



Band Theory of Solids



Some Unresolved Issues

Free electron theory tells gets rid of the specific heat problem, but

- Why are carriers in Al positively charged?
- Why are there insulators?
- Does Wiedemann-Franz law still hold?
- ...

Plan

- “Chemist’s” view of bands – “bonding”
- “Physicist’s” view of bands – “scattering”
- Wavefunctions and Bloch theorem



A Diatomic Molecule

- Why do two hydrogens form a bond?
- Simply put, electrons are delocalised and can reduce kinetic energy
- They have *new states* called molecular orbitals...how do we model this?
- Write a molecular orbital as a linear combination of atomic orbitals $\psi(\mathbf{r}) = a_1\psi_1(\mathbf{r}) + a_2\psi_2(\mathbf{r})$
- Determine a_1 and a_2 by using the fact that the ground state energy is minimum
- $E_g = \langle \psi | H | \psi \rangle$ subject to the condition that $\langle \psi | \psi \rangle = 1$



A Diatomic Molecule

- Under “some assumptions” this reduces to a matrix equation

$$\begin{pmatrix} E_0 & \Delta \\ \Delta & E_0 \end{pmatrix} \begin{pmatrix} a_1 \\ a_2 \end{pmatrix} = E \begin{pmatrix} a_1 \\ a_2 \end{pmatrix}$$

Δ is called “overlap” or “hopping” integral (roughly), that depends on the separation of the two atoms

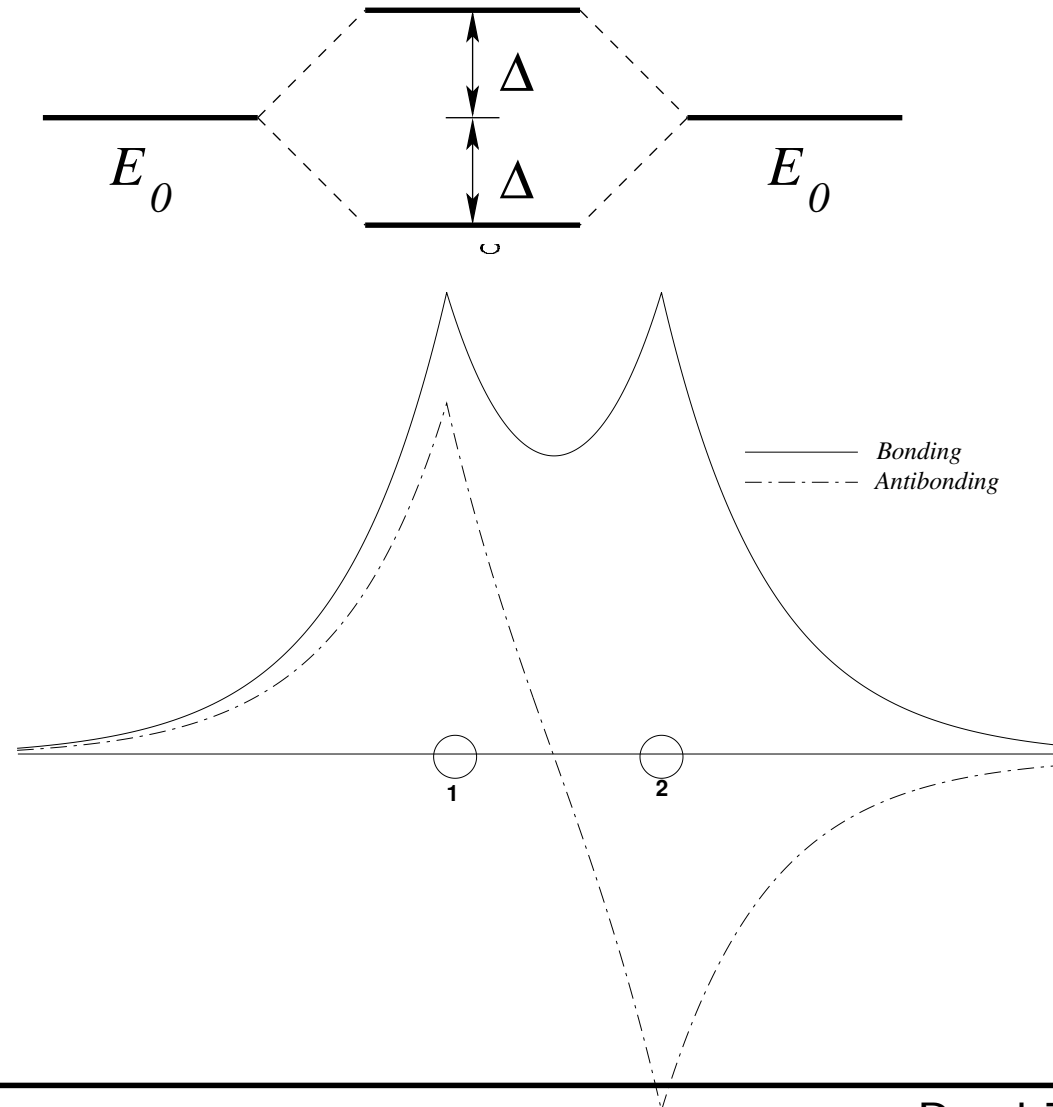
- Two molecular orbitals with energy $E_0 \pm \Delta$
- Bonding orbital, $E_b = E_0 - \Delta$, $|\psi_b\rangle = \frac{1}{\sqrt{2}}(|\psi_1\rangle + |\psi_2\rangle)$
- Antibonding orbital, $E_a = E_0 + \Delta$,
 $|\psi_a\rangle = \frac{1}{\sqrt{2}}(|\psi_1\rangle - |\psi_2\rangle)$

- ~~Two electrons occupy bonding orbital (Pauli to~~

rescue!)

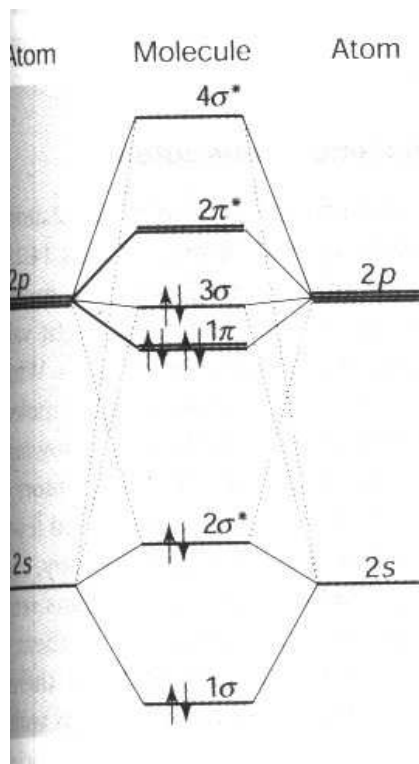
A Diatomic Molecule

● Levels and orbitals

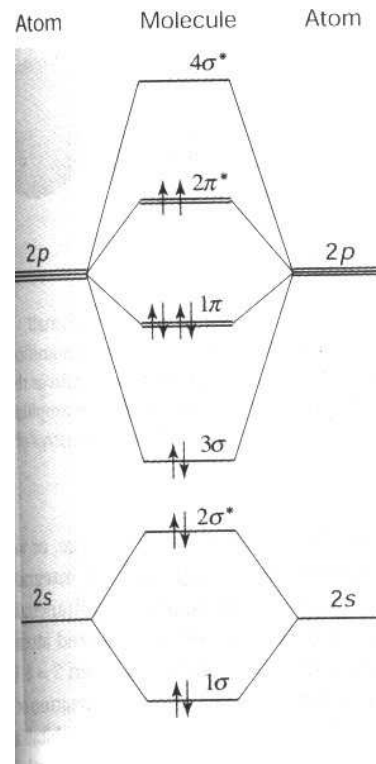


A “Real” Diatomic Molecule

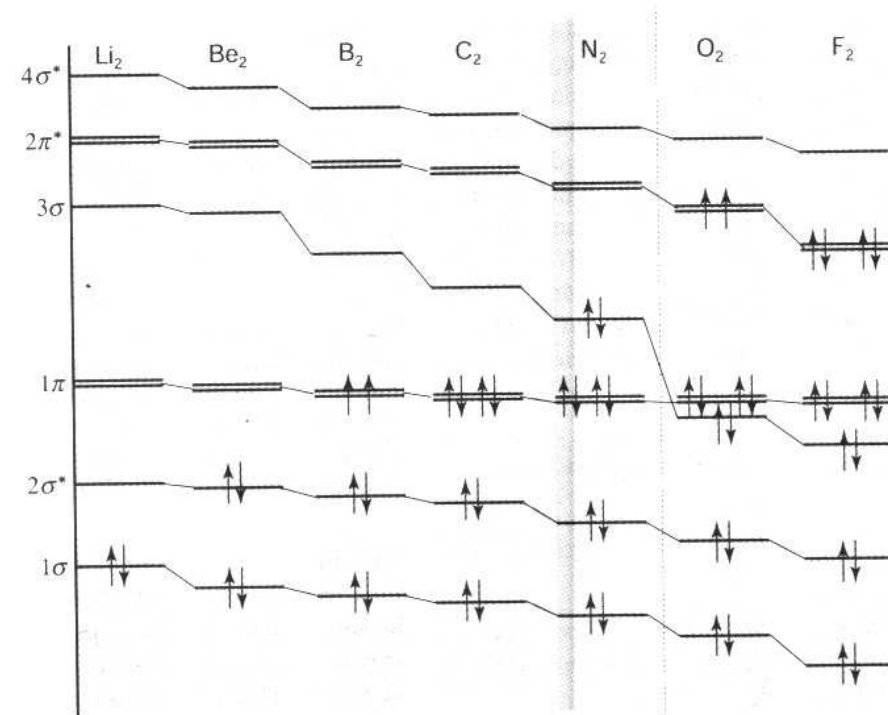
- In a molecule like N_2 or O_2 , s and p orbitals all overlap and one gets a host of molecular orbitals



N_2



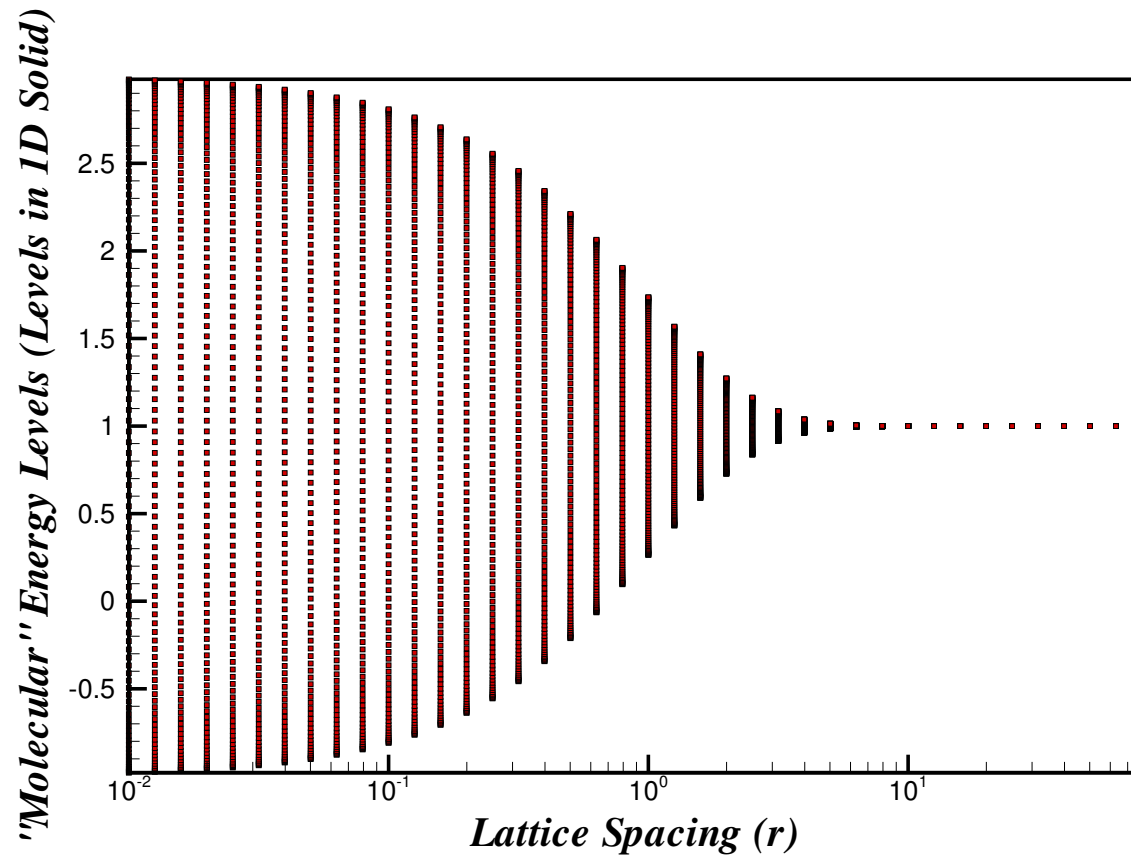
O_2



(Atkins and DePaula)

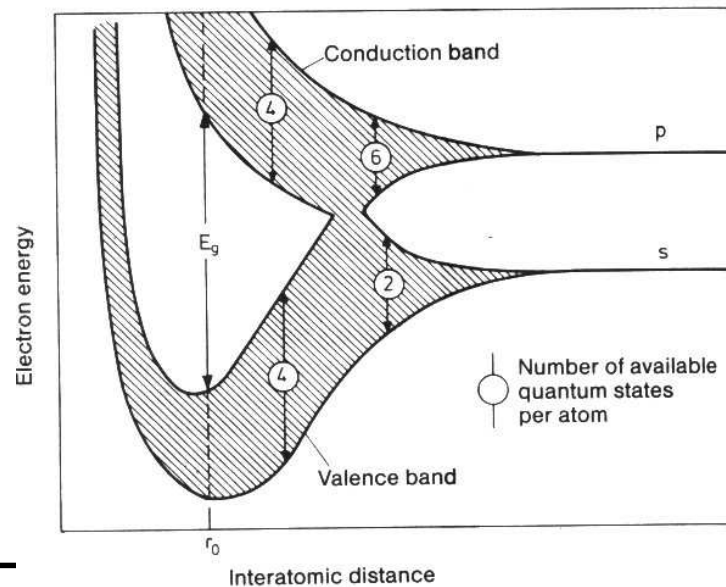
A Model Solid

- A chain of atoms with s -orbital overlap
- “Bands” of energies



A Real Solid – “Chemist’s” view

- Real solids have s, p, d overlaps
- One gets s -band, p -band etc...
- It is possible that the bands overlap...
- Possible that the bands do not overlap! Band gap!
- Further, two atomic orbitals of nearly equal energy can hybridise (say s, p)





Some Preliminaries

- Crystal defined by lattice vectors a_1, a_2, a_3
- Lattice point R defined by integers
$$R = n_1 a_1 + n_2 a_2 + n_3 a_3$$
- Reciprocal lattice defined by vectors b_1, b_2, b_3 which satisfy $b_i \cdot a_j = \delta_{ij}$
- Reciprocal lattice vectors G defined by integers
$$G = m_1 b_1 + m_2 b_2 + m_3 b_3$$



Free Electron needs Repair

- Electrons are not really free!
- They move in a *periodic potential*

$$V(\mathbf{r}) = \sum_{\mathbf{R}} V_a(\mathbf{r} - \mathbf{R})$$

- Schrödinger equation

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

- What are allowed E s and associated ψ s?
- What can we say without solving anything? (Stick to 1D)



1D Solid – Simple Arguments

- Solid with $V(r)$, $V(r + na) = V(r)$, a is lattice parameter
- Imagine that $V(r)$ is a perturbation on free electrons
- What effect does $V(r)$ have on the “free” electron?
- Well, it is like Bragg reflection!
- If the wavelength of the electron is related to the lattice parameter a , then the electron cannot “travel” through the crystal...Bragg reflection will make it a standing wave!
- This happens when the electron wavelength satisfies $n\lambda = 2a$ or when electron wavevector satisfies $k = \frac{n\pi}{a}$!
- Clearly, the electron energies are also changed!

1D Solid – Simple Arguments

- Since the state of the electron for $k = \frac{n\pi}{a}$ is not a propagating one, we can imagine it as a superposition of a forward moving wave and backward moving wave of amplitude to get two types of standing waves

$$\psi_+ = e^{ikx} + e^{-ikx} = 2 \cos(kx),$$

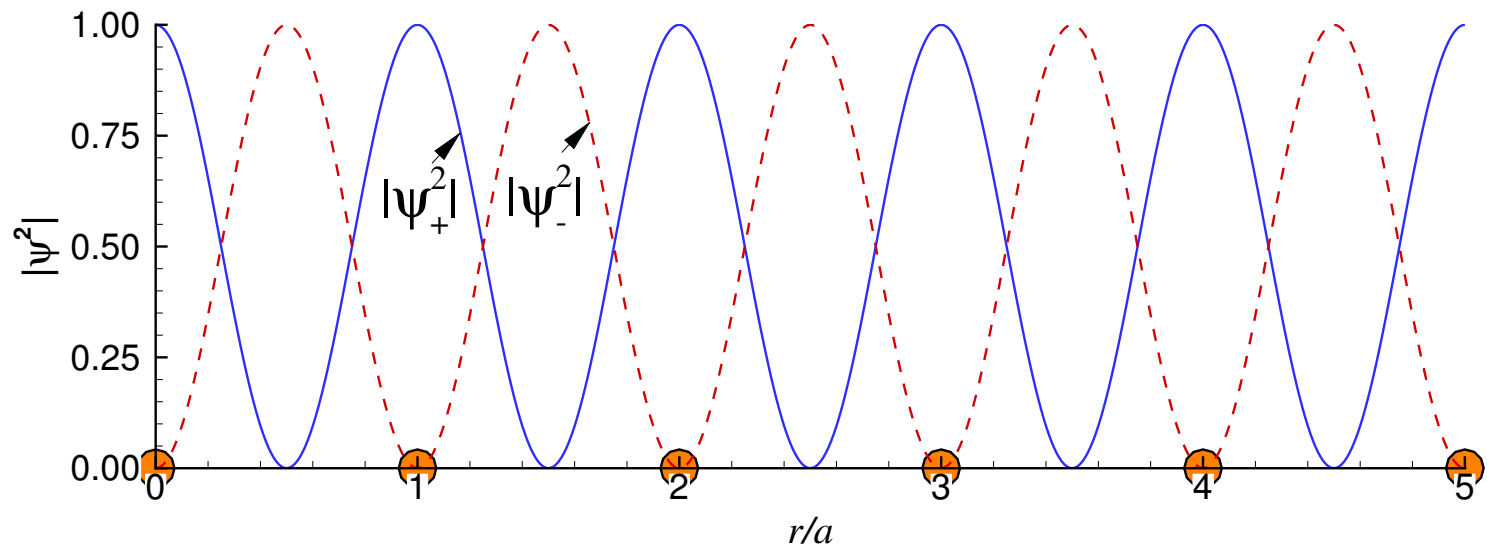
$$\psi_- = e^{ikx} - e^{-ikx} = 2i \sin(kx)$$

Note that these are *standing waves*!

- What are (estimates of) E_{\pm} ?
- To get an idea, think of $|\psi_+|^2$...it is the probability density...if the atomic potential V_a is attractive, then E_+ will be *lower* than E_- , since the electron in ψ_+ state is “located closer to the atom”!

1D Solid – Simple Arguments

- Clearly, ψ_+ has lower energy (for the attractive atomic potential)



- This implies for the same value of free electron wavevector k , there are two possible energy levels...in other words, energy values between these levels are not allowed...a band gap opens up!

1D Solid – A Simple Model

- 1-D solid with lattice parameter a
- Smallest reciprocal vector $G = \frac{2\pi}{a}$
- Simple model “ionic potential” $V(x) = 2V_G \cos Gx$
(Note that $V(x)$ is lattice periodic, V_G is the “strength” of the potential)
- What are eigenvalues and eigenstates of
$$H = -\frac{\hbar^2}{2m} \frac{\partial^2}{\partial x^2} + V(x)?$$
- We know from previous arguments that when $k \approx \frac{G}{2}$ we expect strong Bragg reflection of a plane wave state...based on this it is reasonable to take the energy eigenstate as a linear combination of the forward going wave and the reverse going wave

$|\psi\rangle = C_k |k\rangle + C_{k-G} |k-G\rangle$, where C_k, C_{k-G} are

numbers that we need to determine...

1D Solid – A Simple Model

- Determine C_k, C_{k-G} using $H|\psi\rangle = E|\psi\rangle$; a bit of algebra gives $(\epsilon(k) = \frac{\hbar^2 k^2}{2m})$

$$\begin{pmatrix} \epsilon(k) & V_G \\ V_G & \epsilon(k-G) \end{pmatrix} \begin{pmatrix} C_k \\ C_{k-G} \end{pmatrix} = E \begin{pmatrix} C_k \\ C_{k-G} \end{pmatrix}$$

- Energy eigenvalues are

$$E_{\pm}(k) = \frac{\epsilon(k) + \epsilon(k-G) \pm \sqrt{(\epsilon(k) + \epsilon(k-G))^2 - 4(\epsilon(k)\epsilon(k-G) - V_G^2)}}{2}$$

with associated eigenstates

$$\psi_{\pm}(x) = \underbrace{(C_k^{\pm} + C_{k-G}^{\pm} e^{-iGx})}_{u_{\pm}(x) \dots \text{lattice periodic}} e^{ikx}$$



1D Simple Model – What is learned?

- An energy gap opens up at $k = \frac{G}{2}$, $E_+ - E_- = 2V_G$

