Molecule review

Crystal structure

Review: Molecules I

Every property of a molecule can be calculated using quantum mechanics.

$$H_{\mathrm{mp}} = -\sum_i \frac{\hbar^2}{2m_e}\nabla_i^2 - \sum_a \frac{\hbar^2}{2m_a}\nabla_a^2 - \sum_{a,i} \frac{Z_a e^2}{4\pi\epsilon_0|\vec{r}_i - \vec{r}_a|} + \sum_{i<j} \frac{e^2}{4\pi\epsilon_0|\vec{r}_i - \vec{r}_j|} + \sum_{a<b} \frac{Z_a Z_b e^2}{4\pi\epsilon_0|\vec{r}_a - \vec{r}_b|}$$

Make some approximations.

$$H_{\mathrm{red}} = -\sum_i \frac{\hbar^2}{2m_e}\nabla_i^2 - \cancel{\sum_a \frac{\hbar^2}{2m_a}\nabla_a^2} - \sum_{a,i} \frac{Z_a e^2}{4\pi\epsilon_0|\vec{r}_i - \vec{r}_a|} + \cancel{\sum_{i<j} \frac{e^2}{4\pi\epsilon_0|\vec{r}_i - \vec{r}_j|}} + \sum_{a<b} \frac{Z_a Z_b e^2}{4\pi\epsilon_0|\vec{r}_a - \vec{r}_b|}.$$

$$H_{\mathrm{red}}(\vec{r}_1, \vec{r}_1, \cdots, \vec{r}_N) = H_{\mathrm{mo}}(\vec{r}_1) + H_{\mathrm{mo}}(\vec{r}_2) + \cdots + H_{\mathrm{mo}}(\vec{r}_N).$$

$$\Psi_{\mathrm{red}}(\vec{r}_1, \vec{r}_1, \cdots, \vec{r}_N) = |\psi_{\mathrm{mo}}(\vec{r}_1)\psi_{\mathrm{mo}}(\vec{r}_2)\cdots\psi_{\mathrm{mo}}(\vec{r}_N)\rangle.$$

Molecular orbital Hamiltonian: $$H_{\mathrm{mo}} = -\frac{\hbar^2}{2m_e}\nabla^2 - \sum_a \frac{Z_a e^2}{4\pi\epsilon_0|\vec{r} - \vec{r}_a|}.$$

The exact solution to H_{red} can be constructed from the solutions to H_{mo}.

Review: Molecules II

$$H_{\mathrm{mo}} = -\frac{\hbar^2}{2m_e}\nabla^2 - \sum_a \frac{Z_a e^2}{4\pi\epsilon_0|\vec{r}-\vec{r}_a|}\,.$$

The molecular orbitals are constructed using LCAO.

$$\psi_{\mathrm{mo}}(\vec{r}) = \sum_a \sum_{ao} c_{ao,a}\phi_{ao}^{Z_a}(\vec{r}-\vec{r}_a).$$

Substitute into $H_{\mathrm{mo}}\psi_{\mathrm{mo}} = E\psi_{\mathrm{mo}}$, construct the Roothaan equations.

The many electron wavefunction is constructed as a Slater determinant.

$$\Psi(\vec{r}_1,\vec{r}_2,\cdots,\vec{r}_N) \approx |\psi_{\mathrm{mo1}}\uparrow(\vec{r}_1),\psi_{\mathrm{mo2}}\uparrow(\vec{r}_2),\cdots,\psi_{\mathrm{moN}}\uparrow(\vec{r}_N)\rangle.$$

This is an exact solution to H_{red} and an approximate solution to H_{mp}.

The energy is calculated including the electron-electron interactions.

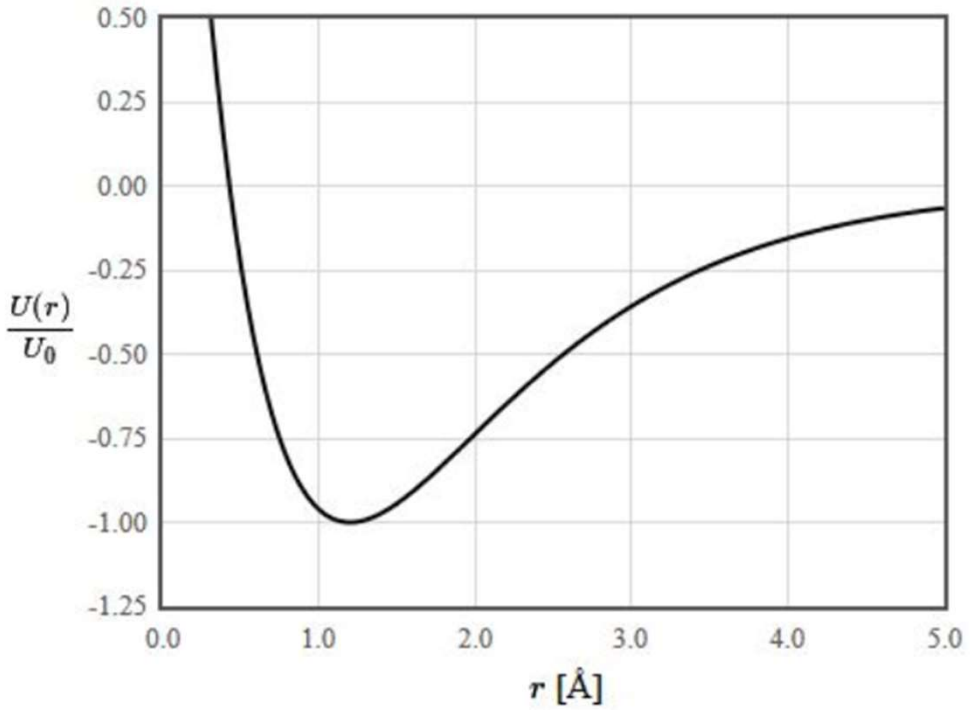
$$E = \frac{\langle\Psi|H_{mp}|\Psi\rangle}{\langle\Psi|\Psi\rangle}$$

Review: Molecules III

$$E = \frac{\langle \Psi | H_{mp} | \Psi \rangle}{\langle \Psi | \Psi \rangle}$$

Calculate the bond potential

Bond lengths, bond angles
⟹ Shape of the molecule



Rotational energy levels: $E_J = \frac{\hbar^2}{2I} J(J+1) = BJ(J+1) \qquad J = 0, 1, 2, \cdots$

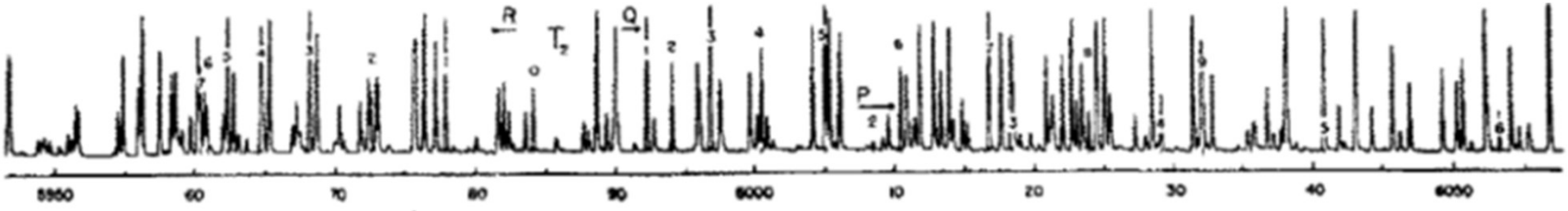
Vibrational energy levels: $E_\nu = \hbar\omega(\nu + 1/2) \qquad \nu = 0, 1, 2, \cdots$

Review: Molecules IV

Calculate the transition rates $\Gamma_{i\to f} = \frac{2\pi}{\hbar}|\langle f|H_1|i\rangle|^2\delta(E_f - E_i)$

Complicated emission and adsorption spectra even for simple molecules

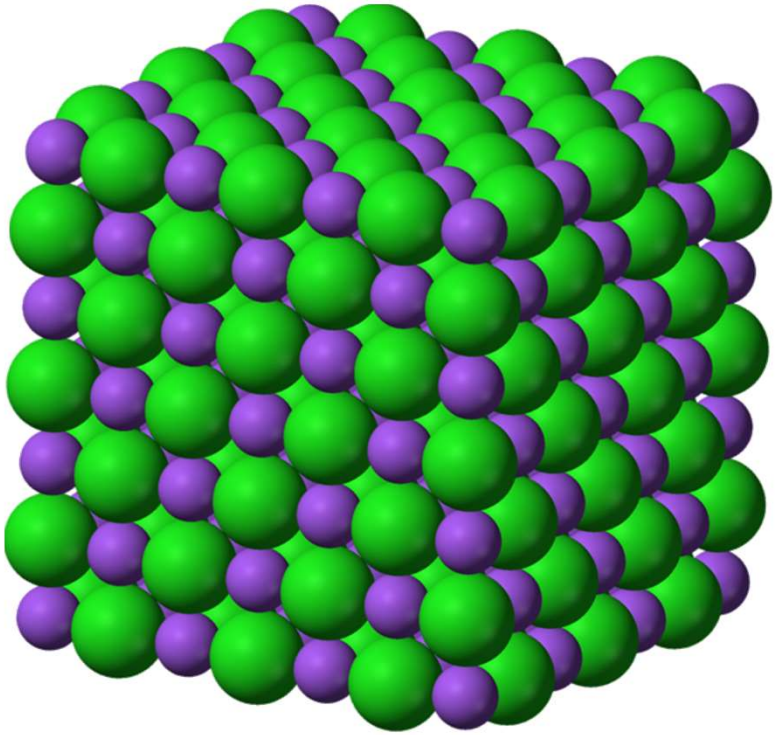
Spectra are a ‘fingerprint’ for a molecule



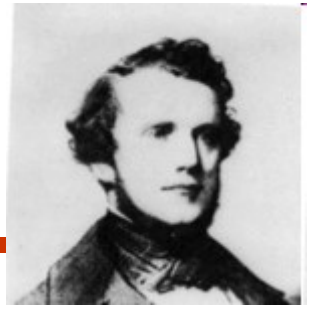
Dieke, Journal of Molecular Spectroscopy 2, p. 494 (1958)

Crystal structure

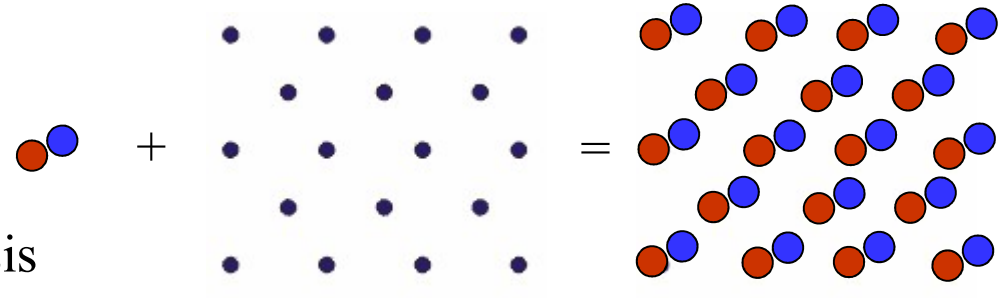
A crystal is a three dimensional periodic arrangement of atoms.



Bravais lattice



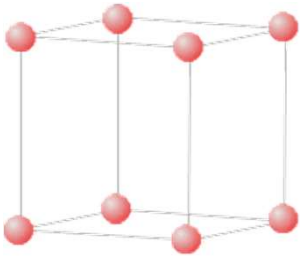
Auguste Bravais



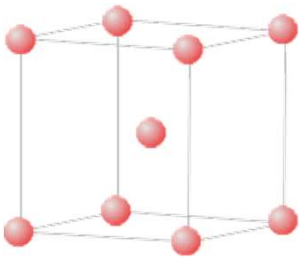
basis

Bravais lattice

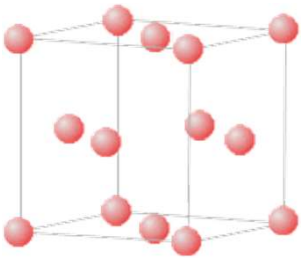
Crystal



simple cubic

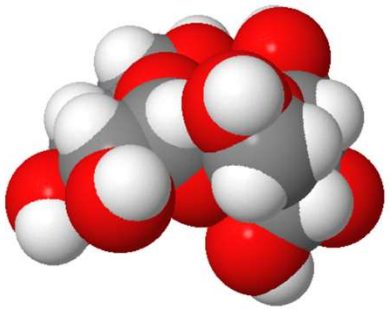


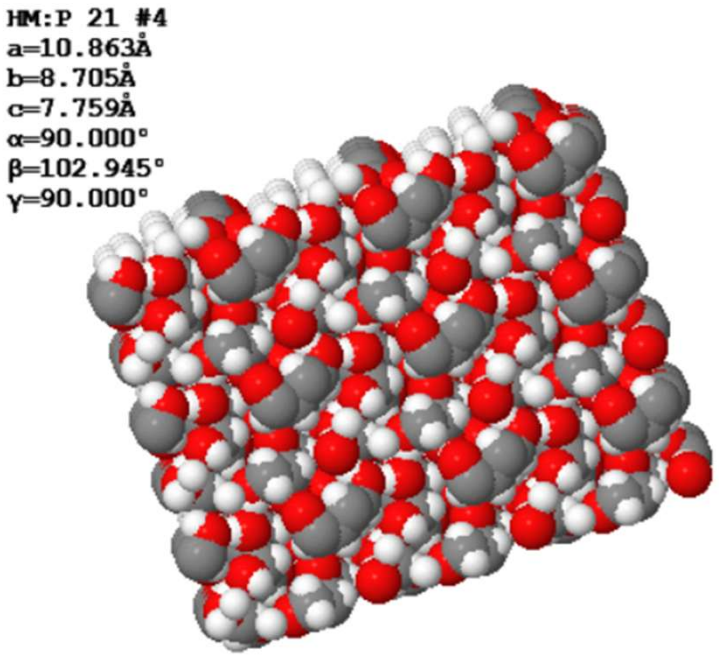
body centered cubic, bcc



face centered cubic, fcc

Sugar (Sucrose)





7 Crystal Systems

triclinic: a ≠ b ≠ c and $\alpha \neq \beta \neq \gamma \neq 90°$

monoclinic: a ≠ b ≠ c and $\alpha \neq 90° \ \beta = \gamma = 90°$

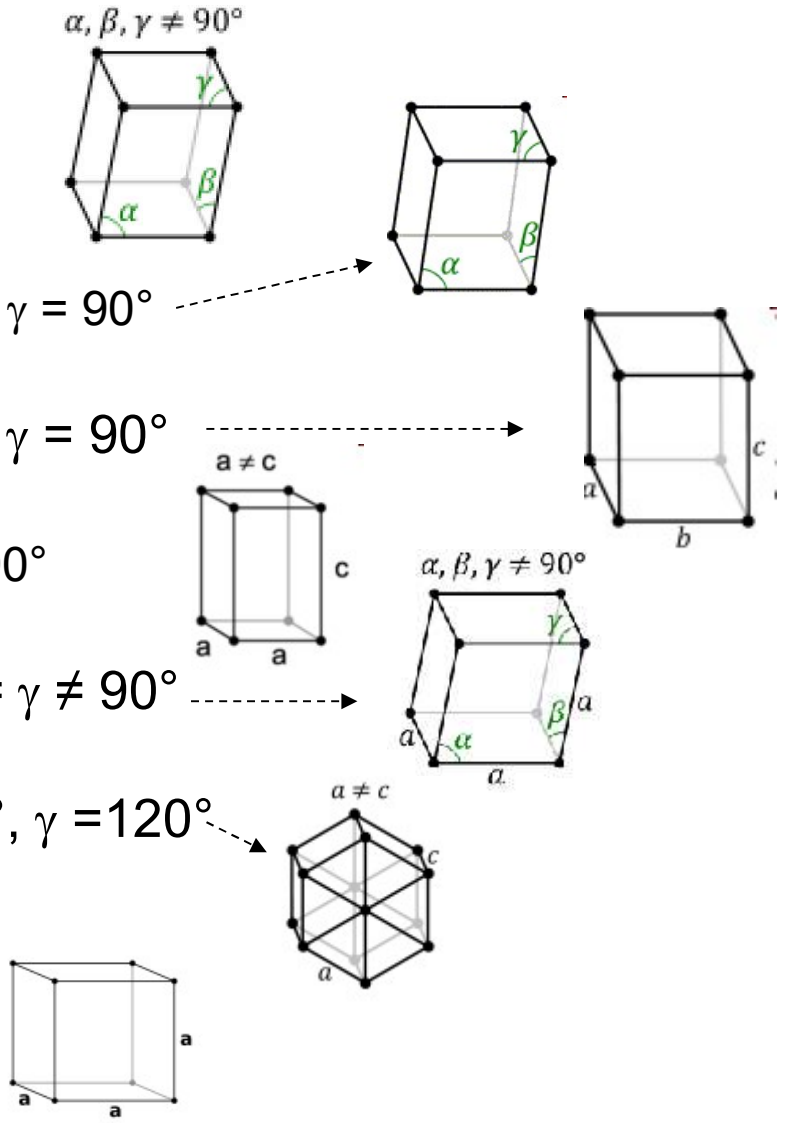
orthorhombic: a ≠ b ≠ c and $\alpha = \beta = \gamma = 90°$

tetragonal: a = b ≠ c and $\alpha = \beta = \gamma = 90°$

rhombohedral: a = b = c and $\alpha \neq \beta \neq \gamma \neq 90°$

hexagonal: a = b ≠ c and $\alpha = \beta = 90°, \gamma = 120°$

cubic a = b = c and $\alpha = \beta = \gamma = 90°$

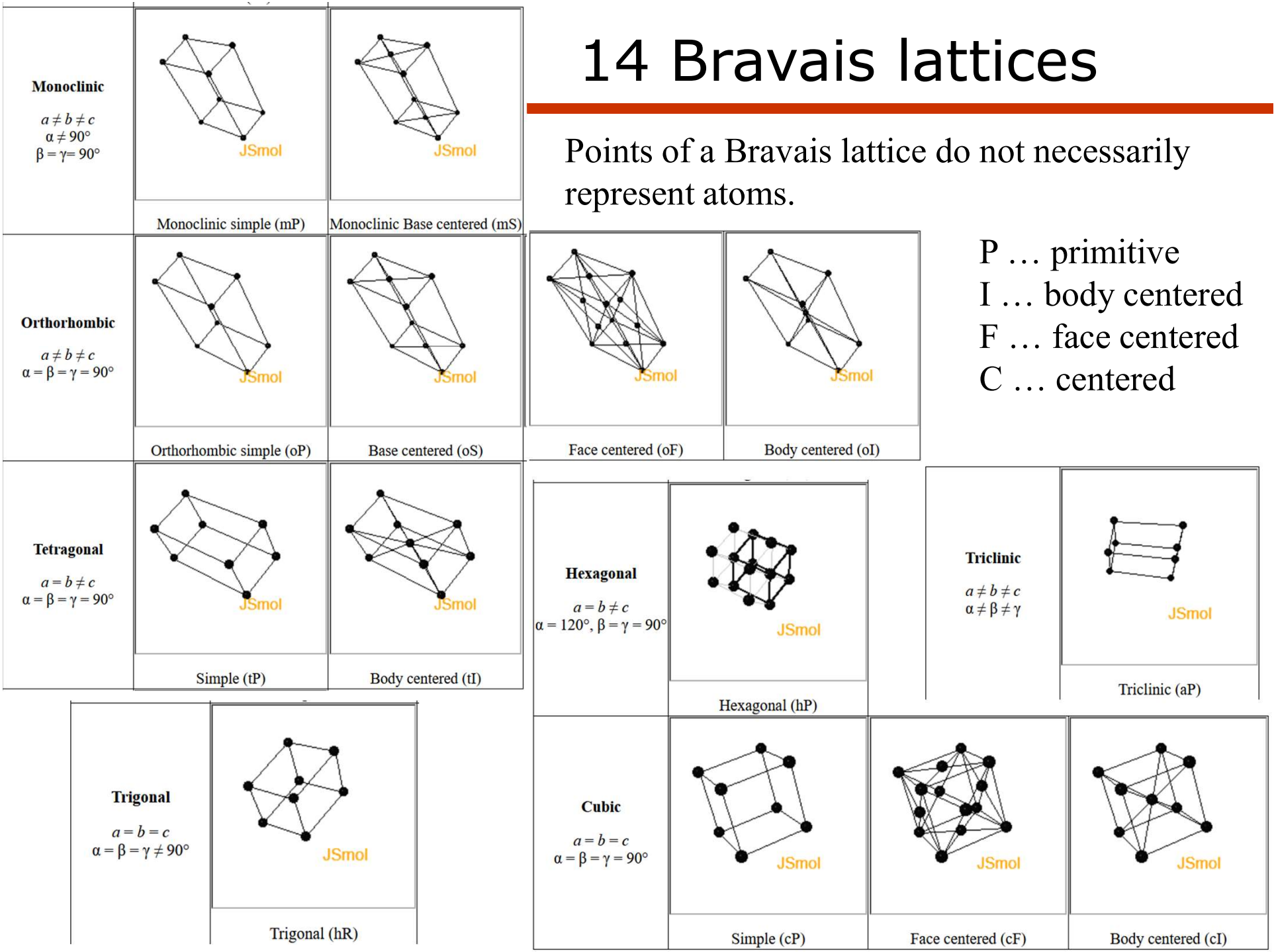


α is the angle between b and c

14 Bravais lattices

Points of a Bravais lattice do not necessarily represent atoms.

P … primitive
I … body centered
F … face centered
C … centered

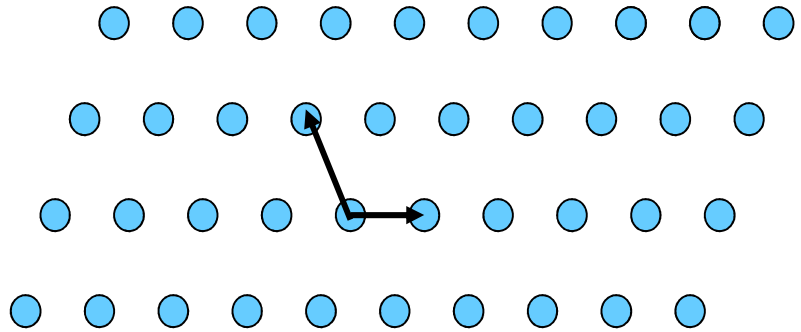


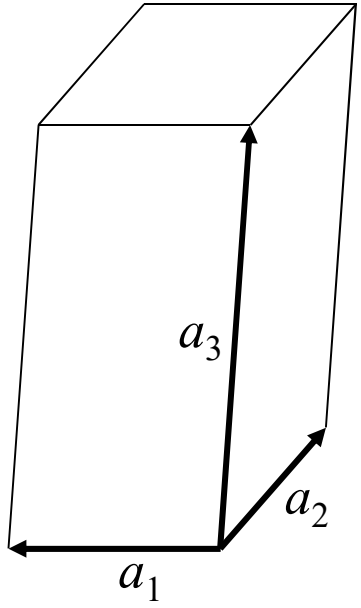
Primitive lattice vectors

Every point of a Bravais lattice can be reached from another point on the lattice by a translation vector

Translation vector

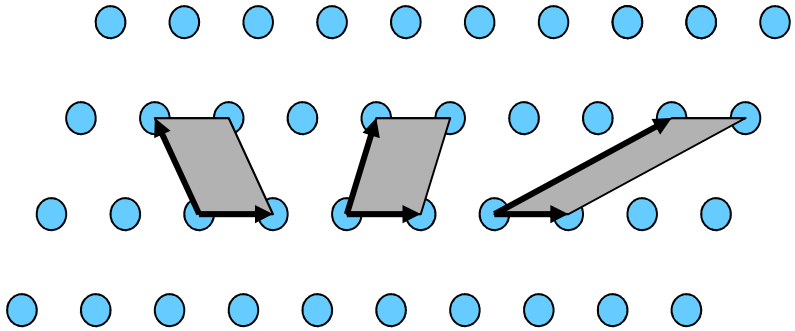
$$\vec{T} = n_1\vec{a}_1 + n_2\vec{a}_2 + n_3\vec{a}_3 \qquad n_1, n_2, n_3 = \cdots -2, -1, 0, 1, 2, \cdots$$



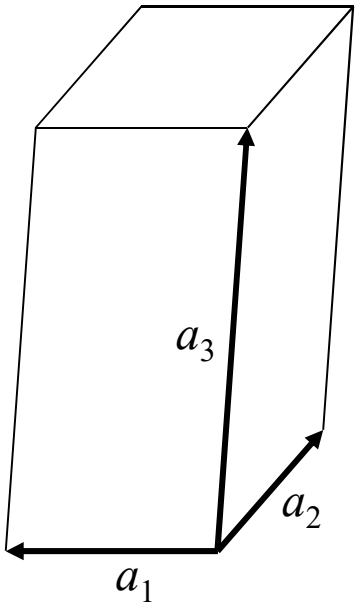


Primitive lattice vectors

Primitive Unit Cell



There is more than one choice for a primitive unit cell



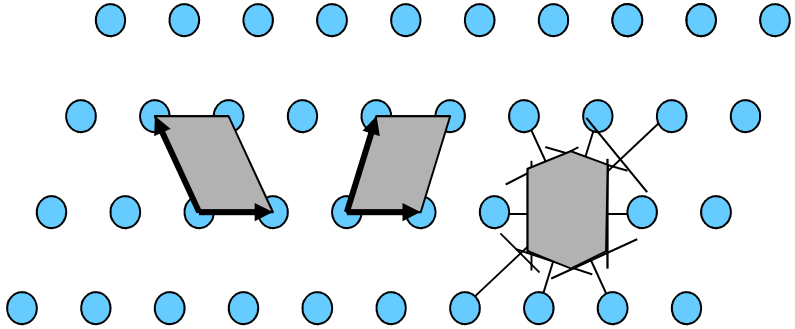
volume of a unit cell =

$$|\vec{a}_1 \cdot (\vec{a}_2 \times \vec{a}_3)|$$

$$\vec{T} = n_1\vec{a}_1 + n_2\vec{a}_2 + n_3\vec{a}_3 \qquad n_1, n_2, n_3 = \cdots -2, -1, 0, 1, 2, \cdots$$

Unit Cells

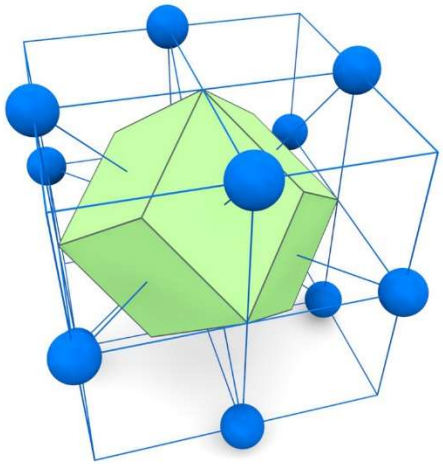
There is more than one choice for a primitive unit cell



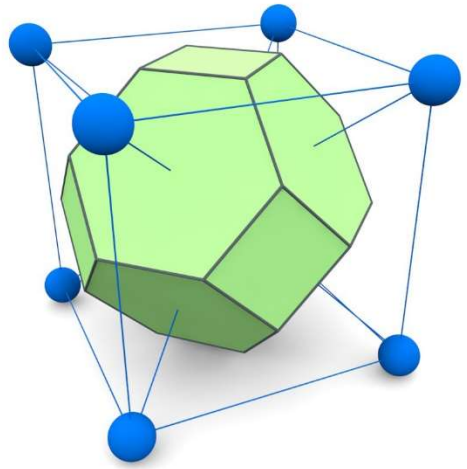
Eugene Wigner

Frederick Seitz

Wigner-Seitz primitive unit cell

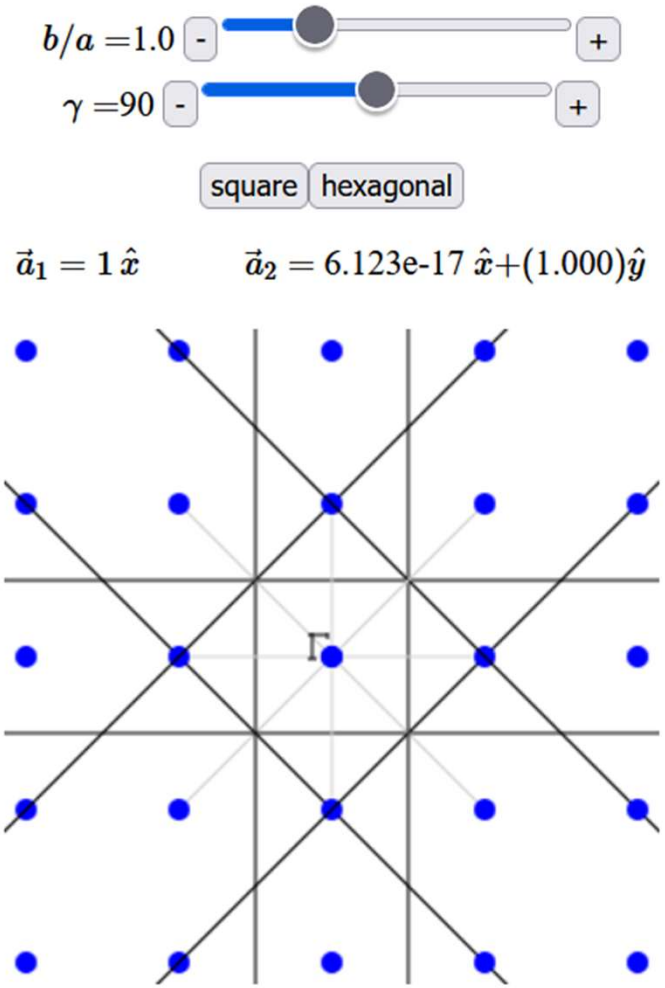


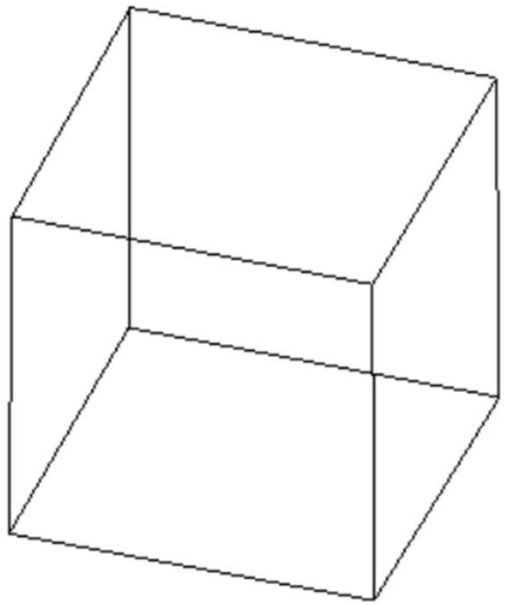
fcc



bcc

Wigner-Seitz cells





https://lampx.tugraz.at/~hadley/ss1/bzones/drawing_WS.php

Drawing Wigner-Seitz Cells

The form below takes the primitive lattice vectors in real space as input and calculates the Bravais lattice vectors $\vec{R}_{hkl}$, the planes (hkl) that form the Wigner-Seitz cell boundaries, and the corners of the Wigner-Seitz cell.

Primitive lattice vectors:

$\vec{a}_1 =$ 3 $\hat{x}+$ 0 $\hat{y}+$ 0 $\hat{z}$ [Å]
$\vec{a}_2 =$ 0 $\hat{x}+$ 3 $\hat{y}+$ 0 $\hat{z}$ [Å]
$\vec{a}_3 =$ 0 $\hat{x}+$ 0 $\hat{y}+$ 3 $\hat{z}$ [Å]

submit
sc fcc bcc hex

A boundary of the Wigner-Seitz cell is a plane normal to $\vec{R}_{hkl}$, that passes through the point $\frac{\vec{R}_{hkl}}{2}$. For the planes that make up the Wigner-Seitz cell boundary, the distance from $\frac{\vec{R}_{hkl}}{2}$ to the origin is smaller than the distance from $\frac{\vec{R}_{hkl}}{2}$ to any of the other Bravais lattice vectors. By computing these distances, the planes that make up the Wigner-Seitz cell can be determined.

The Wigner-Seitz cell consists of 6 planes.

(0 0 1)
(0 0 -1)
(0 1 0)
(0 -1 0)
(1 0 0)
(-1 0 0)

The Miller indices are given in terms of the primitive lattice vectors.

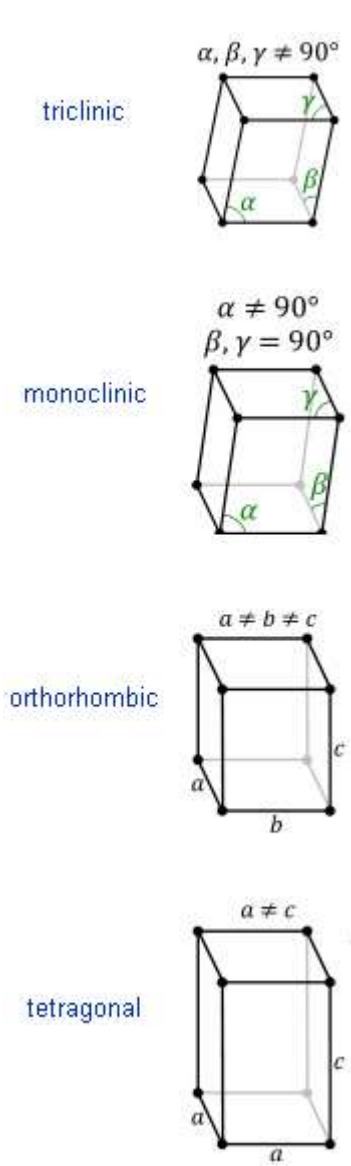
Once the planes are known, the points at the corners of the Wigner-Seitz cell can be determined by considering the intersections of the planes. The formula for the (hkl) plane is,

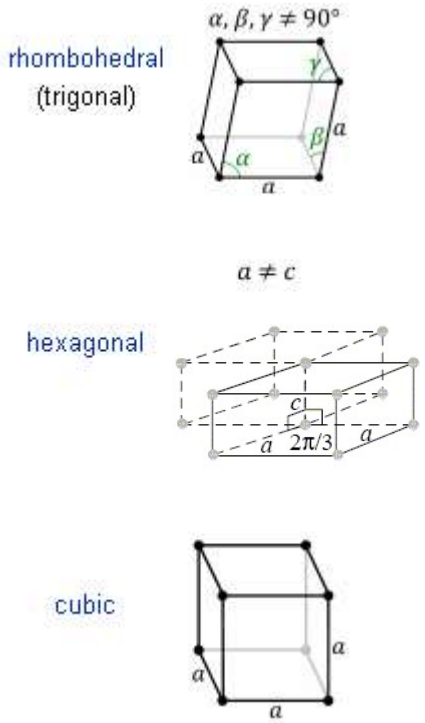
$$R_{hkl,x}k_x + R_{hkl,y}k_y + R_{hkl,z}k_z = \frac{R_{hkl,x}^2}{2} + \frac{R_{hkl,y}^2}{2} + \frac{R_{hkl,z}^2}{2}.$$

By solving the sets of linear equations, the corners can be determined.

There are 8 corners:

Conventional (crystallographic) unit cell





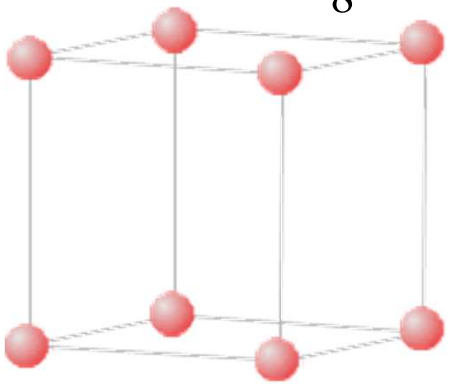
α is the angle between *b* and *c*
β is the angle between *a* and *c*
γ is the angle between *a* and *b*

6 faces, 8 corners

http://en.wikipedia.org/wiki/Bravais_lattice

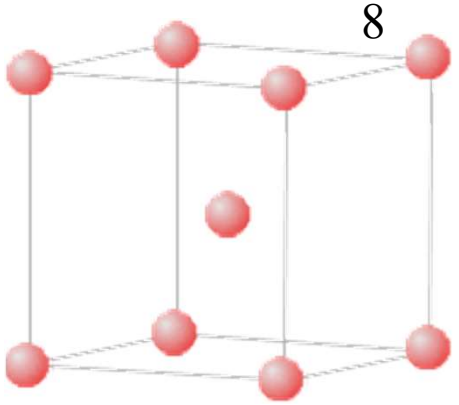
Conventional (crystalographic) unit cell

$$8 \times \frac{1}{8} = 1$$



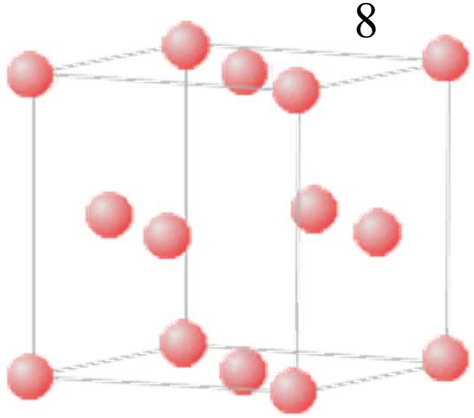
simple cubic

$$8 \times \frac{1}{8} + 1 = 2$$

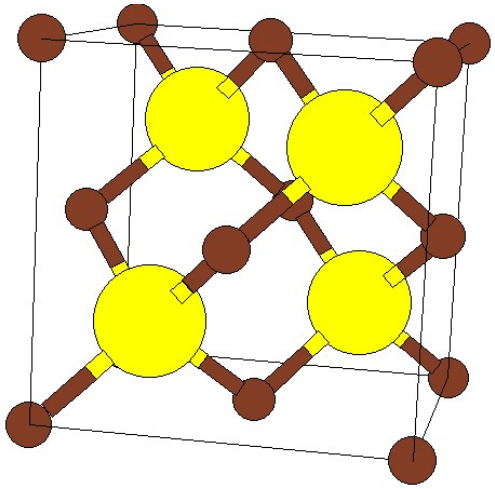


bcc

$$8 \times \frac{1}{8} + 6 \times \frac{1}{2} = 4$$

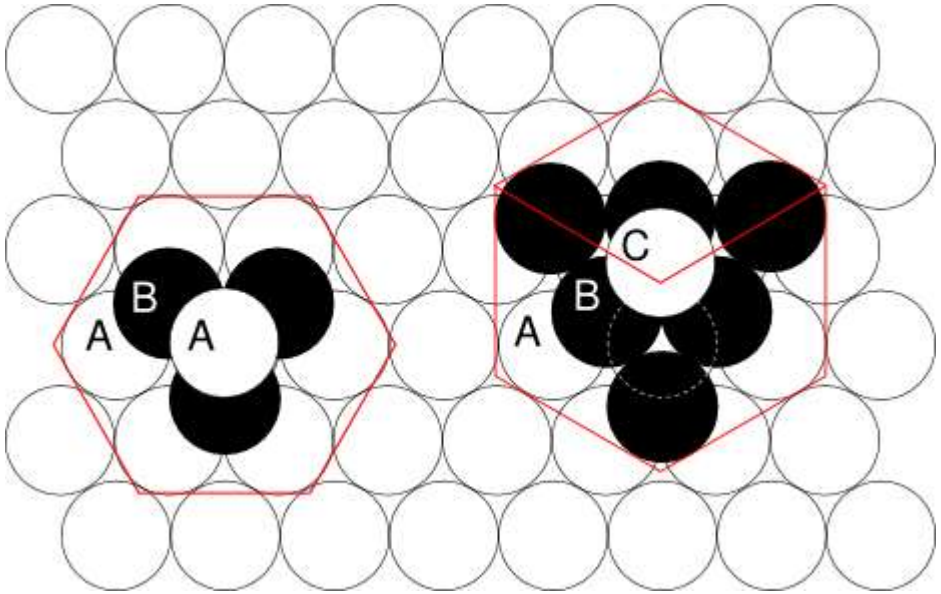


fcc

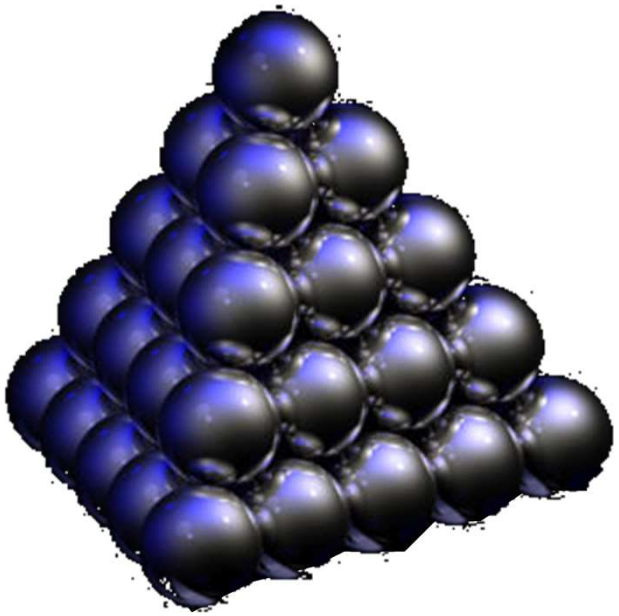


zincblende

Close packing

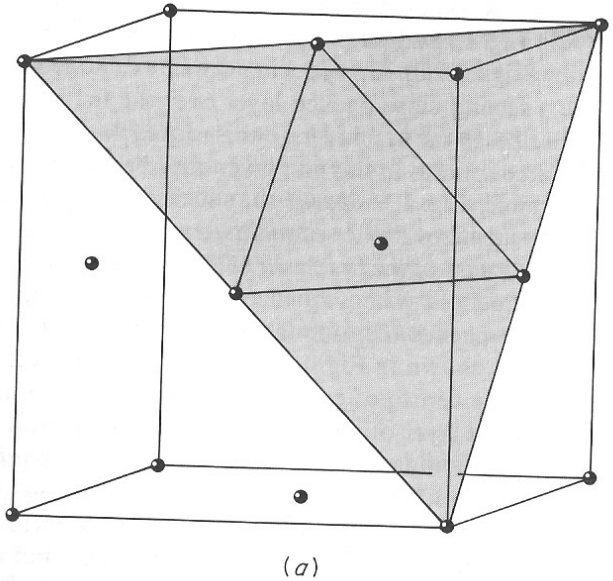


HCP FCC

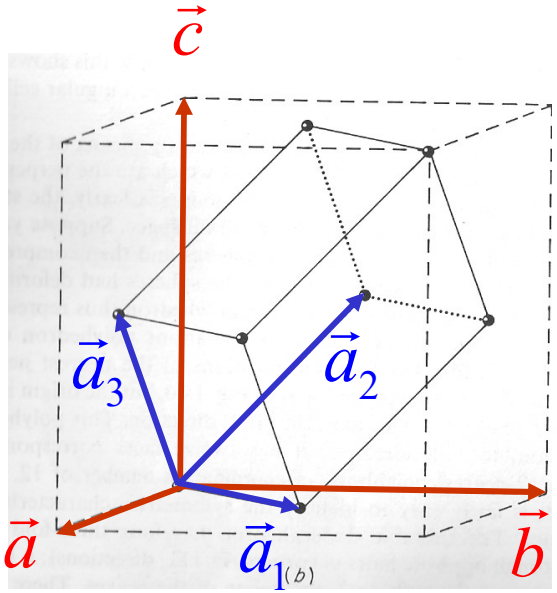


HCP = Hexagonal close pack
Hexagonal Bravais lattice with two atoms in the basis.

Fcc

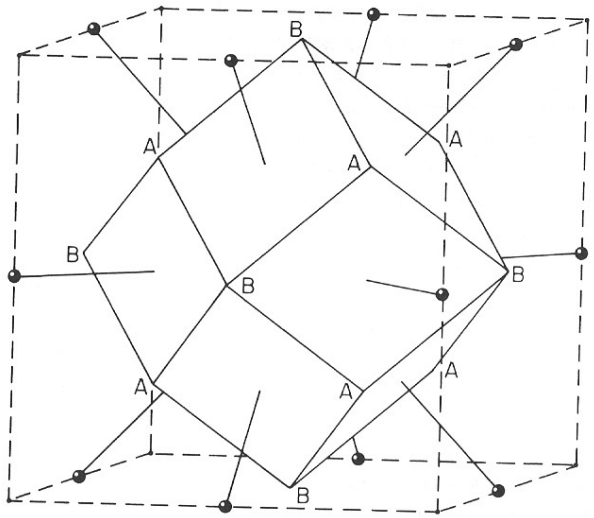


Crystalographic unit cell showing close packed plane



Crystalographic lattice vectors

Primitive lattice vectors



Wigner-Seitz cell

From: Hall, Solid State Physics