac{q^2}{4\pi\varepsilon_0}\left(\frac{1}{|\mathbf{r}-\mathbf{R}_1|} + \frac{1}{|\mathbf{r}-\mathbf{R}_2|} - \frac{1}{|\mathbf{R}_1-\mathbf{R}_2|}\right)$$

It's complicated as N increases!

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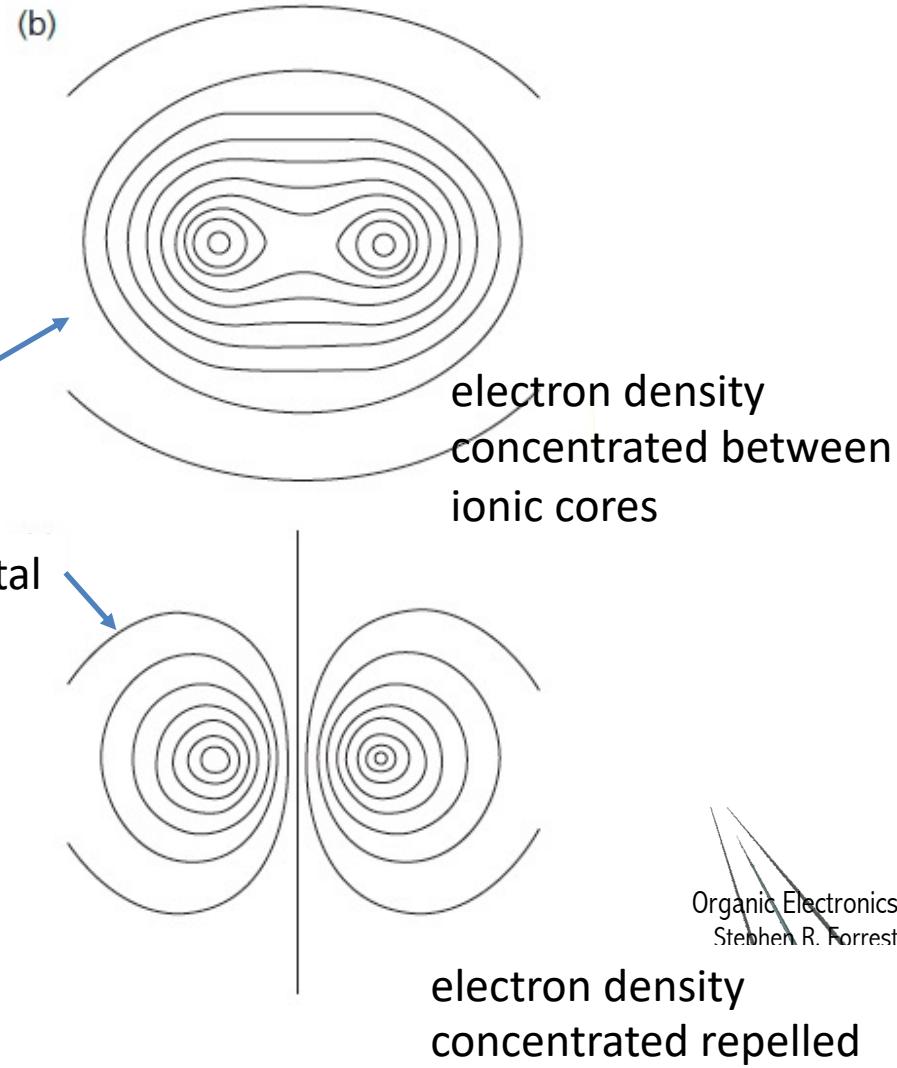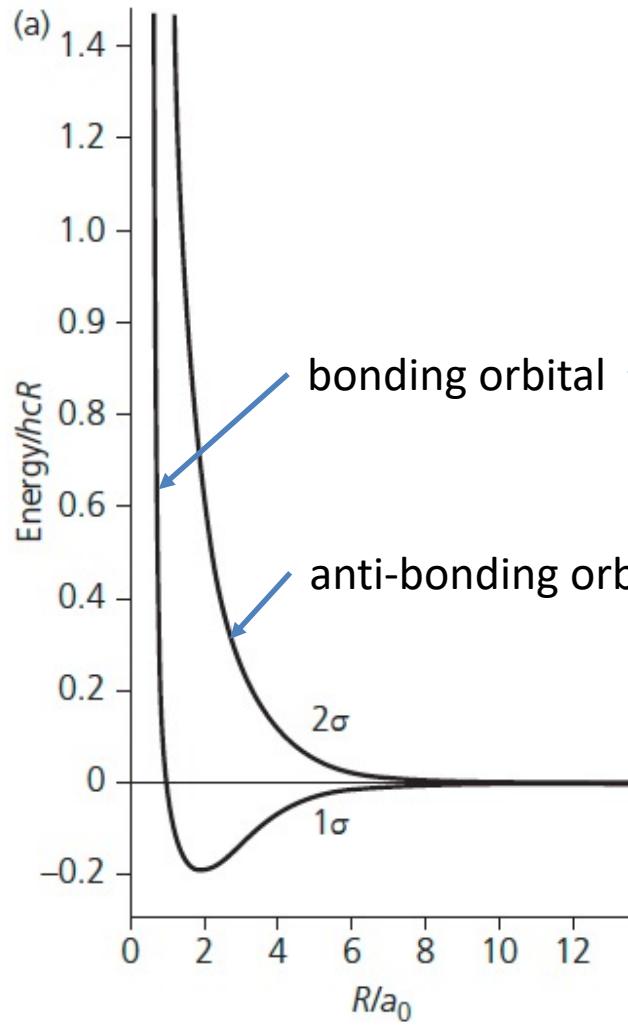
Organic Molecules with C-C bonds
e.g. Anthracene
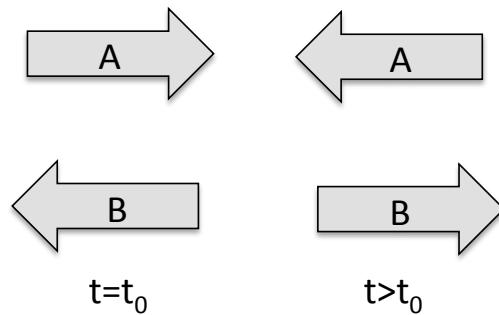
Solutions to the H₂⁺ Molecule

- Two solutions exist

(a)

bonding orbital

anti-bonding orbital

2σ

1σ

R/a_0

Energy/hcR

(b)

electron density concentrated between ionic cores

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electron density concentrated repelled
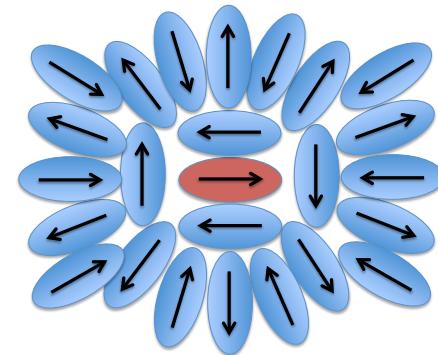
van der Waals bonding

- Purely electrostatic *instantaneous* induced dipole-induced dipole interaction between π-systems of nearby molecules.

Medium around the dipole is *polarized*

Multipole potential is from expansion

$$\Phi(\mathbf{r}) = \frac{1}{4\pi\varepsilon_0\varepsilon_r}\left[\frac{q}{r} + \frac{\mathbf{p}\cdot\mathbf{r}}{r^3} + \frac{1}{2}\sum_{i,j}Q_{ij}\frac{r_i r_j}{r^5} + \cdots\right]$$

Monopole dipole quadropole

$$\mathbf{p} = \int \mathbf{r}\rho(\mathbf{r})d^3\mathbf{r} \quad : \text{Dipole moment}$$
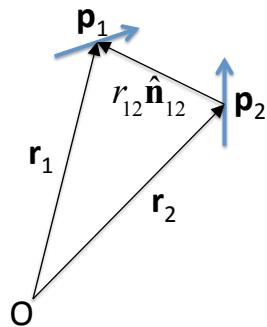
$$\mathbf{F}(\mathbf{r}) = \frac{3\hat{\mathbf{n}}(\mathbf{p}\cdot\hat{\mathbf{n}}) - \mathbf{p}}{4\pi\varepsilon_0\varepsilon_r r^3} \quad : \text{Field from dipole moment}$$

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$$E_r = \frac{2p\cos\theta}{4\pi\varepsilon_0\varepsilon_r r^3}$$

$$E_\theta = \frac{p\sin\theta}{4\pi\varepsilon_0\varepsilon_r r^3}$$

$$E_\phi = 0$$

Dipole interactions

$$E(r) = \frac{3\hat{n}(p \cdot \hat{n}) - p}{4\pi\varepsilon_0\varepsilon_r r^3}$$

<u>Fixed dipoles</u>

For $p_1 = p_2$

$$U = -p \cdot F(r)$$

$$U(r_{12}) = \frac{p_1 \cdot p_2 - 3(\hat{n}_{12} \cdot p_1)(\hat{n}_{12} \cdot p_2)}{4\pi\varepsilon_0\varepsilon_r r_{12}^3} = \frac{p^2}{4\pi\varepsilon_0\varepsilon_r}\left\{\frac{\hat{p}_1 \cdot \hat{p}_2}{r_{12}^3} - \frac{3(r_{12} \cdot \hat{p}_1)(r_{12} \cdot \hat{p}_2)}{r_{12}^5}\right\}$$

Applying Boltzmann statistics to the energy as a function of angle, it can be shown:

Keesom interaction: $\quad U(r_{12}) = -\dfrac{2p^4}{3(4\pi\varepsilon_0\varepsilon_r)kTr^6} = -\dfrac{A_{DD}}{r^6}$
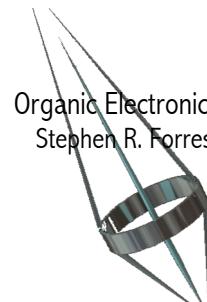
<u>Important relationships:</u>

$U = -\dfrac{1}{2}kx^2$ (in one dimension for an SHO)

$\Rightarrow U' = F = -kx$

$\Rightarrow U'' = -k \quad$ = force constant = compressibility of the solid

$\Rightarrow$ Bulk modulus $= B = Vol(U'') = -Vol(k)$

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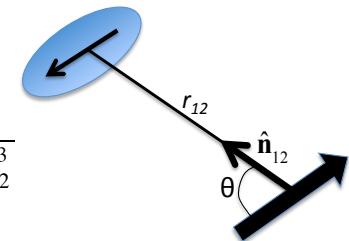
Van der Waals interaction

For van der Waals, the <u>induced dipoles are parallel</u> $(\hat{\mathbf{p}}_1 = \hat{\mathbf{p}}_2)$

Then our energy equation reduces to: $U = \dfrac{p_1 p_2}{4\pi\varepsilon_0\varepsilon_r r_{12}^3}\{1 - 3\cos\theta\} \approx -\dfrac{p_1 p_2}{2\pi\varepsilon_0\varepsilon_r r_{12}^3}$

The field from one dipole at the other: $\mathbf{F}(\mathbf{r}) = \dfrac{3\hat{\mathbf{n}}(\mathbf{p}\cdot\hat{\mathbf{n}}) - \mathbf{p}}{4\pi\varepsilon_0\varepsilon_r r^3} \Rightarrow F(r) \approx \dfrac{p_1}{4\pi\varepsilon_0\varepsilon_r r^3}$
(the induced dipoles must be parallel)

<u>Induced dipoles </u>depend on the polarizability (α) of the molecule (which may different from the medium, ε_r:

$$\mathbf{p}_{ind}(\mathbf{r}) = \alpha\mathbf{F}(\mathbf{r}) \Rightarrow p_2 \approx \dfrac{\alpha p_1}{4\pi\varepsilon_0\varepsilon_r r^3}$$
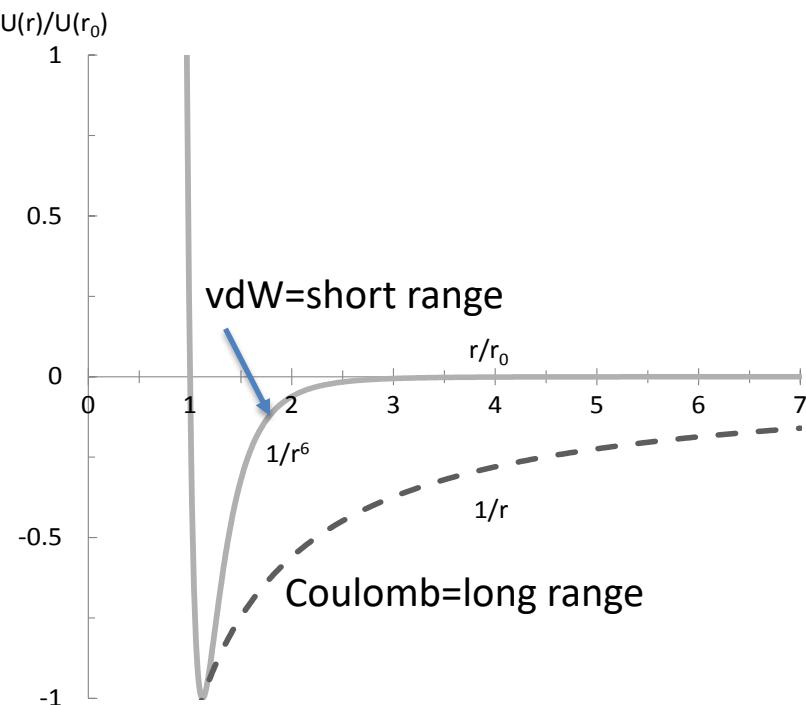
From which we get the "London interaction energy": $\quad U_{vdW} \approx \dfrac{\alpha p_1^2}{\left(4\pi\varepsilon_0\varepsilon_r\right)^2 r^6}$

$$U(r_{12}) = -\dfrac{A_{disp}}{r_{12}^6} \quad : \text{Dispersion interaction}$$

$$U(r) = 4\varepsilon\left[\left(\dfrac{\sigma}{r}\right)^{12} - \left(\dfrac{\sigma}{r}\right)^6\right] \quad : \text{Lennard-Jones 6-12 potential}$$

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van der Waals Coefficients Between atoms

$U(r)/U(r_0)$

vdW=short range

r/r_0

$1/r^6$

$1/r$

Coulomb=long range

Atoms i-j	$r_{0,ij}$ Å	ε_{ij} kcal mol^{-1}
C-C	4.00	0.150
C-N	3.75	0.155
C-O	3.60	0.173
C-S	4.00	0.173
C-H	3.00	0.055
N-C	3.75	0.155
N-N	3.50	0.160
N-O	3.35	0.179
N-S	3.75	0.179
N-H	2.75	0.057
O-C	3.60	0.173
O-N	3.35	0.179
O-O	3.20	0.200
O-S	3.60	0.200
O-H	2.60	0.063
S-C	4.00	0.173
S-N	3.75	0.179
S-O	3.60	0.200
S-S	4.00	0.200
S-H	3.00	0.063
H-C	3.00	0.055
H-N	2.75	0.057
H-O	2.60	0.063
H-S	3.00	0.063
H-H	2.00	0.020

$$\frac{P}{kT} = \frac{N}{V} + B_2(T)\left(\frac{N}{V}\right)^2 + B_3(T)\left(\frac{N}{V}\right)^3 + ...$$

Virial coeff'ts from vdW interactions
- Deviations from ideal gas law
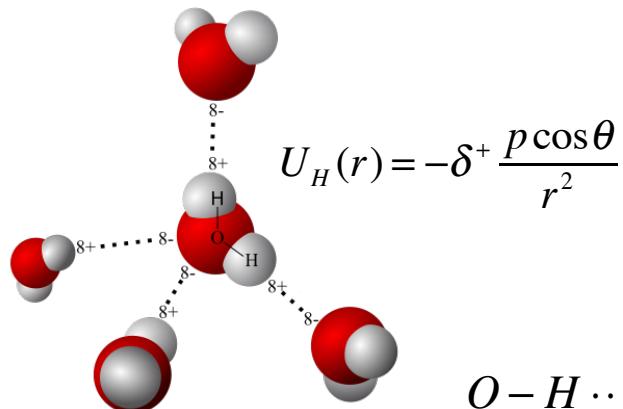
$$U_{crystal} = \frac{1}{2}\sum_{i \neq j} U(R_{ij})$$

: Equilibrium crystal structure found by calculating and then minimizing all atom-atom potentials over N atoms in molecules in solid
- Local vs. global minima?
- Huge numbers of degrees of freedom (6 per molecule!)
- Thermodynamics important (different structures with different k_BT)

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Hydrogen bonds

- Directional
- Coulombic

$$U_H(r) = -\delta^+ \frac{p\cos\theta}{r^2}$$

Israelachvili, *Intermolecular and Surface Forces*, Academic Press, 2011
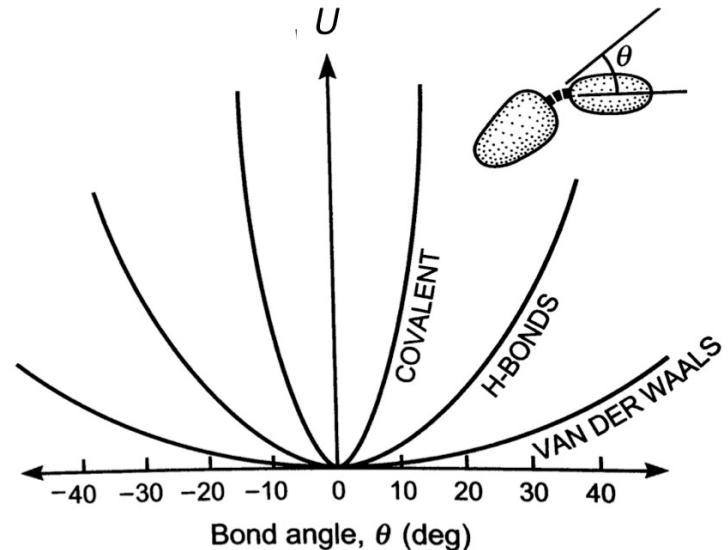
$O - H \cdots O$: Must be linear otherwise O-O repulsion dominates

O-H bond: 1Å
O...H bond: 1.6 -1.8 Å

H$\cdots$O and H$\cdots$N are usually only important

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Precise form of potential (Coulombic, exponential) usually not critical