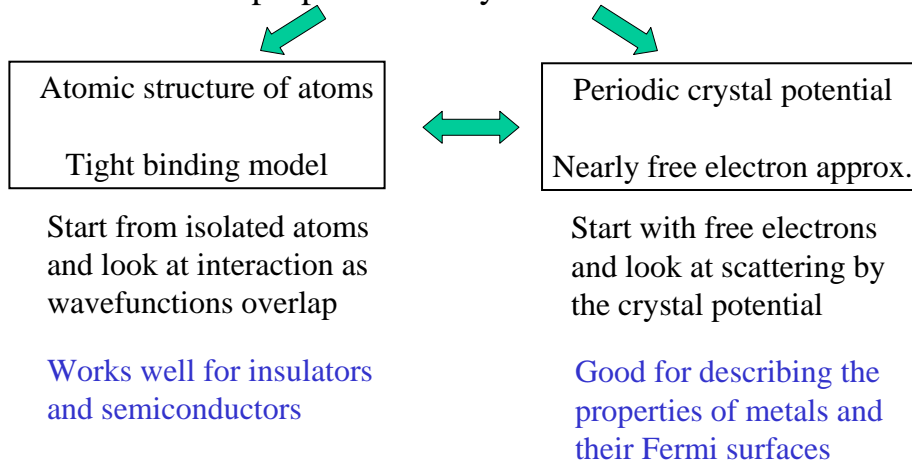


Band Theory

Need to take account of two main factors in understanding the electronic properties of crystals



Nearly Free Electron Approximation

Use a travelling wavefunction for an electron, e^{ikx} , with kinetic energy $\hbar^2 k^2 / 2m$

Assume that this is Bragg scattered by the wavevector $G=2\pi/a$ to give a second wave $e^{i(k-G)x}$ with energy $\hbar^2(k-G)^2/2m$

Crystal potential is periodic in real space. Therefore we can Fourier Transform the potential so that:

$$V(x) = \sum_G V_G \exp(iGx)$$

For a schematic solution we calculate what happens for a single Fourier component V_G so $V(x) = V_G(e^{iGx} + e^{-iGx})$

Formally what we are doing is to solve the Hamiltonian form of Schrödinger equation

$$\mathbf{H} \psi = E \psi$$

where ψ are the two travelling wave solutions. Expanding gives:

$$\begin{pmatrix} H_{11} - \lambda & H_{12} \\ H_{21} & H_{22} - \lambda \end{pmatrix} \begin{pmatrix} e^{ikx} \\ e^{i(k-G)x} \end{pmatrix} = (E - \lambda) \begin{pmatrix} e^{ikx} \\ e^{i(k-G)x} \end{pmatrix}$$

$H_{11} = \left\langle \psi_1^* \left -\frac{\hbar^2}{2m} \frac{\partial^2}{\partial x^2} \right \psi_1 \right\rangle = \frac{\hbar^2 k^2}{2m}, \quad H_{22} = \frac{\hbar^2 (k-G)^2}{2m}$
$H_{12} = \left\langle \psi_1^* \left V(x) \right \psi_2 \right\rangle = V_G$

New Schrödinger equation is: $H\psi = -\frac{\hbar^2}{2m} \frac{\partial^2 \psi}{\partial x^2} + V(x)\psi = E\psi$

if $\psi = e^{ikx}$, $H\psi = \frac{\hbar^2 k^2}{2m} e^{ikx} + V_G e^{i(k \pm G)x}$

so e^{ikx} is no longer a solution.

\therefore Choose a combination of two waves: $A_k e^{ikx} + B_{k'} e^{ik'x}$.

Can then solve the Schrödinger Eq. by writing:

$$\begin{aligned} H\psi &= \frac{\hbar^2 k^2}{2m} A e^{ikx} + \frac{\hbar^2 k'^2}{2m} B e^{ik'x} + V_G [A e^{i(k \pm G)x} + B e^{i(k' \pm G)x}] \\ &= E (A e^{ikx} + B e^{ik'x}), \quad \text{with } k' = k - G \end{aligned}$$

To simplify this we multiply by e^{-ikx} (and again by $e^{-ik'x}$)
and integrate over all space using

$$\frac{1}{L} \int_0^L e^{iqx} dx = 1 \text{ when } q = 0, \text{ and } \int_0^L e^{iqx} dx = 0 \text{ when } q \neq 0$$

Gives a pair of simultaneous equations:

$$E A = \frac{\hbar^2 k^2}{2m} A + V_G B$$

$$E B = V_G A + \frac{\hbar^2 (k - G)^2}{2m} B$$

Solve determinant:

at the Brillouin Zone
boundary

$$|k'| = |k - G| = \pi/a$$

(using $G = 2\pi/a$)

Giving two solutions:

With eigenstates

i.e. Standing waves $\cos\vartheta$ and $\sin\vartheta$

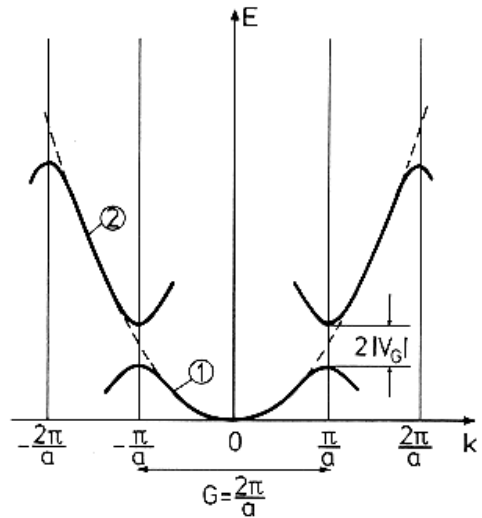
$$\begin{vmatrix} \frac{\hbar^2 (\pi/a)^2}{2m} - E & V_G \\ V_G & \frac{\hbar^2 (\pi/a)^2}{2m} - E \end{vmatrix} = 0$$

$$\lambda = \frac{\hbar^2 (\pi/a)^2}{2m} \pm V_G$$

$$\psi = e^{i(\pi/a)x} \pm e^{-i(\pi/a)x}$$

Around $k = \pi/a - \delta$
 solutions are:
$$\varepsilon(\pm) = \frac{\hbar^2(\pi/a)^2}{2m} \pm V_G + \frac{\hbar^2\delta^2}{2m} \left(1 \pm \frac{\hbar^2(\pi/a)^2}{mV_G} \right)$$

- Around the band gap the solutions are parabolae - almost mirror images
- At the band edge the states are stationary. i.e. zero velocity
- Inverted parabola describes the behaviour of **holes**



Generalise to include scattering by all possible reciprocal lattice vectors

Crystal potential is:
$$V(x) = \sum_G V_G \exp(iGx)$$

travelling wave e^{ikx} is scattered to give:

$$\psi = A e^{ikx} + B e^{i(k-G)x} + C e^{i(k-G')x} + \dots$$

which is:
$$\psi = e^{ikx} (u_0 + u_G e^{-iGx} + u_{G'} e^{-iG'x} + \dots)$$

$$\psi = e^{ikx} u_k(x) = e^{ikx} u_k(x+a)$$

$u_k(x)$ is called a Bloch function, and it has the same periodicity as the crystal lattice (from Fourier series)

Bloch's Theorem

For any periodic potential defined by $V(\mathbf{r}) = V(\mathbf{r} + \mathbf{R})$
the solutions to the Schrödinger equation

$$\left\{ -\frac{\hbar^2}{2m} \nabla^2 + V(\mathbf{r}) \right\} \psi(\mathbf{r}) = E_\psi \psi(\mathbf{r})$$

are

$$\psi_k(\mathbf{r}) = \exp(i\mathbf{k} \cdot \mathbf{r}) u_k(\mathbf{r})$$

$$\text{where } u_k(\mathbf{r}) = u_k(\mathbf{r} + \mathbf{R})$$

Free electron states have $u_k(\mathbf{r}) = \text{constant}$

In real solids $u_k(\mathbf{r})$ looks like the atomic wavefunctions

Proof of Bloch's Theorem

substituting $\mathbf{R} + \mathbf{r}' = \mathbf{r}$

$$\left\{ -\frac{\hbar^2}{2m} \nabla^2 + V(\mathbf{R} + \mathbf{r}') \right\} \psi(\mathbf{R} + \mathbf{r}') = E_\psi \psi(\mathbf{R} + \mathbf{r}')$$

but since $V(\mathbf{R} + \mathbf{r}') = V(\mathbf{r}')$

$$\left\{ -\frac{\hbar^2}{2m} \nabla^2 + V(\mathbf{r}') \right\} \psi(\mathbf{R} + \mathbf{r}') = E_\psi \psi(\mathbf{R} + \mathbf{r}')$$

Therefore $\psi(\mathbf{r})$ and $\psi(\mathbf{r} + \mathbf{R})$ represent solutions with the same energy:

thus they can only differ by a phase factor $\delta\phi = \mathbf{k} \cdot \mathbf{R}$

$$\psi(\mathbf{r} + \mathbf{R}) = e^{i\mathbf{k} \cdot \mathbf{R}} \psi(\mathbf{r}) \text{ where } \mathbf{k} \text{ is a constant and } \mathbf{R} = n_1 \mathbf{a} + n_2 \mathbf{b} + n_3 \mathbf{c}$$

This will be automatically satisfied if we substitute:

$$\psi_k(\mathbf{r}) = \exp(i\mathbf{k} \cdot \mathbf{r}) u_k(\mathbf{r}), \quad \text{where } u_k(\mathbf{r}) = u_k(\mathbf{r} + \mathbf{R})$$

$$\psi_k(\mathbf{r} + \mathbf{R}) = \exp(i\mathbf{k} \cdot (\mathbf{r} + \mathbf{R})) u_k(\mathbf{r} + \mathbf{R}) = \exp(i\mathbf{k} \cdot \mathbf{R}) \psi_k(\mathbf{r})$$

Consequences of Bloch's Theorem

1) **The value of \mathbf{k} is not unique.** It repeats in reciprocal space. If we add a reciprocal lattice vector \mathbf{G} ($=\mathbf{h}\mathbf{a}^* + \mathbf{k}\mathbf{b}^* + \mathbf{l}\mathbf{c}^*$) then:

$$\psi_{\mathbf{k}}(\mathbf{r} + \mathbf{R}) = \exp(i\mathbf{k}\cdot\mathbf{R}) \psi_{\mathbf{k}}(\mathbf{r})$$

$$\psi_{\mathbf{k}+\mathbf{G}}(\mathbf{r} + \mathbf{R}) = \exp(i(\mathbf{k} + \mathbf{G})\cdot\mathbf{R}) \psi_{\mathbf{k}+\mathbf{G}}(\mathbf{r})$$

but as $\exp(i\mathbf{G}\cdot\mathbf{R}) = 1$

$$\psi_{\mathbf{k}+\mathbf{G}}(\mathbf{r} + \mathbf{R}) = \exp(i\mathbf{k}\cdot\mathbf{R}) \psi_{\mathbf{k}+\mathbf{G}}(\mathbf{r})$$

2) **\mathbf{k} is known as the crystal momentum.**

It measures the change in phase ($\mathbf{k}\cdot\mathbf{R}$) from one unit cell to the next.

It is conserved only subject to $\pm\mathbf{G}$.

It does not give us the real momentum for the travelling particle.

Brillouin Zones and dispersion relations

Free electrons have energies

$$\hbar^2\mathbf{k}^2/2m$$

$$\hbar^2(\mathbf{k}-\mathbf{G})^2/2m, \hbar^2(\mathbf{k}+\mathbf{G})^2/2m, \dots$$

Describe the dispersion relations

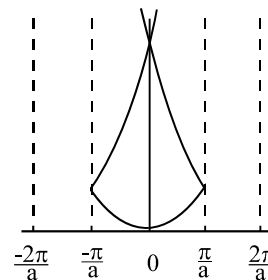
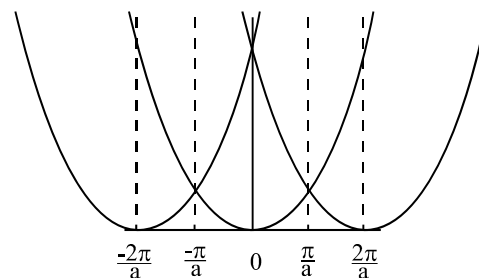
in either the

extended/repeated zone

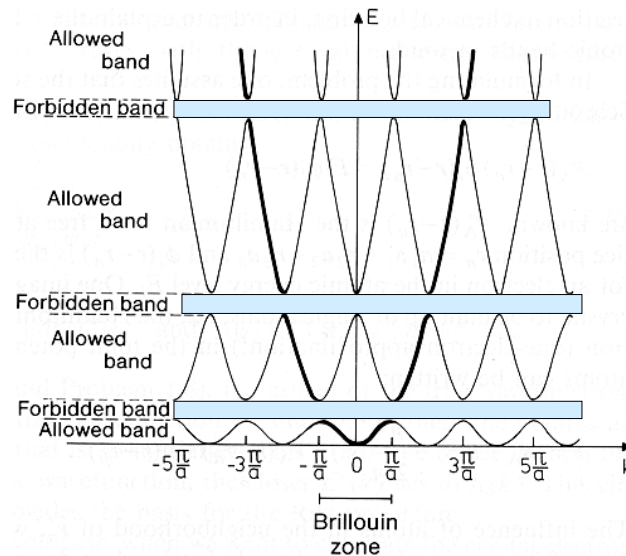
or

reduced zone

Schemes



Repeated Zone Scheme



Number of states per Zone (Band)

Use periodic boundary conditions for electrons:

$$\psi(x) = \psi(x + L), \quad \text{with } \psi(x) = e^{ikx} u_k(x)$$

but as $u_k(x)$ is periodic with lattice constant a , and $L = N_x a$

$$e^{ikN_x a} = 1 \quad \text{and so: } \delta k = 2\pi/N_x a$$

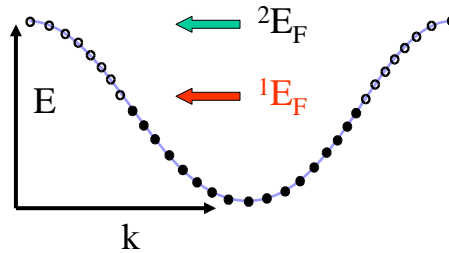
Number of states in one Brillouin Zone is:

$$2 \times \left(\frac{2\pi/a}{\delta k} \right)^3 = 2N_x^3 = 2N$$

$\times 2$ for spin states

1-D Solid

- When we have 1 electron per atom we have a total of N electrons \therefore the first 'band' is half filled
- When we have 2 electrons per atom we have a total of $2N$ electrons \therefore the first 'band' is full

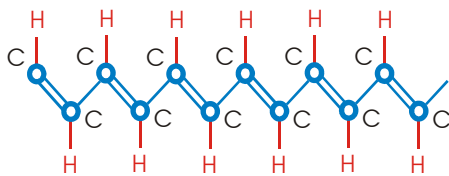


Filled band means electrons have no empty states to move into
 \therefore Filled band = insulating behaviour

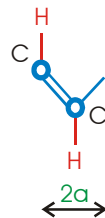
Polymers are 1-D materials

e.g. polyacetylene - $(\text{CH})_x$

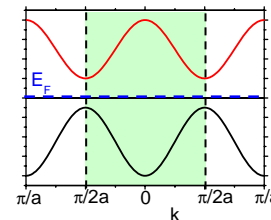
Alternating bonds



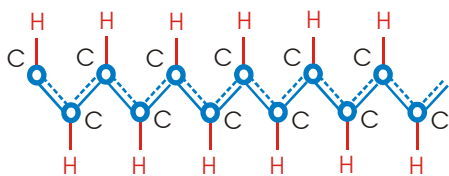
2 e/unit cell



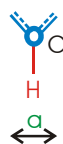
Semiconductor/Insulator



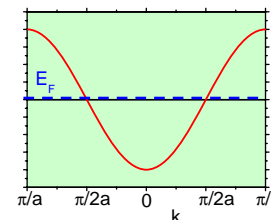
Symmetric configuration



1 e/unit cell

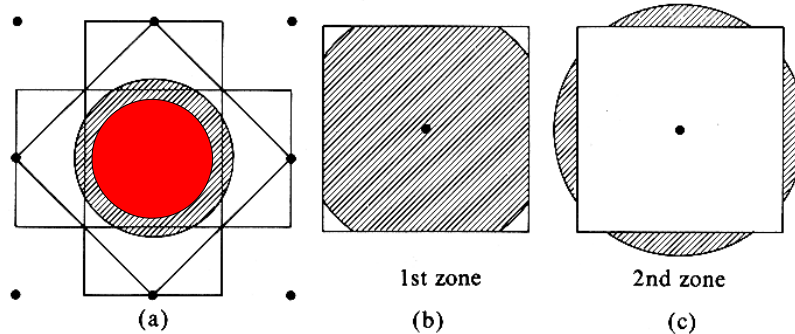


Metal



Fermi Surfaces for **Monovalent** and Divalent metals in 2-D

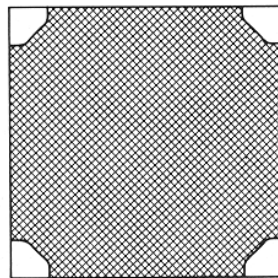
For monovalent metals the volume of the Fermi sphere is only half the first Brillouin Zone



For Divalent metals the two volumes are the same

Divalent Metal with Band structure

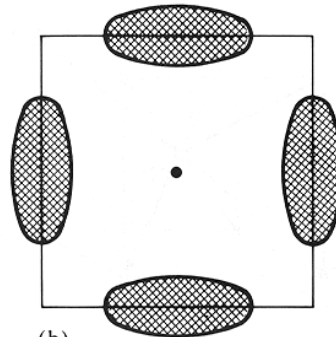
First Brillouin zone



(a)

Nearly filled band with a few **holes**

Second Brillouin zone



(b)

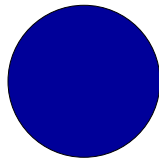
Map pockets of second zone together so that they join up - small number of **electrons**

Divalent Semiconductors and Insulators

If crystal potential V_G is stronger the band gaps get bigger.
Eventually all the overlap between the band edges disappears.

The “Fermi Surface” is a cube, lowest band is filled
→ material is a semiconductor or an insulator depending on
the size of the band gap

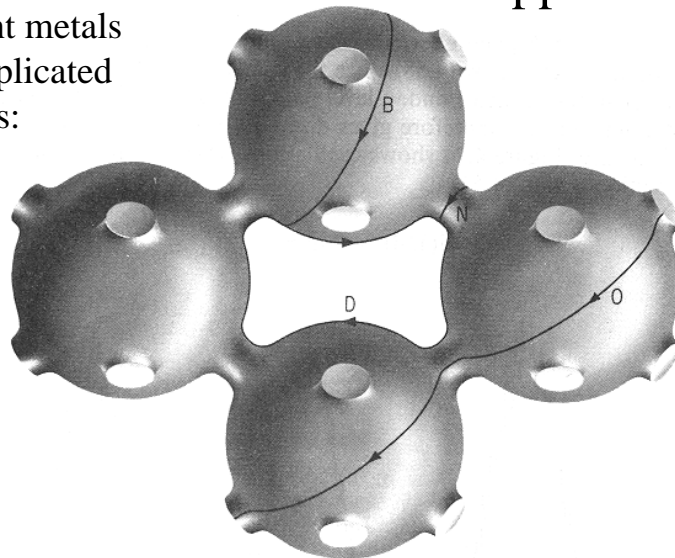
Metal:



Insulator:



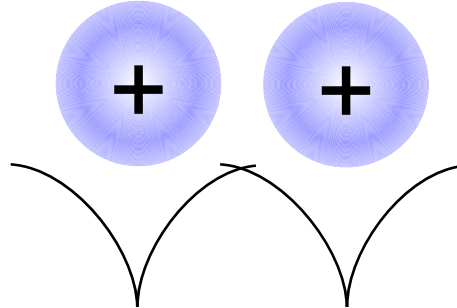
Even monovalent metals
can have complicated
Fermi surfaces:



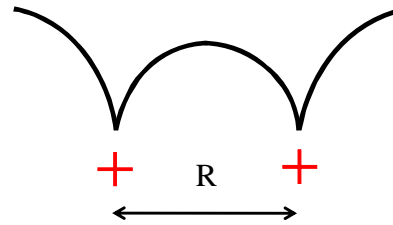
Copper

Tight Binding Model

- Atoms with strongly bound electrons interact quite weakly



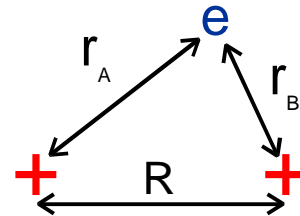
- Simplest example:
Two hydrogen atoms - the hydrogen molecular ion H_2^+



Hydrogen Molecular Ion

Hamiltonian is:

$$H = -\frac{\hbar^2}{2m}\nabla^2 - \frac{e^2}{4\pi\epsilon_0 r_A} - \frac{e^2}{4\pi\epsilon_0 r_B} + \frac{e^2}{4\pi\epsilon_0 R}$$



Trial (i.e. guessed) wavefunctions based on atomic states for single atoms

$$\psi = \psi_A \pm \psi_B, \text{ where } \psi_A = \psi_{1s}(r_A)$$

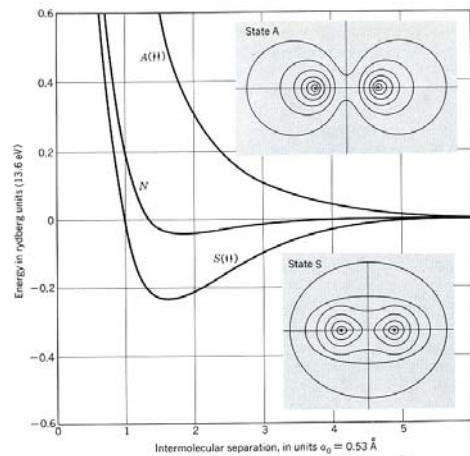
Evaluate Energy from:

$$E = \frac{\int \psi^* H \psi}{\int \psi^* \psi} = \frac{H_{AA} \pm H_{AB}}{1 \pm S}$$

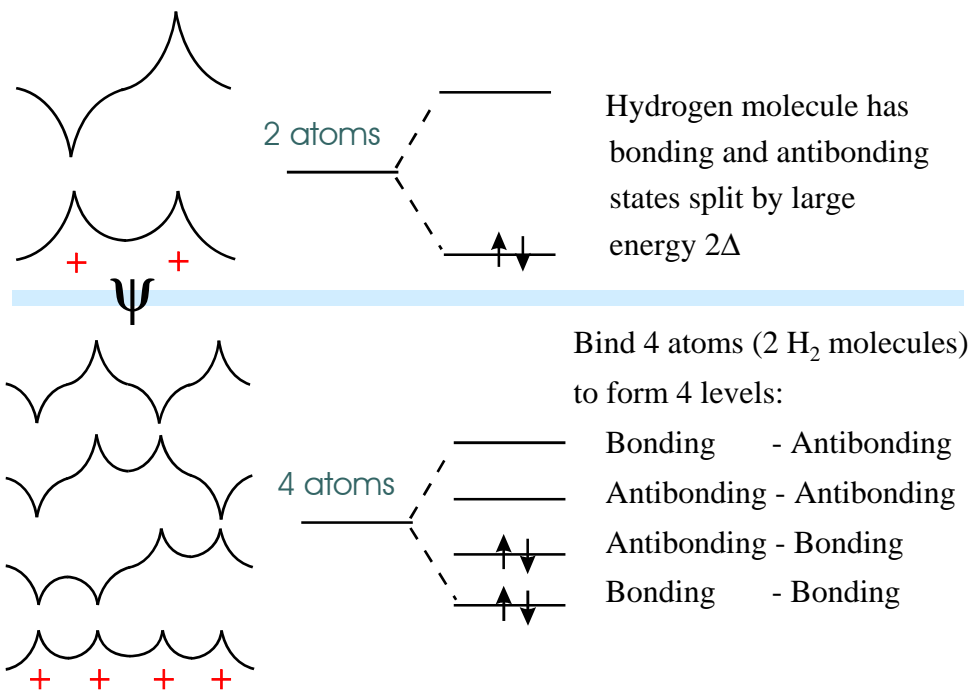
with $H_{AA} = \int \psi_A^* H \psi_A dr$, $H_{AB} = \int \psi_A^* H \psi_B dr$, $S = \int \psi_A^* \psi_B dr$

R large: E_{1s} Δ ≈ 0

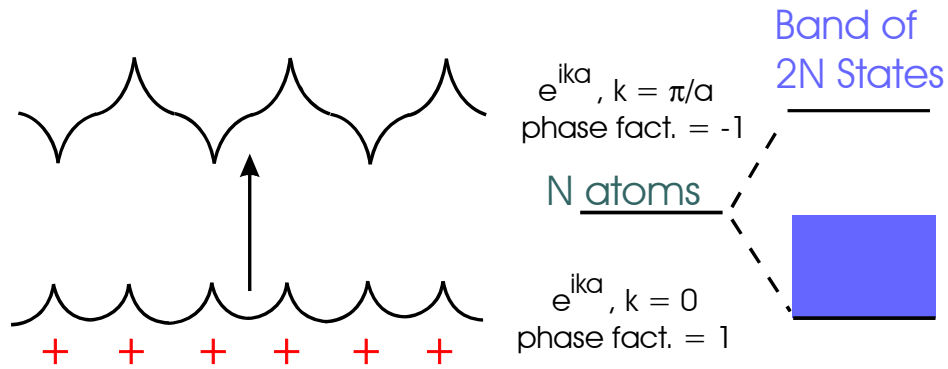
Single particle wavefunctions are:
 symmetric (bonding state)
 and
 antisymmetric (antibonding state)
 To form a Hydrogen **molecule** need **two** electrons. Both in lowest state only with opposite spins + must include electron-electron interaction.



If electron spins are parallel
 → go into antibonding state with much larger energy.
 Energy difference is origin of Exchange Interaction -
 very important for magnetic properties.



Build a solid from long chain of N atoms



- All electrons are still in atomic s-wavefunctions
- Coupled atoms have a phase difference which defines a wavevector

Couple N atoms to form a crystal

2N 1s-states, but spread over an energy band from the symmetric (in-phase) to the antisymmetric (anti-phase) levels

6N 2p-states, 2N 2s-states.....

Overlap of wavefunctions increases for higher levels

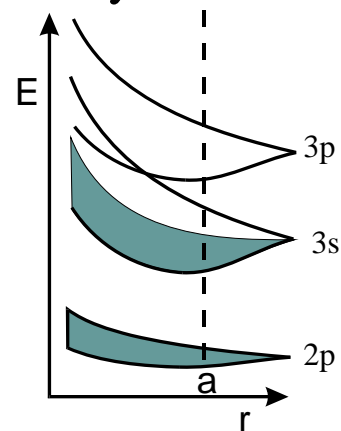
∴ Band width increases

Alkali metals have 1 outer s-electron per atom

- N electrons per crystal

∴ s- Band is half filled - empty states next to filled states - therefore the electrons can move when we apply an electric field

∴ They are metals



2 (outer) electrons per atom

$2N$ electrons in crystal. If bands do not overlap strongly then the n-s band may be filled.

\therefore could be an insulator

But

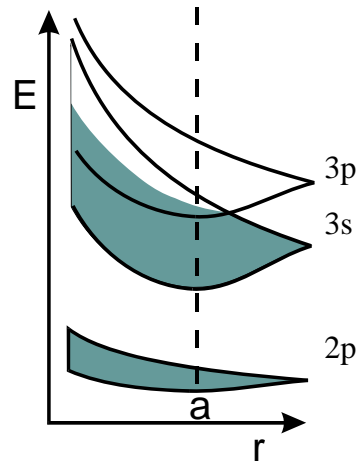
s- and p- orbitals usually give bands broadened enough to overlap.

\therefore can also be a metal

Hence Group II elements (Be, Mg, Ca, Sr, Ba) are still metals due to overlap of bands.

But

nearly filled bands (and p-like bands) can be more complicated - show effects such as a positive Hall effect which says that conduction is by **holes** in some cases.



Periodic Table

Core states have little overlap e.g. in Sodium the 1s, 2s and 2p states. Energy bands are very narrow and filled.

Most electronic properties come from the 3s and 3p levels.

Picture repeats as more shells filled.

Families of materials e.g. *Alkali metals* have similar properties.

Number of electrons per primitive unit cell is odd \rightarrow a metal.

Number of electrons even \rightarrow can have a filled band

\therefore an insulator, **BUT** often bands overlap \therefore still a metal

Periodic Table

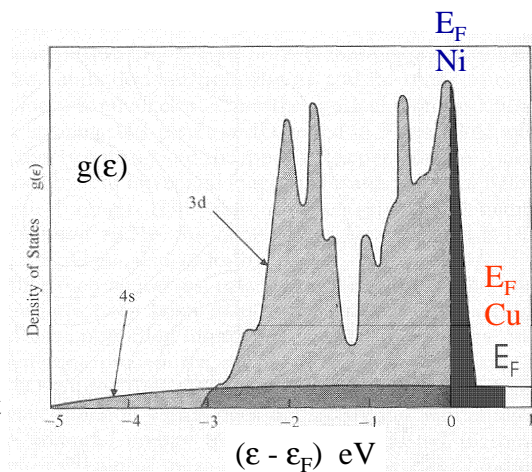
Period	Group**																															
	1 IA 1A	2 IIA 2A											13 IIIA 3A	14 IVA 4A	15 VA 5A	16 VIA 6A	17 VIIA 7A	18 VIIIA 8A														
1	1 H 1.008																	2 He 4.003														
2	3 Li 6.941	4 Be 9.012											5 B 10.81	6 C 12.01	7 N 14.01	8 O 16.00	9 F 19.00	10 Ne 20.18														
3	11 Na 22.99	12 Mg 24.31	3 IIIB 3B	4 IVB 4B	5 VB 5B	6 VIB 6B	7 VIIB 7B	8 ----- VIII ----- ----- 8 -----	9	10	11 IB 1B	12 IIB 2B	13 Al 26.98	14 Si 28.09	15 P 30.97	16 S 32.07	17 Cl 35.45	18 Ar 39.95														
4	19 K 39.10	20 Ca 40.08	21 Sc 44.96	22 Ti 47.88	23 V 50.94	24 Cr 51.94	25 Mn 54.94	26 Fe 55.85	27 Co 58.93	28 Ni 58.69	29 Cu 63.55	30 Zn 65.39	31 Ga 69.72	32 Ge 72.59	33 As 74.92	34 Se 78.96	35 Br 79.90	36 Kr 83.80														
5	37 Rb 85.47	38 Sr 87.62	39 Y 88.91	40 Zr 91.22	41 Nb 92.91	42 Mo 95.94	43 Tc (98)	44 Ru 101.1	45 Rh 106.4	46 Pd 106.4	47 Ag 107.9	48 Cd 112.4	49 In 114.8	50 Sn 118.7	51 Sb 121.8	52 Te 127.6	53 I 126.9	54 Xe 131.3														
6	55 Cs 132.9	56 Ba 137.3	57 La* 138.9	58 Ce 140.1	59 Pr 140.9	60 Nd 144.2	61 Pm (145)	62 Sm 150.4	63 Eu 151.9	64 Gd 157.3	65 Tb 158.9	66 Dy 162.5	67 Ho 164.9	68 Er 167.3	69 Tm 168.9	70 Yb 173.0	71 Lu 174.9	72 Hf 178.5	73 Ta 180.9	74 W 183.8	75 Re 186.2	76 Os 190.2	77 Ir 192.2	78 Pt 195.1	79 Au 197.0	80 Hg 200.6	81 Tl 204.4	82 Pb 207.2	83 Bi 208.9	84 Po (210)	85 At (210)	86 Rn (222)
7	87 Fr (223)	88 Ra (226)	89 Ac~ (227)	90 Th (232)	91 Pa (231)	92 U (238)	93 Np (237)	94 Pu (244)	95 Am (243)	96 Cm (247)	97 Bk (247)	98 Cf (251)	99 Es (252)	100 Fm (257)	101 Md (258)	102 Ds (261)	103 Nh (264)	104 Fl (269)	105 Mc (270)	106 Lv (263)	107 Ts (268)	108 Og (264)										

Transition Metals

The 3d bands and the 4s bands overlap

When the d bands are partly filled in elements such as Ni, Mn, Co and Fe then materials show magnetic properties

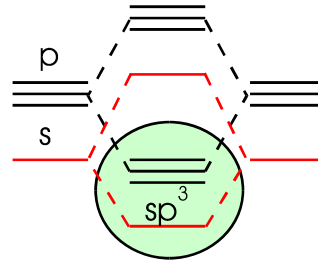
If the 3d bands are filled then they do not influence the properties and we can treat materials such as Copper as free electron metals.



4 electrons per atom (silicon and diamond)

Crystal structure is diamond-like. Each atom has tetrahedral symmetry. Four bonds for each atom. 2 atoms/unit cell.

Carbon ($2s^2 2p^2$) forms bonding and antibonding states for both s and p orbitals. Lowest four states from each atom mix to form sp^3 hybrids with tetrahedral symmetry.

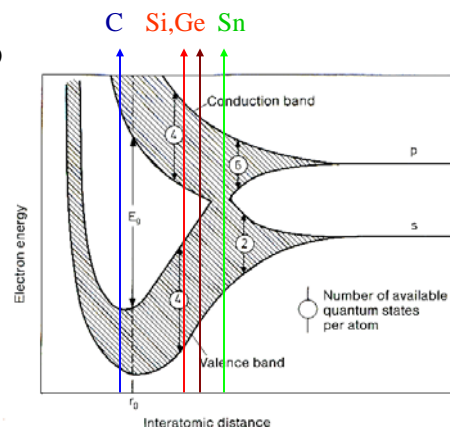


Lower $8N$ sp^3 states overlap to form the (filled) valence band
 \therefore electrons cannot move when a small force is applied.

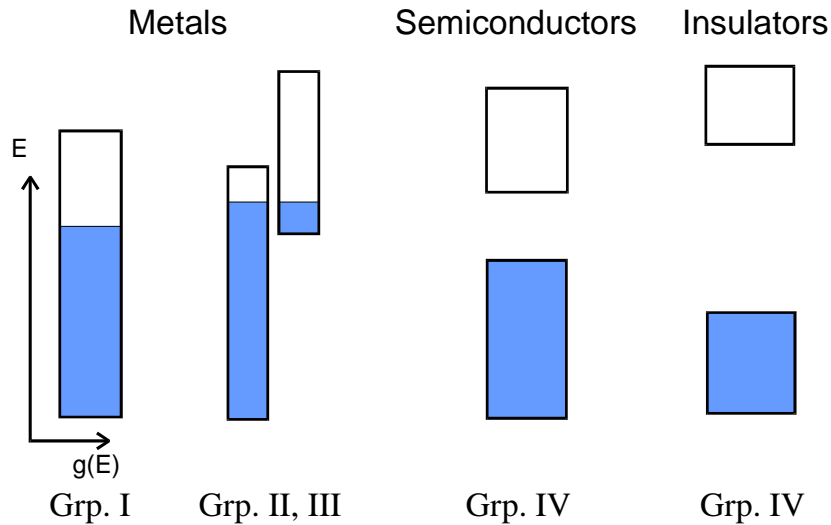
\therefore It is an insulator

Group IV Elements

Element	a_0	Band Gap
• Carbon (Diamond)	0.356	5eV
• Silicon	0.543	1.1 eV
• Germanium	0.566	1.0 eV
• Tin (semimetal)	0.646	a metal



Summary of Band Structure



Successes and Failures of Simple Band Theory

- Explains why some materials are metals, insulators or semiconductors
- Identifies relation between atomic and material properties
- Explains existence of positive charge (negative mass) particles and explains effective masses.
- Independent electron approximation cannot account for collective effects such as ferromagnetism and superconductivity, and phase transitions driven by total electron energy.