

Solid State Theory Physics 545

Band Theory I

Band Theory

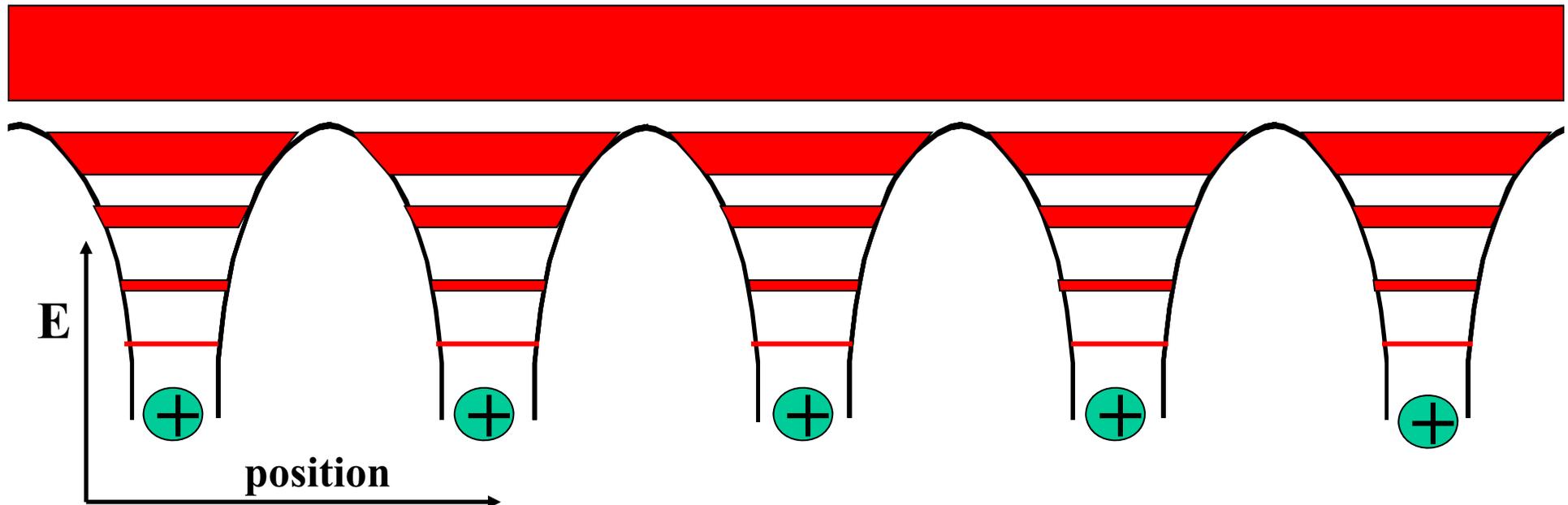
The calculation of the allowed electron states in a solid is referred to as band theory or band structure theory.

To obtain the full band structure, we need to solve Schrödinger's equation for the full lattice potential. This cannot be done exactly and various approximation schemes are used. We will introduce two very different models, the *nearly free electron* and *tight binding models*.

We will continue to treat the electrons as independent, i.e. neglect the electron-electron interaction.

Energy Levels and Bands

- Isolated atoms have precise allowed energy levels.
- In the presence of the periodic lattice potential *bands* of allowed states are separated by energy gaps for which there are no allowed energy states.
- The allowed states in conductors can be constructed from combinations of free electron states (the nearly free electron model) or from linear combinations of the states of the isolated atoms (the tight binding model).



- Chemical bonds and electron bands.

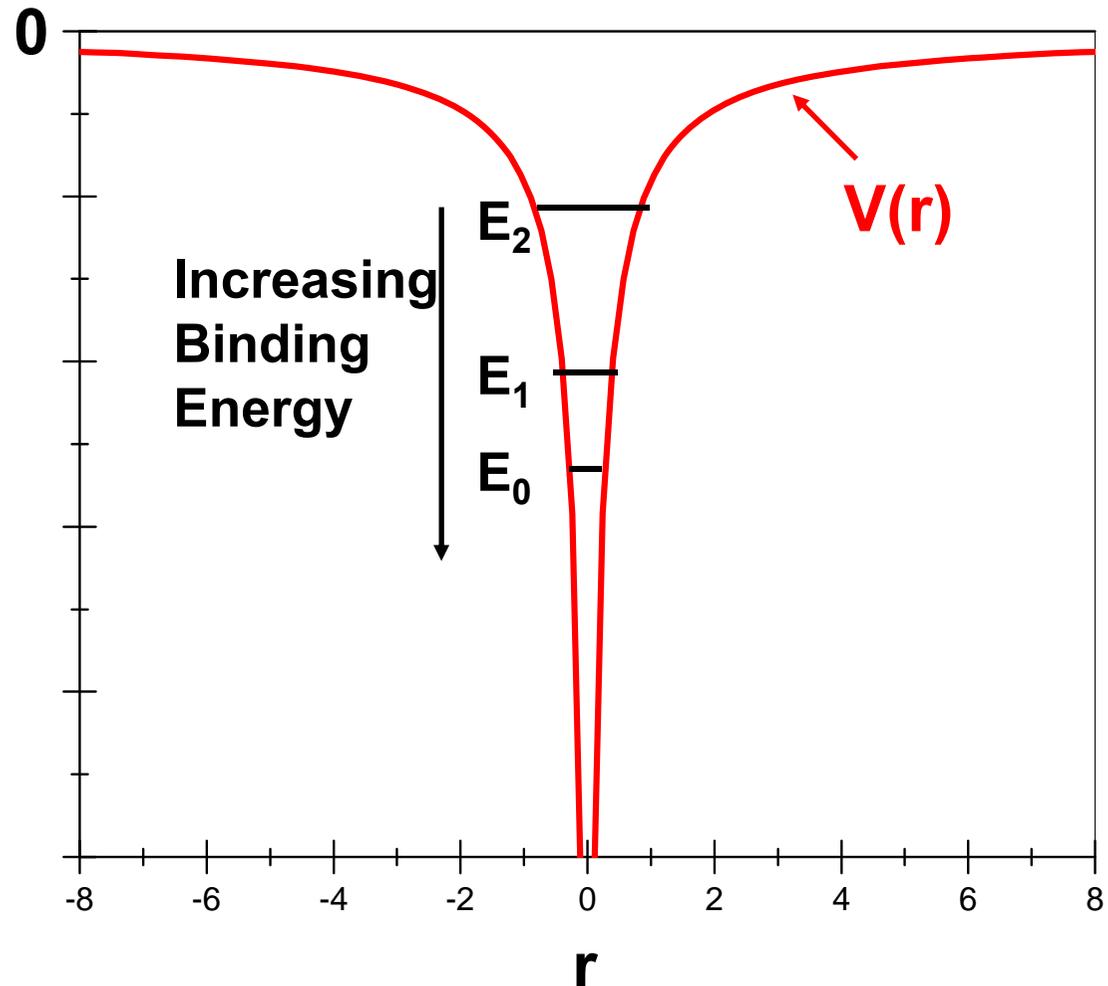
Bands are formed from molecular orbitals.

Bound States in atoms

Electrons in isolated atoms occupy discrete allowed energy levels E_0 , E_1 , E_2 etc. .

The potential energy of an electron a distance r from a positively charge nucleus of charge q is

$$V(r) = \frac{-qe^2}{4\pi\epsilon_0 r}$$

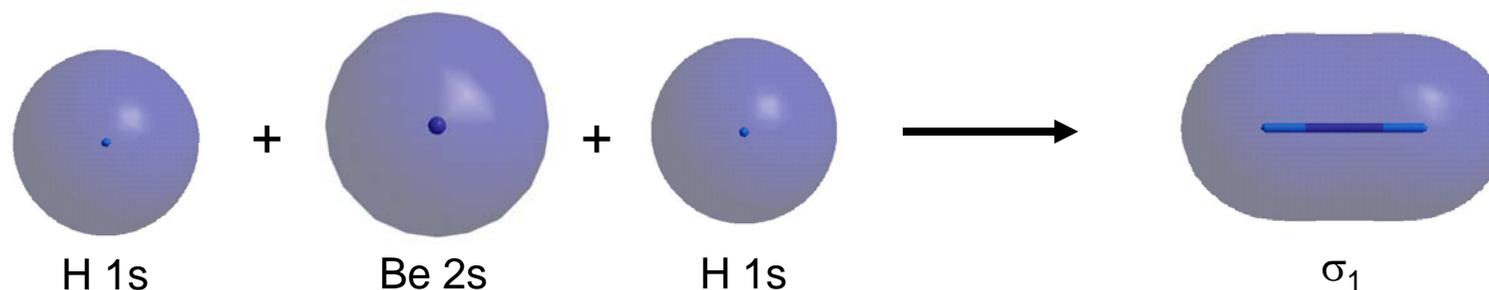


Molecular Orbital Theory

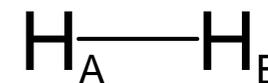
The Molecular Orbitals (MO's) for a molecule is formed from Linear Combinations of Atomic Orbitals (LCAO).

Some basic rules for making MO's using the LCAO method:

- 1) n atomic orbitals must produce n molecular orbitals (e.g. 8 AO's must produce 8 MO's).
- 2) To combine, the atomic orbitals must be of the appropriate symmetry.
- 3) To combine, the atomic orbitals must be of similar energy.
- 4) Each MO must be normal and must be orthogonal to every other MO.



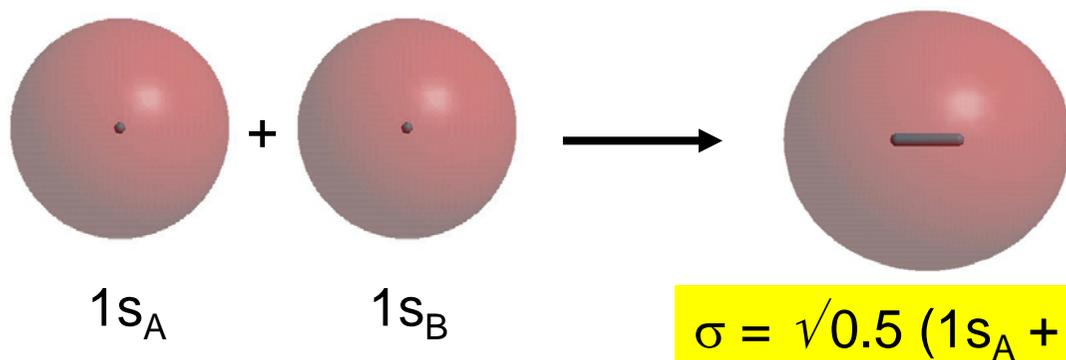
Molecular Orbital Theory



Diatomic molecules: The bonding in H_2

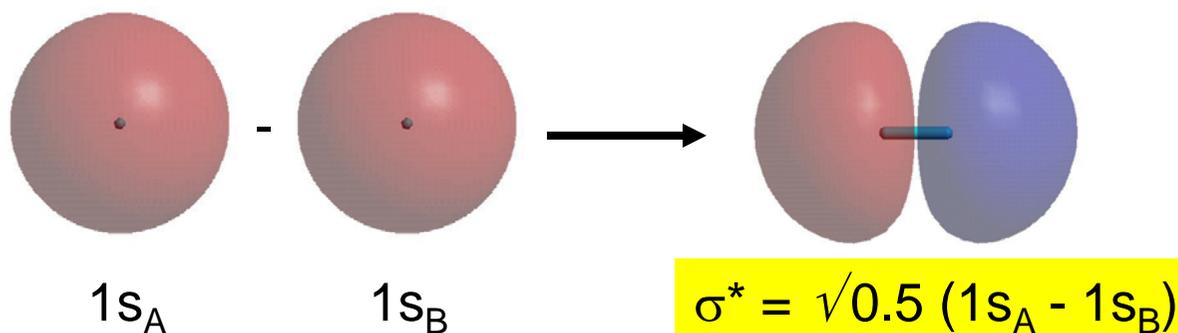
Each H atom has only a 1s orbital, so to obtain MO's for the H_2 molecule, we must make linear combinations of these two 1s orbitals.

Consider the addition of the two 1s functions (with the same phase):



This produces an MO around both H atoms and has the same phase everywhere and is symmetrical about the H-H axis. This is known as a *bonding* MO and is given the label σ because of its symmetry.

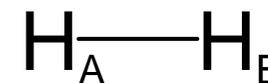
Consider the subtraction of the two 1s functions (with the same phase):



This produces an MO over the molecule with a node between the atoms (it is also symmetrical about the H-H axis). This is known as an *antibonding* MO and is given the label σ^* because of its symmetry. The star indicates antibonding.

Remember that:  is equivalent to: 

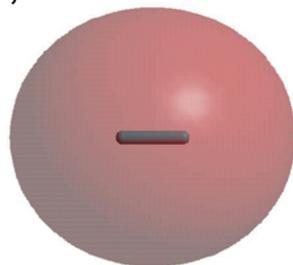
Molecular Orbital Theory



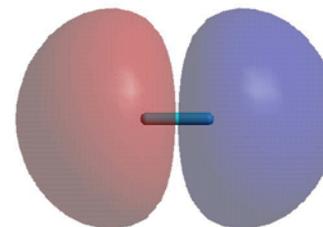
Diatomic molecules: The bonding in H_2

You may ask ... Why is σ called “bonding” and σ^* “antibonding”? What does this mean? How do you know the relative energy ordering of these MO's?

Remember that each 1s orbital is an atomic wavefunction (ϕ_{1s}) and each MO is also a wave function, Ψ , so we can also write LCAO's like this:



$$\sigma = \Psi_1 = \sqrt{0.5} (\phi_{1sA} + \phi_{1sB})$$



$$\sigma^* = \Psi_2 = \sqrt{0.5} (\phi_{1sA} - \phi_{1sB})$$

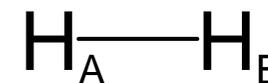
Remember that the square of a wavefunction gives us a probability density function, so the density functions for each MO are:

$$(\Psi_1)^2 = 0.5 [(\phi_{1sA} \phi_{1sA}) + \mathbf{2(\phi_{1sA} \phi_{1sB})} + (\phi_{1sB} \phi_{1sB})]$$

$$\text{and } (\Psi_2)^2 = 0.5 [(\phi_{1sA} \phi_{1sA}) - \mathbf{2(\phi_{1sA} \phi_{1sB})} + (\phi_{1sB} \phi_{1sB})]$$

The only difference between the two probability functions is in the cross term (in bold), which is attributable to the kind and amount of *overlap* between the two 1s atomic wavefunctions (the integral $\int (\phi_{1sA} \phi_{1sA}) \delta\tau$ is known as the “overlap integral”, S). In-phase overlap makes *bonding* orbitals and out-of-phase overlap makes *antibonding* orbitals...why?

Molecular Orbital Theory

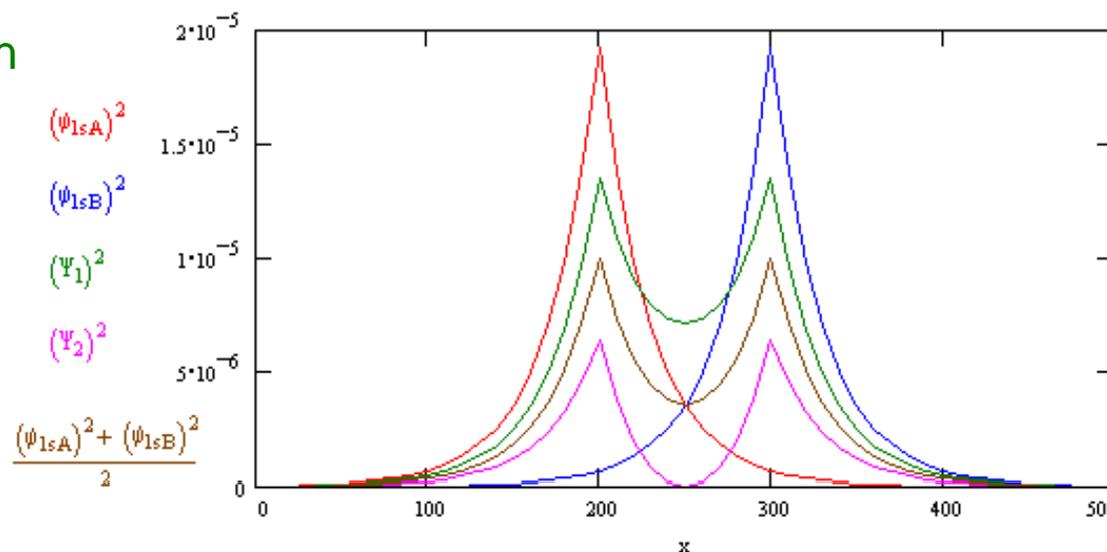


Diatomic molecules: The bonding in H_2

Consider the electron density between the two nuclei: the **red** curve is the probability density for H_A by itself, the **blue** curve is for H_B by itself and the **brown** curve is the density you would get for $\phi_{1sA} + \phi_{1sB}$ without any overlap: it is just $(\phi_{1sA})^2 + (\phi_{1sB})^2$ {the factor of $\frac{1}{2}$ is to put it on the same scale as the normalized functions}.

The function $(\Psi_1)^2$ is shown in **green** and has an extra $+ 2(\phi_{1sA} \phi_{1sB})$ of electron density than the situation where overlap is neglected.

The function $(\Psi_2)^2$ is shown in **pink** and has less electron density between the nuclei $\{- 2(\phi_{1sA} \phi_{1sB})\}$ than the situation where overlap is neglected.



$$(\Psi_1)^2 = 0.5 [(\phi_{1sA} \phi_{1sA}) + 2(\phi_{1sA} \phi_{1sB}) + (\phi_{1sB} \phi_{1sB})]$$

$$(\Psi_2)^2 = 0.5 [(\phi_{1sA} \phi_{1sA}) - 2(\phi_{1sA} \phi_{1sB}) + (\phi_{1sB} \phi_{1sB})]$$

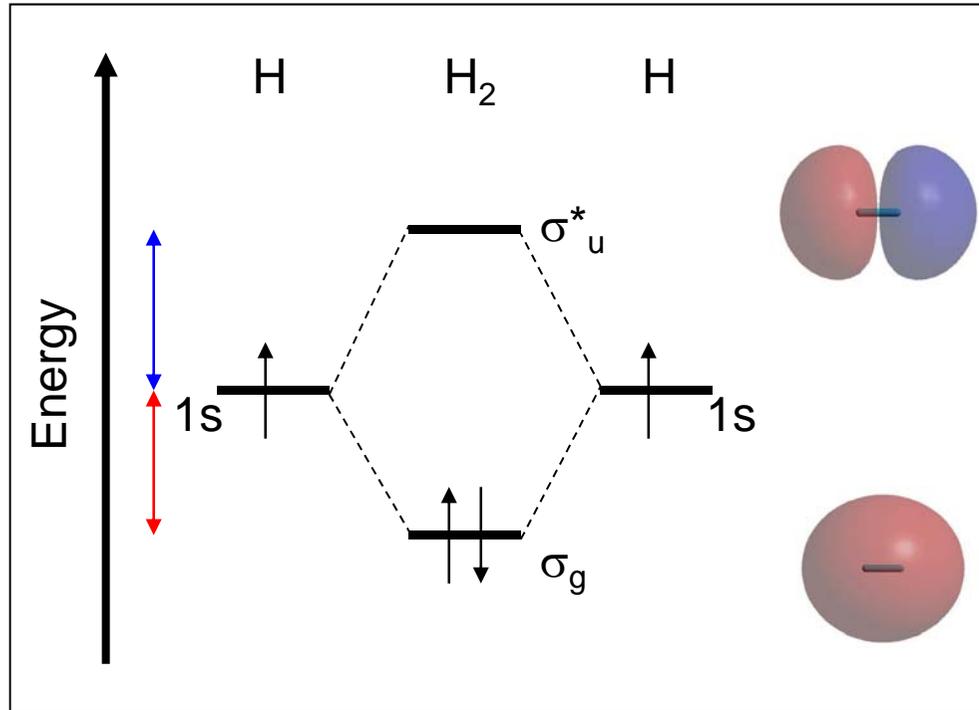
The increase of electron density between the nuclei from the in phase overlap reduces the amount of repulsion between the positive charges. This means that a bonding MO will be lower in energy (more stable) than the corresponding antibonding MO or two non-bonded H atoms.

Molecular Orbital Theory



Diatomic molecules: The bonding in H_2

So now that we know that the σ bonding MO is more stable than the atoms by themselves and the σ^* antibonding MO, we can construct the MO diagram.



To clearly identify the symmetry of the different MO's, we add the appropriate subscripts g (symmetric with respect to the inversion center) and u (anti-symmetric with respect to the inversion center) to the labels of each MO.

Molecular orbitals and bonding

Consider a electron in the ground, 1s, state of a **hydrogen atom**

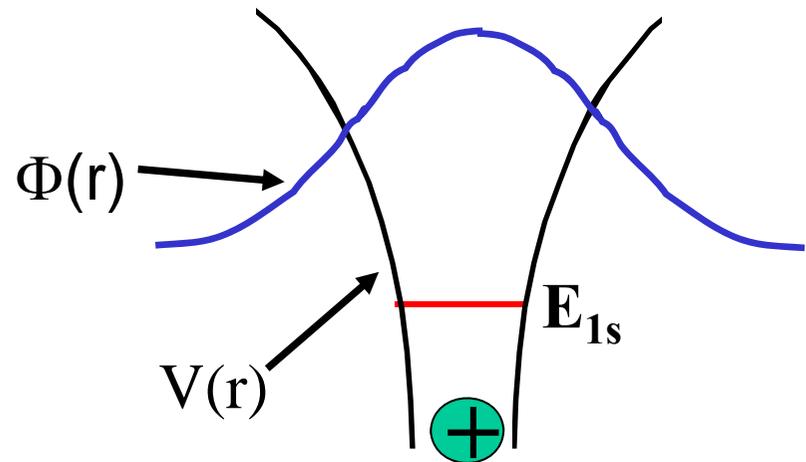
i.e. $\phi(r) = \frac{1}{\sqrt{\pi}} a_0^{3/2} e^{-r/a_0}$ where a_0 is the Bohr Radius

The Hamiltonian is $H = \frac{-\hbar^2 \nabla^2}{2m} - \frac{\alpha}{r}$ where $\alpha = \frac{e^2}{4\pi\epsilon_0}$

The expectation value of the electron energy is

$$\langle E \rangle = \int \phi(r) H \phi(r) dV$$

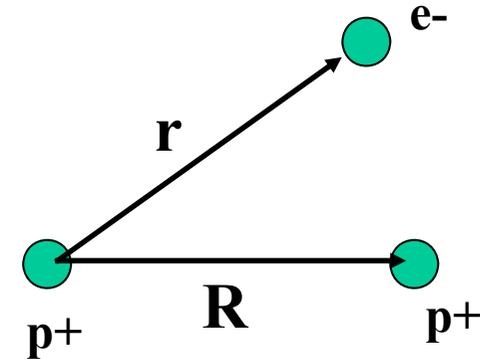
This give $\langle E \rangle = E_{1s} = -13.6\text{eV}$



Hydrogen Molecular Ion

Consider the H_2^+ molecular ion in which one electron experiences the potential of two protons. The Hamiltonian is

$$H = \frac{-\hbar^2 \nabla^2}{2m} + U(\underline{r}) = \frac{-\hbar^2 \nabla^2}{2m} - \frac{\alpha}{r} - \frac{\alpha}{|\underline{r} - \underline{R}|}$$



We approximate the electron wavefunctions as

$$\psi^+(\underline{r}) = A [\phi(\underline{r}) + \phi(|\underline{r} - \underline{R}|)] \equiv A[\phi_1 + \phi_2]$$

and

$$\psi^-(\underline{r}) = B [\phi(\underline{r}) - \phi(|\underline{r} - \underline{R}|)] \equiv B[\phi_1 - \phi_2]$$

Bonding and anti-bonding states

Expectation value of the energy are (see notes)

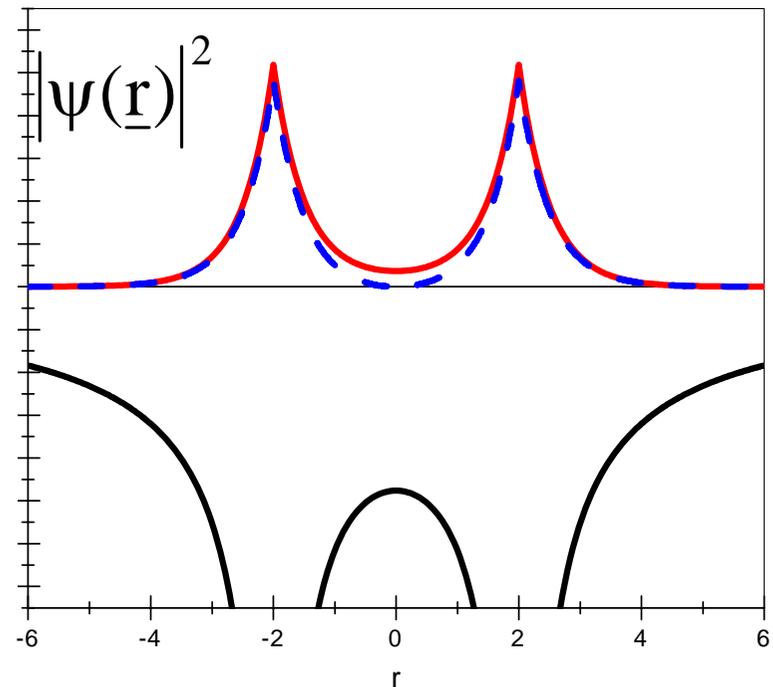
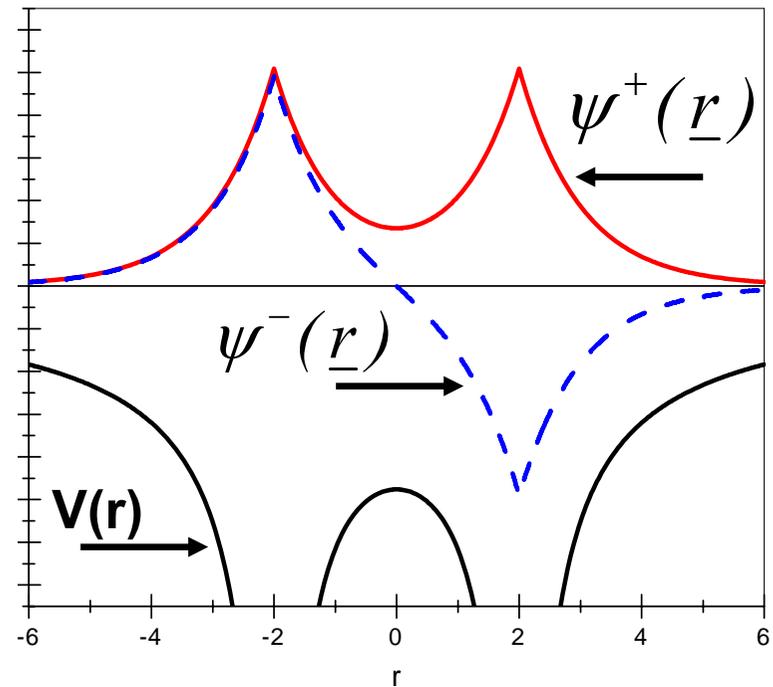
$$E = E_{1s} - \gamma(R) \text{ for } \psi^+(\underline{r})$$

$$E = E_{1s} + \gamma(R) \text{ for } \psi^-(\underline{r})$$

$\gamma(R)$ a positive function

Two atoms: original 1s state leads to two allowed electron states in molecule.

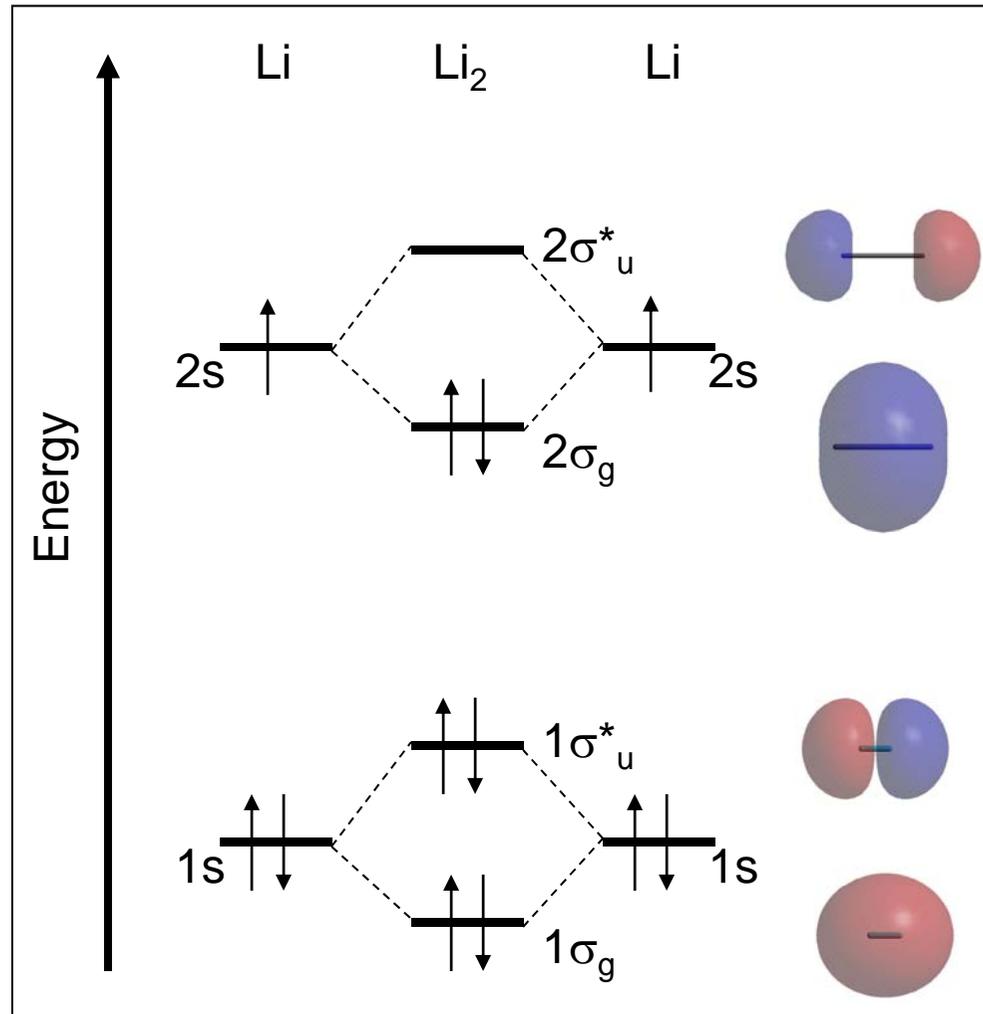
Find for N atoms in a solid have N allowed energy states



Molecular Orbital Theory

Diatomic molecules: Homonuclear Molecules of the Second Period

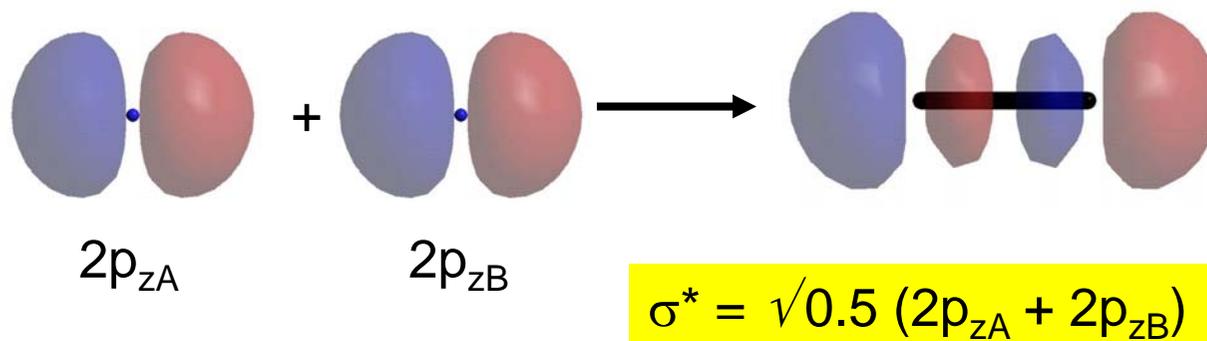
Li has both 1s and 2s AO's, so the MO diagram for the molecule Li_2 can be formed in a similar way to the ones for H_2 and He_2 . The 2s AO's are not close enough in energy to interact with the 1s orbitals, so each set can be considered independently.



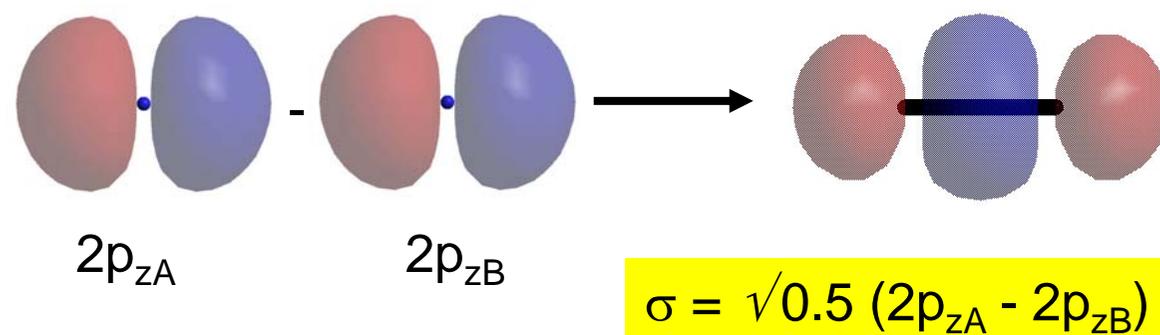
Molecular Orbital Theory

Diatomic molecules: The bonding in F_2

The combinations of σ symmetry:



This produces an MO over the molecule with a node between the F atoms. This is thus an antibonding MO of σ_u^* symmetry.

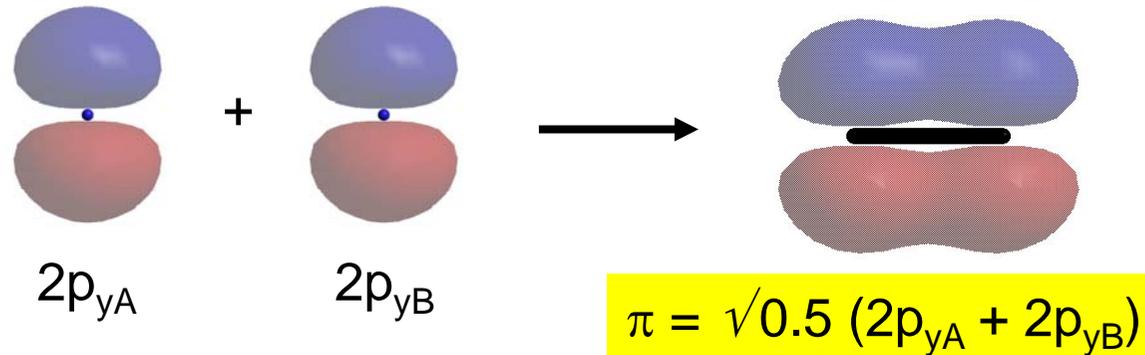


This produces an MO around both F atoms and has the same phase everywhere and is symmetrical about the F-F axis. This is thus a bonding MO of σ_g symmetry.

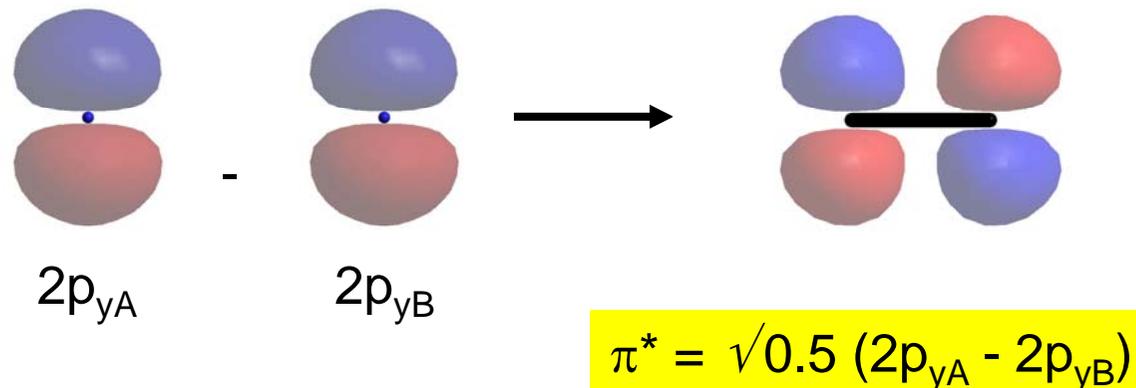
Molecular Orbital Theory

Diatomic molecules: The bonding in F_2

The first set of combinations of π symmetry:



This produces an MO over the molecule with a node on the bond between the F atoms. This is thus a bonding MO of π_u symmetry.

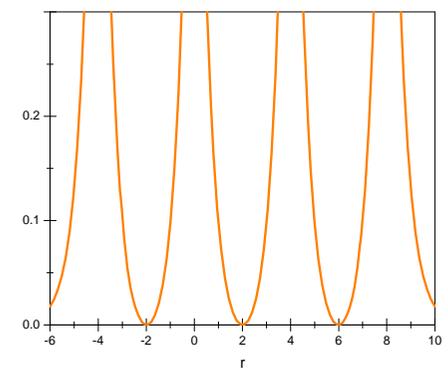
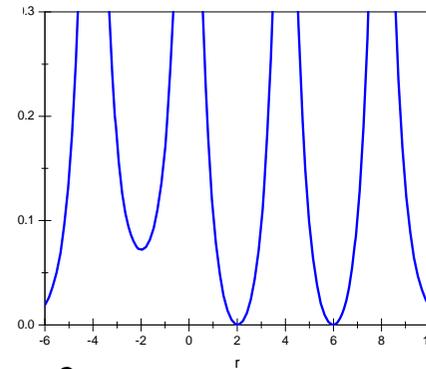
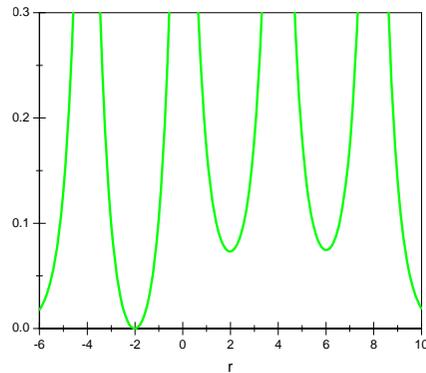
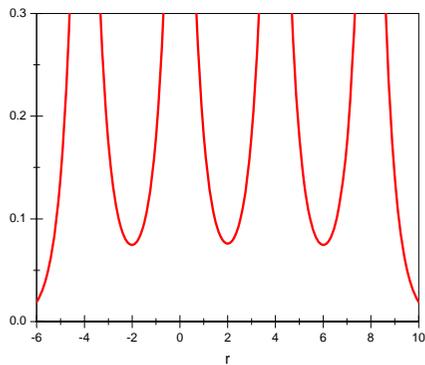
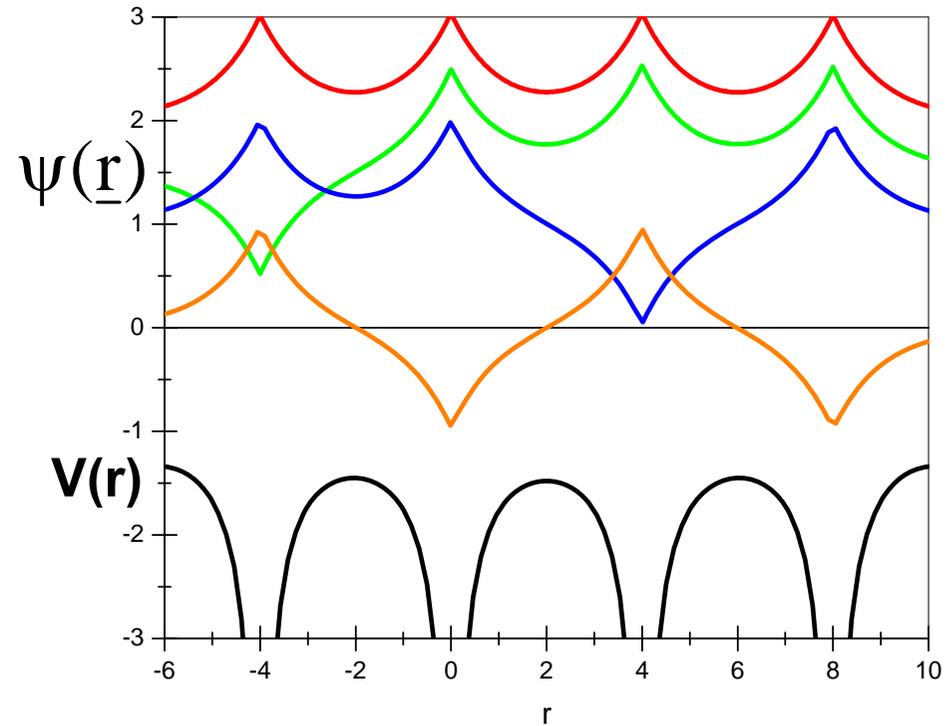


This produces an MO around both F atoms that has two nodes: one on the bond axis and one perpendicular to the bond. This is thus an antibonding MO of π_g^* symmetry.

For N atoms have N allowed energy states

Illustration of why one has the same number of allowed energy states as atoms in a crystal.

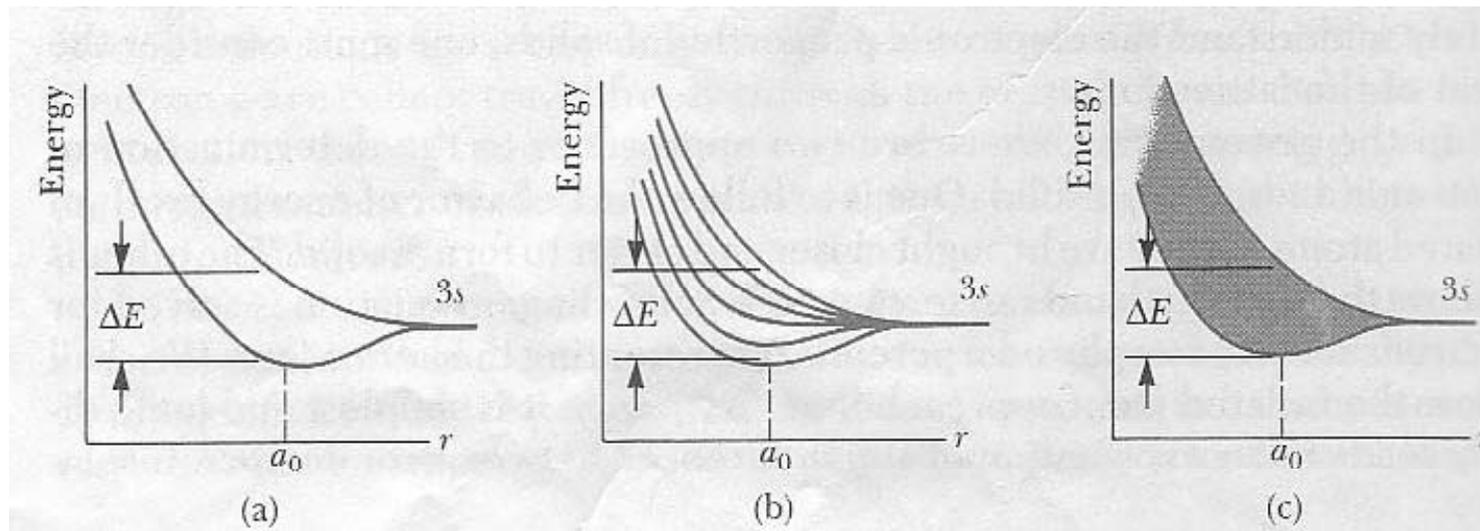
Figures show different linear combinations of 4 atomic wavefunctions for a 1D potential that give 4 different energies. Number of distinct energy states equals the number of zeros in the wavefunction



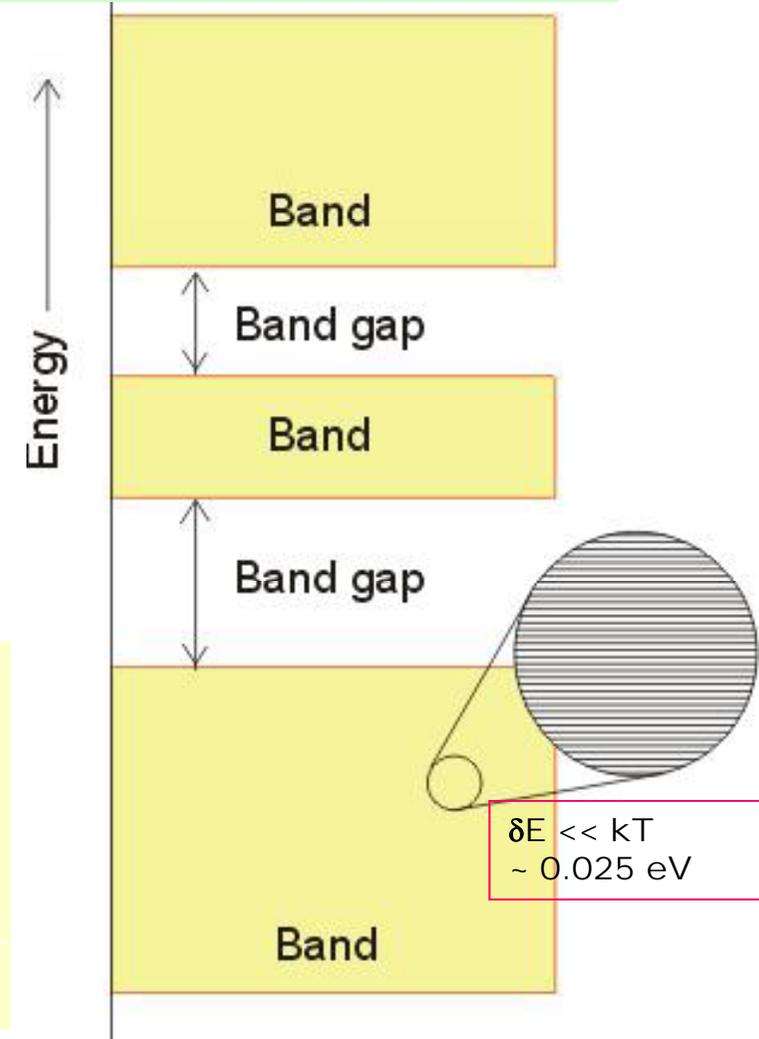
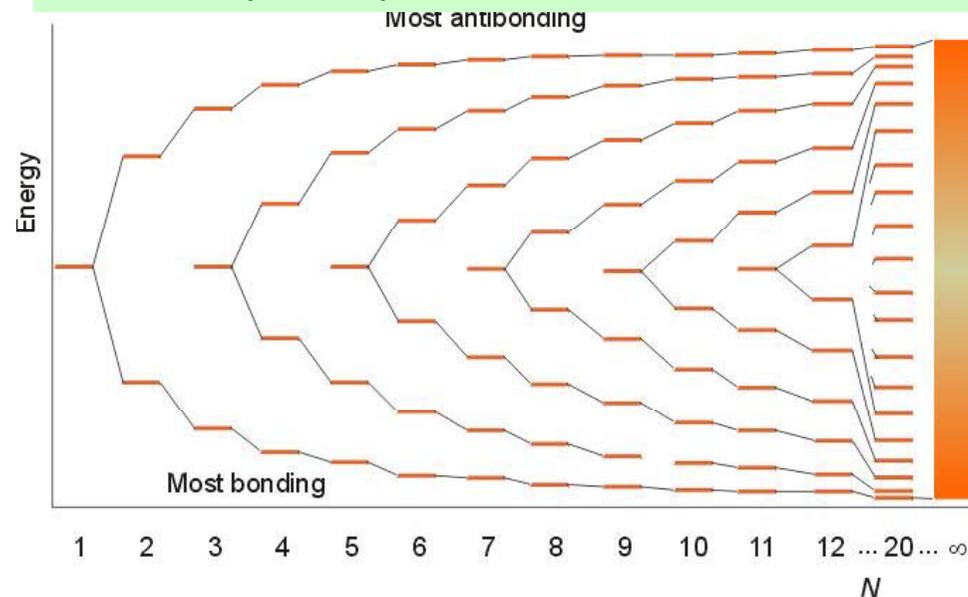
$$|\psi(r)|^2$$

From Two atoms to Many atoms

When a large number of atoms are brought together to form solid crystal, a similar phenomenon occurs. As the atoms are brought together, the various isolated-atom energy levels begin to split. For example, when six atoms are in close proximity, they six degenerate states split into six energy levels, corresponding to six different linear combinations of the isolated atom wave functions. The maximum splitting, ΔE , or the width of the energy band is determined by the interaction between two nearest neighbors, which is independent of the number of atoms. So the energy levels are more closely spaced. Extending the argument to $N=10^{22}$ atoms for a crystal of cm^3 in volume, we have 10^{22} energy levels closely (**or continuously**) spaced and spread over an energy band of ΔE !

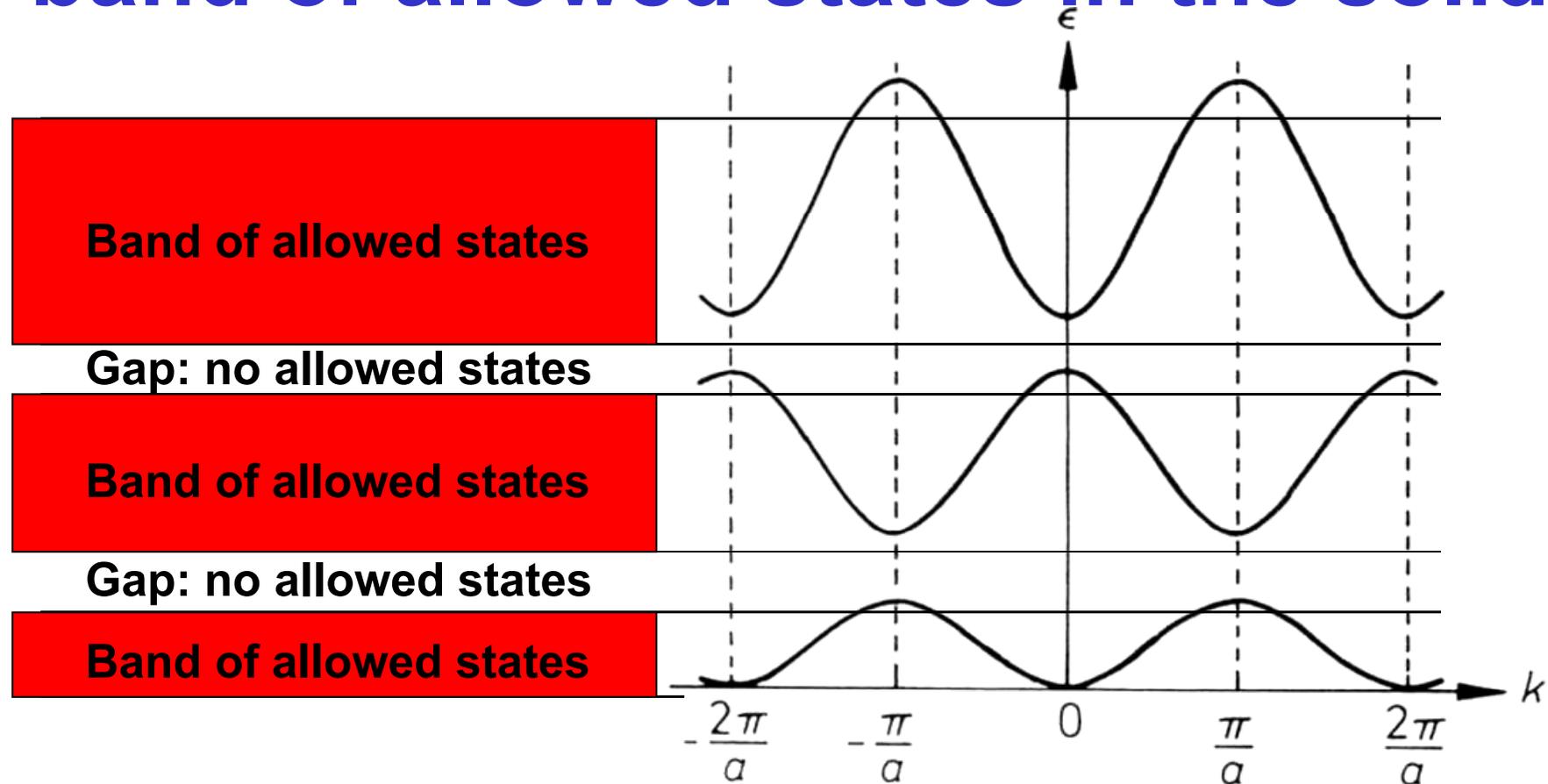


The origin of the simple band model for solids:
Band formation by orbital overlap
(in principle a continuation of the Molecular Orbital model)



the overlap of atomic orbitals in a solid gives rise to the formation of bands separated by gaps (the band width is a rough measure of interaction between neighbouring atoms)

Each atomic orbital leads to a band of allowed states in the solid

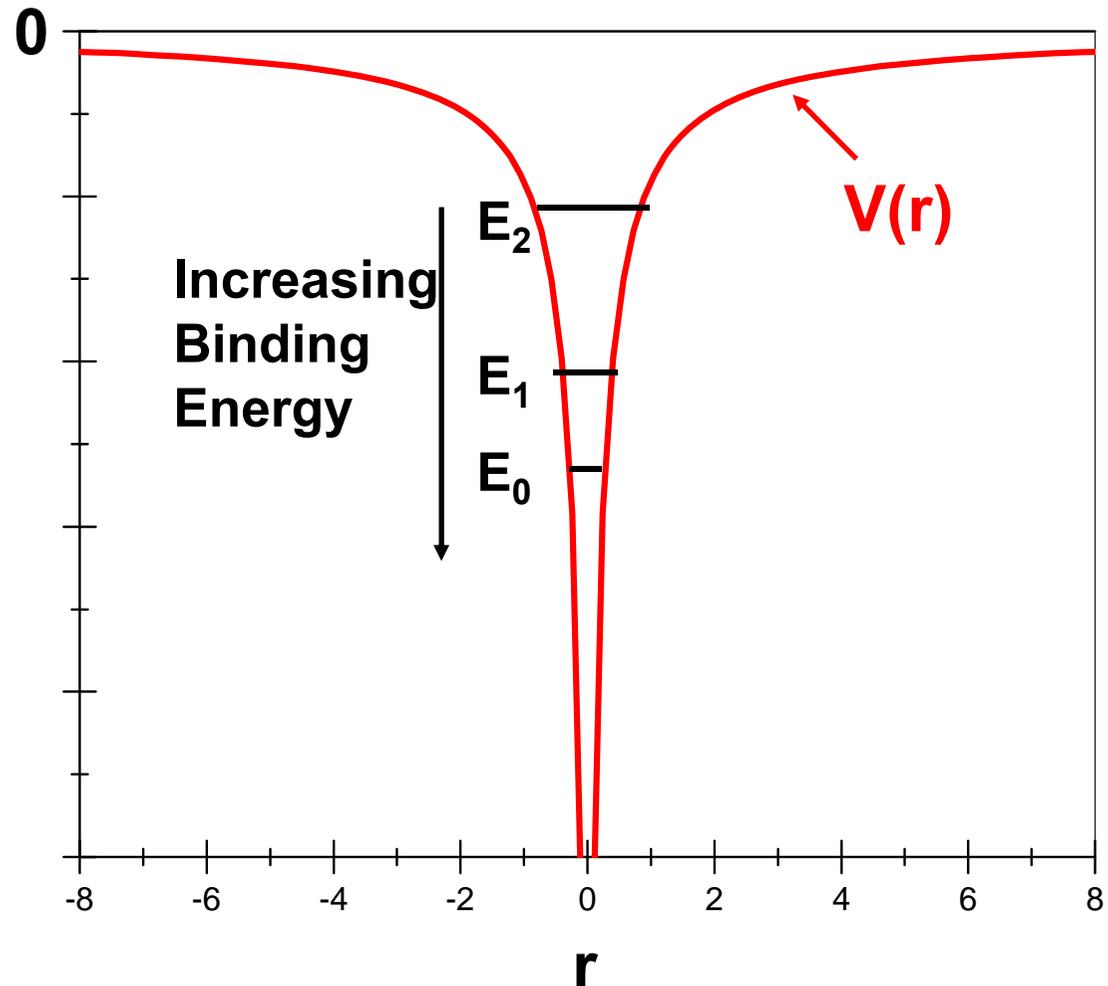


Bound States in atoms

Electrons in isolated atoms occupy discrete allowed energy levels E_0 , E_1 , E_2 etc. .

The potential energy of an electron a distance r from a positively charge nucleus of charge q is

$$V(r) = \frac{-qe^2}{4\pi\epsilon_0 r}$$



Bound and “free” states in solids

The 1D potential energy of an electron due to an array of nuclei of charge q separated by a distance a is

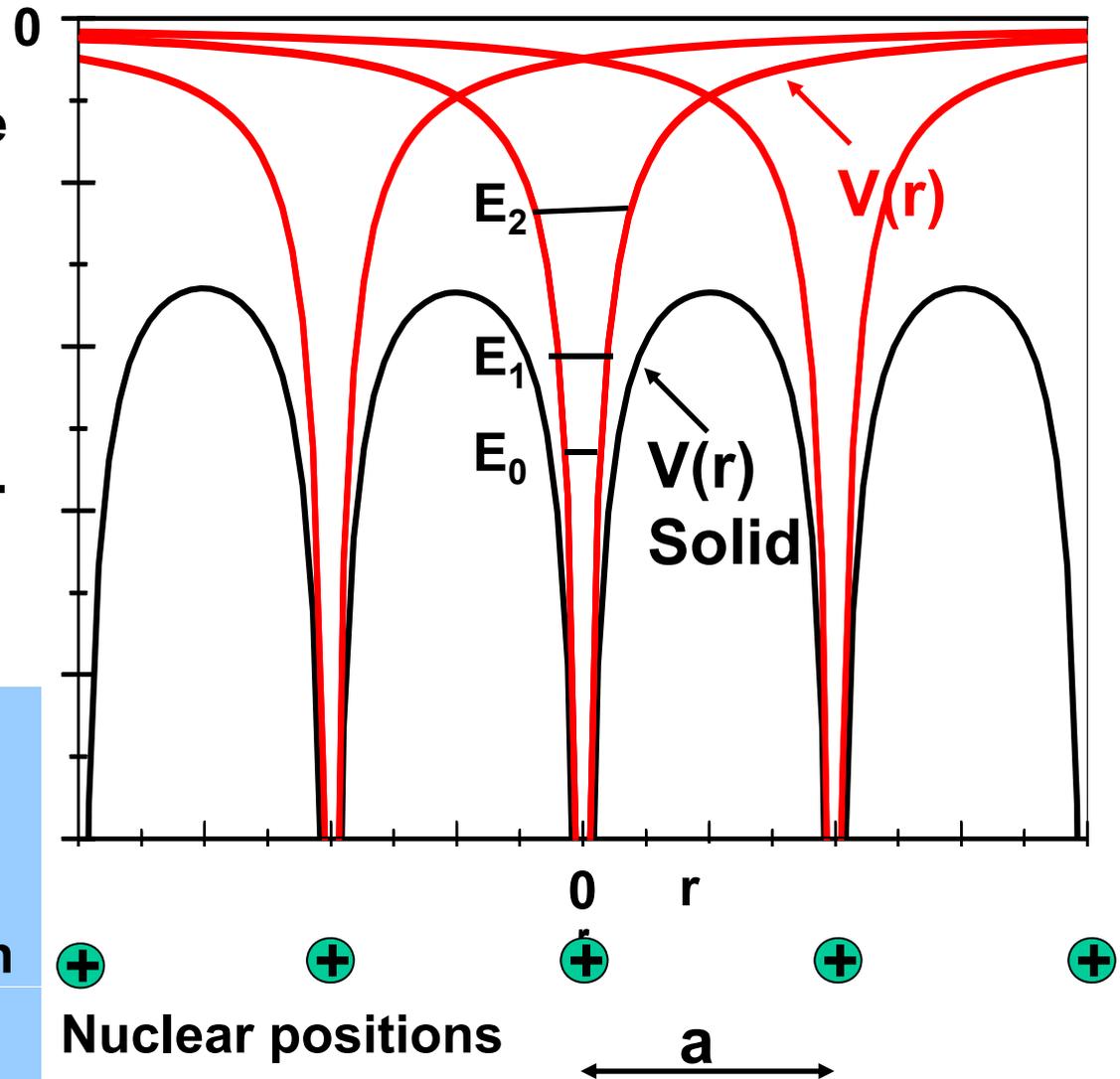
$$V(r) = \sum_n \frac{-qe^2}{4\pi\epsilon_0|r-na|}$$

Where $n = 0, +/-1, +/-2$ etc.

This is shown as the black line in the figure.

$V(r)$ lower in solid (work function).

Naive picture: lowest binding energy states can become free to move throughout crystal



Influence of the lattice periodicity

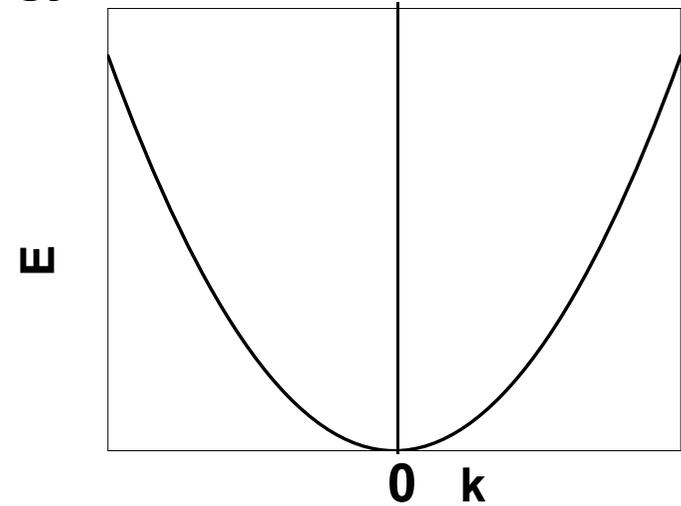
In the free electron model, the allowed energy states are

$$E = \frac{\hbar^2}{2m} (k_x^2 + k_y^2 + k_z^2)$$

where for periodic boundary conditions

$$k_x = \frac{2\pi n_x}{L}; \quad k_y = \frac{2\pi n_y}{L}; \quad k_z = \frac{2\pi n_z}{L}$$

n_x, n_y and n_z positive or negative integers.



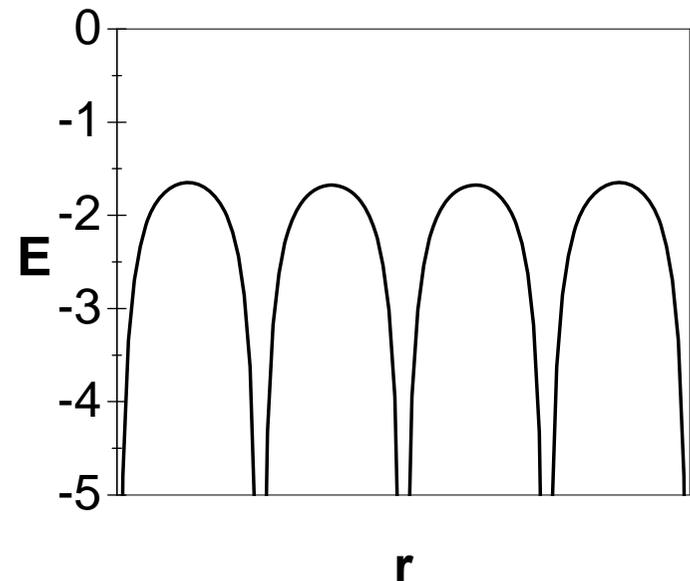
Periodic potential

Exact form of potential is complicated

Has property $V(\underline{r} + \underline{R}) = V(\underline{r})$ where

$$\underline{R} = m_1 \underline{a} + m_2 \underline{b} + m_3 \underline{c}$$

where m_1, m_2, m_3 are integers and $\underline{a}, \underline{b}, \underline{c}$ are the primitive lattice vectors.



Waves in a periodic lattice

Recall X-ray scattering

Consider a wave, wavelength λ moving through a 1D lattice of period a .

Strong backscattering for $\lambda = 2a$

Backscattered waves constructively interfere.

Wave has wavevector $k = 2\pi/\lambda$.

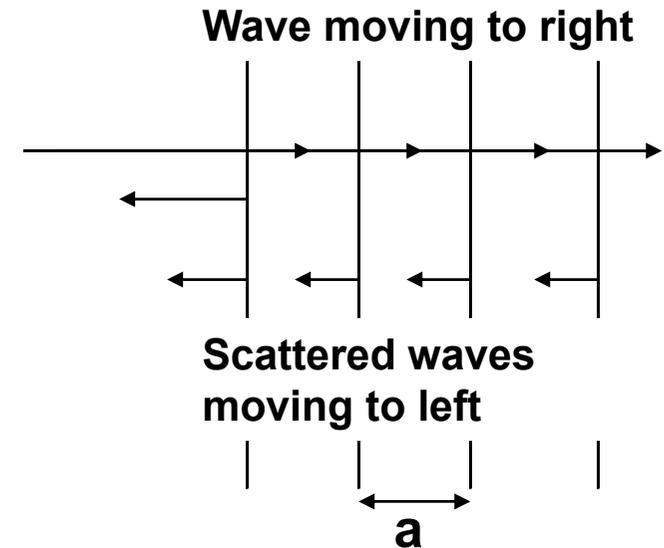
1D Reciprocal lattice vectors are $G = n \cdot 2\pi/a$; n – integer

Bragg condition is $k = G/2$

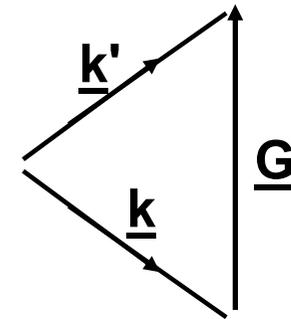
3D lattice: Scattering for \underline{k} to \underline{k}' occurs if $\underline{k}' = \underline{k} + \underline{G}$

where $\underline{G} = h\underline{a}_1 + k\underline{a}_2 + l\underline{a}_3$ h, k, l integer and $\underline{a}_1, \underline{a}_2, \underline{a}_3$

are the primitive reciprocal lattice vectors



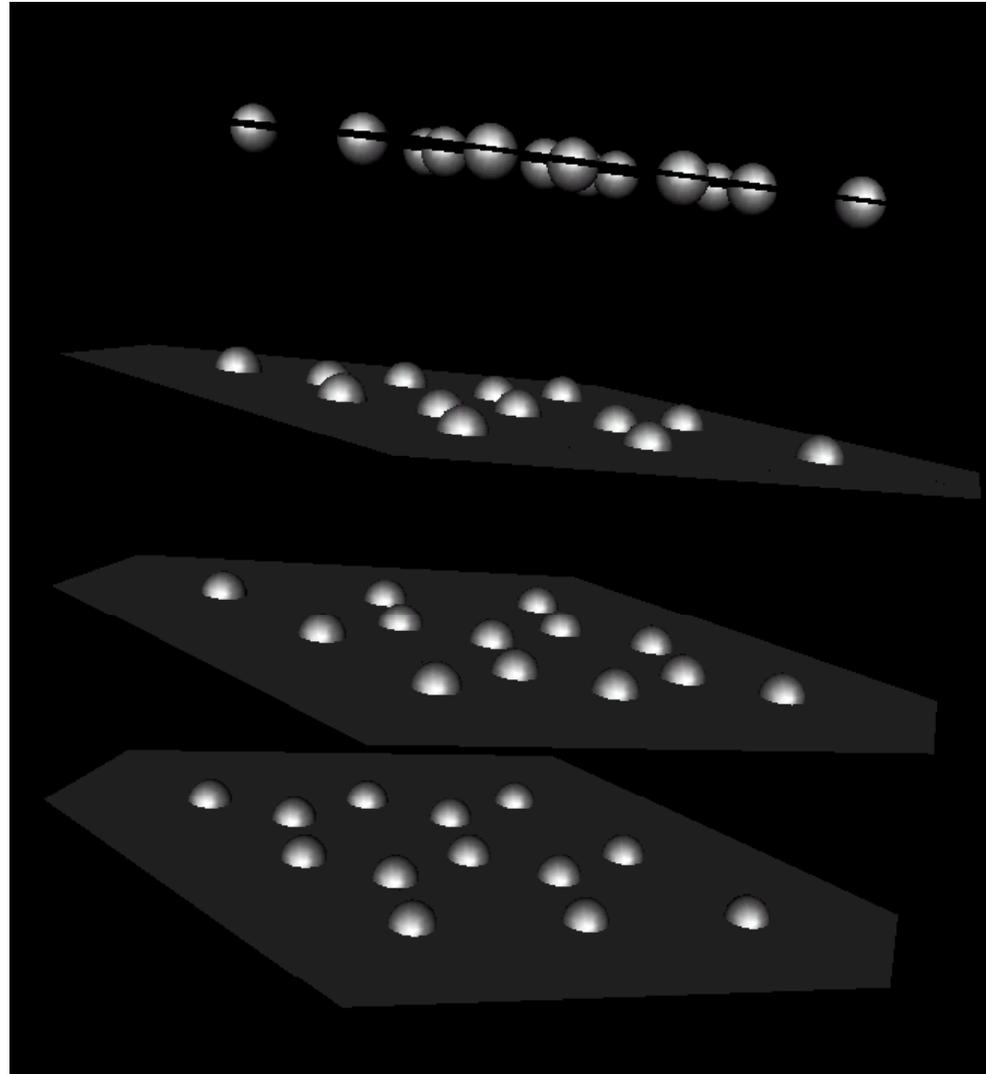
Scattering potential period a



- Band structure is a direct consequence of the crystal lattice periodicity.
 - a) Strongly anisotropic materials may be metals, semiconductors or insulators depending on crystallographic direction.
 - b) External effects influencing crystal periodicity: pressure, mechanical stress and thermal expansion affect the band structure.
 - c) Amorphous materials do not have defined band structure.

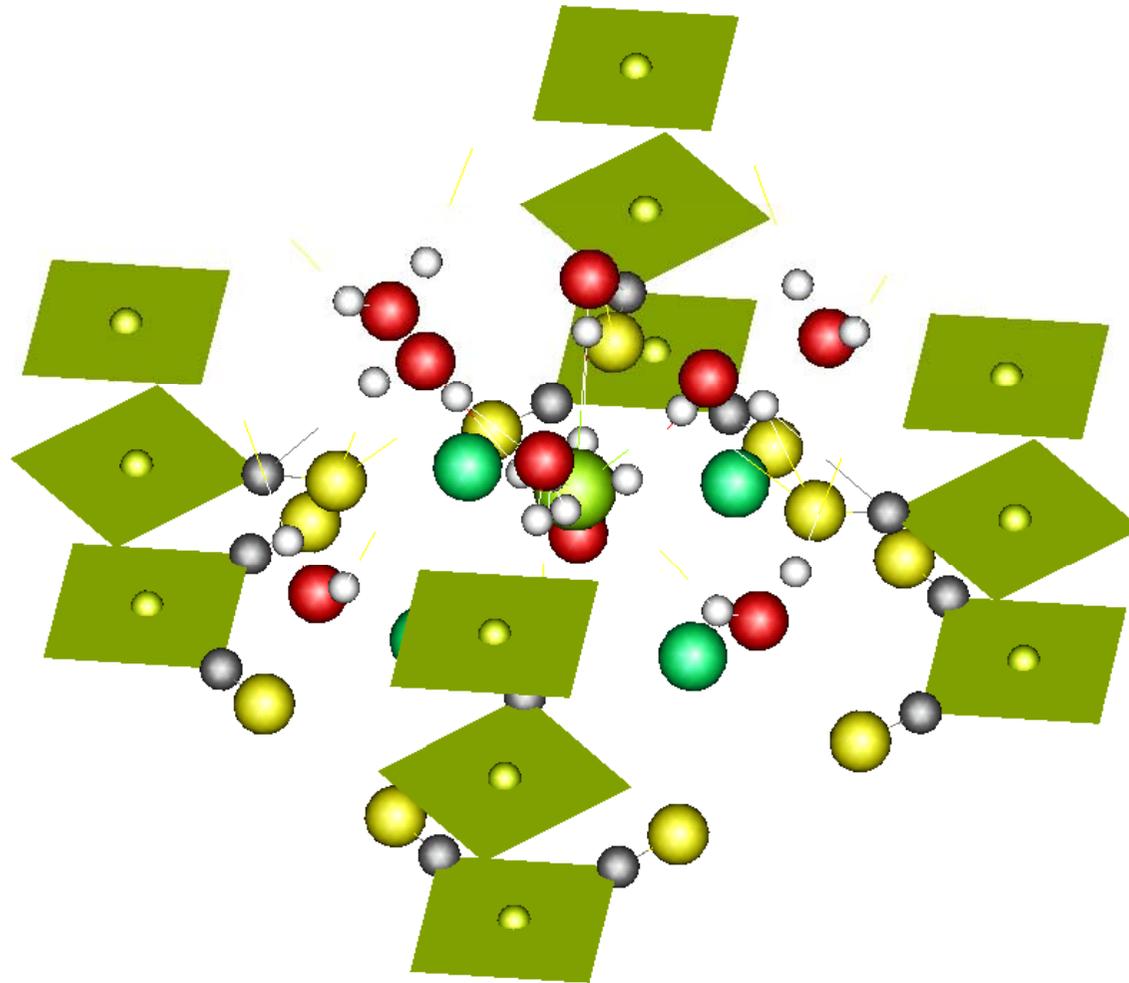
Example 1:

Graphite: 2-D semimetal, 1-D semiconductor



Example 2:

$\text{K}_2\text{Pt}(\text{CN})_4\text{Br}_{0.3}\cdot\text{H}_2\text{O}$: 1-D metal, 2D dielectric

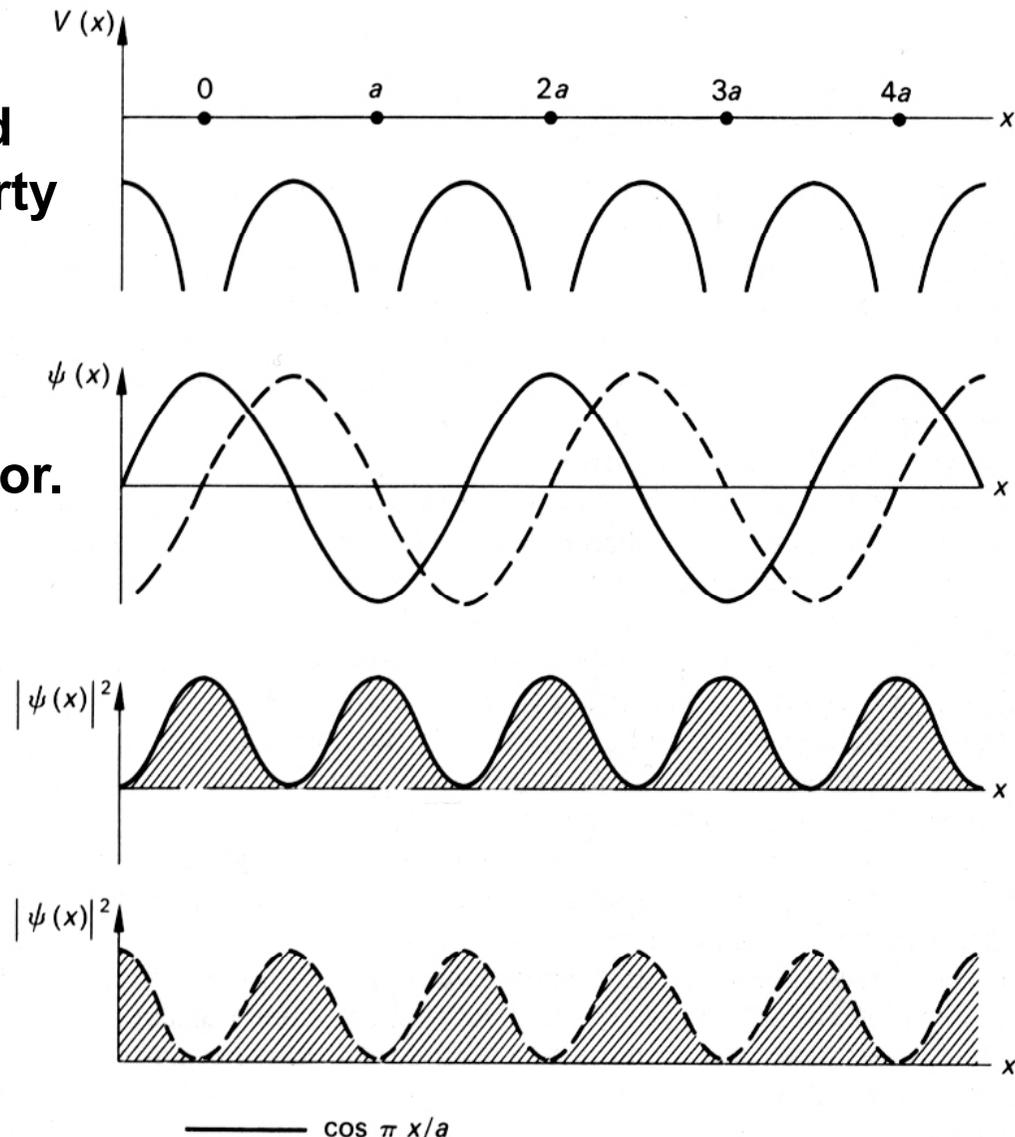


Electron probability density has the same symmetry as the lattice

In a periodic lattice the allowed wavefunctions have the property

$$|\psi(\mathbf{r} + \mathbf{R})|^2 = |\psi(\mathbf{r})|^2$$

where \mathbf{R} is any real lattice vector.



Bloch States

KEY POINT

Bloch's discovery (1928)

- **If** every translation of a system unit with a multiple of a lattice vector leads to identical units
- **And if** the physical environment in every unit is identical
- **Then** every electron state needs to be described only in one unit cell (instead of throughout)
- **And** is connected to other unit cells only via the phase of a plane wave (the simplest periodicity)

Bloch States

In a periodic lattice the allowed wavefunctions have the property

$$|\psi(\mathbf{r} + \mathbf{R})|^2 = |\psi(\mathbf{r})|^2 \quad \text{where } \underline{\mathbf{R}} \text{ is any real lattice vector.}$$

Therefore

$$\psi(\mathbf{r} + \mathbf{R}) = e^{i\alpha(\mathbf{R})} \psi(\mathbf{r})$$

where the function $\alpha(\mathbf{R})$ is **real, independent of \mathbf{r} , and dimensionless.**

Now consider $\psi(\mathbf{r} + \mathbf{R}_1 + \mathbf{R}_2)$. This can be written

$$\psi(\mathbf{r} + \mathbf{R}_1 + \mathbf{R}_2) = e^{i\alpha(\mathbf{R}_1 + \mathbf{R}_2)} \psi(\mathbf{r})$$

Or

$$\psi(\mathbf{r} + \mathbf{R}_1 + \mathbf{R}_2) = e^{i\alpha(\mathbf{R}_1)} \psi(\mathbf{r} + \mathbf{R}_2) = e^{i\alpha(\mathbf{R}_1)} e^{i\alpha(\mathbf{R}_2)} \psi(\mathbf{r})$$

Therefore

$$\alpha(\mathbf{R}_1 + \mathbf{R}_2) = \alpha(\mathbf{R}_1) + \alpha(\mathbf{R}_2)$$

$\alpha(\mathbf{R})$ is linear in \mathbf{R} and can be written $\alpha(\mathbf{R}) = k_x R_x + k_y R_y + k_z R_z = \mathbf{k} \cdot \mathbf{R}$. where k_x, k_y and k_z are the components of **some wavevector \mathbf{k}** so

$$\psi(\mathbf{r} + \mathbf{R}) = e^{i\mathbf{k} \cdot \mathbf{R}} \psi(\mathbf{r}) \quad (\text{Bloch's Theorem})$$

Alternative form of Bloch's Theorem

(Bloch's Theorem) $\psi(r + R) = e^{ik \cdot R} \psi(r)$ (1)

For any k one can write the **general form of any wavefunction** as

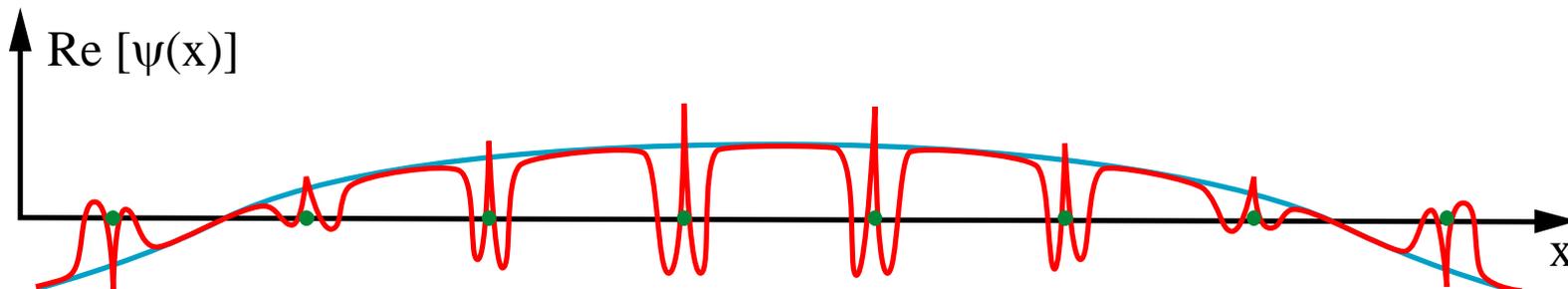
$$\psi(\mathbf{r}) = e^{ik \cdot \mathbf{r}} u(\mathbf{r}) \quad (2)$$

Therefore we have $\psi(r + R) = e^{ik \cdot (r+R)} u(r + R)$ (from..2)

and $\psi(r + R) = e^{ik \cdot R} e^{ik \cdot r} u(r)$ (from..1)

for all r and R . Therefore in a lattice the wavefunctions can be written as

$\psi(\mathbf{r}) = e^{ik \cdot \mathbf{r}} u(\mathbf{r})$
where $u(r)$ has the periodicity (translational symmetry) of the lattice. This is an alternative statement of Bloch's theorem.



Real part of a Bloch function. $\psi \approx e^{ikx}$ for a large fraction of the crystal volume.

Bloch Wavefunctions: allowed k-states

$$\psi(\underline{r}) = \exp[i\underline{k} \cdot \underline{r}]u(\underline{r})$$

Periodic boundary conditions. For a cube of side L we require

$$\psi(x + L) = \psi(x) \text{ etc.. So } e^{ik_x(x+L)}u(x + L) = e^{ik_x x}u(x + L)$$

but $u(x+L) = u(x)$ because it has the periodicity of the lattice therefore

$$\text{Therefore } e^{ik_x(x+L)} = e^{ik_x x} \text{ i.e. } k_x = 2\pi n_x/L \quad n_x \text{ integer.}$$

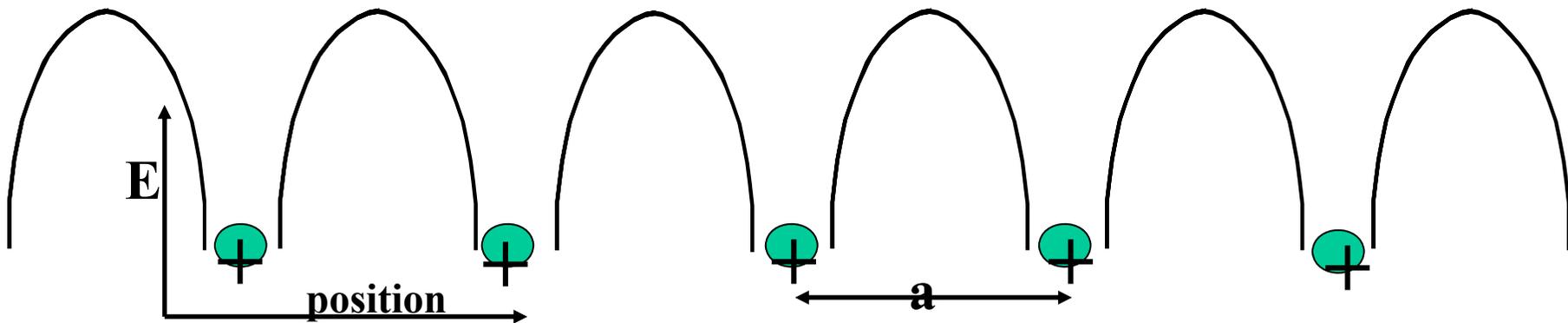
Same allowed k-vectors for Bloch states as free electron states.

Bloch states are not momentum eigenstates i.e. $p \neq \hbar k$

The allowed states can be labelled by a wavevectors k .

Band structure calculations give $E(k)$ which determines the dynamical behaviour.

Bragg scattering & energy gaps



Reminder: De Broglie matter waves

Light: wave-particle duality:

- Light behaves as waves when the characteristic dimensions are comparable to the wavelength of light.
- Light behaves as particles (rays) when the characteristic dimensions are much greater than the wavelength of light.

Wave-particle duality applies to matter such as electrons, atoms, bricks and baseballs

$$\text{Momentum of a particle } p = \frac{E^2}{2m}$$

That is:

De Broglie's hypothesis: Matter has wave character. Wavelength, λ , is given by

$$\lambda = \frac{h}{p} \quad (1)$$

wavenumber $k = \frac{2\pi}{\lambda}$

For free electron

Group velocity of wave packet $v_g = \frac{1}{\hbar} \frac{dE}{dk}$

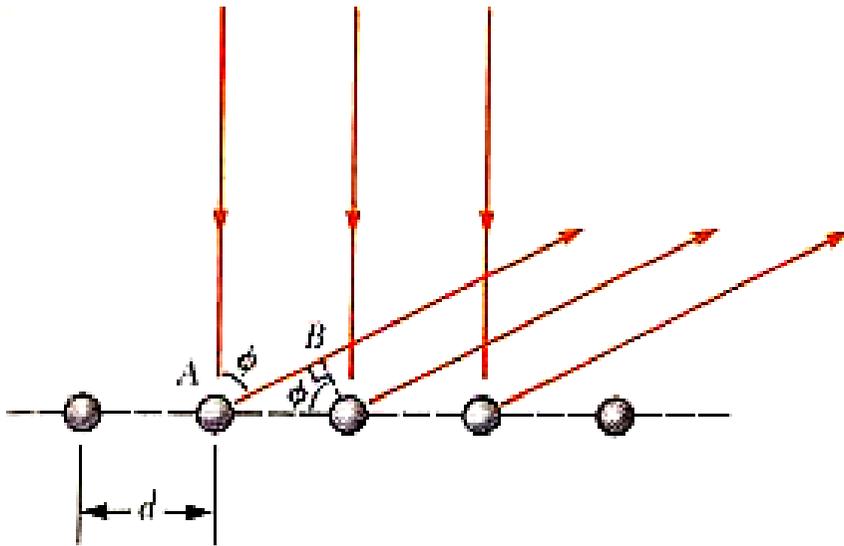
$$E = \frac{\hbar^2 k^2}{2m}$$
$$v_g = \frac{\hbar^2 k}{m} \quad (1a)$$

A direct proof electron waves: The Davisson-Germer Experiment

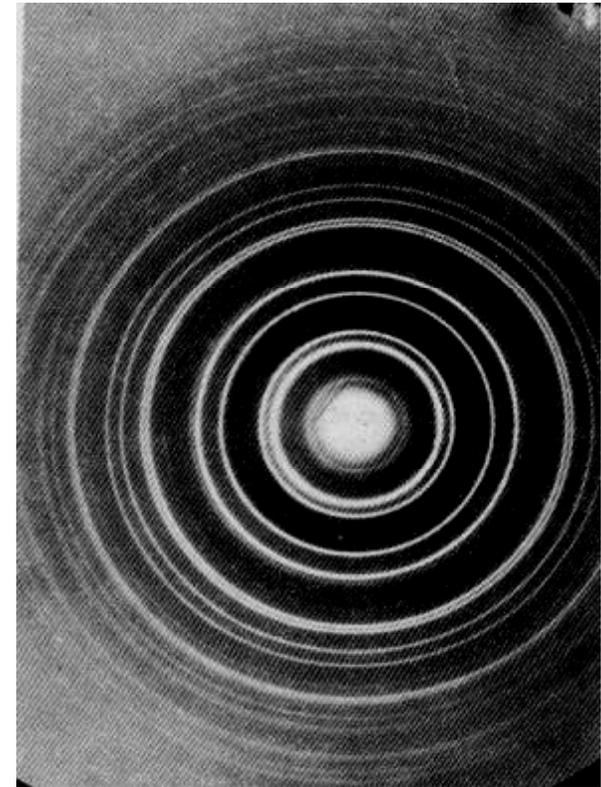
Constructive interference of electrons, scattered by an array of **surface** atoms, at an angle ϕ is described by

$$d \sin(\phi) = n\lambda$$

as found for X-ray diffraction!



Homework: Why surface atoms only?



Diffraction of 50 keV electrons from a Cu_3Au alloy film.

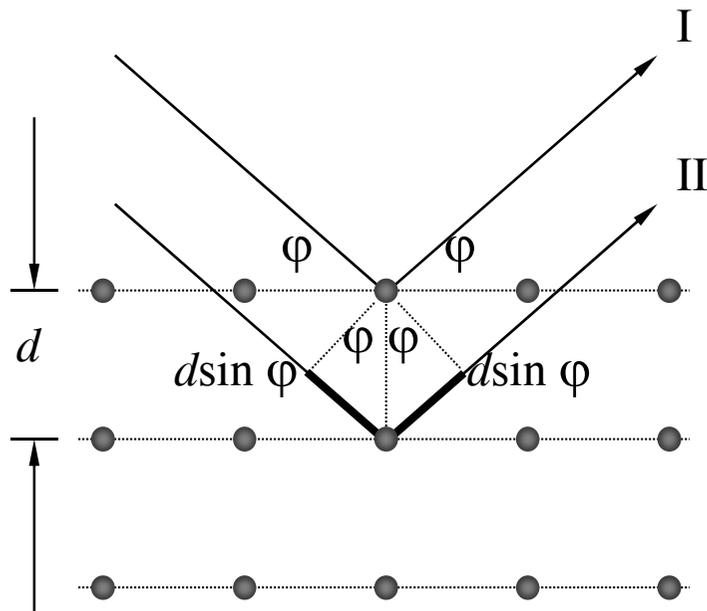
Example: A Ping-Pong ball of mass 1.4 g traveling at a speed of 97.2 km/h (27 m/s) has a wavelength given by

$$\lambda = \frac{h}{p} = \frac{6.63 \cdot 10^{-34}}{1.4 \cdot 10^{-3} \text{ kg} \cdot 27 \text{ m/s}} = 1.75 \cdot 10^{-32} \text{ m} \text{ **Smaller than a nucleus!**}$$

The Nearly-Free-Electron Model

Let us consider the **DIFFRACTION** of waves that is generated by a crystal structure. The diffraction is described by **BRAGG'S LAW**:

$$2d \sin \varphi = n\lambda, \quad n = 1, 2, 3, \dots$$

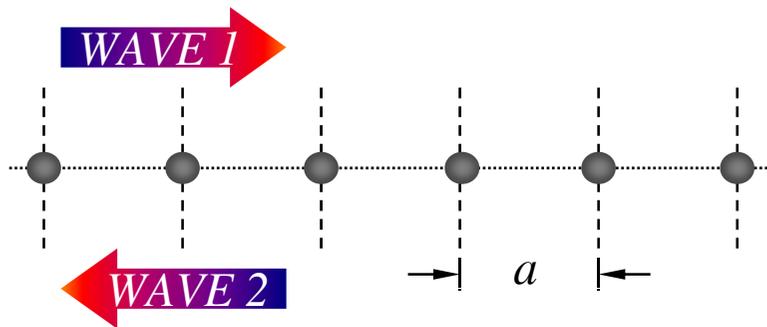


- *Bragg diffraction of waves by a crystal structure*
- *strong reflection of the incident wave will occur for the set of incident angles that satisfy the Bragg condition*
- *the index n defines the path difference between waves- i & ii when the diffraction occurs ... for a given value of n this path difference is $n\lambda$*

Nearly-free electron model

* The main effect of the electron-crystal interaction is to **DIFFRACT** electrons whenever the Bragg condition is satisfied

* For the one-dimensional problem of interest here **EACH** lattice point defines a crystal plane so that the spacing between planes is a while the Bragg angle is restricted to **JUST** 90°



- *Bragg diffraction of waves in a **one-dimensional chain***
- *as wave 1 tries to propagate along the chain it will undergo strong **reflection** whenever the Bragg condition is **satisfied***
- *this gives rise to a reflected component (labeled as wave 2), which propagates in the direction **opposite** to that of wave 1*
- *the **interference** of waves 1 and 2 is **crucial** to understanding the properties of electrons in crystals*

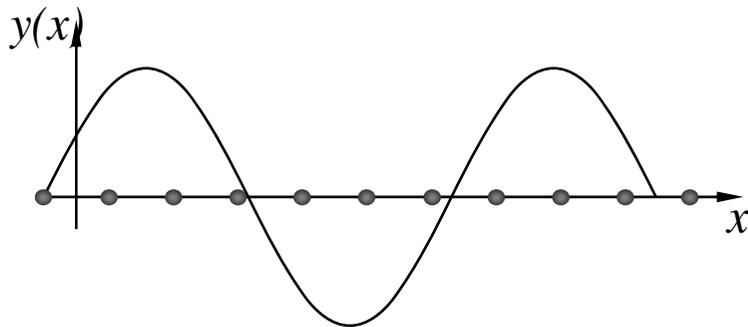
- For the one-dimensional chain the Bragg condition reduces to a very **SIMPLE** form

$$2a = n\lambda, \quad n = 1, 2, 3, \dots \quad (2)$$

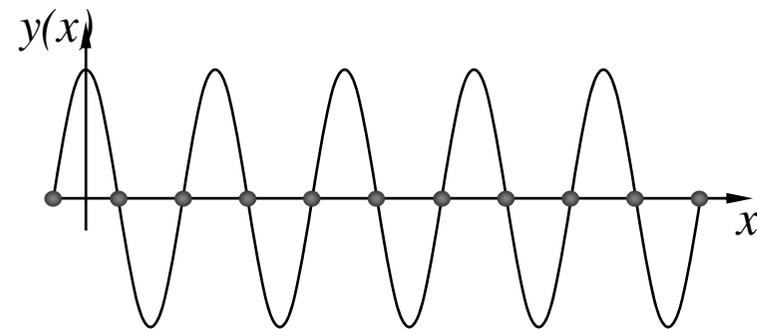
- * Equation (1) implies a corresponding condition on the electron **WAVENUMBER**

$$k_x = \frac{2\pi}{\lambda} = n \frac{\pi}{a} \quad n = \pm 1, \pm 2, \pm 3, \dots \quad (3)$$

⇒ These relations show that diffraction occurs if the wavelength of the electron wave is **COMMENSURATE** with the spacing of atoms in the crystal



Here the wavelength is much **larger** than $2a$ so diffraction of the electron wave does **not** occur.



Here the wavelength is **equal** to $2a$, which corresponds to the first Bragg condition ($n = 1$)

- Consider now the first ($n = 1$) diffraction condition which occurs when

$$k_x = \pm \frac{\pi}{a} \quad (3)$$

- * Diffraction of the original wave gives rise to a reflected component and these two waves **INTERFERE** to produce a standing wave with **ZERO** group velocity
- * The wavefunction of the standing wave can be constructed in **TWO** different ways by superimposing the two **OPPOSITELY** propagating waves

$$\psi_{\pm}(x) = \psi_I(x) \pm \psi_{II}(x) = e^{ik_x x} \pm e^{-ik_x x} \quad (4)$$

or

$$\psi_+(x) = 2 \cos \left[\frac{\pi x}{a} \right] \quad (5)$$

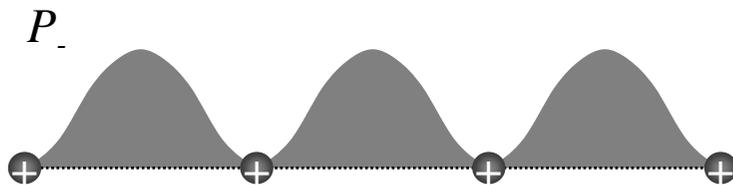
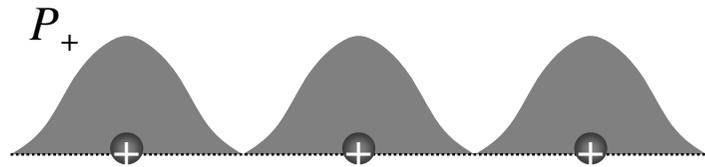
$$\psi_-(x) = -2i \sin \left[\frac{\pi x}{a} \right] \quad (6)$$

- Equations (5) and (6) yield **DIFFERENT** probabilities for finding the electron

$$P_+(x) = \psi_+^*(x)\psi_+(x) = \left(2 \cos\left[\frac{\pi x}{a}\right]\right)^2 = 4 \cos^2\left[\frac{\pi}{a}x\right] \quad (7)$$

$$P_-(x) = \psi_-^*(x)\psi_-(x) = -2i \sin\left[\frac{\pi x}{a}\right] 2i \sin\left[\frac{\pi x}{a}\right] = 4 \sin^2\left[\frac{\pi}{a}x\right] \quad (8)$$

* P_+ gives a high probability of finding electrons **CLOSE** to the ion cores and so has a **LOWER** (more negative) potential energy than P_- .



- P_+ peaks *at* the sites of the ion cores and has a **low** (more negative) potential energy associated with it
- P_- on the other hand peaks at points *between* the ion cores and so has a **larger** (less negative) potential energy than p_+

Cosine solution lower energy than sine solution

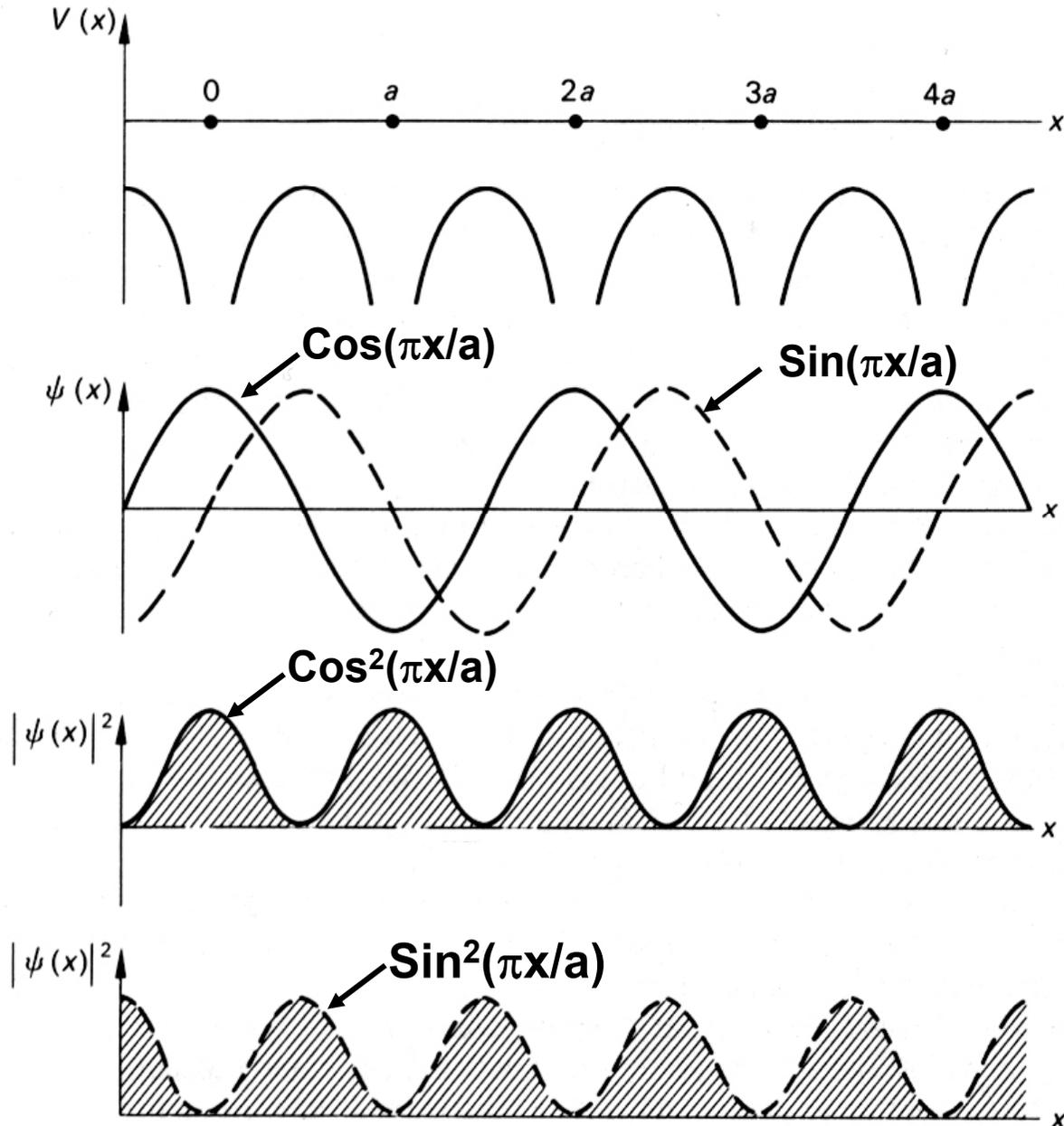
Cosine solution $\psi(+)$ has maximum electron probability density at minima in potential.

Sine solution $\psi(-)$ has maximum electron probability density at maxima in potential.

In a periodic lattice the allowed wavefunctions have the property

$$|\psi(\mathbf{r} + \mathbf{R})|^2 = |\psi(\mathbf{r})|^2$$

where \mathbf{R} is any real lattice vector.

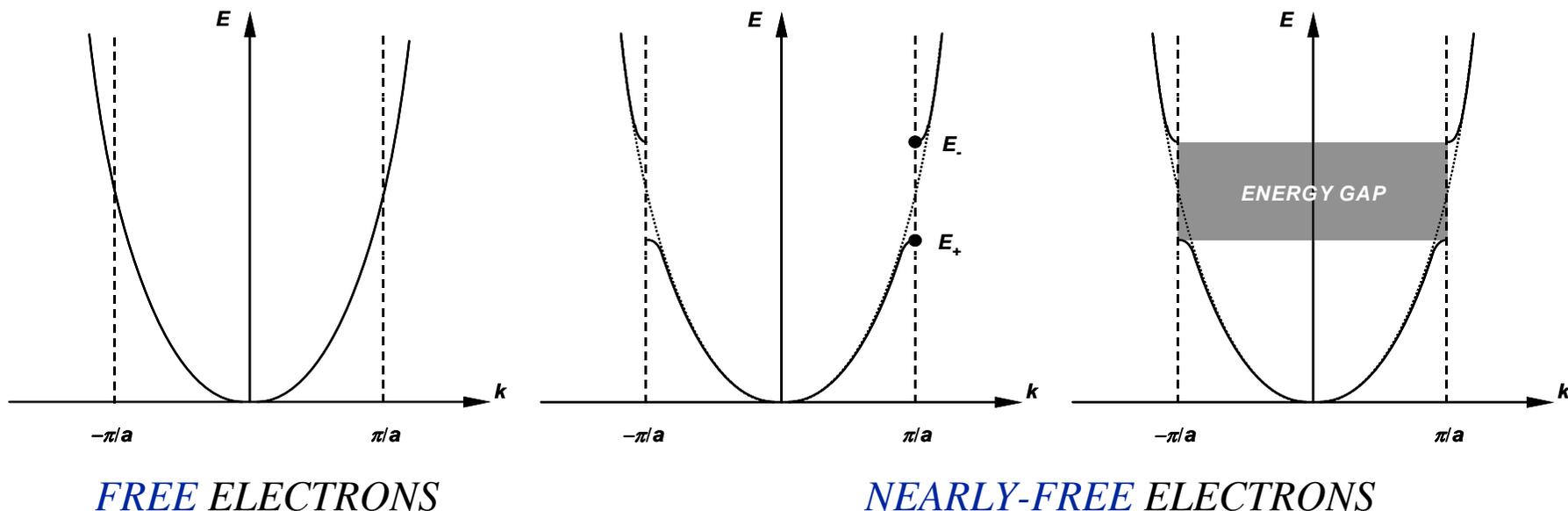


Energy Gaps: At wavenumbers for which Bragg diffraction occurs there are **TWO** possible types of electron wavefunction which in turn have two **DIFFERENT** energies

* In the **FREE**-electron model the energy of the electron is a **CONTINUOUS** function that shows a **PARABOLIC** variation $E = \hbar^2 k^2 / 2m$

* In the nearly-free electron model however the energy becomes **DOUBLE VALUED** at those wavenumbers for which diffraction occurs

⇒ The two energy values are now separated by a forbidden **ENERGY GAP**



- The forbidden gap corresponds to a range of energy inside of which there are **NO** electron states
 - * The **SIZE** of the gap depends on the **STRENGTH** of the crystal potential which we can see by noting that the **AVERAGE** potential energy of the electron may be written as

$$\int \frac{1}{L} (\psi^*(x) \psi(x) V(x)) dx \quad (9)$$

⇒ Here L is the length of the crystal and $V(x)$ describes the periodic potential energy variation of the electron in the crystal

- * Since the crystal potential varies **PERIODICALLY** with position and has periodicity a Equation (9) can be rewritten to yield the potential energy of the **TWO** standing waves

$$V_{\pm} = \int_0^a \frac{1}{a} \begin{bmatrix} 2 \cos^2(\pi x / a) \\ 2 \sin^2(\pi x / a) \end{bmatrix} V(x) dx = \int_0^a \frac{1}{a} \begin{bmatrix} \cancel{1} + \cos(2\pi x / a) \\ \cancel{1} - \cos(2\pi x / a) \end{bmatrix} V(x) dx \quad (10)$$

***AVERAGING CRYSTAL POTENTIAL
FROM 0 TO a YIELDS ZERO!***

- Equation (10) may therefore finally be written as

$$V_{\pm} = \pm \int_0^a \frac{\cos(2\pi x/a)V(x)}{a} dx \equiv \pm V_1 \quad (11)$$

$$\text{where } V_1 = \int_0^a \frac{\cos(2\pi x/a)V(x)}{a} dx .$$

- * The size of the energy gap for $n=1$ is just equal to the **DIFFERENCE** in potential energy of the two standing waves

$$\Delta E_1 = V_- - V_+ = 2V_1 \quad (12)$$

Equation (12) shows that the size of the energy gap is proportional to the **STRENGTH** of the crystal potential. As the crystal potential gets bigger the energy gaps therefore get bigger too. Alternatively if we let the crystal potential **VANISH** the energy gaps also vanish and we **RECOVER** the free-electron result (i.e. a gap-less dispersion)!

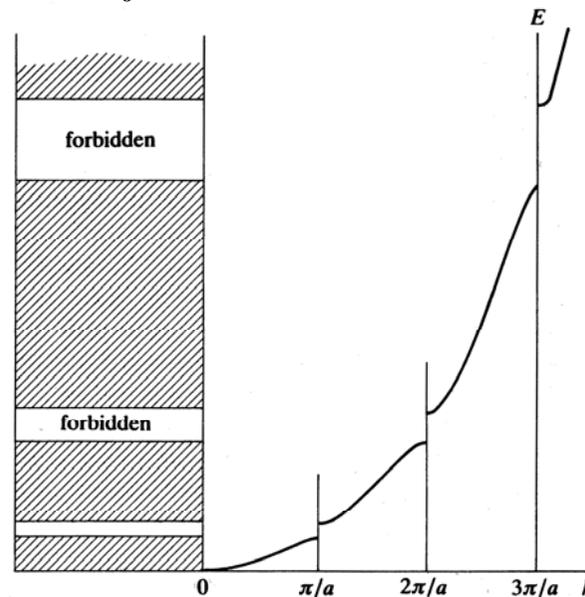
- Thus far we have considered the energy gap that arises from the **FIRST** Bragg condition ($n = 1$). There will also be energy gaps at **HIGHER** energies however for **ALL** wavenumbers that satisfy the Bragg condition

$$k_x = \frac{2\pi}{\lambda} = n \frac{\pi}{a} \quad n = \pm 1, \pm 2, \pm 3, \dots$$

The corresponding energy gap is

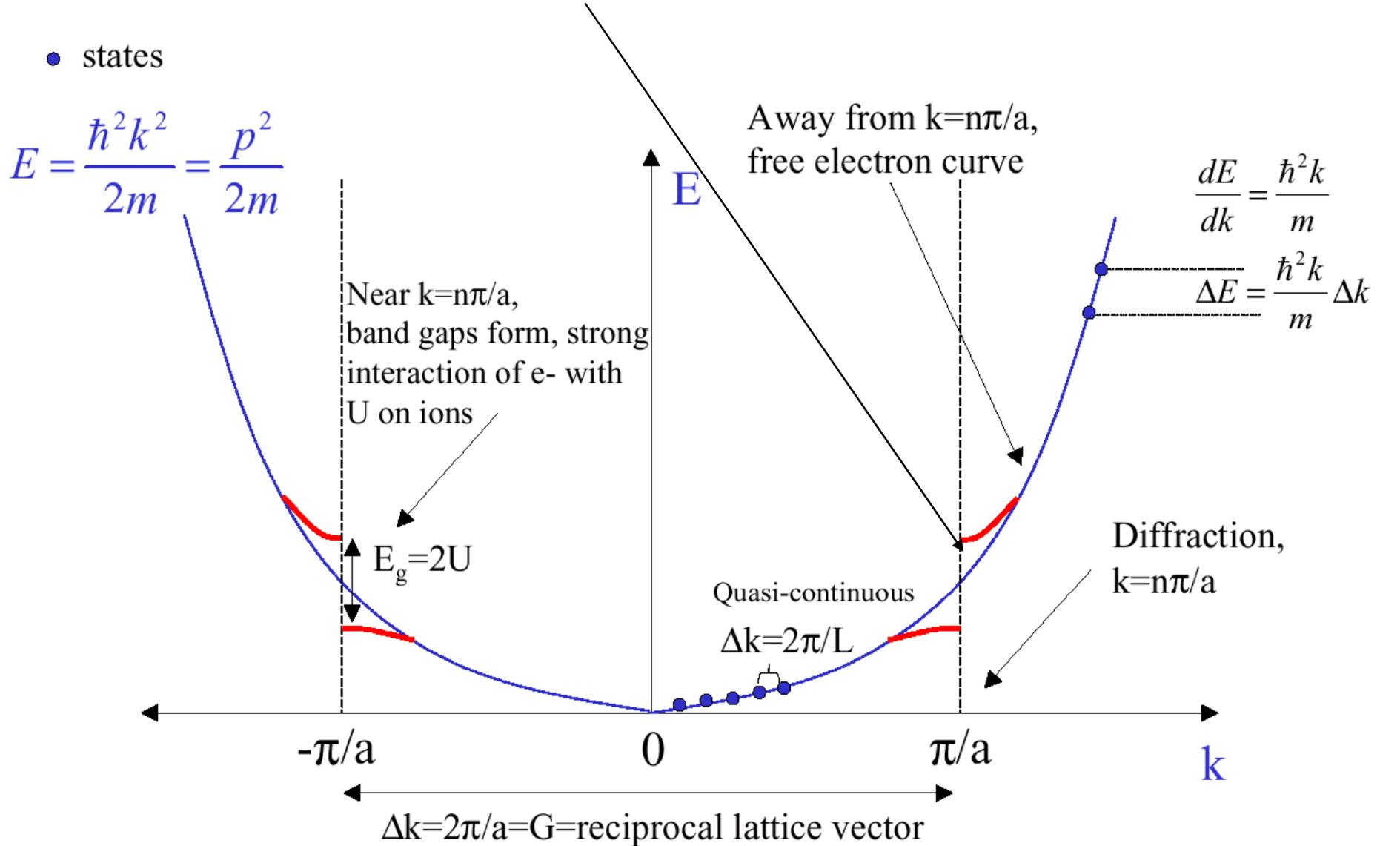
$$\Delta E_n = V_- - V_+ = 2V_n \quad (13)$$

where $V_n = \int_0^a \frac{\cos(2\pi nx/a) V(x)}{a} dx$.



Nearly- Free Electron Model (1- D crystal)

What happens near the band edge?

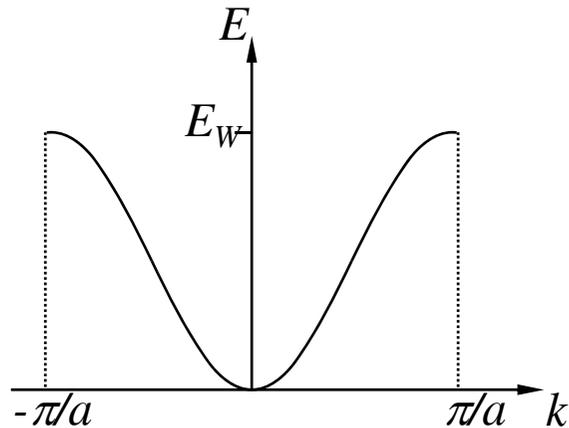


Concept of Effective Mass

- For electrons in a band the variation of energy with wavenumber is different from a free electron and, therefore, we expect that the electron velocity will **DIFFER** from (1a)
- To determine the velocity variation within a band we note that its energy dispersion may be **APPROXIMATED** by the form

$$E(k) = \frac{E_w}{2} - \frac{E_w}{2} \cos(ka) \quad (14)$$

where E_w is the **WIDTH** of the particular energy band

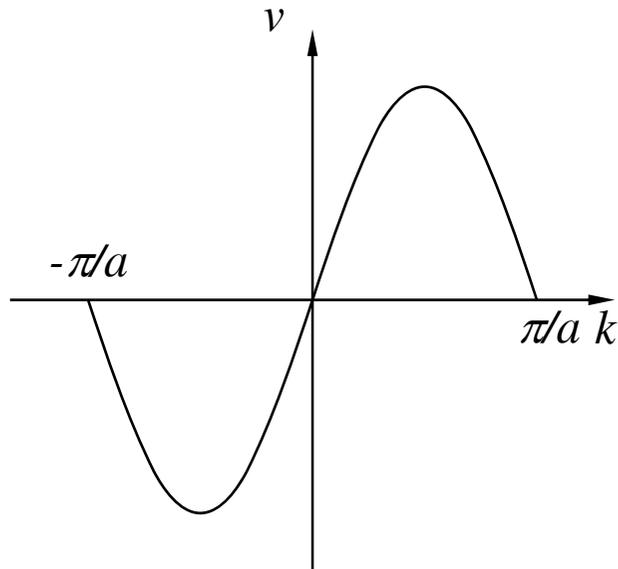


- while equation 7.6 will help us to understand the key aspects of electron dynamics in energy bands it should be emphasized that our conclusions will in fact be quite **general**, regardless of our assumption in equation (14)

- Combining Equations (14) & (1a) we arrive at the following expression for the **VELOCITY** of an electron in the energy band

$$v_g = \frac{1}{\hbar} \frac{dE}{dk} = \frac{E_w a}{2\hbar} \sin(ka) \quad (16)$$

- * This velocity variation is plotted as a function of wavenumber below where we see that it is **VERY DIFFERENT** to that characteristic of free electrons



- Variation of electron *velocity* with wavenumber in an energy band of the form of equation (15)
- note how this variation is very *different* to the linear dependence expected for free electrons
- close to $k = 0$ the sinusoidal variation *approximates* to the *linear* dependence on k as we would expect for free electrons
- the velocity of the electron *vanishes* for values of k corresponding to $\pm\pi/a$ however even though the energy of the electron is *not* zero here

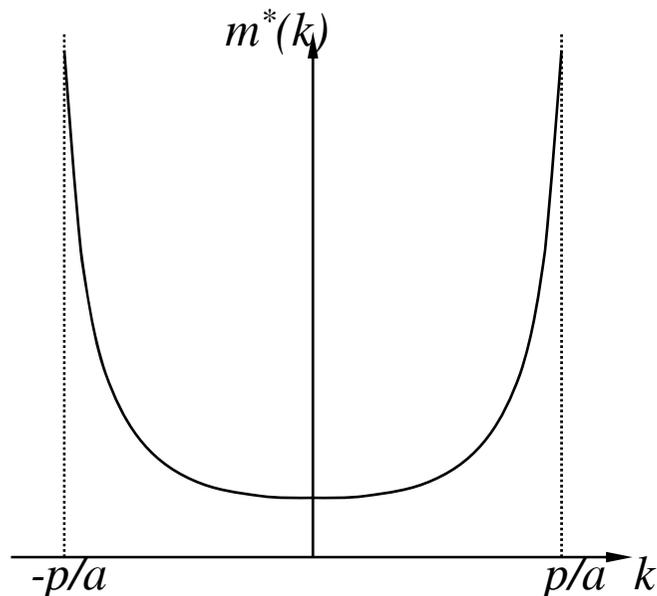
•Equation (14) yields the **WAVENUMBER-DEPENDENT** effective mass

$$\frac{1}{m^*(k)} = \frac{1}{\hbar^2 k} \frac{dE}{dk} = \frac{E_w a \sin(ka)}{2\hbar^2 k}$$

$$\therefore m^*(k) = \frac{2\hbar^2}{E_w a} \frac{k}{\sin(ka)} \quad (16)$$

⇒ For small values of k this mass is essentially **INDEPENDENT** of wavenumber since we can approximate $\sin(ka)$ as ka here

⇒ As k approaches $\pm \pi/a$ however $\sin(ka)$ tends to **ZERO** and so the effective mass becomes **INFINITE!**



⇒ For **SMALL** wavenumbers we see that the mass is essentially **INDEPENDENT** of k indicating that at the **BOTTOM** of the band the electrons behave like **FREE** electrons

⇒ This is not completely surprising since in the nearly-free electron model the energy gaps only modify the dispersion near $k = \pm n\pi/a$

⇒ The divergence of the mass is caused by **BRAGG DIFFRACTION** of electrons once their wavelength becomes commensurate with the lattice spacing