Materials, Electronics and Renewable Energy
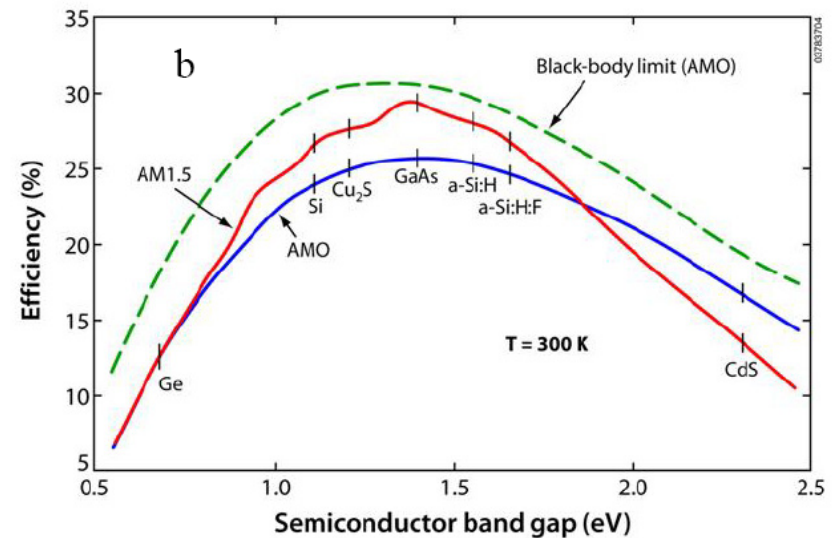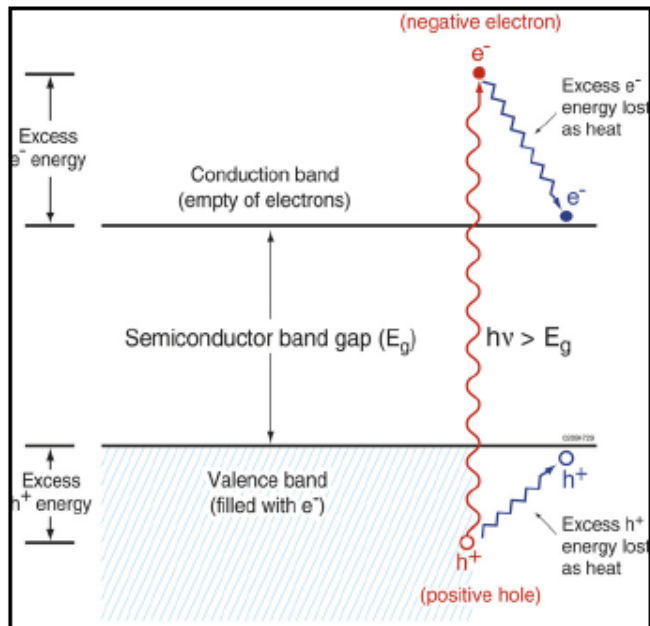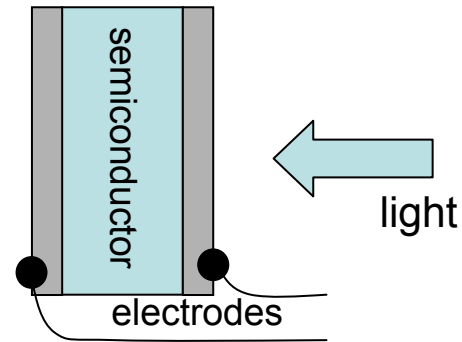
Neil Greenham

ncg11@cam.ac.uk

- Electronic structure of molecules and solids
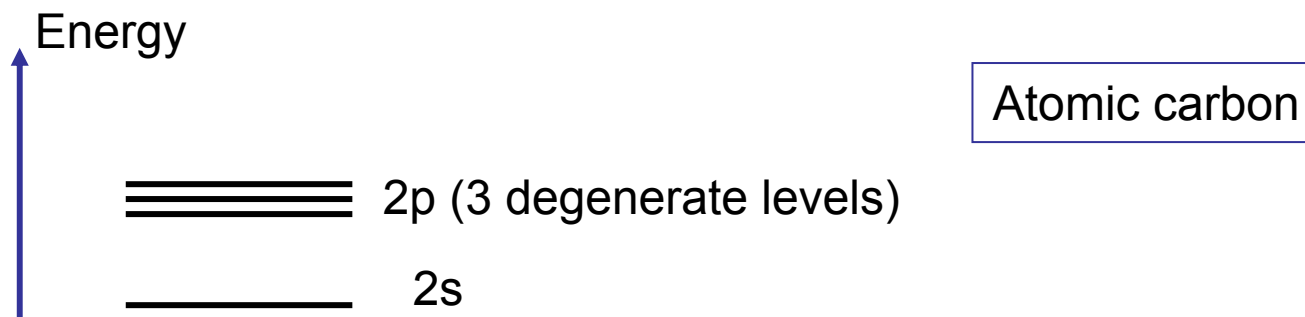
- Interactions with light

Semiconductor Photovoltaics

Need control of bandgap

semiconductor

light

electrodes

(negative electron)

e⁻

Excess e⁻ energy lost as heat

e⁻

Excess e⁻ energy

Conduction band (empty of electrons)

Semiconductor band gap (Eg) $h\nu > E_g$

Excess h⁺ energy

Valence band (filled with e⁻)

Excess h⁺ energy lost as heat

h⁺

h⁺

(positive hole)

Black-body limit (AMO)

AM1.5

Si   Cu₂S   GaAs   a-Si:H   a-Si:H:F

AMO

T = 300 K

Ge

CdS

Efficiency (%)

Semiconductor band gap (eV)

Electronic Structure of Molecules and Solids

Carbon bonding:

Energy

Atomic carbon

2p (3 degenerate levels)

2s
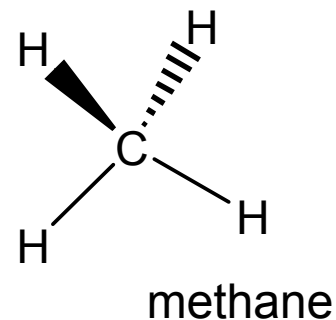
Now add the local environment: carbon usually shows covalent bonding to adjacent atoms – e.g. Methane, CH_4, or diamond – tetrahedral bonding
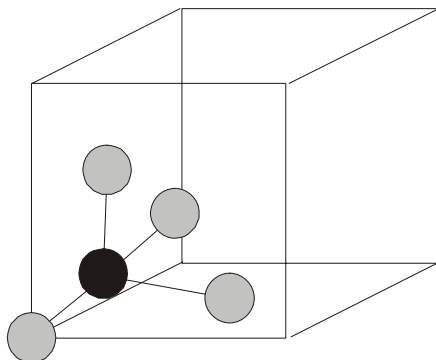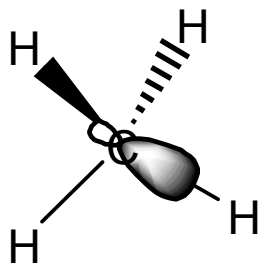
Diamond: Two face-centred cubic lattices, based on (0,0,0) and (¼ , ¼, ¼)

methane

Convenient to re-arrange the atomic orbitals to form
hybrid orbitals:

sp³ hydrid orbitals: $$\phi = \frac{1}{2}\left(\phi_s \pm \phi_{p_x} \pm \phi_{p_y} \pm \phi_{p_z}\right)$$

Hybrid orbitals align along the 4 covalent
bond directions:

Bonding through overlap of wavefunctions in direction of bond

- both electrons (one from each atom forming the bond)
  experience the attractive potential from the two atomic sites.

Describe the resultant molecular orbitals as linear combinations of
the atomic orbitals.   Hückel theory (chemistry), "tight-binding"
model (physics)

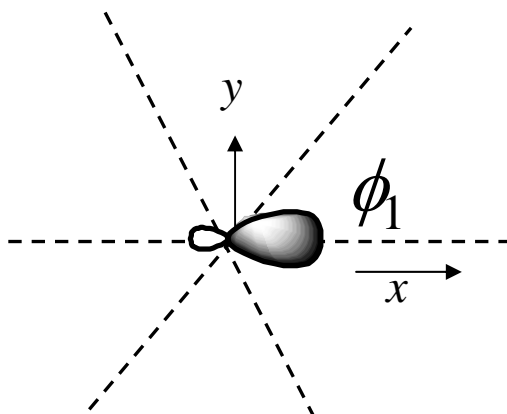The special chemistry of carbon – single and double bonds:

sp² + π bonding

Mix p_x, p_y and s atomic states to form three sp² hybrid orbitals:

$$\phi_1 = \frac{1}{\sqrt{3}}\left(\phi_s + \sqrt{2}\phi_{p_x}\right)$$

$$\phi_2 = \frac{1}{\sqrt{3}}\left(\phi_s - \frac{1}{\sqrt{2}}\phi_{p_x} + \frac{\sqrt{3}}{2}\phi_{p_y}\right)$$

$$\phi_3 = \frac{1}{\sqrt{3}}\left(\phi_s - \frac{1}{\sqrt{2}}\phi_{p_x} - \frac{\sqrt{3}}{2}\phi_{p_y}\right)$$
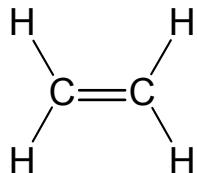

3 orbitals in-plane at 120° to each other

sp² hybrid orbitals leave the p_z non-bonding

Overlap of p_z between adjacent carbon atoms on adjacent sites gives weak π bond formation (double bond)

π-electron molecular orbitals:

Simplest example: ethene

p_z orbitals now experience potential from two carbon sites, A and B

$$V(r) = V_{atomic} + \Delta V(r)$$

Degenerate perturbation theory:

$$\psi_\pi = \frac{1}{\sqrt{2}}\left(\phi_A + \phi_B\right)$$

Mix the two p_z orbitals to form bonding and anti-bonding combinations:

$$\psi_{\pi^*} = \frac{1}{\sqrt{2}}\left(\phi_A - \phi_B\right)$$

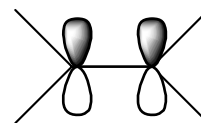$$\psi = \frac{1}{\sqrt{2}}\left(\phi_A \pm \phi_B\right)$$

bonding

$$\hat{H}\psi = \hat{H}_{atomic}\psi + \Delta V\psi$$

$$so:$$
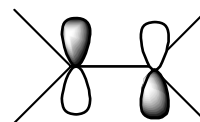
Anti-bonding

$$E\psi = E_{p_z}\psi + \Delta V\psi$$

$$\psi = \frac{1}{\sqrt{2}}\left(\phi_A \pm \phi_B\right)$$

$$\hat{H}\psi = \hat{H}_{atomic}\psi + \Delta V\psi$$

$$E\psi = E_{p_z}\psi + \Delta V\psi$$

Multiply by $\psi*$ and integrate over all space:
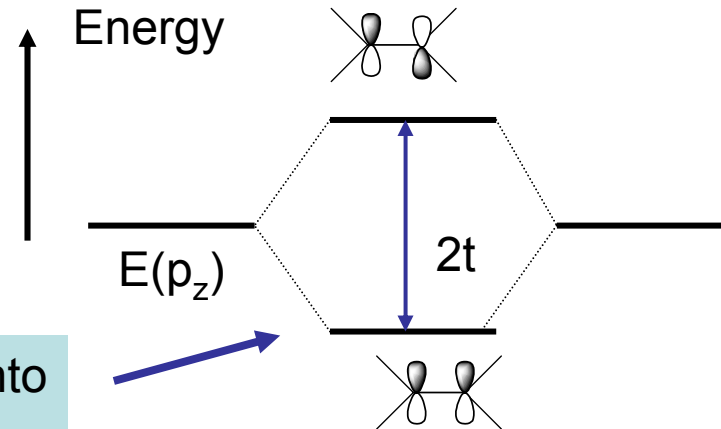
$$E = E_{p_z} + \int \psi^* \Delta V\psi$$

$$\int \psi^* \Delta V\psi = \frac{1}{2}\int\left(\phi_A^* \pm \phi_B^*\right)\Delta V\left(\phi_A \pm \phi_B\right) = -B \mp t$$

where $\quad -B = \int \phi_A^* \Delta V\phi_A$

and $\quad -t = \int \phi_A^* \Delta V\phi_B$
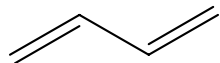
Energy

$E(p_z)$

2t

t is the 'transfer' or 'resonance' integral

Put two electrons into π-bonding orbital

Extend the chain:

n = 4   butadiene

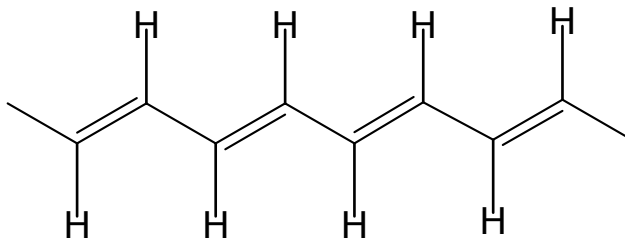4 linear combinations of ϕ_{p_z} orbitals

π^* all antibonding

π all bonding
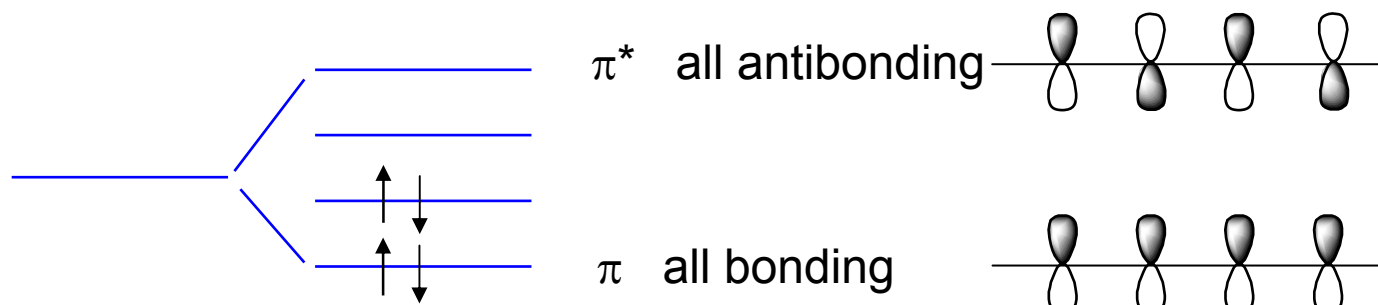
Put two electrons into
lowest π-bonding orbital,
and two into the next lowest
orbital

n = ∞
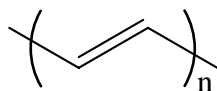
polyacetylene

"trans" isomer

E_{p_z}

π

4 *t*

Band of π states
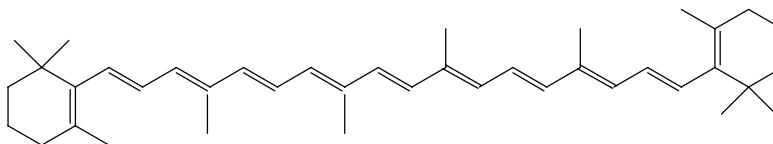
π*
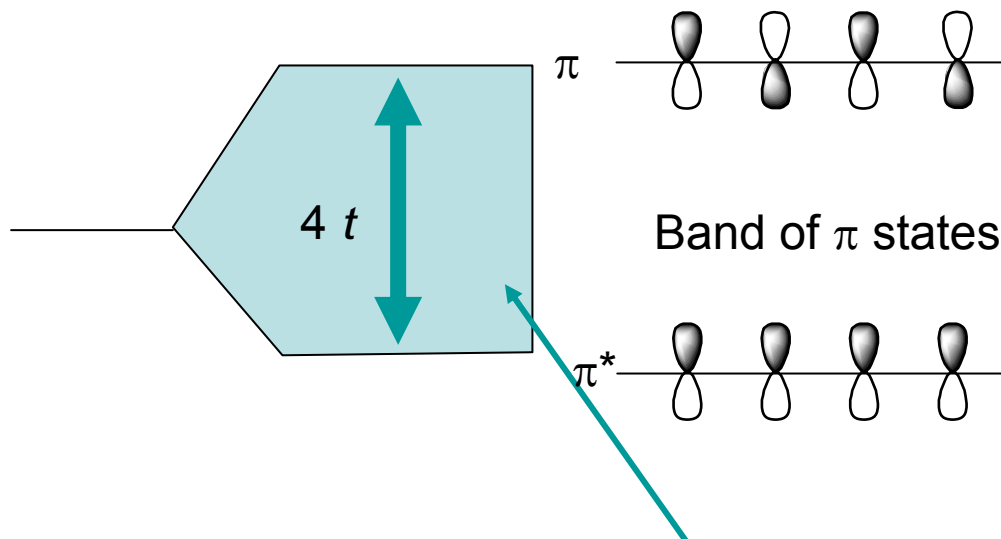
bandwidth = 4 *t*

? Fill half the π molecular orbitals

Natural Products with π-conjugated molecules:

(a) β-carotene

(b) 11-*cis*-retinal:
chromophore in
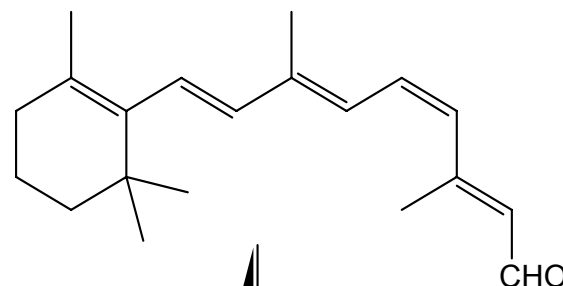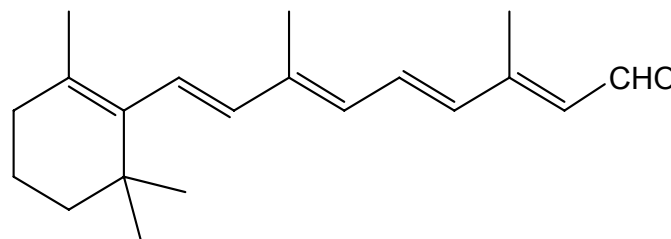**phytochrome protein**

photo-isomerisation $h\nu$

induces conformational change
in rhodopsin protein (visual purple),
gives permeation of Ca^{2+}
across membrane

Periodic structures: crystals (here, a one-dimensional long chain)

Construct the crystal lattice by integer amounts of the three lattice vectors. Identical points, *r* and *r'* are connected by
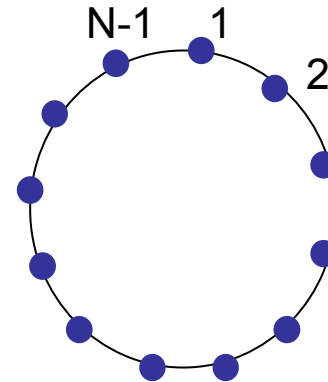
$$\mathbf{r}' = r + u\mathbf{a} + v\mathbf{b} + w\mathbf{c}$$

where **a**, **b**, **c** are the lattice vectors, and *u, v, w* integers

Potential in the lattice is periodic, V(**r** + **T**) = V(**r**) where **T** is a lattice translation vector

Solutions of the Schrodinger equation are wavelike:
- travelling waves require periodic boundary conditions:
- for a one-dimensional chain, loop round to form a ring:

Bloch's theorem: we can write:

$$\psi(k,r) = u_k(r)e^{ikr}$$

Where u(r) is periodic with the lattice,

$$u_k(r) = u_k(r+T)$$

Back to the carbon chain:

We are constructing the molecular orbitals as a linear combination of atomic orbitals (LCAO), and are looking here just at the π molecular orbitals formed from the atomic p_z orbitals:

Choice of Bloch wavefunction:
$$\psi_k(\mathbf{r}) = \sum_{\mathbf{T}} e^{i\mathbf{k}.\mathbf{T}} \phi(\mathbf{r} - \mathbf{T})$$

for the 1-d chain here,
$$\psi_k(x) = \sum_{n=1}^{N-1} e^{ikna} \phi(x - na)$$

Note this gives us exactly N distinct values of k: allowed values of k are spaced by $2\pi/Na$, and all physically-distinct values of k lie within a range $0 < k < 2\pi/a$

p_z orbitals experience potential from *adjacent* carbon sites,

$$V(r) = V_{atomic} + \Delta V(r)$$

$$H_{at} \sum_{n=1}^{N} e^{ikna} \phi(x - na) + \Delta V \sum_{n=1}^{N} e^{ikna} \phi(x - na) = E(k) \sum_{n=1}^{N} e^{ikna} \phi(x - na)$$

Multiply by $\phi^*(x)$ and integrate over all *x:*

$$\int \phi^*(x) H_{at} \sum_{n=1}^{N} e^{ikna} \phi(x - na) dx + \int \phi^*(x) \Delta V \sum_{n=1}^{N} e^{ikna} \phi(x - na) dx = \int \phi^*(x) E(k) \sum_{n=1}^{N} e^{ikna} \phi(x - na) dx$$

$$\boxed{E_{atomic}} \qquad \boxed{\left(e^{ika} + e^{-ika}\right) \int \phi^*(x) \Delta V \phi(x + a) dx + \int \phi^*(x) \Delta V \phi(x) dx} \qquad \boxed{E(k)}$$

we recognise the same
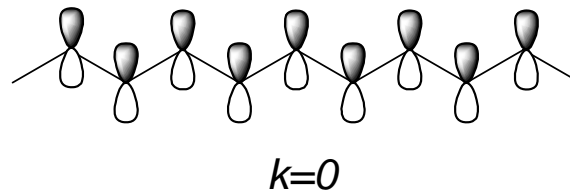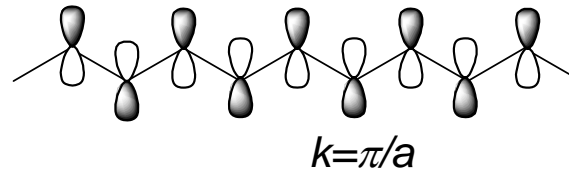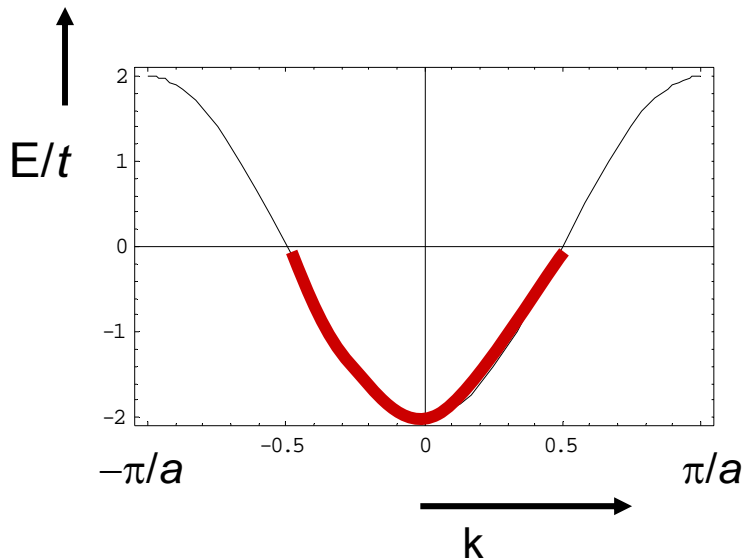*B* and *t* integrals as we
met for the Hückel
treatment of ethene

$$E(k) = E_{atomic} - 2t \cos(ka) - B$$

One-dimensional tight-binding band:

$$E(k) = E_{atomic} - 2t \cos(ka) - B$$

k labels the allowed molecular orbitals on the chain.

There are *k* states are spaced by π/Na and range between $-\pi/a$ and π/a

E/*t*

$-\pi/a$ π/a

k

$k=\pi/a$

$k=0$

Add electrons, one per site, spin-up and spin-down, lowest energy states first – fill ½ of available states, to Fermi energy E_F and values of $k_F = \pm\,\pi/2a$

Describes a metal – unfilled states accessible at E_F

Polyacetylene – shows alternating bond lengths
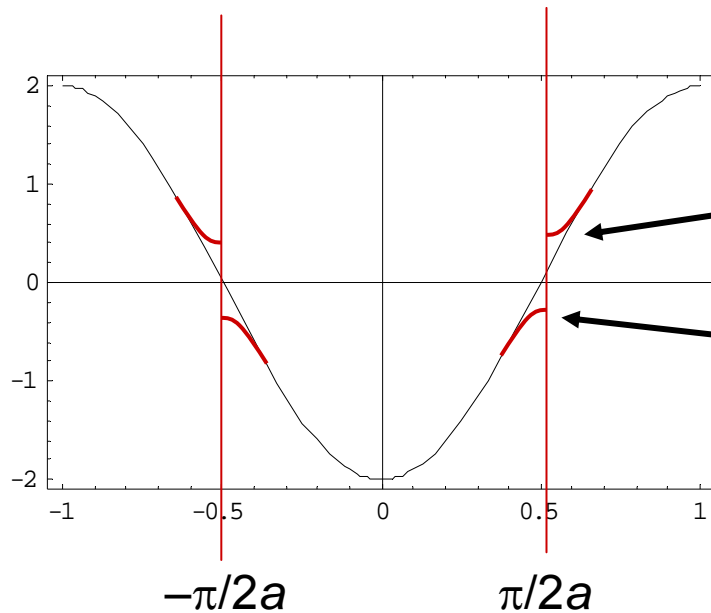along the chain – 'double' and 'single' bonds:

2a
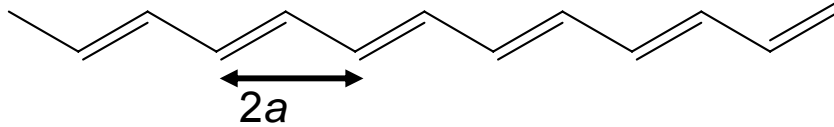
increase in the periodicity from a to 2a
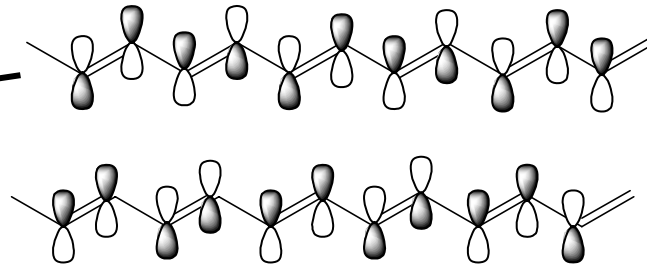
Expect standing wave states at

$k = \pm \pi/2a$?

Look at states at $k = \pi/2a$, real
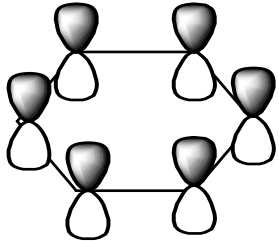space periodicity 4a

$-\pi/2a$ $\pi/2a$

Bonding across long
bonds – higher energy

Bonding across short
bonds – lower energy

Benzene:

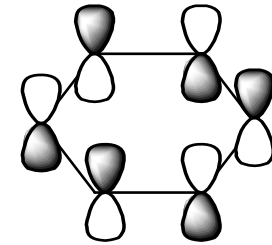6-membered ring. C_6H_6

L=6a, allowed values of k are:
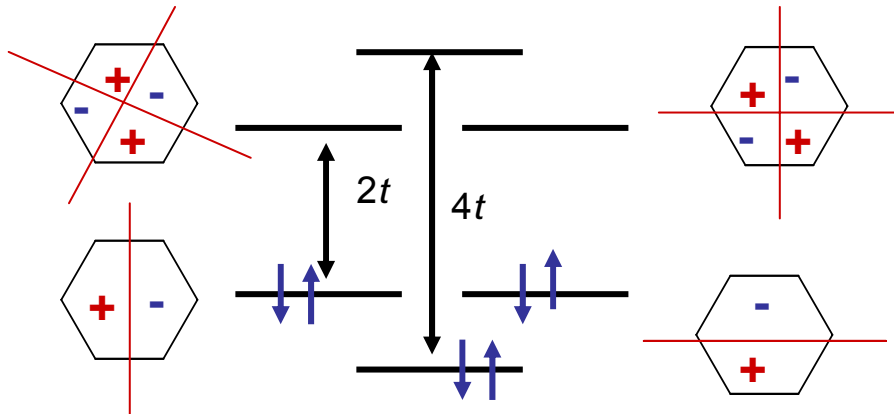
$$0, \quad \pm\frac{\pi}{3a}, \quad \pm\frac{2\pi}{3a}, \quad \pm\frac{\pi}{a}$$

Clockwise and counter-clockwise travelling waves

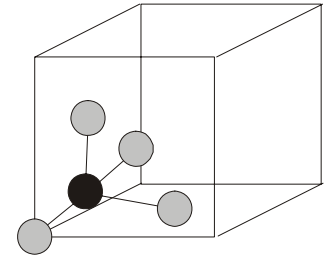$k = \pm\dfrac{\pi}{a}$ describes the same, all anti-bonding standing wave

$2t$ $4t$

6 electrons into π bonding orbitals

$$E(k) = E_{atomic} - 2t\cos(ka) - B$$

$E = -2t, \ -t, \ +t, \ +2t$

Inorganic semiconductors used for photovoltaics

Material	Bandgap (eV) (at 300K)	direct/ indirect
Si (crystalline)	1.1	i
Ge	0.66	i
GaAs	1.43	d
CdSe	1.74	d
CdTe	1.44	d
ZnO	3.2	?
$CuInSe_2$	1.0	d
"$CuInGaSe_2$", CIGS	1.2 or greater	d
amorphous-Si	1.7 (typical)	d

diamond, Si, Ge: both sites same

GaAs: Ga on (0,0,0), As on (¼ ¼ ¼)

CdSe, CdTe – similar, but based on hexagonal close-packed lattice

In general – increased ionicity causes a larger band-gap

Amorphous silicon – preparation under conditions of rapid cooling - locks in disordered 'liquid-like' structure. Short-range order similar to crystal, but no long range order.   Disorder primarily in bond angle rotations.

Electronic states are no longer delocalised k states, but are spatially localised.
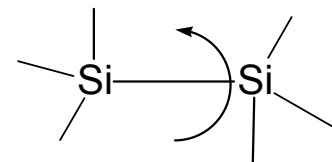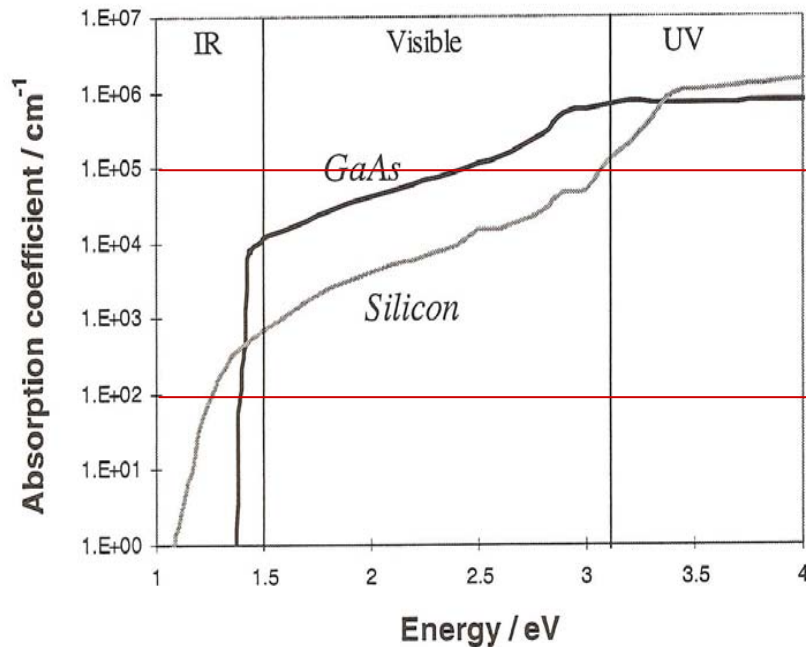
Optical properties of semiconductors

Macroscopic absorption coefficient α describes attenuation of light through a material.
Photons of energy E and intensity I_0 incident normally on a slab of material.

Fraction $\alpha(E)\,dx$ of the photons are absorbed, so: $dI/dx = -\alpha x$

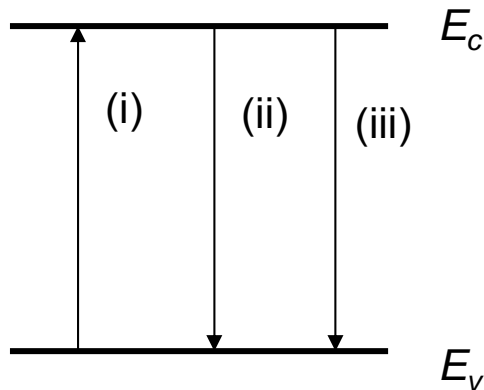integrating, $\quad I(x) = I_0 e^{-\alpha x} \quad$ (the Beer-Lambert law)

absorption coefficient for Si (indirect gap) and for GaAs (direct gap):

$\alpha = 10^5$ cm^{-1} – thickness to absorb 1/e of incident light is 10^{-7} m, or 0.1 μm

$\alpha = 10^2$ cm^{-1} – thickness to absorb 1/e of incident light is 10^{-4} m, or 100 μm

Optical properties of semiconductors

Microscopic description of absorption and emission: start with a 2-level system

(i)   stimulated absorption, rate $B_{vc}u(\omega)$

(ii) stimulated emission, rate $B_{cv}u(\omega)$

(iii) spontaneous emission, rate A

$u(\omega)$ is the energy density of radiation per unit ω

A and B are the Einstein coefficients. Fermi golden rule requires $B_{(absorption)}$ = $B_{(stimulated\ emission)}$.

Thermal equilibrium in reservoir of black body radiation at temperature T sets relation between A and B:

$$A = B\frac{\hbar\omega^3}{\pi^2 c^3}$$

Einstein B coefficient:

Fermi Golden rule to calculate transition rate between initial and final states caused by EM electric field:

$$B_{vc} = \frac{\pi e^2}{\varepsilon_0 \hbar^2} \left| \langle v | x | c \rangle \right|^2$$

Einstein A coefficient gives radiative decay rate, e.g. hydrogen 2s to 1s, A_{21} = 6 x 10^8 s^{-1}, and $\tau_{rad.}$ = 1.6 ns

Optical absorption for band-to-band transitions:

transitions between valence and conduction band Bloch states:

$$\psi_v(k, r) = u_v(r) e^{ikr}$$

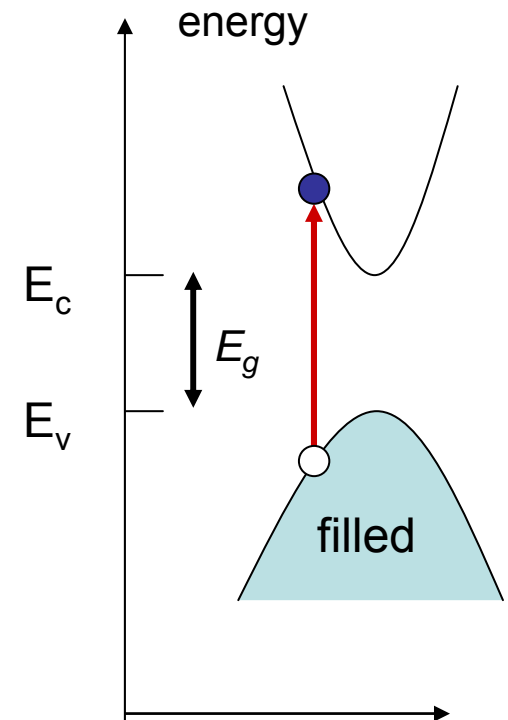$$\psi_c(k', r) = u_c(r) e^{ik'r}$$
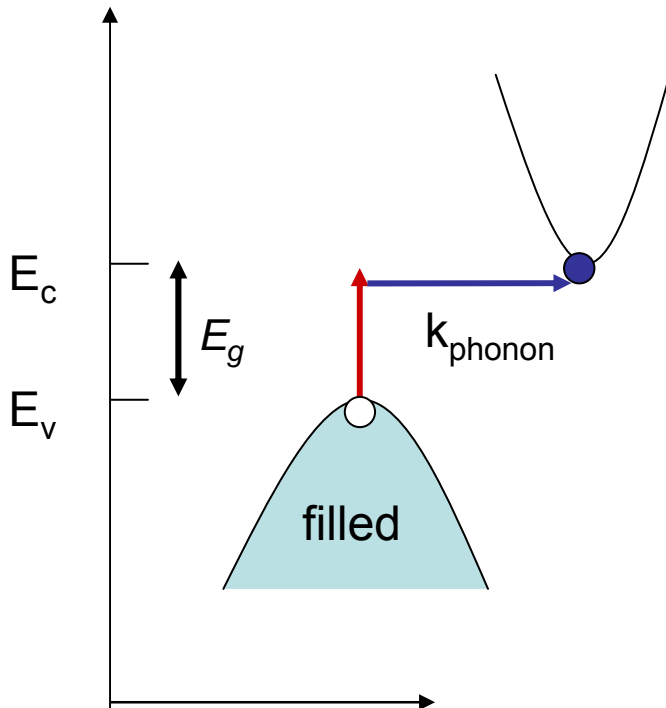
dipole matrix element includes the term
- non-zero only when $k = k'$

$$\int e^{i(k'-k)r} d^3 r$$

standard matrix element 'atomic' selection rules, (s to p etc.) also hold

energy

E_c

E_g

E_v

filled

Indirect gap semiconductors

transition requires participation of a phonon, which provides energy $\hbar\omega$ and momentum $\hbar k$

requires thermal population of phonons, so temperature-dependent absorption coefficient (near the band edge), and weak absorption coefficient.

absorption coefficient only large at threshold energy for direct transitions – a relatively high energy for silicon

E_c

E_g

k_{phonon}

E_v

filled
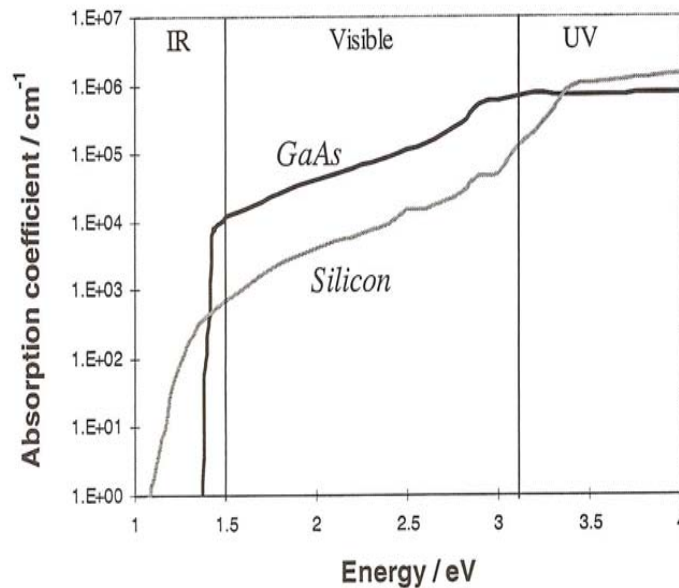
Excitons in inorganic semiconductors

independent treatment of electrons and holes for optically-excited states – is this realistic?

Mott-Wannier Excitons: Coulomb interaction between electron and hole – treat this using a modified Bohr model for the H atom: [c.f. dopant states in extrinsic semiconductors]

$$E_{binding} = \frac{e^4 \mu}{2(4\pi\varepsilon\varepsilon_0\hbar)^2} = \frac{\mu/m}{\varepsilon^2} \times 13.6\,eV$$

where μ is the reduced mass for the e-h system:

$$\frac{1}{\mu} = \frac{1}{m_e^*} + \frac{1}{m_h^*}$$

Minimum energy for absorption is therefore *lower* by the exciton binding energy.

Photon energy in eV

Cu$_2$O
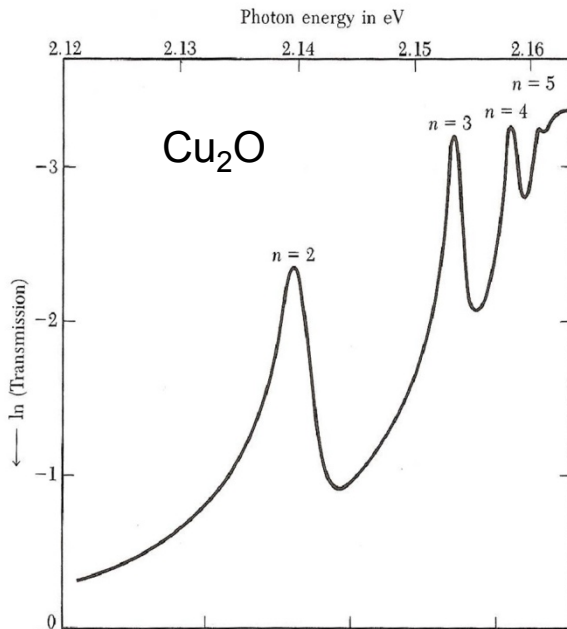
large dielectric constants and low effective masses give very low exciton binding energies for lower-gap semiconductors such as Si and GaAs:

Si	15 meV
GaAs	4 meV
CdS	29 meV

confinement to smaller size causes increase in exciton binding energy – seen for 2-dimensional semiconductor heterostructures, and nanocrystals
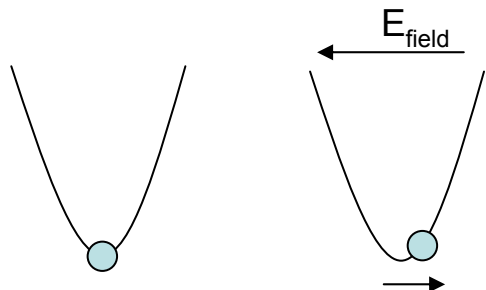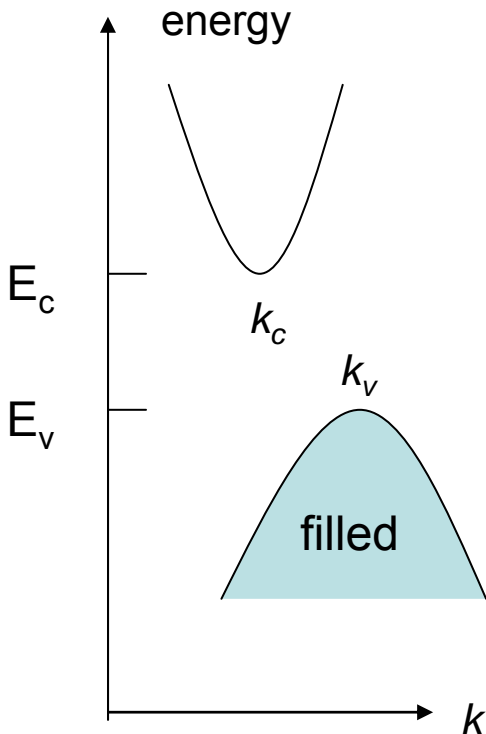
Electron dynamics in semiconductors

Energy vs. momentum for a free particle

$$E = \frac{p^2}{2m} = \frac{\hbar^2 k^2}{2m}$$

energy

For electron in conduction band, E(k) is locally parabolic about band minimum

E_c

k_c

k_v

E_v

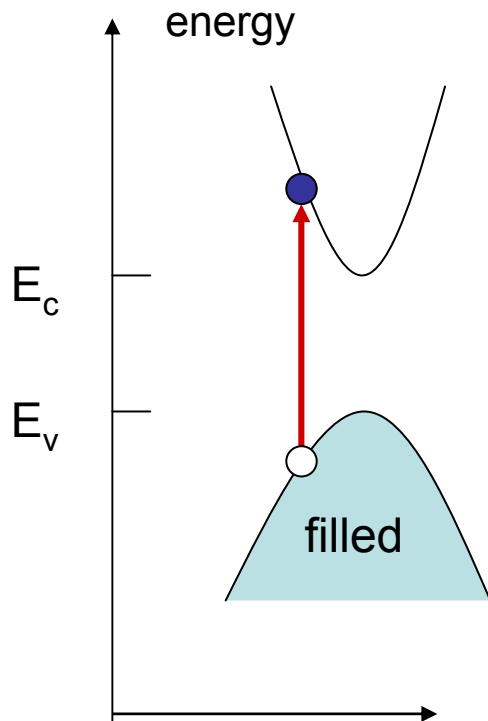$$E = \frac{\hbar^2 (k - k_0)^2}{2m_e^*}$$

effective mass   ≠ free electron mass due to interactions with lattice

filled

To describe a localised electron in an electric field
- make a wavepacket with k values around k_0
- field increases k's with time
- electron moves like classical particle with mass m_e^* and charge $-e$
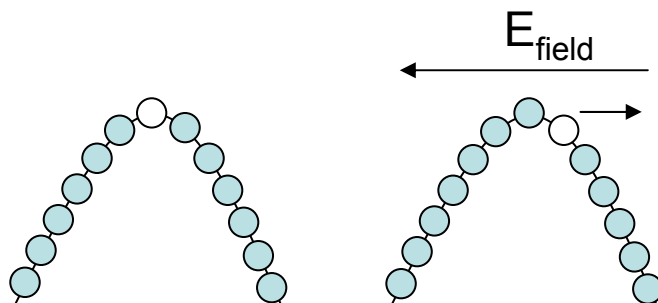- due to scattering, k's never get far from k_0

k

E_{field}

energy

E_c

E_v

filled

E_{field}

• Remove one electron from full valence band

• Consider remaining "hole" as a new particle

  • Positive effective mass
  • Positive charge

related to curvature of top of band, as before

• electrons move to right (increase k) as before
• empty state moves with them
• but $k_{hole} = -k_{electron\ removed}$
• momentum of system (hole) increases to left
• equivalent to motion of positive particle
• energy also increases, as expected