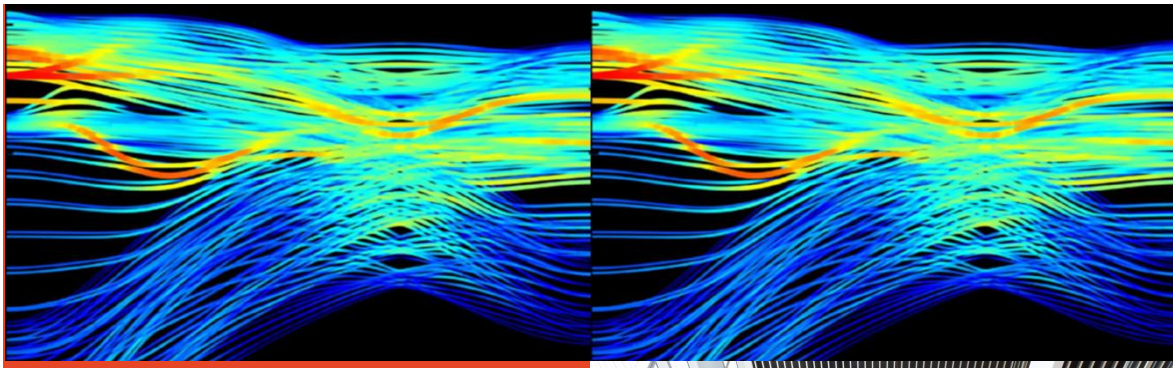
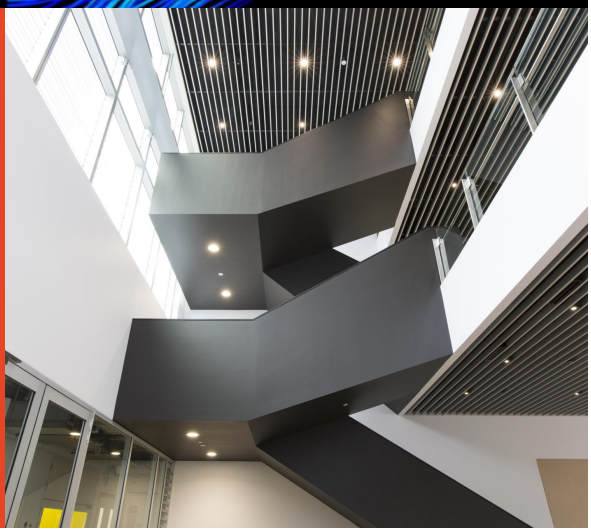


CMP Lecture 11

School of Physics
The University of Sydney

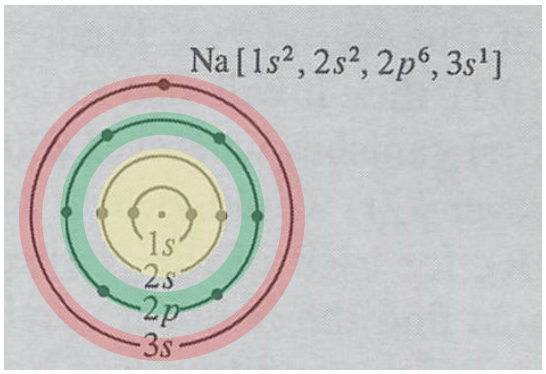
THE UNIVERSITY OF SYDNEY



Tight binding electron model

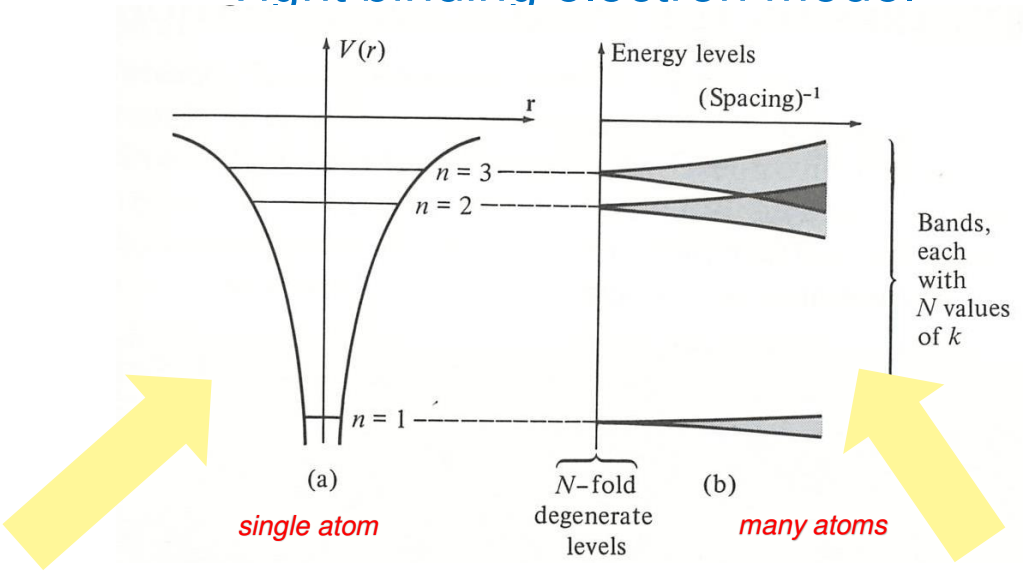
Opposite approach to nearly-free-electron model, where the free electron is only perturbed slightly by a weak potential.

In this model we consider how the electronic configuration of the free *atoms* change as they are brought together to form a solid. Assumes electrons sufficiently tightly bound to the atoms of the solid to be identified with quantum states in the free atom.
To a good approximation, valid for core electrons, not for valence electrons.



Ch. 6, 11 Oxford Solid State Basics
Ch. 10 Ashcroft & Mermin

Tight binding electron model



Electronic levels in an atomic potential

Energy levels for N such atoms in a periodic array, plotted vs inverse interatomic spacing. Atoms far apart: levels nearly degenerate, atomic-like; closer together: levels broaden into bands.

Tight binding electron model

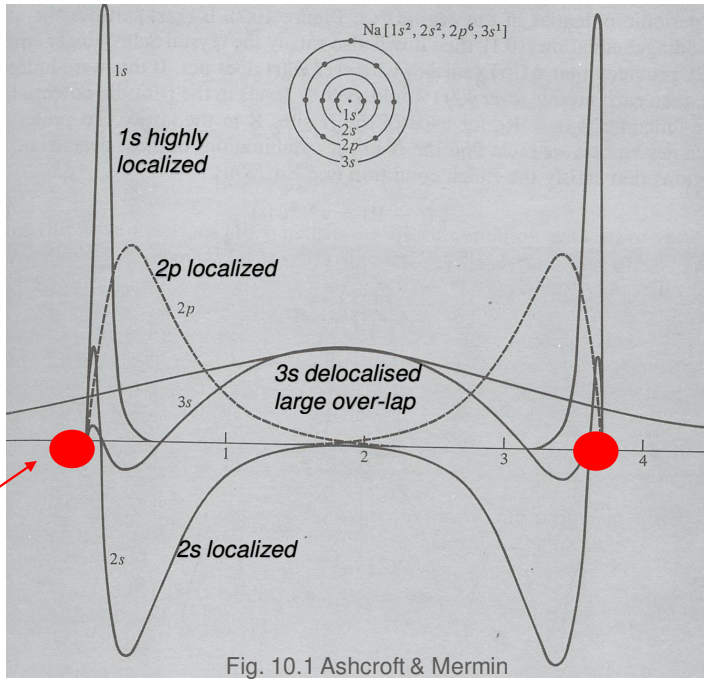


Fig. 10.1 Ashcroft & Mermin

Two Na atoms, interatomic spacing apart (3.7 Å)

Radial wave functions $r\psi(r)$

Calculation by D. R. Hartree and W. Hartree, Proc. Royal Soc. A193, 299 (1948) (former famous for numerical analysis and application of Hartree-Fock equation, latter his father)

Tight binding electron model

- The tight-binding approximation deals with the case in which the overlap of atomic wave functions is enough to require corrections to the picture of isolated atoms, but not so much as to render the atomic description completely irrelevant.
- The approximation is most useful for describing the energy bands that arise from the partially filled d-shells of transition metal atoms and for describing the electronic structure of insulators.
- Quite apart from its practical utility, the tight-binding approximation provides an instructive way of viewing Bloch levels complementary to that of the nearly free electron picture, permitting a reconciliation between the apparently contradictory features of localized atomic levels on the one hand, and free electron-like plane-wave levels on the other.

Tight binding electron model

See - first for 2 atoms: Ch. 6.2.2 Oxford Basics

Hamiltonian for two H atoms. Solve the Schrödinger eq. (S.E.) for the electrons as a function of distance.
Consider a single electron and two positive nuclei.
The Hamiltonian: $H = K + V_1 + V_2$ the kinetic energy of the electron: $K = \frac{\mathbf{p}^2}{2m}$

Coulomb interaction: $V_i = \frac{e^2}{4\pi\epsilon_0|\mathbf{r} - \mathbf{R}_i|}$ $\mathbf{R}_i$ is position of atom *i*

Trial wavefunction: $|\psi\rangle = \phi_1|1\rangle + \phi_2|2\rangle$

Want to find the best ϕ_1, ϕ_2 that will lower the energy to get the ground state

where the ϕ are complex coefficients and |1> and |2> are "tight-binding" or "atomic" orbitals. This form is called "linear combination of atomic orbitals LCAO".

The orbitals can be taken as the ground state solutions of the S.E. when there is only one nucleus present.

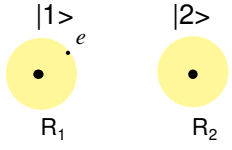
$$(K + V_1)|1\rangle = \epsilon_0|1\rangle$$ - If only have nucleus 1

$$(K + V_2)|2\rangle = \epsilon_0|2\rangle$$ - If only have nucleus 2,

ϵ_0 is the ground state energy of the single atom. Going to take |1>, |2> orthogonal.

Can write an effective S.E. $\sum_j H_{ij}\phi_j = E\phi_i$

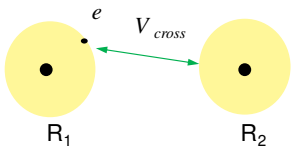
With H_{ij} being matrix element between state |i> and |j> $H_{ij} = \langle i|H|j\rangle$



Tight binding electron model

Hamiltonian (2x2) matrix with elements

$$
\begin{aligned}
H_{11} &= \langle 1|H|1\rangle = \langle 1|K + V_1|1\rangle + \langle 1|V_2|1\rangle = \epsilon_0 + V_{cross} \\
H_{22} &= \langle 2|H|2\rangle = \langle 2|K + V_2|2\rangle + \langle 2|V_1|2\rangle = \epsilon_0 + V_{cross} \\
H_{12} &= \langle 1|H|2\rangle = \langle 1|K + V_2|2\rangle + \langle 1|V_1|2\rangle = 0 \; - \; t \\
H_{21} &= \langle 2|H|1\rangle = \langle 2|K + V_2|1\rangle + \langle 2|V_1|1\rangle = 0 \; - \; t^* \; .
\end{aligned}
$$



$$V_{cross} = \langle 1|V_2|1\rangle = \langle 2|V_1|2\rangle$$

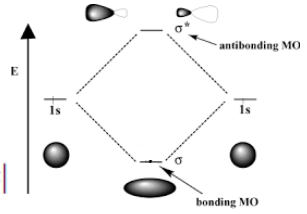
is the Coulomb potential felt by orbital |1> due to nucleus 2 (and vice versa).

$$t = -\langle 1|V_2|2\rangle = -\langle 1|V_1|2\rangle.$$

is called the "hopping" term – determines how much hopping or tunnelling the electron can do between the 2 atoms

Obtain below matrix equation:

$$\begin{pmatrix} \epsilon_0 + V_{cross} & -t \\ -t^* & \epsilon_0 + V_{cross} \end{pmatrix} \begin{pmatrix} \phi_1 \\ \phi_2 \end{pmatrix} = E \begin{pmatrix} \phi_1 \\ \phi_2 \end{pmatrix}.$$



Diagonalizing, we obtain eigenenergies: $E_\pm = \epsilon_0 + V_{cross} \pm |t|$ where lower energy one is the bonding, higher lying one is the antibonding orbital.

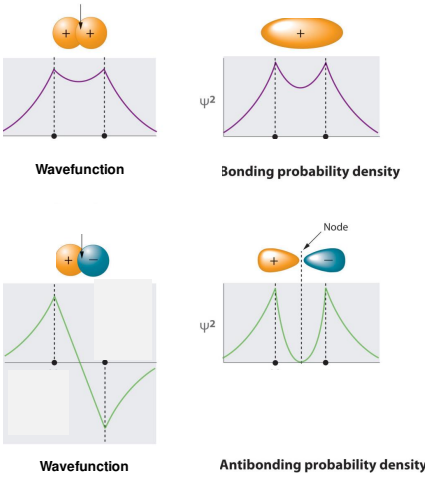
Tight binding electron model

Can think of $E_\pm = \epsilon_0 + V_{cross} \pm |t|$ such that both $|1\rangle$, $|2\rangle$ have energies shifted by V_{cross} due to the presence of the other nucleus. In addition the electron can "hop" from one orbital to the other by the off-diagonal *t* term.

$$|\psi\rangle = \phi_1|1\rangle + \phi_2|2\rangle$$

The corresponding wavefunctions are then,

$$
\begin{aligned}
|\psi_{bonding}\rangle &= \frac{1}{\sqrt{2}}(\,|1\rangle \pm |2\rangle\,) \\
|\psi_{antibonding}\rangle &= \frac{1}{\sqrt{2}}(\,|1\rangle \mp |2\rangle\,).
\end{aligned}
$$

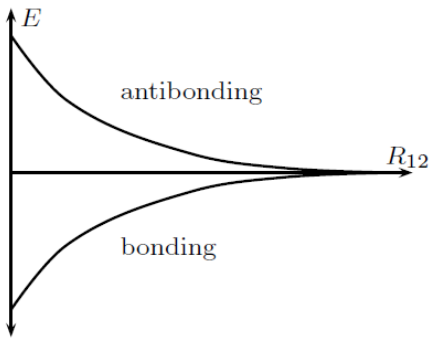


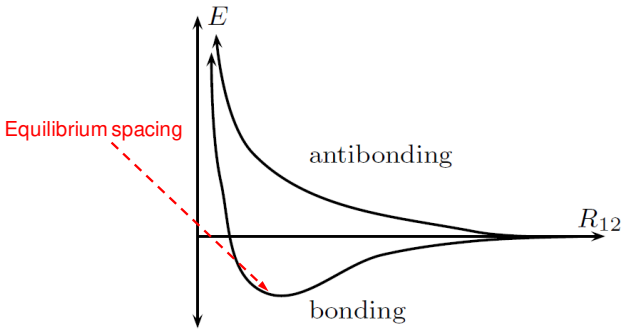
i.e. symmetric and antisymmetric superpositions of orbitals, where

$$\phi_1 = 1/\sqrt{2} \text{ and } \phi_2 = \pm 1/\sqrt{2}$$

$$\phi_1 = 1/\sqrt{2} \text{ and } \phi_2 = \mp 1/\sqrt{2}.$$

Tight binding electron model



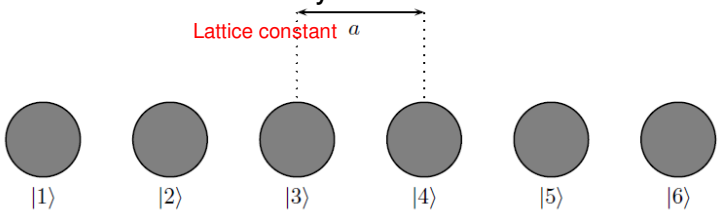


Model tight binding energy levels as a function of distance between the nuclei of the atoms, R_{12}.

More realistic energy levels as a function of distance between the nuclei of the atoms. The energy diverges as the nuclei get pushed together (this is from the Coulomb repulsion between nuclei).

Tight binding model -1D

Now consider a one-dimensional array of *N* atoms:



Consider a single orbital on atom n, called $|n\rangle$
Assume *N* sites, and periodic boundary conditions
(so site *N* is same as site 0)

Assume orthogonal to each other $\langle n|m\rangle = \delta_{n,m}$

Take a general trial wave function: $|\Psi\rangle = \sum_n \phi_n |n\rangle$

Going to let the electrons hop from one atom to the neighbouring site

Effective Schrodinger equation can be written as:

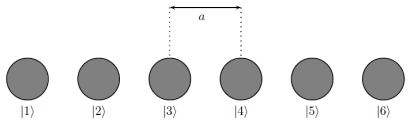
$$\sum_m H_{nm}\phi_m = E\phi_n \qquad (1)$$

where the matrix element is: $H_{nm} = \langle n|H|m\rangle$

Oxford Basics Ch. 11

Tight binding model – 1D

Write Hamiltonian as $H = K + \sum_j V_j$



where K is the kinetic energy
and V_j is the Coulomb interaction
of the electron with the nucleus at site j

$K = p^2/(2m)$

p is the "crystal momentum"

$V_j = V(r - \boldsymbol{R}_j)$

$$H|m\rangle = (K + V_m)|m\rangle + \sum_{j \neq m} V_j|m\rangle$$

Takes into account the interaction of an atom with all the other atoms

First term on RHS is Hamiltonian for only a single nucleus, *m.*
Take the tight-binding orbitals to be the atomic orbitals:

$$(K + V_m)|m\rangle = \epsilon_{atomic}|m\rangle$$

ϵ_{atomic} is the energy of an electron on nucleus m in absence of other nuclei.

Tight binding model – 1D

Can then obtain

$$H_{n,m} = \langle n|H|m\rangle = \epsilon_{atomic}\,\delta_{n,m} + \sum_{j \neq m} \langle n|V_j|m\rangle$$

Need to find second term on RHS. It describes an interaction such that an electron on the m^{th} atom can be transferred to the n^{th} atom. Generally only possible if n and m very close in energy.
Can write:

$$\sum_{j \neq m} \langle n|V_j|m\rangle = \begin{cases} V_0 & n = m \\ -t & n = m \pm 1 \\ 0 & \text{otherwise} \end{cases}$$

Here, no electron transferred, just shift energy on site

Can hop one step to left or right, with amplitude *t*

$$H_{n,m} = \epsilon_0 \delta_{n,m} - t\,(\delta_{n+1,m} + \delta_{n-1,m})$$

$$\epsilon_0 = \epsilon_{atomic} + V_0$$

"tight binding chain" well studied, *t* known as "hopping term"
has dimensions of energy – large when orbitals close, small when far away

Tight binding model – 1D

Trial wavefunction: linear combination of atomic orbitals

$$|\Psi\rangle = \sum_n \phi_n |n\rangle$$

Solution: Ansatz $\phi_n = \frac{e^{-ikna}}{\sqrt{N}}$

$\sqrt{N}$ for normalization, N sites in system

Solving time-independent SE equation

Substitute into LHS of SE (1) $\sum_m H_{nm}\phi_m = E\phi_n$ (1)

$$H_{n,m} = \epsilon_0 \delta_{n,m} - t\left(\delta_{n+1,m} + \delta_{n-1,m}\right)$$

$$\sum_m H_{n,m}\phi_m = \epsilon_0 \frac{e^{-ikna}}{\sqrt{N}} - t\left(\frac{e^{-ik(n+1)a}}{\sqrt{N}} + \frac{e^{-ik(n-1)a}}{\sqrt{N}}\right) \quad (2)$$

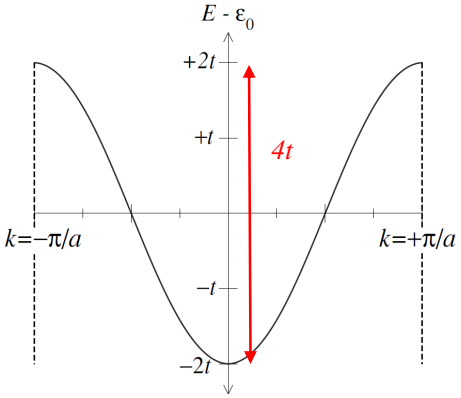
Is equal to the RHS of SE (1) $E\phi_n = E\frac{e^{-ikna}}{\sqrt{N}}$

Obtain: $E = \epsilon_0 - 2t\cos(ka)$

-Has a maximum and a minimum energy

-Electrons only have eigenstates within a certain energy band

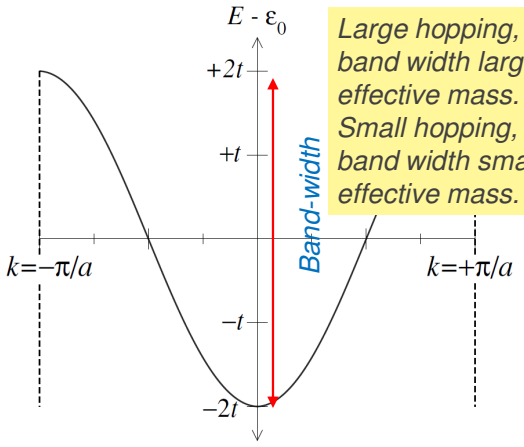
Energy difference between top and bottom of band called the "band width"



Working

Tight binding model

$$E = \epsilon_0 - 2t\cos(ka)$$



Large hopping, t is large, band width large, get small effective mass.
Small hopping, t is small, band width small, get large effective mass.

Near bottom band, dispersion parabolic: expanding $E = \epsilon_0 - 2t\cos(ka)$ for small k

$$E(k) = \text{Constant} + ta^2k^2$$

also quadratic in k

Bottom of band of similar form to that for free electrons:

quadratic in k

$$E_{free}(k) = \frac{\hbar^2 k^2}{2m}$$

View bottom of band as almost being like free electrons, except define new mass

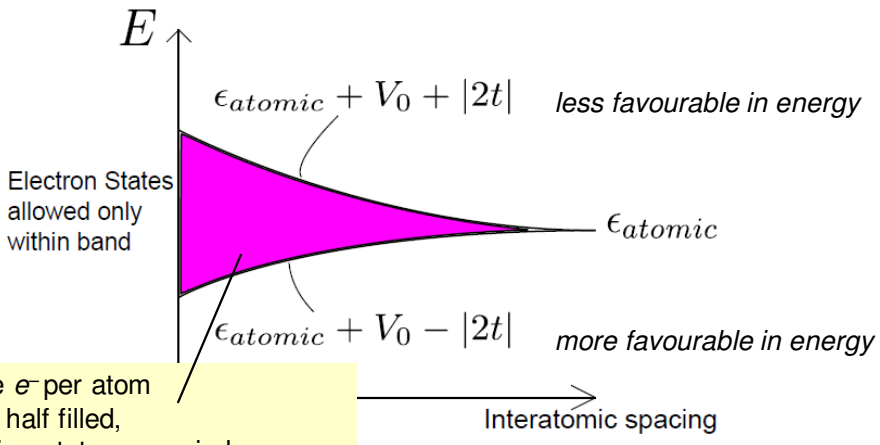
$$\frac{\hbar^2 k^2}{2m^*} = ta^2k^2$$

$$m^* = \frac{\hbar^2}{2ta^2}$$

Effective mass within tight-binding approximation

(Nothing to do with actual mass of electron, depends on hopping, *t*)

Tight binding model



If one e^- per atom
band half filled,
bonding states occupied,
total energy decreases.
Lower energy due to
reduced kinetic energy
via delocalization of wavefunction
through hopping of electrons.

The bandwidth depends on magnitude of *t*, which depends on distance between nuclei. To the right there are *N* states each belonging to an atomic orbital. On left, these *N* states form a band.

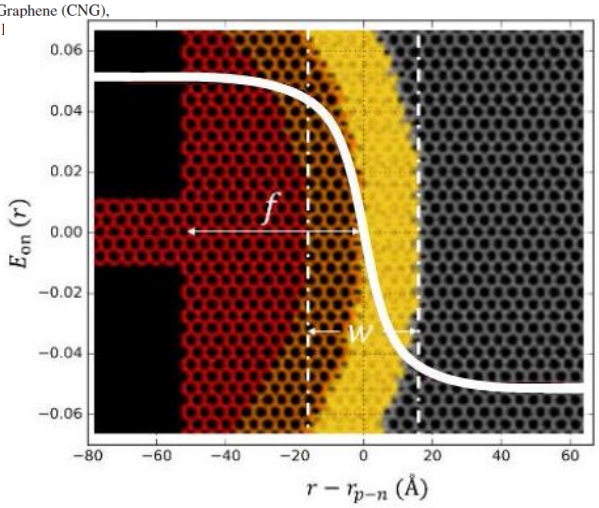
IOP Publishing
J. Phys.: Condens. Matter 30 (2018) 364001 (13pp)
Journal of Physics: Condensed Matter
https://doi.org/10.1088/1361-648X/aad6f1

Large-scale tight-binding simulations of quantum transport in ballistic graphene

Gaetano Calogero, Nick R Papior, Peter Bøggild and Mads Brandbyge

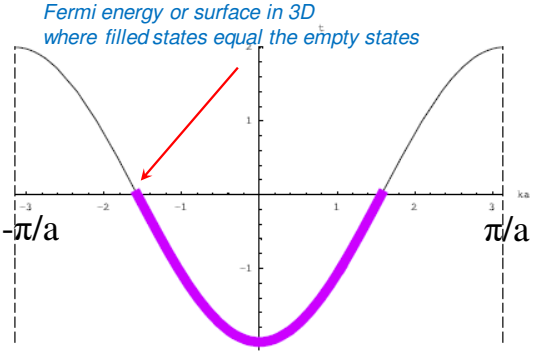
Department of Micro- and Nanotechnology, Center for Nanostructured Graphene (CNG), Technical University of Denmark, Ørsteds Plads, Bldg. 345E, DK-2800 l

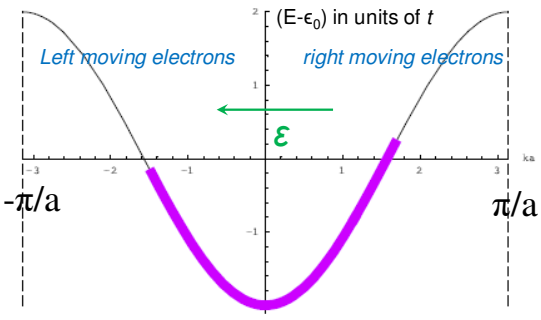
Electron transport across,
p-n junctions of different shape,
magnetic field



Tight binding model – filling bands

For a 1-D monovalent chain with one orbital per unit cell





N nuclei, length of system *L=Na*
allowed *k's: k=2πn/L*
number of different *k* = (size of BZ)/(spacing between *k*) = *(2π/a)/(2π/L)=L/a=N (nr. unit cells)*
means band ½ occupied.

If small electric field applied, costs a small energy to shift the Fermi surface, populating few *k*-states moving right and depopulating some moving left – more right moving electrons than left, so current induced; system is a metal.

Often monovalent materials are metals e.g. Na
If atoms donate two electrons, **band entirely full** – small electric field, no freedom to populate states; **carries no current**

Equation of motion

$$\hbar \frac{dk}{dt} = -e\varepsilon$$

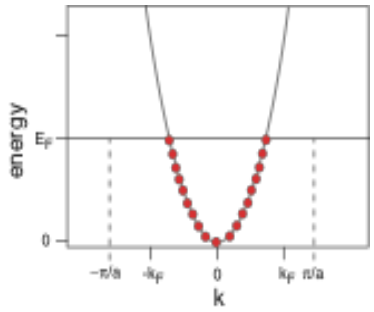
Force on electron due to ε-field

Remember also

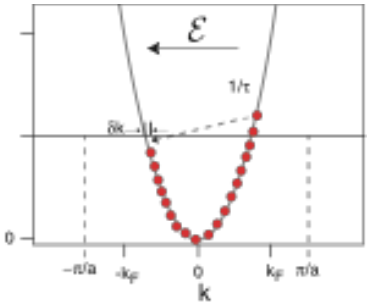
$$v_g = \frac{1}{\hbar}\frac{dE}{dk}$$

Electric field applied to the left; electrons move to the right

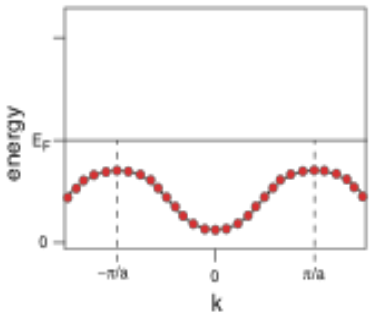
No field



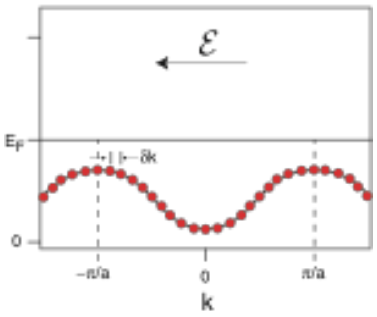
Finite field



Recall: momentum $p = \hbar k$



$$\frac{d}{dt}(\hbar k) = \hbar\left(\frac{dk}{dt}\right) = F$$

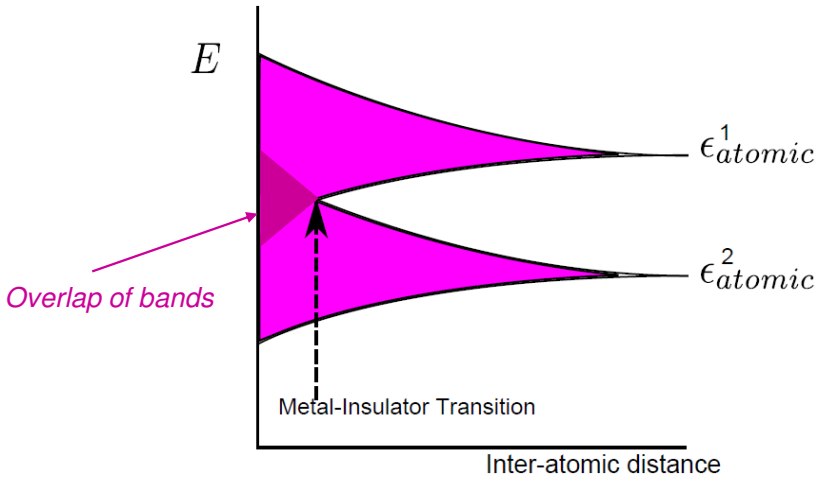


Electric field leads to an increase in *k* after some time *t*. Average group velocity opposite to field direction. Filled band: nothing changes – insulating.

Tight binding model – multiple bands

Oxford Basics Ch. 11.4

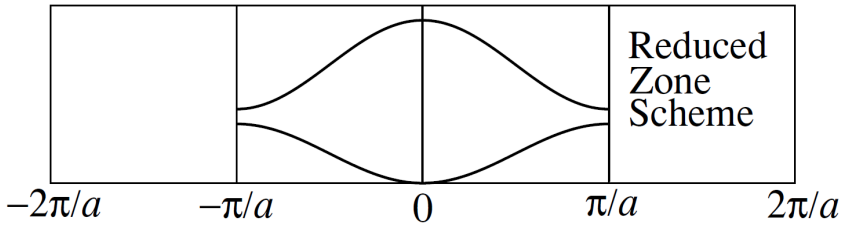
Consider one atom per unit cell, but with two orbitals

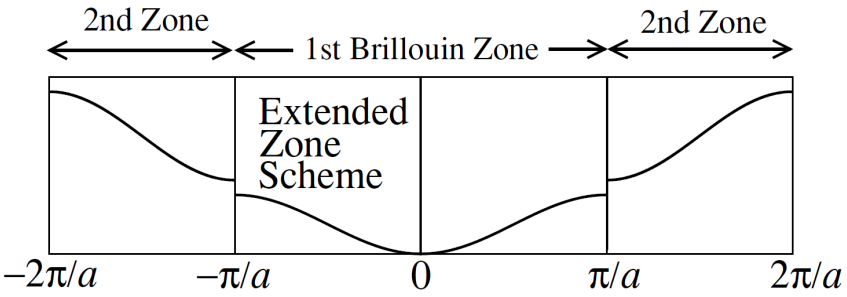


If system has two electrons per cell (one orbital occupied), lower orbital filled and upper one empty. As atoms come together lower band remains filled, upper empty, till bands overlap when both partially filled and becomes a metal.

Tight binding model

Two atoms per cell, each with one orbital





Now two possible energy eigen-values for each *k* – two bands.

If each atom is monovalent, lower band completely filled, upper empty (2N electrons).

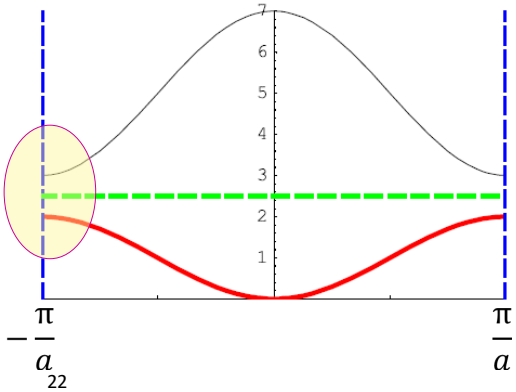
If each atom divalent both bands completely filled (4N electrons).

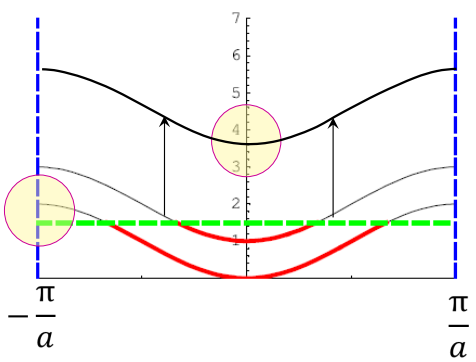
Energy bands – 1D

Two orbitals per unit cell, with 2 electrons per atom (one atom per cell): exactly enough electrons to fill one band – two possibilities:

Get insulator with "***direct*** band gap" (valence band maximum and conduction band minimum at same *k*)

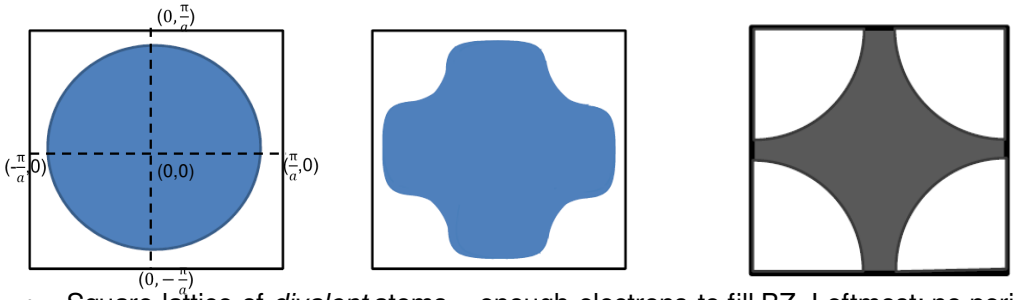
Get metal - two bands both partially filled. If greater separation of bands, would get insulator again with ***indirect*** band gap.





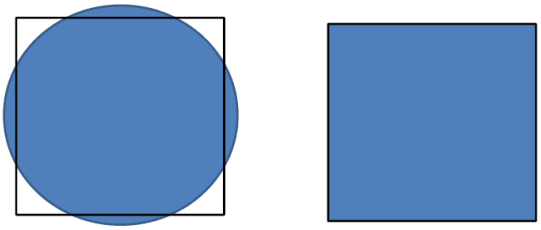
Energy bands – 2D

- Consider square lattice of *monovalent* atoms. The Brillouin zone is square. Since one electron per atom, enough electrons to half fill BZ.
- If no periodic potential, get Fermi circle. With periodic potential gaps open at BZ boundaries, with strong potential can touch BZ boundary.



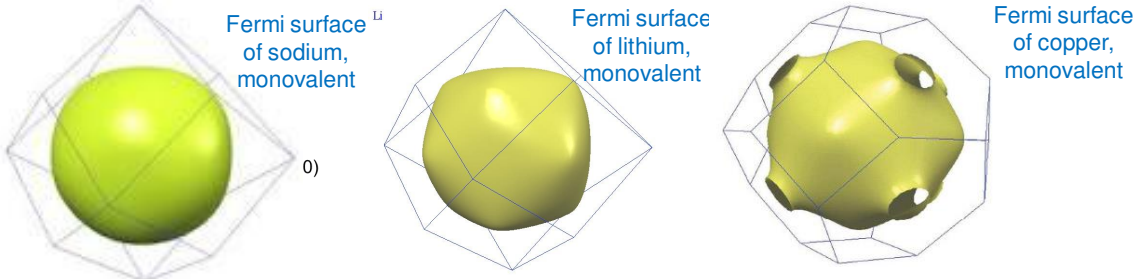
- Square lattice of *divalent* atoms – enough electrons to fill BZ. Leftmost: no periodic potential; right: with strong periodic potential all states filled (gap at zone boundary)

Area of circle equal to that of BZ



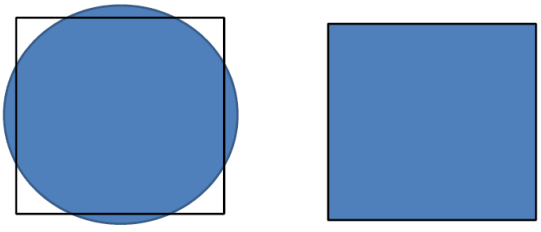
Energy bands – 2D

- Consider square lattice of *monovalent* atoms. The Brillouin zone is square. Since one electron per atom, enough electrons to half fill BZ.
- If no periodic potential, get Fermi circle. With periodic potential gaps open at BZ boundaries, with strong potential can touch BZ boundary.

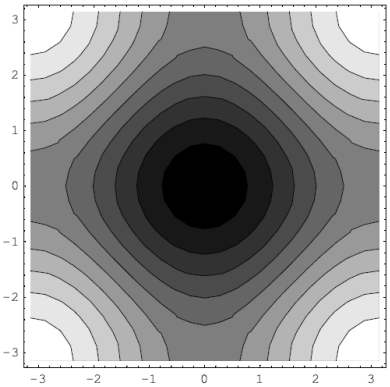


- Square lattice of *divalent* atoms – enough electrons to fill BZ. Leftmost: no periodic potential; right: with strong periodic potential all states filled (gap at zone boundary)

Area of circle equal to that of BZ



Tight binding model – 2D



Similar to expectation for band-gap opening at zone-boundary from nearly-free electron model

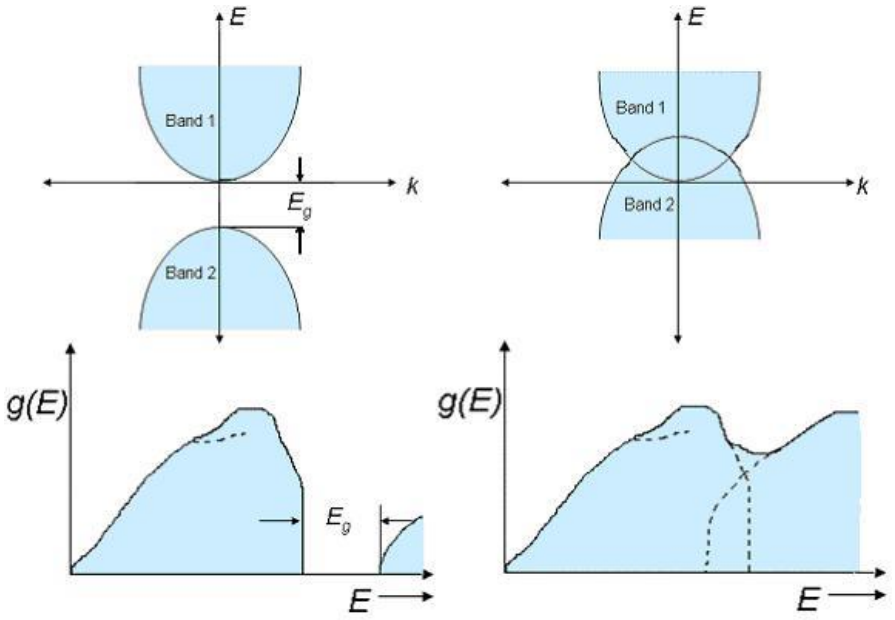
$$E(k) = \epsilon_0 - 2t\cos(k_x a) - 2t\cos(k_y a)$$

For single atomic orbital on a square lattice

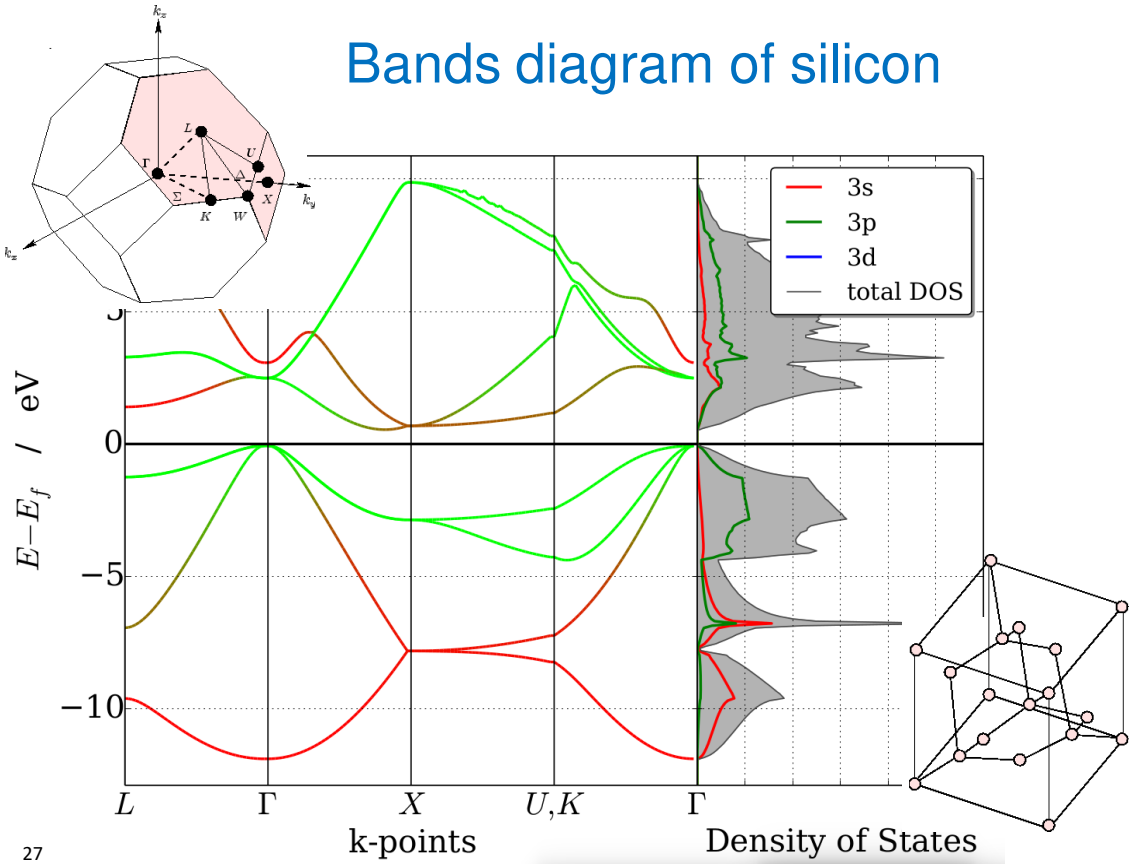
Shortcomings of TB: neglect of electron-electron interactions means

- can't describe magnetism
- can't describe why for some materials with even numbers of electrons where we would expect filled bands and an insulator/semiconductor, they are metals
- can't describe Mott insulators (class of materials that are expected to conduct electricity according to conventional band theories, but turn out to be insulators)

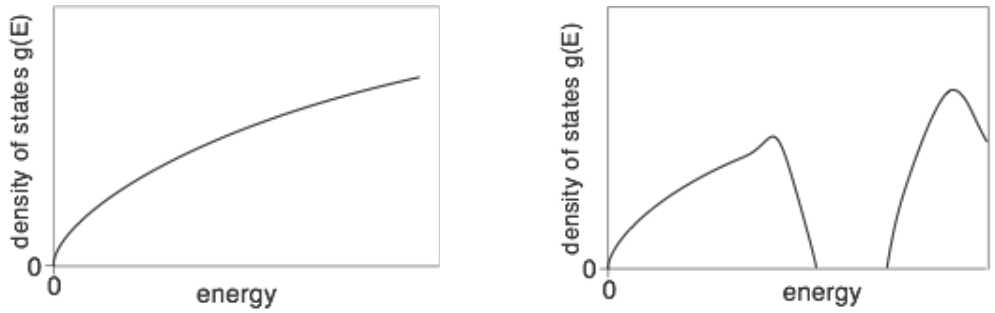
Relationship – band structure and density of states



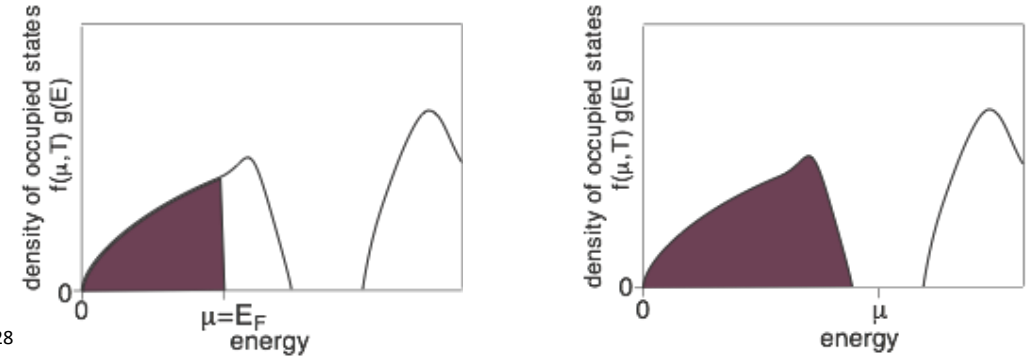
Bands diagram of silicon



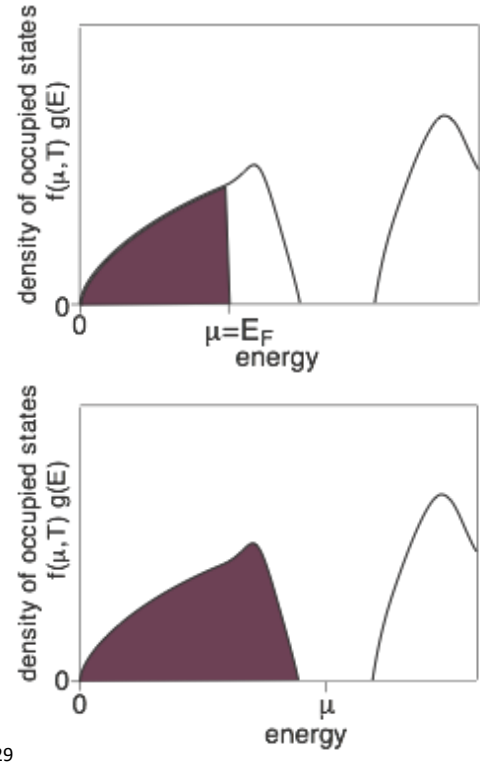
Metals and insulators / semiconductors



The difference between metal and insulator is more obvious when looking at the DOS.
A metal is a material with a finite density of states at the Fermi energy (chemical potential).



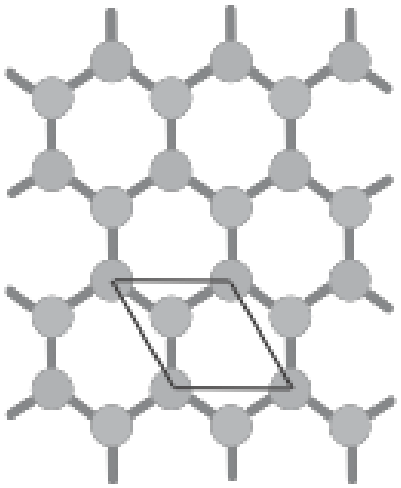
Metals and insulators / semiconductors



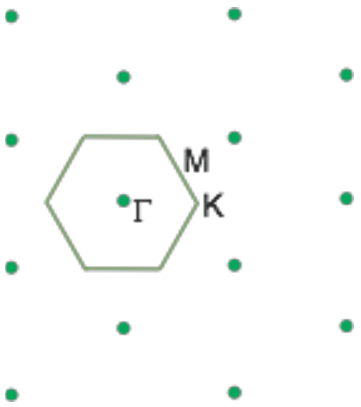
- A metal has a finite density of states at the chemical potential (Fermi energy).
- A semiconductor must have an absolute gap in its band structure (only necessary criterion, not sufficient).
- The number of electrons per unit cell must be such that all the bands are exactly filled up to this gap.

Semimetals: graphene, structure

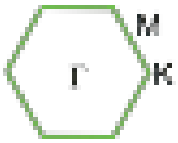
Real space structure
primitive unit cell



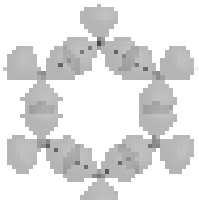
Reciprocal space structure
Brillouin zone



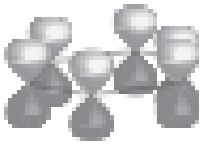
Semimetals: graphene, band structure

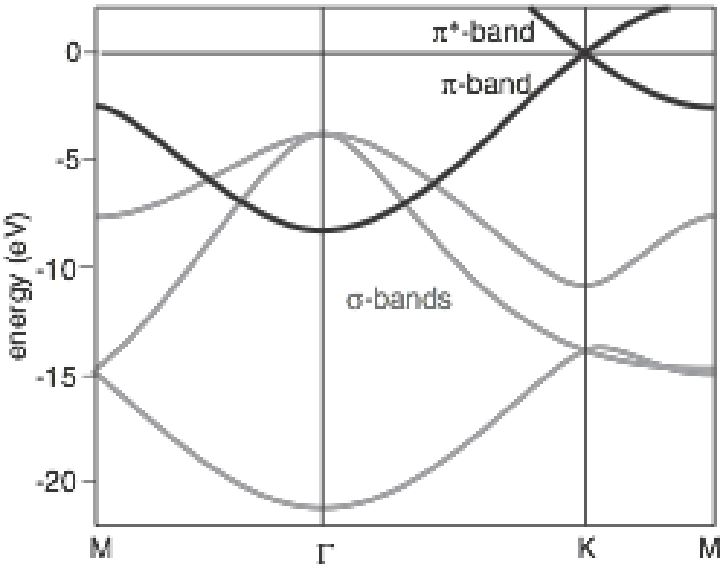


sp^2 orbitals



p_z orbitals



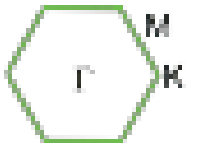


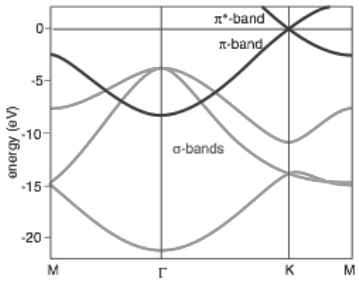
4 electrons per atom, 2 atoms per cell -> 8 electrons per cell, 4 occupied bands

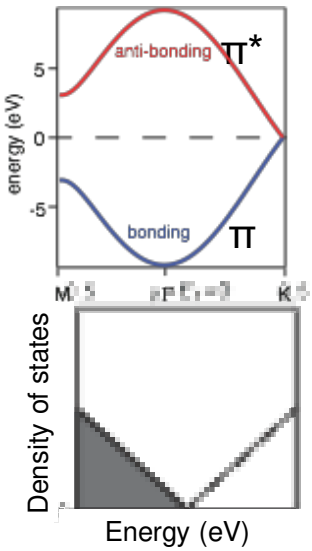
sp^2: 3 states per atom, 6 states per unit cell, 3 σ states, 3 σ* states (not shown)

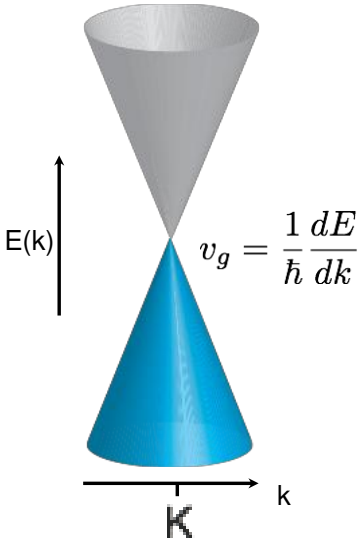
p_z orbitals: 1 state per atom, 2 states per unit cell, 1 π state, 1 π* state

Graphene: electronic structure







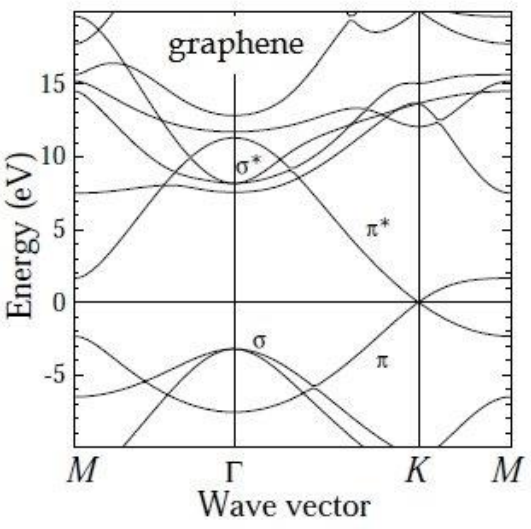


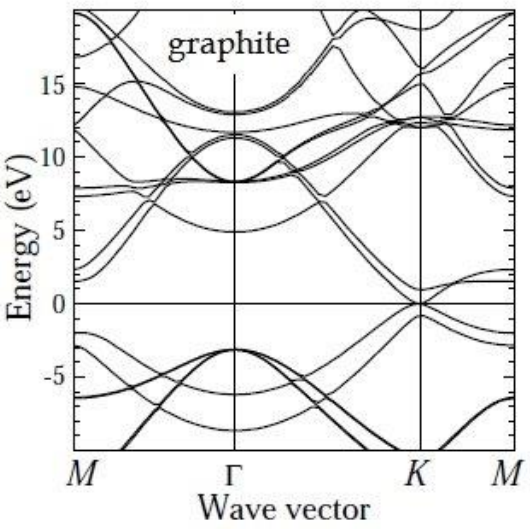
Dirac cone
linear dispersion
group velocity 10^6 ms^{-1}
linear g(E)

Interesting part is the π band at the Fermi energy.
Dispersion is locally linear with a high group velocity.
In 2D *k*-space, this forms a cone, the Dirac cone.
No band gap, but zero density of states at the Fermi energy.

A semimetal

Graphene: electronic structure





End