Week 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

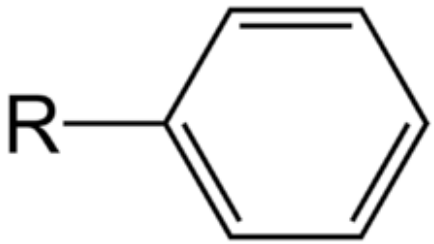
First: Establishing a vocabulary

(Without a common language, there can be no common understanding)

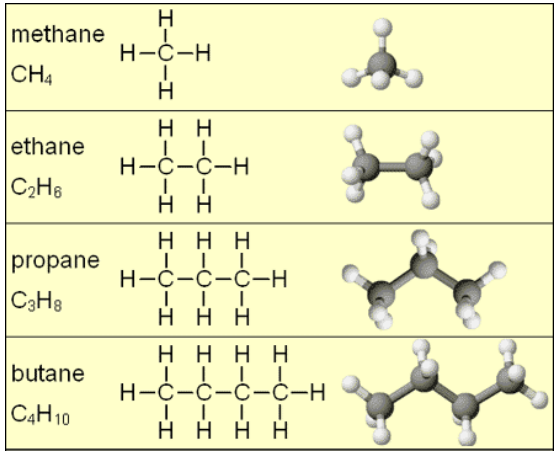
- Illustration of molecular structure
- Basic molecular units and structures
- Standard terminologies

Benzene, phenyl, aryl

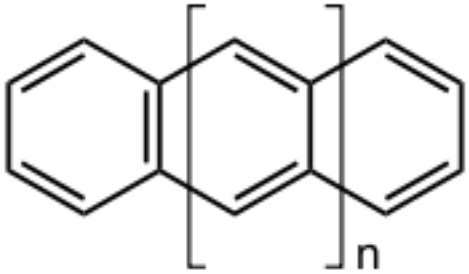
- **Benzene**: C_6H_6
- **Phenyl**: the phenyl group or phenyl ring is a cyclic group of atoms with the formula **C_6H_5**. Phenyl groups are closely related to benzene.
- **Aryl**: A functional group of the form C_6H_5 attached to a molecule



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



- **Polyacenes**: The acenes or polyacenes are a class of organic compounds. Polycyclic aromatic hydrocarbons made up of linearly fused benzene rings.



Aromatics and Radicals

- **Aromaticity**: materials consisting of closed carbon rings where the C bonds are in resonance.

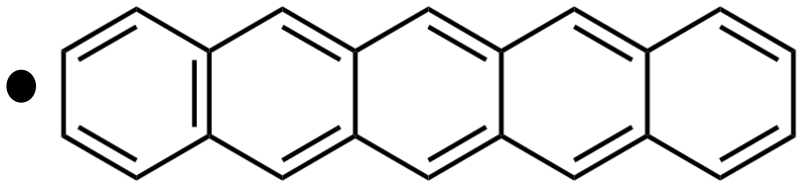
  - Double-single bond structure of the molecule allows the bond arrangement to alternate between C atom pairs in the ring.

  - To be aromatic the molecule must be planar and have an ODD number of π electron pairs. (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)

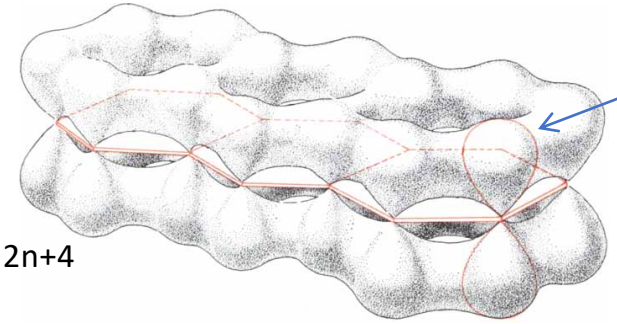
- **Radical**: A charged molecule that is either anionic or cationic. A cation is a positively charged molecule, and an anion is negatively charged. An excess electron is typically denoted by a solid dot.

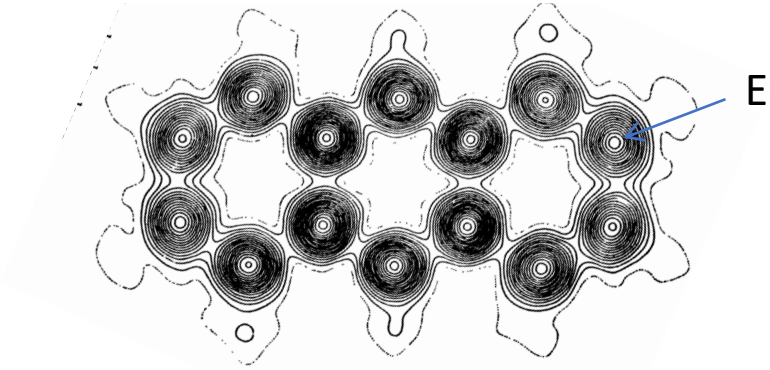
Pentacene anion

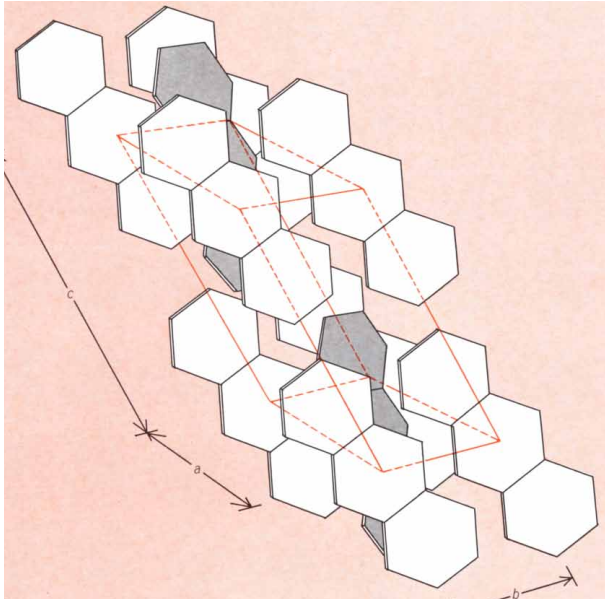


Anthracene: A classic aromatic molecule

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







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

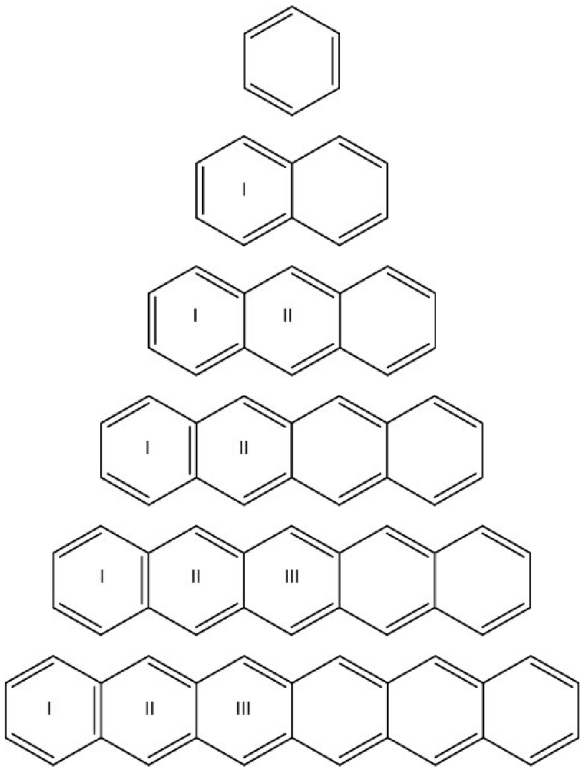
Naphthalene

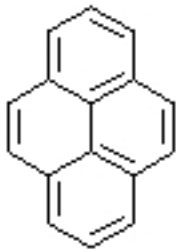
Anthracene

Tetracene

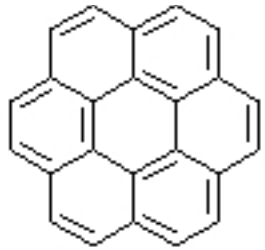
Pentacene

Hexacene

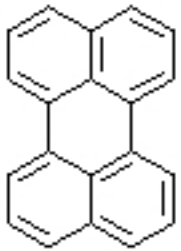




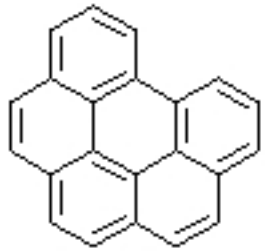
Pyrene



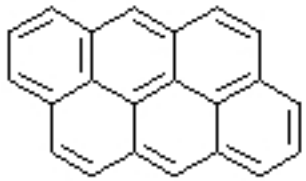
Coronene



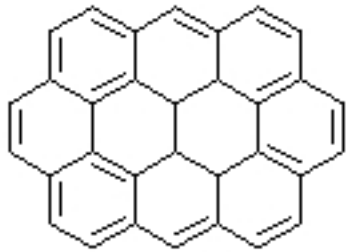
Perylene



Benzoperylene



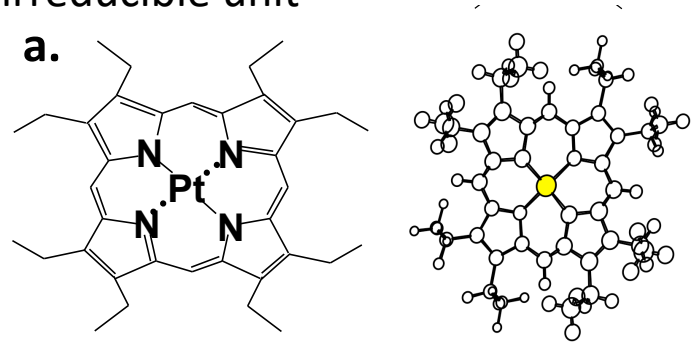
Antanthrene



Ovalene

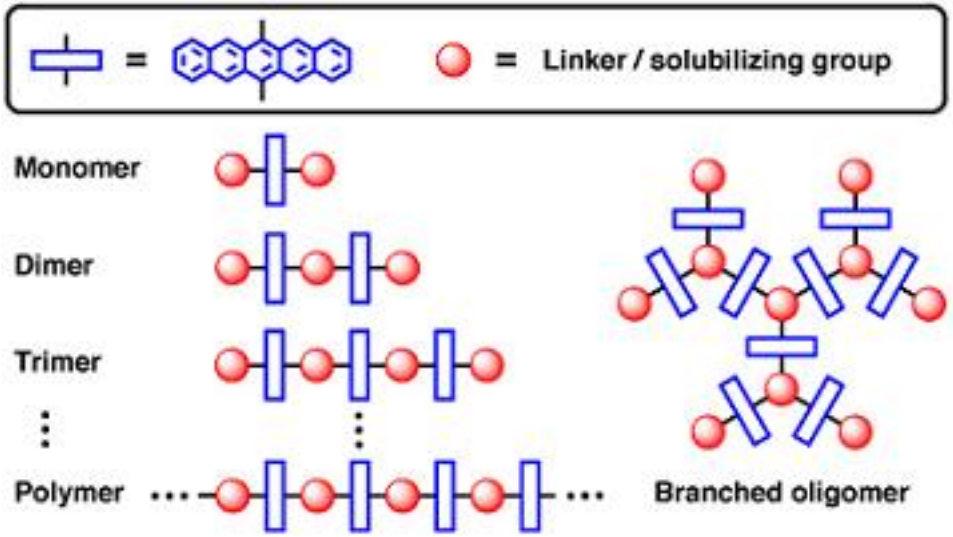
Monomer, Oligomer

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

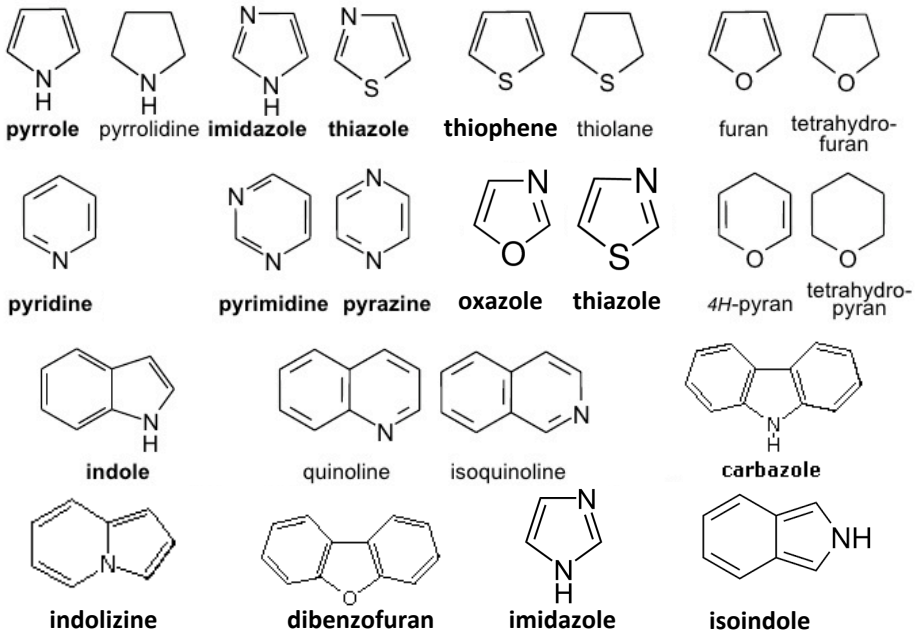


mer (Greek: meros)-part

- **Oligomer:** a molecular complex that consists of a few monomer units, where the number of monomers is, in principle, not limited but is always well defined. (e.g. dimer, trimer, tetramer, etc.)



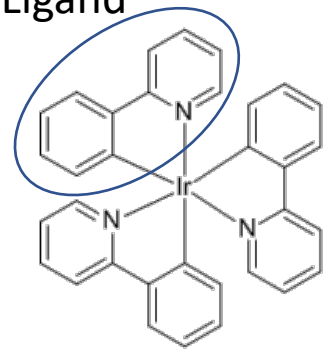
Heterocycles



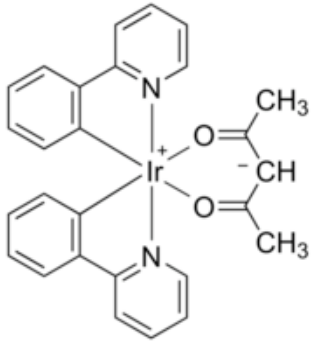
ligand: Latin: can be tied

Metalorganics

Ligand

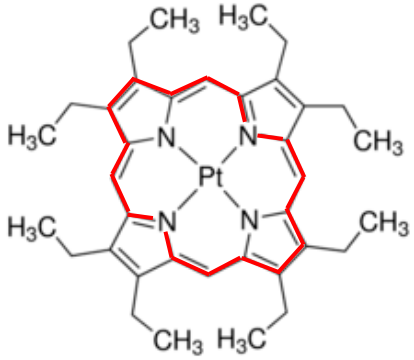


$Ir(ppy)_3$



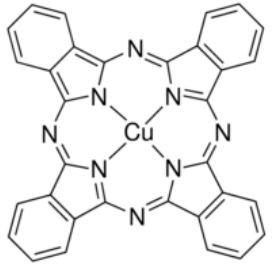
$Ir(ppy)_2acac$

Porphyrins



PtOEP

Phthalocyanines

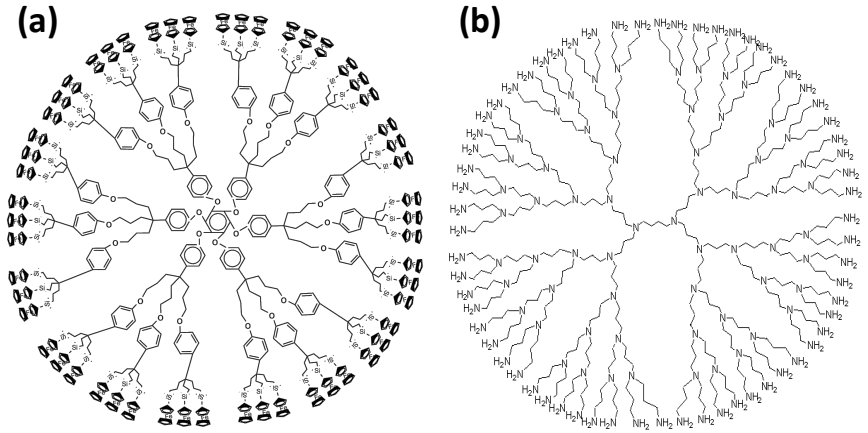


CuPc

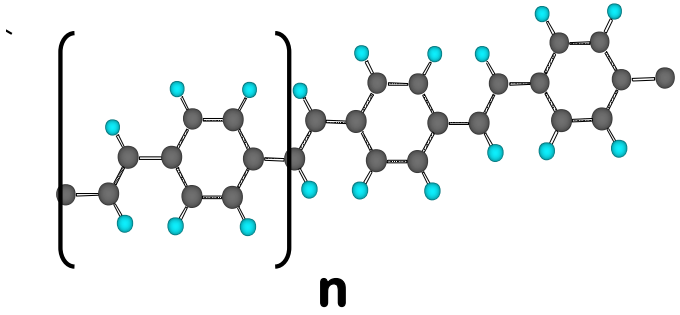
ic Electronics
hen R. Forrest

Dendrimer, Polymer

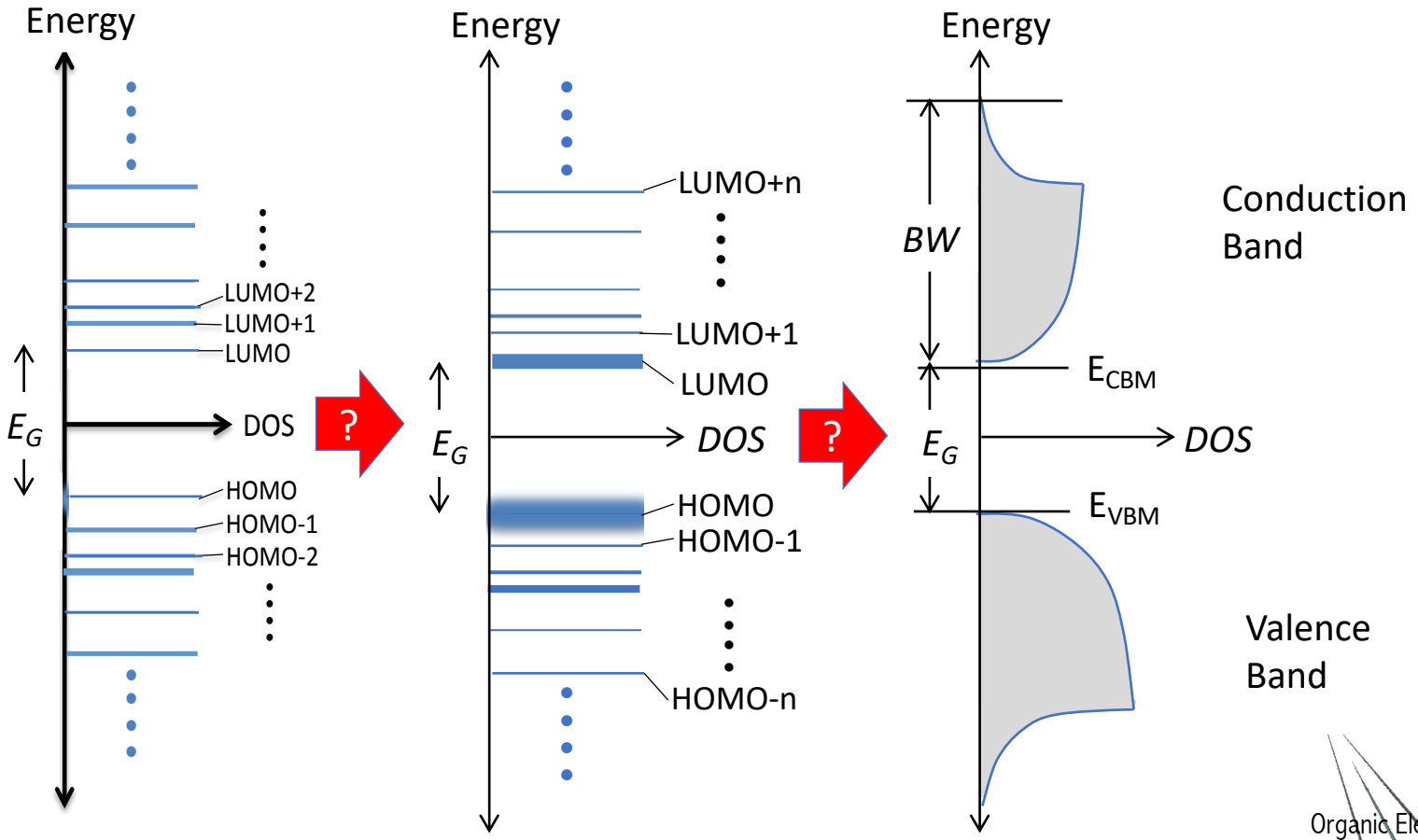
- **Dendrimer**: An oligomer that is built with repeat units radiating (like dendrites) from a central core. Each concentric repeat unit is a *generation*. (a) 54 ferrocene (so named due to the 54 ferrocene groups on its periphery), and (b) a 4th generation dendrimer.



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



At what point does the molecular picture give way to the solid?

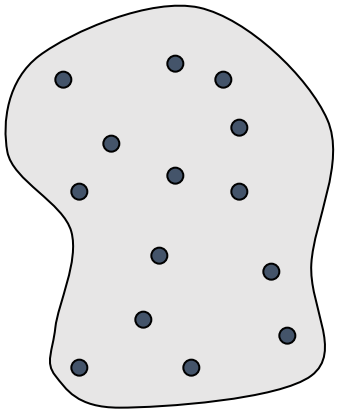


Crystal Morphologies

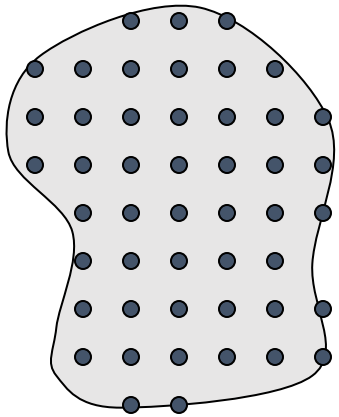
Structure determines electronic properties

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

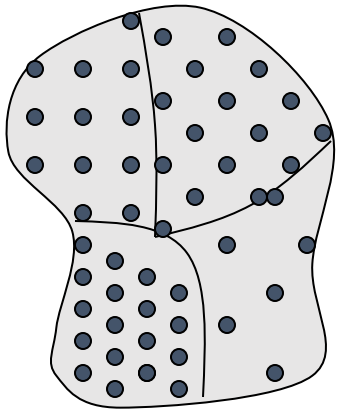
Types of solids



Amorphous



Crystalline



Polycrystalline

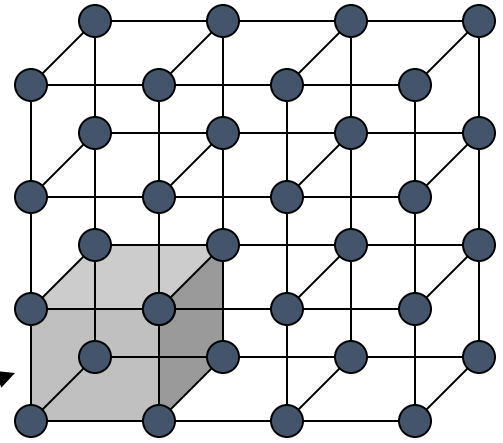
Crystal Structure

Lattice

Periodic arrangement of atoms in a crystal

Unit cell

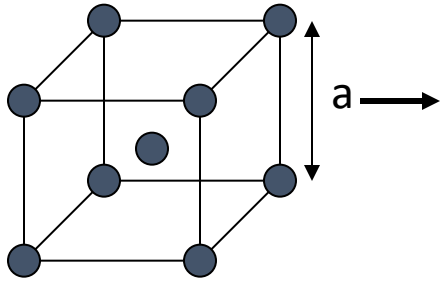
Small volume of crystal that may be used to reproduce the entire crystal—**space filling**



Simple cubic

Primitive unit cell

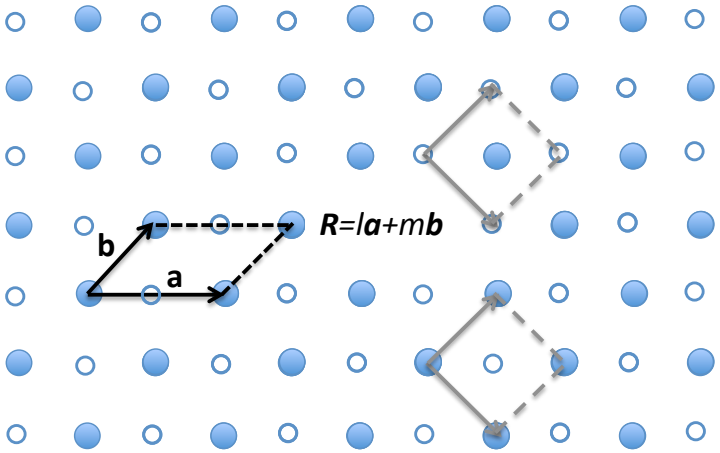
Smallest unit cell that describes the crystal



Body centered cubic (BCC)

Lattice constant is a *material parameter*

Lattices



Translation vector: R=*l*a+*m*b+*n*c

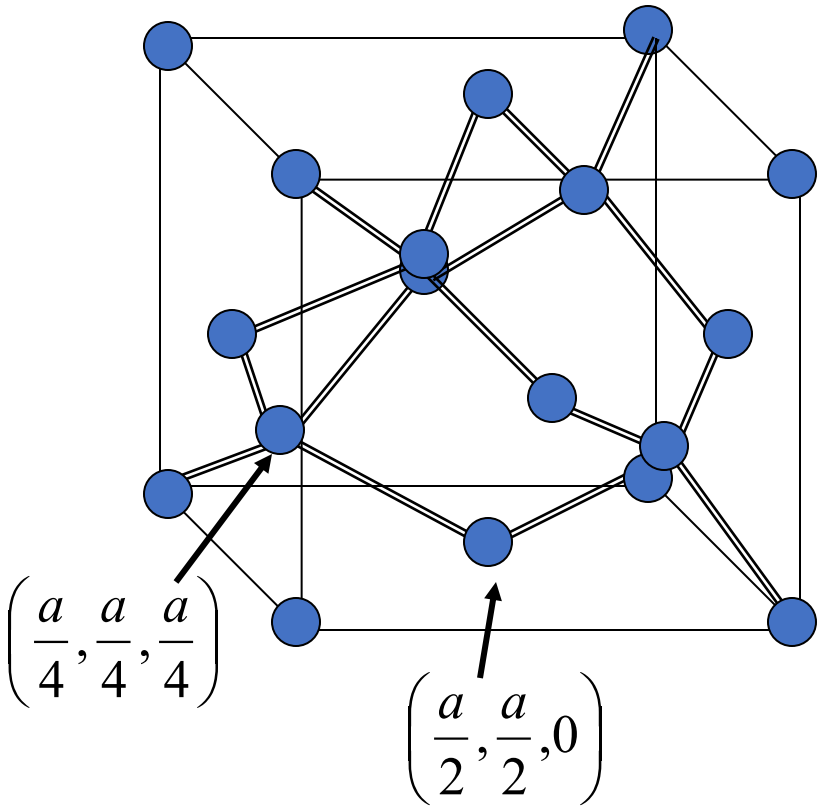
A translation vector moves a **R** point to an equivalent point in the lattice

Volume: $V_{Cell} = \mathbf{a} \bullet (\mathbf{b} \times \mathbf{c})$

Common Semiconductor Crystal Structures

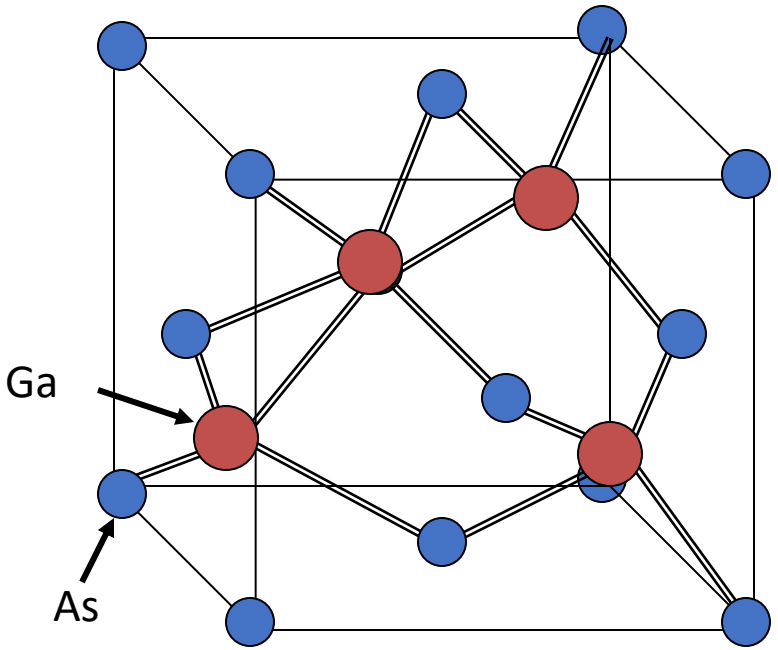
Diamond

(Si, Ge)



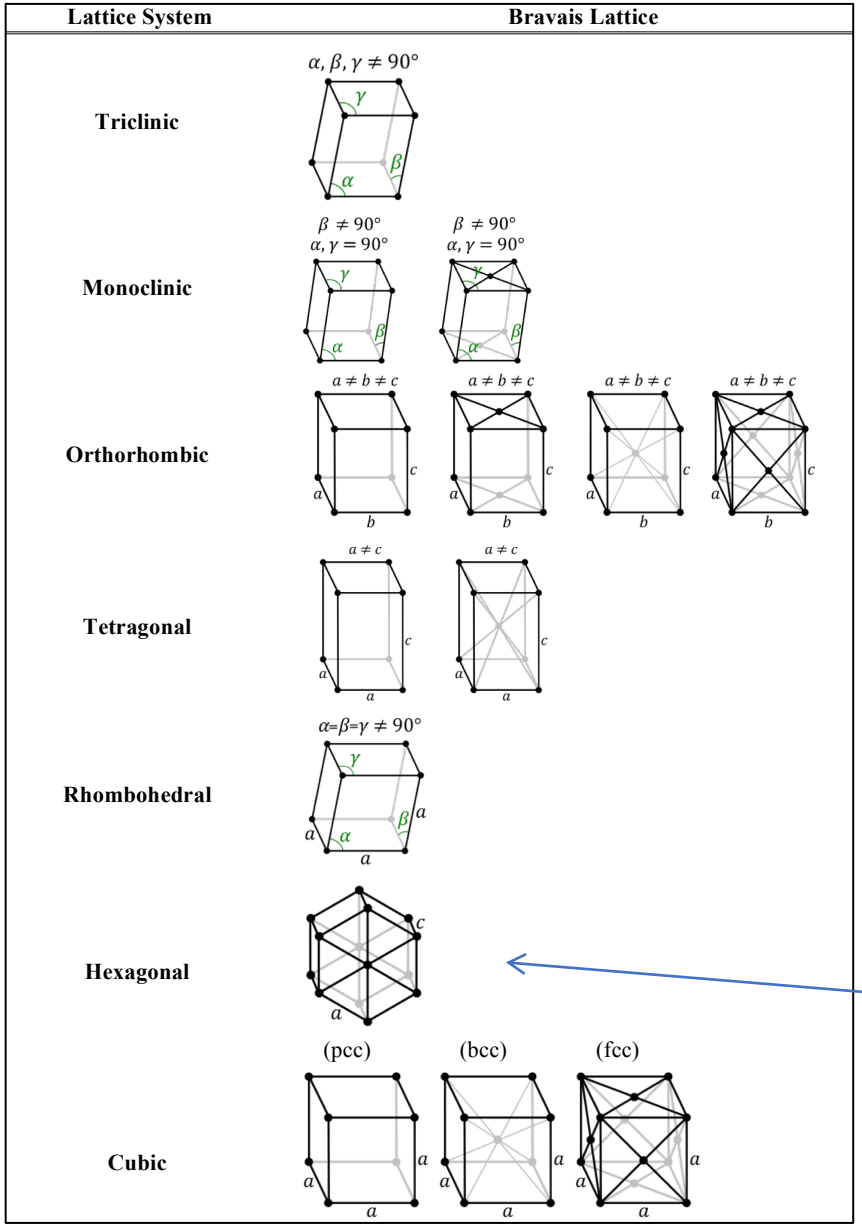
Zinc Blende

(GaAs, InP, AlSb, …)



Bravais Lattices

- These lattices define the crystal structure



Almost all organics fall Into these lattice types

Can you think of an organic material that fits this structure?

coordination #=12 (fcc)

Reciprocal Lattice

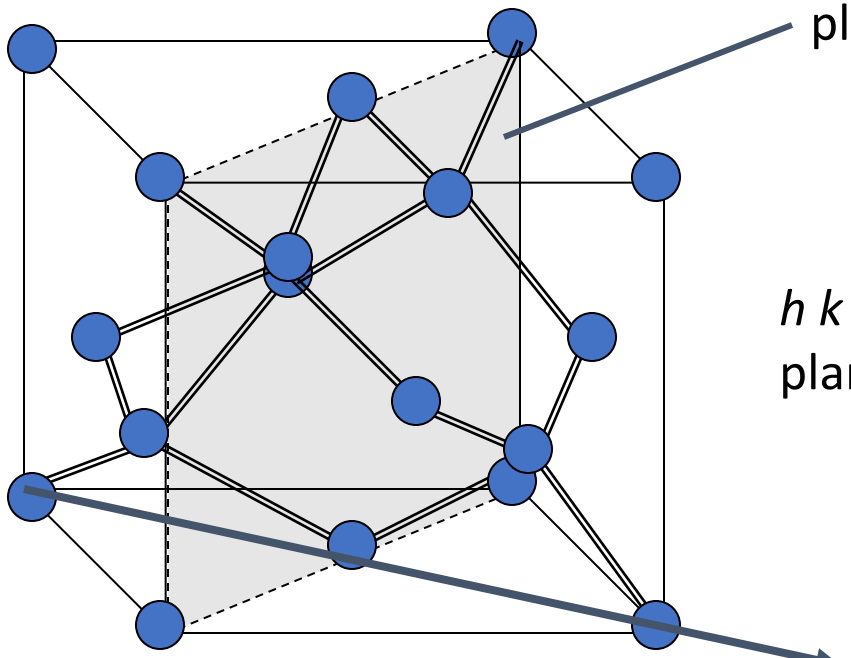
- Condition of self transformation: $\psi(\mathbf{r})=\psi(\mathbf{r}+\mathbf{R}) \sim e^{i\mathbf{G}\cdot\mathbf{r}} = e^{i\mathbf{G}\cdot(\mathbf{R}+\mathbf{r})}$
- Then **G** is the reciprocal lattice vector: $\mathbf{G}\cdot\mathbf{R} = 2\pi$
- The reciprocal lattice defined by **G**, has an identical symmetry to the physical lattice defined by **R**.
- It is then straightforward to show that the primitive reciprocal lattice vectors are defined by the following relationships:

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

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

Miller Indices

Need a method to describe crystalline direction/planes



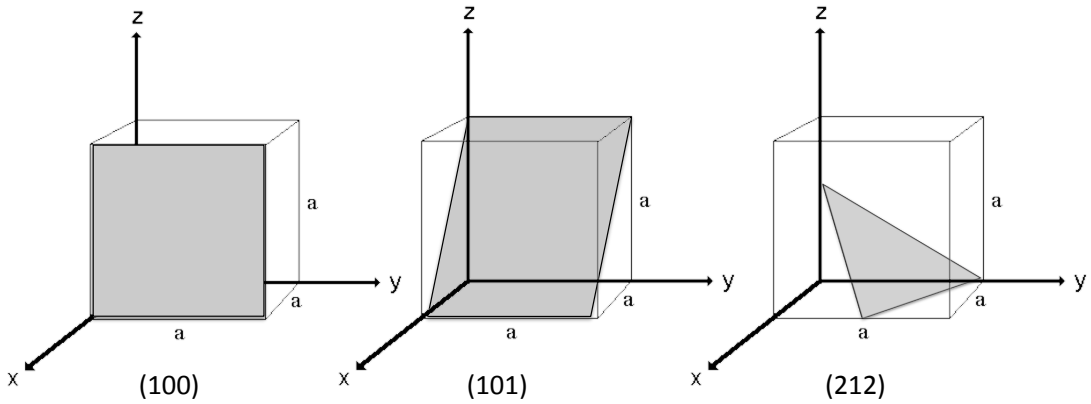
plane (*h k l*)

h k l are Miller indices defining the plane or direction

direction [*h k l*]

Defining Crystal Directions and Planes

- Miller indicies



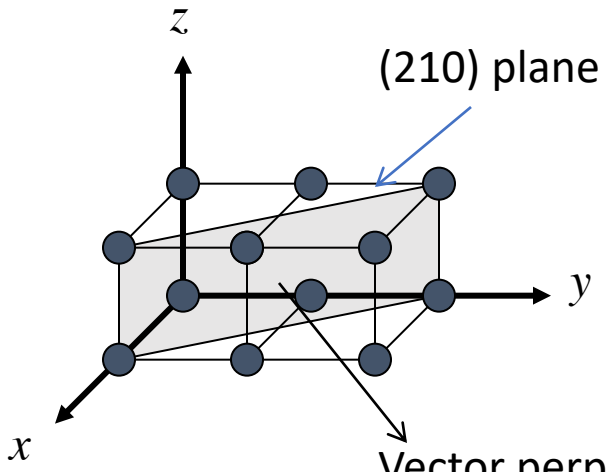
- Miller indices: *h, k, l*, are the lowest integers that are the inverse of the intercepts between the plane and the axes
- (a,b,c) define plane
- {a,b,c} define set of equivalent planes (e.g. (100), (010), (001), etc. for cubic lattice)
- [a,b,c] for lattice direction
- <a,b,c> for set of equivalent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

Determining Miller Indices

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

2. Take reciprocal

3. Multiply by lowest common denominator



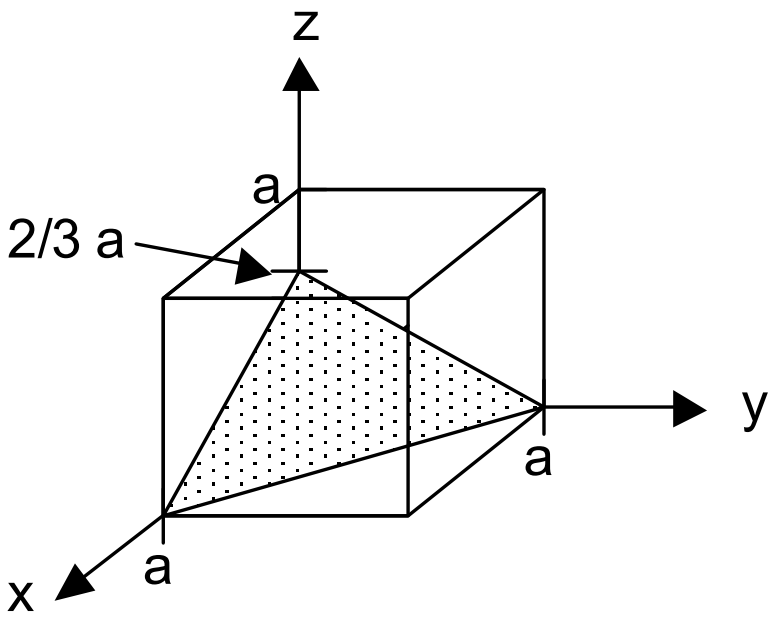
intercepts at (1, 2, ∞)

reciprocal (1, 1/2, 0)

LCM (2, 1, 0)

Example: Miller Index

Determine the representation of the plane below



Ionic Bonds

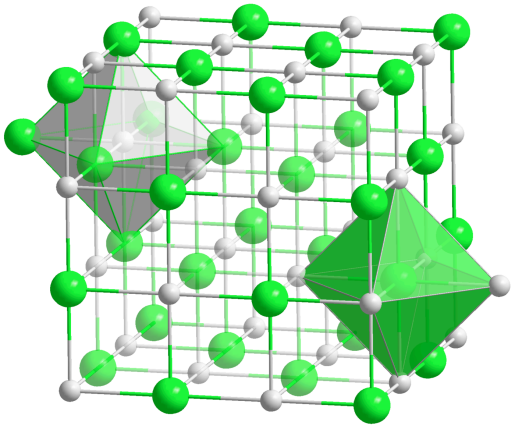
$$U_{ij}(\mathbf{r}) = \pm \frac{q^2}{4\pi\varepsilon_0 |\mathbf{r}_i - \mathbf{r}_j|}$$

For a solid, pairwise ionic interactions must be summed over all *N* ions, which leads to a net attractive energy of:

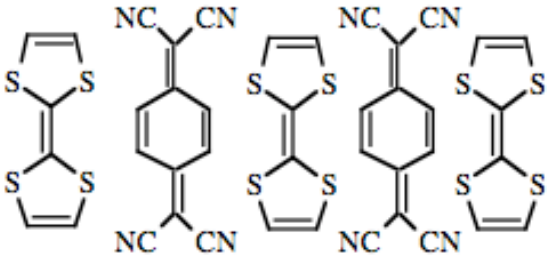
$$U_{attract}(\mathbf{r}) = \frac{q^2}{4\pi\varepsilon_0} \sum_{i,j}^{N} \left(\frac{1}{\mathbf{R}_{ij}} - \frac{1}{|\mathbf{R}_{ij} - \mathbf{a}|} \right)$$

Similar atoms

Oppositely charged atoms



δ- δ+



NaCl (fcc)

TTF-TCNQ: charge transfer complex

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

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

Equilibrium Crystal Structure

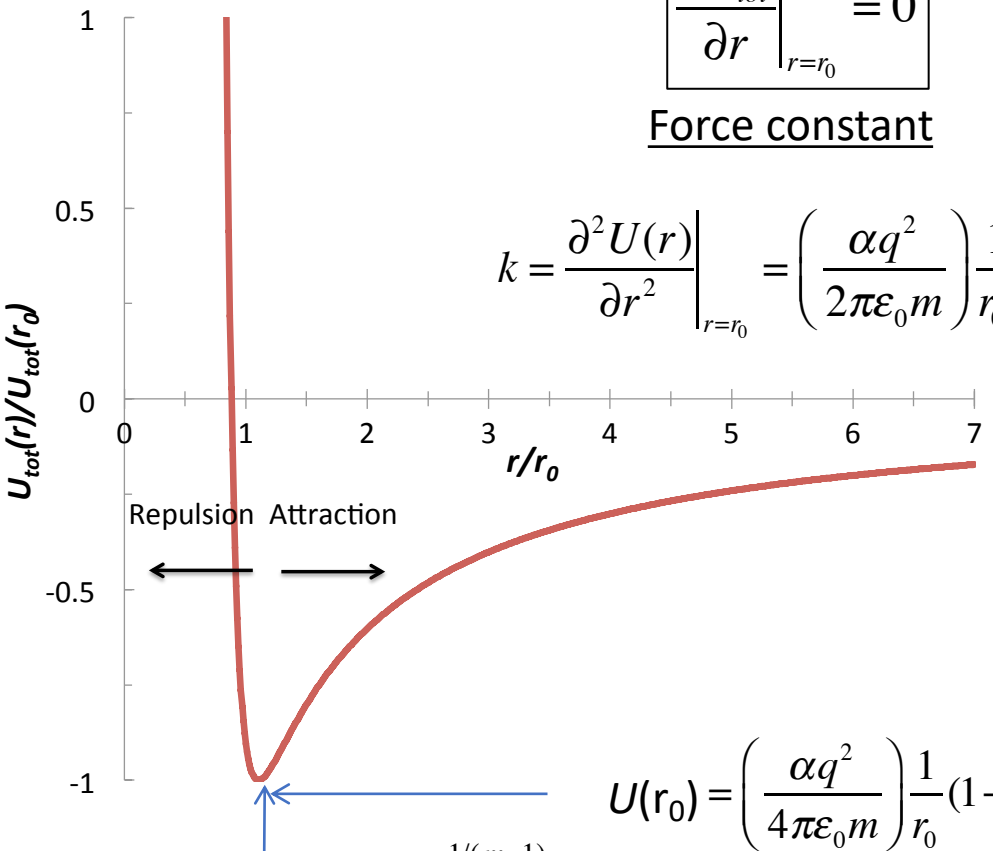
$$U_{tot}(r) = \frac{\sigma}{r^m} - \frac{\alpha q^2}{4\pi\varepsilon_0}\frac{1}{r}$$

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

Equilibrium condition

Force constant

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

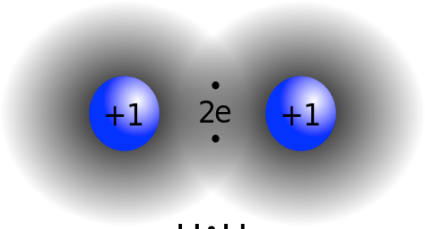


$$U(r_0) = \left(\frac{\alpha q^2}{4\pi\varepsilon_0 m}\right)\frac{1}{r_0}(1-m)$$

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

Covalent Bonding

Shared electron systems between ionic cores



H:H

H – H

H_2, Si, Ge, C….

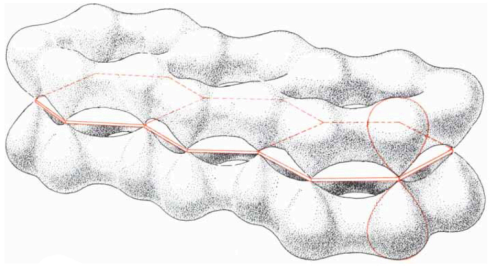
H_2^+

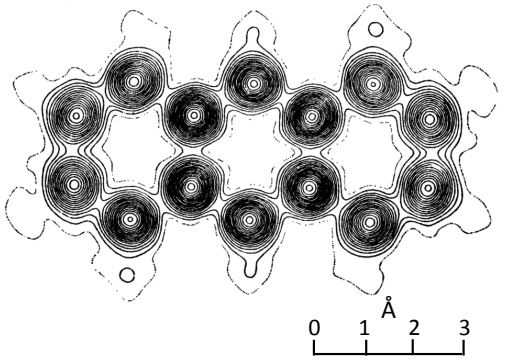
$$H\Psi(\mathbf{r},\mathbf{R}) = E\Psi(\mathbf{r},\mathbf{R})$$

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

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

It's complicated as N increases!



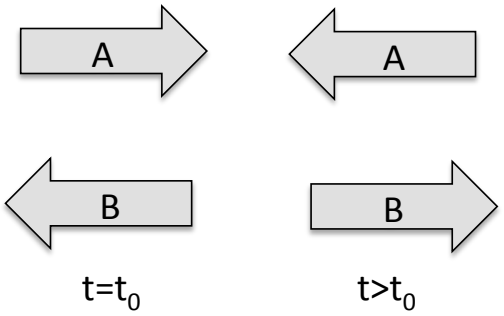


Organic Molecules with C-C bonds

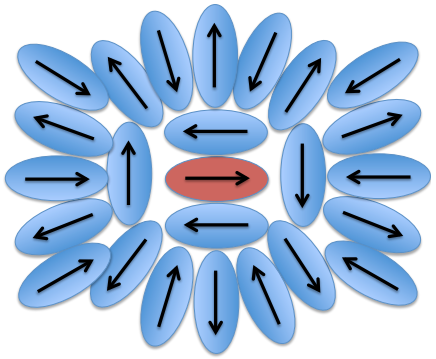
e.g. Anthracene

van der Waals bonding

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



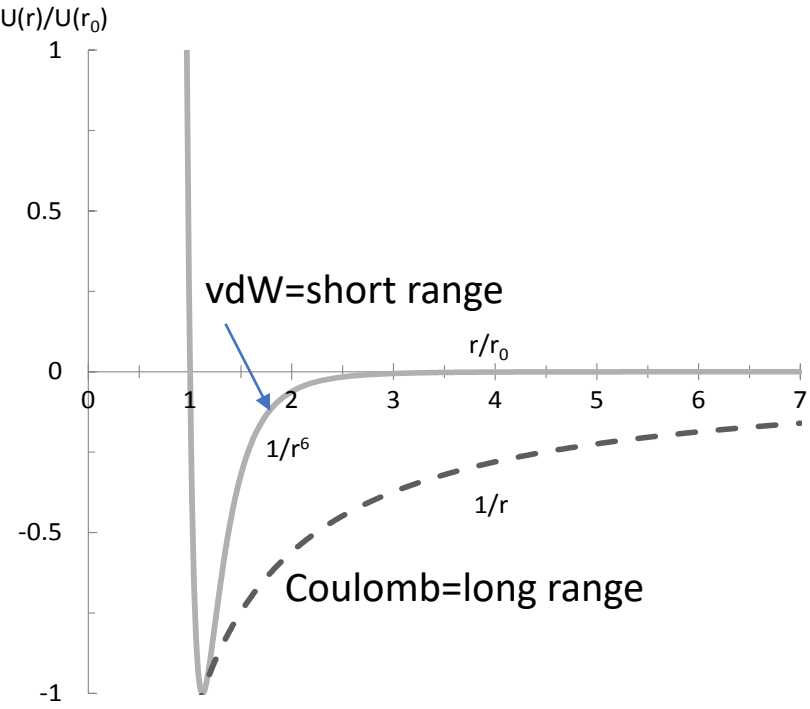
Medium around the dipole is *polarized*



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

$$U(r) = 4\varepsilon\left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^{6}\right]$$: Lennard-Jones 6-12 potential (includes core repulsion)

van der Waals Coefficients Between atoms



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

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

Virial coeff'ts from vdW interactions

- Deviations from ideal gas law

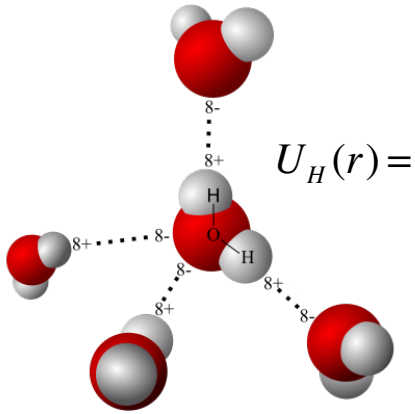
$$U_{crystal} = \frac{1}{2}\sum_{i \neq j} U(R_{ij})$$

: Equilibrium crystal structure found by calculating and then minimizing all atom-atom potentials over N atoms in molecules in solid

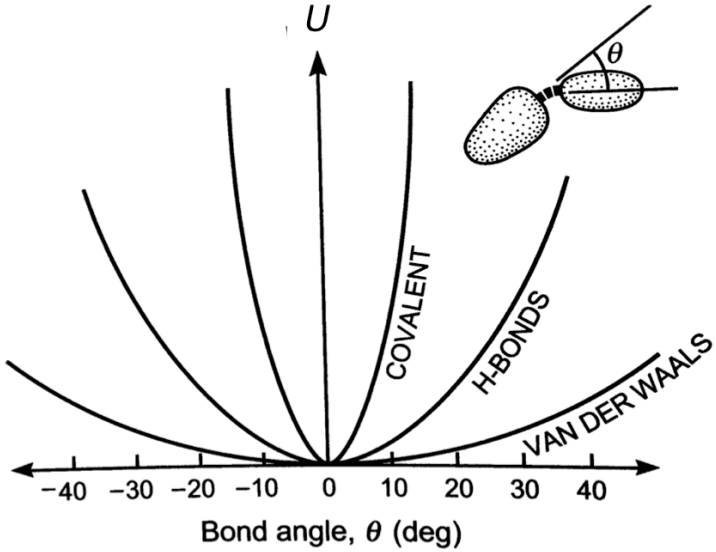
- Local vs. global minima?
- Huge numbers of degrees of freedom (6 per molecule!)
- Thermodynamics important (different structures with different $k_B T$)

Hydrogen bonds: Weak but Important

- Directional
- Coulombic



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



$O-H\cdots O$: Must be linear otherwise O-O repulsion dominates

H···O and H···N are usually only important

O-H bond: 1Å
O…H bond: 1.6 -1.8 Å

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

Summary: Comparison of Bond Strengths

Bond strength determines the physical properties of materials

Bond type	Material	Melting point (°C)	Boiling point (°C)	Sublimation point* (°C)	Density+ (g/cm^3) STP	Bond energy* (kJ/mol)
Covalent	Si	1414	3265		2.33	222
	Ge	938	2833		5.35	188
	GaAs	1238			5.32	210
Ionic	NaCl	801	1413		2.17	787
	LiF	845	1676		2.64	1046
van der Waals	Anthracene	216	340		1.28	129
	Alq_3			350		162
	PTCDA			550	1.70	240
	Pentacene	>300		372	1.3	166
Hydrogen	Water	0	100		1	21
	Ammonia	−77	−33		0.82 (*s*)	46
	Ethanol	−114	78		0.79 (*l*)	38

*Approximate values are given for sublimation points and several bond energies.
+STP = standard temperature and pressure, *s* = solid, *l* = liquid.