Session 3: Advanced Solid State Physics

Reciprocal Lattice

Outline

1.
2.
3.
4.
5.

- Atomic Physics

Hydrogen Atom

1.
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4.
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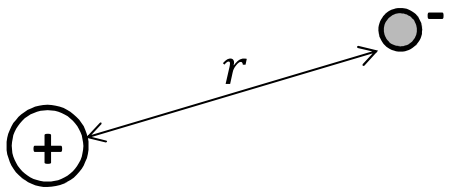

Uncertainty Principle:

$$\Delta p \Delta x \geq h/2\pi$$

Total Energy = K.E. + P.E.

Confinement Energy of Hydrogen Atom

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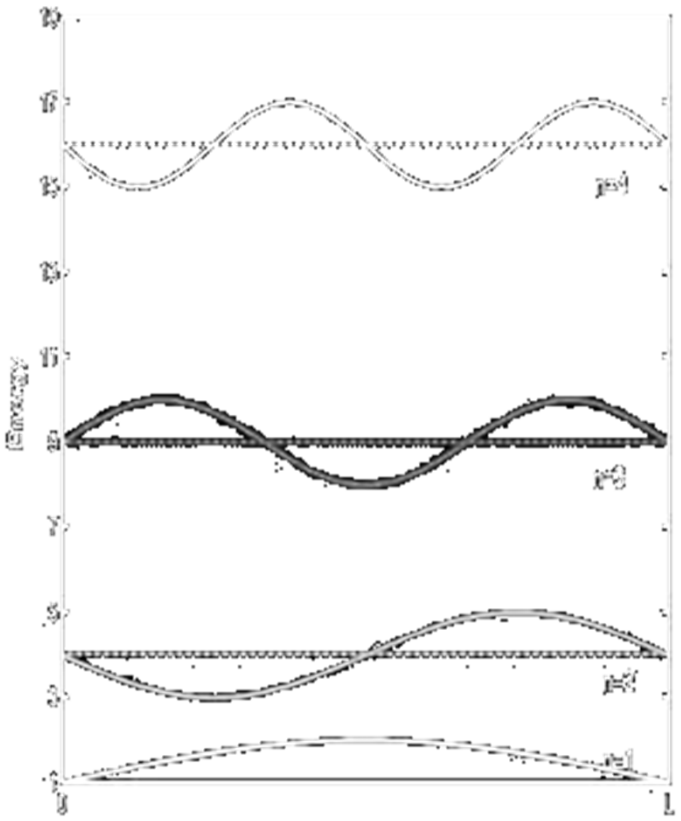
Using the energy levels of ideal 1-D well we can estimate the confinement energy of H atom!



Wave function of Hydrogen Atom

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$$-\frac{\hbar^2}{2m_0}\nabla^2\Psi - \frac{e^2}{4\pi\epsilon_0 r}\Psi = E\Psi$$

B.C. : $\Psi \to 0$ as $r \to 0$

assume:

$$\Psi(r,\theta,\varphi\,) = R(r)\Theta(\theta)\Phi(\varphi)$$

Check slides:

Helium Atom

1.
2.
3.
4.
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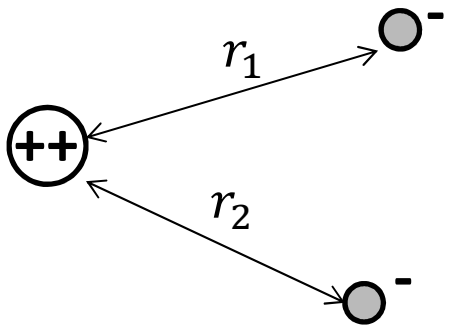

$$-\frac{\hbar^2}{2m_0}(\nabla_1^2\Psi + \nabla_2^2\Psi) - \frac{2e^2}{4\pi\epsilon_0|\vec{r}_1|}\Psi - \frac{2e^2}{4\pi\epsilon_0|\vec{r}_2|}\Psi + \frac{e^2}{4\pi\epsilon_0|\vec{r}_1 - \vec{r}_2|}\Psi = E\Psi$$

$\Psi(r_1, r_2)$ = probability of finding one of the electrons at r_1 and 2nd on at r_2

assuming: $\Psi(r_1, r_2) = \Psi_1(r_1)\Psi_2(r_2)$

Helium Atom

1.
2.
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$$-\frac{\hbar^2}{2m}\nabla_1^2\Psi_1\Psi_2 - \frac{2e^2}{4\pi\epsilon_0|\vec{r}_1|}\Psi_1\Psi_2 = \frac{\hbar^2}{2m}\nabla_2^2\Psi_1\Psi_2 + \frac{2e^2}{4\pi\epsilon_0|\vec{r}_2|}\Psi_1\Psi_2 + E\Psi_1\Psi_2$$

Separate variables:

$$-\frac{\hbar^2}{2m\Psi_1}\nabla_1^2\Psi_1 - \frac{2e^2}{4\pi\epsilon_0|\vec{r}_1|} = C = \frac{\hbar^2}{2m\Psi_2}\nabla_2^2\Psi_2 + \frac{2e^2}{4\pi\epsilon_0|\vec{r}_2|} + E$$

$$-\frac{\hbar^2}{2m}\nabla_1^2\Psi_1 - \frac{2e^2}{4\pi\epsilon_0|\vec{r}_1|}\Psi_1 = C\Psi_1$$

$$-\frac{\hbar^2}{2m}\nabla_2^2\Psi_2 - \frac{2e^2}{4\pi\epsilon_0|\vec{r}_2|}\Psi_2 = (E-C)\Psi_2$$

Indistinguishable Particles

1.
2.
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5.

$$|\Psi(r_1, r_2)|^2 = |\Psi(r_2, r_1)|^2$$

$$\Psi(r_1, r_2) = \pm\Psi(r_2, r_1)$$

Bosons:
$\Psi(r_1, r_2) = \Psi(r_2, r_1)$

Fermions:
$\Psi(r_1, r_2) = -\Psi(r_2, r_1)$

Fermions: $\Psi(r_1, r_2) = \frac{1}{\sqrt{2}}(\Psi_1(r_1)\Psi_2(r_2) - \Psi_1(r_2)\Psi_2(r_1))$

If $\Psi_1(r_1)\Psi_2(r_2) \rightarrow \Psi(r_1, r_2) = 0$ Pauli's exclusion principle

Relativistic QM: $\Psi(r_1, r_2) = \frac{1}{\sqrt{2}}\Psi_1(r_1)\Psi_2(r_2)(\alpha(r_1)\beta(r_2) - \alpha(r_2)\beta(r_1))$

Hamiltonian of a molecule

1.
2.
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Hamiltonian of a molecule (holds for any molecule)

$$H = -\sum_i \frac{\hbar^2}{2m_e}\nabla_i^2 - \sum_A \frac{\hbar^2}{2m_A}\nabla_A^2 - \sum_{i,A} \frac{Z_A e^2}{4\pi\epsilon_0 r_{iA}} - \sum_{i<j} \frac{e^2}{4\pi\epsilon_0 r_{ij}} - \sum_{A,B} \frac{Z_A Z_B e^2}{4\pi\epsilon_0 r_{AB}}$$

K.E. of electrons

K.E. of nucleus

Potential energies

Born Oppenheimer Approximation

1.
2.
3.
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5.

Fix the positions of the nuclei

$$H = -\sum_i \frac{\hbar^2}{2m_e}\nabla_i^2 - \sum_{i,A}\frac{Z_A e^2}{4\pi\epsilon_0 r_{iA}} - \sum_{i<j}\frac{e^2}{4\pi\epsilon_0 r_{ij}} - \sum_{A,B}\frac{Z_A Z_B e^2}{4\pi\epsilon_0 r_{AB}}$$

still too difficult. Neglect the electron-electron interactions

$$H = -\sum_i \frac{\hbar^2}{2m_e}\nabla_i^2 - \sum_{i,A}\frac{Z_A e^2}{4\pi\epsilon_0 r_{iA}} - \sum_{B,A}\frac{Z_A Z_B e^2}{4\pi\epsilon_0 r_{AB}}$$

Separation of variables

$$H_t(r_1, r_2, \ldots, r_n) = H_1(r_1) + H_2(r_2) + \ldots + H_n(r_n)$$

Fix the positions of the nuclei.
Solve the Schrödinger equation for 1e → (molecular orbitals) ground state and the excited states.

$$H_{MO} = -\frac{\hbar^2}{2m_e}\nabla_1^2 - \sum_A \frac{Z_A e^2}{4\pi\epsilon_0 r_{1A}}$$

Linear Combination of Atomic Orbitals

1.
2.
3.
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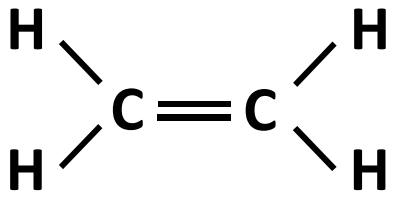
Ethene



Guess which atomic orbitals should be used to construct the molecular orbitals
A safe guess is to take them all.

$$\Psi_{MO} = c_1\psi_{1s1} + c_2\psi_{1s2} + c_3\psi_{2s1} + c_4\psi_{2s2} + c_5\psi_{2px1} + c_6\psi_{2px2} + c_7\psi_{2py1} + c_8\psi_{2py2} + c_9\psi_{2pz1} + c_{10}\psi_{2pz2} + c_{11}\psi_{1s3} + c_{12}\psi_{1s4} + c_{13}\psi_{1s5} + c_{14}\psi_{1s6}$$

$$H\Psi_{MO} = E\Psi_{MO}$$

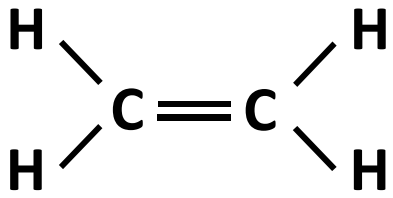
14 variables ?

$$\langle\psi^*_{1s1}|H|\Psi_{MO}\rangle = c_1\langle H_{11}\rangle + c_2\langle H_{12}\rangle + \cdots c_{14}\langle H_{1,14}\rangle$$

Linear Combination of Atomic Orbitals

1.
2.
3.
4.
5.

Ethene



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$$H\Psi_{MO} = E\Psi_{MO}$$

14 variables ?

$$\langle\psi^*_{1s1}|H|\Psi_{MO}\rangle = c_1\langle H_{11}\rangle + c_2\langle H_{12}\rangle + \cdots c_{14}\langle H_{1,14}\rangle =$$
$$= E\{c_1\langle S_{11}\rangle + c_2\langle S_{12}\rangle + \cdots c_{14}\langle S_{1,14}\rangle\}$$

How many of these we can write?

Linear Combination of Atomic Orbitals

1.
2.
3.
4.
5.

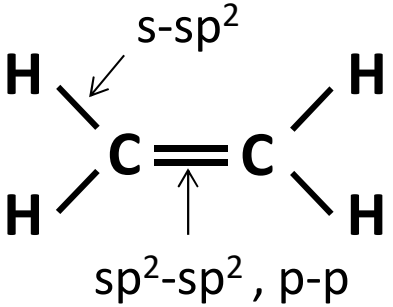
$$\begin{vmatrix} H_{11} & H_{12} & \cdots & H_{1N} \\ H_{21} & H_{22} & & \\ \vdots & & \ddots & \\ H_{N1} & & & H_{NN} \end{vmatrix} - E \begin{vmatrix} S_{11} & S_{12} & \cdots & S_{1N} \\ S_{21} & S_{22} & & \\ \vdots & & \ddots & \\ S_{N1} & & & S_{NN} \end{vmatrix} \begin{vmatrix} c_1 \\ c_2 \\ \vdots \\ c_N \end{vmatrix} = 0$$

Solve for c's and E.

For Ethene, the valence orbitals are

$$\Psi_{2pz1} \text{and } \psi_{2pz2}$$

$$\Psi_{\text{MO}} = c_1\psi_{2pz1} + c_2\psi_{2pz2}$$



Linear Combination of Atomic Orbitals

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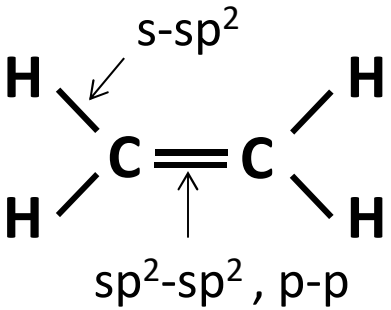
$$\Psi_{\mathrm{MO}} = c_1\psi_{2pz1} + c_2\psi_{2pz2}$$



Notation:

$$H_{ij} = \langle \psi_i | H | \psi_j \rangle$$

$$S_{ij} = \langle \psi_i | \psi_j \rangle$$

$$\begin{bmatrix} H_{11} - E & H_{12} - ES_{12} \\ H_{21} - ES_{21} & H_{22} - S \end{bmatrix} \begin{bmatrix} c_1 \\ c_2 \end{bmatrix} = 0$$

Solves for:

$$E^+ = \frac{H_{11} + H_{12}}{1 + S_{12}} \qquad E^- = \frac{H_{11} - H_{12}}{1 - S_{12}}$$

bounding anti-bounding

Atomic Bonding

1.
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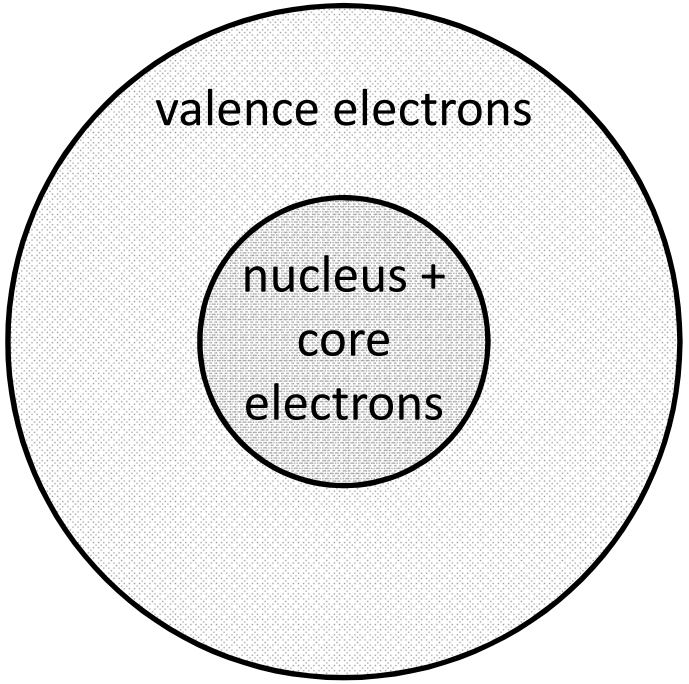
Atoms vibrate with small amplitudes about fixed equilibrium positions. We assume that atoms are fixed, unless phonons are considered.
Atoms look like outer valence electrons orbiting around the core. Core consists of nucleus plus inner core electrons.



Ionic bond: $Na^{+}Cl^{-}$
Covalent bond: sharing e^{-} to complete an octet
H need only one atom to complete the octet and therefore we only have H_2. Silicon needs 4 e^{-} and so can bond to four other Si atoms, forming a crystal.
Metallic bond:
Van derWaals:

Ionic Bonding

1.
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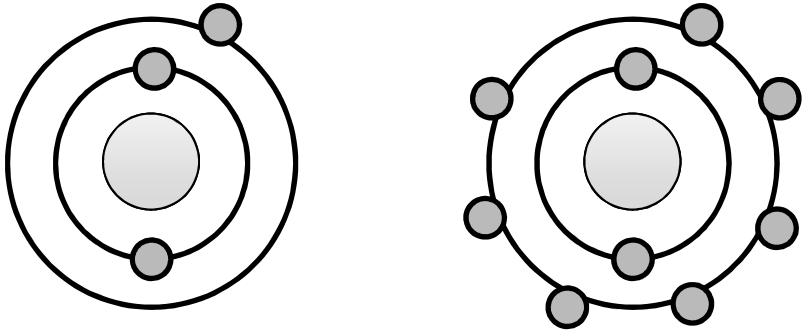
Complete transfer of electrons from one atom (usually a metal) to another (non metal ion) (compounds only, not elemental solids). Bond comes from electrostatic attraction between ions.

$$Na + Cl \rightarrow Na^{+} + Cl^{-} \rightarrow NaCl$$



All ionic compounds have a degree of covalent bonding. The larger the difference in electronegativity between two atoms, the more ionic the bond is.

- Bond is strong (high melting point, large elastic modulus)
- Not directional (high density, high coordination number)
- Compounds only
- Good insulators (except near melting point)
- Transparent up to UV (strong bonds →electrons need a lot of energy to become free)

Mathematical form: Energy ~ 1/r , Example: Sodium Chloride

Ionic Bonding

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Coulomb force:

$$F = \frac{e^2}{4\pi\epsilon_0 r^2}$$

Energy needed to separate charges e and -e

$$E = \int F.dr = \int_{0.2nm}^{\infty} \frac{-e^2}{4\pi\epsilon_0 r^2} dr = 7eV$$

Covalent Bonding

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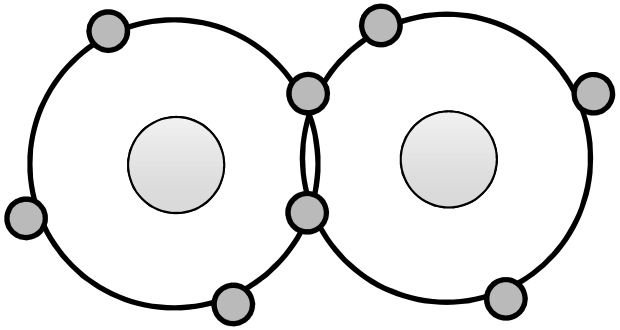

Equal sharing of electrons between atoms → both atoms have full shells
(Example: Diamond, Silicon)
Note continuum of behavior, ionic → covalent (e.g. III-V compounds GaAs, InSb, are partially covalent and partially ionic.)

- Bond is strong (high melting point, large elastic modulus)
- Directional (from orientation of QM orbitals) → low density
- Saturable (limited number of bonds per atom) ↑
- Good insulators

Covalent Bonding: Square well potential

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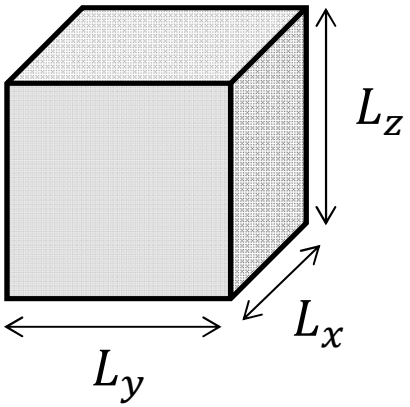

$$V = \begin{cases} 0 & \text{inside cube} \\ \infty & \text{outside cube} \end{cases}$$

$$-\frac{\hbar^2}{2m_0}\nabla^2\Psi = E\Psi$$

$$\Psi = \frac{2\sqrt{2}}{\sqrt{L_x L_y L_z}} \sin\frac{n_x \pi x}{L_x} \sin\frac{n_y \pi y}{L_y} \sin\frac{n_z \pi z}{L_z}$$

$$E_{n_x n_y n_z} = \frac{\hbar^2 \pi^2}{2m}\left(\frac{n_x^2}{L_x^2} + \frac{n_y^2}{L_y^2} + \frac{n_z^2}{L_z^2}\right)$$

Covalent Bonding: Square well potential

1.
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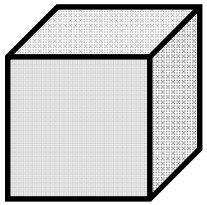
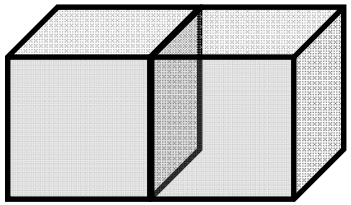
5.

$$E_{n_x n_y n_z} = \frac{\hbar^2 \pi^2}{2m}\left(\frac{n_x^2}{L_x^2} + \frac{n_y^2}{L_y^2} + \frac{n_z^2}{L_z^2}\right)$$



Energy of a particle confined to a cube L×L×L

$$E = \frac{3h^2}{8ml^2}$$



Energy of a particle confined to a cube L×L×2L

$$E = \frac{9h^2}{32ml^2}$$

Decrease in energy:

$$E = \frac{3h^2}{16ml^2}$$

For L= 0.2 nm: ΔE =14eV

Metallic Bonding

1.
2.
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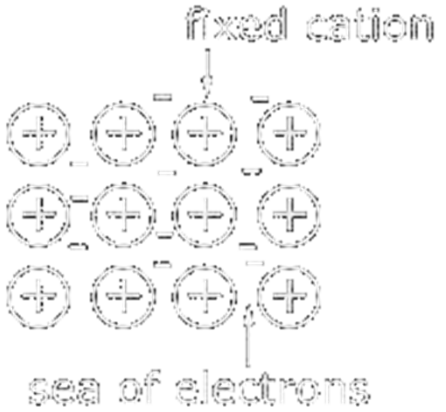
Positive ions plus gas (sea) of electrons. Think of this as the limiting case of ionic bonding in which the negative ions are electrons. (BUT electrons can't be forced to sit at lattice points from Uncertainty Principle: $\Delta p \Delta x \geq h/2$ as for electrons m is small so the zero point energy $\Delta E = \Delta p^2/2m$ is very large; the electrons would
shake themselves free and are therefore delocalized)

• Bonds are non directional (high coordination number, high density, malleable and ductile)

• Variable strength

• Free electrons → high electrical conductivity, shiny (Electric field associated with incident light makes free electrons at surface move back and forth, re-radiating the light, as a reflected beam)



Metallic Bonding

1.
2.
3.
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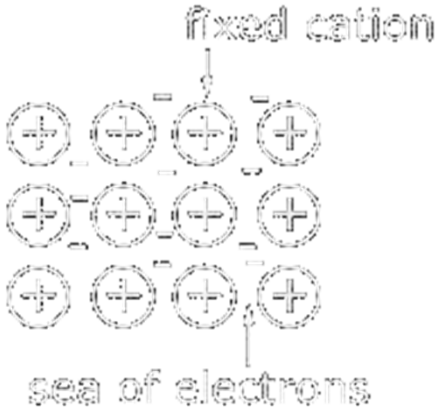
The electron wave functions spread out over the entire crystal.
A three dimensional potential square well is a simple model for a metal.

$$E_{n_x n_y n_z} = \frac{\hbar^2 \pi^2}{2m}\left(\frac{n_x^2}{L_x^2} + \frac{n_y^2}{L_y^2} + \frac{n_z^2}{L_z^2}\right)$$



Energy mostly determines by Electrostatic force!

Van der Waals Bond

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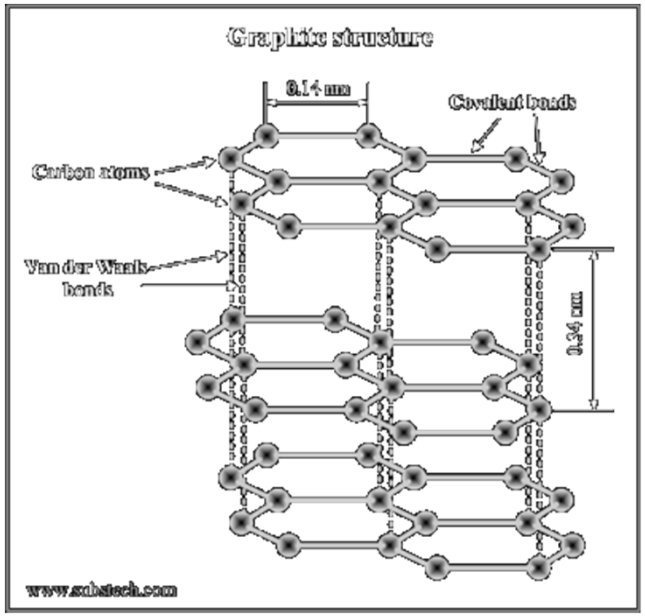

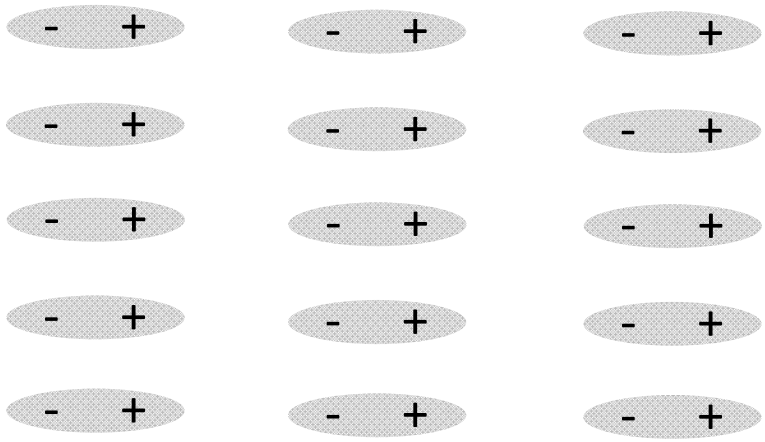

Even a neutral atom with a full shell, can, at a given instant, have a dipole moment (i.e. one side of the atom more positive than the other) This instantaneous dipole will induce a dipole in a neighboring atom, and the resulting dipole-dipole interaction is the origin of the van der Waals bond. Although the original dipole time-averages to zero, the interaction does not – it is always attractive. Energy ~ $1/r^6$

- Bond is weak (→low melting point, large expansion coefficient)
- Non directional so high coordination number BUT
- Long bond lengths (→low density)

Examples: Solid inert gases (Argon, Neon), molecular solids (solid Oxygen)

Hydrogen Bonding

1.
2.
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Hydrogen loses its electron and becomes positively charged particularly easily. Therefore the region of a molecule around a hydrogen atom is often quite positive, and this allows an electrostatic bond to form between it and negative parts of neighboring molecules.
Example: ice – the strength of the hydrogen bond explains the anomalously high melting point of ice

Valence Bond Theory

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$$H = -\sum_i \frac{\hbar^2}{2m_e}\nabla_i^2 + U(r)$$

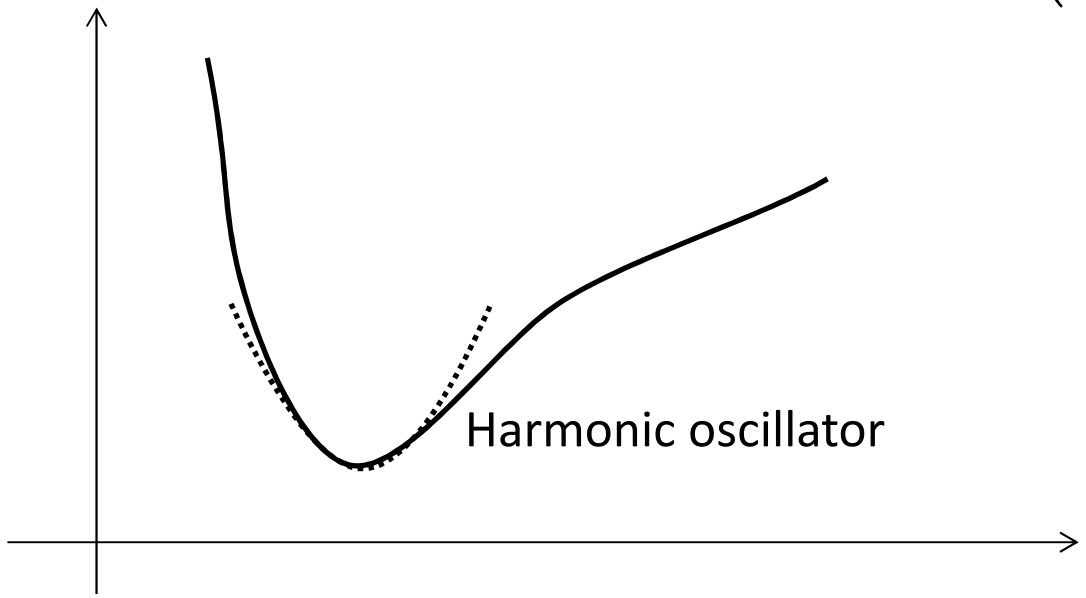
Bond potentials

Morse (covalent)

$$U(r) = U_0\left(e^{-2(r-r_0)/a} - 2e^{-(r-r_0)/a}\right)$$

Lennard-Jones (van der Waals)

$$U(r) = 4E_0\left(\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^{6}\right)$$



Diffraction , Reciprocal Lattice

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Diffraction

1.
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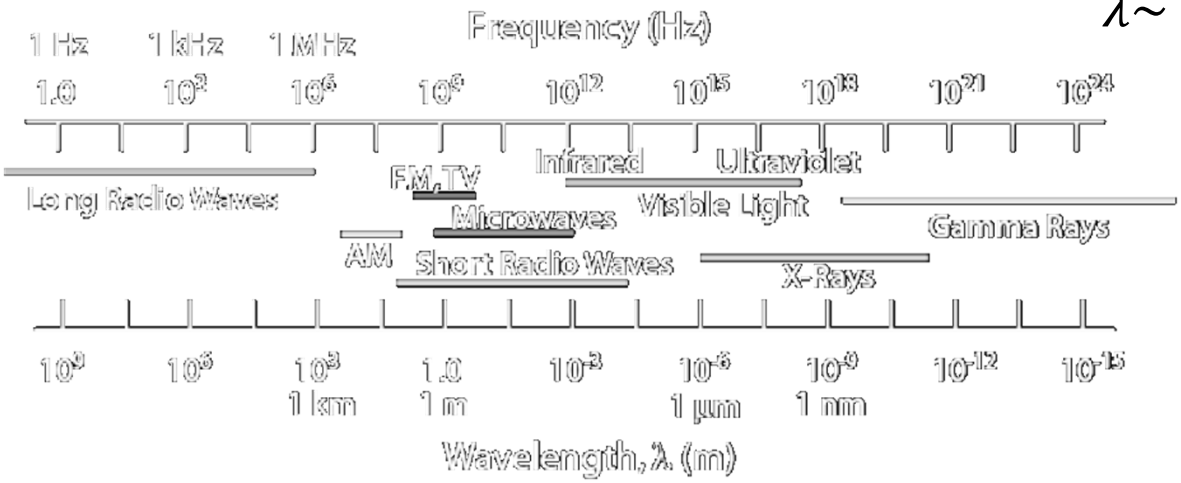
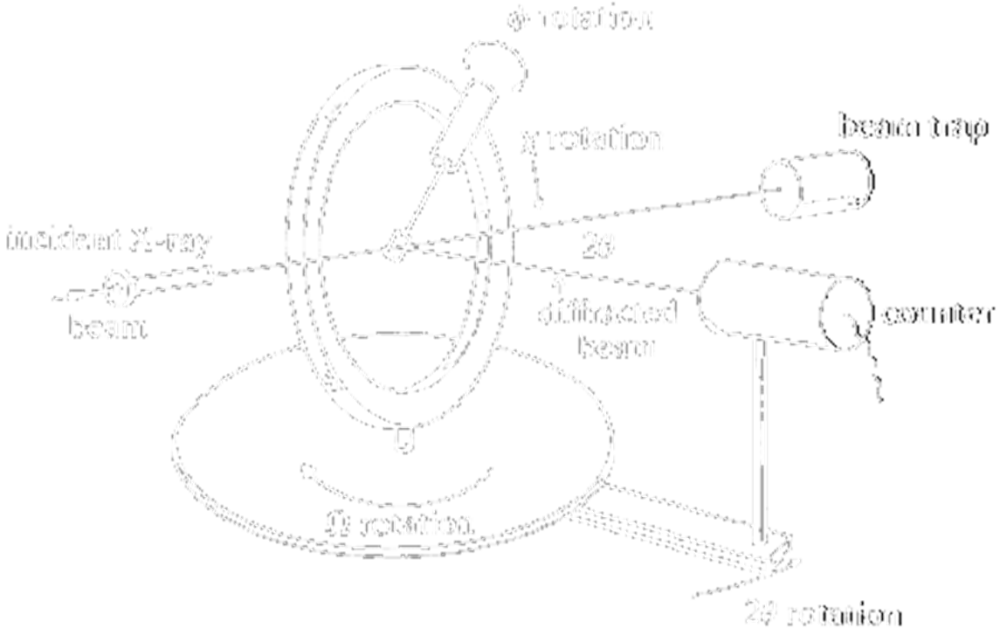
5.

Electromagnetic Spectrum



$\lambda\sim$ or < lattice constant

→ Diffraction at angles different from incident direction



Applications of X-Ray Diffraction: Determination of
– crystal structure and its lattice parameters
– spacing between lattice planes (hkl Miller indices)

Bragg Law

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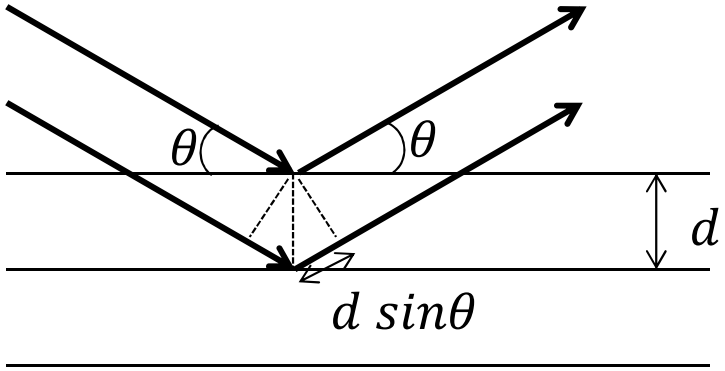
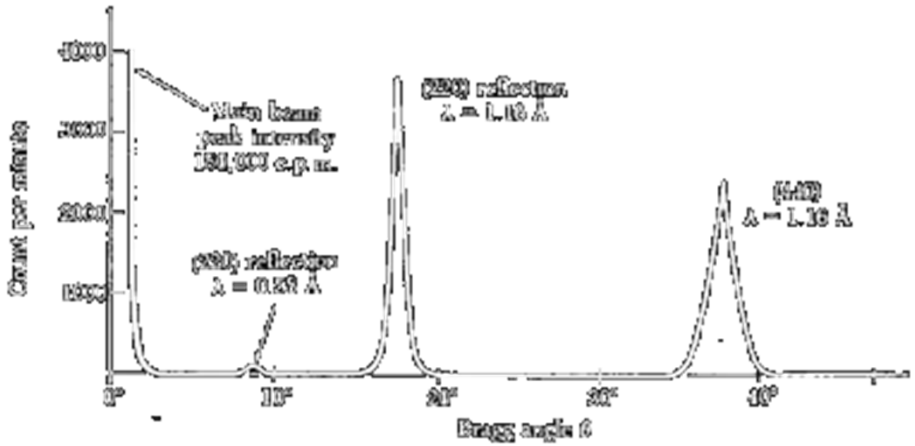


elastic scattering of X-ray

Constructive interference: $2dsin\theta = n\lambda$



Fourier series

1.
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3.
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1-D $$f(x) = \sum_{G=-\infty}^{+\infty} f_G e^{iGx}$$

$$f(x) = f(x + a)$$

$$G = \frac{2\pi n}{a} \qquad n = 0,1,2,3, \ldots$$

Reciprocal lattice vector

Allowed terms in Fourier series

3-D $$f(\vec{r}) = \sum_{\vec{G}} f_{\vec{G}} e^{i\vec{G}\cdot\vec{r}}$$

$G \in$ Reciprocal space

Reciprocal space = Wave vector space = k-space

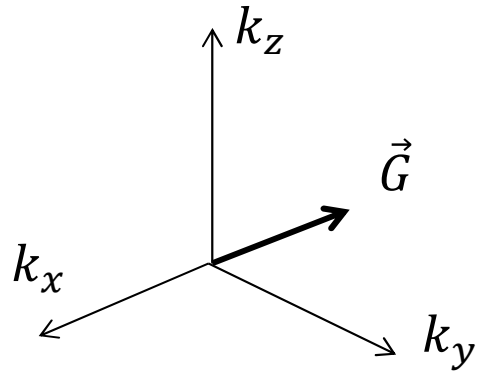
$$f_{\vec{G}} = \frac{1}{V} \iiint_{Unit\ cell} f(\vec{r}).\, e^{i\vec{G}\cdot\vec{r}} d^3r$$

$V =$ volume of the primitive unit cell

Reciprocal space (k-space)

1.
2.
3.
4.
5.

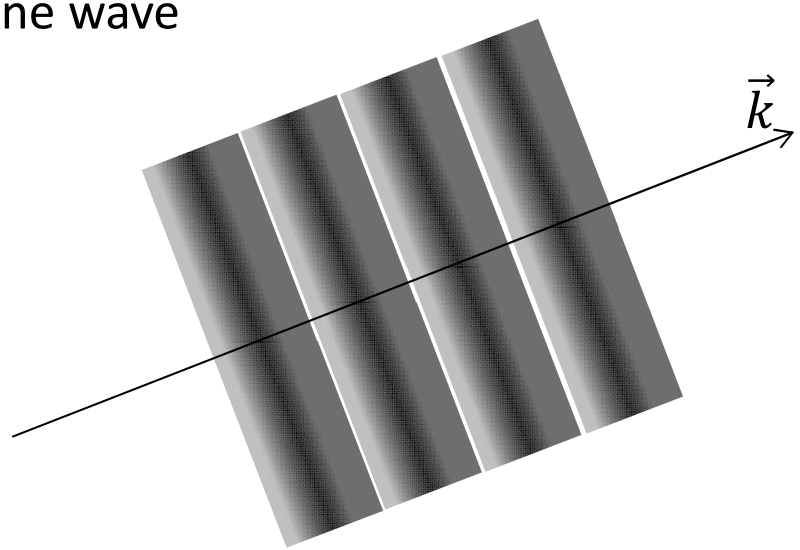
k-space is the space of all wave-vectors



wavelength: $\lambda = \frac{2\pi}{|\vec{k}|}$

momentum: $\vec{p} = \hbar\vec{k}$

Plane wave



Reciprocal (momentum) space (k-space)

1.
2.
3.
4.
5.

The reciprocal lattice of a lattice (usually a Bravais lattice) is the lattice in which the Fourier transform of the spatial function of the original lattice (or direct lattice) is represented.

real space primitive vectors: $\mathbf{T} = n_1\boldsymbol{a_1} + n_2\boldsymbol{a_2} + n_3\boldsymbol{a_3}$ sc , fcc, bcc

reciprocal lattice primitive vectors: : $\mathbf{G} = \upsilon_1\boldsymbol{b_1} + \upsilon_2\boldsymbol{b_2} + \upsilon_3\boldsymbol{b_3}$ sc , bcc, fcc

$$V = \boldsymbol{a}_1 \cdot (\boldsymbol{a}_2 \times \boldsymbol{a}_3)$$

$$\boldsymbol{b}_1 = \frac{2\pi}{V}(\boldsymbol{a}_2 \times \boldsymbol{a}_3)$$

$$\boldsymbol{b}_2 = \frac{2\pi}{V}(\boldsymbol{a}_3 \times \boldsymbol{a}_1)$$

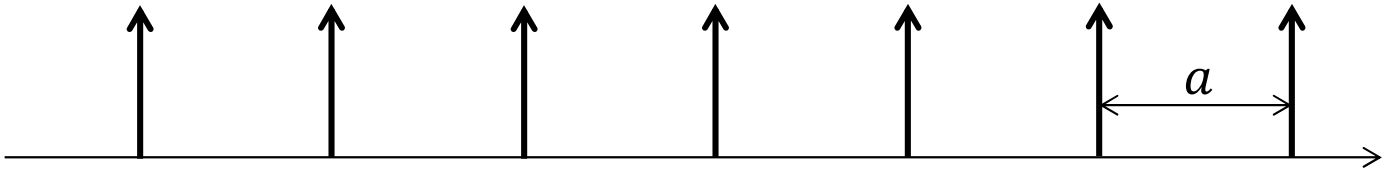
$$\boldsymbol{b}_3 = \frac{2\pi}{V}(\boldsymbol{a}_1 \times \boldsymbol{a}_2)$$

$$f(\vec{r}) = f(\vec{r} + \boldsymbol{T}) = \sum_{\vec{G}} f_{\vec{G}} e^{i\vec{G}\cdot\vec{r}}$$

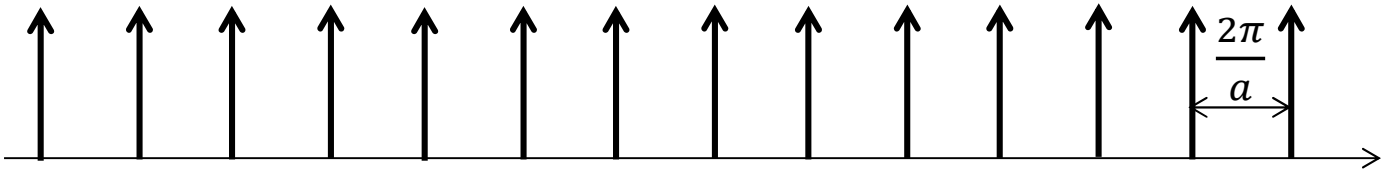
Dirac Comb

1.
2.
3.
4.
5.

real space

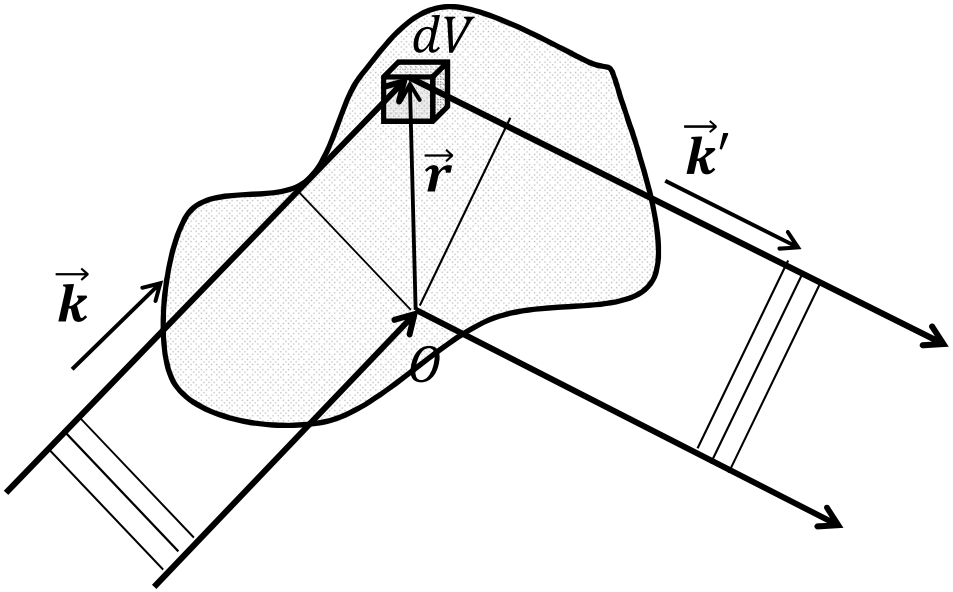


reciprocal space

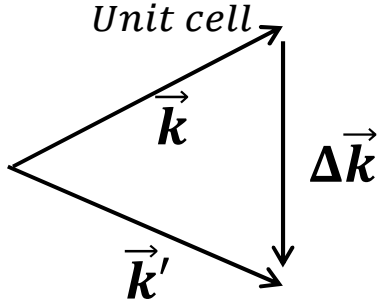


Diffraction Condition

1.
2.
3.
4.
5.



$$f_{\vec{G}} = \frac{1}{V} \iiint_{Unit\ cell} f(\vec{r}).e^{i\vec{G}\cdot\vec{r}} d^3r$$



Total difference in phase angle= $(\vec{k} - \vec{k}') \cdot \vec{r}$

Phase factor between wave scattered from O and dV = $e^{i(\vec{k}-\vec{k}')\cdot\vec{r}}$

Scattering condition: $\Delta\vec{k} = \boldsymbol{G}$

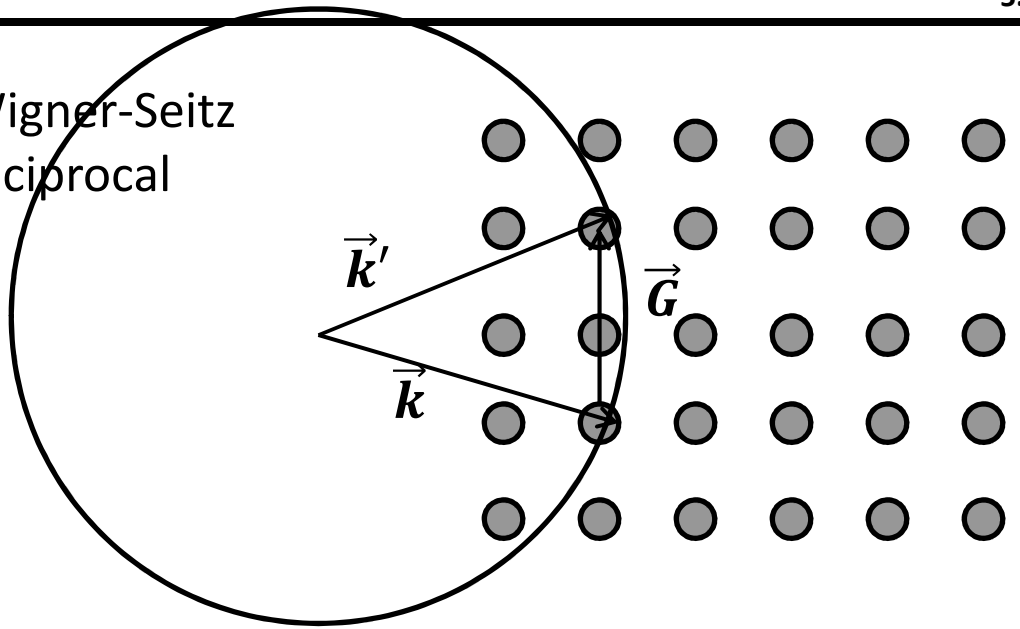
elastic scattering $|\vec{k}| = |\vec{k}'|$

$$2\vec{k} \cdot \vec{G} = G^2$$

Brillouin Zone

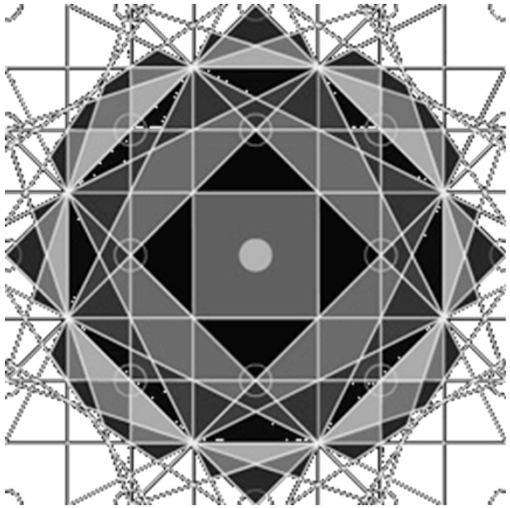
1.
2.
3.
4.
5.

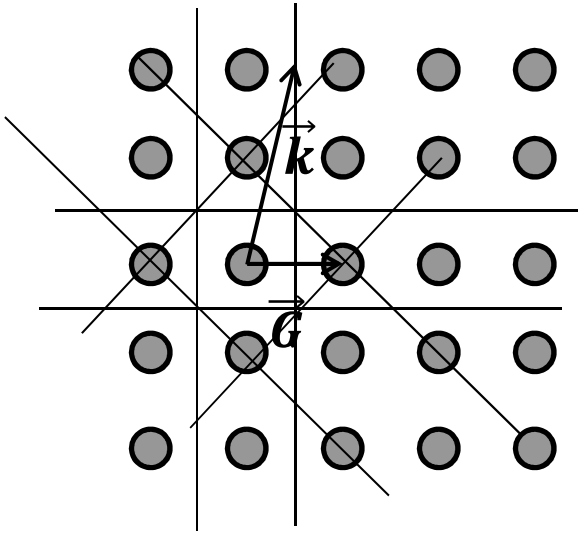
Brillouin zone = Wigner-Seitz primitive cell in reciprocal space



$$2\vec{k}\cdot\vec{G} = G^2$$

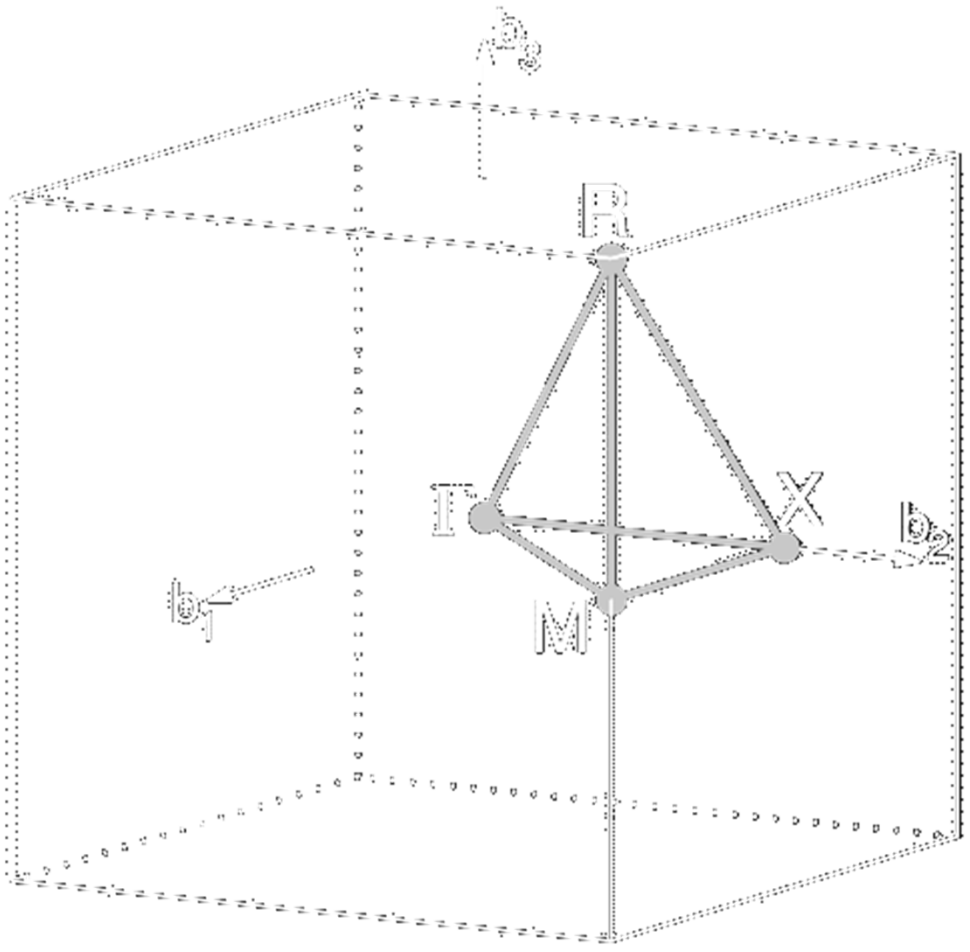
$$\vec{k}\cdot\left(\tfrac{1}{2}\vec{G}\right) = \left(\tfrac{1}{2}G\right)^2$$





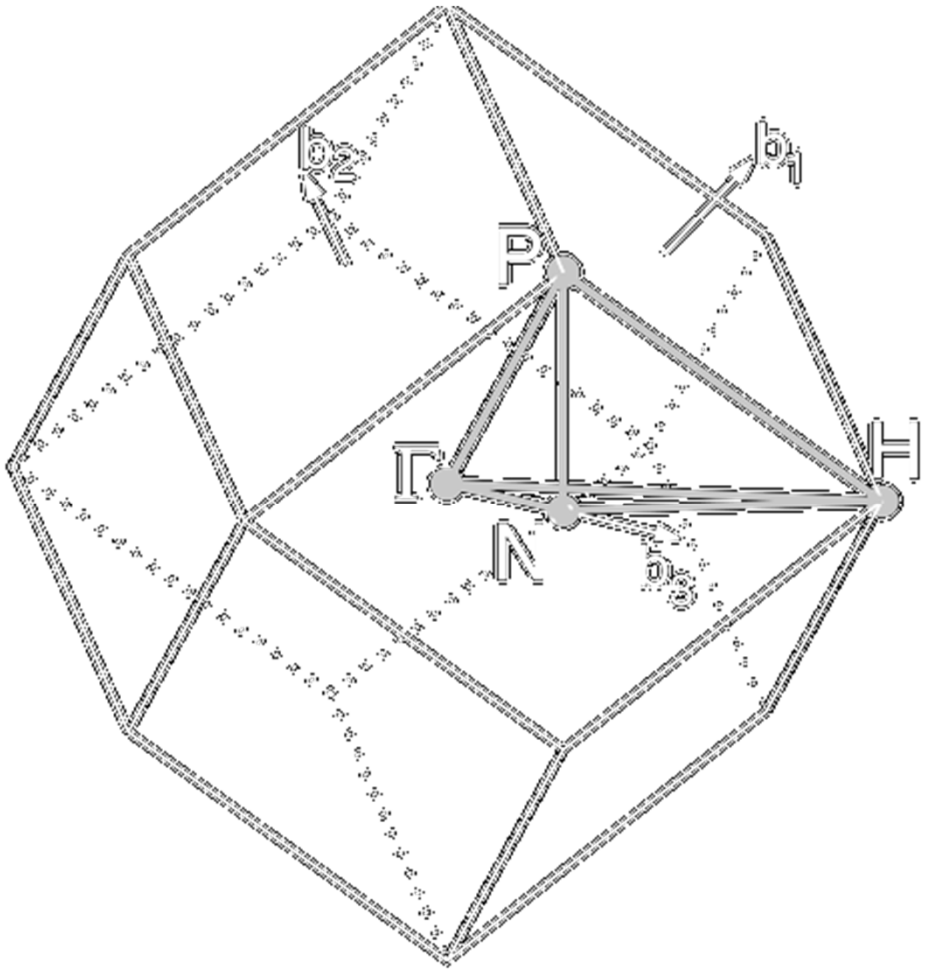
Brillouin Zone of Simple Cubic lattice

1.
2.
3.
4.
5.



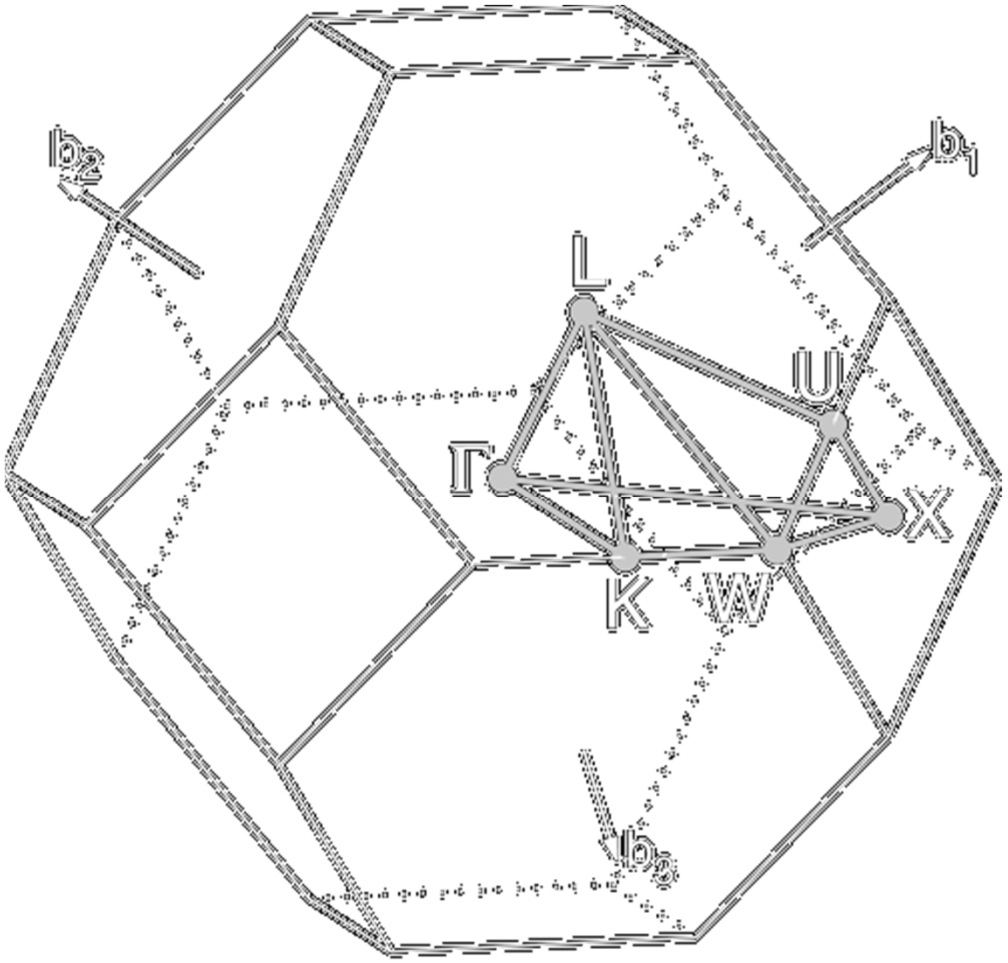
Brillouin Zone of Body-Centered Cubic Lattice

1.
2.
3.
4.
5.



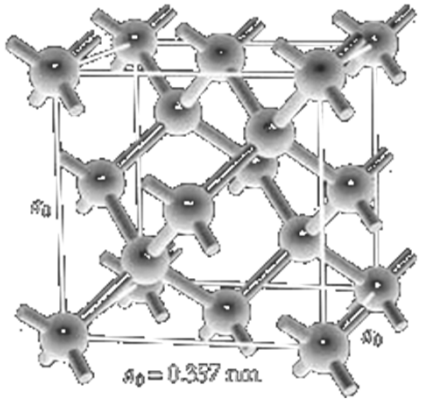
Brillouin Zone of Face-Centered Cubic Lattice

1.
2.
3.
4.
5.



Diamond

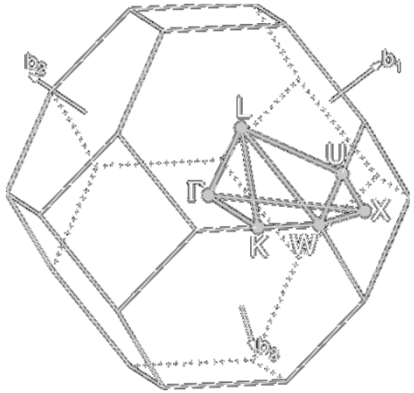
1.
2.
3.
4.
5.



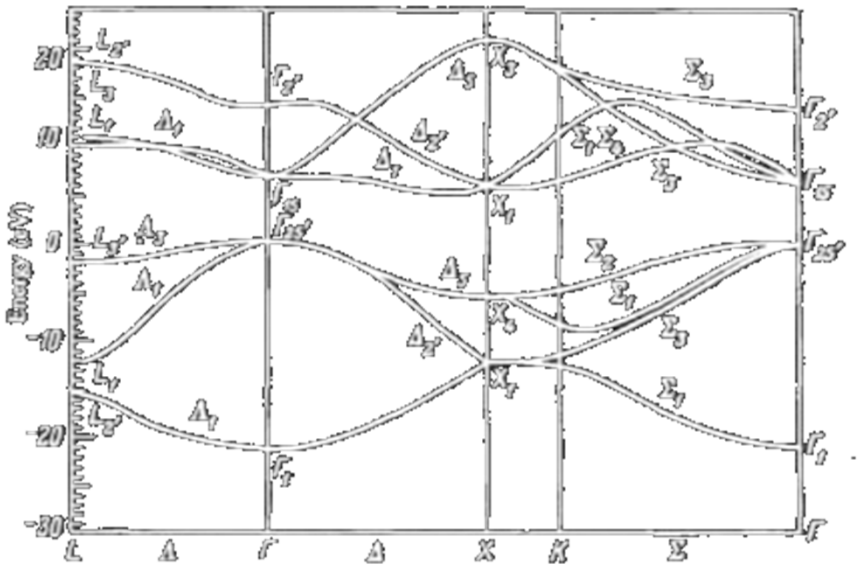
Diamond = FCC with 2 atoms / UC

C @ $[0 \quad 0 \quad 0]$

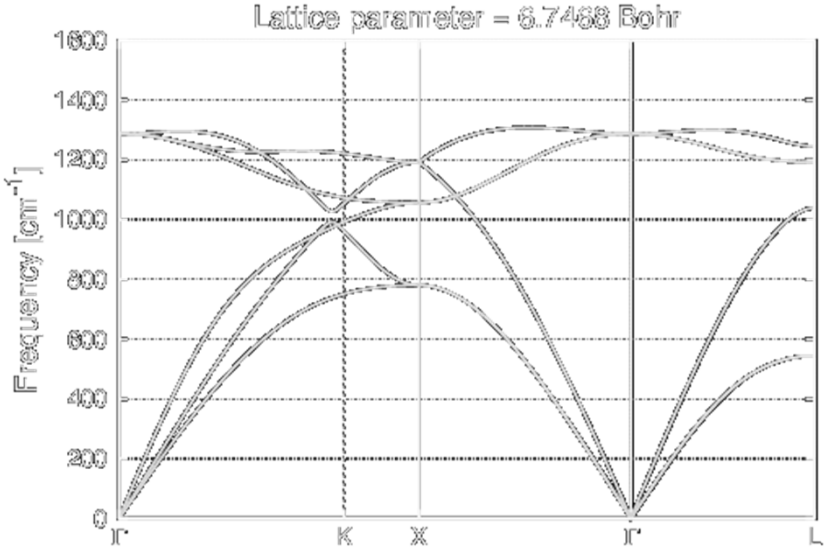
C @ $\left[\frac{1}{4} \quad \frac{1}{4} \quad \frac{1}{4}\right]$



diamond electronic band structure



diamond phonon dispersion



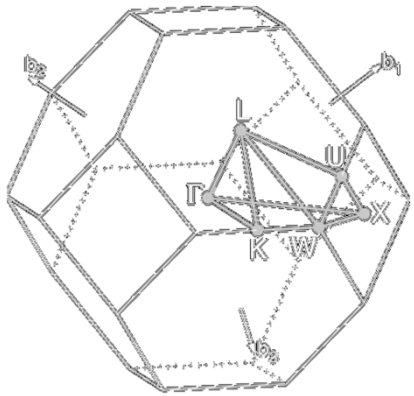
Silicon Carbide

1.
2.
3.
4.
5.

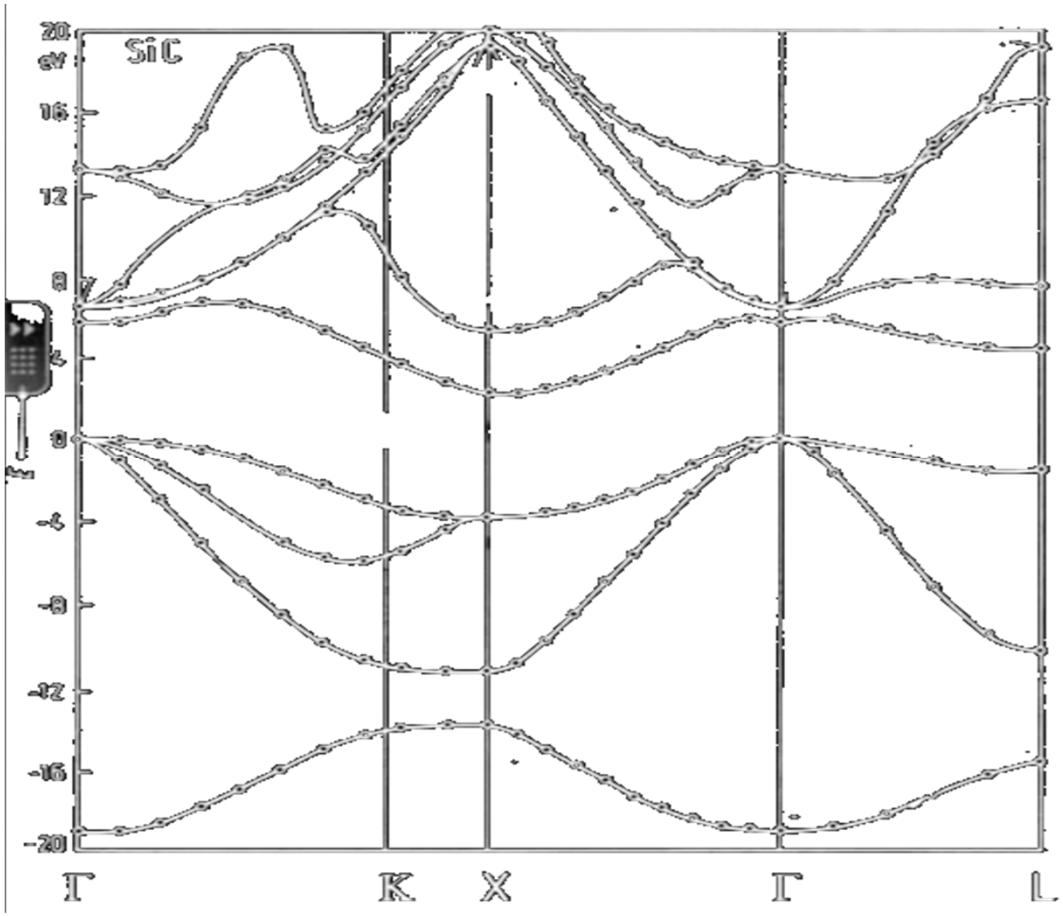
Silicon Carbide = FCC with 2 atoms / UC

Si @ $[0 \quad 0 \quad 0]$

C @ $\left[\frac{1}{4} \quad \frac{1}{4} \quad \frac{1}{4}\right]$



electronic band structure



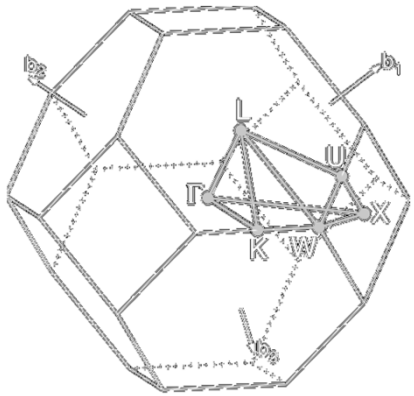
Silicon

1.
2.
3.
4.
5.

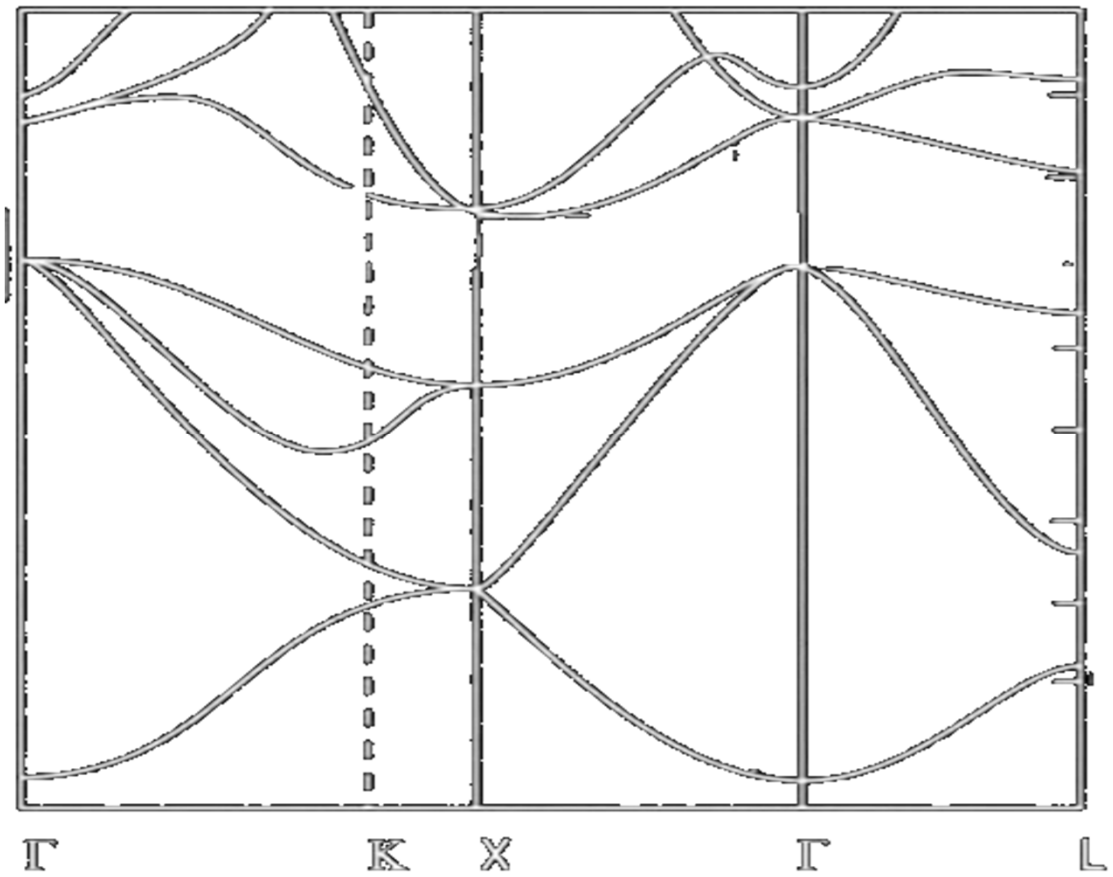
Silicon = FCC with 2 atoms / UC

Si @ $[0 \quad 0 \quad 0]$

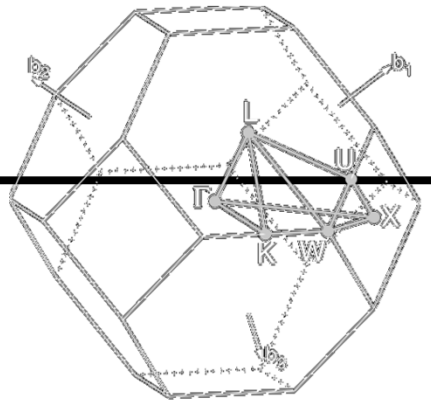
Si @ $\left[\frac{1}{4} \quad \frac{1}{4} \quad \frac{1}{4}\right]$



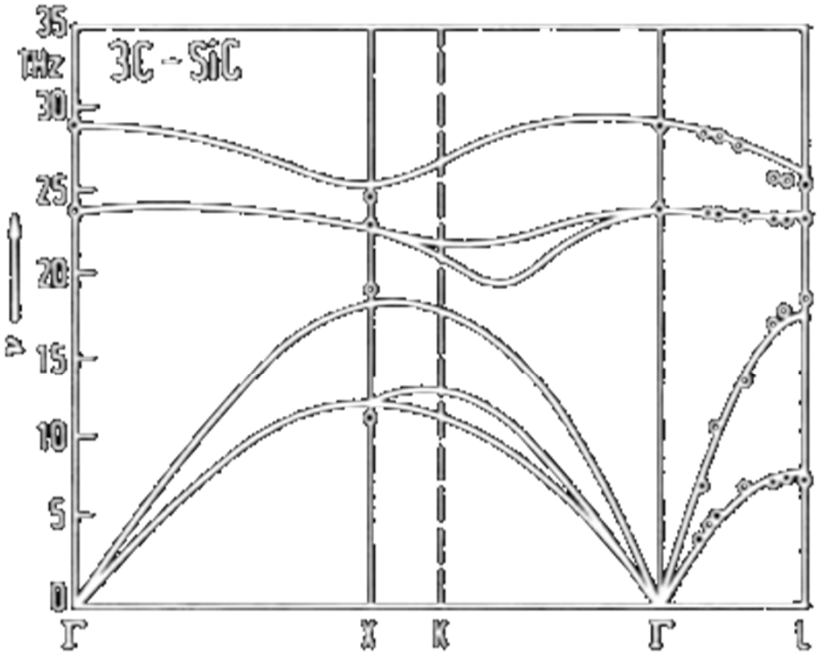
electronic band structure



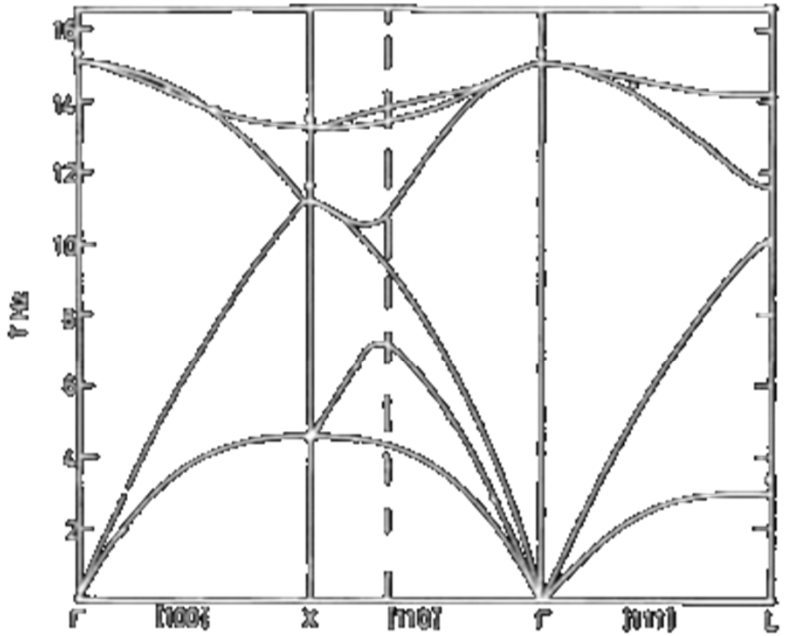
Phonons



1.
2.
3.
4.
5.



Silicon Carbide Phonons



Silicon Phonons

Fourier Analysis of Basis

1.
2.
3.
4.
5.

$$f(\vec{r}) = \sum_{\vec{G}} f_{\vec{G}} e^{i\vec{G}\cdot\vec{r}} \qquad f_{\vec{G}} = \frac{1}{V} \iiint_{Unit\ cell} f(\vec{r}).e^{-i\vec{G}\cdot\vec{r}} d^3r$$

Electron concentration $n(\vec{r})$

$$S_{\vec{G}} = \iiint_{Unit\ cell} n(\vec{r}).e^{-i\vec{G}\cdot\vec{r}} d^3r$$ Structure factor

$$n(\vec{r}) = \sum_{j-1}^{s} n_j(\vec{r} - \vec{r}_i)$$ $\vec{r}_i$ = vector to the center of atom j

$$\vec{\rho} = \vec{r} - \vec{r}_i$$

$$S_{\vec{G}} = \sum_j \iiint_{Unit\ cell} n_j(\vec{r} - \vec{r}_i).e^{-i\vec{G}\cdot\vec{r}} d^3r = \sum_j e^{-i\vec{G}\cdot\vec{r}_j} \iiint_{Unit\ cell} n_j(\vec{\rho}).e^{-i\vec{G}\cdot\vec{\rho}} d^3r$$

Atomic form factor f_j

$$S_{\vec{G}} = \sum_j f_j e^{-i\vec{G}\cdot\vec{r}_j}$$

Energy Bands

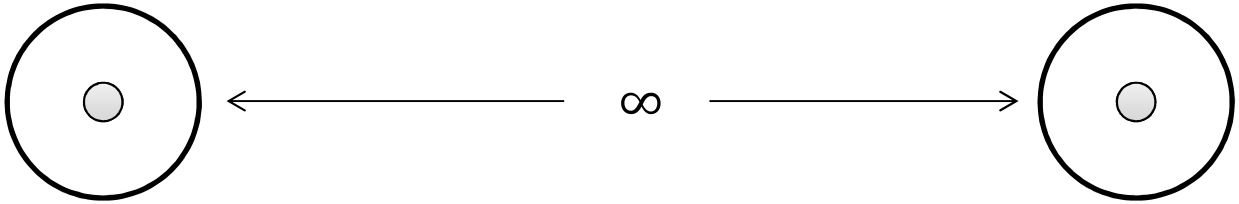
1.
2.
3.
4.
5.

Always simplify!

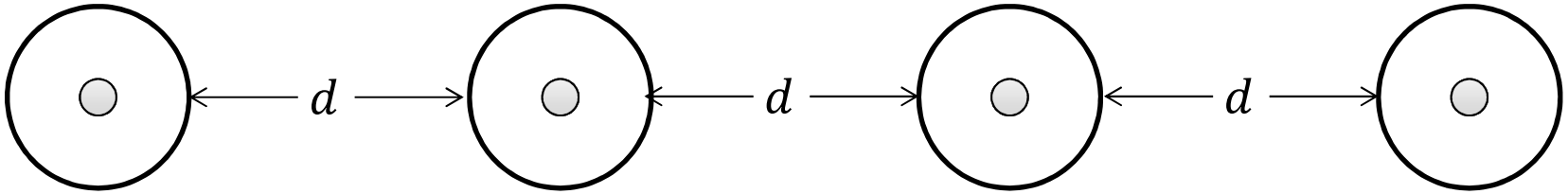
Our life is frittered away by detail. Simplify, simplify, simplify! I say, let your affairs be as two or three, and not a hundred or a thousand; instead of a million count half a dozen, and keep your accounts on your thumb-nail.
Thoreau, Henry David

Henry David Thoreau
(July 12, 1817 – 1862)

Simplest state: Isolated atom

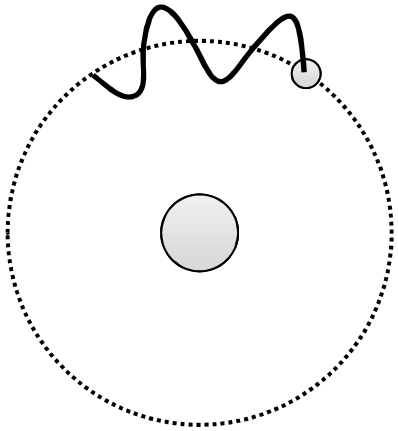


Periodic atoms:



Bohr Atomic Model

1.
2.
3.
4.
5.

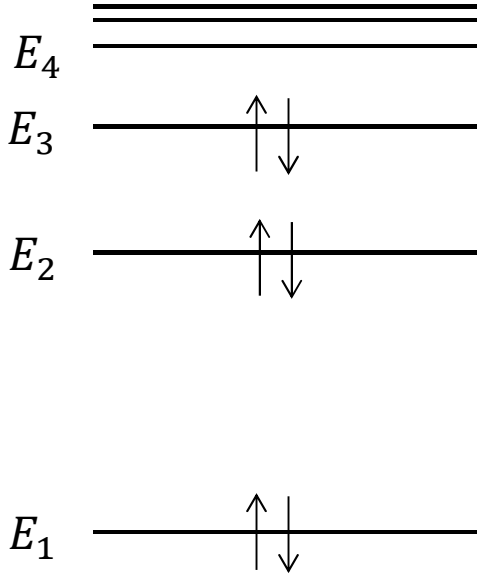


wave-particle duality $\lambda = h/p$

$$mvr = n\hbar$$

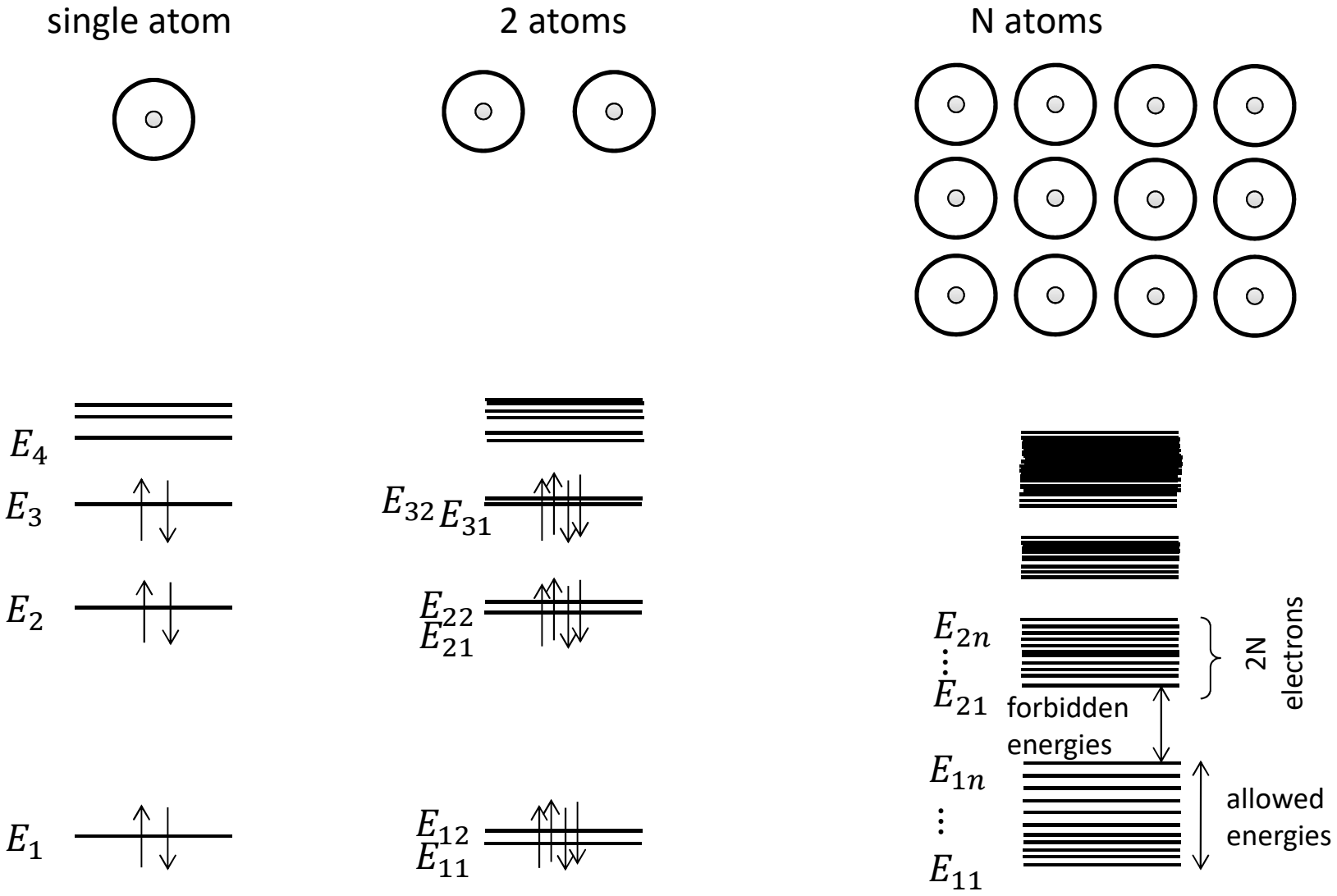
de Broglie standing wave

Energy Bands:



Bohr Atomic Model

1.
2.
3.
4.
5.



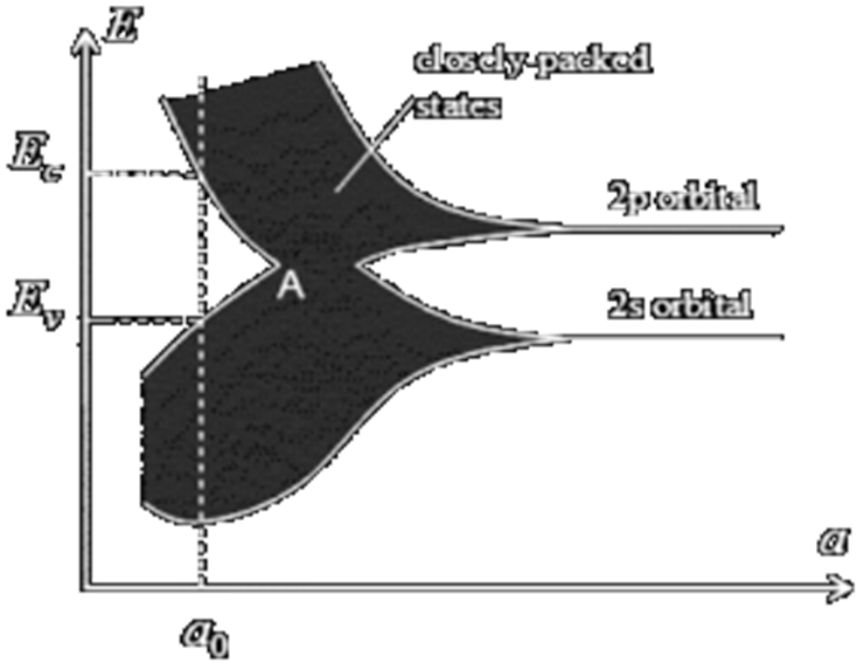
Pauli exclusion principle

Electrons in Solids

1.
2.
3.
4.
5.

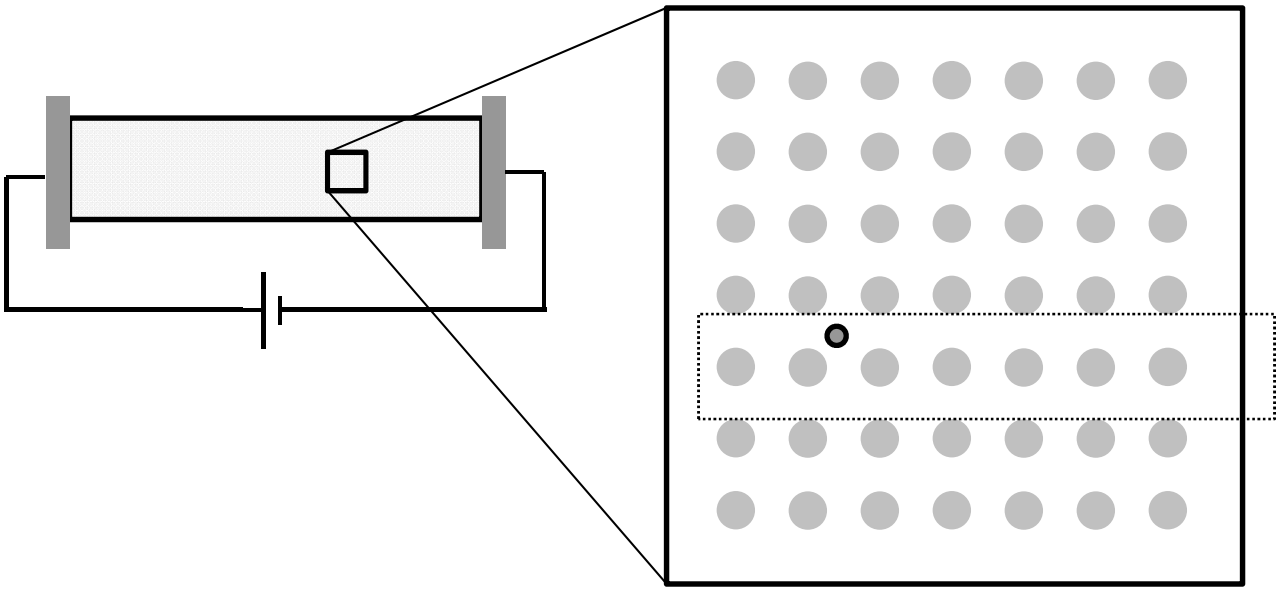
In a solid, there are so many electrons with energies very near each other that ‘bands’
of states develop.

Formation of energy bands as a diamond lattice crystal is formed by bringing isolated silicon atoms together



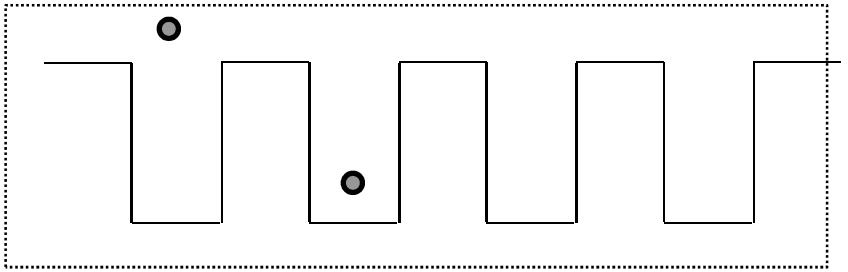
Solid State Problem!

1.
2.
3.
4.
5.



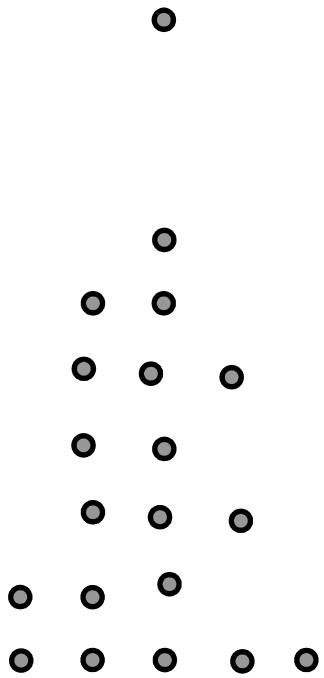
Talking about macroscopic properties by microscopic analysis!

Electrons in periodic potential:



Carrier Density

1.
2.
3.
4.
5.

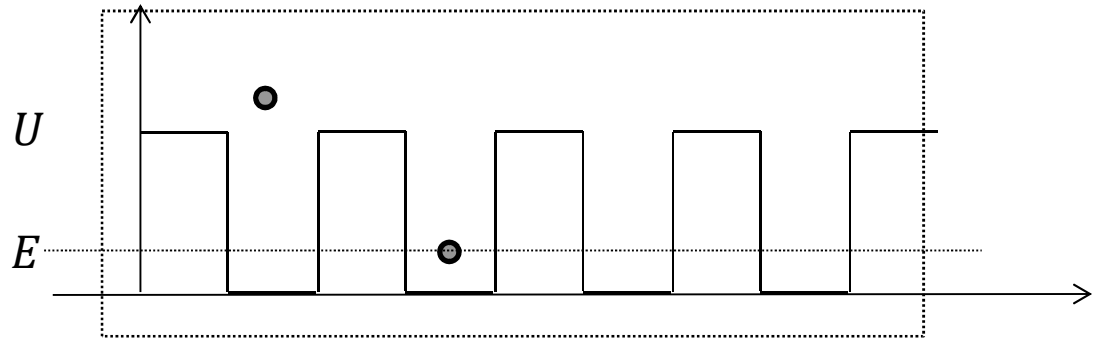


Carrier number = Number of states x filling factor

$$D(E) \qquad f(E)$$

Solid State Problem!

1.
2.
3.
4.
5.



$$-\frac{\hbar^2}{2m_0}\frac{d^2\psi}{dx^2} + V(r)\psi = E\psi$$

$$\frac{d^2\psi}{dx^2} + \frac{2m}{\hbar^2}(E-U)\psi = 0$$

$E > U$:

$$\frac{d^2\psi}{dx^2} + k^2\psi = 0 \qquad k = \frac{1}{\hbar}\sqrt{2m(E-U)}$$

$$\psi = A_+ e^{ikx} + A_- e^{-ikx}$$

$E < U$:

$$\frac{d^2\psi}{dx^2} - \alpha^2\psi = 0 \qquad \alpha = \frac{1}{\hbar}\sqrt{2m(U-E)}$$

$$\psi = De^{-\alpha x} + Ee^{\alpha x}$$

Five Steps for Analytical Solution,N regions

1.
2.
3.
4.
5.

1. $\frac{d^2\psi}{dx^2} + k^2\psi = 0$ — *2N unknowns for N regions*

2. $\psi(\infty) \to 0 \qquad \psi(-\infty) \to 0$ — *Reduces 2 unknowns*

3. $\psi\Big|_{x_B^-} = \psi\Big|_{x_B^+} \qquad \frac{d\psi}{dx}\Big|_{x_B^-} = \frac{d\psi}{dx}\Big|_{x_B^+}$ — *2N-2 equations*

4. Det (coefficient matrix)=0 — *1 equation for E*

5. $\int_{-\infty}^{\infty} |\psi|^2 dx = 1$ — *normalization*

Bound-levels in Finite Well

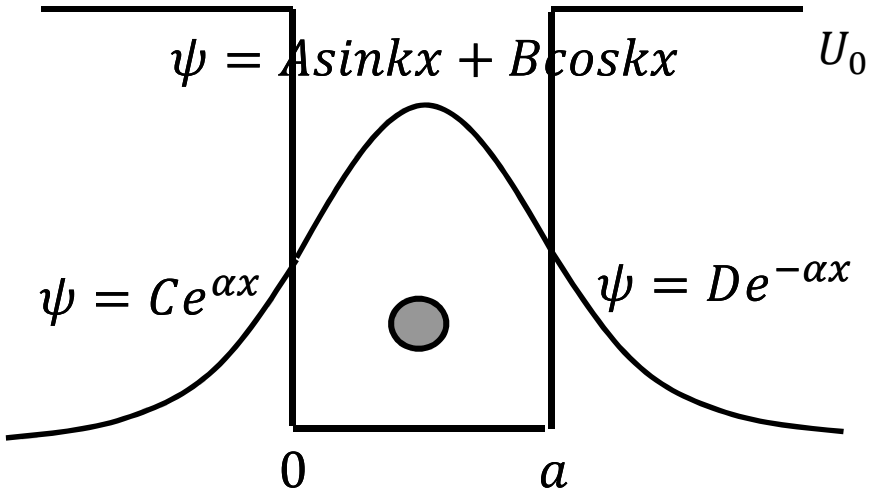
1.
2.
3.
4.
5.

$$\psi\Big|_{x_B^-} = \psi\Big|_{x_B^+}$$

$$\frac{d\psi}{dx}\Big|_{x_B^-} = \frac{d\psi}{dx}\Big|_{x_B^+}$$

$$C = B$$

$$\alpha C = kA$$



$$Asinka + Bcoska = De^{-\alpha a}$$

$$kAcoska - kBsinka = -\alpha De^{-\alpha a}$$

$$\begin{pmatrix} 0 & 1 & -1 & 0 \\ k & 0 & \alpha & 0 \\ \sin ka & \cos ka & 0 & -e^{-\alpha a} \\ \cos ka & -\sin ka & 0 & \alpha e^{-\alpha a}/k \end{pmatrix} \begin{bmatrix} A \\ B \\ C \\ D \end{bmatrix} = \begin{bmatrix} 0 \\ 0 \\ 0 \\ 0 \end{bmatrix}$$

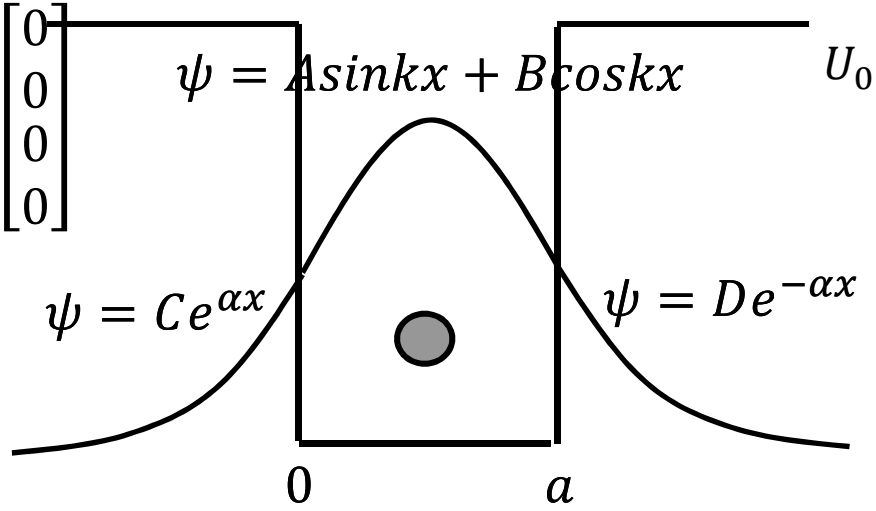
Bound-levels in Finite Well

1.
2.
3.
4.
5.

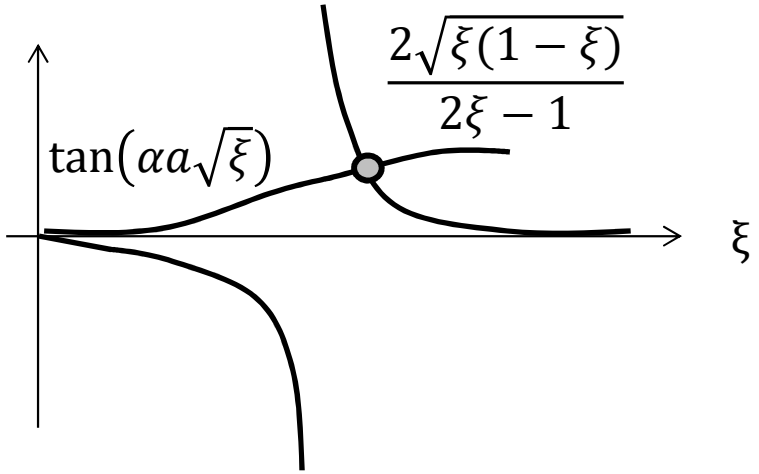
$$\begin{pmatrix} 0 & 1 & -1 & 0 \\ k & 0 & \alpha & 0 \\ \sin ka & \cos ka & 0 & -e^{-\alpha a} \\ \cos ka & -\sin ka & 0 & \alpha e^{-\alpha a}/k \end{pmatrix} \begin{bmatrix} A \\ B \\ C \\ D \end{bmatrix} = \begin{bmatrix} 0 \\ 0 \\ 0 \\ 0 \end{bmatrix}$$

$$\det(\quad) = 0$$

$$\xi = E/U_0 \qquad \alpha = \frac{1}{\hbar}\sqrt{2m(U-E)}$$



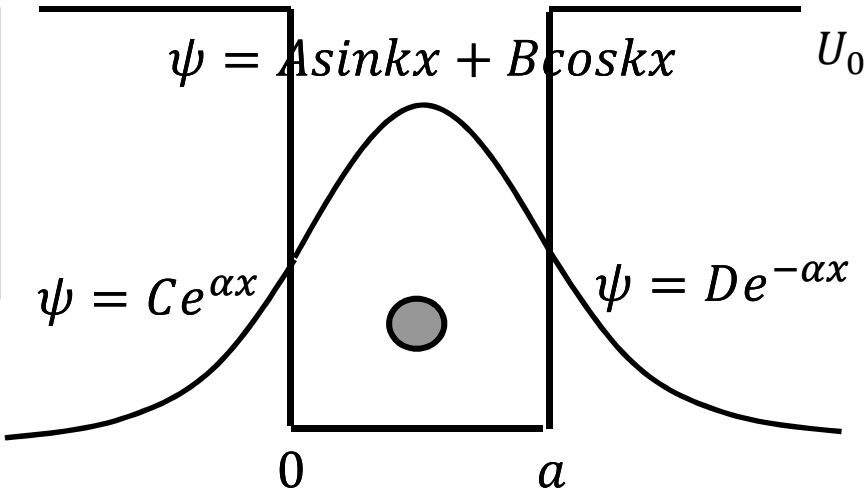
$$\tan\left(\alpha a\sqrt{\xi}\right) = \frac{2\sqrt{\xi(1-\xi)}}{2\xi - 1}$$



Bound-levels in Finite Well, wave function

1.
2.
3.
4.
5.

$$\begin{pmatrix} 0 & 1 & -1 & 0 \\ k & 0 & \alpha & 0 \\ \sin(ka) & \cos(ka) & 0 & e^{-\alpha a} \\ \cos(ka) & -\sin(ka) & 0 & -\alpha D e^{-\alpha a}/k \end{pmatrix} \begin{vmatrix} A \\ B \\ C \\ D \end{vmatrix} = \begin{vmatrix} 0 \\ 0 \\ 0 \\ 0 \end{vmatrix}$$



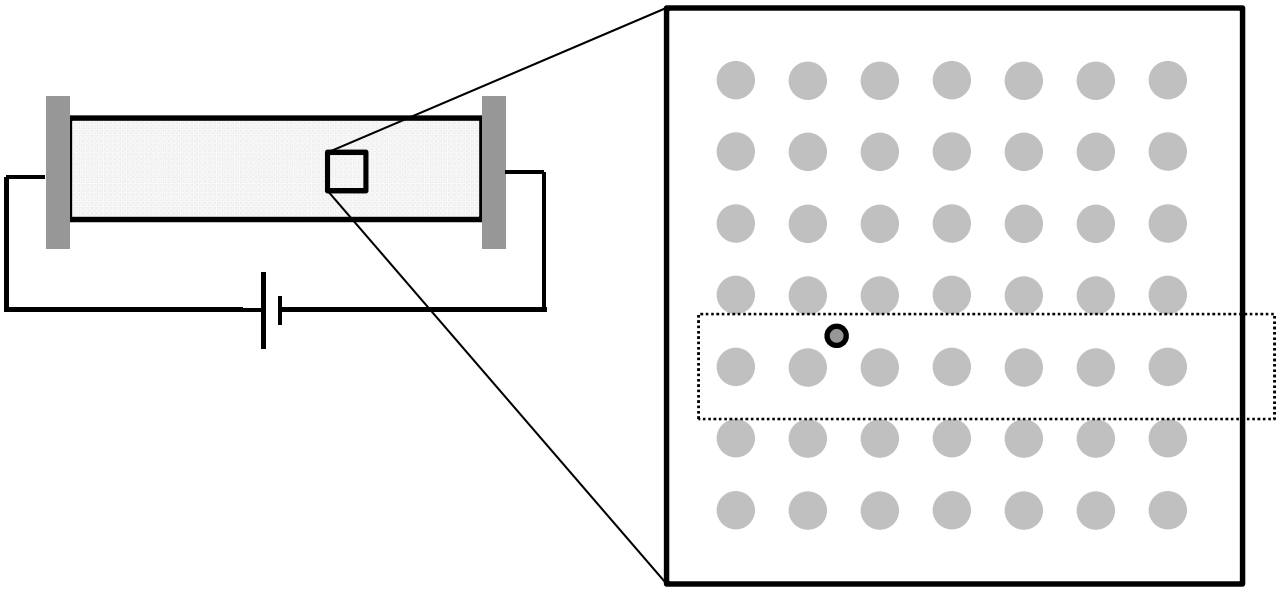
$$\begin{vmatrix} B \\ C \\ D \end{vmatrix} = \begin{pmatrix} 1 & -1 & 0 \\ 0 & \alpha & 0 \\ \cos(ka) & 0 & e^{-\alpha a} \end{pmatrix}^{-1} \begin{vmatrix} 0 \\ kA \\ A\sin(ka) \end{vmatrix}$$

$$\int_{-\infty}^{\infty} \psi^2 dx = 1 \quad \text{=>}$$

$$\int_{-\infty}^{0} C^2 e^{2\alpha x} dx + \int_{0}^{a} \left| A\sin(kx) + B\sin(kx) \right|^2 dx + \int_{a}^{\infty} D^2 e^{-2\alpha x} dx$$

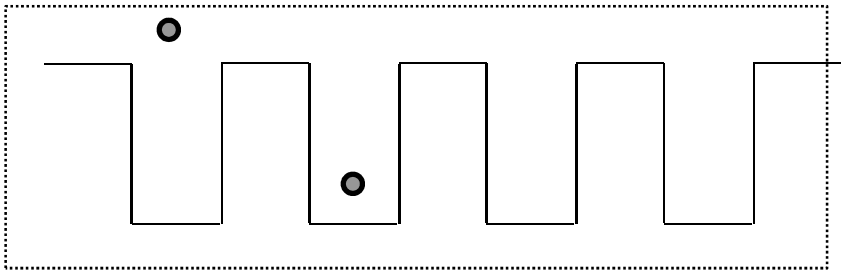
Back to Solid State Problem!

1.
2.
3.
4.
5.



Talking about macroscopic properties by microscopic analysis!

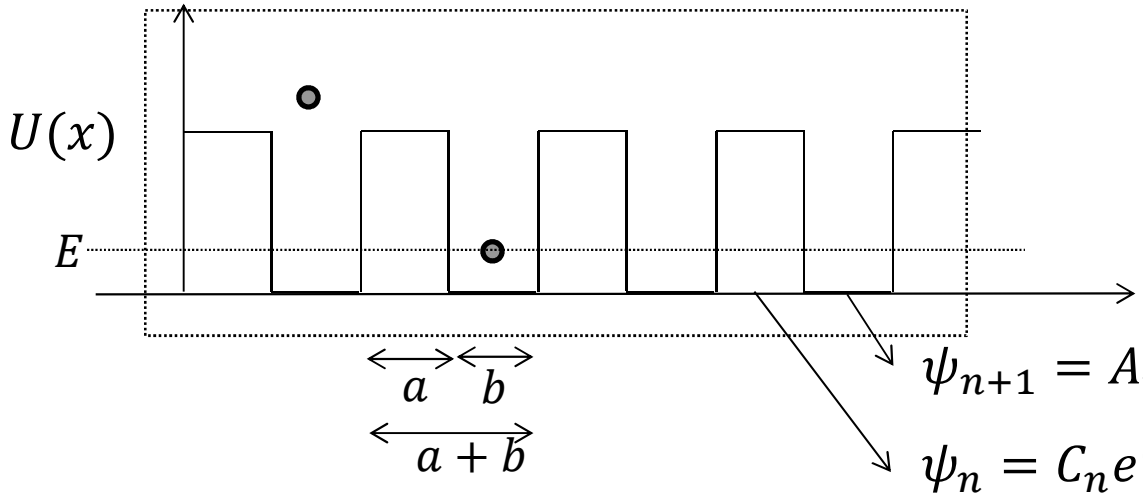
Electrons in periodic potential:



Real Problem?!

1.
2.
3.
4.
5.

Electrons in periodic potential:



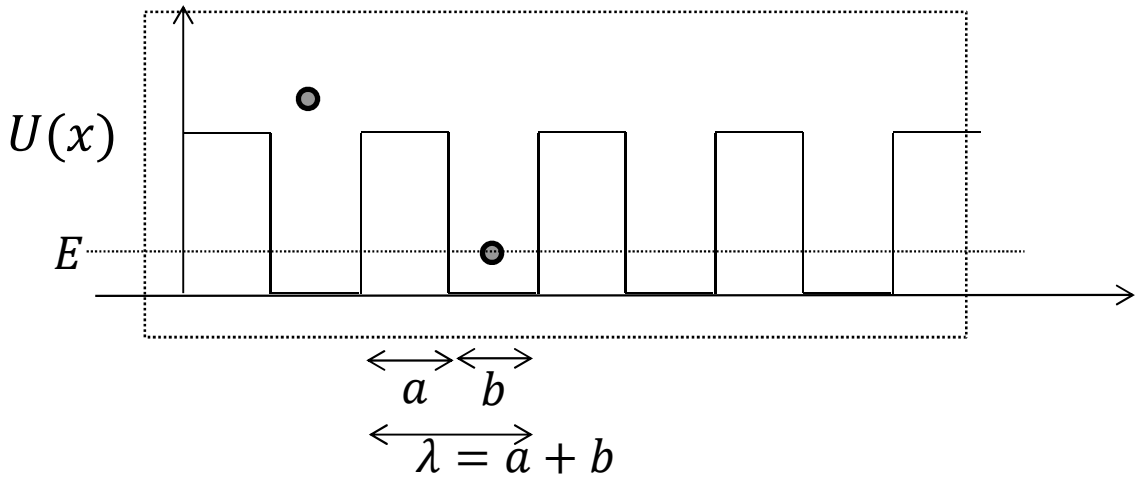
$$\psi_{n+1} = A_{n+1}\sin kx + B_{n+1}$$

$$\psi_n = C_n e^{\alpha x} + D_n e^{-\alpha x}$$

Can we solve it only for one unit cell!?

Bloch Theorem

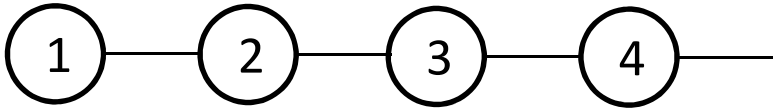
1.
2.
3.
4.
5.

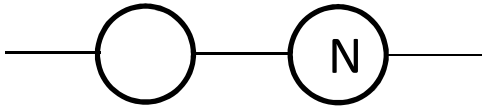


$$P(x) = P(x + \lambda)$$

$$|\psi(x)|^2 = |\psi(x + \lambda)|^2$$

$$\psi(x + \lambda) = \psi(x)e^{ik\lambda}$$





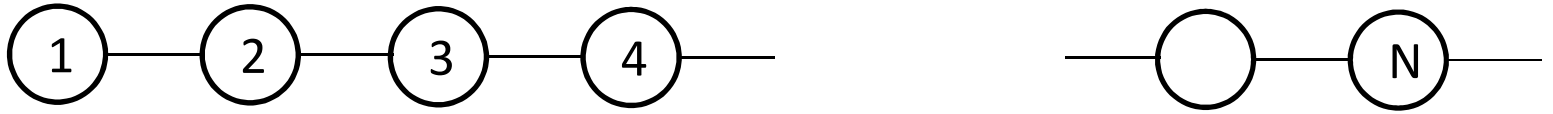
$$\psi(x + \lambda) = \psi(x)e^{ik\lambda}$$

$$\psi(x + 2\lambda) = \psi(x)e^{i2k\lambda}$$

$$\psi(x + N\lambda) = \psi(x)e^{iNk\lambda}$$

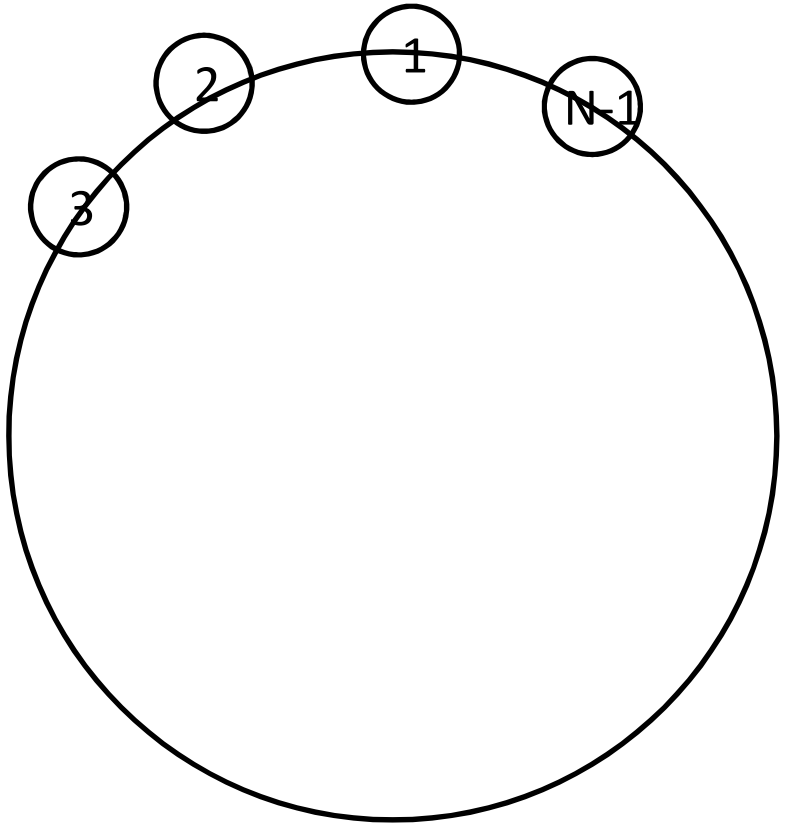
Periodic Boundary Condition

1.
2.
3.
4.
5.



$$\psi(x+\lambda) = \psi(x)e^{ik\lambda}$$

$$\psi(x+2\lambda) = \psi(x)e^{i2k\lambda}$$



$$\psi(x+N\lambda) = \psi(x)e^{iNk\lambda}$$

$$\psi(x+N\lambda) = \psi(x)e^{iNk\lambda} = \psi(x)$$

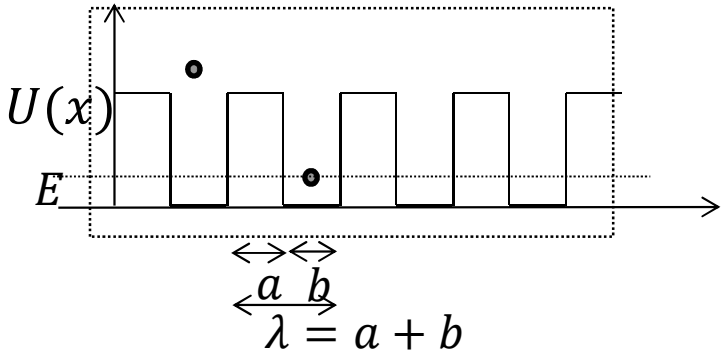
$$Nk\lambda = \pm 2\pi n$$

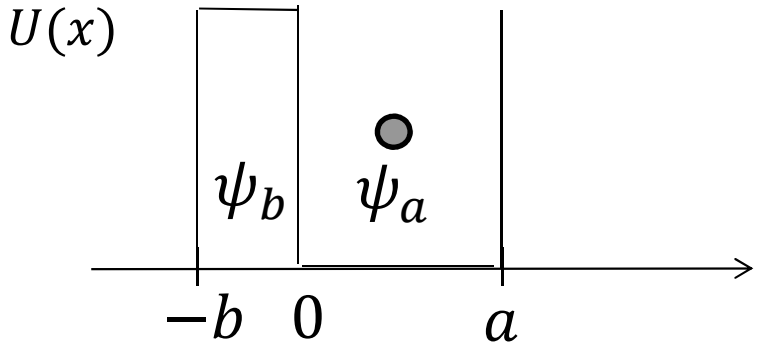
$$k = \pm\frac{2\pi n}{N\lambda} \qquad n = -\frac{N}{2}, \dots, -1, 0, 1, \dots, \frac{N}{2}$$

$$k_{max} = \frac{\pi}{\lambda}\ , k_{min} = -\frac{\pi}{\lambda}$$

Boundary Conditions

1.
2.
3.
4.
5.





$$\psi_a = A_a \sin \alpha x + B_a \cos \alpha x \qquad \alpha = \sqrt{2mE}/\hbar$$

$$\psi_b = A_b \sinh \beta x + B_b \cosh \beta x \qquad \beta = \sqrt{2m(U_0 - E)}/\hbar$$

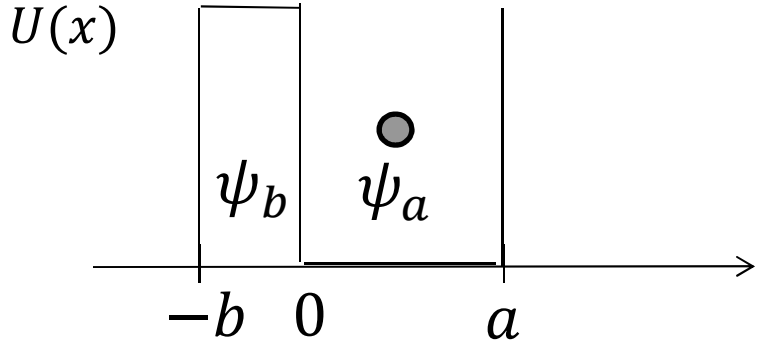
$$\psi\Big|_{0^+} = \psi\Big|_{0^-} \qquad \psi_a\Big|_{x=a} = \psi\Big|_{x=b} e^{ik\lambda}$$

$$\psi'\Big|_{0^+} = \psi'\Big|_{0^-} \qquad \psi'_a\Big|_{x=a} = \psi'\Big|_{x=b} e^{ik\lambda}$$

Calculating Energy-levels

1.
2.
3.
4.
5.

$$\begin{pmatrix} 0 & 1 & 0 & -1 \\ \alpha & 0 & \beta & 0 \\ ? & ? & ? & ? \\ ? & ? & ? & ? \end{pmatrix} \begin{bmatrix} A_a \\ B_a \\ A_b \\ B_b \end{bmatrix} = \begin{bmatrix} 0 \\ 0 \\ 0 \\ 0 \end{bmatrix}$$



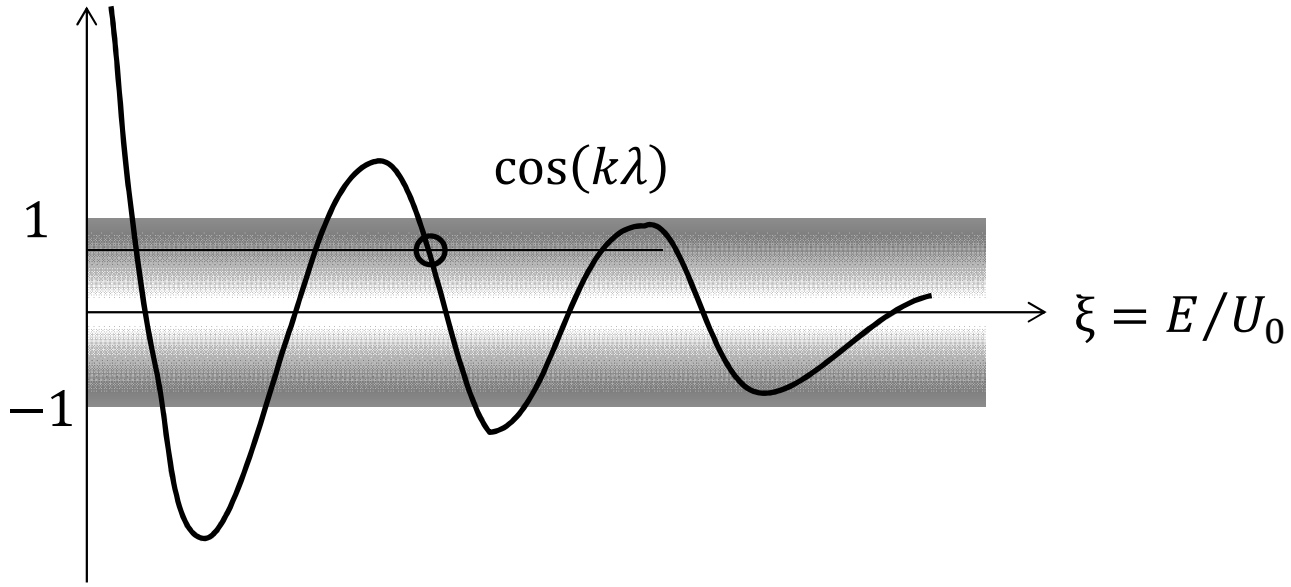
$$\xi = E/U_0 \qquad \alpha_0 = \frac{1}{\hbar}\sqrt{2mU_0}$$

$$\frac{1-2\xi}{2\xi\sqrt{1-\xi}} \times \ \ldots = \cos(k\lambda)$$

Graphical solution to Energy Levels

1.
2.
3.
4.
5.

$$\frac{1-2\xi}{2\xi\sqrt{1-\xi}} \times \ \ldots = \cos(k\lambda)$$

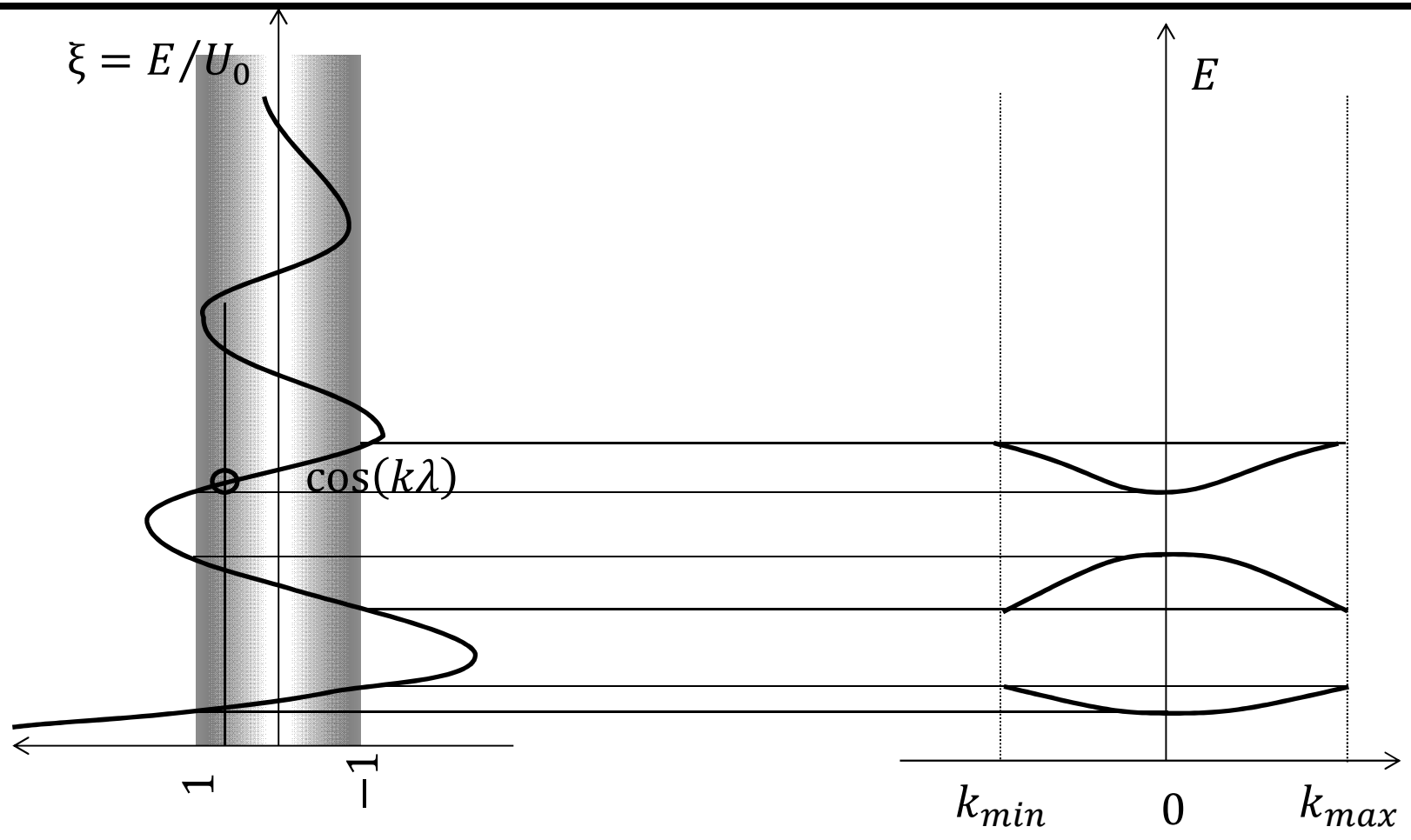


$$k = \pm\frac{2\pi n}{N\lambda} \qquad n = -\frac{N}{2}, \ldots, -1,0,1, \ldots, \frac{N}{2}$$

$$k_{max} = \frac{\pi}{\lambda} \ , k_{min} = -\frac{\pi}{\lambda}$$

(E-K) Energy Band Diagram

1.
2.
3.
4.
5.



$$k = \pm\frac{2\pi n}{N\lambda} \qquad n = -\frac{N}{2}, \ldots, -1,0,1, \ldots, \frac{N}{2}$$

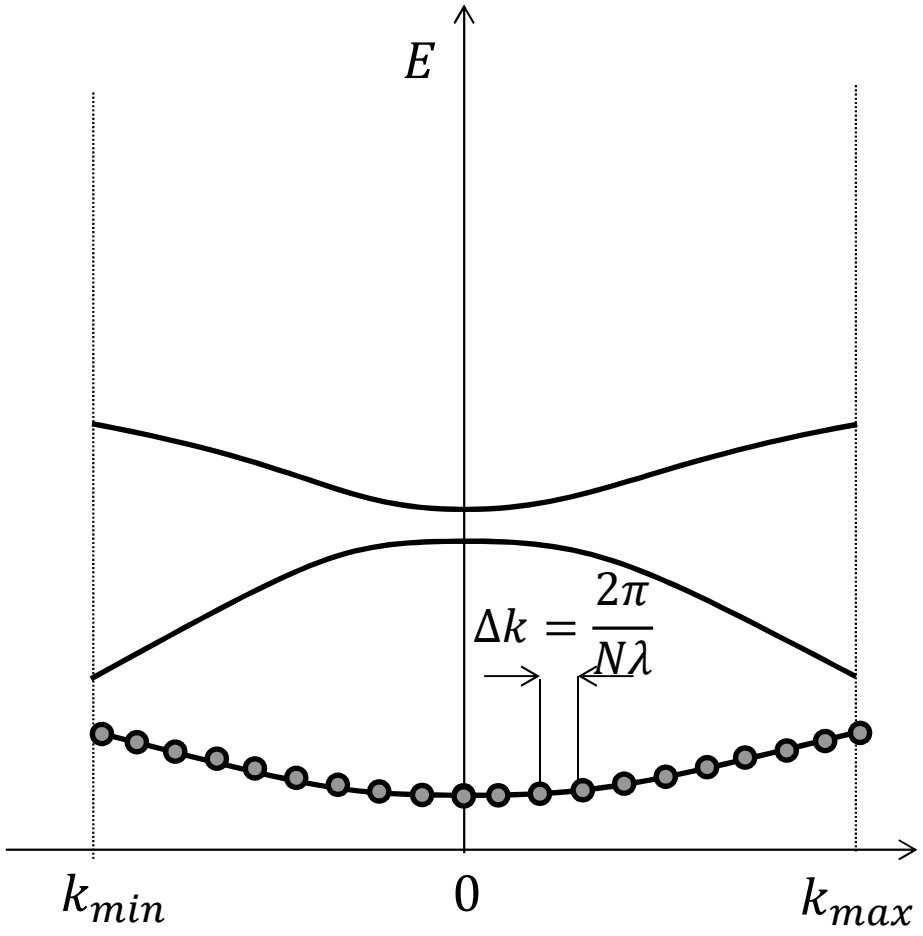
$$k_{max} = \frac{\pi}{\lambda}\ , k_{min} = -\frac{\pi}{\lambda}$$

Brillouin Zone and Number of States

1.
2.
3.
4.
5.

$$\frac{STATES}{BAND} = \frac{k_{max} - k_{min}}{\Delta k}$$

$$= \frac{\frac{2\pi}{\lambda}}{\frac{2\pi}{N\lambda}} = N$$

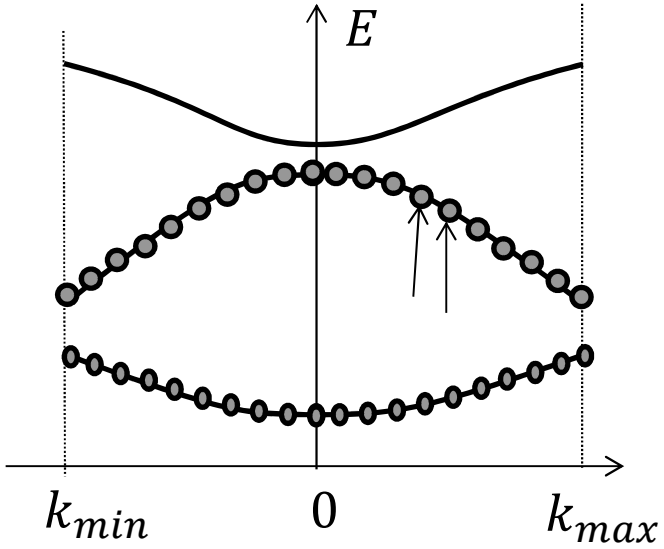


$$k = \pm\frac{2\pi n}{N\lambda} \qquad n = -\frac{N}{2}, \ldots, -1,0,1, \ldots, \frac{N}{2}$$

$$k_{max} = \frac{\pi}{\lambda}\ , k_{min} = -\frac{\pi}{\lambda}$$

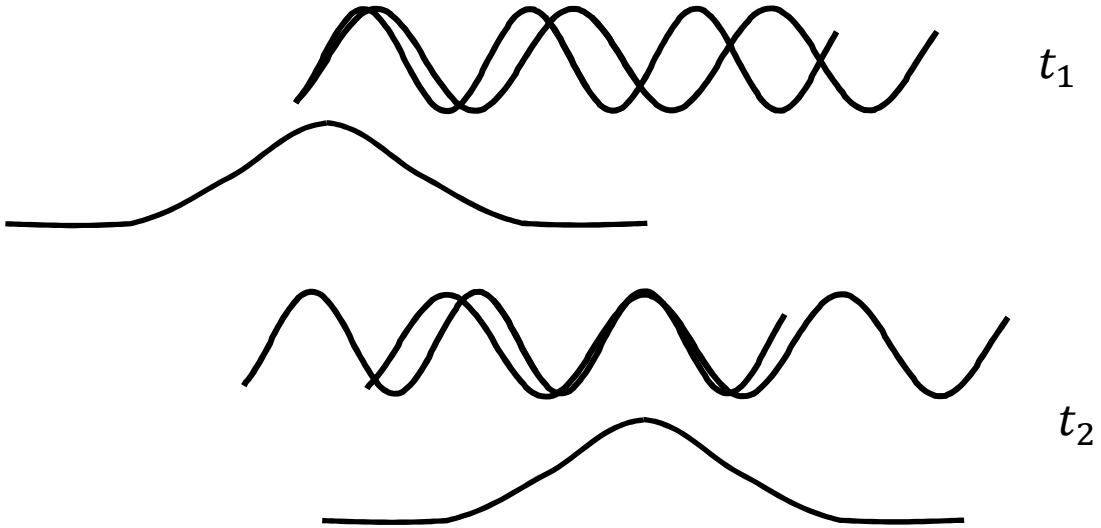
Wave Packet and Group Velocity

1.
2.
3.
4.
5.



$$\psi(x,t) = Ae^{ikx - i\frac{E}{\hbar}t} + Ae^{i(k+\Delta k)x - i\frac{E+\Delta E}{\hbar}t}$$

$$= Ae^{ikx - i\frac{E}{\hbar}t}\left[1 + e^{i\Delta k.x - i\frac{\Delta E}{\hbar}t}\right]$$

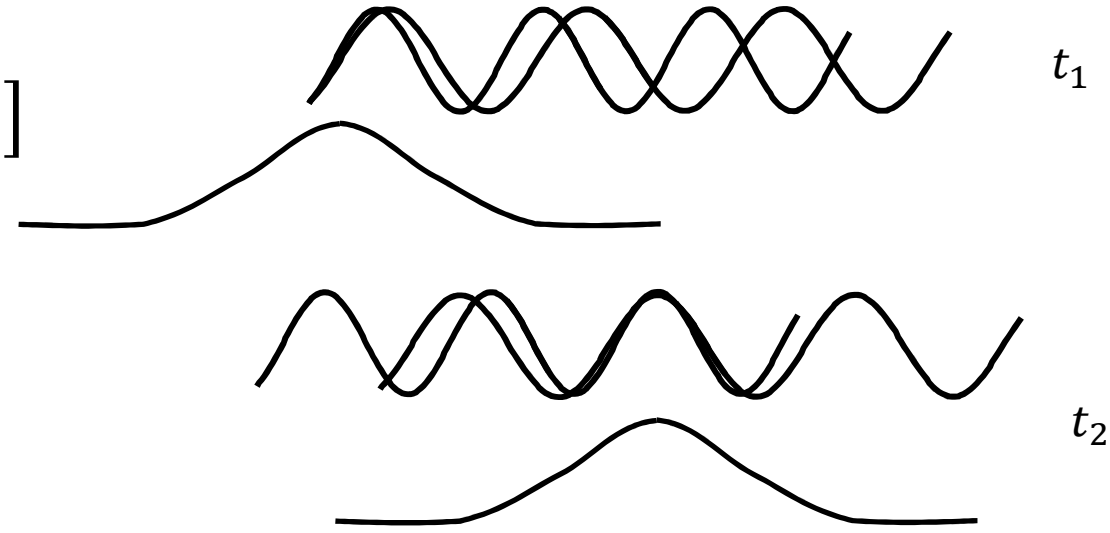


Group Velocity for a Given Band

1.
2.
3.
4.
5.

$$\psi(x,t) = Ae^{ikx - i\frac{E}{\hbar}t}\left[1 + e^{i\Delta k.x - i\frac{\Delta E}{\hbar}t}\right]$$

$$= Ae^{ikx - i\frac{E}{\hbar}t}\left[1 + e^{i\times const}\right]$$



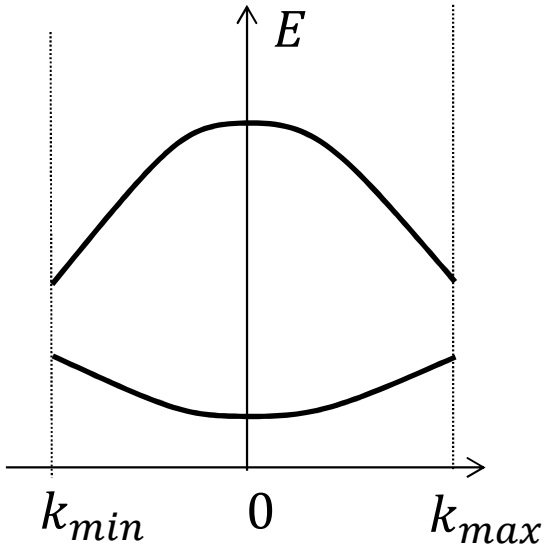
$$v = \frac{\Delta x}{\Delta t} = \frac{\Delta E}{\hbar \Delta k}$$

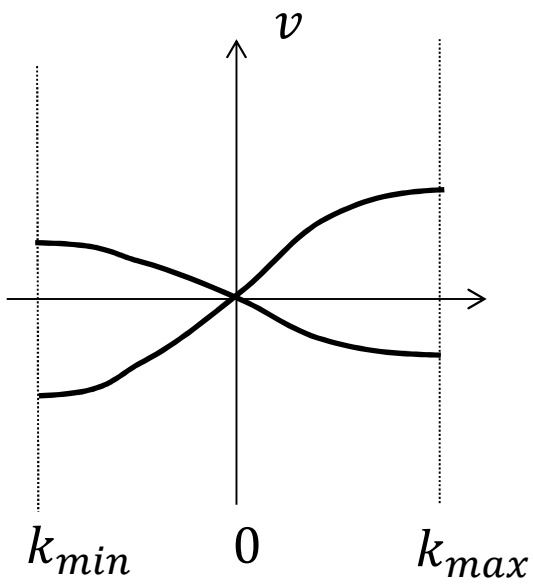
$$\therefore \quad \left[x\Delta k - t\frac{\Delta E}{\hbar \Delta k}\right] = cte$$

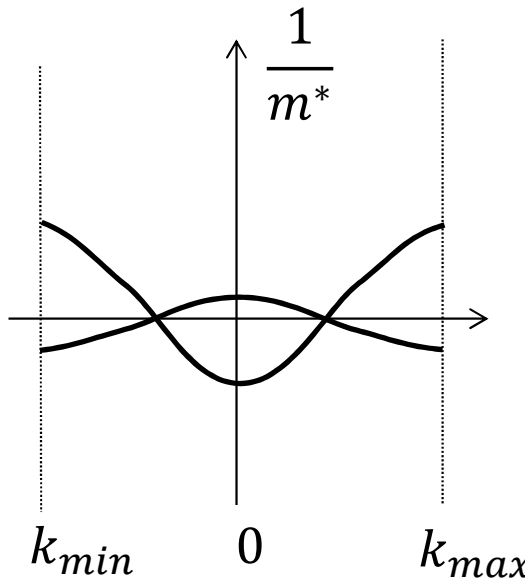
$$a = \frac{\Delta v}{\Delta t} = \frac{1}{\hbar}\frac{d}{dt}\left(\frac{\Delta E}{\Delta k}\right) = \frac{1}{\hbar^2}\frac{d}{dk}\left(\frac{\Delta E}{\Delta k}\right)\frac{d(\hbar k)}{dt} = \frac{F}{m^*}$$

Effective Mass for a Given Band

1.
2.
3.
4.
5.







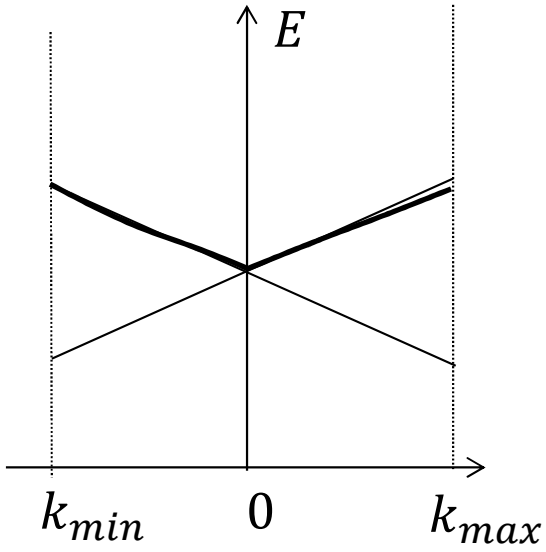
$$v = \frac{\Delta E}{\hbar \Delta k}$$

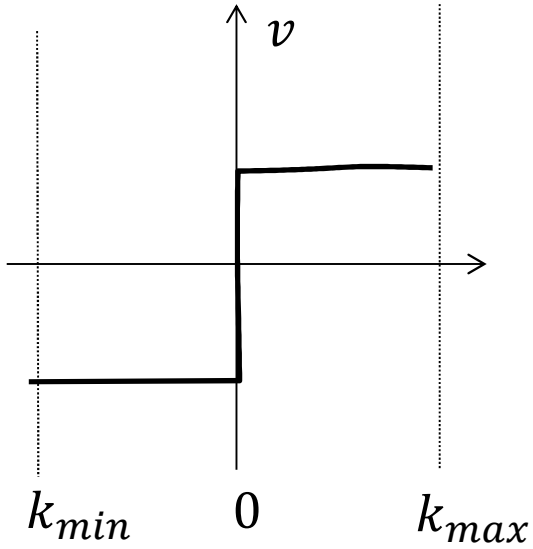
$$\frac{1}{m^*} = \frac{1}{\hbar^2} \frac{d^2 E}{dk^2}$$

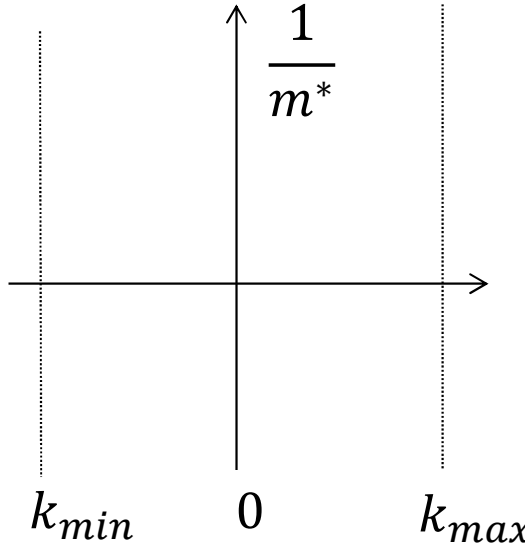
Effective Mass is not Essential …

1.
2.
3.
4.
5.

Effective mass is not a fundamental concept. There are systems for which effective mass can not be defined.







$$F = \hbar \frac{\Delta k}{\Delta t}$$

$$v = \frac{\Delta E}{\hbar \Delta k}$$

$$\frac{1}{m^*} = \frac{1}{\hbar^2} \frac{d^2 E}{dk^2}$$

Electron / Hole fluxes: Filled/Empty Bands

1.
2.
3.
4.
5.

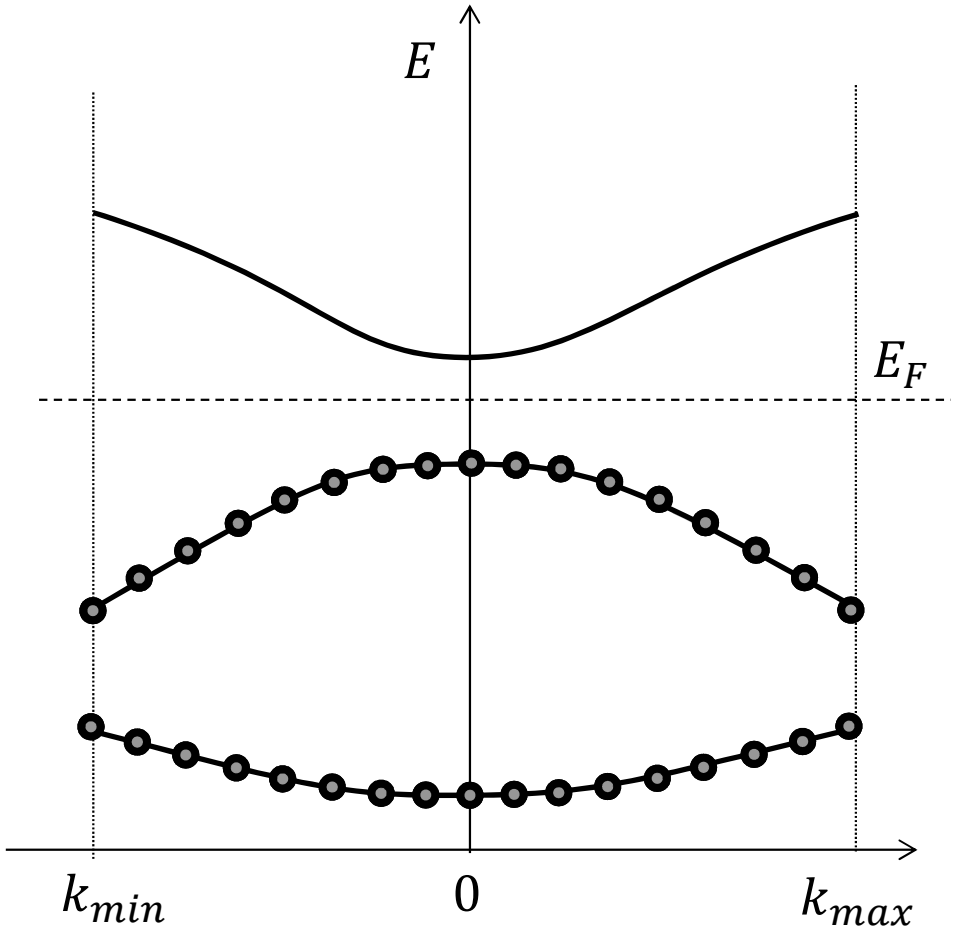
$$J = -\frac{q}{L}\sum_{i(filled)} v_i = 0$$

$$J = -\frac{q}{L}\sum_{i(filled)} v_i$$

$$= -\frac{q}{L}\sum_{0}^{k_{max}} v_i$$

$$-\frac{q}{L}\sum_{-k_{min}}^{0} -|v_i|$$

$$= 0$$



Filled and empty bands carry no current !

$$k = \pm\frac{2\pi n}{N\lambda} \qquad n = -\frac{N}{2}, \ldots, -1,0,1, \ldots, \frac{N}{2}$$

$$k_{max} = \frac{\pi}{\lambda}\ , k_{min} = -\frac{\pi}{\lambda}$$

Electron/Hole Fluxes: Partially Filled Bands

1.
2.
3.
4.
5.

$$J = -\frac{q}{L}\sum_{i(filled)} v_i = 0$$

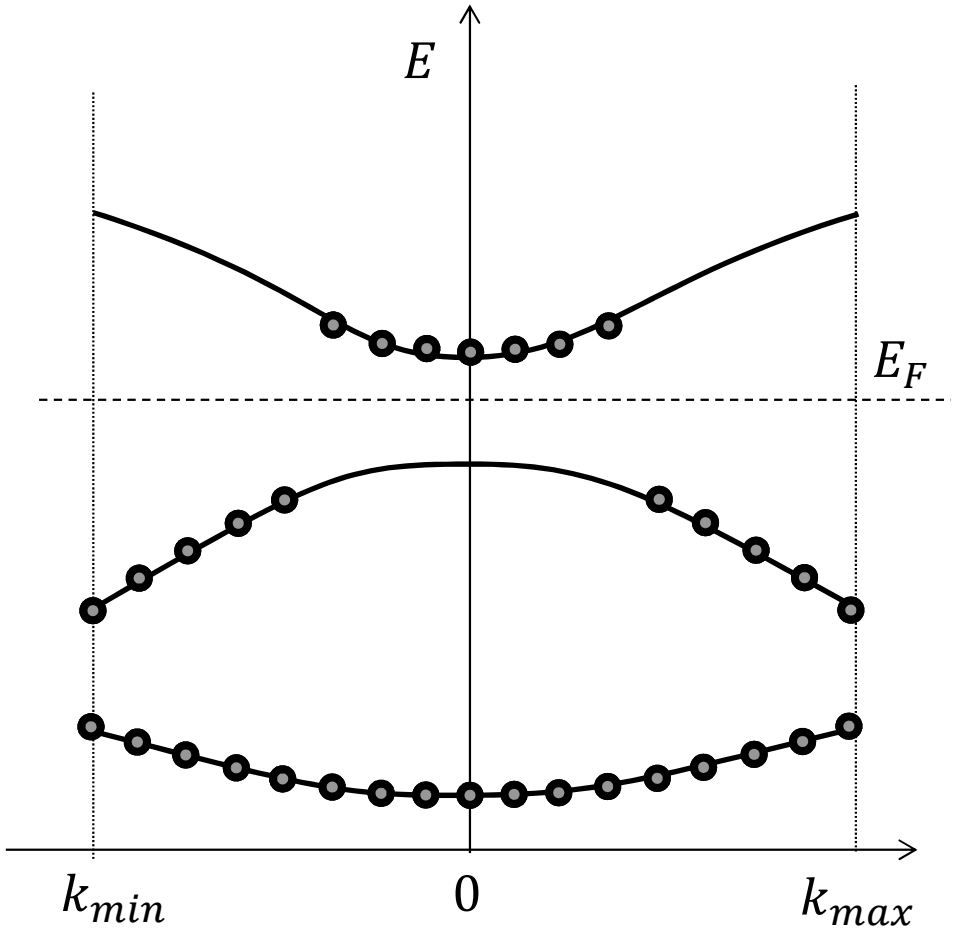
$$J = -\frac{q}{L}\sum_{i(filled)} v_i$$

$$= -\frac{q}{L}\sum_{0}^{k_{max}} v_i$$

$$-\frac{q}{L}\sum_{-k_{min}}^{0} -|v_i|$$

$$= 0$$

Filled and empty bands carry no current !



$$k = \pm\frac{2\pi n}{N\lambda} \qquad n = -\frac{N}{2}, \ldots, -1,0,1, \ldots, \frac{N}{2}$$

$$k_{max} = \frac{\pi}{\lambda}\ , k_{min} = -\frac{\pi}{\lambda}$$

Electron/Hole Fluxes: Partially Filled Bands

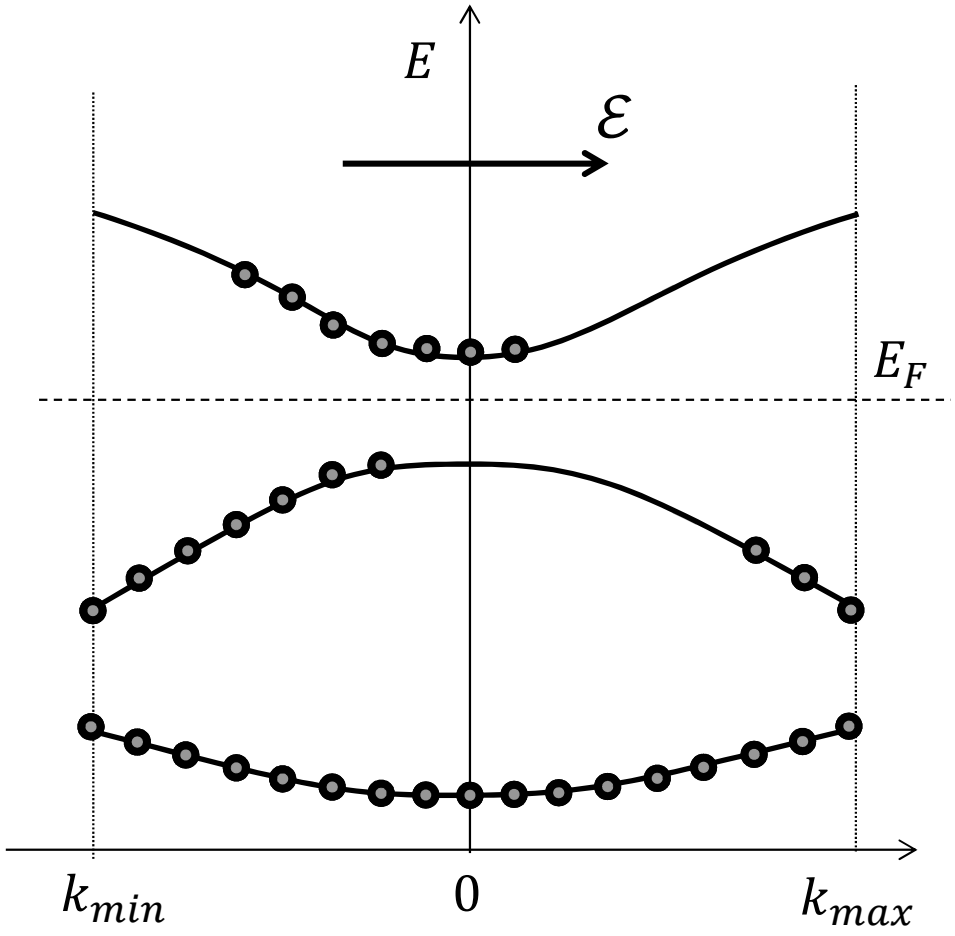
1.
2.
3.
4.
5.

$$J = -\frac{q}{L}\sum_{i(filled)} v_i \neq 0$$

$$J = -\frac{q}{L}\sum_{i(filled)} v_i$$

$$= -\frac{q}{L}\sum_{all} v_i + \frac{q}{L}\sum_{i(empty)} |v_i|$$

$$= \frac{q}{L}\sum_{i(empty)} |v_i|$$



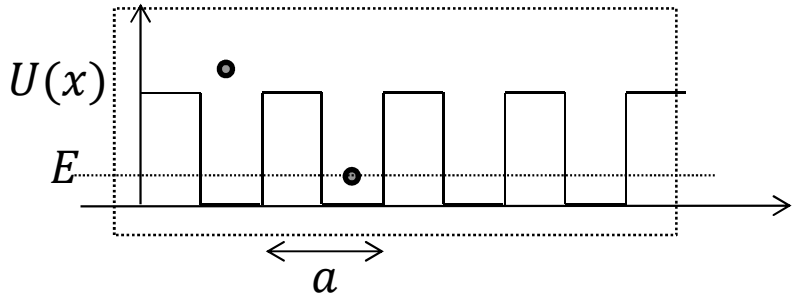
$$k = \pm\frac{2\pi n}{N\lambda} \qquad n = -\frac{N}{2}, \ldots, -1,0,1, \ldots, \frac{N}{2}$$

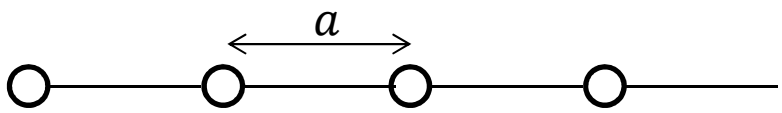
$$k_{max} = \frac{\pi}{\lambda}\ , k_{min} = -\frac{\pi}{\lambda}$$

Brillouin Zone for 1-D Solids

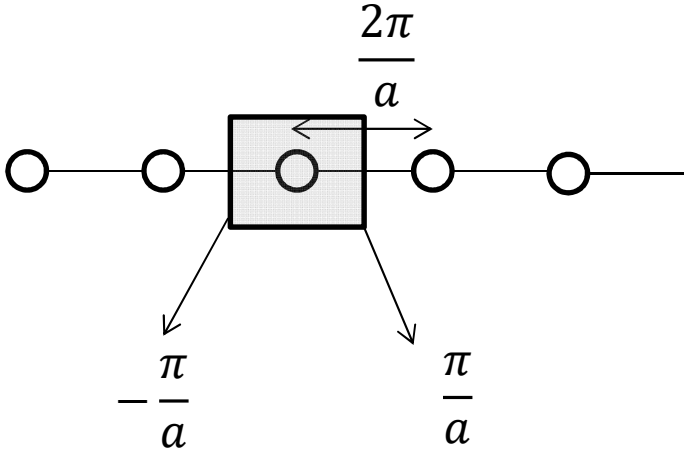
1.
2.
3.
4.
5.

Electrons in periodic potential:

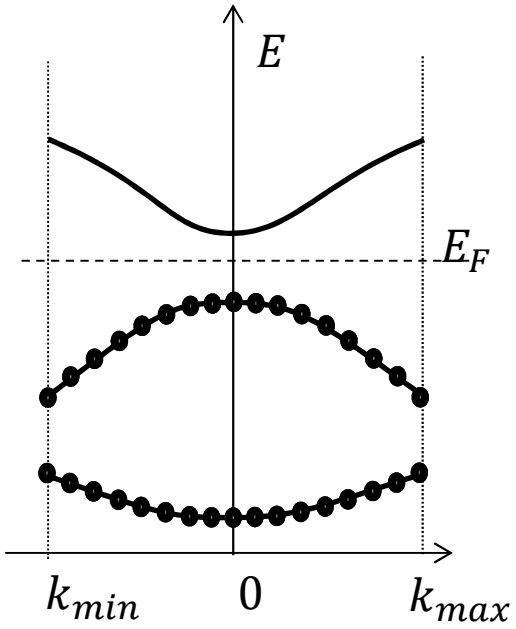




Lattice:
Real space



Lattice:
K-space



$$k = \pm\frac{2\pi n}{Na}$$

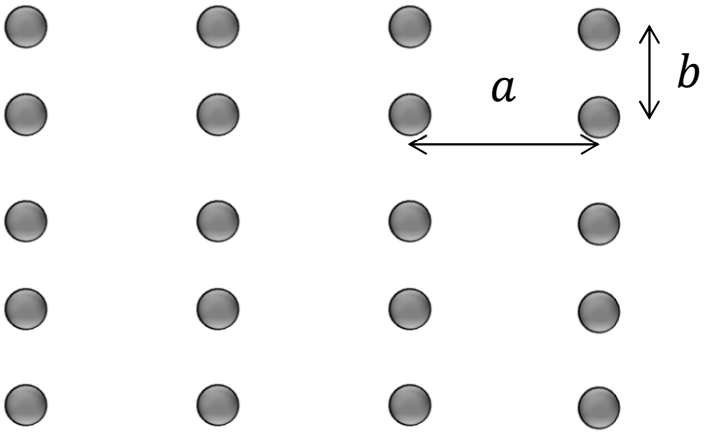
$$n = -\frac{N}{2}, \dots, -1,0,1, \dots, \frac{N}{2}$$

$$k_{max} = \frac{\pi}{a}\ , k_{min} = -\frac{\pi}{a}$$

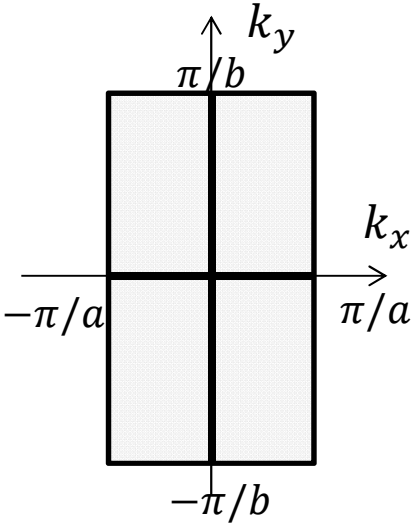
E-k diagram in 2-D solids

1.
2.
3.
4.
5.

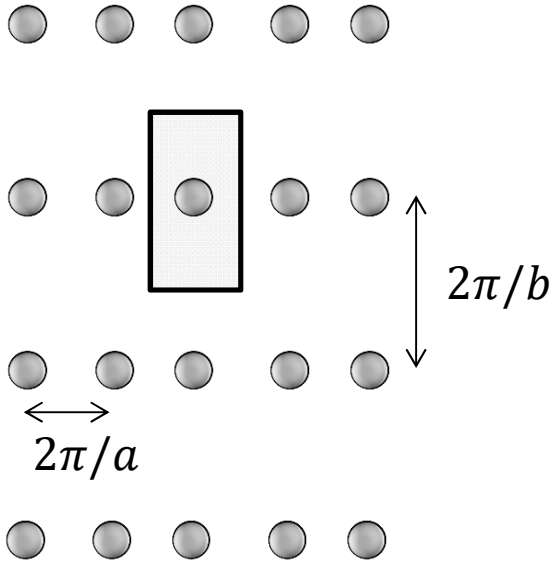
Lattice:
Real space

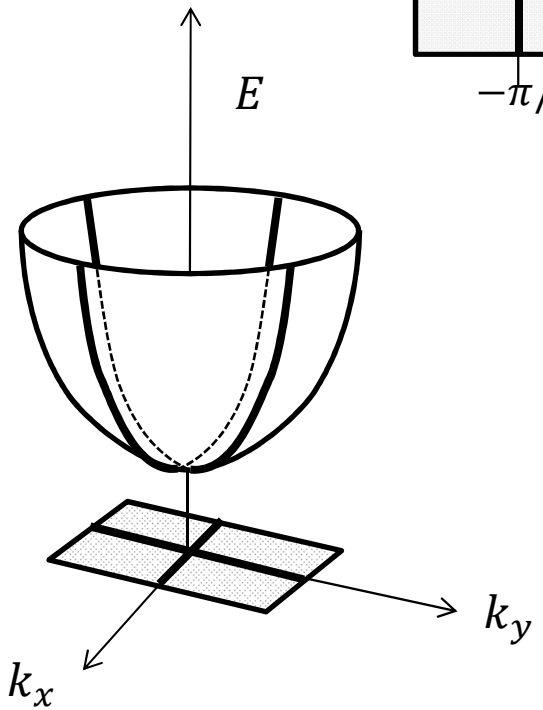


E-k diagram



Lattice:
K space

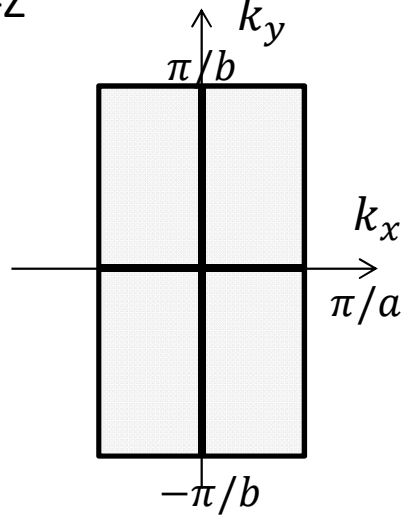




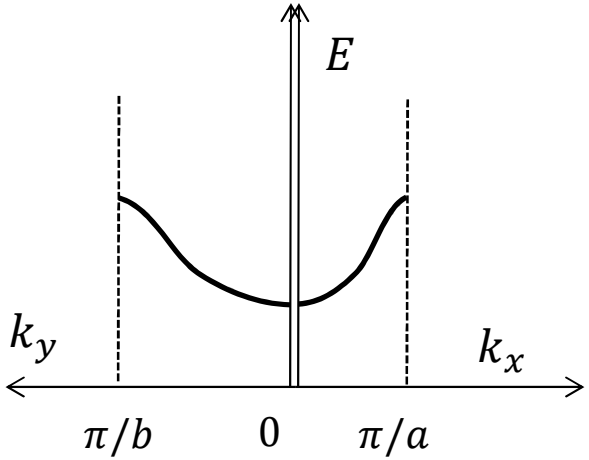
Constant Energy-surface in 2-D

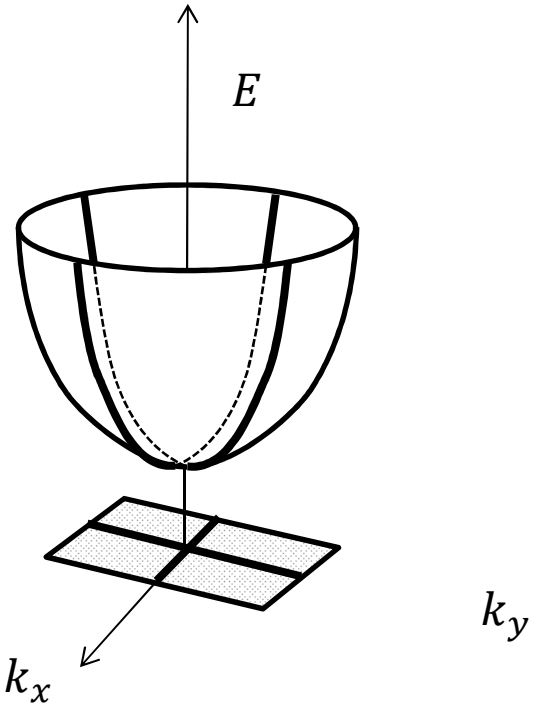
1.
2.
3.
4.
5.

1st B-Z

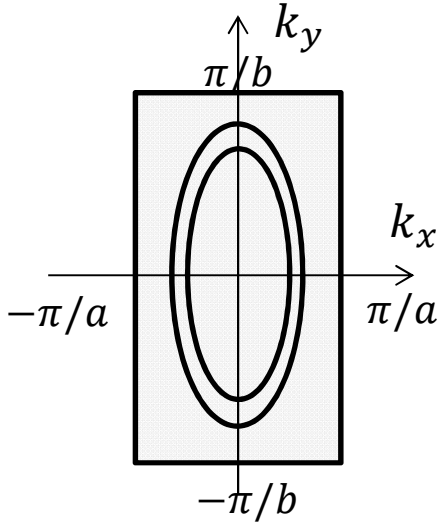


E-k diagram





Const. Energy Surface



1.
2.
3.
4.
5.