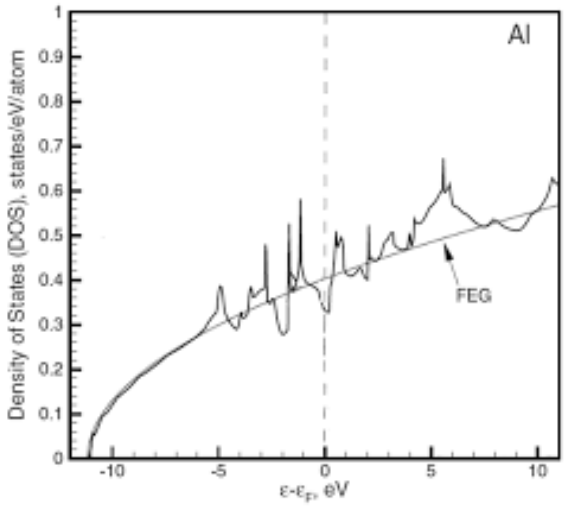
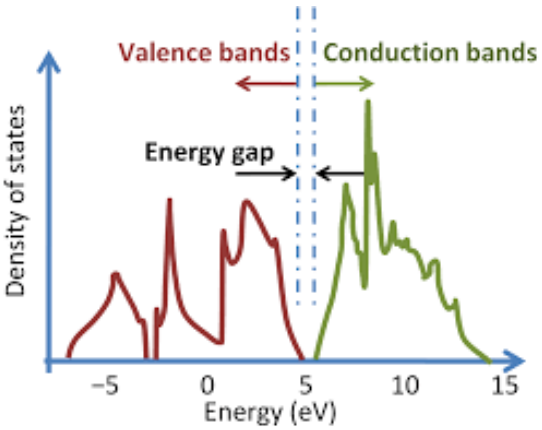
## Week 4: Electrons in Crystalline Solids

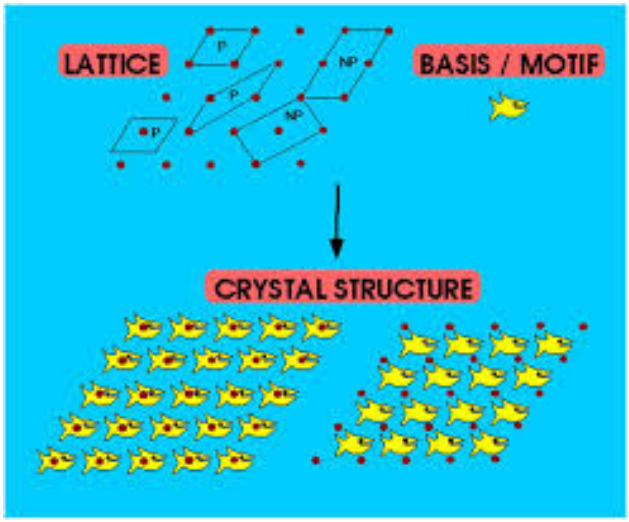
- Free electron model and real materials. Density of states:




- Incorporate crystal structure. Effects of the translational symmetry on the electronic states.

- A perfect crystal can be generated by decorating each point in a lattice with the same basis. A lattice is an infinite array of mathematical points in space with translational symmetry.

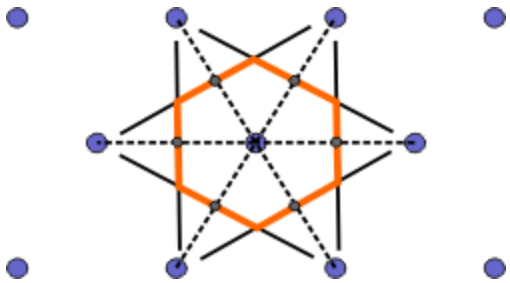


## Points on a Lattice and Unit Cells

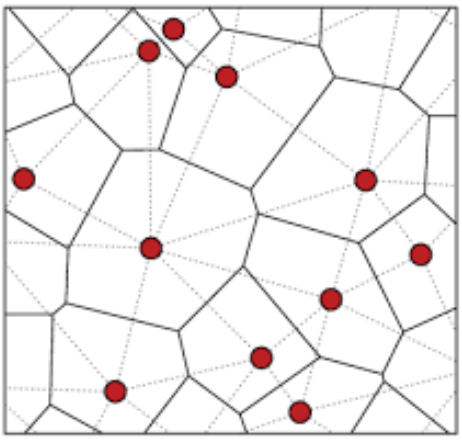
- In 3D, points on lattice given by $\mathbf{R}_{n_1,n_2,n_3} = n_1\mathbf{a} + n_2\mathbf{b} + n_3\mathbf{c}$ where $\mathbf{a}$, $\mathbf{b}$ and $\mathbf{c}$ are 3 'primitive vectors' and $n_1$, $n_2$ and $n_3$ are integers.

- There are just 14 3D crystal structures with different symmetries (*Bravais lattices*). They are in 7 groups: cubic, tetragonal, orthorhombic, hexagonal, trigonal (also called rhombohedral), monoclinic and triclinic. See document on Moodle in *Term 2, Week 4: Lectures 7 and 8*

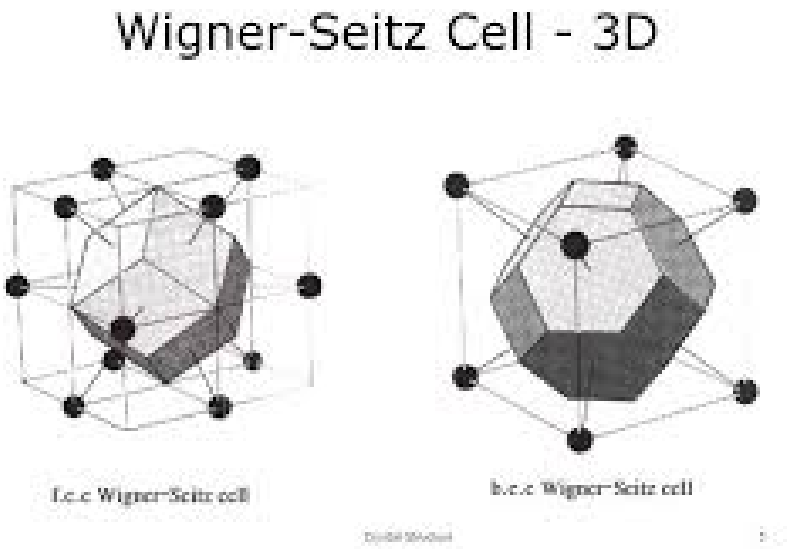
- Filling space, one unit cell per each lattice point. For example, the Wigner-Seitz unit cells. A cell is constructed around a lattice point from planes that bisect and with normals aligned with the vectors connecting the point to its nearest neighbours. In 2D:



The process for a random set of points:



- A couple of 3D examples, b.c.c. and f.c.c. WS unit cells.




- Find the volume of a unit cell of a hexagonal close packed (hcp) structure as a function of the ratio $c/a$.

- The hcp structure has a simple hexagonal Bravais lattice with primitive vectors, $\mathbf{a} = (a, 0, 0)$, $\mathbf{b} = (a/2, \sqrt{3}a/2, 0)$ and $\mathbf{c} = (0, 0, c)$. There is a basis of 2 atoms, one at $(0, 0, 0)$ and the other at $(\mathbf{a}/3 + \mathbf{b}/3 + \mathbf{c}/2)$, i.e.

there are two interleaved hexagonal lattices. The volume of the hcp unit cell is the area of the base hexagon times the height $c$. The base area is six times the area of the equilateral triangle of side $a$, which is $\frac{a^2\sqrt{3}}{4}$. The volume is $\frac{3\sqrt{3}a^2c}{2}$.

## The Reciprocal Lattice and Reciprocal Space.

- Since a crystal structure has periodicity, properties will also be periodic, e.g. the electron probability density, the potential that the electrons 'see' etc.

- For a 1D lattice comprising a chain of atoms with spacing $a$, a function $f(x) = f(x + na)$ can be expressed as a Fourier Series.
  $f(x) = a_0 + \sum_{n\neq 0}\left(a_n \cos(\frac{2\pi nx}{a}) + b_n \sin(\frac{2\pi nx}{a})\right) = \sum_n f_n e^{iG_n x}$ where $G_n = \frac{2\pi n}{a}$ and $f_n = \frac{1}{a}\int_0^a f(x)e^{-iG_n x}\,dx$.

- The $G_n$'s also describe a chain of points, a lattice, this time spaced apart by $2\pi/a$. This is the Reciprocal Lattice. N.B. $e^{iG_n a} = 1$.

- For a 3D lattice with points $\mathbf{R}_{n_1,n_2,n_3} = n_1\mathbf{a} + n_2\mathbf{b} + n_3\mathbf{c}$, a reciprocal lattice can be specified from the imposition $e^{i\mathbf{G}_{h,k,l}\cdot\mathbf{R}_{n_1,n_2,n_3}} = 1$. The $\mathbf{G}_{h,k,l}$'s ($h$, $k$, $l$ are integers) describe the reciprocal lattice.

- $\mathbf{G}_{h,k,l} = h\mathbf{A} + k\mathbf{B} + l\mathbf{C}$ and $\mathbf{A} = \frac{2\pi(\mathbf{b}\times\mathbf{c})}{\mathbf{a}\cdot(\mathbf{b}\times\mathbf{c})}$, $\mathbf{B} = \frac{2\pi(\mathbf{c}\times\mathbf{a})}{\mathbf{a}\cdot(\mathbf{b}\times\mathbf{c})}$ and $\mathbf{C} = \frac{2\pi(\mathbf{a}\times\mathbf{b})}{\mathbf{a}\cdot(\mathbf{b}\times\mathbf{c})}$. Show that $e^{i(\mathbf{G}_{h,k,l}\cdot\mathbf{R}_{n_1,n_2,n_3})} = 1$.

- $\mathbf{A}$, $\mathbf{B}$ and $\mathbf{C}$ are the primitive vectors of the reciprocal lattice.

- X-ray diffraction experiments directly measure the reciprocal lattice.

## The Crystalline Potential

- The potential describing an electron's interaction with the nuclei and the other electrons must also have the symmetry of the lattice. Hence, $V(\mathbf{r}) = \sum_h \sum_k \sum_l V_{h,k,l} e^{i\mathbf{G}_{h,k,l}\cdot\mathbf{r}}$. Show that $V(\mathbf{r} + \mathbf{R}_{n_1,n_2,n_3}) = V(\mathbf{r})$.

- We will go on to look at the quantum mechanics of electrons moving in such crystalline potentials. We will find that the energies $E$ will have a dependence on the values of the wavevectors $\mathbf{k}$ which can have *any* value in reciprocal space, $E(\mathbf{k})$. Note that for free electrons $E(\mathbf{k}) = \frac{\hbar^2 k^2}{2m}$.

- A Wigner-Seitz unit cell in the reciprocal space is called the first Brillouin Zone (BZ). It is constructed in the same way as the real space counterpart. In 1D, for a chain of atoms separated by $a$, the values of wavevector $k$ in the first BZ are $-\pi/a < k < \pi/a$. 3D example for a f.c.c. lattice: