

# Electrons in Crystals

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PHYSICS TEXTBOOK

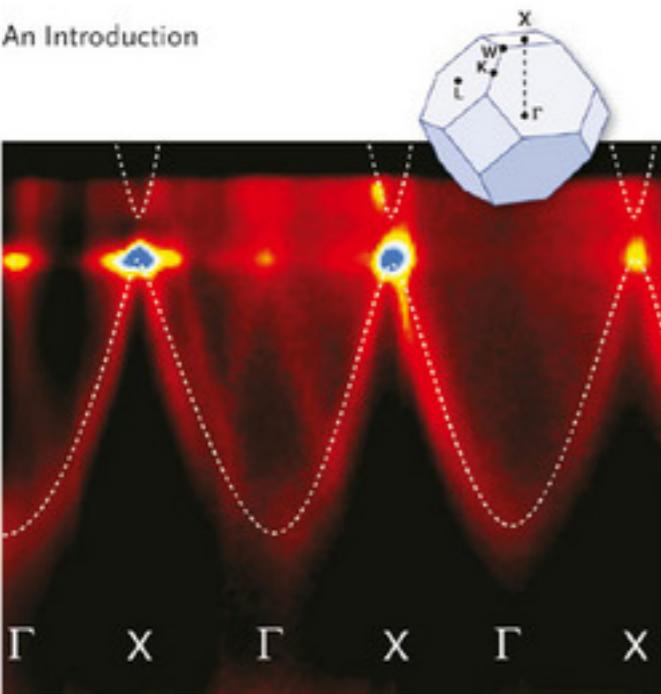
Philip Hofmann

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OXFORD MASTER SERIES IN CONDENSED MATTER PHYSICS

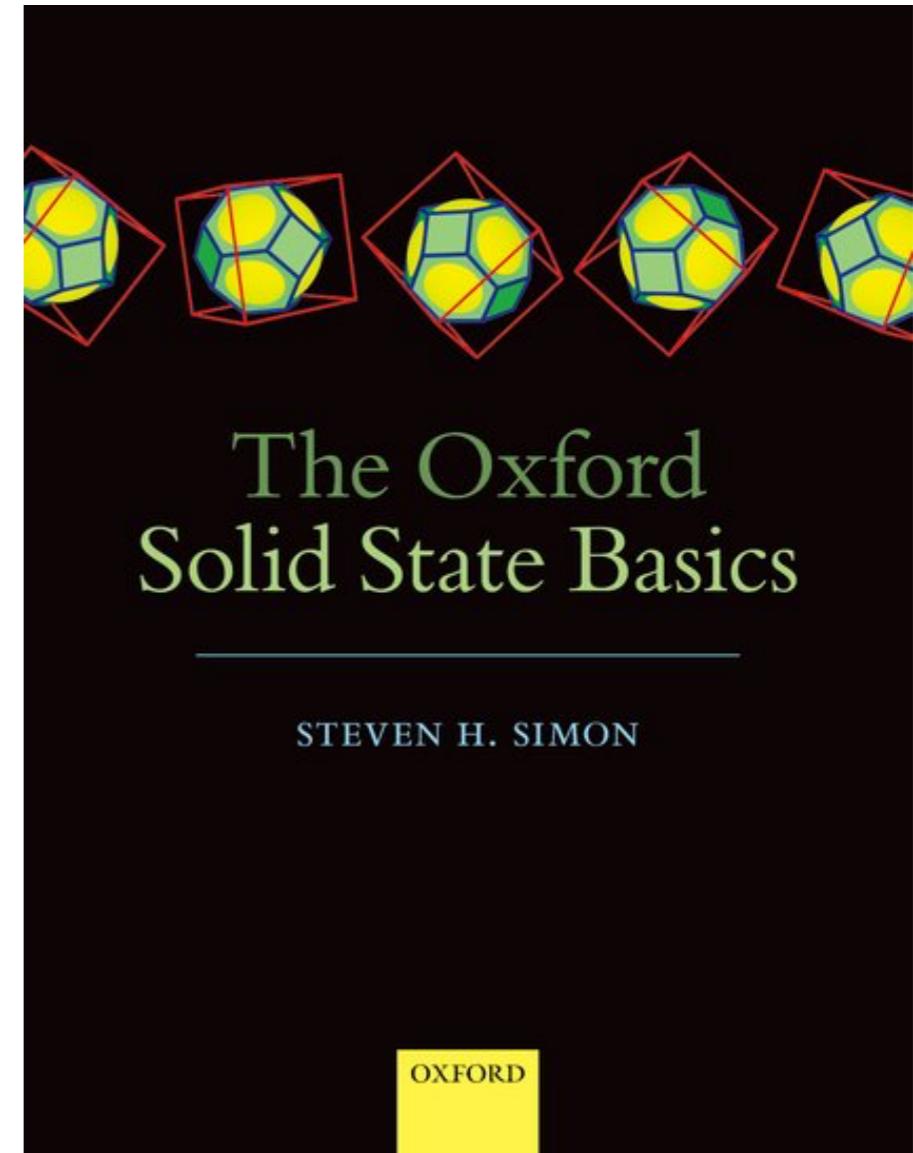
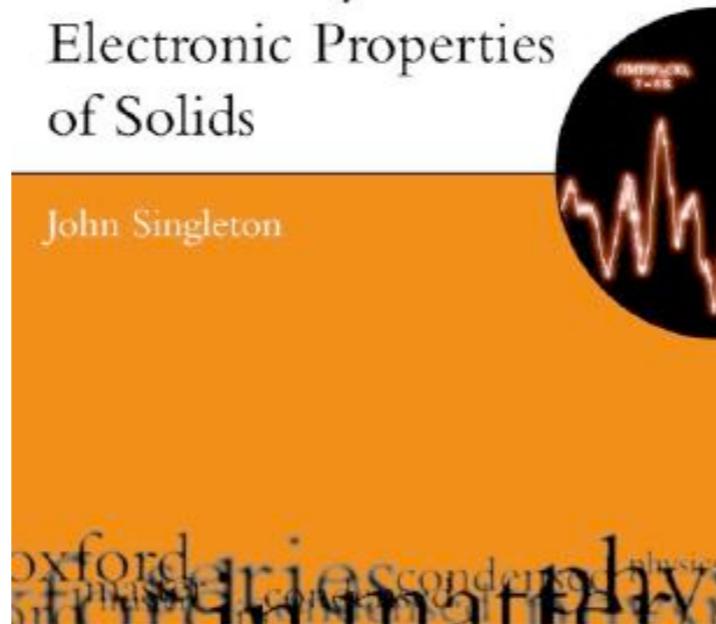
# Solid State Physics

An Introduction



Band Theory and  
Electronic Properties  
of Solids

John Singleton



Harald Ibach  
Hans Lüth

## Solid-State Physics

An Introduction to  
Principles of Materials Science

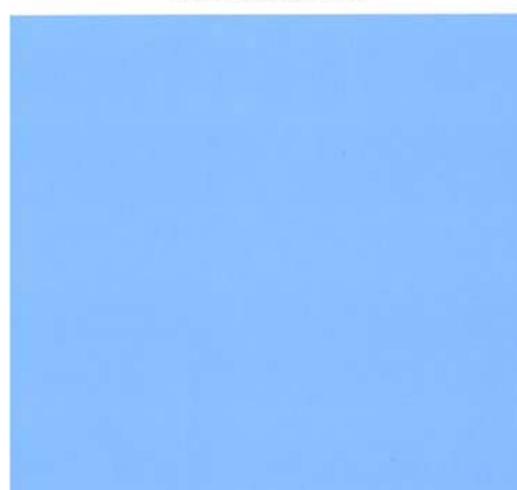
Fourth Edition

Springer

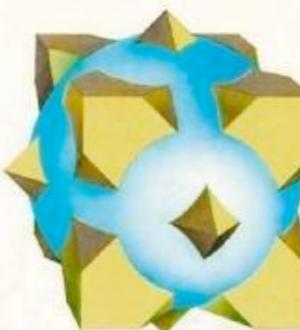
EIGHTH EDITION

## Introduction to Solid State Physics

CHARLES KITTEL



ASHCROFT / MERMIN



SOLID STATE PHYSICS

You might also find this to be useful background later on :

*Physica Scripta* **91** 053009 (2016)

**OPEN ACCESS**

**IOP Publishing | Royal Swedish Academy of Sciences**

Physica Scripta

Phys. Scr. **91** (2016) 053009 (13pp)

[doi:10.1088/0031-8949/91/5/053009](https://doi.org/10.1088/0031-8949/91/5/053009)

**Invited Comment**

**Life on the edge: a beginner's guide to the Fermi surface**

**S B Dugdale**

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# Prologue

**Q. How many atoms  
are there in one cm<sup>3</sup>  
of a crystalline solid?**

**A.  $\sim 10^{23}$  ( $N_A$ )**

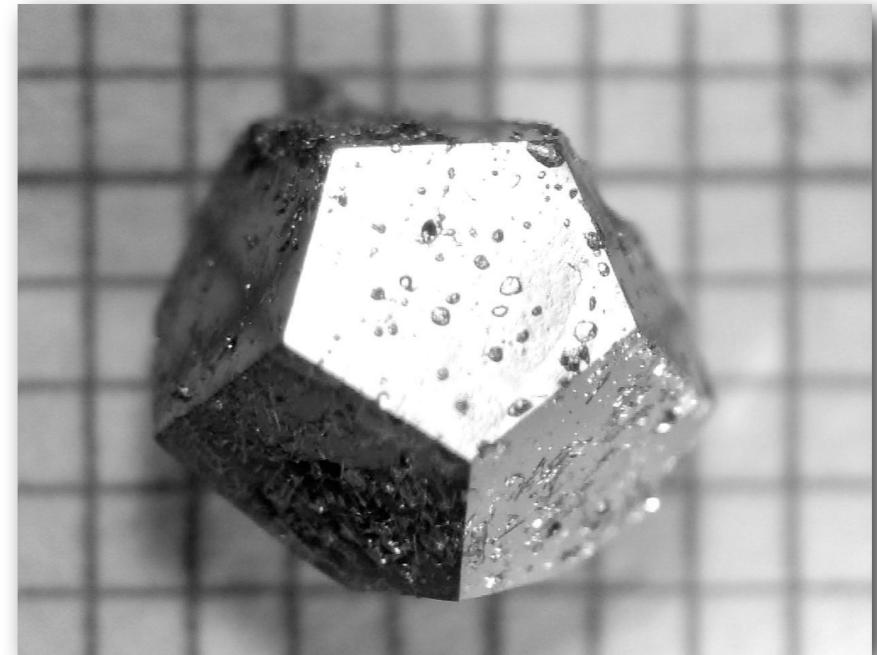


Image (Fisher Group, Stanford):  
an Al-Pd-Re quasicrystal (\*)

**How can we possibly deal with this number?**

This course will not only show you how, but also start to hint at how this complexity actually leads to “emergent” phenomena...

\* As you'll appreciate later on, the existence of quasicrystals was something of a surprise (2011 Chemistry Nobel Prize for Dan Shechtman). They are beyond the scope of this course, and it is included here as a pretty picture of a “crystal”

# “More is different”

4 August 1972, Volume 177, Number 4047

## SCIENCE

### More Is Different

Broken symmetry and the nature of the hierarchical structure of science.

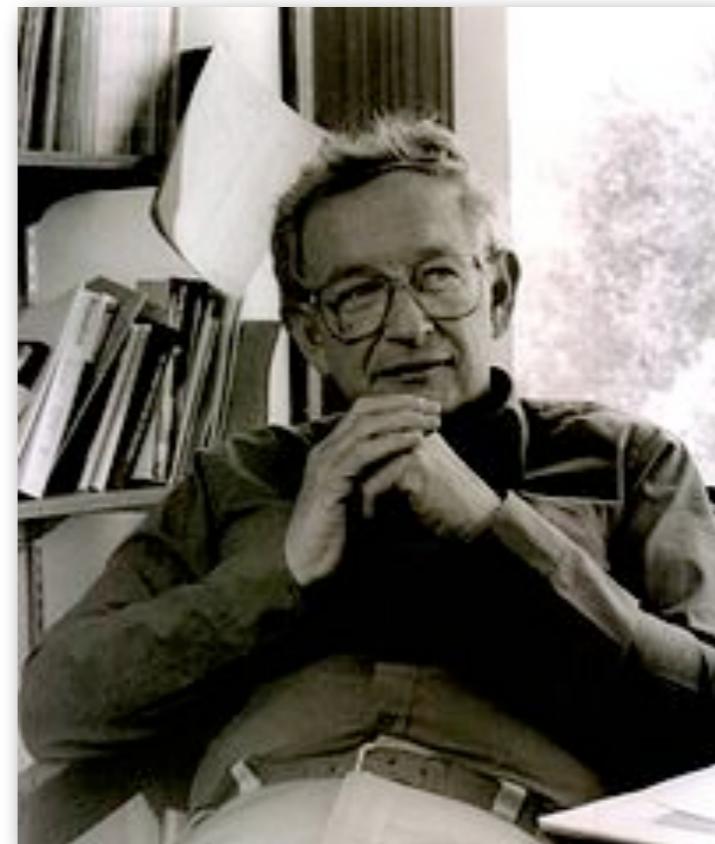
P. W. Anderson

The reductionist hypothesis may still be a topic for controversy among philosophers, but among the great majority

planation of phenomena in terms of known fundamental laws. As always, distinctions of this kind are not unambiguous, but they are clear in most cases. Solid

less relevance they seem to have to very real problems of the rest of science, much less to those of society.

The constructionist hypothesis breaks down when confronted with the difficulties of scale and complexity. behavior of large and complex aggregates of elementary particles, it turns out, is not to be understood in terms of a simple extrapolation of the properties of a few particles. Instead, each level of complexity entirely new properties appear, and the understanding of the new behaviors requires a search which I think is as fundamental in its nature as any other. That seems to me that one may arrange sciences roughly linearly in a hierarchy according to the idea: The elements of science X obey the law



DOI: 10.1126/science.177.4047.393

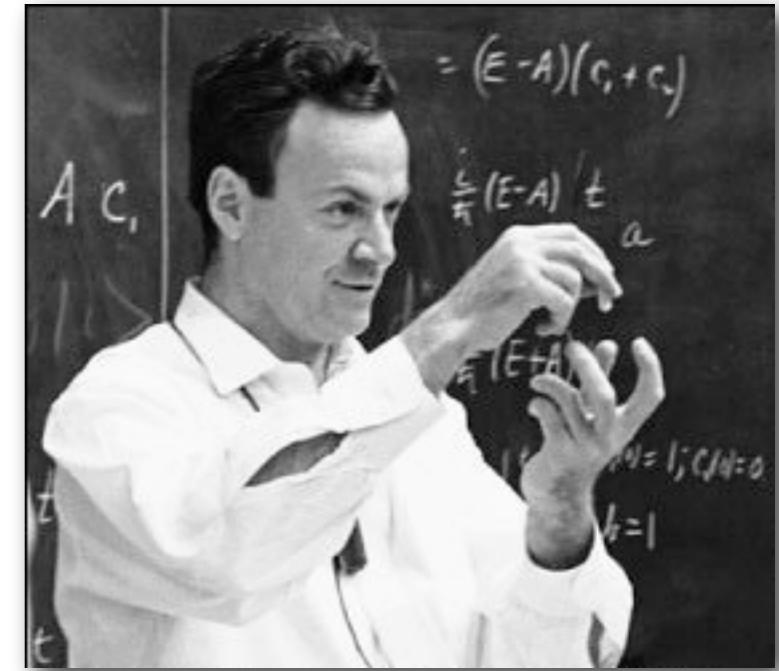
# Chapter I - Crystal Structures

In this course, we are concerned with crystalline solids in which the atoms are arranged on a perfect lattice (i.e. no defects, impurities, or boundaries). This is because translational symmetry allows us to generate excellent models in spite of the complexity associated with dealing with  $\sim N_A$  atoms.

Note that there are some solids which are not crystalline. We call these “amorphous” solids, and are characterised by the absence of long-range order; there may, however, be short-range order. Although this is a very interesting class of materials, we will not be dealing with them in this course.

We will start with some preliminaries which should mostly be revision, before starting to look properly at crystal structures.

Chemical bonding is a delicate balance of attractive and repulsive forces



We will discuss the attractive part in a moment, but where does the repulsion come from?

Richard Feynman



→ Pauli exclusion principle means that when the electron “clouds” of atoms start to overlap, they need to maintain orthogonality - this costs energy

(Revision - first year)

# Chemical bonding in crystalline solids

covalent  
e.g. diamond

ionic  
e.g. NaCl

metallic

primary

van der Waals  
e.g. noble gases

hydrogen  
e.g. ice, DNA

secondary

# Atoms, orbitals and electron configuration

Schrödinger equation for hydrogenic atom : note :  $\psi = \psi(r, \theta, \phi)$

$$\frac{1}{r^2} \frac{\partial}{\partial r} \left( r^2 \frac{\partial \psi}{\partial r} \right) + \frac{1}{r^2 \sin \theta} \frac{\partial}{\partial \theta} \left( \sin \theta \frac{\partial \psi}{\partial \theta} \right) + \frac{1}{r^2 \sin^2 \theta} \frac{\partial^2 \psi}{\partial \phi^2} + \frac{2m}{\hbar^2} (E - U) \psi = 0$$

Separation of variables gives radial part  $R_{nl}(r)$  and an angular part

$$R_{10} = 2 \left( \frac{Z}{a_0} \right)^{\frac{3}{2}} e^{-Zr/a_0}$$

Bohr radius :  $a_0 = \frac{\hbar}{\alpha mc}$

$$R_{21} = \frac{1}{2\sqrt{6}} \left( \frac{Z}{a_0} \right)^{\frac{3}{2}} \left( \frac{Zr}{a_0} \right) e^{-Zr/2a_0}$$

$$R_{20} = \frac{1}{\sqrt{2}} \left( \frac{Z}{a_0} \right)^{\frac{3}{2}} \left( 1 - \frac{1}{2} \frac{Zr}{a_0} \right) e^{-Zr/2a_0}$$

$$R_{32} = \frac{1}{9\sqrt{30}} \left( \frac{Z}{a_0} \right)^{\frac{3}{2}} \left( \frac{2Zr}{3a_0} \right)^2 e^{-Zr/3a_0}$$

$$R_{31} = \frac{2\sqrt{2}}{9\sqrt{3}} \left( \frac{Z}{a_0} \right)^{\frac{3}{2}} \left( \frac{2Zr}{3a_0} \right) \left( 1 - \frac{1}{4} \frac{2Zr}{3a_0} \right) e^{-Zr/3a_0}$$

$$R_{30} = \frac{2}{3\sqrt{3}} \left( \frac{Z}{a_0} \right)^{\frac{3}{2}} \left( 1 - \frac{2Zr}{3a_0} + \frac{1}{6} \left( \frac{2Zr}{3a_0} \right)^2 \right) e^{-Zr/3a_0}$$

$$\psi_{nlm}(r, \theta, \phi) = R_{nl}(r) Y_{lm}(\theta, \phi)$$



these are the spherical harmonics

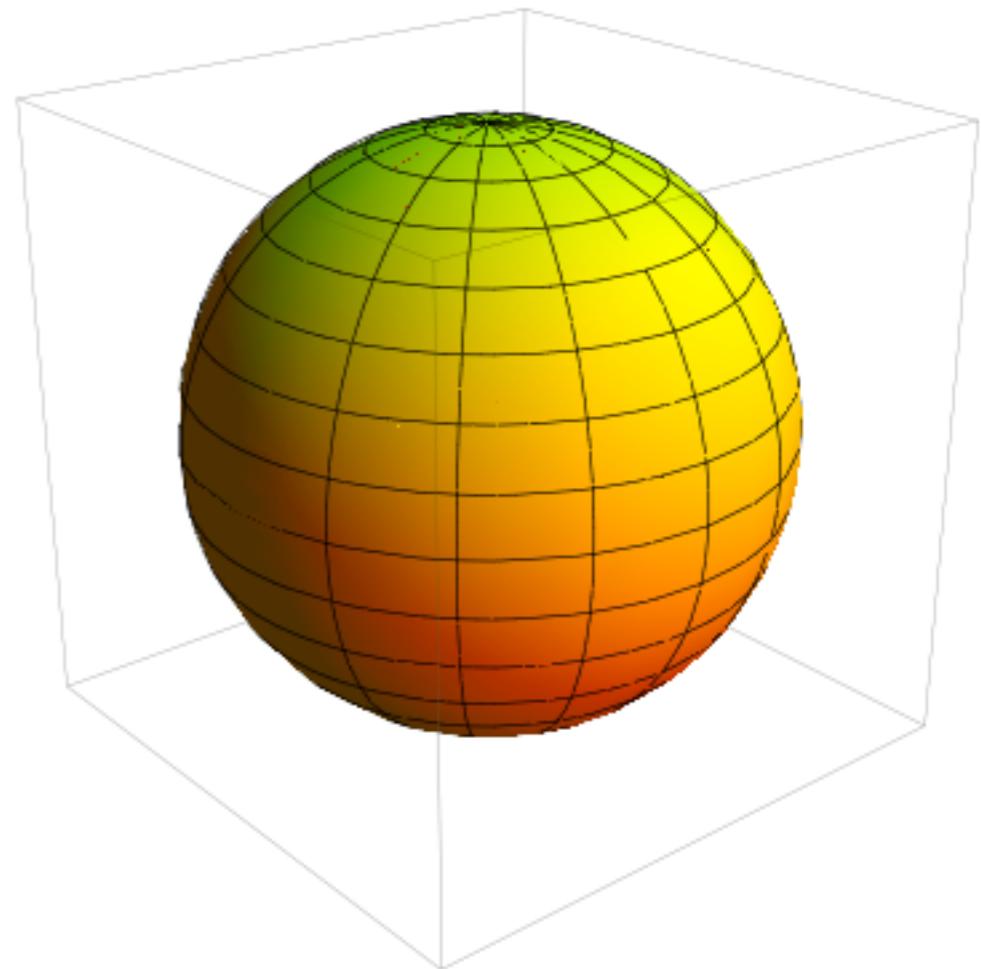
## s orbitals

e.g.  $\psi_{n00} = R_{n0}(r)Y_{00}$

$$Y_{00} = \frac{1}{\sqrt{4\pi}}$$

How many electrons can an orbital accommodate? It's  $2(2l + 1)$

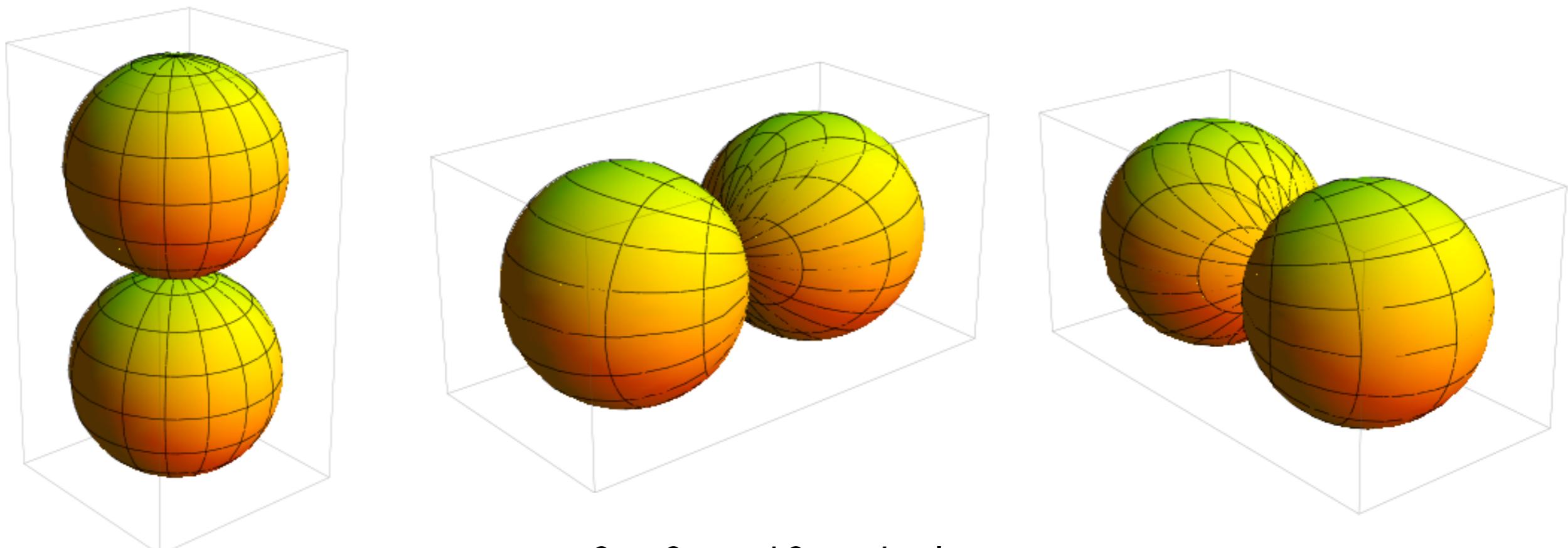
Thus an s orbital ( $l = 0$ ) will take 2 electrons



[http://demonstrations.wolfram.com/  
VisualizingAtomicOrbitals/](http://demonstrations.wolfram.com/VisualizingAtomicOrbitals/)

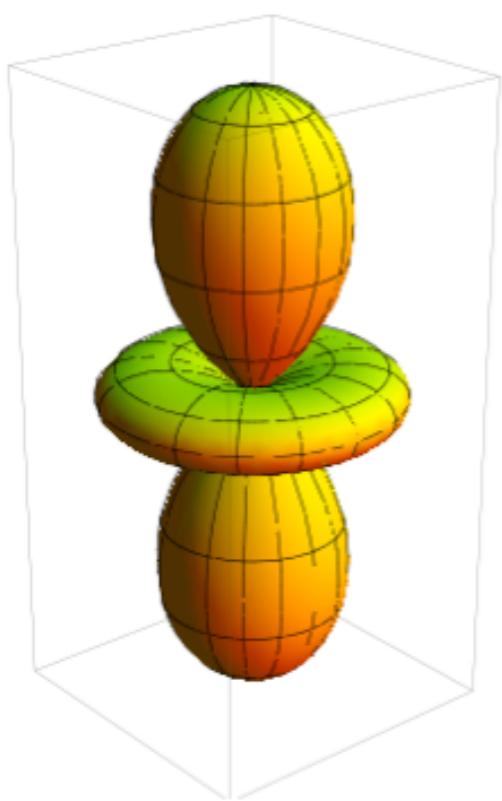
# p orbitals

There are three p orbitals ( $p_x$ ,  $p_y$  and  $p_z$ ), each of which will take 2 electrons, so a total of 6 electrons can be accommodated.

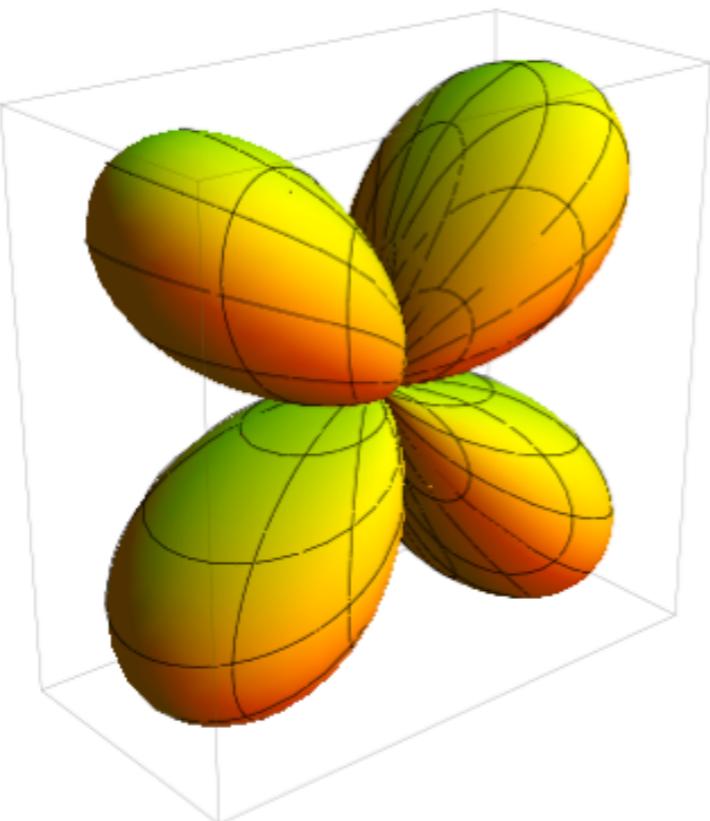


$2p_z$  ,  $2p_x$  and  $2p_y$  orbitals  
[http://demonstrations.wolfram.com/  
VisualizingAtomicOrbitals/](http://demonstrations.wolfram.com/VisualizingAtomicOrbitals/)

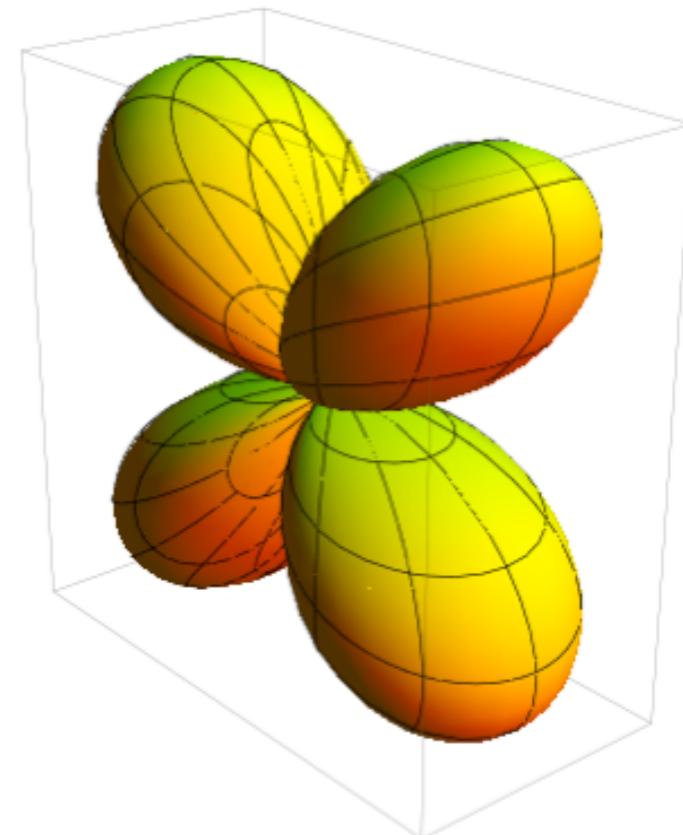
# d orbitals : 10 electrons in five orbitals



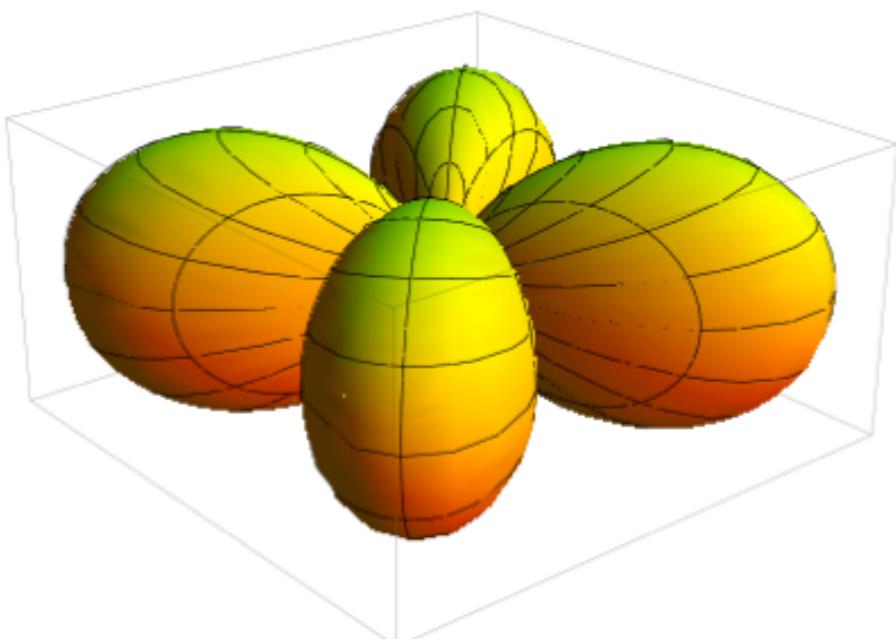
$d_{z^2}$



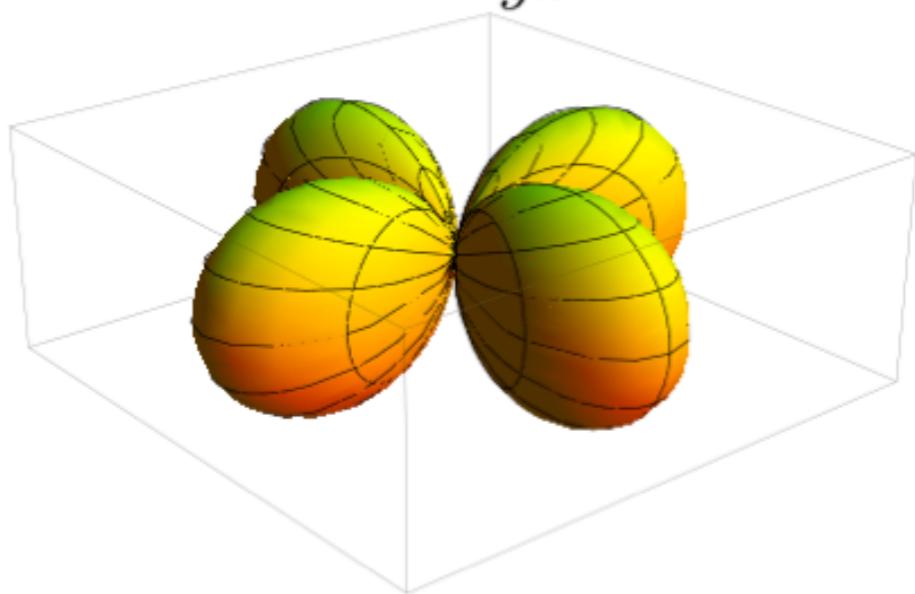
$d_{zx}$



$d_{yz}$



$d_{xy}$



$d_{x^2-y^2}$

3d orbitals  
[http://demonstrations.wolfram.com/  
VisualizingAtomicOrbitals/](http://demonstrations.wolfram.com/VisualizingAtomicOrbitals/)

# Atoms, orbitals and electron configuration

# Periodic Table of Chemical Elements

	1 IA	Periodic Table of Chemical Elements																		18 VIIIA																		
1	1 H Hydrogen 1.0079	2 IIA																			2 He Helium 4.0025																	
2	3 Li Lithium 6.941	4 Be Beryllium 9.0122																			10 Ne Neon 20.180																	
3	11 Na Sodium 22.990	12 Mg Magnesium 24.305																			18 Ar Argon 39.948																	
4	19 K Potassium 39.098	20 Ca Calcium 40.078	21 Sc Scandium 44.956	22 Ti Titanium 47.867	23 V Vanadium 50.942	24 Cr Chromium 51.996	25 Mn Manganese 54.938	26 Fe Iron 55.845	27 Co Cobalt 58.933	28 Ni Nickel 58.693	29 Cu Copper 63.546	30 Zn Zinc 65.39	31 Ga Gallium 69.723	32 Ge Germanium 72.64	33 As Arsenic 74.921	34 Se Selenium 78.96	35 Br Bromine 79.904	36 Kr Krypton 83.8																				
5	37 Rb Rubidium 85.468	38 Sr Strontium 87.62	39 Y Yttrium 88.906	40 Zr Zirconium 91.224	41 Nb Niobium 92.906	42 Mo Molybdenum 95.94	43 Tc Technetium 96	44 Ru Ruthenium 101.07	45 Rh Rhodium 102.91	46 Pd Palladium 106.42	47 Ag Silver 107.87	48 Cd Cadmium 112.41	49 In Indium 114.82	50 Sn Tin 118.71	51 Sb Antimony 121.76	52 Te Tellurium 127.6	53 I Iodine 126.9	54 Xe Xenon 131.29																				
6	55 Cs Caesium 132.91	56 Ba Barium 137.33	57-71 La-Lu Lanthanide 178.49	72 Hf Hafnium 180.95	73 Ta Tantalum 183.84	74 W Tungsten 186.21	75 Re Rhenium 190.23	76 Os Osmium 192.22	77 Ir Iridium 195.08	78 Pt Platinum 196.97	79 Au Gold 200.59	80 Hg Mercury 204.38	81 Tl Thallium 207.2	82 Pb Lead 208.99	83 Bi Bismuth 209	84 Po Polonium 210	85 At Astatine 210	86 Rn Radon 222																				
7	87 Fr Francium 223	88 Ra Radium 226	89-103 Ac-Lr Actinide 226	104 Rf Rutherfordium 261	105 Db Dubnium 262	106 Sg Seaborgium 266	107 Bh Bohrium 264	108 Hs Hassium 277	109 Mt Meitnerium 268	110 Ds Darmstadtium 281	111 Rg Roentgenium 280	112 Uub Ununbium 285	113 Uut Ununtrium 284	114 Uuq Ununquadium 289	115 Uup Ununpentium 288	116 Uh Ununhexium 293	117 Uus Ununseptium 292	118 Uuo Ununoctium 294																				

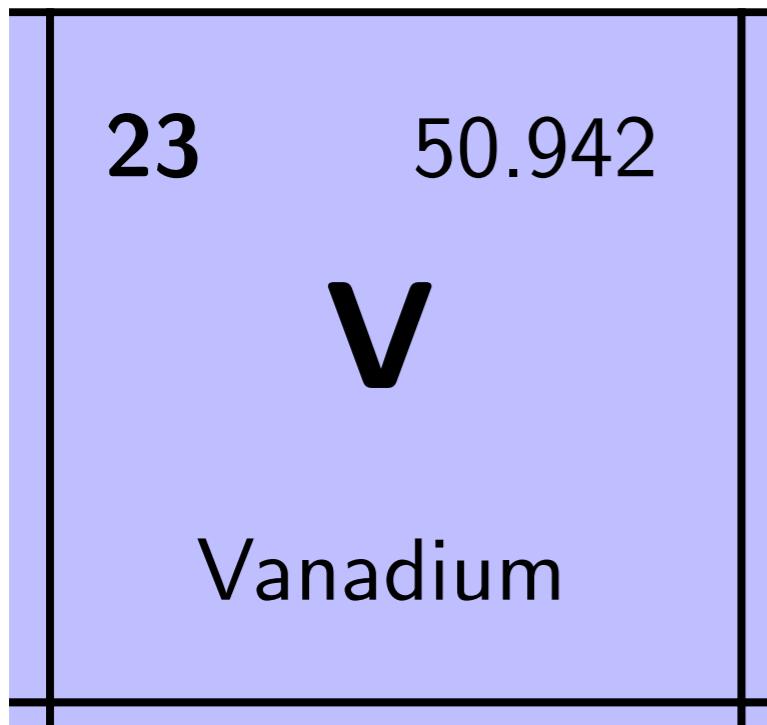
- █ Alkali Metal
- █ Alkaline Earth Metal
- █ Metal
- █ Metalloid
- █ Non-metal
- █ Halogen
- █ Noble Gas
- █ Lanthanide/Actinide

57 La Lanthanum 138.91	58 Ce Cerium 140.12	59 Pr Praseodymium 140.91	60 Nd Neodymium 144.24	61 Pm Promethium 145	62 Sm Samarium 150.36	63 Eu Europium 151.96	64 Gd Gadolinium 157.25	65 Tb Terbium 158.93	66 Dy Dysprosium 162.50	67 Ho Holmium 164.93	68 Er Erbium 167.26	69 Tm Thulium 168.93	70 Yb Ytterbium 173.04	71 Lu Lutetium 174.97
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z <b>Symbol</b>	mass	name	man-made
89 Ac Actinium	227	90 Th Thorium	232.04
91 Pa Protactinium	231.04	92 U Uranium	238.03
93 Np Neptunium	237	94 Pu Plutonium	244
95 Am Americium	243	96 Cm Curium	247
97 Bk Berkelium	247	98 Cf Californium	251
99 Es Einsteinium	252	100 Fm Fermium	257
101 Md Mendelevium	258	102 No Nobelium	259
103 Lr Lawrencium	262		

# Electron configuration

How are the electrons divided into various orbitals, in say, the 3d transition metal V?



Periodic Table of Chemical Elements

The table includes the following sections:

- Groups:** 1 IA, 2 IIA, 3 IIIA, 4 IVB, 5 VB, 6 VIB, 7 VIIB, 8 VIIIB, 9 VIIIB, 10 VIIIB, 11 IB, 12 IIB, 13 IIIA, 14 IVA, 15 VA, 16 VIA, 17 VIIA, 18 VIIIA.
- Periods:** 1 through 7.
- Elements:** Hydrogen, Helium, Lithium, Beryllium, Sodium, Magnesium, Potassium, Calcium, Scandium, Titanium, Vanadium, Chromium, Manganese, Iron, Cobalt, Nickel, Copper, Zinc, Gallium, Germanium, Arsenic, Selenium, Bromine, Krypton, Rubidium, Strontium, Yttrium, Zirconium, Niobium, Molybdenum, Technetium, Ruthenium, Rhodium, Palladium, Silver, Cadmium, Indium, Tin, Antimony, Tellurium, Iodine, Xenon, Cs, Ba, La-Lu, Hf, Ta, W, Re, Os, Ir, Pt, Au, Hg, Tl, Pb, Bi, Po, At, Rn, Fr, Ra, Ac-Lr, Rf, Db, Sg, Bh, Hs, Mt, Ds, Rg, Uub, Ut, Uup, Uuh, Uus, Uuo, La, Ce, Pr, Nd, Pm, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Lu, Yb, Lu, Ac, Th, Pa, U, Np, Pu, Am, Cm, Bk, Cf, Es, Fm, Md, No, Lr.
- Legend:** Alkali Metal, Alkaline Earth Metal, Metal, Metalloid, Non-metal, Halogen, Noble Gas, Lanthanide/Actinide.
- Bottom Row:** Z (mass) Symbol Name, m.p.-m.d.

23 electrons in total, so we have  $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^3$

Bit tedious to write out the whole thing, so we can abbreviate as



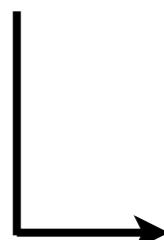
[Ar] is closest closed shell,  
so we count from there

# I.1 Description of Crystal Structures

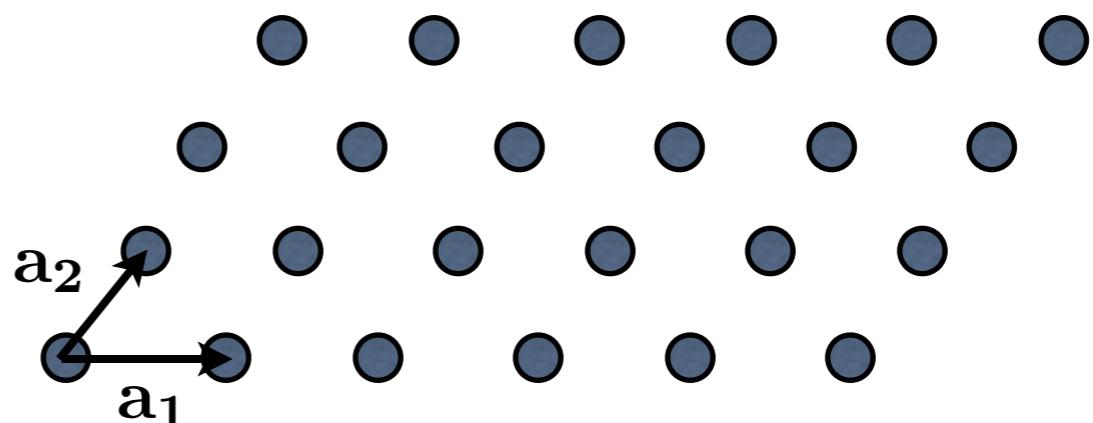
A crystal can be described through a mathematical description of the lattice. This lattice is a set of points which are generated by multiples  $(m,n,o)$  of some generating vectors  $(\mathbf{a}_1, \mathbf{a}_2, \mathbf{a}_3)$ :

$$\mathbf{R} = m\mathbf{a}_1 + n\mathbf{a}_2 + o\mathbf{a}_3$$

Such a lattice of points is also called a *Bravais lattice*, and the vectors are called *primitive vectors*. How many Bravais lattices are there that have a different symmetry?



in 2D : 5  
in 3D : 14



An example of a 2D Bravais lattice

# The 14 Bravais Lattices

[www.quimica3d.com](http://www.quimica3d.com)

November, 2009

Last updated: January, 2011



UNICAMP Pintor Pedro Marenco

# An aside for general interest : Space Groups

7 crystal systems  
14 Bravais lattices  
230 Space Groups

## In practice, we work with Space Groups

Ref : J. Cryst. Growth 312, 3204 (2010)

### **Lu<sub>5</sub>Ir<sub>4</sub>Si<sub>10</sub> whiskers: morphology, crystal structure, superconducting and charge density wave transition studies**

C. Opagiste<sup>1</sup>, M. Leroux<sup>1</sup>, P. Rodière<sup>1</sup>, G. Garbarino<sup>2</sup>, S. Pairis<sup>1</sup>, P. Bordet<sup>1</sup> and P. Lejay<sup>1</sup>

<sup>1</sup>Institut Néel, CNRS / UJF, PB 166, 38042 Grenoble Cedex 9, France

<sup>2</sup>European Synchrotron Radiation Facility (ESRF), BP 220, 6 Rue Jules Horowitz,  
38043 Grenoble Cedex, France

#### **Abstract**

Highly perfect single crystal whiskers of Lu<sub>5</sub>Ir<sub>4</sub>Si<sub>10</sub> were successfully grown out of the melt. Details of the surface and morphology of the whiskers are presented. X-ray diffraction data confirmed that the whisker structure has the same tetragonal P4/mmb space group symmetry as bulk single crystals with lattice parameters  $a = 12.484(1)$  Å and  $c = 4.190(2)$  Å. By

*Table 1: Atomic coordinates and isotropic displacement parameters for Lu<sub>5</sub>Ir<sub>4</sub>Si<sub>10</sub>.*

Atom	Wyckoff pos.	X	Y	Z	Uiso (Å <sup>2</sup> )
Ir	8i	0.018812(18)	0.245589(17)	0	0.00530(5)
Lu1	2a	0	0	0	0.00691(8)
Lu2	4h	0.17411(2)	0.32589(2)	0.5	0.00760(6)
Lu3	4h	-0.11531(2)	0.38469(2)	0.5	0.00815(6)
Si1	4g	0.06628(15)	0.43372(15)	0	0.0064(4)
Si2	8i	0.19999(16)	0.16501(16)	0	0.0095(4)
Si3	8j	0.0035(2)	0.15636(17)	0.5	0.0157(5)

The next important concept is that of the *primitive unit cell*.

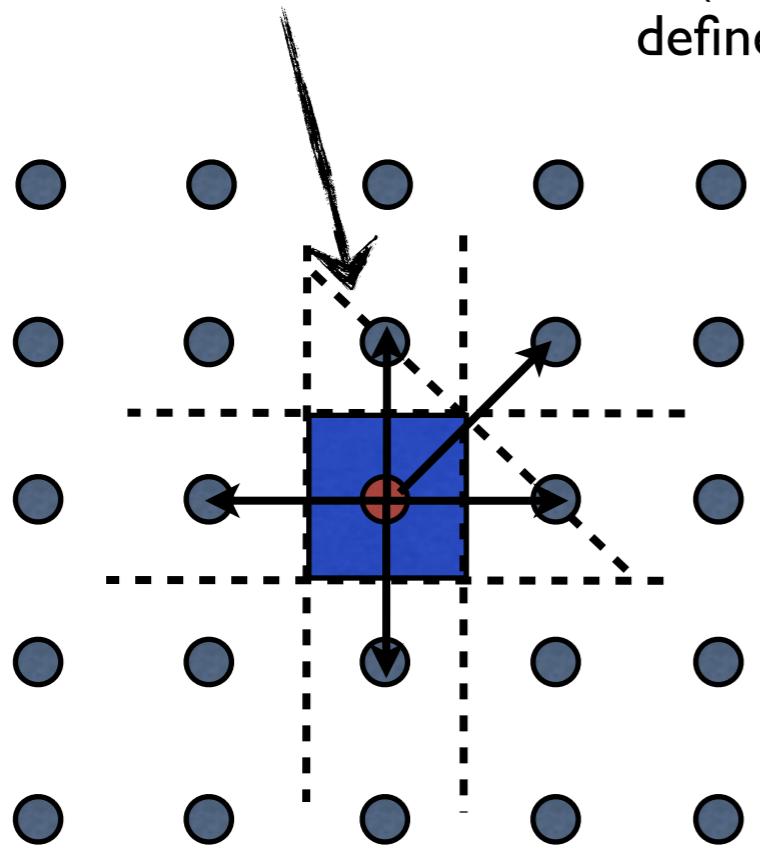
*Definition* : The primitive unit cell is the volume of space which, when translated through **all** of the vectors of the Bravais lattice, fills space without overlapping or leaving any voids.

The primitive unit cell contains *only* one lattice point. Of course, one can easily imagine any number of other (non-primitive) unit cells which contain more than one lattice point, and these will fill space without overlap by using some subset of the primitive vectors.

A special choice of primitive unit cell is the Wigner-Seitz cell; this is the region of space which is closer to one given lattice point than any other. It is constructed by drawing the planes defined by the perpendicular bisectors of lattice vectors. The volume surrounding the lattice point is then the Wigner-Seitz unit cell.

# How to construct the Wigner-Seitz unit cell :

this bisecting “plane” doesn’t contribute to the Wigner Seitz cell for this lattice, but when we introduce the idea of Brillouin zones (with the same construction) you can see that it is starting to define the 2nd Brillouin zone



Draw on the primitive vectors (and if necessary the other combinations which take you to neighbouring lattice sites - in fact, you could just draw on lines connecting the red atom with *all* its neighbours)  
and the planes (\*) which are their perpendicular bisectors



is the Wigner-Seitz unit cell

\* In 2D, the bisecting planes, are of course, just lines. In 3D, they really are planes.

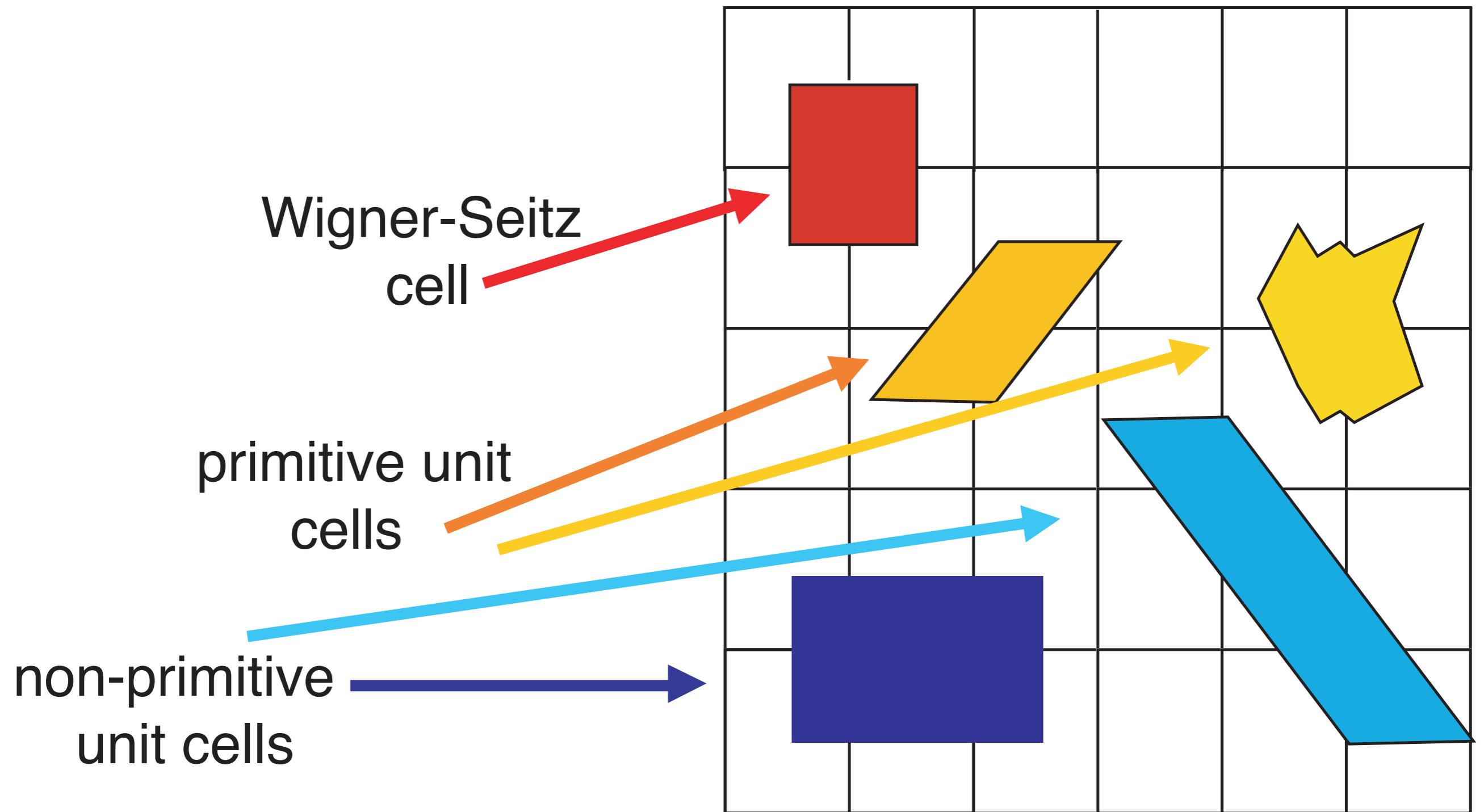
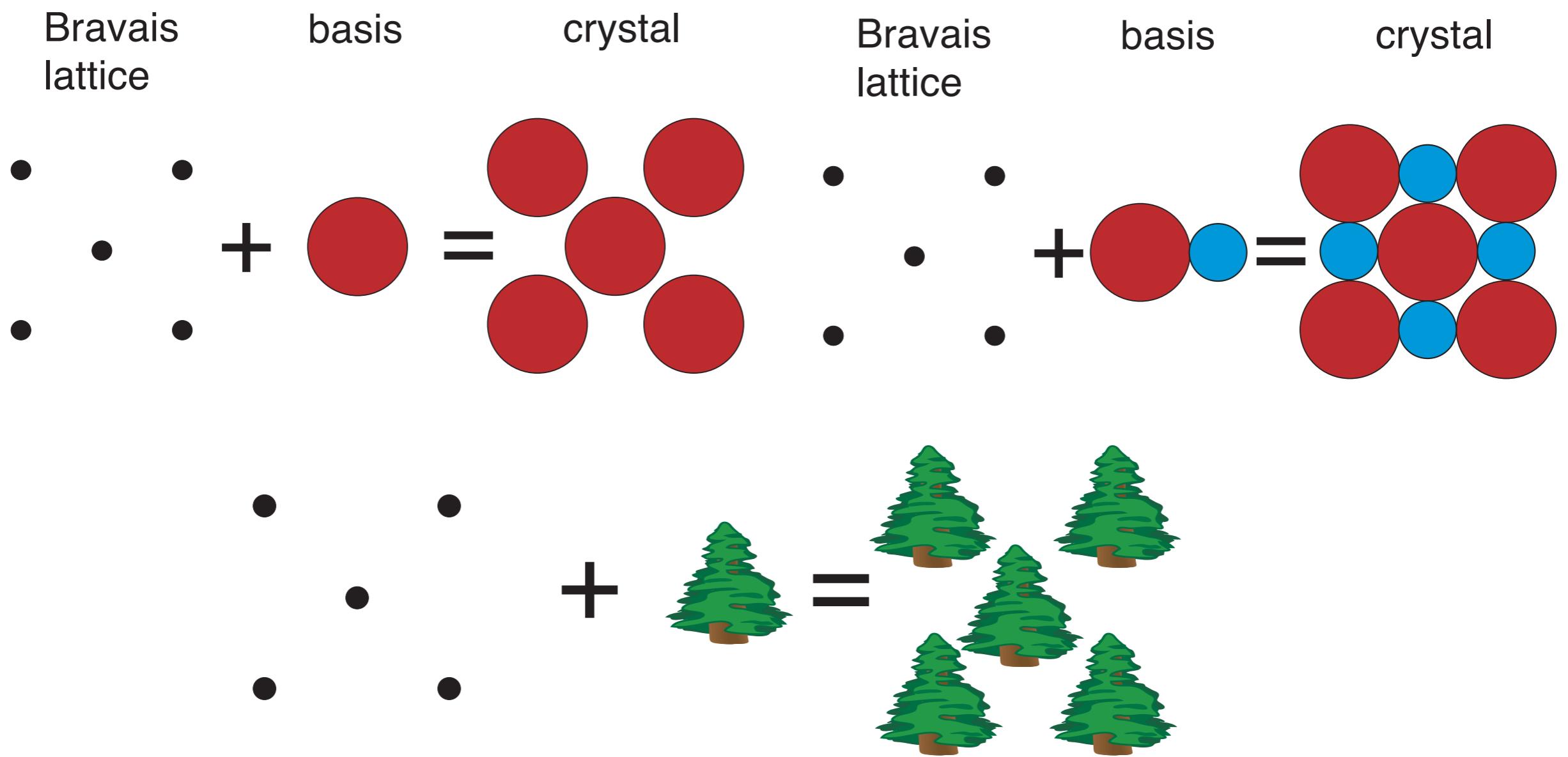


Illustration of several different unit cells (image : Hofmann)

To be able to describe an actual crystal structure, we need to introduce the concept of a *basis*. This is what we actually “place” on each lattice site, and can be a single atom, a few atoms, or even a complex molecule (in the case of a protein crystal).

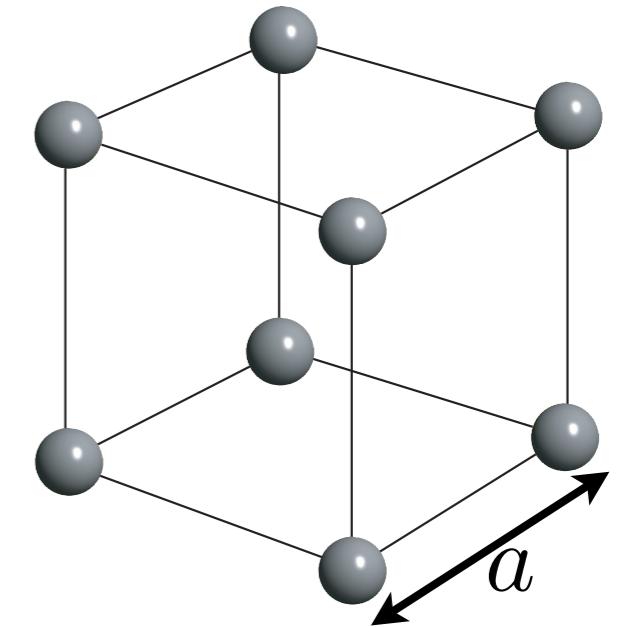


Illustrations of the concept of *basis* (image : Hofmann)

# I.2 Some Simple Crystal Structures

## Simple Cubic (sc)

This is not a very common structure amongst the elements. We will see why shortly.



Conventional unit cell of the sc structure  
(image : adapted from Hofmann)

### Primitive vectors:

$$\mathbf{a}_1 = a\hat{\mathbf{x}}$$

$\hat{\mathbf{x}}$  is unit vector in the x direction

$$\mathbf{a}_2 = a\hat{\mathbf{y}}$$

$$\mathbf{a}_3 = a\hat{\mathbf{z}}$$

Examples include  $\text{Cu}_3\text{Au}$ , cubic perovskites such as  $\text{PbTiO}_3$

Why is the simple cubic structure so rare amongst the elements?

Hint - ask a greengrocer.

It's all about the packing!



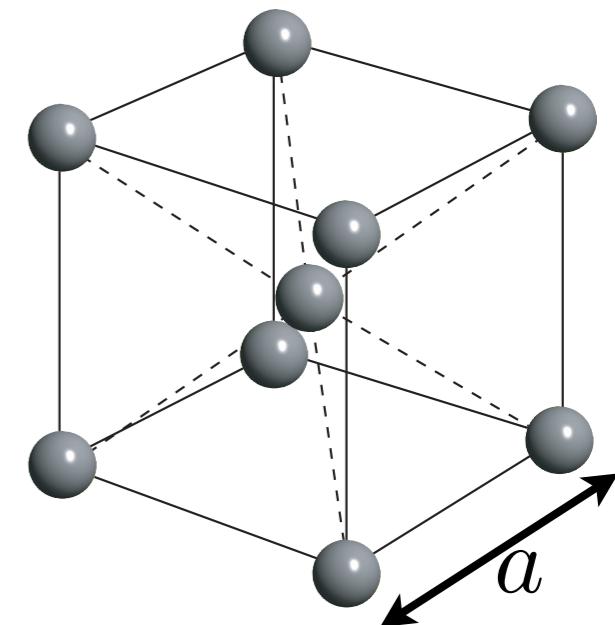
Stacked fruit  
(image : Peter Griffin -  
public domain)

Exercise - show that the packing fraction for hard spheres (no overlap!) in the simple cubic structure is 0.52.

We can do a little better (0.68) by putting something in the middle - we call this the body-centred cubic or bcc structure

# Body-centred cubic (bcc)

This is a much common structure amongst the elements e.g. alkali metals (e.g. Li, Na), some 3d transition metals such as Cr, V.



Primitive vectors:

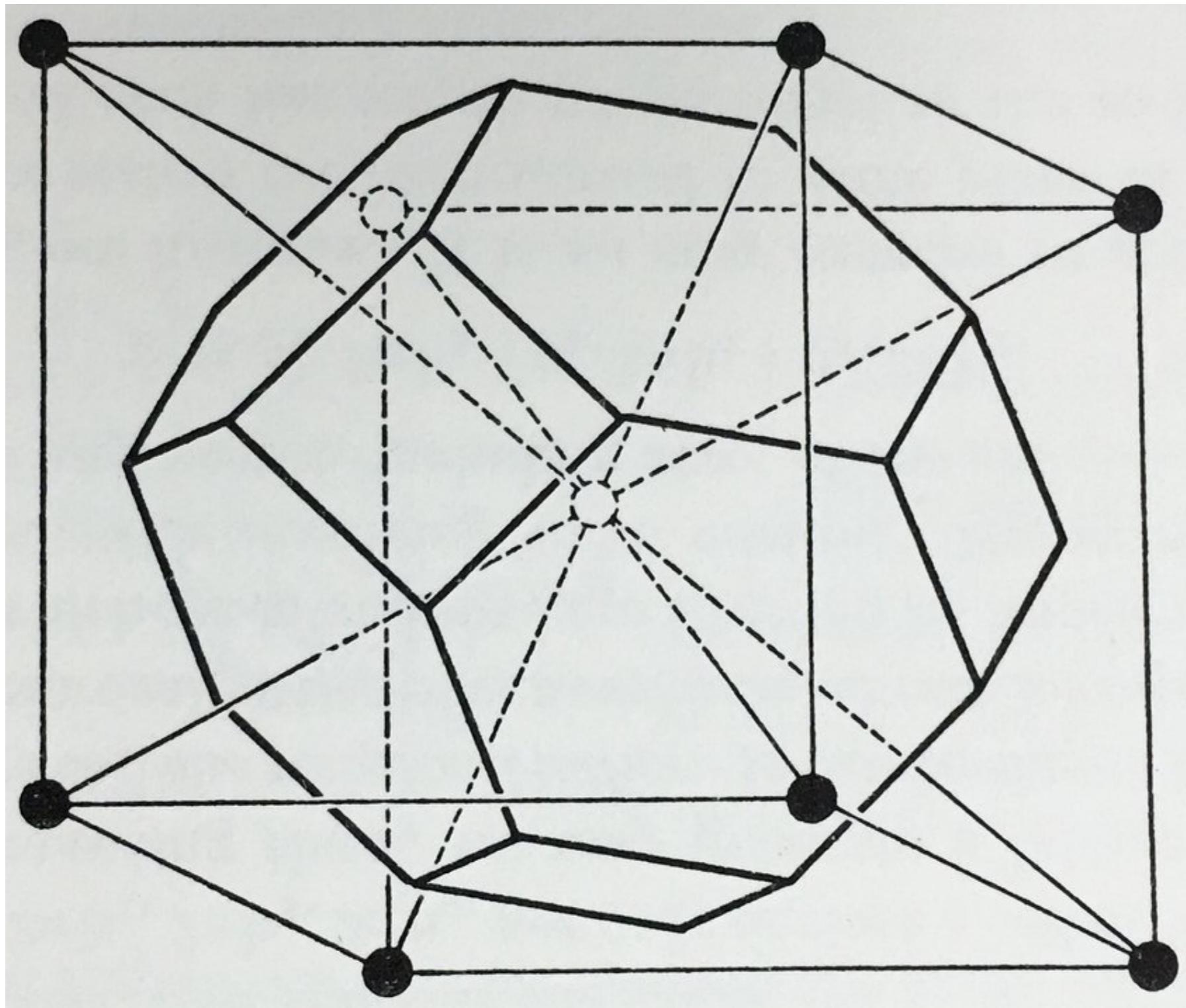
Conventional unit cell of  
the bcc structure  
(image : Hofmann)

$$\mathbf{a}_1 = \frac{a}{2}(\hat{\mathbf{x}} + \hat{\mathbf{y}} - \hat{\mathbf{z}})$$

$$\mathbf{a}_2 = \frac{a}{2}(-\hat{\mathbf{x}} + \hat{\mathbf{y}} + \hat{\mathbf{z}})$$

$$\mathbf{a}_3 = \frac{a}{2}(\hat{\mathbf{x}} - \hat{\mathbf{y}} + \hat{\mathbf{z}})$$

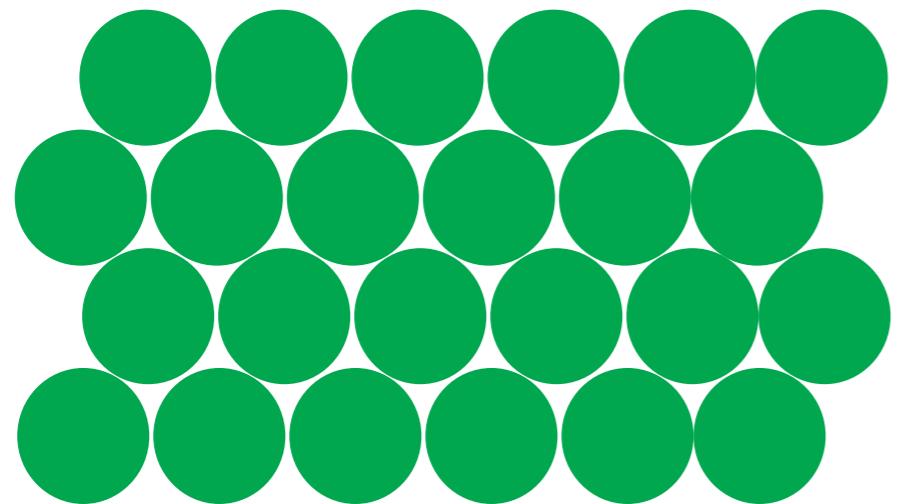
But it's still not close-packed.



Wigner-Seitz (primitive) unit cell for bcc structure  
(the truncated octahedron, sitting **inside** the cube)  
c.f. “conventional unit cell” drawn on previous slide

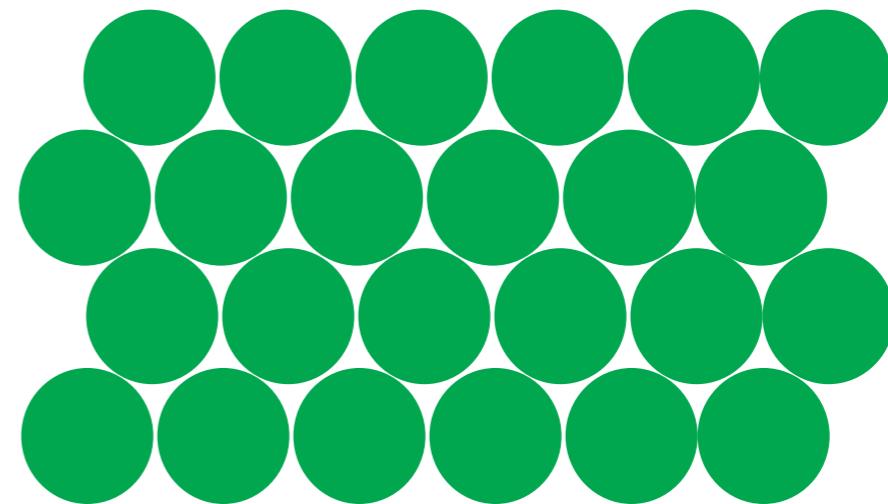
Close-packed structures are **face-centred cubic (fcc)** and **hexagonal closed packed (hcp)**

hcp



ABABAB...

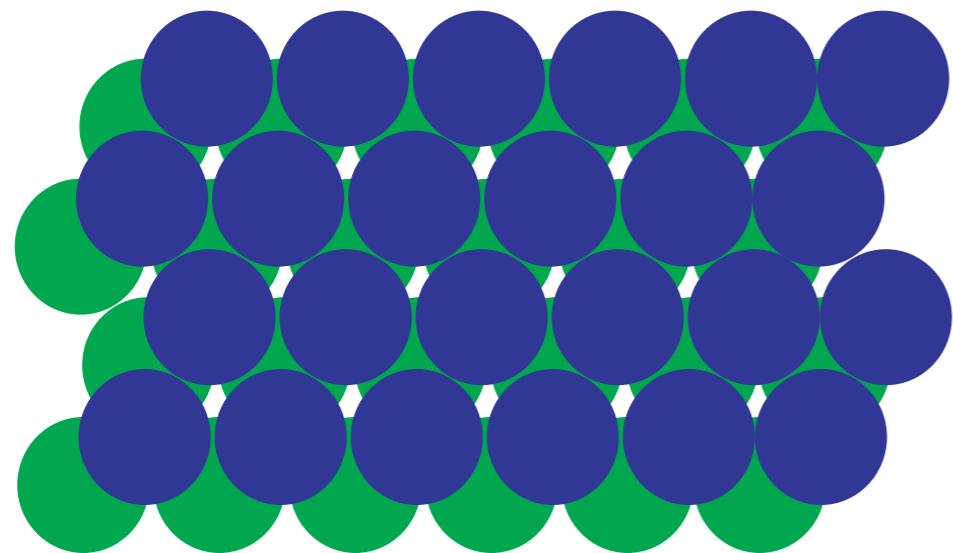
fcc



ABCABCABC...

Illustrations of close-packed planes (sequence of images : Hofmann)

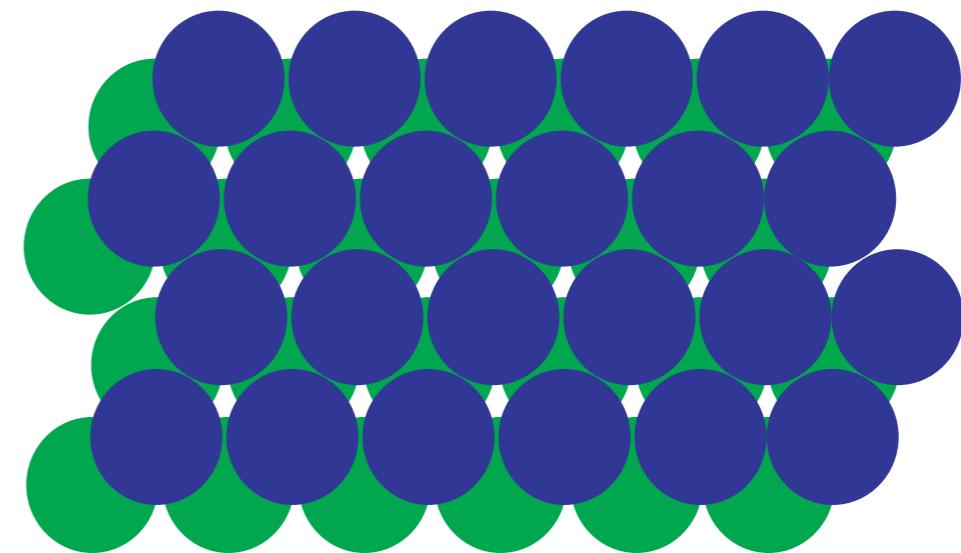
hcp



**ABABAB...**

Moving perpendicular  
to hexagonal planes

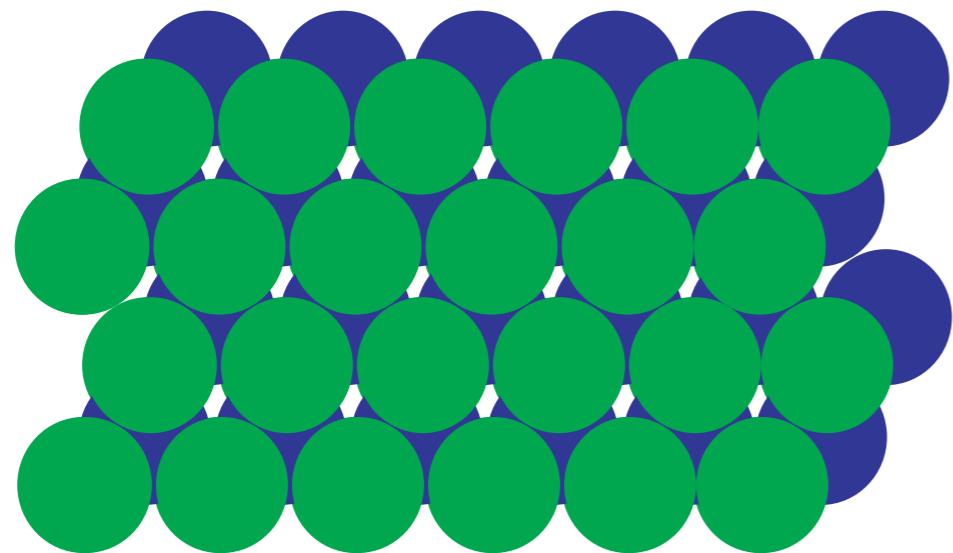
fcc



**ABCABCABC...**

Moving in direction of cube  
diagonal (i.e.  $\langle 111 \rangle$  direction - see later!)

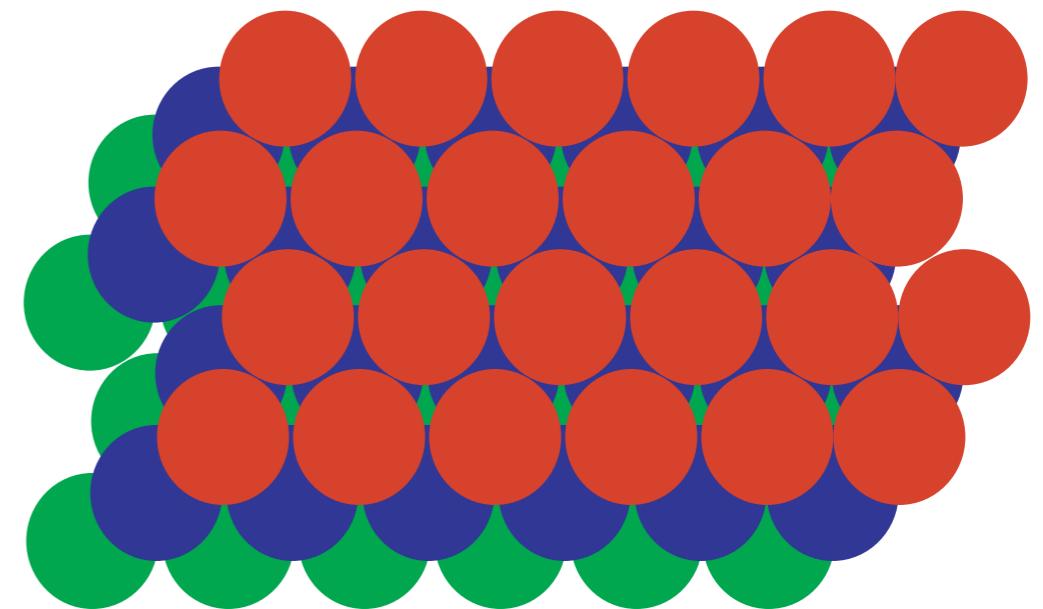
hcp



**ABABAB...**

Moving perpendicular  
to hexagonal planes

fcc

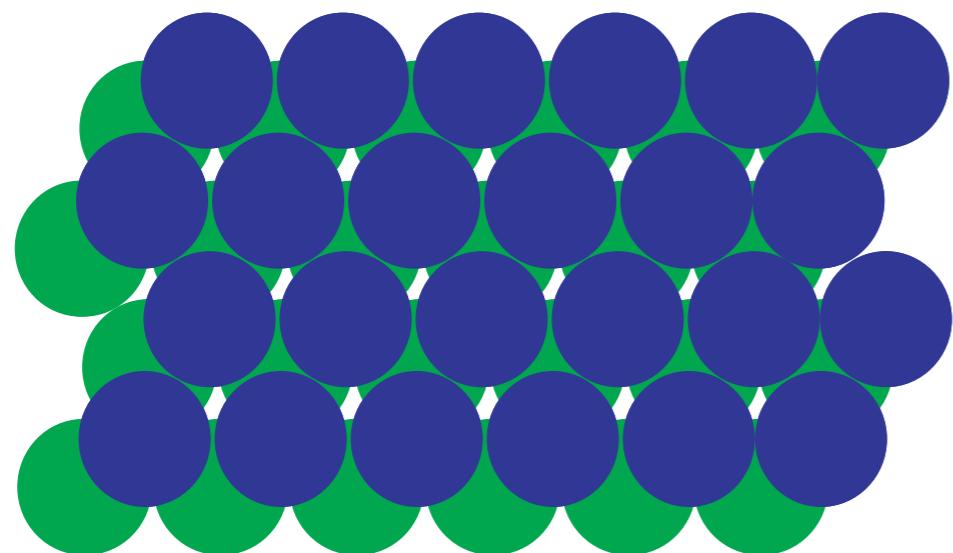


**ABCABCABC...**

Moving in direction of cube  
diagonal (i.e.  $\langle 111 \rangle$  direction - see later!)

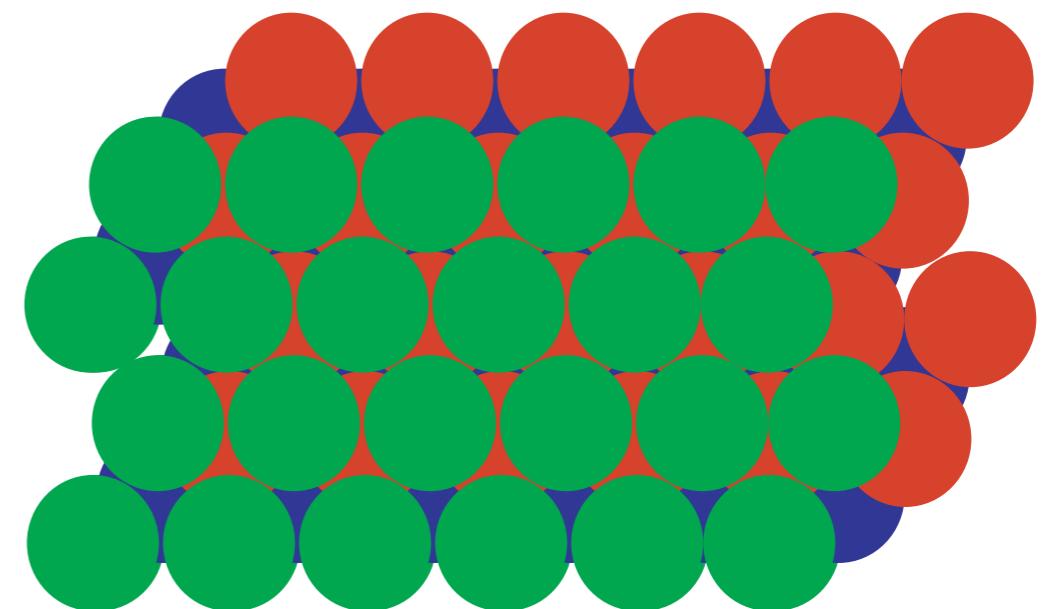
Packing fractions of both these structures is 0.74

hcp



ABABAB...

fcc



ABCABCABC...

There are some nice interactive demonstrations here

<http://demonstrations.wolfram.com/CubicClosePackingVersusHexagonalClosePacking>

# Face-centred cubic (fcc)

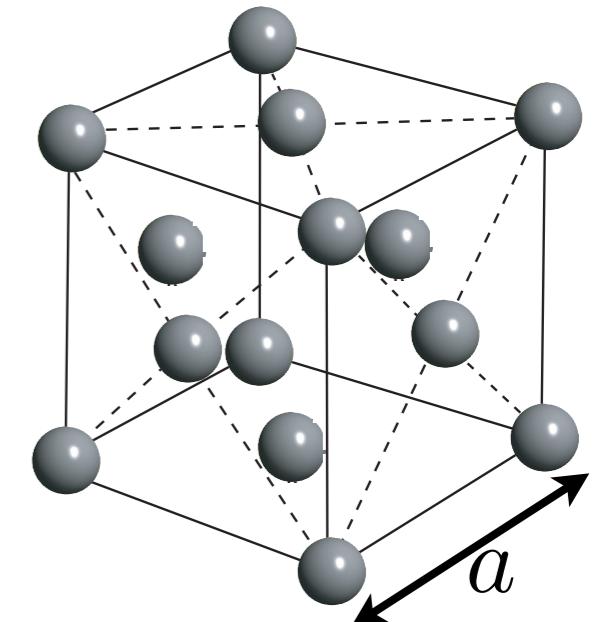
Again, this is a much common structure amongst the elements e.g. noble metals (Cu, Ag, Au), simple metals such as Al, and the 3d transition metal Ni.

Primitive vectors:

$$\mathbf{a}_1 = \frac{a}{2}(\hat{\mathbf{x}} + \hat{\mathbf{y}})$$

$$\mathbf{a}_2 = \frac{a}{2}(\hat{\mathbf{y}} + \hat{\mathbf{z}})$$

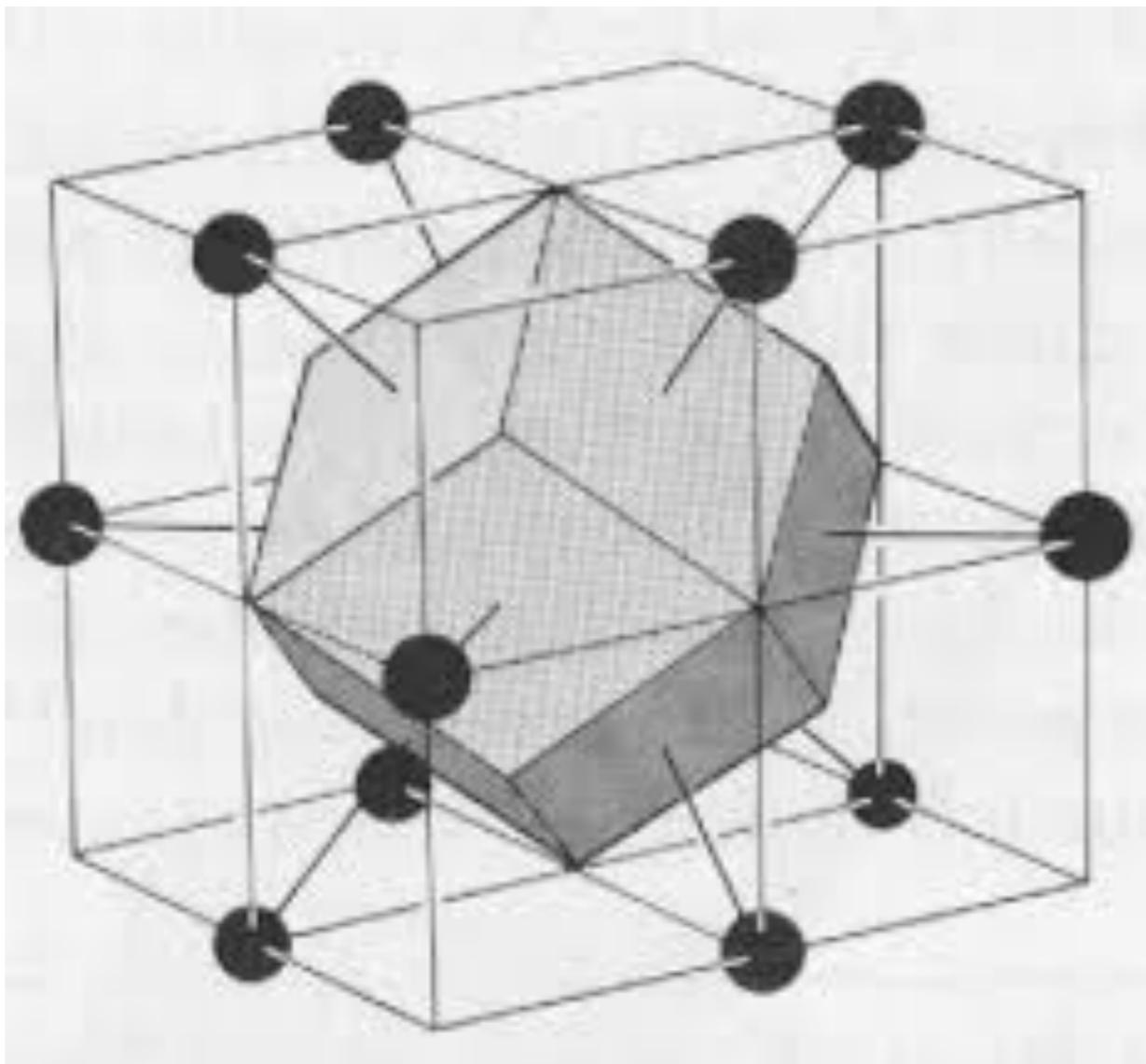
$$\mathbf{a}_3 = \frac{a}{2}(\hat{\mathbf{z}} + \hat{\mathbf{x}})$$



Conventional unit cell (\*) of the fcc structure  
(image : Hofmann)

Just like sc and bcc, this structure is also a Bravais lattice

\* If you're a little confused about different unit cells, then have a look at this video :  
<https://www.youtube.com/watch?v=KhDIIstODC8>



Wigner-Seitz (primitive) unit cell for fcc structure  
c.f. “conventional unit cell” drawn on previous slide

# Hexagonal close-packed (hcp)

Note that this structure is not a Bravais lattice as we need to associate two atoms with each point on an underlying hexagonal Bravais lattice. Examples include many rare-earth elements (e.g. Gd) and the transition metal Co.

Primitive vectors:

$$\mathbf{a}_1 = a \left( \frac{1}{2} \hat{\mathbf{x}} - \frac{\sqrt{3}}{2} \hat{\mathbf{y}} \right)$$

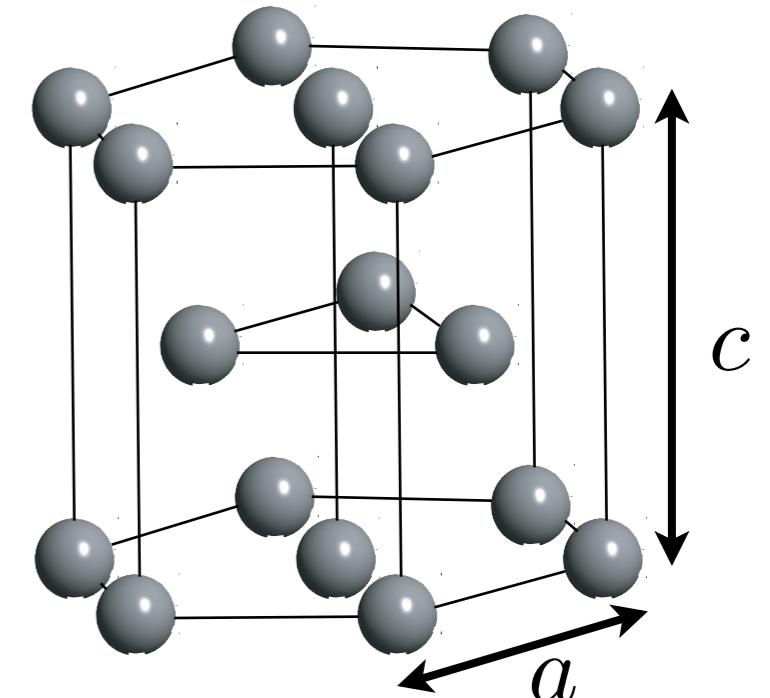
$$\mathbf{a}_2 = a \left( \frac{1}{2} \hat{\mathbf{x}} + \frac{\sqrt{3}}{2} \hat{\mathbf{y}} \right)$$

$$\mathbf{a}_3 = c \hat{\mathbf{z}}$$

Basis vectors :

$$\begin{aligned} \mathbf{R}_1 &= \frac{1}{3} \mathbf{a}_1 + \frac{2}{3} \mathbf{a}_2 + \frac{1}{4} \mathbf{a}_3 \\ \mathbf{R}_2 &= \frac{2}{3} \mathbf{a}_1 + \frac{1}{3} \mathbf{a}_2 + \frac{3}{4} \mathbf{a}_3 \end{aligned}$$

these vectors tell us where the (two) atoms in the basis are in the cell, and are expressed here in terms of the primitive vectors



Earlier it was said that there are 7 crystal systems

Cubic  
Hexagonal  
Rhombohedral  
Tetragonal  
Orthorhombic  
Monoclinic  
Triclinic

The seven crystal systems

and then we have

Primitive  
Body  
Face  
Base (x 3)

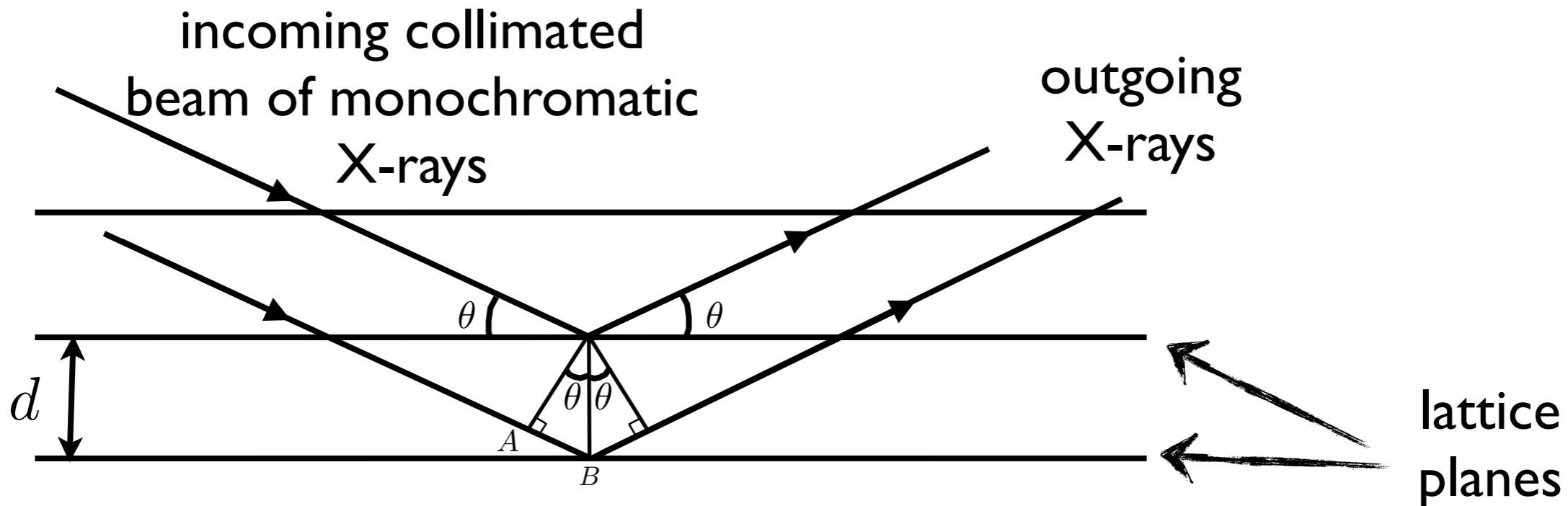
(but not all exist in all systems!)

# I.3 Determining Crystal Structures

How do we know what structures crystals have? By far the most common way of measuring crystal structures is by X-ray diffraction. In this section, we will look at X-ray diffraction, and see how it naturally leads into the idea of the *reciprocal lattice* which is the natural habitat of crystallographers and solid-state physicists.

X-rays interact with the charge distribution in a solid, and do so rather weakly. This means we can assume that they only scatter once, something which we call the *kinematic approximation*. We also assume that the source of X-rays, and the detector are sufficiently far away from the sample being studied that we can consider both the ingoing and outgoing waves as plane waves. The first observation, and explanation of X-ray diffraction was that of M. von Laue (1912), but we will first look at an alternative, simpler description due to W.L. and W.H. Bragg.

### I.3.1 The Bragg Theory of Diffraction



Consider the two rays which are specularly reflected by successive planes. For *constructive interference* to occur, the extra path length ( $2AB$ ) must be a whole number ( $n$ ) of wavelengths, i.e.

$$n\lambda = 2AB$$

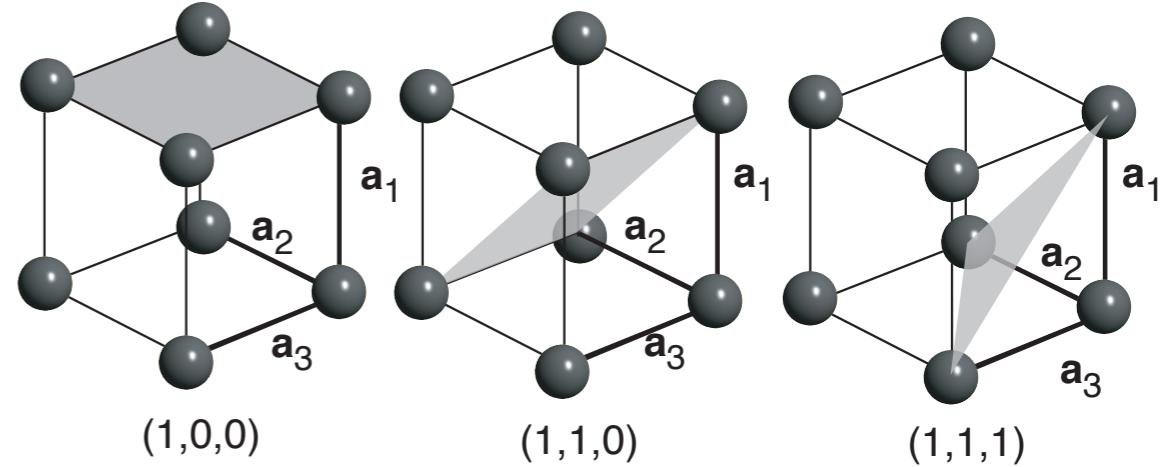
or  $n\lambda = 2d \sin \theta$  (“Bragg condition”)

We consider the planes to be uniform - but on what scale? Clearly, it is in comparison to wavelength of X-rays. But is this true? What do we need wavelength to be in order to see diffraction at all?

## I.3.2 Lattice Planes and Miller Indices

In the Bragg theory, we speak of “lattice planes”, but what precisely do we mean by a lattice plane? In fact, we can define it as containing at least three (\*) non-collinear points of a given Bravais lattice. We characterise these planes by their “Miller indices”. Here’s how :

- (i) Find where the plane intercepts the crystallographic axes (in lattice vector units)
- (ii) Take the reciprocal values of these three numbers
- (iii) Reduce these numbers to the smallest set of integers having the same ratio (if necessary) by multiplying by a factor



Three different lattice planes for the simple cubic structure (image : Hofmann)

\* If it contains only three, then the translational symmetry means that it will contain infinitely many

Let's look at an example.

- (i) Find where the plane intercepts the crystallographic axes

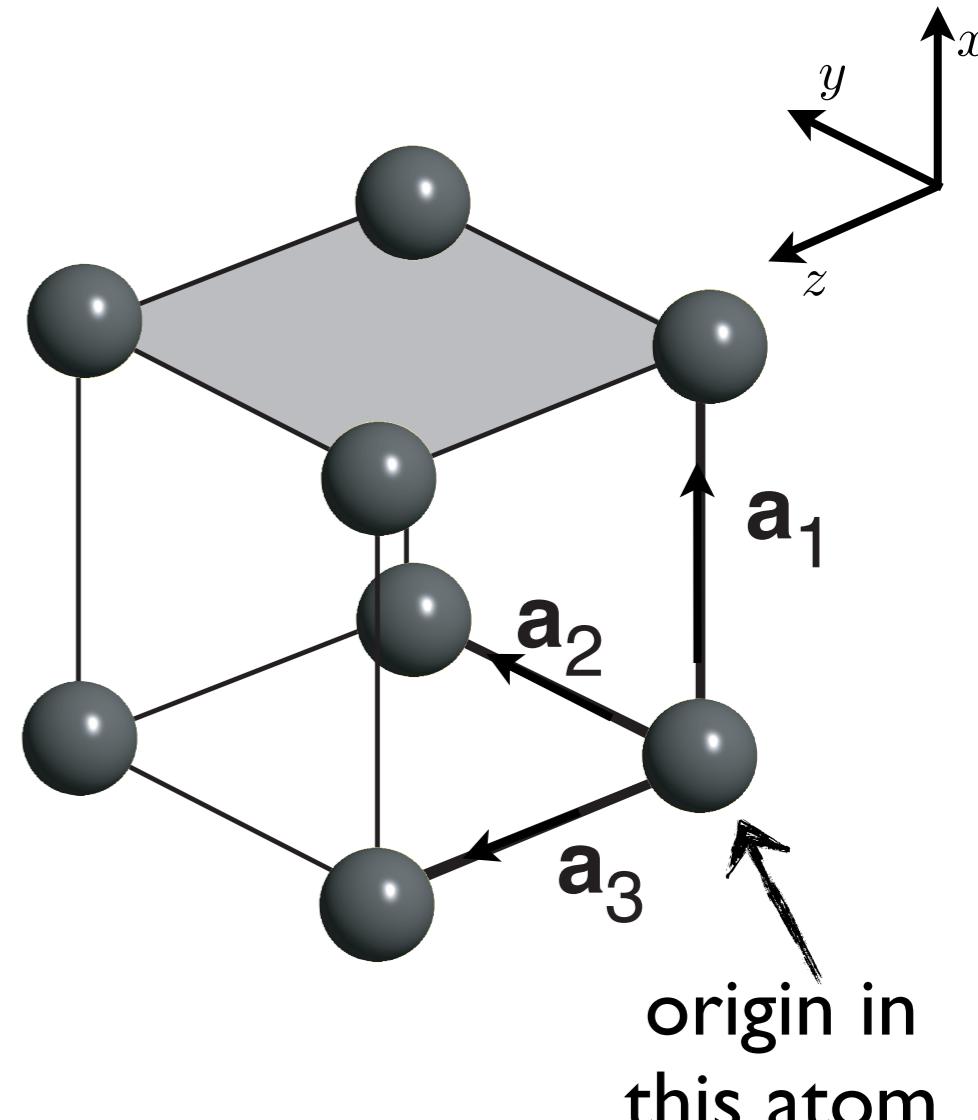
The plane cuts the x-axis at 1, but will never cross the y or z axes (i.e. will only do so at  $\infty$ ). So our three values are  $(1, \infty, \infty)$

- (ii) Take the reciprocal values of these three numbers

This is simply  $(1/1, 1/\infty, 1/\infty)$  or  $(1, 0, 0)$

- (iii) Reduce these numbers to the smallest set of integers having the same ratio (if necessary) by multiplying by a factor

We can't reduce these any further, so the Miller indices are  $(1, 0, 0)$



Miller indices, then are expressed (\*\*) in the form  $(h,k,l)$ . The family of planes e.g.  $(2,0,0)$ ,  $(5,0,0)$ ,  $(167,0,0)$  are all “ $(1,0,0)$ -type” planes, and can be described as  $\{1,0,0\}$  planes. (Note the use of curly brackets).

What if, in step (i), we cross the axis at a negative number, leading to, for example  $\left(-\frac{1}{2}, \frac{1}{3}, \frac{1}{4}\right)$  ?

In such a case, we would write the Miller indices as  $(\bar{2}, 3, 4)$  . Note the little “bar” above the 2, to show that it is really “-2”.

Also note (\*\*) that the direction  $[h,k,l]$  is perpendicular to the plane  $(h,k,l)$ . Similarly, the set of directions  $\langle 1,1,1 \rangle$  would include directions such as  $[3,3,3]$ ,  $[21,21,21]$  and  $[-1,-1,-1]$ , which, of course, we should write as  $[\bar{1}, \bar{1}, \bar{1}]$  .

What are the limitations of this Bragg theory? Firstly, it doesn’t tell us anything about what the lattice is made of (i.e. what the *basis* is). Secondly, why the X-rays should be reflected off the lattice planes is also rather obscure.

\*\*We normally write  $(hkl)$  and don’t include the commas.

\*\* For cubic systems



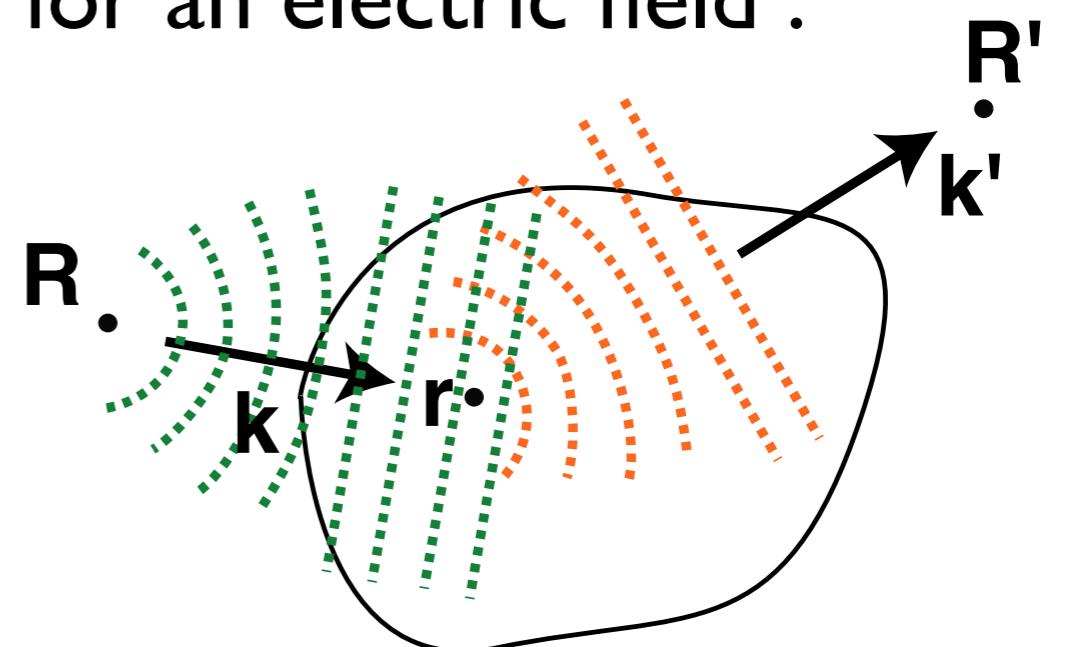
### I.3.3 The von Laue Theory of Diffraction

So how does an X-ray interact with the crystal? In fact, the scattering of the X-ray is due to its electromagnetic field causing the electrons in the material to oscillate at the same frequency as that of the field. These electrons then emit new X-rays, and this gives rise to an interference pattern.

Let's start with a general expression for an electric field :

$$\mathbf{E}(\mathbf{r}, t) = \mathbf{E}_0 e^{i\mathbf{k} \cdot \mathbf{r} - i\omega t}$$

$\mathbf{k}$  points in direction of wave propagation, with a magnitude of  $2\pi/\lambda$



Schematic of X-ray scattering from a sample. The source is at  $\mathbf{R}$  and the detector at  $\mathbf{R}'$ , both far from the sample such that we have plane waves  
(image : Hofmann)

Let's start by writing down the electric field at  $\mathbf{r}$  :

$$\mathbf{E}(\mathbf{r}, t) = \mathbf{E}_0 e^{i\mathbf{k}\cdot(\mathbf{r}-\mathbf{R}) - i\omega t}$$

Dropping the  $\mathbf{E}_0$ , since this will only affect the magnitude, this becomes :

$$\mathbf{E}(\mathbf{r}, t) \propto e^{i\mathbf{k}\cdot(\mathbf{r}-\mathbf{R}) - i\omega t}$$

Now consider the scattering generated by a small volume  $dV$  at  $\mathbf{r}$ . This will be isotropic, but we're interested in the direction towards the detector at  $\mathbf{R}'$ . The amplitude of the wave scattered in this direction is going to be proportional to *incoming* field and something which is related to the probability that scattering has occurred (which will be proportional to the charge density,  $\rho(\mathbf{r})$ ).

Noting that the outgoing wave propagates in the direction of  $\mathbf{k}'$ , this gives :

$$d\mathbf{E}(\mathbf{R}', t) \propto \mathbf{E}(\mathbf{r}, t) \rho(\mathbf{r}) dV e^{i\mathbf{k}' \cdot (\mathbf{R}' - \mathbf{r})}$$

Substituting in the expression we had for  $\mathbf{E}(\mathbf{r}, t)$ :

$$d\mathbf{E}(\mathbf{R}', t) \propto e^{i\mathbf{k} \cdot (\mathbf{r} - \mathbf{R})} \rho(\mathbf{r}) dV e^{i\mathbf{k}' \cdot (\mathbf{R}' - \mathbf{r})} e^{-i\omega t}$$

$$\propto e^{i(\mathbf{k}' \cdot \mathbf{R}' - \mathbf{k} \cdot \mathbf{R})} \rho(\mathbf{r}) dV e^{i(\mathbf{k} - \mathbf{k}') \cdot \mathbf{r}} e^{-i\omega t}$$



note that  $\mathbf{k}'$  is (approximately) the same for all points in the sample so in a moment we'll lose this whole term into the proportionality

So now we have the contribution to the electric field at the detector, coming from the small volume  $dV$  in the sample. To get the total, we need to integrate over the volume of the sample :

$$\mathbf{E}(\mathbf{R}', t) \propto e^{-i\omega t} \int_V \rho(\mathbf{r}) e^{i(\mathbf{k} - \mathbf{k}') \cdot \mathbf{r}} dV$$

Noting that the outgoing wave propagates in the direction of  $\mathbf{k}'$ , this gives :

$$d\mathbf{E}(\mathbf{R}', t) \propto \mathbf{E}(\mathbf{r}, t) \rho(\mathbf{r}) dV e^{i\mathbf{k}' \cdot (\mathbf{R}' - \mathbf{r})}$$

Substituting in the expression we had for  $\mathbf{E}(\mathbf{r}, t)$ :

$$d\mathbf{E}(\mathbf{R}', t) \propto e^{i\mathbf{k} \cdot (\mathbf{r} - \mathbf{R})} \rho(\mathbf{r}) dV e^{i\mathbf{k}' \cdot (\mathbf{R}' - \mathbf{r})} e^{-i\omega t}$$

$$\propto e^{i(\mathbf{k}' \cdot \mathbf{R}' - \mathbf{k} \cdot \mathbf{R})} \rho(\mathbf{r}) dV e^{i(\mathbf{k} - \mathbf{k}') \cdot \mathbf{r}} e^{-i\omega t}$$



note that  $\mathbf{k}'$  is (approximately) the same for all points in the sample so in a moment we'll lose this whole term into the proportionality

So now we have the contribution to the electric field at the detector, coming from the small volume  $dV$  in the sample. To get the total, we need to integrate over the volume of the sample :

$$\mathbf{E}(\mathbf{R}', t) \propto e^{-i\omega t} \int_V \rho(\mathbf{r}) e^{i(\mathbf{k} - \mathbf{k}') \cdot \mathbf{r}} dV$$

In practice, only the intensity of the X-rays will be measured, and not the field itself, and so :

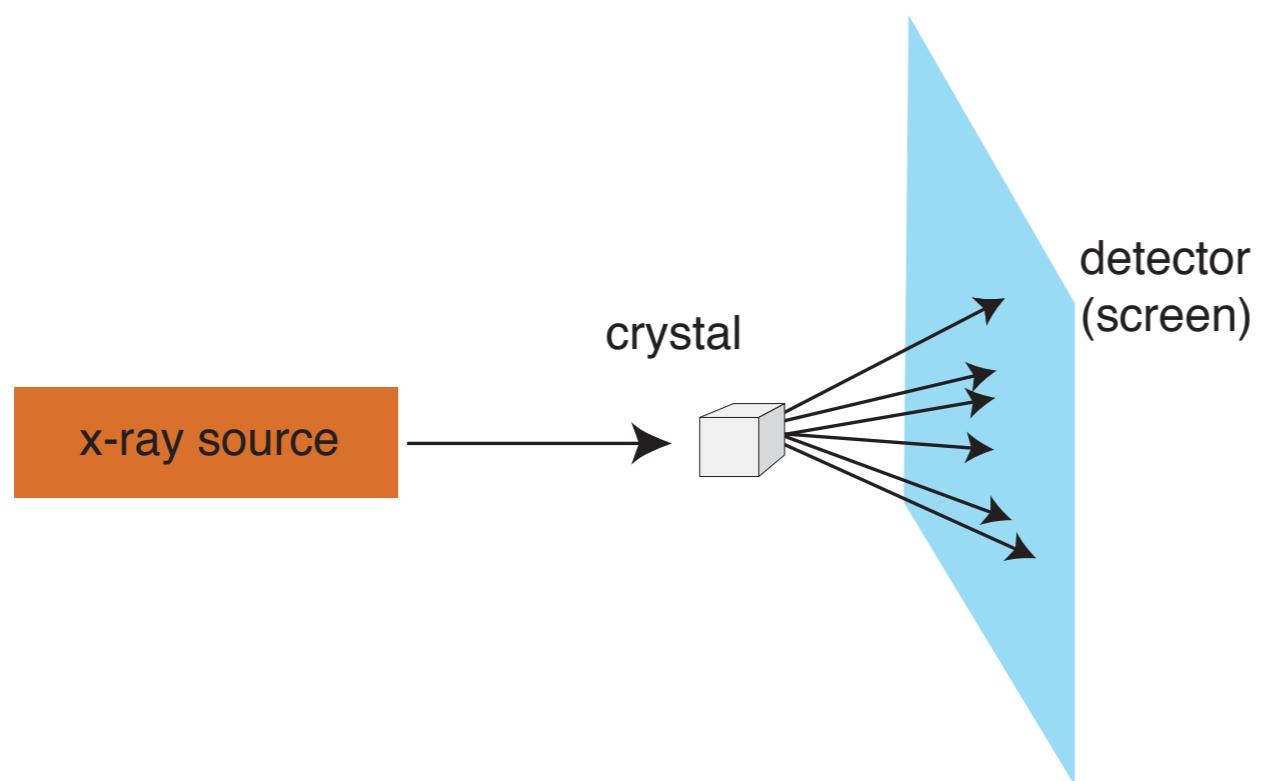
$$I(\mathbf{R}') \propto \left| \int_V \rho(\mathbf{r}) e^{i(\mathbf{k}-\mathbf{k}') \cdot \mathbf{r}} dV \right|^2$$

It is going to be useful to introduce a quantity  $\mathbf{K}$ , which we call the scattering vector since it is  $\mathbf{k}' - \mathbf{k}$ . Then :

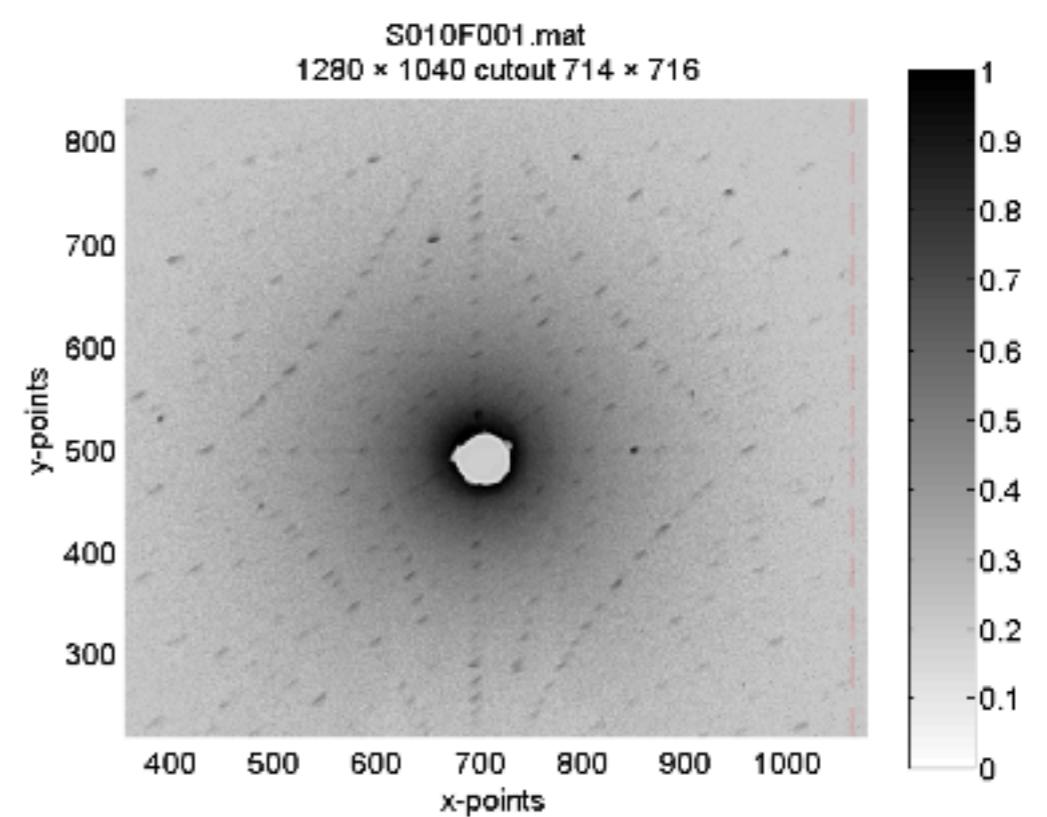
$$I(\mathbf{K}) \propto \left| \int_V \rho(\mathbf{r}) e^{-i\mathbf{K} \cdot \mathbf{r}} dV \right|^2$$

Note : What I'm saying here is that it is going to be more useful to think about considering measuring the intensity as a function of  $\mathbf{K}$ , rather than as a function of position ( $\mathbf{R}'$ ) ; we are considering the scattering to be *elastic*, so that  $|\mathbf{k}'| = |\mathbf{k}|$  and thus changing  $\mathbf{K}$  is like changing  $\mathbf{R}'$ .

So this looks good. Since the charge density is strongly concentrated on the atomic sites, by measuring the intensity of the scattered X-rays at a large number of different values of  $K$ , we should be able to figure out what the structure is. It is still a hugely difficult task; if the structure is periodic, however, the problem can be simplified, particularly if we introduce the concept of the *reciprocal lattice*.



Determining structure through X-ray diffraction  
(image : Hofmann)



“Laue” X-ray of a quartz single crystal

### I.3.4 The Reciprocal Lattice

It turns out that the concept of the reciprocal lattice is of fundamental importance in describing and understanding behaviour in periodic structures. We shall see that it helps us understand how we can determine crystalline structures, and it will be of central importance when we soon begin to describe how electrons behave in crystals. You may not immediately see why it is so useful, but hopefully this will change as we progress through the course. So let's just start by defining it.

For a given Bravais lattice,

$$\mathbf{R} = m\mathbf{a}_1 + n\mathbf{a}_2 + o\mathbf{a}_3 ,$$

we define its reciprocal lattice as the set of vectors,  $\mathbf{G}$ , for which

$$\mathbf{G} \cdot \mathbf{R} = 2\pi l , \text{ where } l \text{ is an integer}$$

An equivalent way of expressing this is :

$$e^{i\mathbf{G} \cdot \mathbf{R}} = 1$$

Just as we expressed  $\mathbf{R}$  in terms of a set of generating vectors, we can do the same for  $\mathbf{G}$  :

$$\mathbf{G} = m' \mathbf{b}_1 + n' \mathbf{b}_2 + o' \mathbf{b}_3 ,$$

where the coefficients ( $m'$  etc.) are integers and we call the  $\mathbf{b}$  vectors *reciprocal lattice vectors*.

The  $\mathbf{b}$  vectors can be calculated directly from the  $\mathbf{a}$  vectors :

$$\mathbf{b}_1 = 2\pi \frac{\mathbf{a}_2 \times \mathbf{a}_3}{\mathbf{a}_1 \cdot (\mathbf{a}_2 \times \mathbf{a}_3)}$$

$$\mathbf{b}_2 = 2\pi \frac{\mathbf{a}_3 \times \mathbf{a}_1}{\mathbf{a}_1 \cdot (\mathbf{a}_2 \times \mathbf{a}_3)}$$

$$\mathbf{b}_3 = 2\pi \frac{\mathbf{a}_1 \times \mathbf{a}_2}{\mathbf{a}_1 \cdot (\mathbf{a}_2 \times \mathbf{a}_3)}$$



Note that the denominator is the same in all three expressions. In fact, it represents the volume of the parallelepiped formed by the primitive real-space ( $\mathbf{a}$ ) lattice vectors

There are some other useful properties which follow from this definition. Firstly,

$$\mathbf{a}_i \cdot \mathbf{b}_j = 2\pi\delta_{ij}$$

the Kronecker delta is unity if  $i=j$ , or zero otherwise

Secondly, the Miller indices  $(h,k,l)$  define a plane which is perpendicular to the reciprocal lattice vector  $h\mathbf{b}_1 + k\mathbf{b}_2 + l\mathbf{b}_3$ .

But what is the *meaning* of this reciprocal lattice? Let's see how we can use it to describe the charge density of a periodic solid. We'll work in one dimension for simplicity, but the result can be straightforwardly generalised to three dimensions. Mathematically, how do we describe periodic functions in an efficient manner? Answer : *Fourier series*.

Let's start with a one-dimensional chain of atoms, separated by a lattice spacing of  $a$ . The charge density will have the periodicity of the lattice i.e.  $\rho(x) = \rho(x + a)$ .

This is just a periodic function, and as such we can represent it as a Fourier series :

$$\rho(x) = \rho_0 + \sum_{n=1}^{\infty} \left\{ C_n \cos(x2\pi n/a) + S_n \sin(x2\pi n/a) \right\}$$

sum starts from one, not zero as the constant term ( $\rho_0$ ) has been taken out of the sum.

with real coefficients  $C_n$  and  $S_n$ . There is a more compact way of writing this Fourier series which uses complex coefficients,  $\rho_n$  :

$$\rho(x) = \sum_{n=-\infty}^{\infty} \rho_n e^{ixn2\pi/a}$$

The charge density has to be a *real* quantity, and for this to be the case,

$$\rho_{-n}^* = \rho_n$$

note that the \* here means complex conjugate

What's the reciprocal lattice of a one-dimensional real-space lattice which has a spacing of  $a$ ? (*Hint* - use the expression involving the Kronecker delta we wrote down a little earlier). In fact, it is a one-dimensional lattice with a spacing of  $2\pi/a$ . So a general reciprocal lattice “vector” is :

$$g = n \frac{2\pi}{a}$$



the reason for the quotes is that we're working in one-dimension, hence calling it a vector is a little too much!

This is precisely what appears in the complex Fourier series we've just written down, i.e.

$$\rho(x) = \sum_g \rho_g e^{ixg}$$

where we are now summing over the set of reciprocal lattice “vectors”. This series can trivially be extended to the three-dimensional case :

$$\rho(\mathbf{r}) = \sum_{\mathbf{G}} \rho_{\mathbf{G}} e^{i\mathbf{G} \cdot \mathbf{r}}$$

So we can now substitute this into our earlier expression for the diffraction intensity :

$$I(\mathbf{K}) \propto \left| \int_V \rho(\mathbf{r}) e^{-i\mathbf{K} \cdot \mathbf{r}} dV \right|^2$$

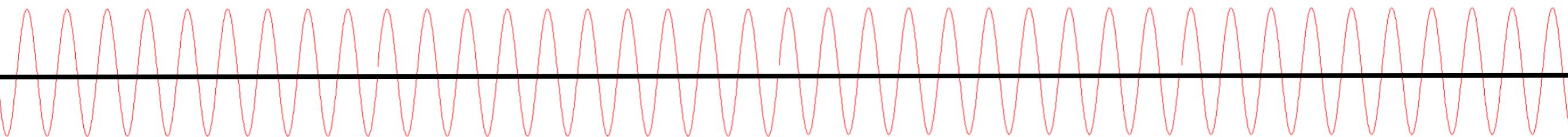
the integrand is a plane wave  
with a wavevector  $\mathbf{G} - \mathbf{K}$

giving

$$I(\mathbf{K}) \propto \left| \sum_{\mathbf{G}} \rho_{\mathbf{G}} \int_V e^{i(\mathbf{G} - \mathbf{K}) \cdot \mathbf{r}} dV \right|^2$$

If you look carefully at the integral for some general  $\mathbf{K}$ , it's going to be zero (or very close to zero) because we're integrating a function with lots of peaks and troughs. However, for some special values of  $\mathbf{K}$ , namely those that are equal to  $\mathbf{G}$ , the integrand becomes unity. This is *constructive interference*, and it occurs only when  $\mathbf{K} = \mathbf{G}$ , which is the so-called *Laue condition*.

Over a whole number  
of wavelengths,  
function is positive as  
much as it is negative



integral is zero

(This refers to the previous slide - just pointing out how  
the integral of an oscillating function over a whole number  
of wavelengths is zero)

So we can now substitute this into our earlier expression for the diffraction intensity :

$$I(\mathbf{K}) \propto \left| \int_V \rho(\mathbf{r}) e^{-i\mathbf{K} \cdot \mathbf{r}} dV \right|^2$$

the integrand is a plane wave  
with a wavevector  $\mathbf{G} - \mathbf{K}$

giving

$$I(\mathbf{K}) \propto \left| \sum_{\mathbf{G}} \rho_{\mathbf{G}} \int_V e^{i(\mathbf{G} - \mathbf{K}) \cdot \mathbf{r}} dV \right|^2$$

If you look carefully at the integral for some general  $\mathbf{K}$ , it's going to be zero (or very close to zero) because we're integrating a function with lots of peaks and troughs. However, for some special values of  $\mathbf{K}$ , namely those that are equal to  $\mathbf{G}$ , the integrand becomes unity. This is *constructive interference*, and it occurs only when  $\mathbf{K} = \mathbf{G}$ , which is the so-called *Laue condition*.

When the Laue condition is satisfied, then if we measure the intensity of the scattering for some particular scattering vector,  $\mathbf{G}$ , then we get intensity which is proportional to  $|\rho_{\mathbf{G}}|^2$ . Recalling that the quantity  $\rho_{\mathbf{G}}$  is a *complex* Fourier coefficient, we cannot know what  $\rho_{\mathbf{G}}$  is directly from a measurement of the diffraction intensity; we can only know the modulus and not the phase. This is the well-known *phase problem* of X-ray diffraction.

The standard way to deal with this problem is to guess a solution (that is, guess the  $\rho_{\mathbf{G}}$ ), and then calculate what the scattering would look like (take the square modulus). By doing this for lots of different scattering vectors which satisfy the Laue condition (that is, calculating the intensities of lots of “Bragg peaks” or “reflections”) and comparing them with the set of experimentally measured ones, it is possible to “refine” the structure.

### I.3.5 Further Examples of Reciprocal Lattices

Having defined and seen how useful the reciprocal lattice can be, let's look a little more closely at the reciprocal lattice. Starting with the simple cubic lattice, application of :

$$\mathbf{b}_1 = 2\pi \frac{\mathbf{a}_2 \times \mathbf{a}_3}{\mathbf{a}_1 \cdot (\mathbf{a}_2 \times \mathbf{a}_3)}$$

$$\mathbf{b}_2 = 2\pi \frac{\mathbf{a}_3 \times \mathbf{a}_1}{\mathbf{a}_1 \cdot (\mathbf{a}_2 \times \mathbf{a}_3)}$$

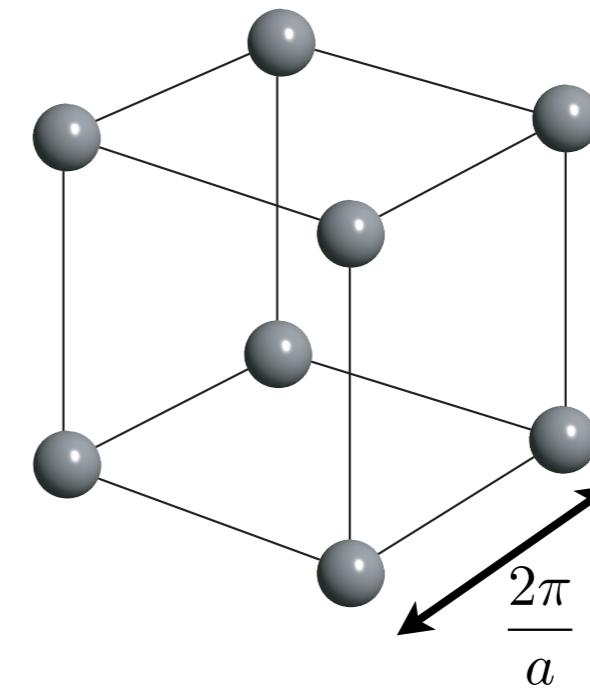
$$\mathbf{b}_3 = 2\pi \frac{\mathbf{a}_1 \times \mathbf{a}_2}{\mathbf{a}_1 \cdot (\mathbf{a}_2 \times \mathbf{a}_3)}$$

gives

$$\mathbf{b}_1 = \frac{2\pi}{a} \hat{\mathbf{x}}$$

$$\mathbf{b}_2 = \frac{2\pi}{a} \hat{\mathbf{y}}$$

$$\mathbf{b}_3 = \frac{2\pi}{a} \hat{\mathbf{z}}$$

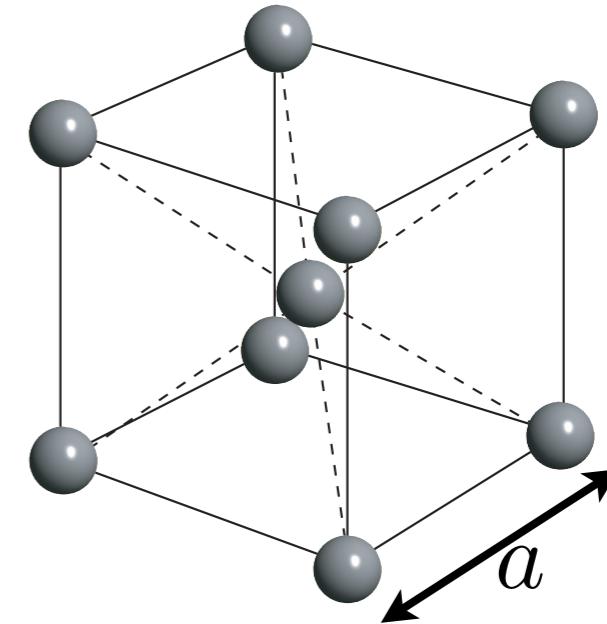


The reciprocal lattice of a sc lattice  
(image : adapted from Hofmann)

i.e. reciprocal lattice is another sc lattice, but with side  $\frac{2\pi}{a}$

What about the reciprocal lattice of the real space bcc lattice?  
If we apply the formula, we go from :

$$\begin{aligned}\mathbf{a}_1 &= \frac{a}{2}(\hat{\mathbf{x}} + \hat{\mathbf{y}} - \hat{\mathbf{z}}) \\ \mathbf{a}_2 &= \frac{a}{2}(-\hat{\mathbf{x}} + \hat{\mathbf{y}} + \hat{\mathbf{z}}) \\ \mathbf{a}_3 &= \frac{a}{2}(\hat{\mathbf{x}} - \hat{\mathbf{y}} + \hat{\mathbf{z}})\end{aligned}$$

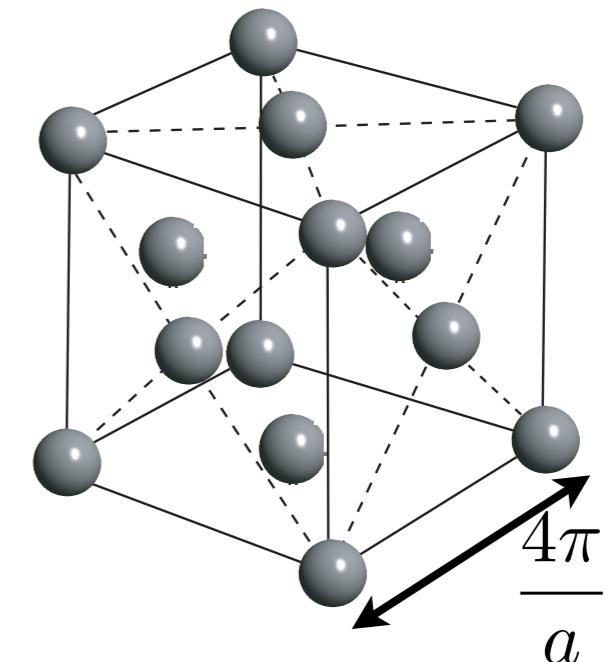


The bcc Bravais lattice  
(image : Hofmann)

to:

$$\begin{aligned}\mathbf{b}_1 &= \frac{2\pi}{a}(\hat{\mathbf{x}} + \hat{\mathbf{y}}) \\ \mathbf{b}_2 &= \frac{2\pi}{a}(\hat{\mathbf{y}} + \hat{\mathbf{z}}) \\ \mathbf{b}_3 &= \frac{2\pi}{a}(\hat{\mathbf{z}} + \hat{\mathbf{x}})\end{aligned}$$

these vectors describe  
an fcc lattice of  
“side”  $\frac{4\pi}{a}$



Reciprocal lattice is an fcc  
Bravais lattice  
(image : Hofmann)

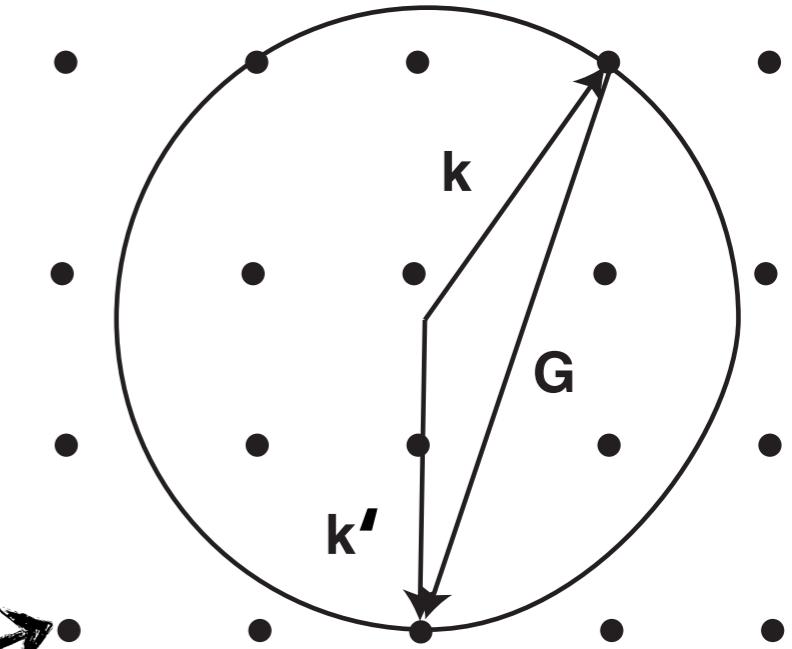
Similarly, the reciprocal lattice of an fcc lattice is a bcc lattice (but with cube side  $\frac{4\pi}{a}$ ).

You should be able to work out what the reciprocal lattice of the hexagonal lattice is - this is left as an exercise.

## I.3.6 Visualising the Laue Condition : the Ewald Construction

There is an intuitive geometrical construction, due to P. Ewald (1913), to visualise the Laue condition. In two dimensions, it is illustrated in the figure on the right which is drawn as follows:

these are reciprocal  
lattice points



The Ewald construction is a way of visualising what the Laue condition (image by Hofmann)

- (i) Draw the incoming wave vector  $\mathbf{k}$  so that it ends at the origin of the reciprocal lattice (we can, of course, choose where this origin is).
- (ii) Draw a circle (\*) of radius  $|\mathbf{k}|$  about the origin of the  $\mathbf{k}$ .
- (iii) Whenever the circle intersects a reciprocal lattice point, the Laue condition is satisfied, and we will find diffraction intensity in the direction of  $\mathbf{k}'$ .

\* In three dimensions, the circle would, of course, become a sphere

### I.3.7 Connection Between the Bragg and Laue Theories

The Laue condition is a vector condition, and therefore it is really *three* separate conditions on the three components of the vectors. In the Bragg picture of specular reflection, it is automatically fulfilled for two of the three components as the wave vector parallel to the planes is not changed. So the Laue condition just becomes a scalar relationship on the perpendicular component:

elastic scattering so  $|\mathbf{k}'| = |\mathbf{k}|$

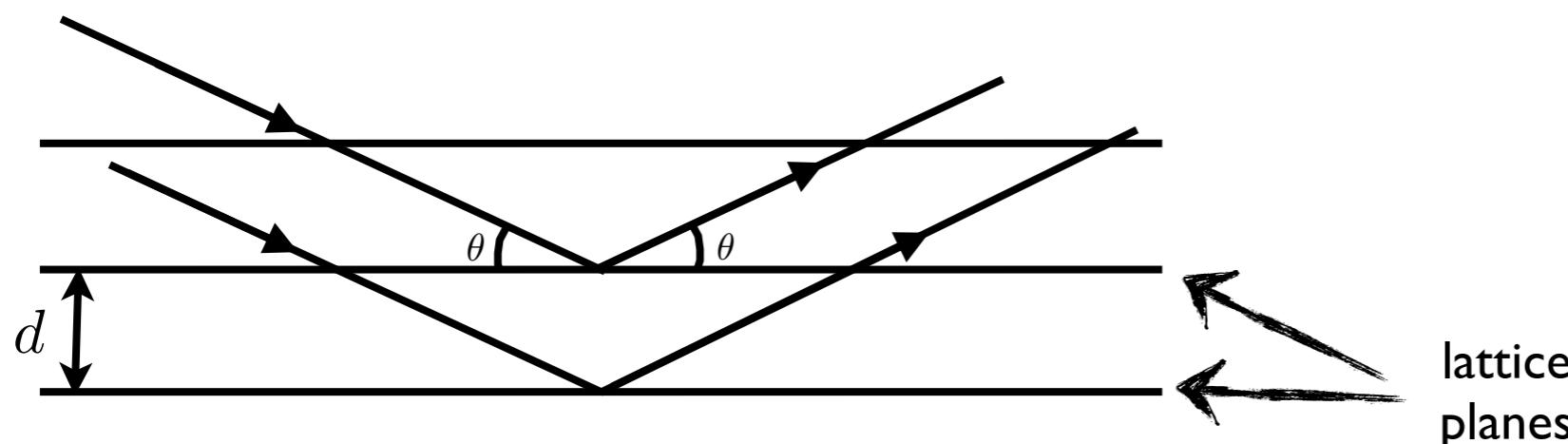
$$k'_\perp - k_\perp = 2k_\perp = 2\frac{2\pi}{\lambda} \sin \theta = G_\perp$$

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

perpendicular component  
of  $\mathbf{G}$  vector

Since  $G_\perp = n\frac{2\pi}{d}$ , where  $n$  is an integer, we get

$$n\lambda = 2d \sin \theta \text{ which is the Bragg condition}$$



### 1.3.8 The Structure Factor

We argued earlier that the intensity of scattering at a **K** vector which satisfies the Laue condition (**K=G**) was :

$$I(\mathbf{G}) \propto |\rho_{\mathbf{G}}|^2$$

and that these  $\rho_{\mathbf{G}}$  were just the (complex) Fourier coefficients of the charge density :

$$\rho(\mathbf{r}) = \sum_{\mathbf{G}} \rho_{\mathbf{G}} e^{i\mathbf{G} \cdot \mathbf{r}}$$

For historical reasons, these  $\rho_{\mathbf{G}}$  are also called the *structure factors*, and are written as  $F_{\mathbf{K}}$  or  $F_{hkl}$  (or sometimes  $S_{hkl}$ ). These structure factors also exist for the diffraction of other probes (e.g. electrons, neutrons), but for X-rays,

$$\rho_{\mathbf{G}} \equiv F_{hkl}$$



these  $hkl$  are the  
Miller indices again

The structure factors are expressed like this :

$$F_{hkl} = \sum_{j=1}^n f_j e^{(i\mathbf{G}_{hkl} \cdot \mathbf{r}_j)}$$

I've labelled the **G** vector with the Miller indices to make it explicit that we're looking at a particular structure factor and thus a particular Fourier component

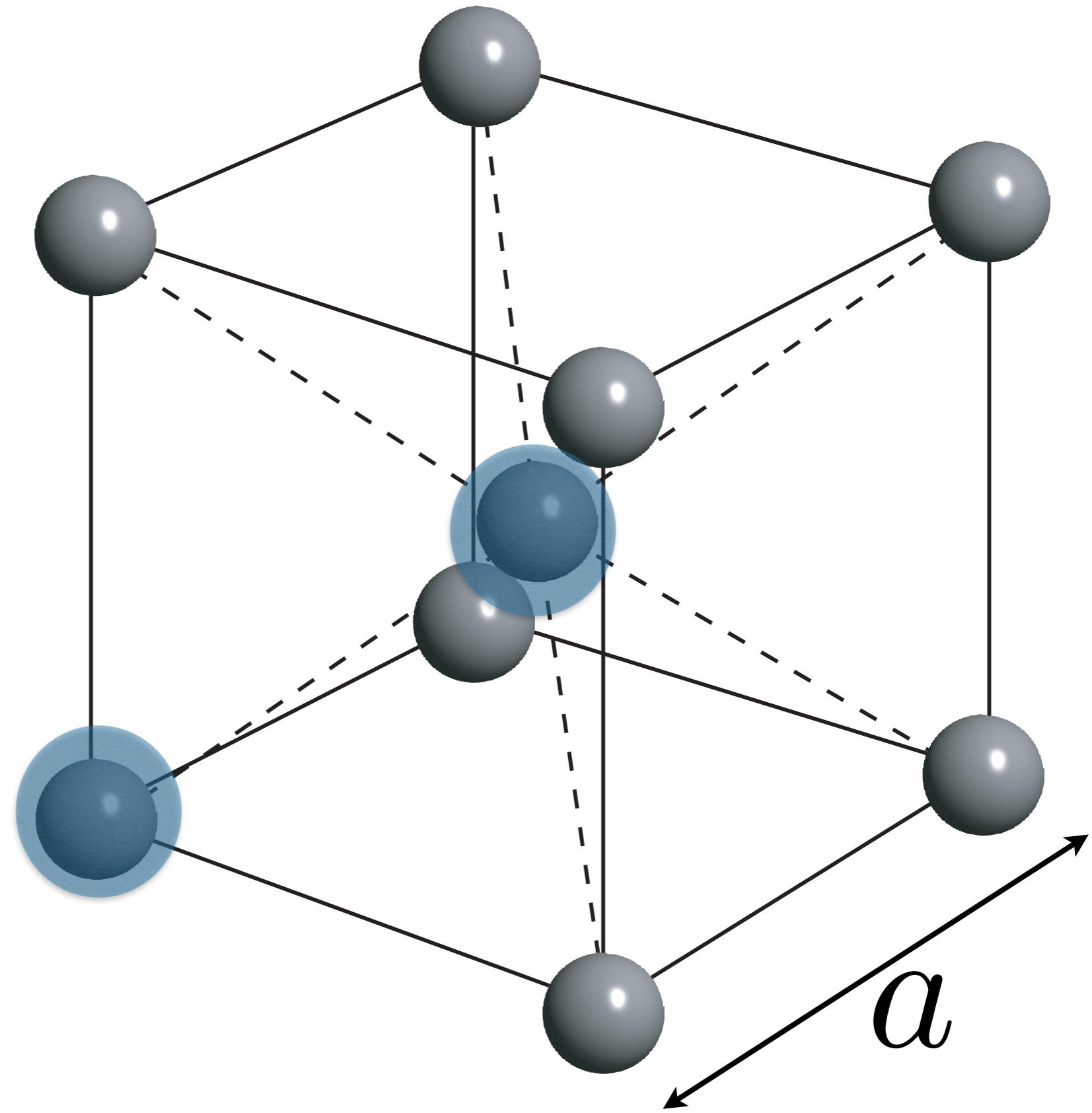
where the sum runs over all atoms in the unit cell, and  $\mathbf{r}_j$  is the position vector of the  $j^{\text{th}}$  atom within the cell. The quantity  $f_j$  is called the *atomic form factor* and describes the scattering power of the particular atom.

Let's consider a diffracted beam from a plane in the crystal which has Miller indices  $(h,k,l)$ . Remember that the direction  $[h,k,l]$  is perpendicular to the plane  $(h,k,l)$ , and thus the beam will have a wave vector :

$$\mathbf{G}_{hkl} = h\mathbf{b}_1 + k\mathbf{b}_2 + l\mathbf{b}_3 ,$$

where the **b**'s are the reciprocal lattice vectors.

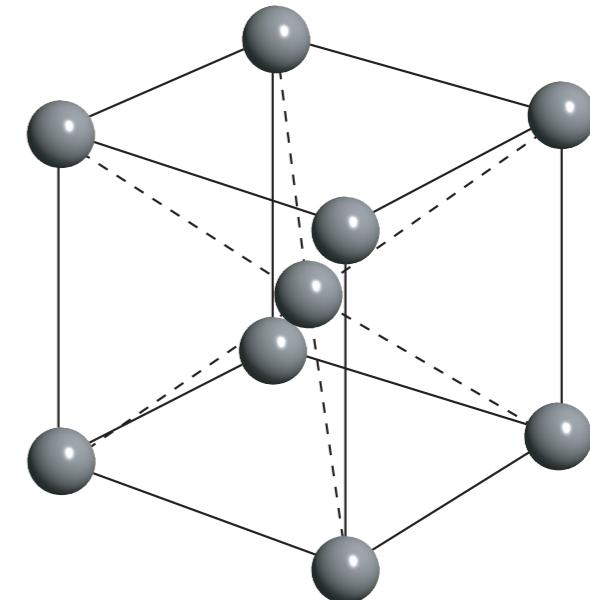
Only the two highlighted atoms are in the basis - the other ones are picked up by translations using the Bravais lattice vectors



Let's look at the bcc structure, which we can think of as being a simple cubic lattice with a basis of two identical atoms located at  $(0,0,0)$  and  $(1/2,1/2,1/2)$  (in units of the lattice vectors).

We don't know what the atomic form factor  $f$  is, but it must be the same for both identical atoms. Let's just call it  $f$ . So now we just plug this information into here:

$$F_{hkl} = \sum_{j=1}^n f_j e^{(i\mathbf{G}_{hkl} \cdot \mathbf{r}_j)}$$



The bcc structure  
(image : Hofmann)

First let's look at the scalar product  $\mathbf{G}_{hkl} \cdot \mathbf{r}_j$  for each of the two atoms in the cell. For the one at the origin, the scalar product is simply zero. For the atom at  $(1/2,1/2,1/2)$ , we have

$$2\pi \times \left( \frac{h}{2} + \frac{k}{2} + \frac{l}{2} \right).$$

 note that the "a" coming from the position vector has cancelled with the  $1/a$  in the reciprocal lattice vector

So the structure factor is :

$$F_{hkl} = \underbrace{f \times e^0}_{\text{atom at } (0,0,0)} + \underbrace{f \times e^{2\pi i \times \left( \frac{h}{2} + \frac{k}{2} + \frac{l}{2} \right)}}_{\text{atom at } (1/2, 1/2, 1/2)}$$

which simplifies to :

$$F_{hkl} = f \left( 1 + e^{i\pi(h+k+l)} \right)$$

What does this mean? What happens if  $(h + k + l)$  is odd?

$$F_{hkl} = 0 \text{ if } (h + k + l) \text{ odd}$$

and  $F_{hkl} = 2f$  if  $(h + k + l)$  even

In Bravais lattices where there is centring, planes of lattice points can give rise to *destructive interference* for some reflections, giving a structure factor of zero.

### I.3.9 Brillouin Condition for Diffraction and the Brillouin Zone

From the Laue condition,  $\mathbf{k}' - \mathbf{k} = \mathbf{G}$ , a new condition for diffraction can be derived :

$$\mathbf{k}' = \mathbf{k} + \mathbf{G}$$

Taking scalar product of both sides with themselves

$$\mathbf{k}' \cdot \mathbf{k}' = (\mathbf{k} + \mathbf{G}) \cdot (\mathbf{k} + \mathbf{G})$$

$$k'^2 = 2\mathbf{k} \cdot \mathbf{G} + G^2 + k^2$$

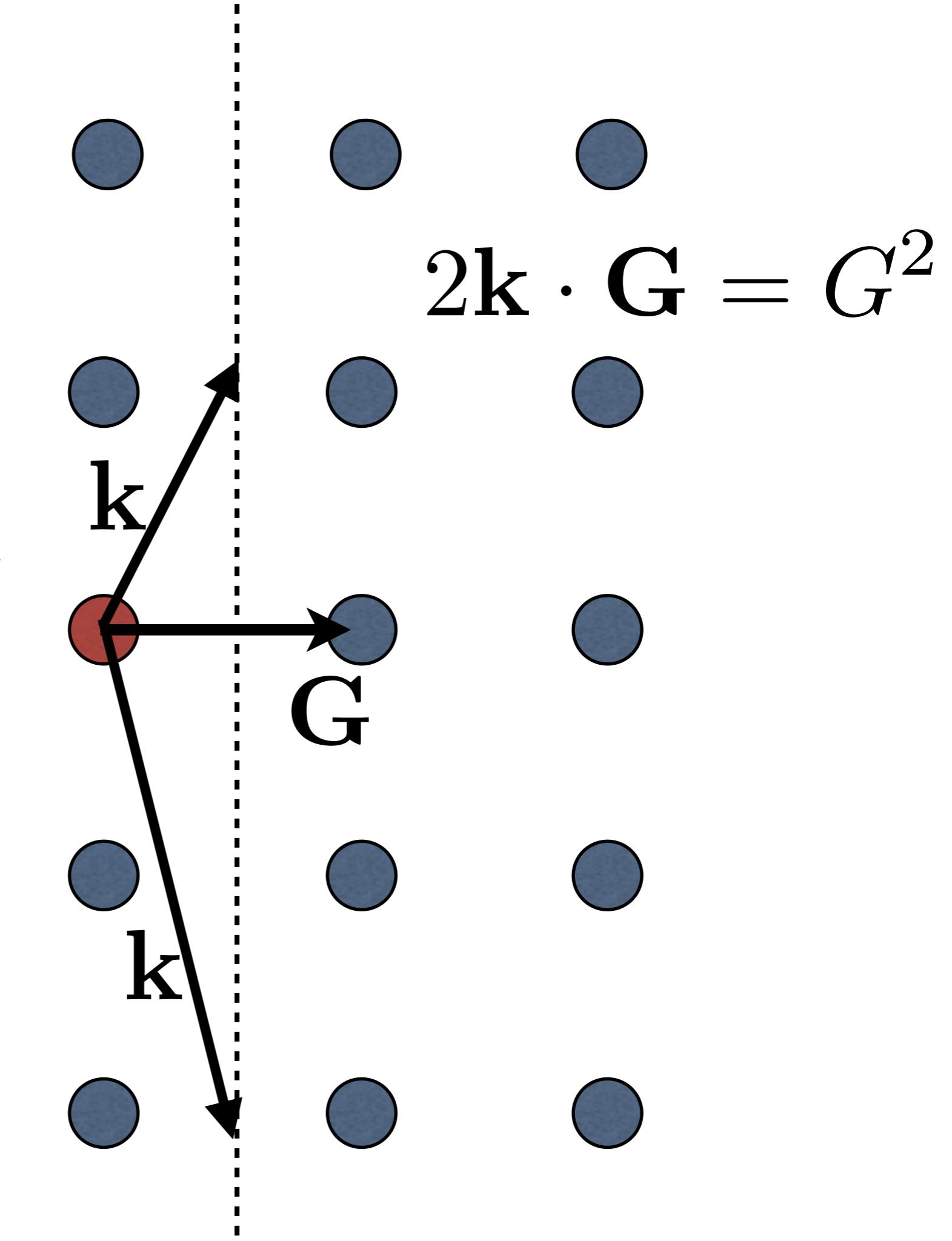
Recalling that interaction is elastic ( $\mathbf{k}' = \mathbf{k}$ ), we have :

$$2\mathbf{k} \cdot \mathbf{G} = -G^2$$

$$2\mathbf{k} \cdot \mathbf{G} = G^2$$

If  $\mathbf{G}$  is a reciprocal lattice vector, then so is  $-\mathbf{G}$ , so we shouldn't worry about losing this minus sign

For whatever  
k you choose that  
ends on the BZ boundary  
(dashed lines),  
you satisfy the  
Brillouin condition  
automatically!



## So what's this telling us?

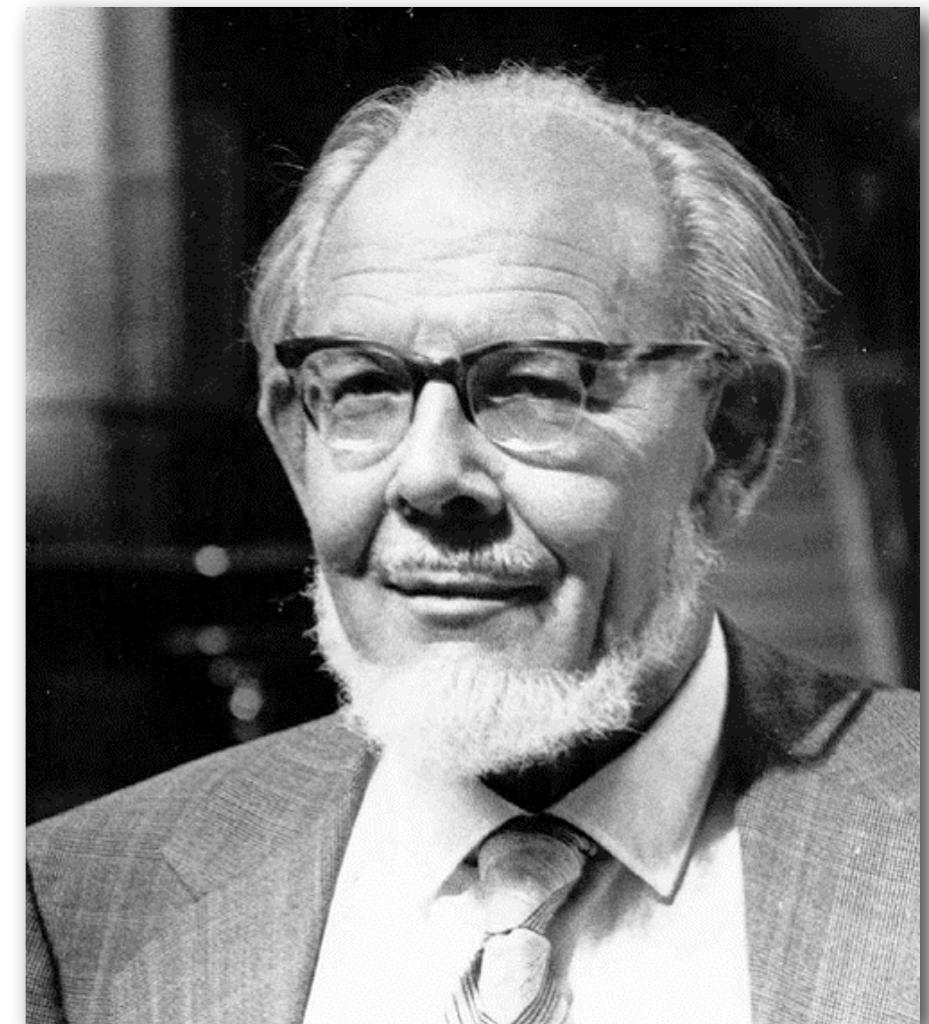
It's telling us that the diffraction condition is satisfied in planes which are the perpendicular bisectors of  $\mathbf{G}$  vectors. Remember when we last looked at planes which were the perpendicular bisectors of the primitive (Bravais lattice) vectors? It was when we were constructing the Wigner-Seitz unit cell.

We now have a new unit cell, this time in reciprocal space, defined by planes which satisfy the diffraction condition. This cell is called the *Brillouin Zone (BZ)* (\*). It is the “Wigner-Seitz unit cell of reciprocal space”.

\* Strictly speaking, this is the first Brillouin zone, but we will come back to this later

## An aside : Is there such a thing as a perfect crystal?

“Crystals are like people -  
it's the defects in them that make  
them interesting”



Prof. Sir Charles Frank, FRS  
(Image : University of Bristol)

In reality, no crystal is perfect (\*). There will be vacancies, interstitials, dislocations etc., and of course, there are vibrations (“phonons”) of the ion cores, all of which conspire to destroy perfect periodicity - in fact, it is the deviation from periodicity which is the source of electrical resistance.

\* Creating a defect will cost energy, but entropy will increase. Equilibrium (minimum free energy) will be balance between defect formation energy and entropy increase.

# **Chapter 2 - Electrons in Metals**

In this chapter, we are going to look at how electrons behave in the crystalline environments that we now know how to describe.

What kinds of properties are we trying understand? Electrical and thermal conductivities, interaction with electromagnetic radiation (e.g. reflectivity), specific heat...

As hinted at earlier, it seems like a hopeless task - how can we ever understand what  $\sim 10^{23}$  electrons are doing when we struggle to make analytic solutions for anything beyond the hydrogen atom?

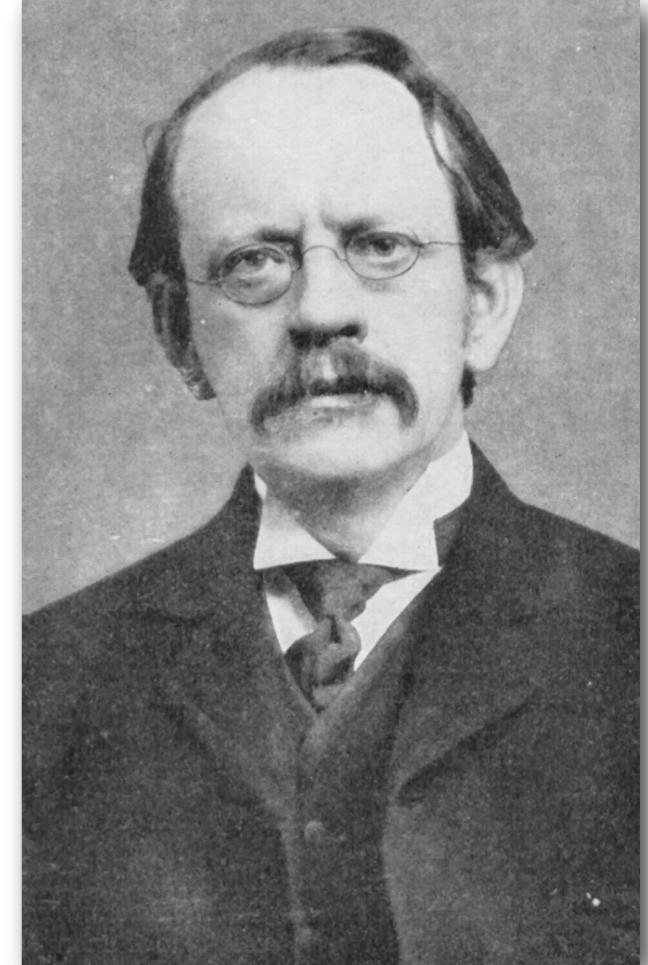
## 2.1 Beginnings

JJ Thomson's discovery of the electron (1897) paved the way for the rapid development in our understanding of electrons in metals.

**Big question** - if all solids contain electrons, why do some conduct electricity and others do not?



Paul Drude  
(Image: public domain)



"JJ" Tompson, OM FRS  
(Image: public domain)

Drude (1900) was quick to apply the (classical) kinetic theory to the “gas” of these recently discovered electrons. He imagined this gas of electrons moving freely in the space between the positively charged ion cores.

## 2.2 The Drude Model

Assumptions :

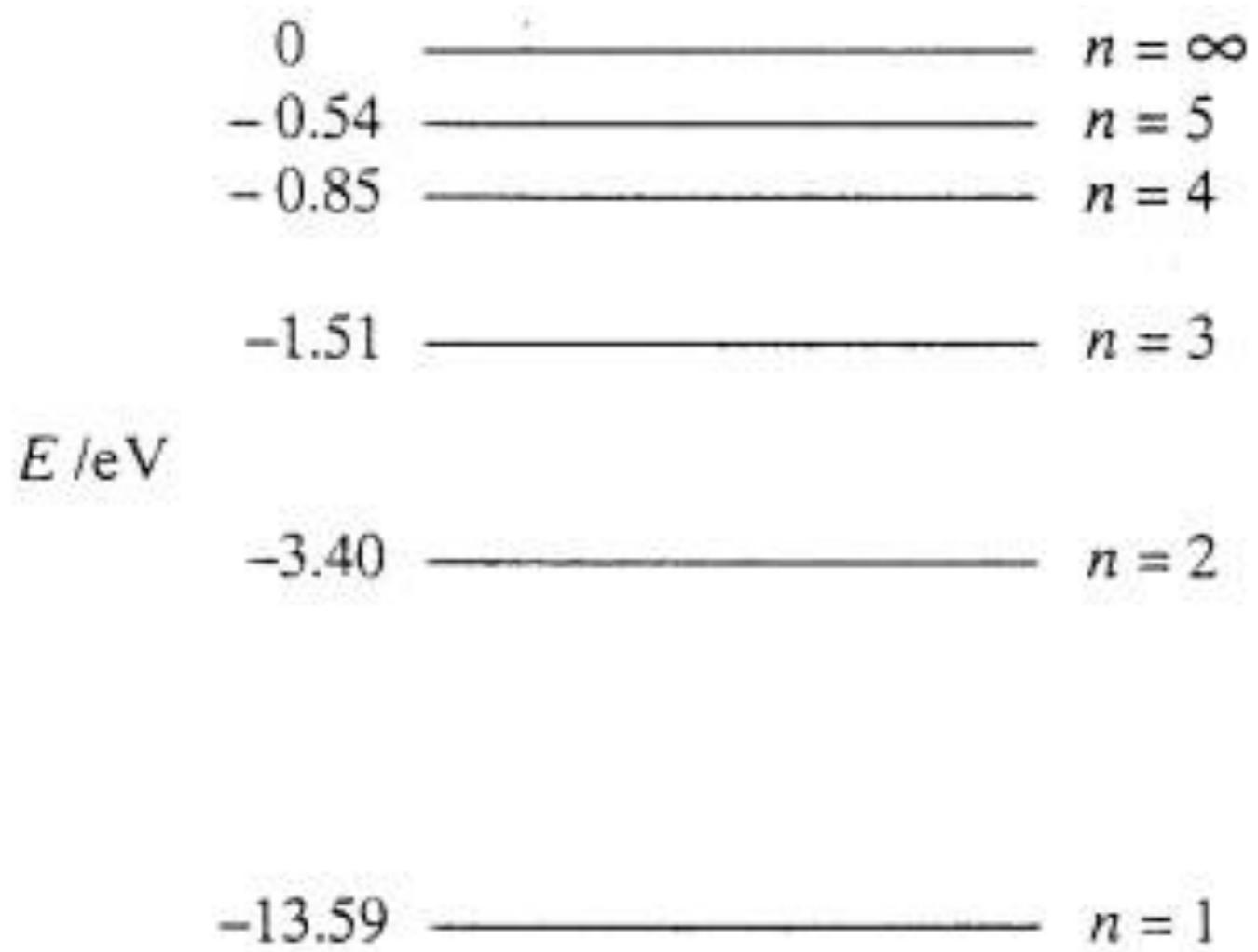
- (i) Electrons scatter only through *collisions* with the ion cores.
- (ii) Between collisions, they do not interact with each other (*independent electron approximation*) or with the ion cores (*free electron approximation*).
- (iii) Collisions are instantaneous and result in the velocity of the electrons changing.
- (iv) Probability of an electron suffering a collision per unit time is  $1/\tau$ ; i.e.  $\tau$  is the inverse scattering rate.
- (v) Thermal equilibrium is reached through collisions.

So what does this model predict?

If each atom is considered to contribute one or more electrons to this *conduction* electron gas, the prediction is that each electron moves with the average K.E. ( $\frac{3}{2}k_B T$ ), meaning that the specific heat will be  $\frac{3}{2}nk_B$ , where  $n$  is the electron density.

i.e. it is *independent* of temperature

In spite of this failure (we will see later on that it *is* a failure as this prediction is wrong), the Drude model's longevity is due to the importance of some of the concepts it introduced (such as the scattering rate). Moreover, it did have some successes, such as being able to explain the DC electrical conductivity, Hall effect, optical reflectivity and perhaps most importantly of all, the Wiedemann-Franz Law (that the ratio of the electrical and thermal conductivities was a constant). This latter success was made even more impressive because it even gave the correct value for the ratio due to an unnoticed mistake Drude had made.

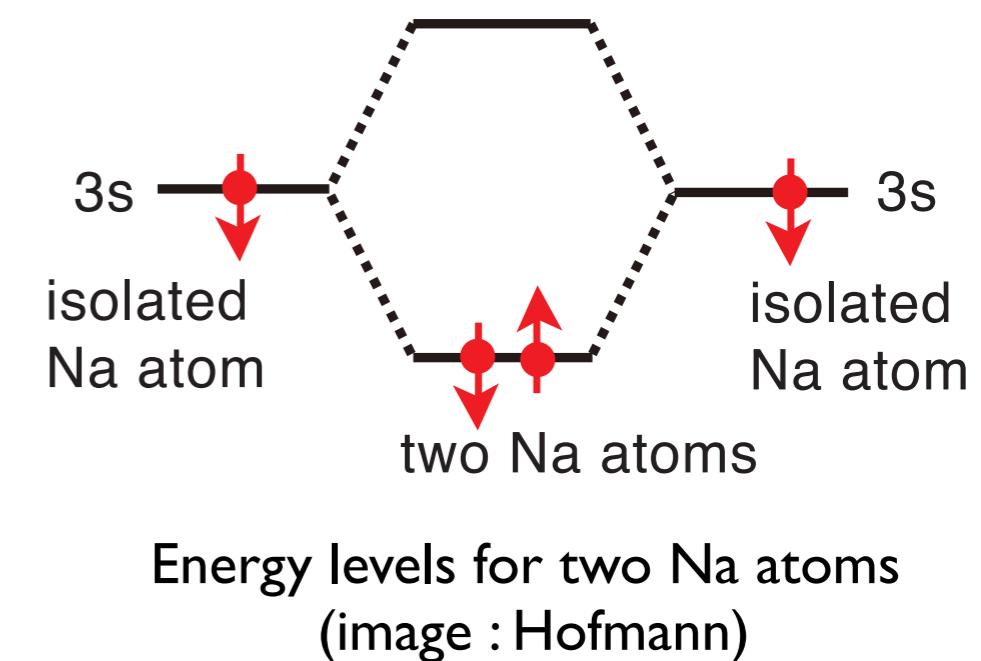


**Energy levels in an isolated hydrogen atom**

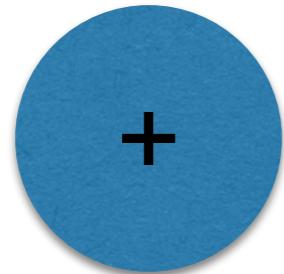
What happens to these levels as we bring another atom close?

## 2.3 The Origin of Energy Bands in Solids

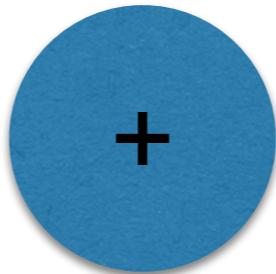
Very shortly, we will see that the energy levels that electrons can occupy in a crystal form a *band*. It is instructive to see how those energy bands arise, at least from a qualitative perspective. Let's start by thinking about two isolated Na atoms (electron configuration is  $[\text{Ne}]3s^1$ ).



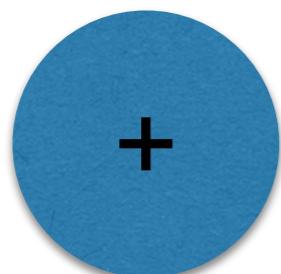
So each atom has one electron in the 3s shell. What happens to the energy levels when we bring these two atoms together and allow the wavefunctions of these two electrons to overlap? A new “molecular” wavefunction will be born, which is a result of the **interference** between the two original wavefunctions. It will be either constructive or destructive, and will lead to there being two energy levels associated with *bonding* or *anti-bonding* states.



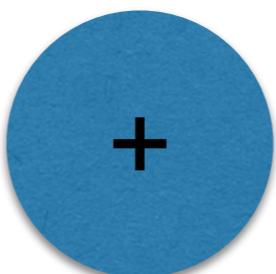
increased  
electron  
density



bonding

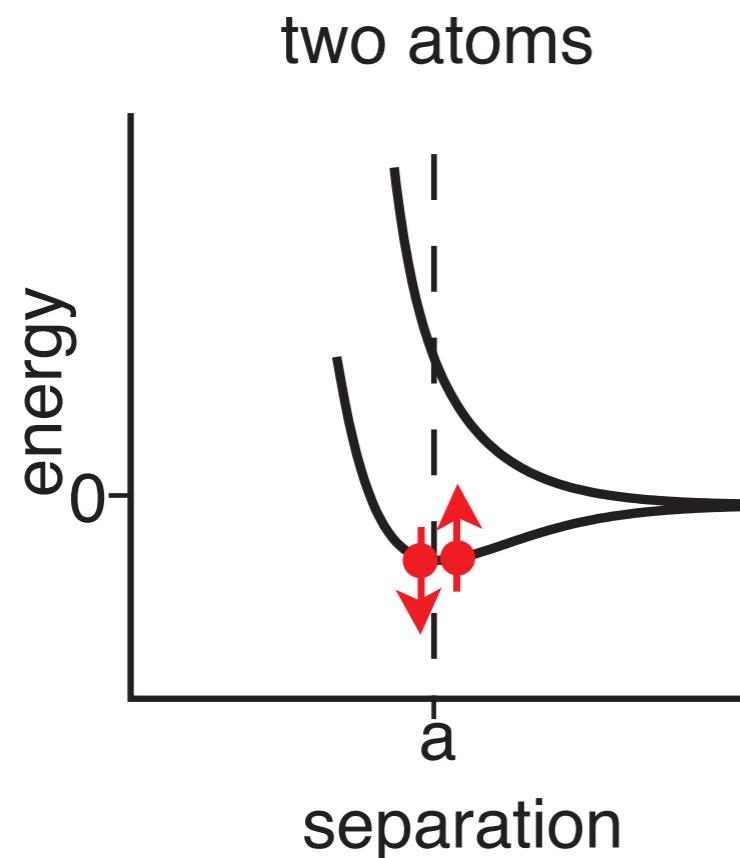


decreased  
electron  
density



anti-bonding

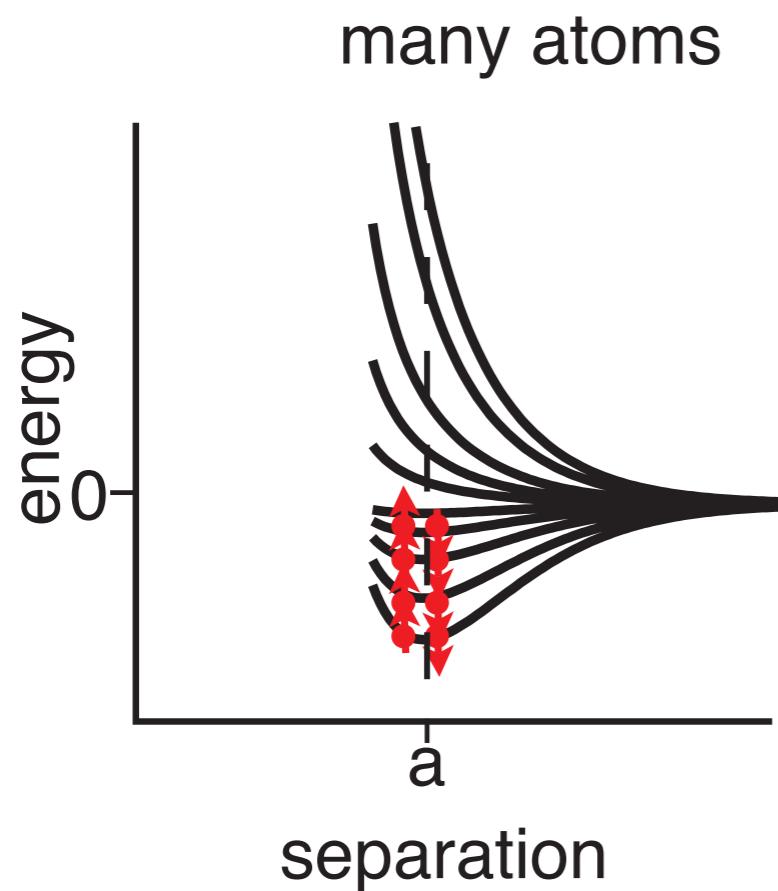
The bonding state come from the constructive interference which puts extra electron density between the nuclei. The anti-bonding state is a result of destructive interference which suppresses the electron density between the nuclei.



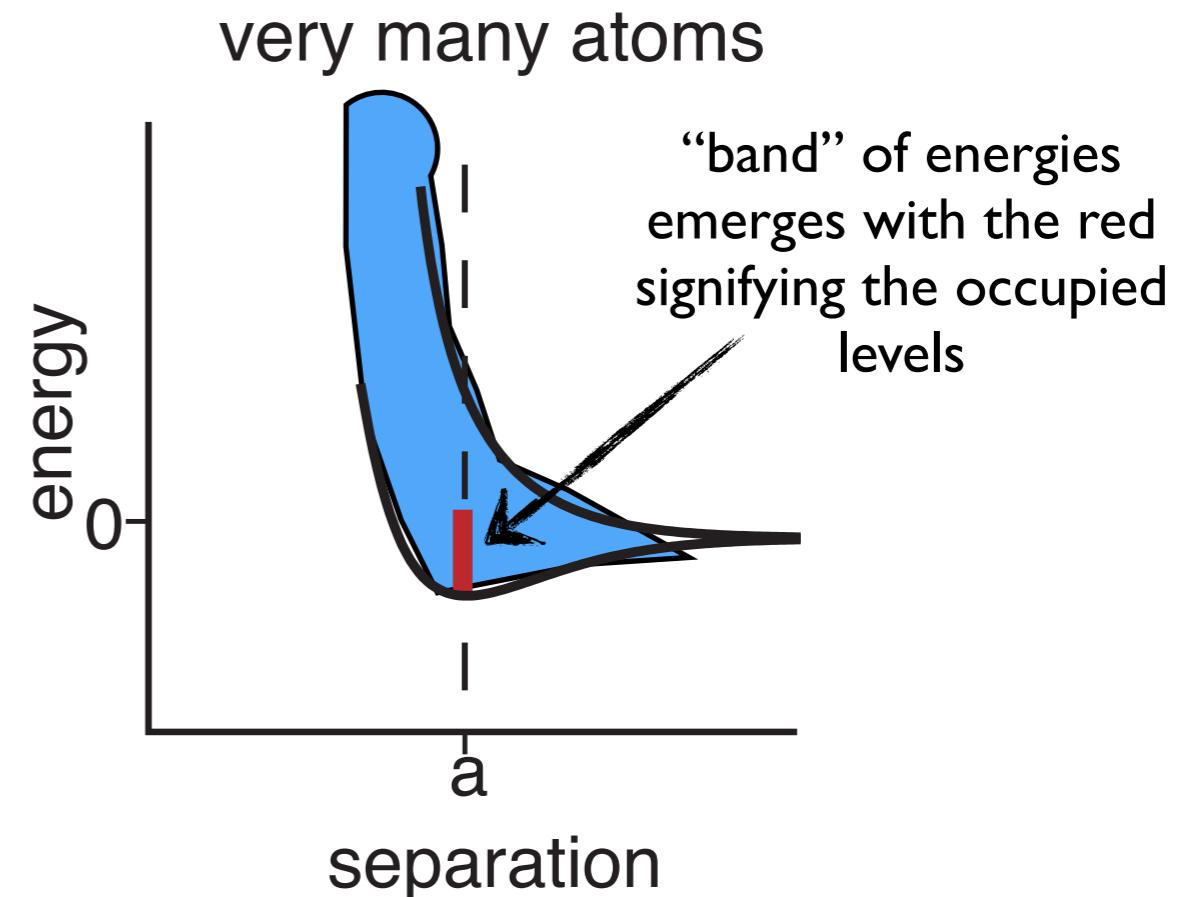
So as the separation decreases, and the overlap increases, the original  $3s^1$  energies split into separate bonding and anti-bonding levels.

Illustration of how the energy levels evolve as two Na atoms are brought together. The dashed line is the equilibrium separation  
(image : Hofmann)

We can imagine our solid, then, as being a large molecule. As we add more and more atoms, we will end up with more and more non-degenerate (\*) levels, and in the case of Na we will only be populating half of these (the lowest energy ones).



Energy levels for many Na atoms  
(image : Hofmann)



Energy levels for even more Na atoms  
(image : Hofmann)

\* There may, of course, be accidental degeneracies due to symmetry

## 2.4.1 The Sommerfeld “Free Electron” Model

This is, in essence, a quantum mechanical version of the Drude theory. Without further approximation, the calculation of the wavefunctions of  $\sim 10^{23}$  electrons is an impossible task.

Approximations :

- (i) Ignore the motion of the ions (separation of electronic and ionic motion is the so-called *Born-Oppenheimer approximation*).
- (ii) Encapsulate all the interactions between an electron and ion-cores and between it and other electrons into an effective potential,  $U(\mathbf{r})$ .  
  
any potential, must, of course, have the periodicity of the lattice i.e.  $U(\mathbf{r}) = U(\mathbf{r} + \mathbf{R})$ .

So *all* we have to solve is this time-independent Schrödinger equation with the appropriate boundary conditions:

$$-\frac{\hbar^2 \nabla^2}{2m_e} \psi(\mathbf{r}) + U(\mathbf{r})\psi(\mathbf{r}) = E\psi(\mathbf{r})$$

In the Sommerfeld model, we treat the electrons as being “free” (not interacting with either the ion cores or the other electrons), which is equivalent to saying that  $U(\mathbf{r}) = 0$ . So what should these boundary conditions on the wavefunction be? The quantum mechanical problem that we are trying to solve is just that of a particle in a box, and the simplest possible boundary conditions would be for wavefunction to vanish at the surface of the box; this would lead to standing wave solutions, and we’re not really interested in those. It is much better to use *Born-von Kármán* (or *periodic*) boundary conditions. Let’s assume our box is cubic with a macroscopic side of length  $L$  (and hence volume  $V=L^3$ ), and thus the boundary conditions are :

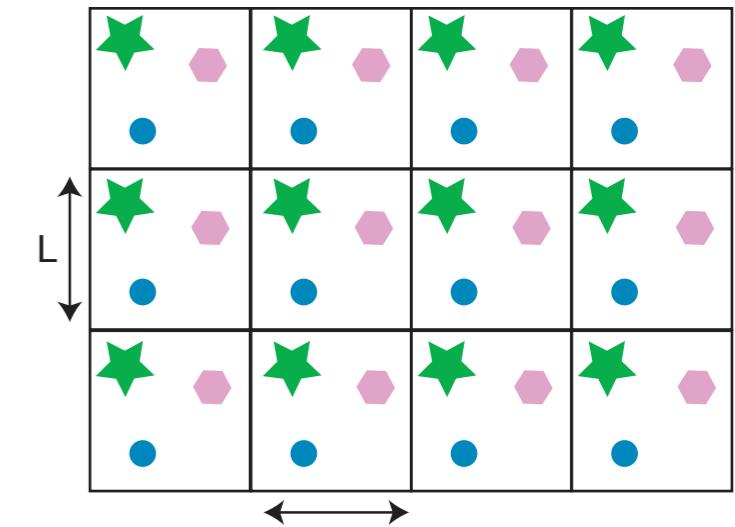


Illustration (in 2D) of periodic or Born-von Kármán boundary conditions

(image : Hofmann)

$$\psi(\mathbf{r}) = \psi(x, y, z) = \psi(x + L, y, z) = \psi(x, y + L, z) = \psi(x, y, z + L)$$

The normalised solution to this Schrödinger equation with these boundary conditions is :

$$\psi(\mathbf{r}) = \frac{1}{\sqrt{V}} e^{i\mathbf{k} \cdot \mathbf{r}}$$

← solutions are plane waves

But the boundary conditions have also imposed some restrictions on the allowed values of  $\mathbf{k}$ . Hopefully you can see this as follows:

Let's look at the wavefunction at  $\mathbf{r} = (x + L, y, z)$  :

$$\begin{aligned}\psi(x + L, y, z) &= \frac{1}{\sqrt{V}} e^{i(k_x(x+L) + k_y y + k_z z)} \\ &= \frac{1}{\sqrt{V}} e^{i(k_x L)} e^{i(k_x x + k_y y + k_z z)} \\ &= \psi(x, y, z) \text{ if } e^{i(k_x L)} = 1\end{aligned}$$

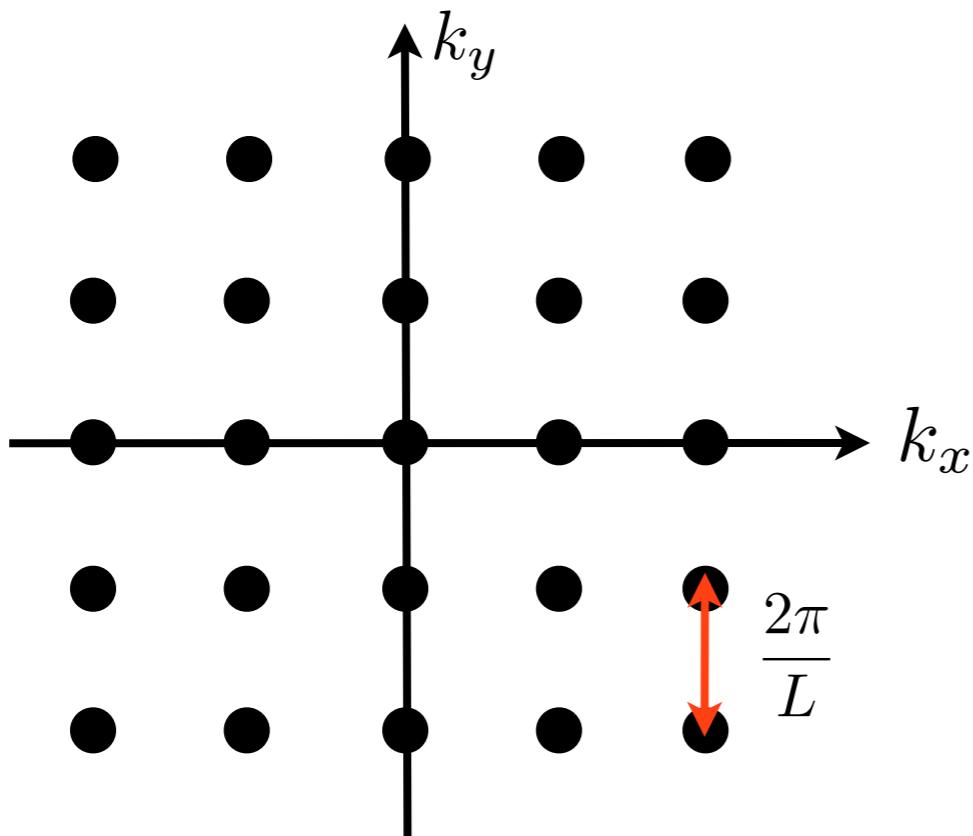
← which it has to in order to satisfy the boundary condition

The allowed values of  $\mathbf{k}$  are therefore:

$$\mathbf{k} = (k_x, k_y, k_z) = \left( \frac{n_x 2\pi}{L}, \frac{n_y 2\pi}{L}, \frac{n_z 2\pi}{L} \right),$$

where  $n_x, n_y$  and  $n_z$  are integers ( $0, \pm 1, \pm 2, \dots$ ).

Thus there are a discrete set of values for the wavevector.



Allowed values of  $\mathbf{k}$  in two dimensions

Let's now look at the discrete set of energies, which are of course the **energy eigenvalues**:

$$-\frac{\hbar^2 \nabla^2}{2m_e} \psi(\mathbf{r}) = E \psi(\mathbf{r})$$

Putting  $\psi(\mathbf{r}) = \frac{1}{\sqrt{V}} e^{i\mathbf{k}\cdot\mathbf{r}}$  into this Schrödinger equation, we get :

$$\frac{\hbar^2 k^2}{2m_e} \frac{1}{\sqrt{V}} e^{i\mathbf{k}\cdot\mathbf{r}} = E \frac{1}{\sqrt{V}} e^{i\mathbf{k}\cdot\mathbf{r}}$$

which means that

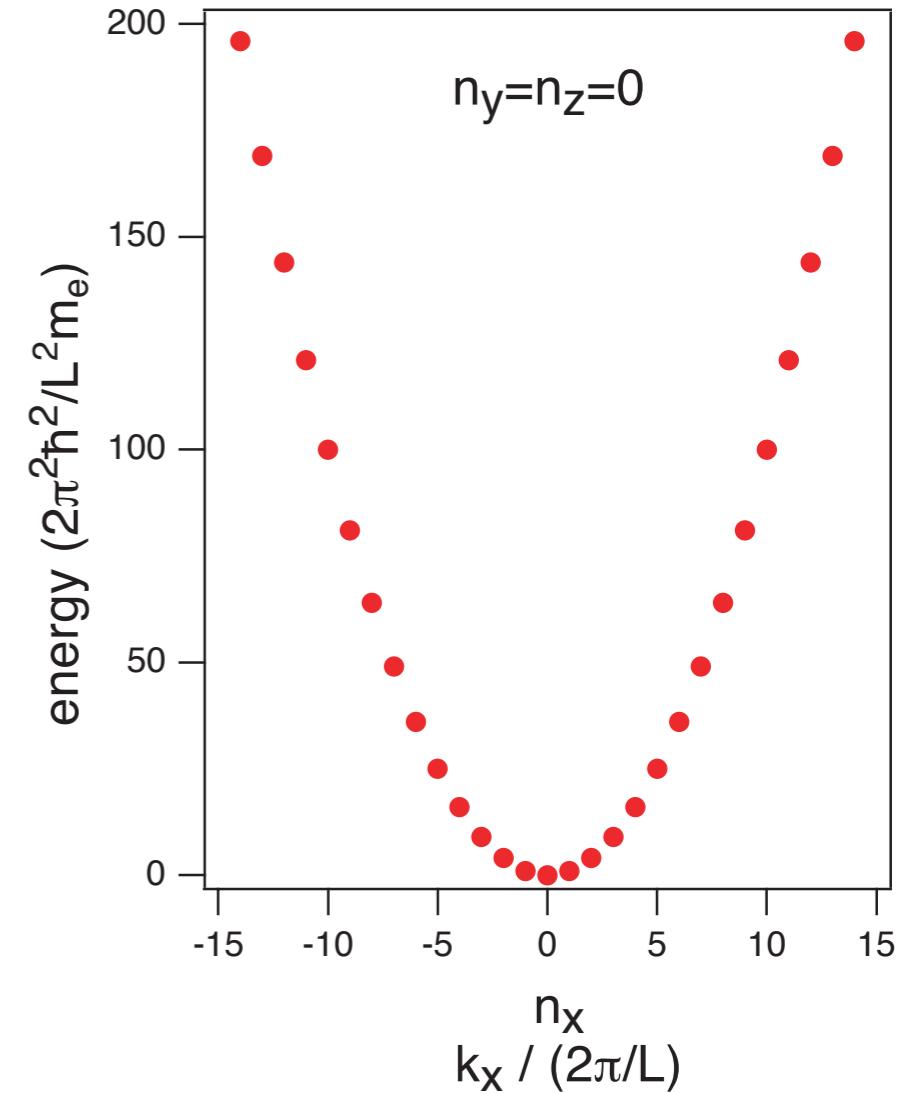
$$E(\mathbf{k}) = \frac{\hbar^2 k^2}{2m_e} = \frac{\hbar^2}{2m_e} (k_x^2 + k_y^2 + k_z^2)$$

where we have made the  **$k$ -dependence explicit.** We now have a *quasi-continuous band* (\*) of energies just as we argued we should in §2.3, which depend quadratically on the magnitude of the wavevector.

\* I say “quasi-continuous” because of course the energy eigenvalues are discrete. However, the separation is very small, of order  $\frac{\hbar^2}{2m_e} \left( \frac{2\pi}{L} \right)^2$

Since all electron-electron interactions are ignored in this model, these are “one-electron” levels in the sense that we’ve solved the Schrödinger equation for a single electron. Each of these levels can be populated by two electrons without violating the Pauli Exclusion Principle. Starting at the lowest energy, we carry on populating these levels with two electrons until we have assigned levels to all electrons in the solid (\*).

Let’s calculate what the highest energy will be, if we have  $N$  electrons to accommodate; this means we are going to need  $N/2$  levels. What  $n$  will this correspond to?



Energy levels for free electrons  
(image : Hofmann)

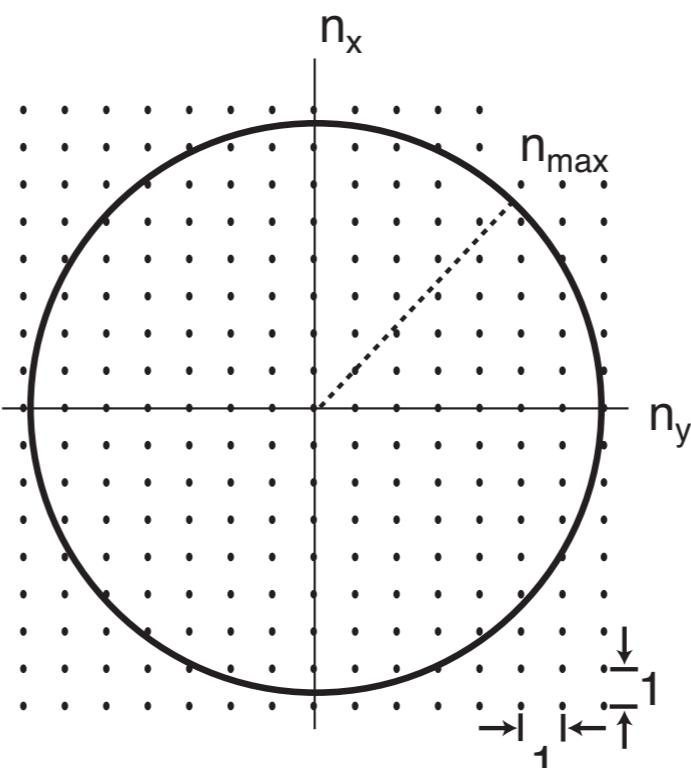
\*This is where the Sommerfeld model is most different from the Drude model in that we are populating the states according to Fermi-Dirac distribution, rather than the classical Maxwell-Boltzmann distribution

Perhaps the simplest way of figuring this out is geometrically. How many states lie within a sphere of radius  $n_{max}$ ? As the states (in  $n_x$ ,  $n_y$ ,  $n_z$ ) are separated in units of one, the total number of states is just the volume of the sphere. Thus:

$$\frac{N}{2} = \frac{4}{3}\pi n_{max}^3$$

number of states we  
need to  
accommodate

volume of a sphere of  
radius  $n_{max}$



Hence :

$$n_{max} = \left( \frac{3N}{8\pi} \right)^{1/3}$$

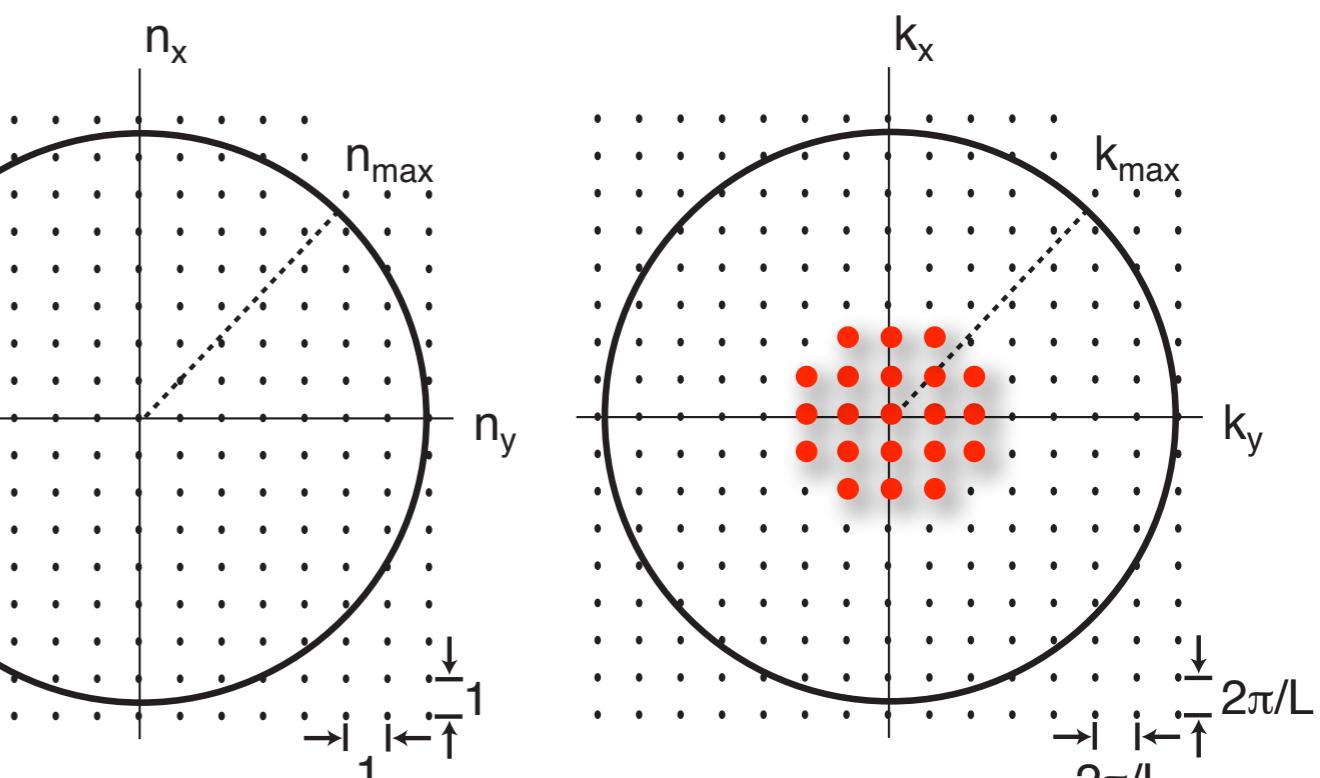
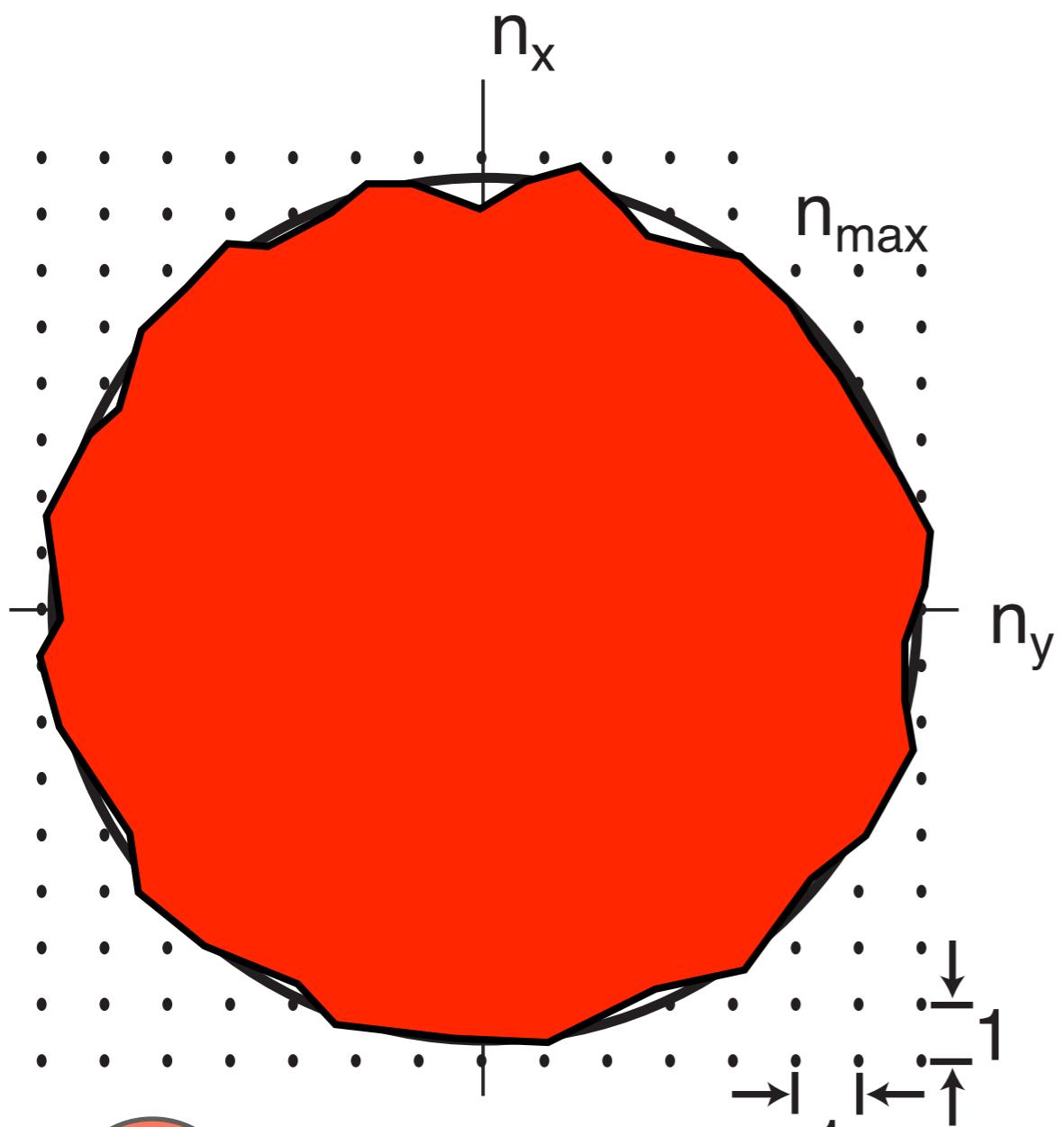


Illustration (in 2D) of the discrete set of levels  
expressed both in terms of  $n$  and  $\mathbf{k}$   
(image : Hofmann)



$$\frac{N}{2} = \frac{4}{3} \pi n_{\max}^3$$

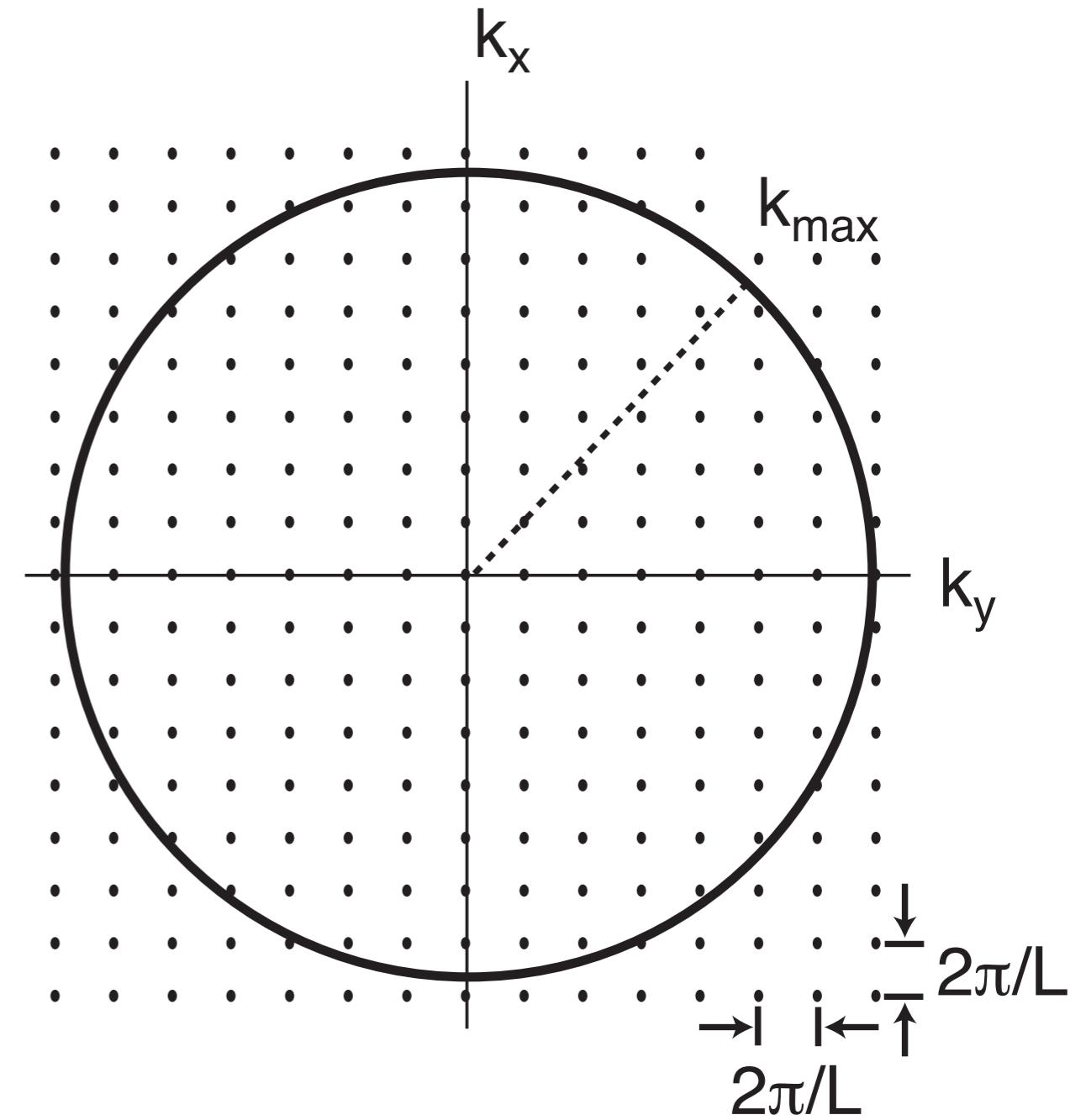


Illustration (in 2D) of the discrete set of levels expressed both in terms of  $n$  and  $\mathbf{k}$   
(image : Hofmann)

Therefore the maximum energy is :

$$\begin{aligned} E_{\max} &= \frac{\hbar^2 k_{\max}^2}{2m_e} = \frac{\hbar^2}{2m_e} \left( \frac{2\pi}{L} \right)^2 n_{\max}^2 \\ &= \frac{\hbar^2}{2m_e} \left( \frac{8\pi^3}{L^3} \frac{3N}{8\pi} \right)^{2/3} \\ &= \frac{\hbar^2}{2m_e} (3\pi^2 n)^{2/3} \end{aligned}$$

$n$  here is the number density of electrons (i.e.  $N/L^3$  or  $N/V$ ) so do not confuse it with  $n_{\max}$  which was the radius of our sphere of states

We call this maximum energy the *Fermi Energy* ( $E_F$ ). For most metals it is of the order of a few eV.

So,

$$E_F = \frac{\hbar^2}{2m_e} (3\pi^2 n)^{2/3}$$

We can also express this quantity in terms of the maximum wavevector, which we call the *Fermi wavevector*,  $k_F$  :

$$E_F = \frac{\hbar^2}{2m_e} k_F^2$$

meaning that

$$k_F = (3\pi^2 n)^{1/3}$$

Metal	$n (10^{22} \text{ cm}^{-3})$	$k_F (10^8 \text{ cm}^{-1})$	$E_F (\text{eV})$
Li	4.62	1.11	4.7
Na	2.53	0.91	3.14
Cs	0.86	0.63	1.53
Al	18.07	1.75	11.65
Cu	8.47	1.36	7.03
Ag	5.86	1.2	5.5
Au	5.9	1.2	5.52

Electron density, Fermi wavevector and Fermi energy for a few metals (Lüth and Lüth,  
 Solid State Physics (Fourth Edition), Springer)

## 2.4.2 The Density of States

In calculating many important quantities, it turns out that it is crucial to know how many allowed states (coming from the quantisation) there are within some small energy interval  $dE$  at some energy particular energy,  $E$ . It might be clearer, though, if we start in  $k$ -space, as after all, that is where the quantisation occurs.

Let's look at some large volume (\*) of  $k$ -space. One unit of volume in  $k$ -space is  $(2\pi/L)^3$ , and so the number of allowed levels per unit volume of  $k$ -space is  $(L/2\pi)^3$  or, in  $d$  dimensions,  $(L/2\pi)^d$ .



$L^3$  is, of course, the volume  $V$  of the crystal



We might be looking at some problems in one-dimension of two dimensions, so it is worth generalising this now.

\* Large on the scale of the discretisation i.e. large compared with  $(2\pi/L)^3$

Each allowed level can contain 2 electrons (one of each spin), and therefore the number of allowed states between  $k$  and  $k+dk$  is :

$$D(k)dk = 4\pi k^2 dk \times \left(\frac{L}{2\pi}\right)^3 \times 2$$

Note : This expression is for three dimensions (3D)  
- equivalent expressions will exist in 1D and 2D

Having derived the expression for the number of allowed states between  $k$  and  $(k+dk)$  in terms of  $k$ , we can straightforwardly convert to energy using the relationship between  $E$  and  $k$  in the free electron model.

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

$$\therefore dE = \frac{\hbar^2 k dk}{m}$$

$$D(k)dk = D(E)dE = 4\pi k^2 \frac{mdE}{\hbar^2 k} \times \frac{V}{8\pi^3} \times 2$$

$V=L^3$

this term is  $dk$

$$\therefore D(E)dE = V \left( \frac{2mE}{\hbar^2} \right)^{1/2} \frac{1}{\hbar^2 \pi^2} mdE$$

Simplifying, and dropping the  $dE$  (as we want an expression for the *density of states*, not the number of states),

density of states (DOS)  
for free electrons  $\rightarrow$

$$D(E) = \frac{V}{2\pi^2} \left( \frac{2m}{\hbar^2} \right)^{3/2} E^{1/2}$$

We could derive this another way. Earlier when we were calculating the maximum energy (the Fermi energy) associated with accommodating our  $N$  electrons we had an expression :

$$E = \frac{\hbar^2}{2m_e} \left( \frac{3\pi^2 N}{V} \right)^{2/3}$$

Or making the dependence on  $N$  explicit:

$$E(N) = \frac{\hbar^2}{2m_e} \left( \frac{3\pi^2 N}{V} \right)^{2/3}$$

The number of states ( $dN$ ), then, in a small energy interval  $dE$  is:

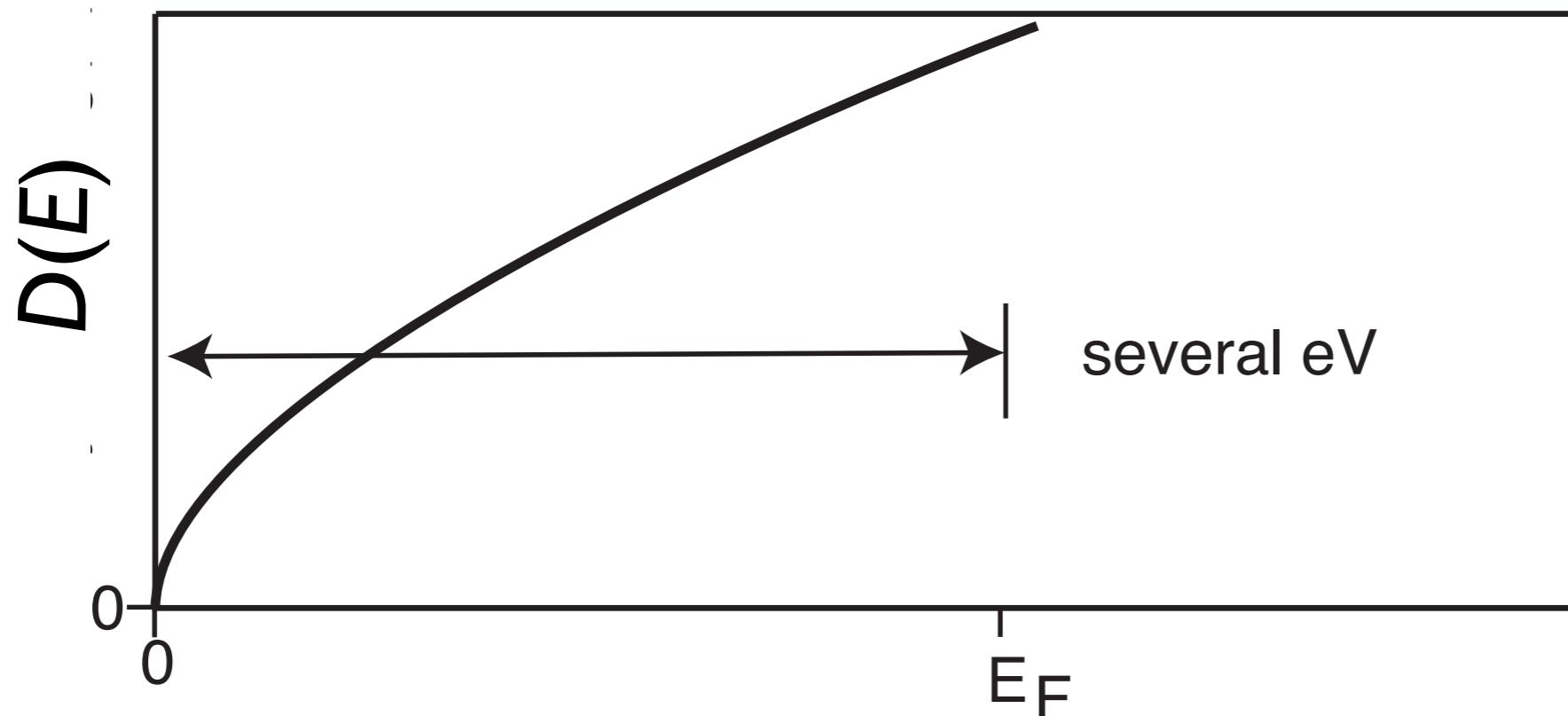
$$D(E)dE = dN = \frac{dN}{dE}dE = \frac{V}{2\pi^2} \left( \frac{2m}{\hbar^2} \right)^{3/2} E^{1/2}dE$$

giving us the same expression for  $D(E)$  as before.

The density of states for 3D free electrons behaves like  $\sqrt{E}$

Fermi energy is determined by area under  $D(E)$  graph between zero and the Fermi energy being  $N$  electrons i.e.

$$N = \int_0^{E_F} D(E) dE \quad \xleftarrow{\text{true at zero temperature}}$$



We now know how the states are distributed in energy; but how they are actually *populated* is going to depend on temperature, and so far we have only considered zero temperature.

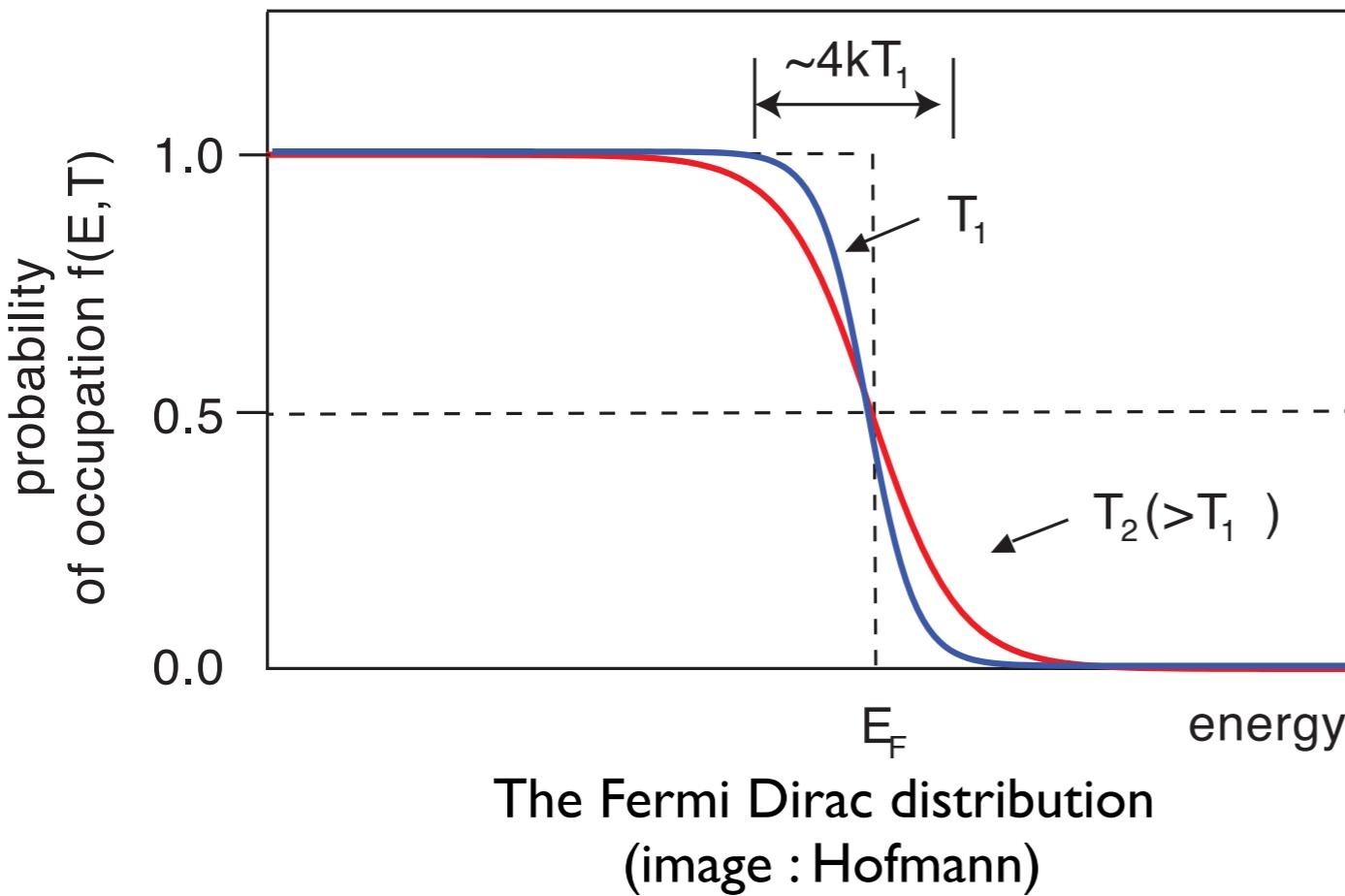
## 2.4.3 The Electron Distribution at Finite Temperature

Electrons are fermions, and so will be distributed according to the *Fermi-Dirac distribution* :

$$f(E, T) = \frac{1}{e^{(E-\mu)/k_B T} + 1},$$

where  $\mu$  is the chemical potential.

For metals, we can put the chemical potential equal to the Fermi energy ; this is strictly only true at zero temperature, but it's good enough for metals.

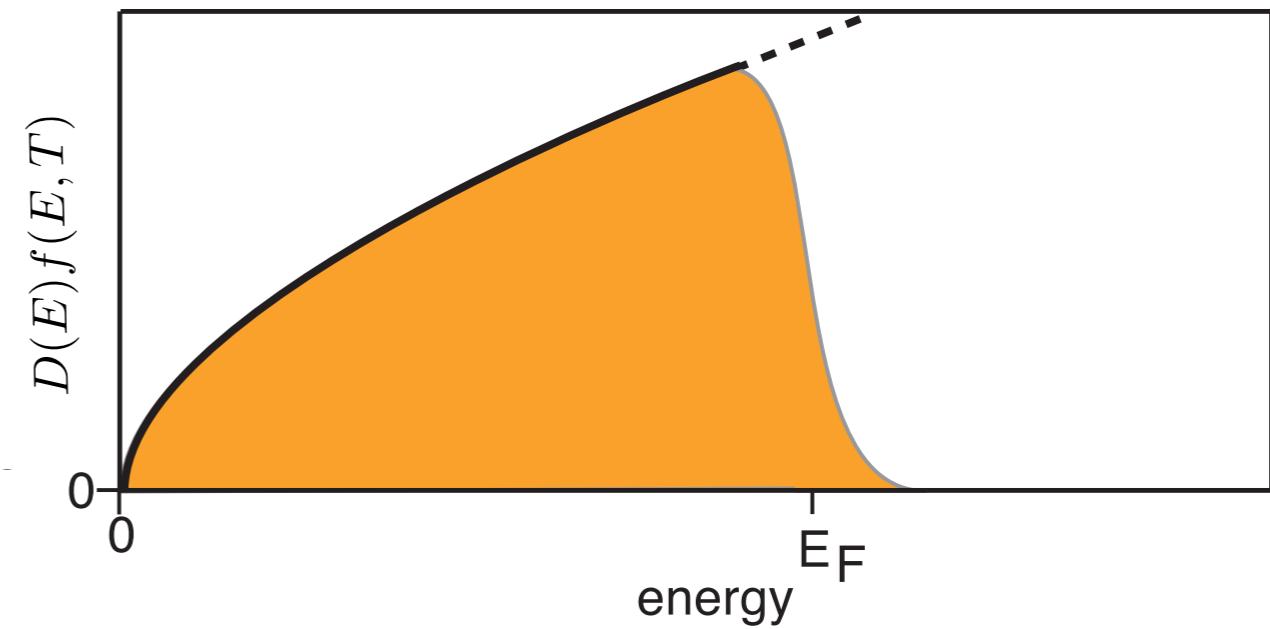


At finite temperature, there is a smearing of the distribution function at the chemical potential, meaning that states below it are unoccupied and states above are occupied. We can think of this as a “soft zone”.

This “soft zone” has an energy width of  $\sim 4k_B T$ . Recalling that  $k_B T$  is about 25meV at room temperature, this means that we have a “soft zone” of about 0.1eV at room temperature. At finite temperature, our expression for the number of electrons becomes :

$$N = \int_0^{\infty} D(E) f(E, T) dE ,$$

and the Fermi energy is now “hidden” within the Fermi-Dirac distribution which affects the cut off to contributions to the integral around the chemical potential (which, for metals, is effectively the Fermi energy).



Density of occupied states at finite temperature  
(Image : Hofmann)

## 2.4.4 The Fermi Surface

Let's go back to zero temperature again, so that we have a sharp cut-off between occupied and unoccupied states at the Fermi energy (\*). In §2.3.1 we introduced the idea of a Fermi wavevector,  $k_F$ , which defined the maximum wavevector for a given electron density,  $n$  :

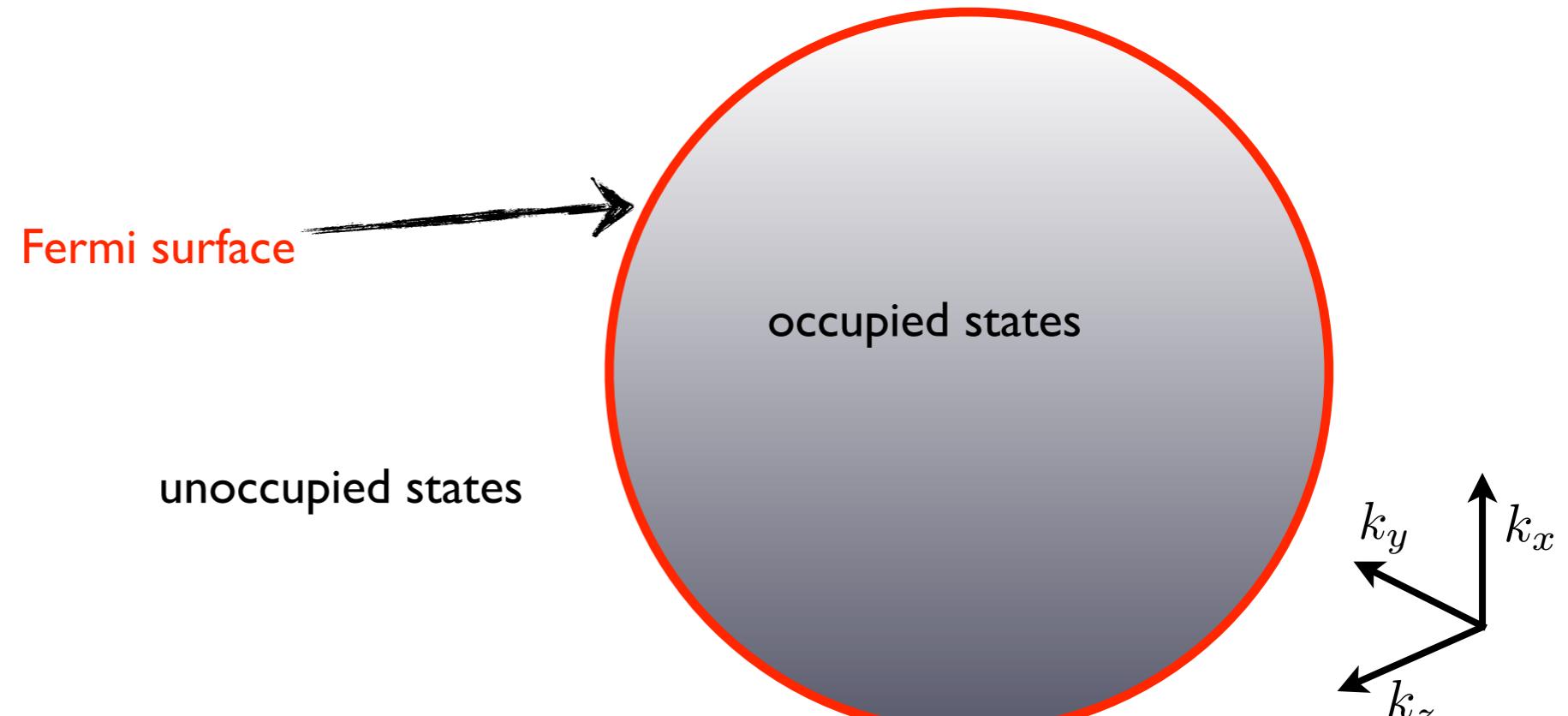
$$k_F = (3\pi^2 n)^{1/3}$$

This means that we have a sphere of occupied states in wavevector ( $k$ -)space, the sphere having a radius of  $k_F$ . We call this sphere the free-electron *Fermi surface*. We will see later on when we “switch on” the interaction between the electrons and the lattice so that these electrons stop being free that this surface no longer has to be a sphere, but the idea of a Fermi surface will still remain.

\* At finite temperature, the Fermi surface we are about to introduce will just be smeared out over an energy range of  $\sim 4k_B T$

A definition :

“The Fermi surface is the surface of constant energy in reciprocal space (\*) which separates occupied states from unoccupied ones”



The free electron Fermi surface is a sphere of radius  $k_F$

\* Reciprocal space is another way of saying wavevector space or  $k$ -space.

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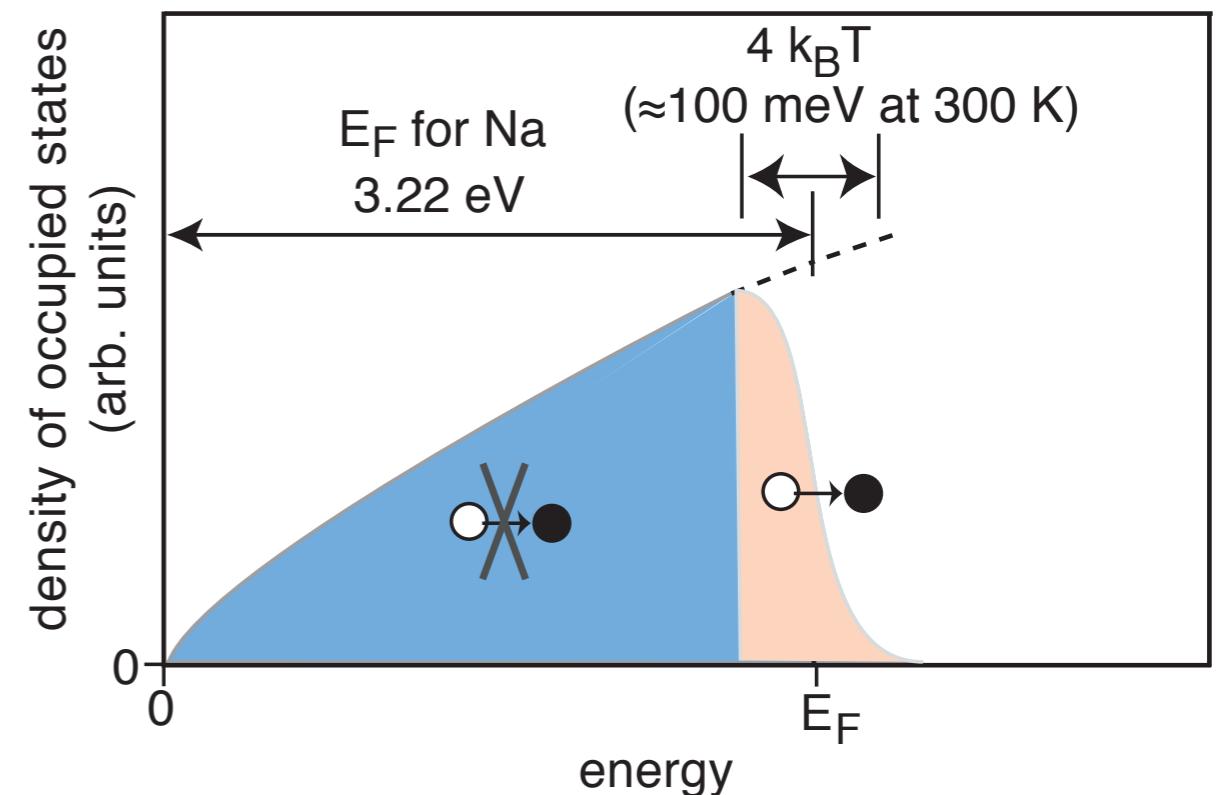
**Invited Comment**

## **Life on the edge: a beginner's guide to the Fermi surface**

**S B Dugdale**

H.H. Wills Physics Laboratory, University of Bristol, Tyndall Avenue, Bristol BS8 1TL, UK

Why is it so important? The very existence of a Fermi surface is due to the Pauli principle which forbids fermions (electrons) to be in the same quantum state, forcing electrons to occupy higher and higher energies until all have been accommodated. The Pauli principle also means that most of the electrons below (\*) the Fermi level are effectively inert as they cannot reach (scatter into) unoccupied states if their energy changes by just a small amount, leaving just a small number of electrons in this “soft zone” around the Fermi energy. Put simply, it’s only electrons on the Fermi surface (or very close to it) that matter.



The scattering of electrons in states below  $E_F$  is restricted because there are no easily accessible states for them to scatter into.

(image : Hofmann)

\* Only electrons with a few  $k_B T$  of the Fermi energy are relevant.

## 2.4.5 Heat Capacity Within the Sommerfeld Model

Experimentally, how does the heat capacity depend on temperature?

PHYSICAL REVIEW

VOLUME 118, NUMBER 4

MAY 15, 1960

### Heat Capacity of Sodium and Potassium at Temperatures below 1°K

WILLIAM H. LIEN AND NORMAN E. PHILLIPS

Department of Chemistry and Lawrence Radiation Laboratory, University of California, Berkeley, California

(Received December 17, 1959)

The heat capacities of sodium and potassium have been measured from about 0.15°K to just above 1°K. No anomaly was observed in either case: the heat capacity could be represented by the sum of a term linear in temperature and a cubic term. Values of the Debye temperatures and effective masses of the conduction electrons are given.

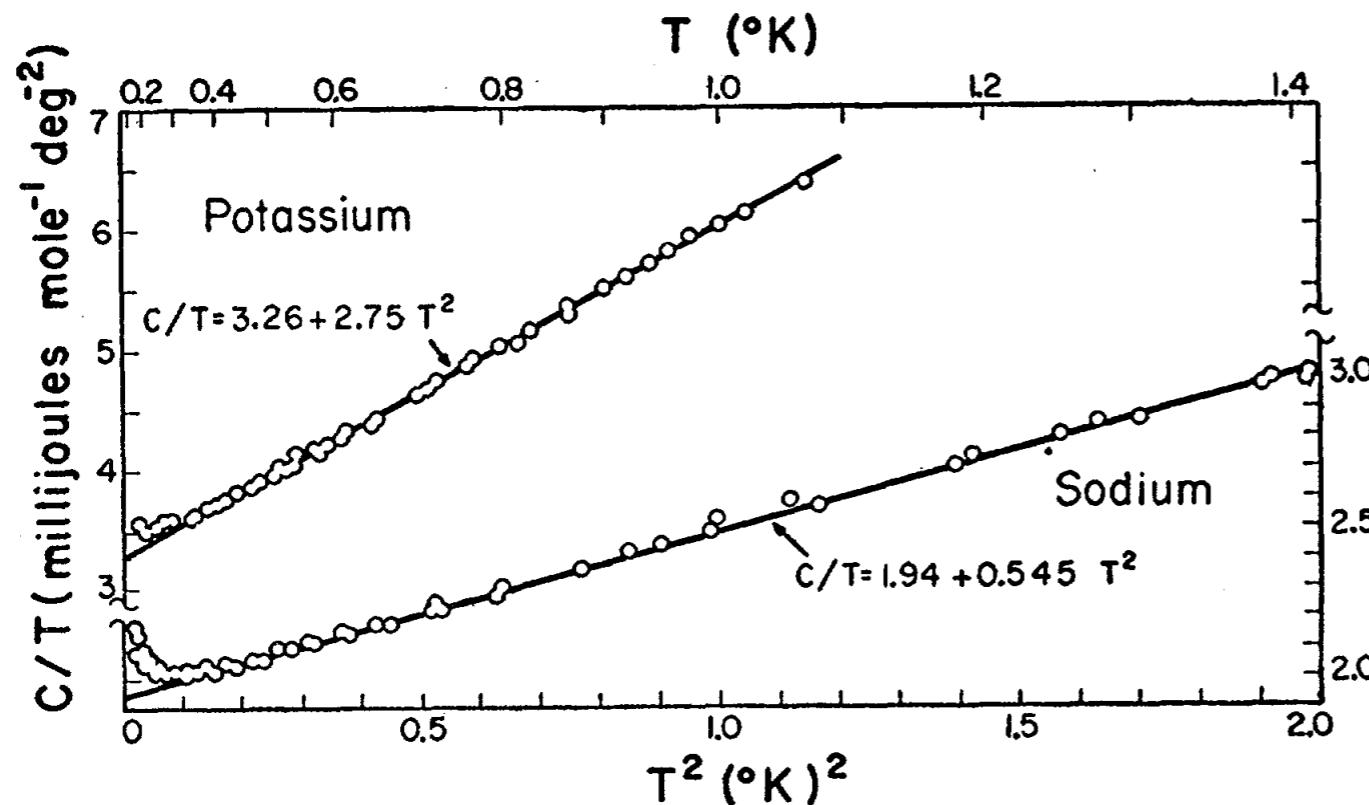


FIG. 1.  $C/T$  vs  $T^2$ .  $C$  is the heat capacity of sample plus calorimeter per mole of sample. The corrections to  $C/T$  for the calorimeters were estimated from the known heat capacities of the material used (largely copper) and are  $0.49 + 0.036T^2$  and  $1.02 + 0.07T^2$  millijoules/mole deg<sup>2</sup> for sodium and potassium, respectively.

$$C = \gamma T + \beta T^3$$

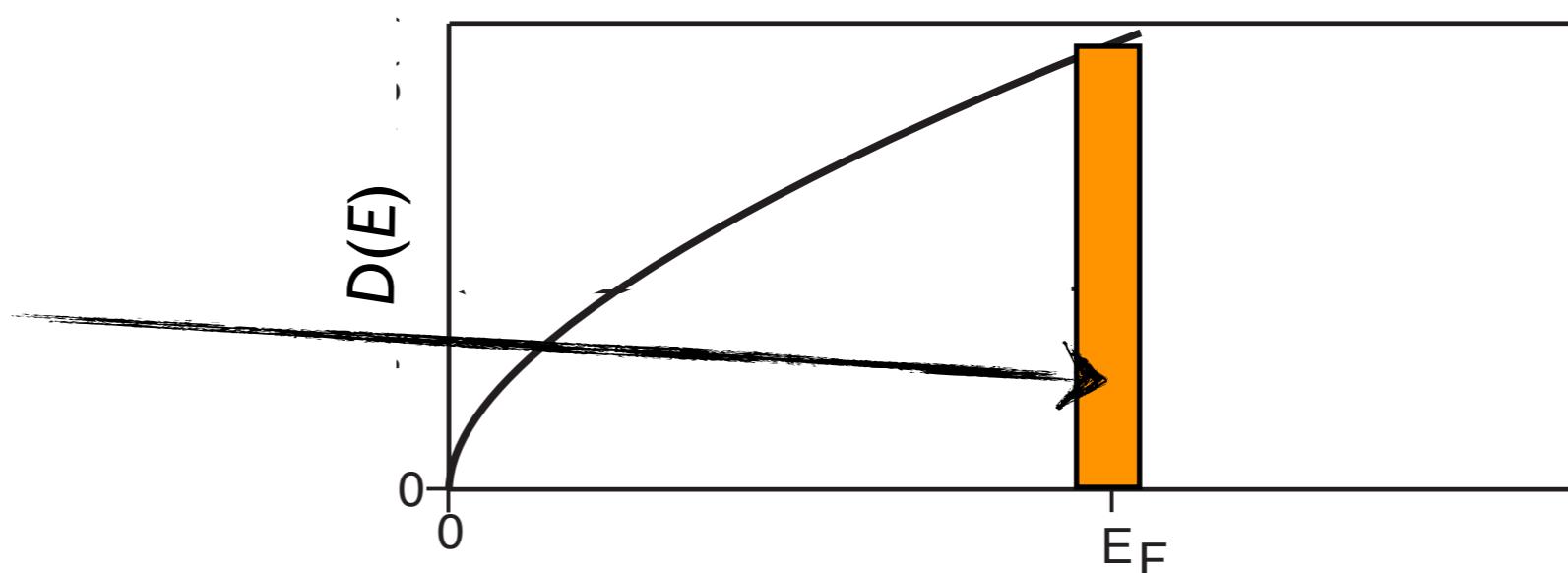
linear term due to electrons  
cubic term due to phonons  
this is the term we'll be trying to understand

What does the Sommerfeld theory predict? We need to work out the internal energy at finite temperature i.e.

$$U_{\text{int}} = \int_0^{\infty} ED(E)f(E, T)dE$$

We would then work out the heat capacity from  $C_V = \left(\frac{\partial U}{\partial T}\right)_V$ . The problem is that the above integral is a rather complicated to evaluate at finite temperature. An approximation can be made as follows. Let's assume that as we raise the temperature, a number of electrons will be excited from below the Fermi energy to above the Fermi energy, and that in doing so they gain an energy of the order of  $k_B T$ . We can estimate the number of electrons that do this by taking it to be the number within  $k_B T$  of the Fermi energy which again we can approximate as being  $D(E_F)k_B T$ .

$k_B T$  window around  
Fermi energy not to  
scale! Area of rectangle  
is  $D(E_F)k_B T$



Therefore the change in internal energy with respect to zero temperature (  $\Delta U = U - U_{0K}$  ) is going to be of the order of :

$$\begin{aligned}\Delta U &\sim D(E_F)k_B T \times k_B T \\ &\sim D(E_F)k_B^2 T^2\end{aligned}$$

and therefore

$$C_V \sim 2D(E_F)k_B^2 T$$

The exact result (doing those nasty integrals) is :

$$C_V = \frac{\pi^3}{3} D(E_F) k_B^2 T$$



Note that the heat capacity is proportional to temperature - as in the experiment

We know what the density of states at the Fermi level is for free electrons :

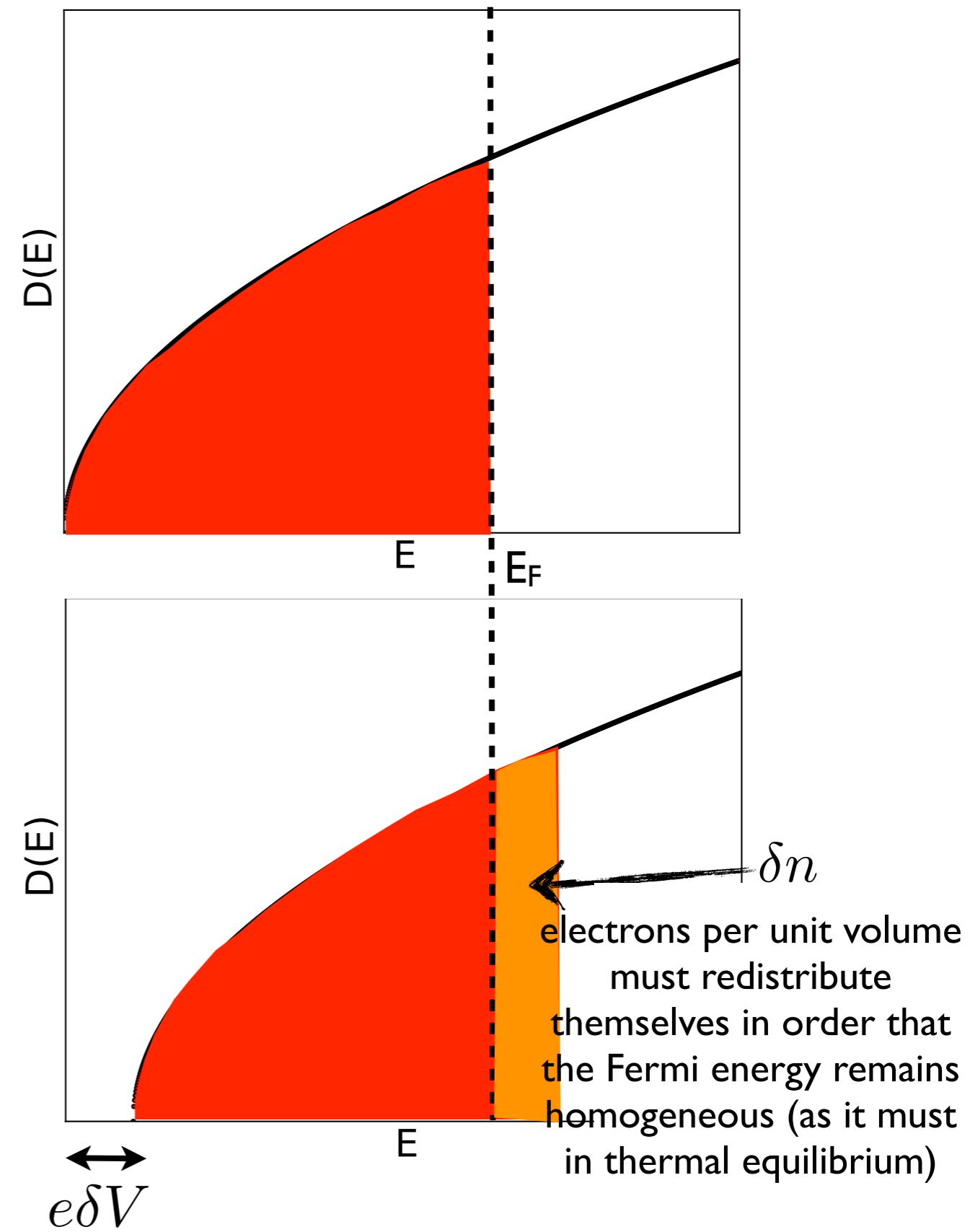
$$D(E_F) = \frac{V}{2\pi^2} \left( \frac{2m_e}{\hbar^2} \right)^{3/2} E_F^{1/2}$$

and therefore it is possible to evaluate the constant which appears in the temperature dependence of the specific heat ( $C = \gamma T$ ). Real materials have  $\gamma$  constants that can vary quite substantially from the free electron value, and the usual way to interpret this is through “mass enhancement” i.e. somehow the electrons are not behaving as though they have the free electron mass, but a different one.

How can this be? It is because in reality electrons are not free, and you will see that electrons in real bands behave as if they have a mass which is different from their rest mass - this is called their “effective mass”. This mass is further influenced by their interactions, with for example, lattice vibrations - this lies at the heart of conventional superconductivity.

## 2.4.6 Electrostatic Screening and the Mott Transition

What happens when we introduce a small charge into a metal? The otherwise homogeneous electron distribution is going to be perturbed, and will rearrange itself in order to compensate the electric field created by the charge. We call this “screening” and we can model it as follows. Let’s assume the charge impurity creates some local perturbation potential  $\delta V$ , which will have the effect of shifting the  $D(E)$  by an energy  $e\delta V$ .



We can assume that this is a small perturbation and therefore obeys  $|e\delta V| \ll E_F$ .

Recall that Poisson's equation relates charge density to potential:

$$\begin{aligned}
 \nabla^2(\delta V) &= -\frac{-\delta\rho}{\epsilon_0} \\
 &= -\frac{e\delta n}{\epsilon_0} \quad \leftarrow \text{δn is (approximately) } D(E_F)e\delta V \\
 &= -\frac{e^2 D(E_F)}{\epsilon_0} \delta V
 \end{aligned}$$

Assuming spherical symmetry, and using the form of the Laplacian in spherical polar coordinates

$$\begin{aligned}
 \nabla^2(\delta V) &\equiv \frac{1}{r^2} \frac{\partial}{\partial r} r^2 \frac{\partial}{\partial r} (\delta V) \\
 &\equiv \left( \frac{\partial^2}{\partial r^2} + \frac{2}{r} \frac{\partial}{\partial r} \right) \delta V
 \end{aligned}
 \quad \dots$$

... it can be shown that :

$$\delta V(r) = \frac{e}{4\pi\epsilon_0} \frac{e^{-\lambda r}}{r}$$

where

$$\lambda^2 = \frac{e^2 D(E_F)}{\epsilon_0}$$

The quantity

$$r_{TF} = \left( \frac{e^2 D(E_F)}{\epsilon_0} \right)^{-1/2}$$



$r_{TF}$  is just  $1/\lambda$

so that

$$\delta V(r) = \frac{e}{4\pi\epsilon_0} \frac{e^{-r/r_{TF}}}{r}$$

is called the Thomas-Fermi screening length.

In the free-electron model, the Thomas-Fermi screening length is given by :

$$\begin{aligned}\frac{1}{r_{\text{TF}}^2} &= \frac{me^2}{\pi^2 \hbar^2 \epsilon_0} (3\pi^2 n)^{1/3} \\ &= \frac{4}{\pi} (3\pi^2)^{1/3} \frac{n^{1/3}}{a_0}\end{aligned}$$

where  $a_0$  is the Bohr radius ( $\approx 0.529$  Å). To a good approximation then,

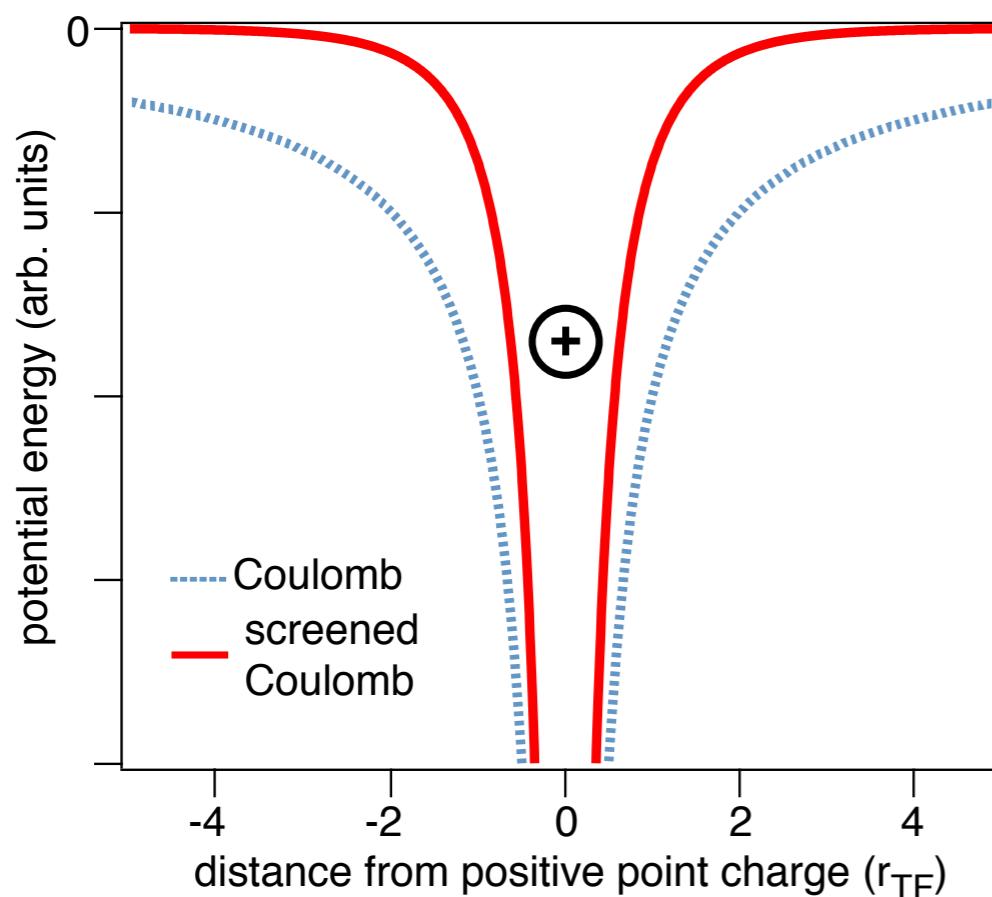
$$\frac{1}{r_{\text{TF}}} \approx 2 \frac{n^{1/6}}{a_0^{1/2}}$$

or

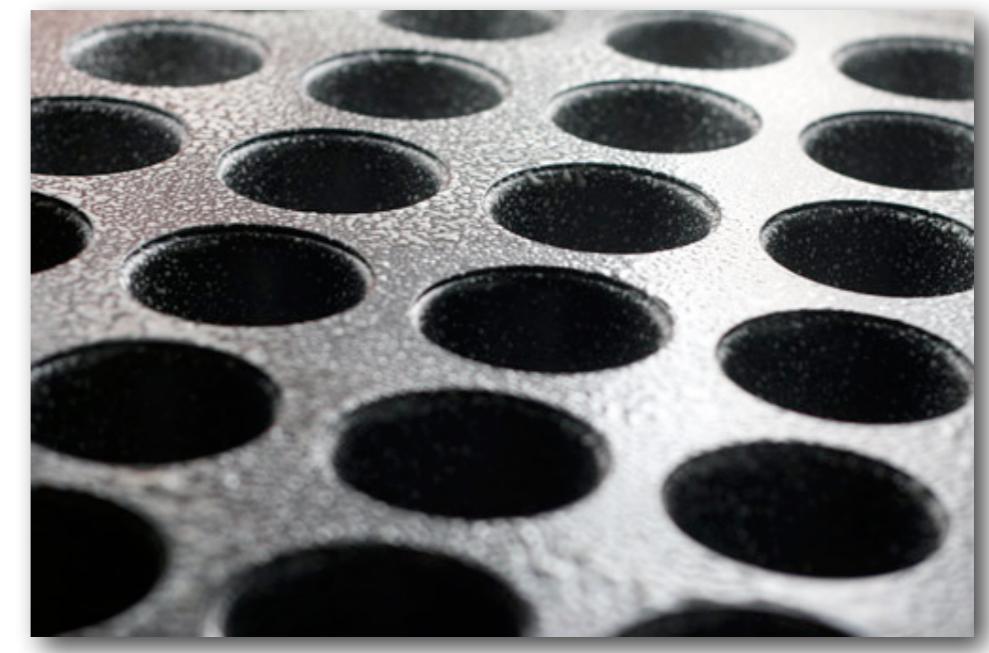
$$r_{\text{TF}} \approx 0.5 \left( \frac{n}{a_0^3} \right)^{-1/6}$$

For Cu, this is about 0.55 Å !

This starts to explain, then, why metals have conduction electrons in the first place. The Coulomb interaction has had its infinite range curtailed by the exponential term, and therefore bound states do not exist. In fact, this is the essence of the Mott transition...



The “screened” Coulomb potential  
(Image: Hofmann)



The so-called “muffin-tin potential”  
(Image: public domain)

Mott used an argument similar to this to explain why at some critical doping (corresponding to some critical electron density  $n$ ) in a material it could suddenly go from being insulating to metallic.

It goes like this. If you look at the form of this screened Coulomb potential (also called a Yukawa potential), then by solving the Schrödinger equation with this potential it is possible (but tricky) to show that it will not support bound states for all values of  $\lambda$ , and therefore there will be a critical value of the Thomas-Fermi screening length, below which the potential cannot bind the electron. This critical value is

$$r_{TF} < 0.84a_0$$



Prof. Sir Neville Mott, FRS  
(Image : University of Bristol)

Within the free electron model, then, we can convert this condition on the Thomas-Fermi screening length to a condition on the lattice spacing e.g. let's assume a simple cubic structure, with lattice spacing  $a$ , and assume that each atom provides one electron. Therefore,

$$n = \frac{1}{a^3}$$

So the condition for the solid being a metal, then, is that the screened Coulomb potential can no longer bind its electron, and therefore (using the definition of  $r_{TF}$ ) that :

$$a < 3.4a_0$$

Mott used a slightly more sophisticated argument, and got :

$$a < 4.5a_0$$

## 2.4.7 Sommerfeld - Successes and Shortcomings

The Sommerfeld model of free electrons is undoubtedly a great improvement on the Drude theory. Amongst other successes, it predicts the correct temperature dependence of the low temperature heat capacity (\*).

There are a number of shortcomings, but we should focus on just two. Firstly, we are no closer to understanding why some solids are insulators and others are metals. Secondly, as we shall see in the latter part of this course, Fermi surfaces of real metals are never spherical (although some of the alkali metals e.g. Na are nearly spherical. See <http://www.phys.ufl.edu/fermisurface/>).

To go further, we are going to need to *switch on* the lattice potential, and deal with the complications it will introduce. Our electrons will go from being *free* to being merely *nearly free*.

\* I say “low temperature” because at low temperatures the  $T^3$  term due to phonons can be neglected in comparison with the  $T$ -linear term due to electrons.

## 2.5.1 Nearly Free Electrons

In §2.4.1 we solved the Schrödinger equation for a vanishing potential (i.e.  $U=0$ ). We are now going to tackle it for a finite (but still small) potential. We are still going to use the independent electron approximation (the electrons are not interacting with each other), but our electrons are no longer free; they are now only *nearly free*. Let's start by reminding ourselves of what we're going to solve :

$$-\frac{\hbar^2 \nabla^2}{2m_e} \psi(\mathbf{r}) + U(\mathbf{r})\psi(\mathbf{r}) = E\psi(\mathbf{r})$$

where the potential must have the periodicity of the lattice :

$$U(\mathbf{r}) = U(\mathbf{r} + \mathbf{R})$$

We still adopt the same Born-von Kármán boundary conditions (which will place the same constraints on the allowed values of  $\mathbf{k}$ ).

## 2.5.2 Bloch's Theorem

We are now going to prove a very important theorem which expresses perhaps the most remarkable fact about the wavefunctions of electrons in crystalline solids and explains how the electrons can travel so far without “bumping” into the ion cores. We begin with a very general statement : Every solution of this Schrödinger equation consistent with periodic boundary conditions can be written in terms of a sum of plane waves :

$$\psi(\mathbf{r}) = \sum_{\mathbf{k}} c_{\mathbf{k}} e^{i\mathbf{k}\cdot\mathbf{r}}$$

We can assume that the  $\mathbf{k}$ 's can only take values allowed by the boundary conditions, and that the overall wavefunction has a normalisation that is taken care of by the plane wave coefficients,  $c_{\mathbf{k}}$ . We can also make a Fourier expansion of the potential, just like we did for the charge density earlier :

$$U(\mathbf{r}) = \sum_{\mathbf{G}} U_{\mathbf{G}} e^{i\mathbf{G}\cdot\mathbf{r}}$$

Note that since the potential also has to be a real quantity, the Fourier coefficients have to obey :

$$U_{-\mathbf{G}} = U_{\mathbf{G}}^*$$

Let's look at the kinetic and potential energy terms in the Schrödinger equation in turn. First, the kinetic energy term is :

$$-\frac{\hbar^2 \nabla^2}{2m_e} \psi(\mathbf{r}) = \sum_{\mathbf{k}} \frac{\hbar^2 k^2}{2m_e} c_{\mathbf{k}} e^{i\mathbf{k}\cdot\mathbf{r}}$$

Next, the potential energy term is :

$$\begin{aligned} U(\mathbf{r})\psi(\mathbf{r}) &= \left( \sum_{\mathbf{G}} U_{\mathbf{G}} e^{i\mathbf{G}\cdot\mathbf{r}} \right) \left( \sum_{\mathbf{k}} c_{\mathbf{k}} e^{i\mathbf{k}\cdot\mathbf{r}} \right) \\ &= \sum_{\mathbf{k}\mathbf{G}} U_{\mathbf{G}} c_{\mathbf{k}} e^{i(\mathbf{G}+\mathbf{k})\cdot\mathbf{r}} \\ &= \sum_{\mathbf{k}'\mathbf{G}} U_{\mathbf{G}} c_{\mathbf{k}'-\mathbf{G}} e^{i\mathbf{k}'\cdot\mathbf{r}} \end{aligned}$$

In this last step, we've introduced  $\mathbf{k}'=\mathbf{k}+\mathbf{G}$  in order that we have the same form of plane wave as we had for the K.E. term. We can do this because the sum is over all  $\mathbf{k}$  vectors consistent with the boundary conditions, and the reciprocal lattice vectors are clearly a subset of these

The new summation over  $\mathbf{k}'$  (rather than over  $\mathbf{k}$ ) is completely arbitrary, so I can just replace the  $\mathbf{k}'$  with  $\mathbf{k}$  to give :

$$U(\mathbf{r})\psi(\mathbf{r}) = \sum_{\mathbf{kG}} U_{\mathbf{G}} c_{\mathbf{k}-\mathbf{G}} e^{i\mathbf{k}\cdot\mathbf{r}}$$

Therefore our original Schrödinger equation can be written :

$$\sum_{\mathbf{k}} e^{i\mathbf{k}\cdot\mathbf{r}} \left\{ \left( \frac{\hbar^2 k^2}{2m_e} - E \right) c_{\mathbf{k}} + \sum_{\mathbf{G}} U_{\mathbf{G}} c_{\mathbf{k}-\mathbf{G}} \right\} = 0$$

This is known as the *central equation*. It is just the Schrödinger equation in a periodic lattice written as a set of *algebraic equations* rather than as the more familiar differential equation. In principle, this set of equations is infinite in extent (our wavefunction and potential could have infinitely many Fourier components), but in practice we can take a finite number.

How do we go about solving this set of equations? To get the whole “band structure”, we would need to do this for all the values of  $\mathbf{k}$  separately i.e. we will have to solve the set of equations at each **k**-point where we want to know the wavefunction (the coefficients  $c_{\mathbf{k}}$ ) or the energy,  $E$ . Note that the plane waves are orthogonal, so the term  $\{\dots\}$  has to vanish for each  $\mathbf{k}$ . Before we try and solve this, let’s get back to our derivation of Bloch’s Theorem by looking at the set of equations for some particular value of  $\mathbf{k}$ . We get :

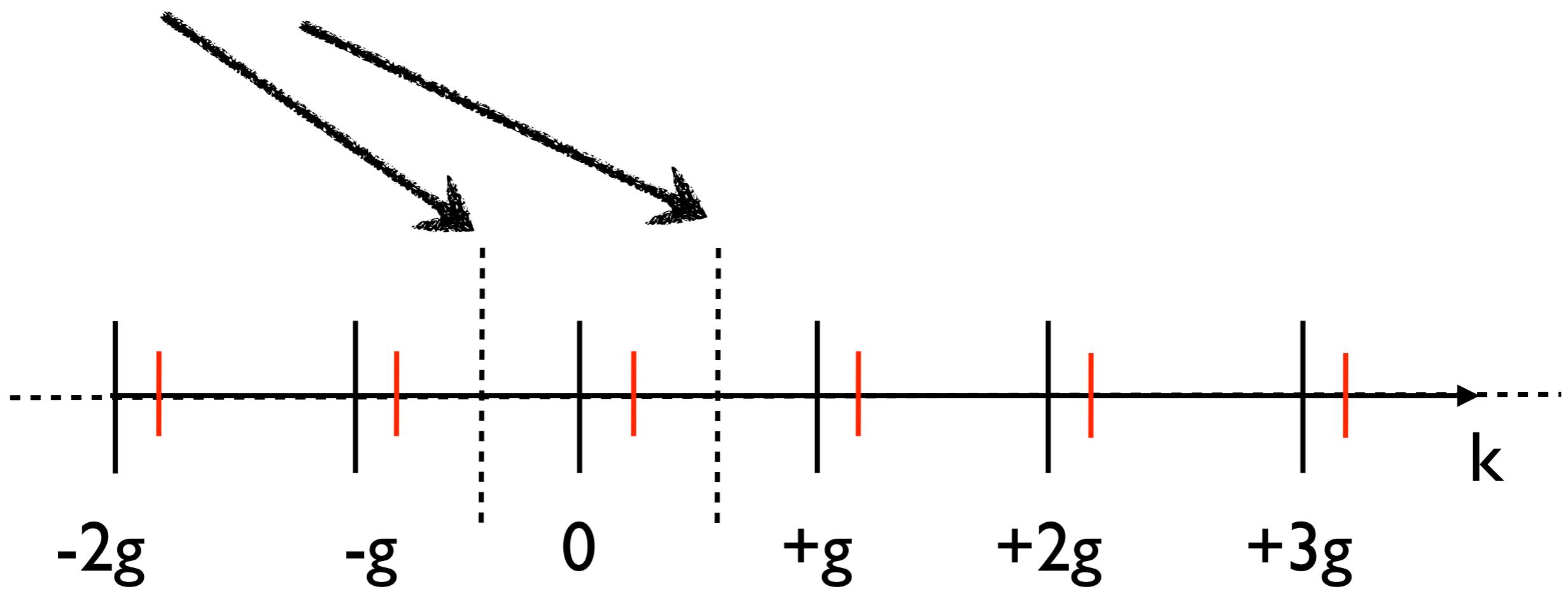
$$\left( \frac{\hbar^2 k^2}{2m_e} - E \right) c_{\mathbf{k}} + \sum_{\mathbf{G}} U_{\mathbf{G}} c_{\mathbf{k}-\mathbf{G}} = 0$$

Notice how this equation only couples coefficients ( $c_{\mathbf{k}}$ ) that differ by a  $\mathbf{G}$  vector. This means that the wavefunction for electrons with wavevector  $\mathbf{k}$ ,  $\psi_{\mathbf{k}}(\mathbf{r})$ , can be written as

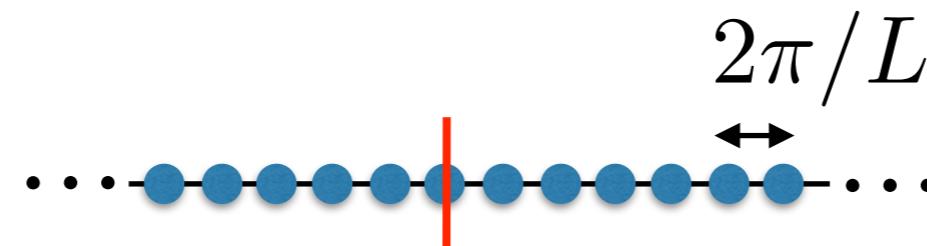
$$\psi_{\mathbf{k}}(\mathbf{r}) = \sum_{\mathbf{G}} c_{\mathbf{k}-\mathbf{G}} e^{i(\mathbf{k}-\mathbf{G}) \cdot \mathbf{r}}$$

edges of first Brillouin zone  $\pm\pi/a$

$$\left( \frac{\hbar^2 k^2}{2m_e} - E \right) c_{\mathbf{k}} + \sum_{\mathbf{G}} U_{\mathbf{G}} c_{\mathbf{k}-\mathbf{G}} = 0$$



Cartoon to show how only  $k$  values separated by a  $g$  are coupled together



We can re-arrange this to give :

$$\psi_{\mathbf{k}}(\mathbf{r}) = e^{i\mathbf{k}\cdot\mathbf{r}} \left( \sum_{\mathbf{G}} c_{\mathbf{k}-\mathbf{G}} e^{-i\mathbf{G}\cdot\mathbf{r}} \right)$$

the term in brackets is another of these Fourier expansions in  $\mathbf{G}$  vectors, and thus has to have the lattice periodicity

which describes a plane wave multiplied by a function which has the periodicity of the lattice i.e.

$$\psi_{\mathbf{k}}(\mathbf{r}) = e^{i\mathbf{k}\cdot\mathbf{r}} u_{\mathbf{k}}(\mathbf{r})$$

where

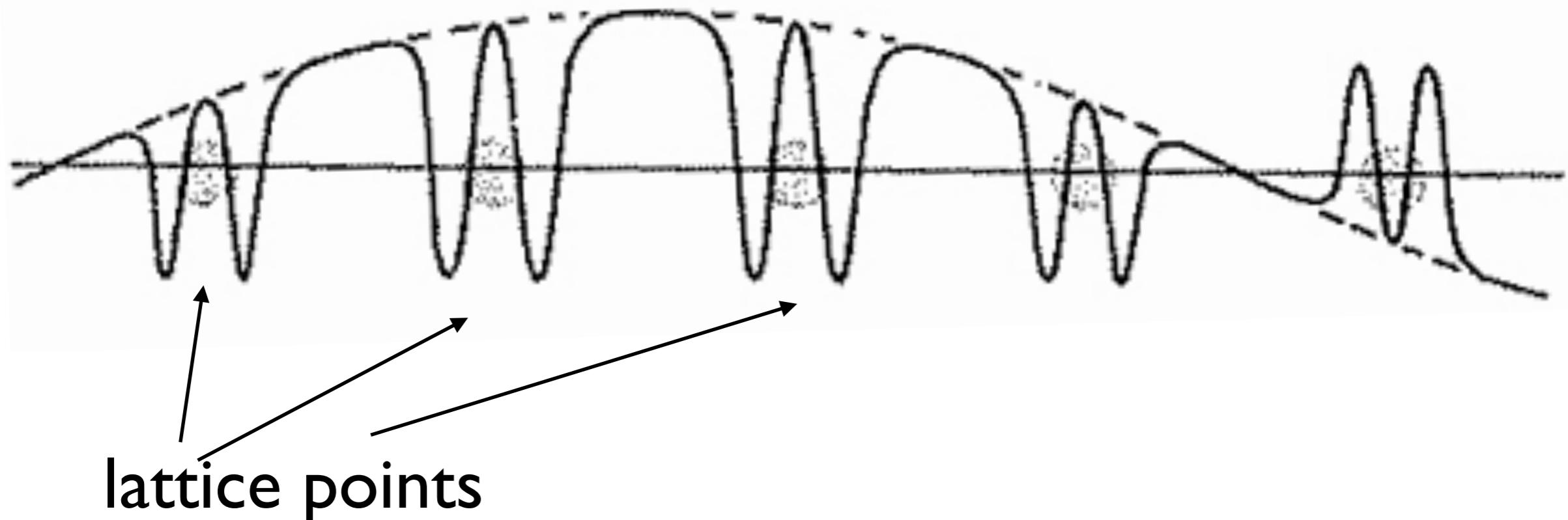
$$u_{\mathbf{k}}(\mathbf{r}) = u_{\mathbf{k}}(\mathbf{r} + \mathbf{R}) .$$

$u_{\mathbf{k}}(\mathbf{r})$  is just a function which has the periodicity of the lattice

We call this *Bloch's Theorem*.

$$\psi_{\mathbf{k}}(\mathbf{r}) = e^{i\mathbf{k} \cdot \mathbf{r}} u_{\mathbf{k}}(\mathbf{r})$$

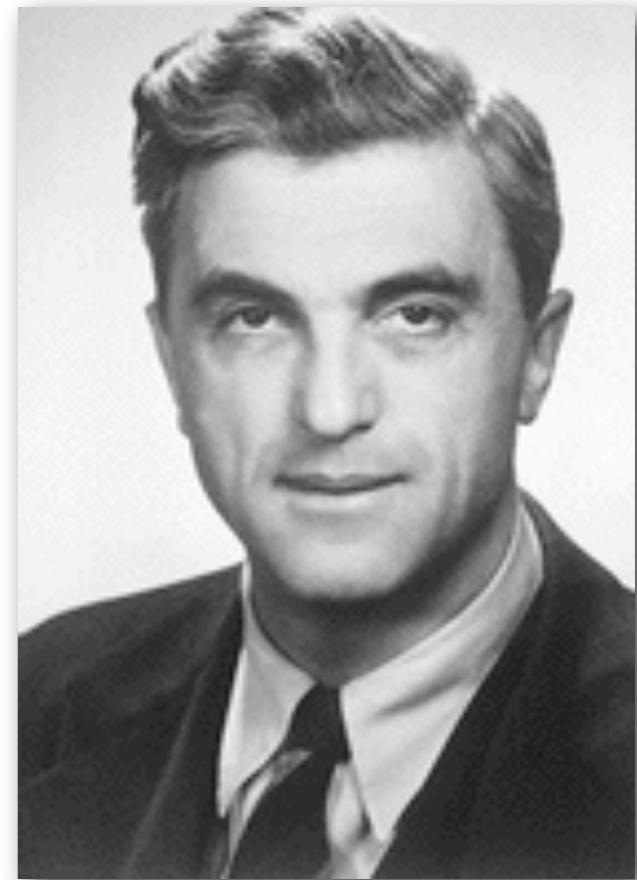
dashed line is the plane wave



**Sketch of a Bloch wave**  
(well, its real part  
because in general it is complex)

*When I started to think about it, I felt that the main problem was to explain how the electrons could sneak by all the ions in a metal so as to avoid a mean free path of the order of atomic distances. Such a distance was much too short to explain the observed resistances, which even demanded that the mean free path become longer and longer with decreasing temperature. But Heitler and London had already shown how electrons could jump between two atoms in a molecule to form a covalent bond, and the main difference between a molecule and a crystal was only that there were many more atoms in a periodic arrangement. To make my life easy, I began by considering wave functions in a one dimensional periodic potential. By straight Fourier analysis I found to my delight that the wave differed from a plane wave of free electron only by a periodic modulation.*

*This was so simple that I didn't think it could be much of a discovery, but when I showed it to Heisenberg he said right away, "That's it." Well, that wasn't quite it yet, and my calculations were only completed in the summer when I wrote my thesis on "The Quantum Mechanics of Electrons in Crystal Lattices."*



Felix Bloch  
(Image: Nobel website)

## 2.5.3 Some Consequences of Bloch's Theorem

Let's begin by looking at some properties of these *Bloch states* (or *Bloch waves*). Firstly, we write down the wavefunction for some wavevector  $\mathbf{k}+\mathbf{G}'$ :

$$\begin{aligned}\psi_{\mathbf{k}+\mathbf{G}'}(\mathbf{r}) &= \sum_{\mathbf{G}} c_{\mathbf{k}+\mathbf{G}'-\mathbf{G}} e^{i(\mathbf{k}+\mathbf{G}'-\mathbf{G}) \cdot \mathbf{r}} \\ &= \left( \sum_{\mathbf{G}''} c_{\mathbf{k}-\mathbf{G}''} e^{-i\mathbf{G}'' \cdot \mathbf{r}} \right) e^{i\mathbf{k} \cdot \mathbf{r}} \\ &= \psi_{\mathbf{k}}(\mathbf{r})\end{aligned}$$

dummy summation  
index of  $\mathbf{G}'' = \mathbf{G}-\mathbf{G}'$

i.e. Bloch waves that differ by a reciprocal lattice vector are identical.

Next, let's look at the energy eigenvalues. We label these energies  $E(\mathbf{k})$  (or  $E_{\mathbf{k}}$ ) and they appear in the Schrödinger equations for  $\mathbf{k}$  and  $\mathbf{k}+\mathbf{G}'$ :

$$\hat{H}\psi_{\mathbf{k}}(\mathbf{r}) = E_{\mathbf{k}}\psi_{\mathbf{k}}(\mathbf{r})$$

$$\hat{H}\psi_{\mathbf{k}+\mathbf{G}'}(\mathbf{r}) = E_{\mathbf{k}+\mathbf{G}'}\psi_{\mathbf{k}+\mathbf{G}'}(\mathbf{r})$$

Therefore, since  $\psi_{\mathbf{k}+\mathbf{G}'}(\mathbf{r}) = \psi_{\mathbf{k}}(\mathbf{r})$ , it follows that

$$E_{\mathbf{k}} = E_{\mathbf{k}+\mathbf{G}'}$$

and hence the eigenvalues are periodic functions of  $\mathbf{k}$ . Therefore, we only need to know the eigenvalues within the first Brillouin zone (\*) and we know then for all possible  $\mathbf{k}$ .

Now we can move on and start to calculate these eigenvalues. In other words, we can start to look at the *electronic bandstructure* ( $E(\mathbf{k})$  or  $E_{\mathbf{k}}$ ) of a periodic solid.

\* Recall that the first Brillouin zone is the equivalent of the Wigner-Seitz unit cell in reciprocal space

## 2.5.4 Solving the Central Equation

We're trying to solve this set of equations

$$\sum_{\mathbf{k}} e^{i\mathbf{k} \cdot \mathbf{r}} \left\{ \left( \frac{\hbar^2 k^2}{2m_e} - E \right) c_{\mathbf{k}} + \sum_{\mathbf{G}} U_{\mathbf{G}} c_{\mathbf{k}-\mathbf{G}} \right\} = 0$$

for which, we earlier argued, the  $\{ \dots \}$  has to be zero for every  $\mathbf{k}$  we choose to look at. Let's begin by making some simplifications. Firstly, let's work in one dimension (say with lattice constant  $a$ ) so that we can drop some of the vector notation, and we can call the shortest reciprocal lattice vector  $\mathbf{g}$  ( $= 2\pi/a$ ). Secondly, let's set all the Fourier coefficients  $U_{\mathbf{g}}$  equal to zero, except for  $U_1$  and  $U_{-1}$  and since we can make them real coefficients, since  $U_{-\mathbf{g}}^* = U_{\mathbf{g}}$  we can simply call them both  $U$ . Then,

$$U(x) = U(e^{-i2\pi x/a} + e^{i2\pi x/a})$$

$$( = 2U \cos(2\pi x/a))$$

Remember that  
 $e^{i\theta} = \cos \theta + i \sin \theta$

So let's look at what we have for a particular  $k$  by writing out the central equation

$$\left\{ \left( \frac{\hbar^2 k^2}{2m_e} - E \right) c_k + \sum_G U_G c_{k-G} \right\} = 0$$

in matrix form :

$$\begin{pmatrix} \ddots & & & & & & \\ & \frac{\hbar^2(k-2g)^2}{2m_e} - E & U & 0 & 0 & 0 & \\ & U & \frac{\hbar^2(k-g)^2}{2m_e} - E & U & 0 & 0 & \\ & 0 & U & \frac{\hbar^2 k^2}{2m_e} - E & U & 0 & \\ & 0 & 0 & U & \frac{\hbar^2(k+g)^2}{2m_e} - E & U & \\ & 0 & 0 & 0 & U & \frac{\hbar^2(k+2g)^2}{2m_e} - E & \\ & & & & & & \ddots \end{pmatrix} \begin{pmatrix} \vdots \\ c_{k-2g} \\ c_{k-g} \\ c_k \\ c_{k+g} \\ c_{k+2g} \\ \vdots \end{pmatrix} = 0$$

This is, in principle, an infinitely large matrix, (and so we're only looking at some part of it here); but in practice, we don't need an infinite number of coefficients ( $c_k$ ) to describe the electronic wavefunctions which means we can deal with a much simpler problem.

Let's simplify things radically for now, and assume that the wavefunction only has three non-zero components,  $c_k$ ,  $c_{k-g}$  and  $c_{k+g}$ . The matrix equation then becomes :

$$\begin{pmatrix} \frac{\hbar^2(k-g)^2}{2m_e} - E & U & 0 \\ U & \frac{\hbar^2 k^2}{2m_e} - E & U \\ 0 & U & \frac{\hbar^2(k+g)^2}{2m_e} - E \end{pmatrix} \begin{pmatrix} c_{k-g} \\ c_k \\ c_{k+g} \end{pmatrix} = 0$$

the  $E$ 's are the (energy) eigenvalues of the matrix below

this set of coefficients are the eigenfunctions

$$\begin{pmatrix} \frac{\hbar^2(k-g)^2}{2m_e} & U & 0 \\ U & \frac{\hbar^2 k^2}{2m_e} & U \\ 0 & U & \frac{\hbar^2(k+g)^2}{2m_e} \end{pmatrix}$$

Let's make our lives even simpler for a moment, by now letting  $U$  go to zero (\*) (we'll turn it back on again a little later) :

$$\begin{pmatrix} \frac{\hbar^2(k-g)^2}{2m_e} - E & 0 & 0 \\ 0 & \frac{\hbar^2k^2}{2m_e} - E & 0 \\ 0 & 0 & \frac{\hbar^2(k+g)^2}{2m_e} - E \end{pmatrix}$$

and therefore the secular (characteristic) equation is :

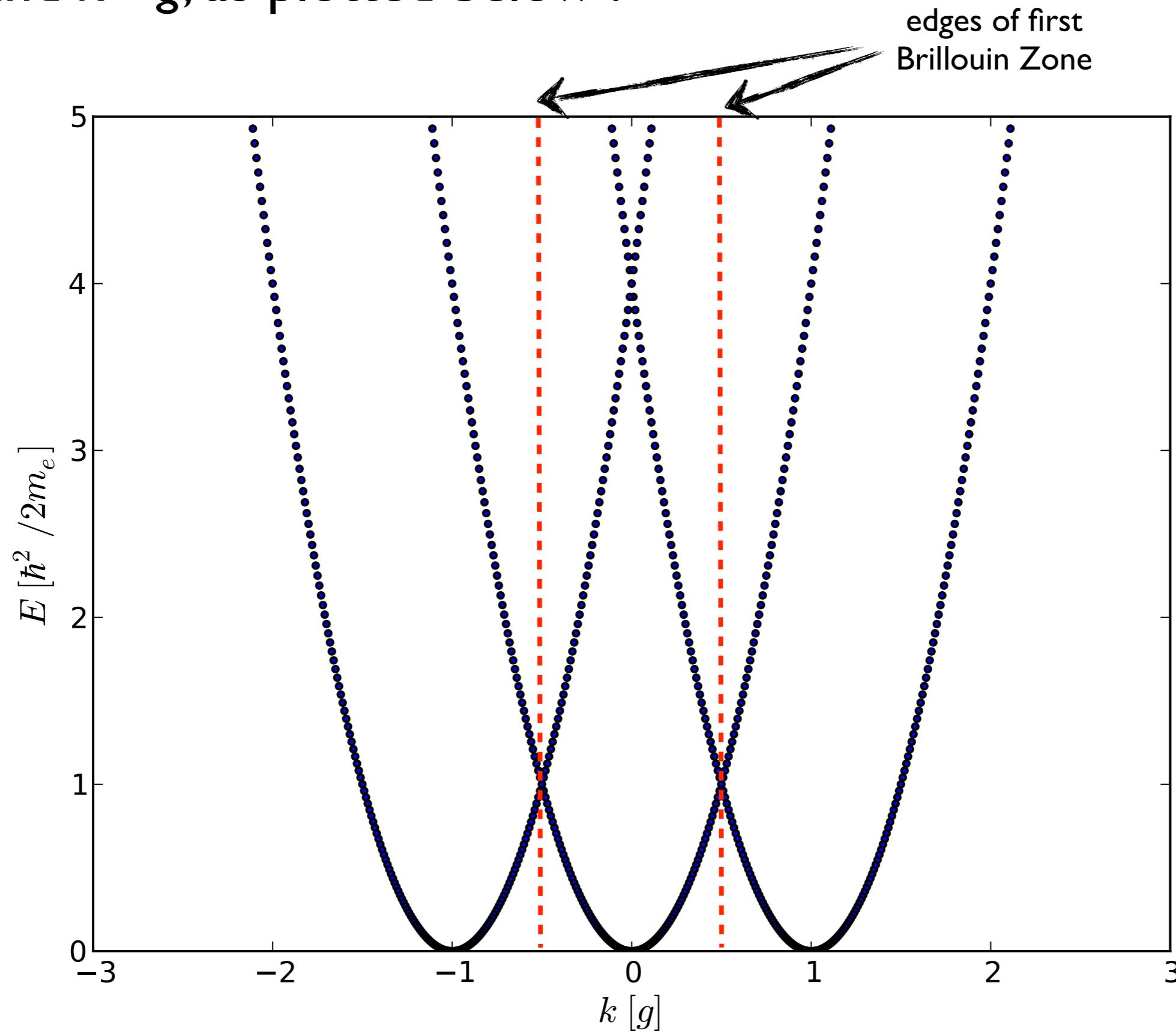
$$\begin{vmatrix} \frac{\hbar^2(k-g)^2}{2m_e} - E & 0 & 0 \\ 0 & \frac{\hbar^2k^2}{2m_e} - E & 0 \\ 0 & 0 & \frac{\hbar^2(k+g)^2}{2m_e} - E \end{vmatrix} = 0$$

which will give three eigenvalues (three values of  $E$  which satisfy the condition of the determinant being zero) which are :

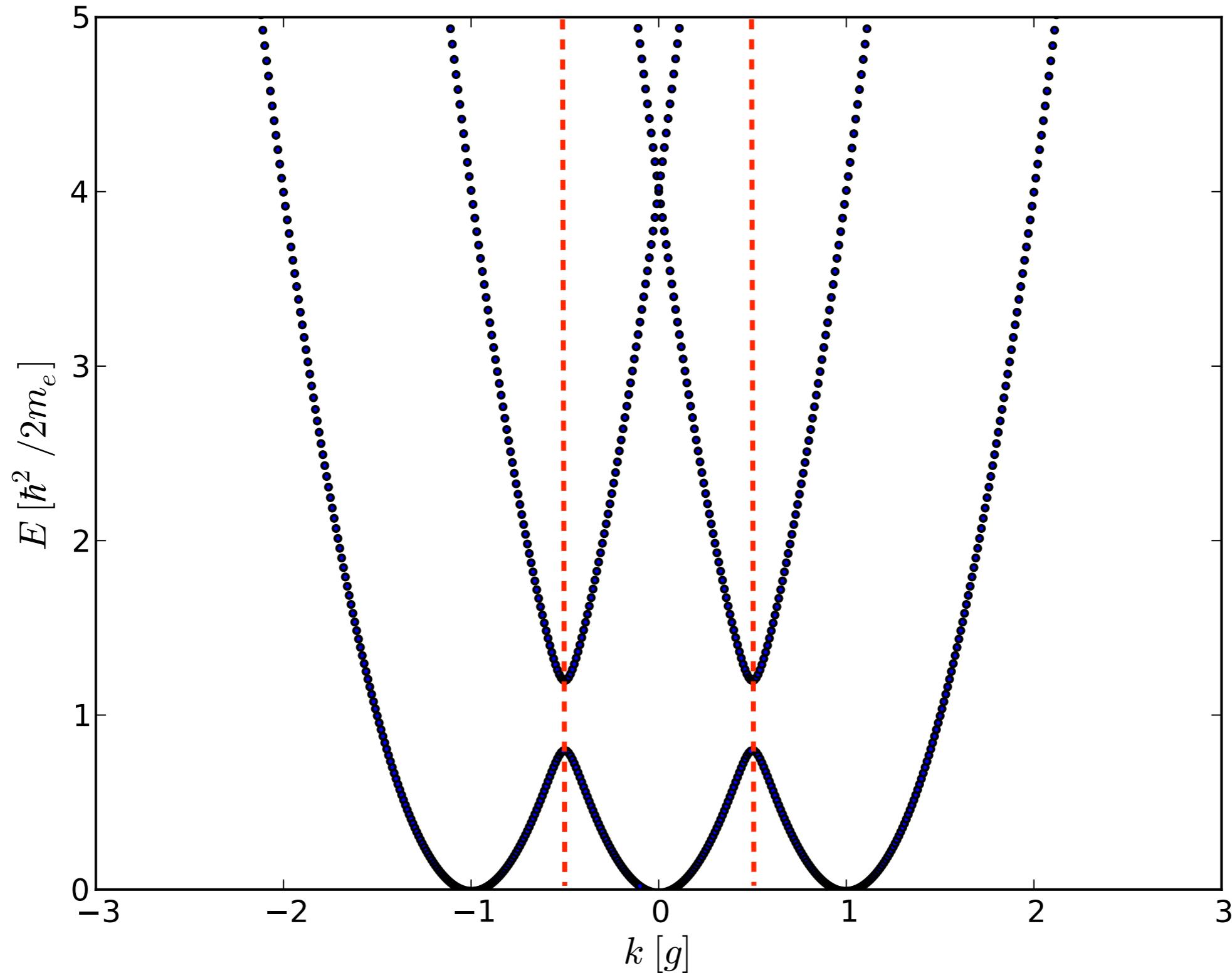
$$E = \frac{\hbar^2(k-g)^2}{2m_e}, E = \frac{\hbar^2k^2}{2m_e}, E = \frac{\hbar^2(k+g)^2}{2m_e}$$

\* This is the so-called empty lattice approximation

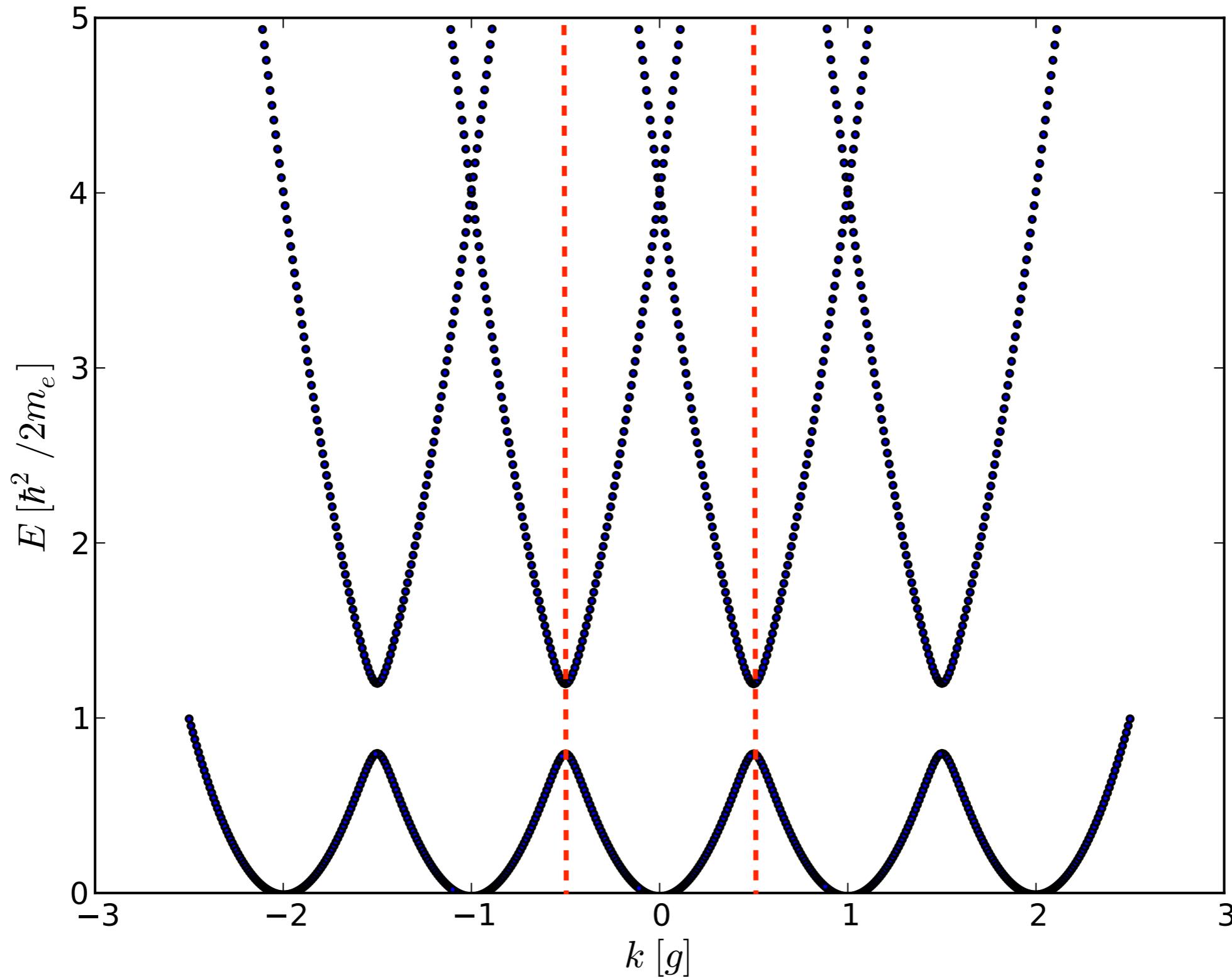
These are just three “free electron” parabolas, centred on  $k=0$ ,  $k=g$  and  $k=-g$ , as plotted below :



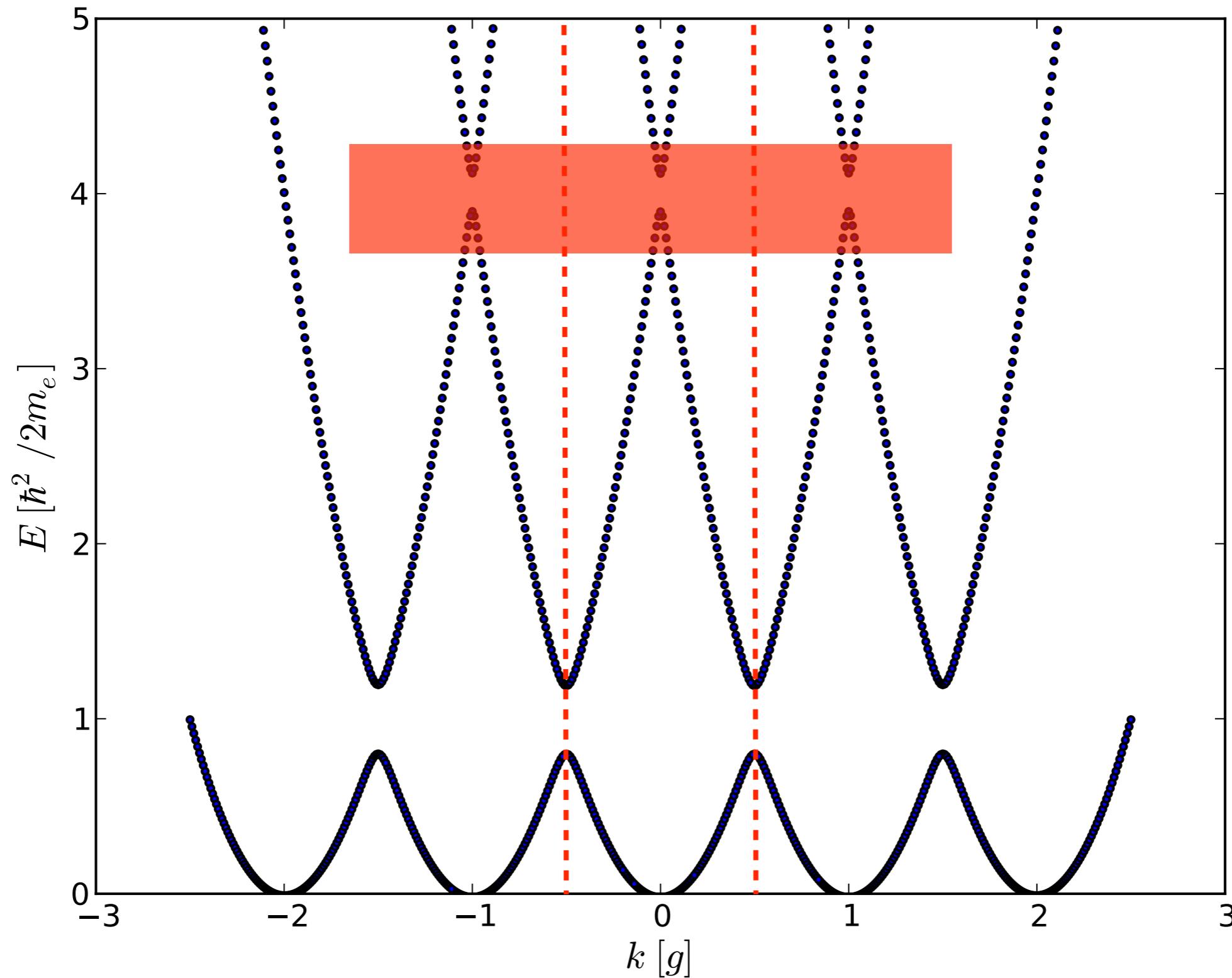
Now, let's turn the  $U$  back on, and solve again. We find that some gaps have now appeared at the first Brillouin zone boundary :



We can add another couple of coefficients ( $c_{k+2g}$  and  $c_{k-2g}$ ) and we get some more parabolas. It's starting to look pretty good in the first Brillouin zone now.



If we want to introduce the next set of gaps, then we need to add a second Fourier coefficient - the matrix is on the next slide :



This was the equation that was solved to get the bandstructure plot on the previous page :

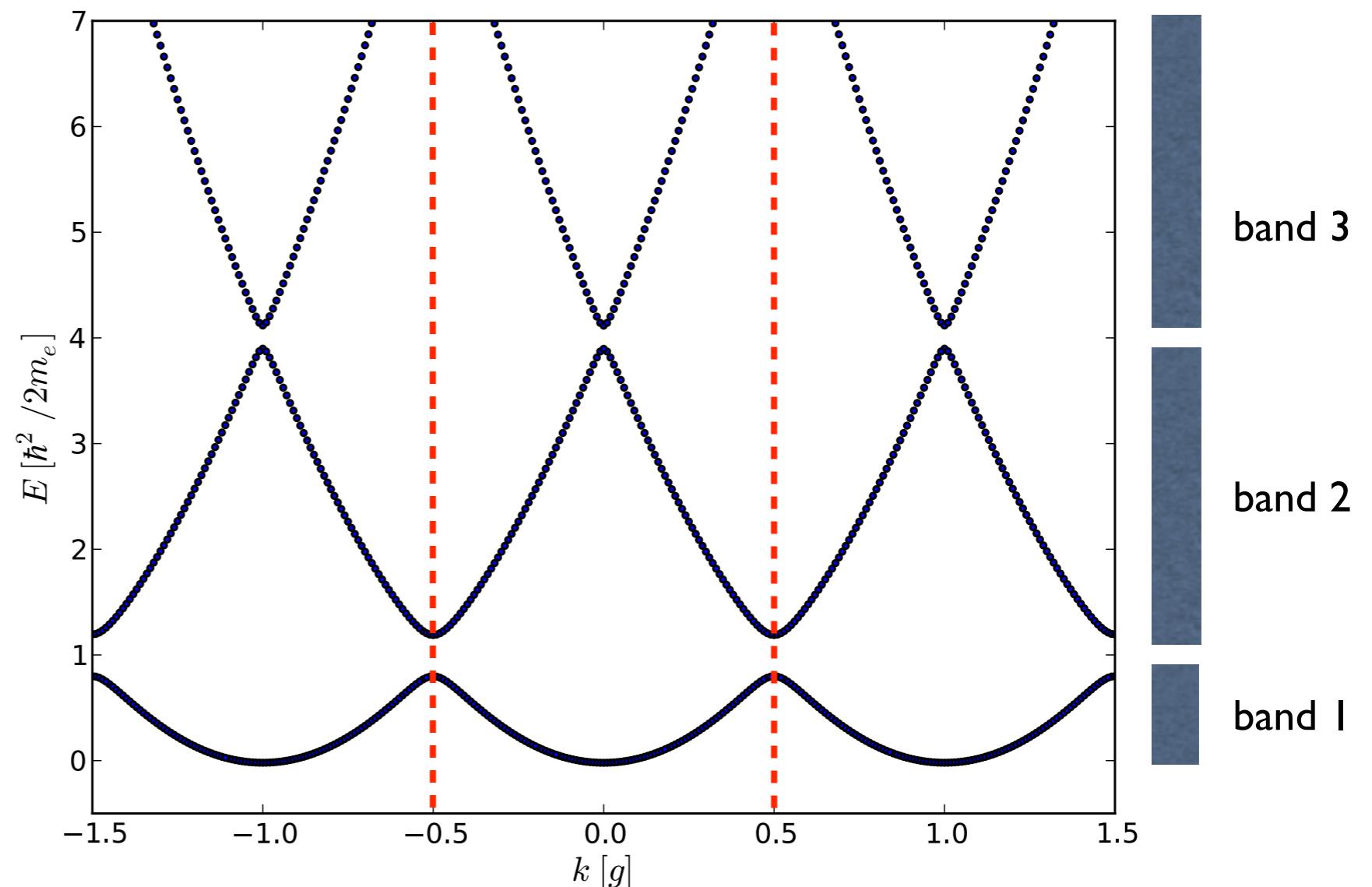
$$\begin{pmatrix} \frac{\hbar^2(k-2g)^2}{2m_e} - E & U_1 & U_2 & 0 & 0 \\ U_1 & \frac{\hbar^2(k-g)^2}{2m_e} - E & U_1 & U_2 & 0 \\ U_2 & U_1 & \frac{\hbar^2k^2}{2m_e} - E & U_1 & U_2 \\ 0 & U_2 & U_1 & \frac{\hbar^2(k+g)^2}{2m_e} - E & U_1 \\ 0 & 0 & U_2 & U_1 & \frac{\hbar^2(k+2g)^2}{2m_e} - E \end{pmatrix} \begin{pmatrix} c_{k-2g} \\ c_{k-g} \\ c_k \\ c_{k+g} \\ c_{k+2g} \end{pmatrix} = 0$$

with different values for  $U_1$  and  $U_2$  (in fact,  $U_2$  was  $U_1/2$ ).

By this simplistic approach we are getting the correct result in the first BZ at low energies (\*), and to improve things further we would need to include more coefficients and more Fourier components in the potential.

\* At higher energies we need the contributions from “parabolas” centred in higher zones  
(i.e centred at higher multiples of g)

The bandstructure has regions where there are no allowed states (so-called *band gaps*). From what we have just done (in terms of playing with the  $U$ 's, and the absence of these gaps in the free-electron model), we can probably guess that it has something to do with the presence of the potential.



## 2.5.5 The Energy Gap at the Brillouin Zone Boundary

Let's look at an even simpler set of equations, this time with just two wavefunction coefficients (and we can go back to having just one non-zero Fourier coefficient, as this was enough to open up the gap at the zone boundary) :

$$\begin{pmatrix} \ddots & & & & & \\ & \frac{\hbar^2(k-2g)^2}{2m_e} - E & U & 0 & 0 & 0 \\ & U & \frac{\hbar^2(k-g)^2}{2m_e} - E & U & 0 & 0 \\ & 0 & U & \frac{\hbar^2k^2}{2m_e} - E & U & 0 \\ & 0 & 0 & U & \frac{\hbar^2(k+g)^2}{2m_e} - E & U \\ & 0 & 0 & 0 & U & \frac{\hbar^2(k+2g)^2}{2m_e} - E \\ & & & & & \ddots \end{pmatrix} \begin{pmatrix} \vdots \\ c_{k-2g} \\ c_{k-g} \\ c_k \\ c_{k+g} \\ c_{k+2g} \\ \vdots \end{pmatrix} = 0$$

i.e. the secular equation is :

$$\left| \begin{array}{cc} \frac{\hbar^2(k-g)^2}{2m_e} - E & U \\ U & \frac{\hbar^2k^2}{2m_e} - E \end{array} \right| = 0$$

$$\therefore \left( \frac{\hbar^2(k-g)^2}{2m_e} - E \right) \left( \frac{\hbar^2 k^2}{2m_e} - E \right) - U^2 = 0$$

or

$$(\mu(k-g)^2 - E)(\mu k^2 - E) - U^2 = 0$$

**where we are using  $\mu = \frac{\hbar^2}{2m_e}$  to save some writing!**

$$\mu^2 k^2 (k-g)^2 + E^2 - E\mu(k-g)^2 - E\mu k^2 - U^2 = 0$$

**At the zone boundary,  $k=g/2$ , and therefore we have :**

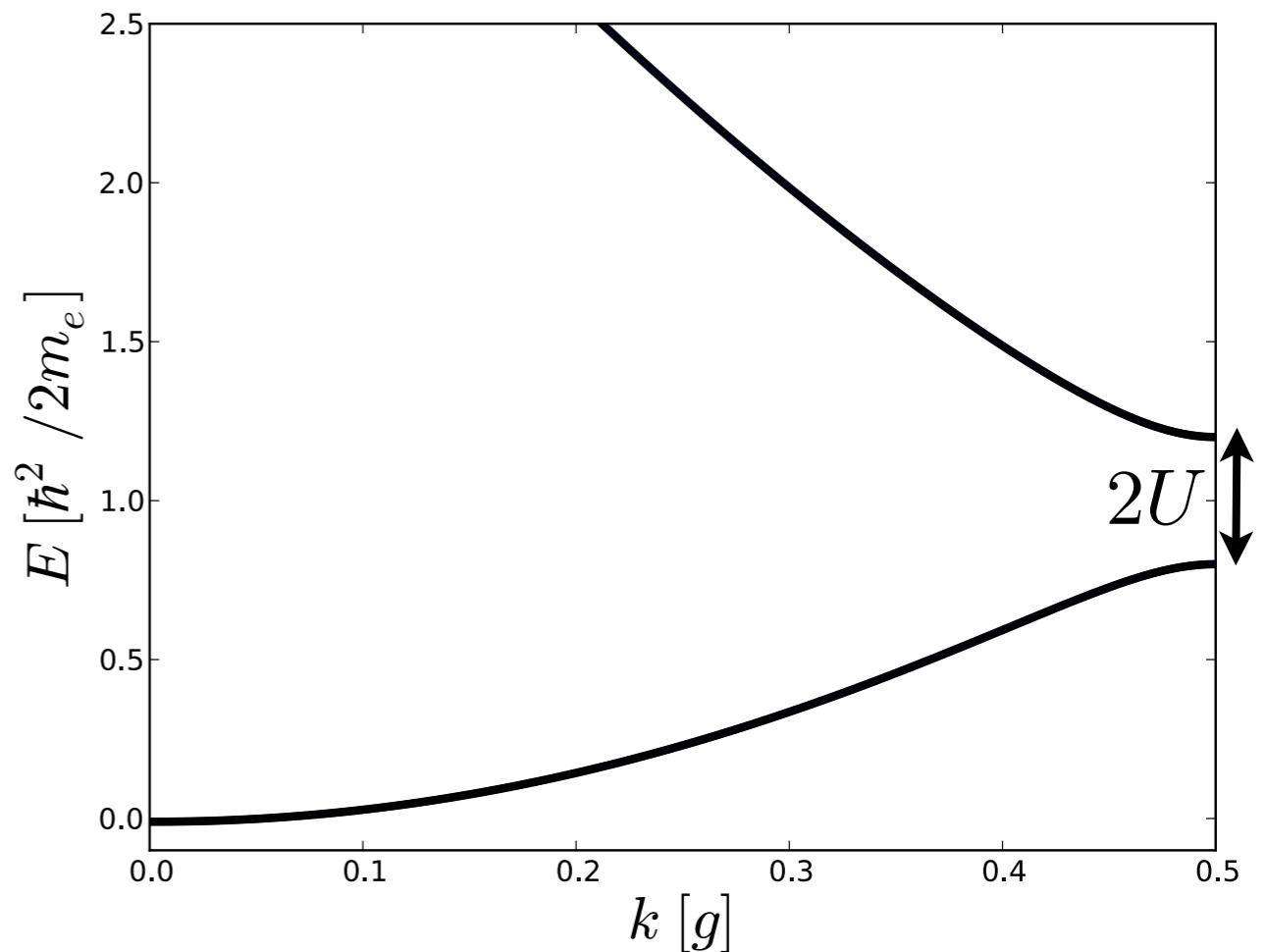
$$\mu^2 \frac{g^2}{4} \left( \frac{g}{2} - g \right)^2 + E^2 - E\mu \left( \frac{g}{2} - g \right)^2 - E\mu \frac{g^2}{4} - U^2 = 0$$

$$\therefore \mu^2 \frac{k^2 g^2}{4} + E^2 - E\mu \frac{g^2}{4} - E\mu \frac{g^2}{4} - U^2 = 0$$

$$\therefore E^2 - E\mu \frac{g^2}{2} + \left( \frac{\mu^2 g^4}{16} - U^2 \right) = 0$$

Solving the quadratic,

$$\begin{aligned}
 E &= \frac{\frac{\mu g^2}{2} \pm \sqrt{\frac{\mu^2 g^4}{4} - 4 \left( \frac{\mu^2 g^4}{16} - U^2 \right)}}{2} \\
 &= \frac{\frac{\mu g^2}{2} \pm \sqrt{\frac{\mu^2 g^4}{4} - \frac{\mu^2 g^4}{4} + 4U^2}}{2} \\
 &= \frac{\frac{\mu g^2}{2} \pm 2U}{2} \\
 &= \frac{\mu g^2}{4} \pm U \\
 &= \frac{\hbar^2}{2m_e} \frac{g^2}{4} \pm U
 \end{aligned}$$



i.e. there is a gap of  $2U$  (twice the Fourier coefficient) at the zone boundary.

## 2.5.6 Origin of the Energy Gap

We've just been solving

$$\begin{pmatrix} \frac{\hbar^2(k-g)^2}{2m_e} - E & U \\ U & \frac{\hbar^2k^2}{2m_e} - E \end{pmatrix} \begin{pmatrix} c_{k-g} \\ c_k \end{pmatrix} = 0$$

at the zone boundary ( $k=g/2$ ) i.e.

$$\begin{pmatrix} \frac{\hbar^2(-g/2)^2}{2m_e} - E & U \\ U & \frac{\hbar^2(g/2)^2}{2m_e} - E \end{pmatrix} \begin{pmatrix} c_{-g/2} \\ c_{g/2} \end{pmatrix} = 0$$

and we want to look at the wavefunction at the zone boundary, so we are going to need to figure out the two Fourier coefficients of the wavefunction (the two c's which make up the eigenfunction). As before, to save some writing, let's define

$$\alpha = \frac{\hbar^2 g^2}{8m_e}$$

and continue...

Thus we have :

$$\begin{pmatrix} \alpha - E & U \\ U & \alpha - E \end{pmatrix} \begin{pmatrix} c_{-g/2} \\ c_{g/2} \end{pmatrix} = 0$$

and we can multiply out

$$(\alpha - E)c_{-g/2} + Uc_{g/2} = 0$$

$$Uc_{-g/2} + (\alpha - E)c_{g/2} = 0$$

From either of these equations we can figure out the ratio of the two coefficients. Let's do it with the first one :

$$(\alpha - E)c_{-g/2} + Uc_{g/2} = 0$$

$$\therefore c_{g/2} = \frac{(E - \alpha)c_{-g/2}}{U}$$

$$\therefore \frac{c_{g/2}}{c_{-g/2}} = \frac{(E - \alpha)}{U}$$

We already know what the two eigenvalues (the  $E$ 's) are :

$$E = \frac{\hbar^2}{2m_e} \frac{g^2}{4} \pm U ,$$

so we can substitute for them to get :

$$\frac{c_{g/2}}{c_{-g/2}} = \frac{U}{U} = 1$$

$$\text{or } \frac{c_{g/2}}{c_{-g/2}} = \frac{-U}{U} = -1$$

Our Bloch wave, therefore is:

$$\psi_{g/2}(x) = c_{g/2} e^{igx/2} + c_{-g/2} e^{-igx/2}$$

$$\psi_{g/2}(x) = c_{g/2} \left( e^{igx/2} + \frac{c_{-g/2}}{c_{g/2}} e^{-igx/2} \right)$$

Given that the ratios of the coefficients are  $\pm 1$ , we can write the Bloch wave as :

$$\psi_{g/2}(x) = c_{g/2} \left( e^{igx/2} \pm e^{-igx/2} \right)$$

which describe two standing waves (corresponding to the “+” and “-” solutions) produced by the Bragg reflection at the zone boundary (recall the Brillouin condition). We can go further and calculate the charge density :

$$\rho^+(x) = |\psi_{g/2}^+(x)|^2$$



you could simplify all of this by spotting that this ( ) is already  $\cos(gx/2)$  and therefore just squaring it for the result!

$$\propto \left( e^{igx/2} + e^{-igx/2} \right) \left( e^{-igx/2} + e^{igx/2} \right)$$

$$\propto (2 + e^{igx} + e^{-igx})$$

$$\propto 2 + 2 \cos(gx)$$

$$\propto 2 + 2(\cos^2(gx/2) - 1)$$

$$\propto \cos^2(gx/2)$$

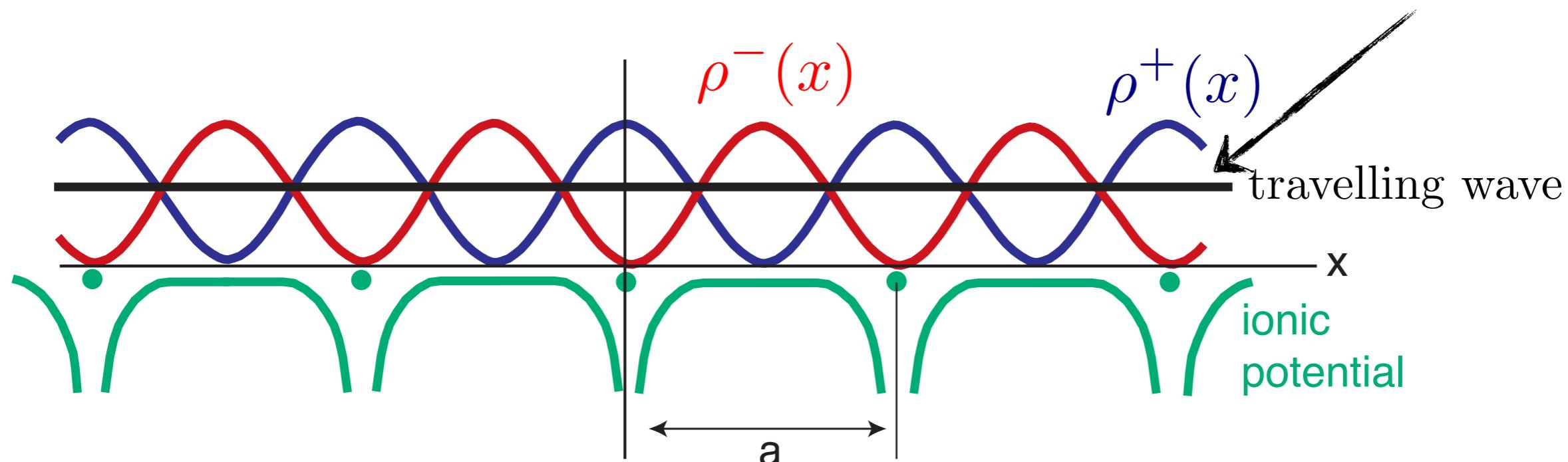
Recalling that the g “vector” is  $2\pi/a$  ,

$$\rho^+(x) \propto \cos^2(\pi x/a)$$

Similarly,

$$\rho^-(x) \propto \sin^2(\pi x/a)$$

For states well away from the zone boundary, the solutions can be approximated by travelling plane waves. Plotted below is the *delocalised density* for a free electron for comparison



The potential is normally attractive (that is *negative*) so  $U$  is normally a negative number. Therefore, the + solution actually corresponds to the lower energy eigenvalue (we’re adding a negative number). Physically, with the electronic charged piled up on the ion cores, the potential energy is lowered with respect to a travelling plane wave.

## Recap :

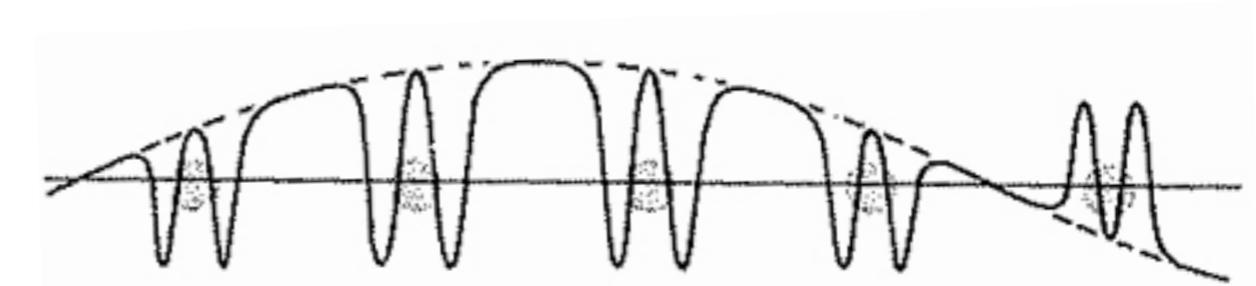
Switch back on interaction  
between electrons and ion cores

$$U(\mathbf{r}) = \sum_{\mathbf{G}} U_{\mathbf{G}} e^{i\mathbf{G} \cdot \mathbf{r}}$$

$$\psi_{\mathbf{k}}(\mathbf{r}) = e^{i\mathbf{k} \cdot \mathbf{r}} u_{\mathbf{k}}(\mathbf{r})$$

where

$$u_{\mathbf{k}}(\mathbf{r}) = u_{\mathbf{k}}(\mathbf{r} + \mathbf{R}) .$$



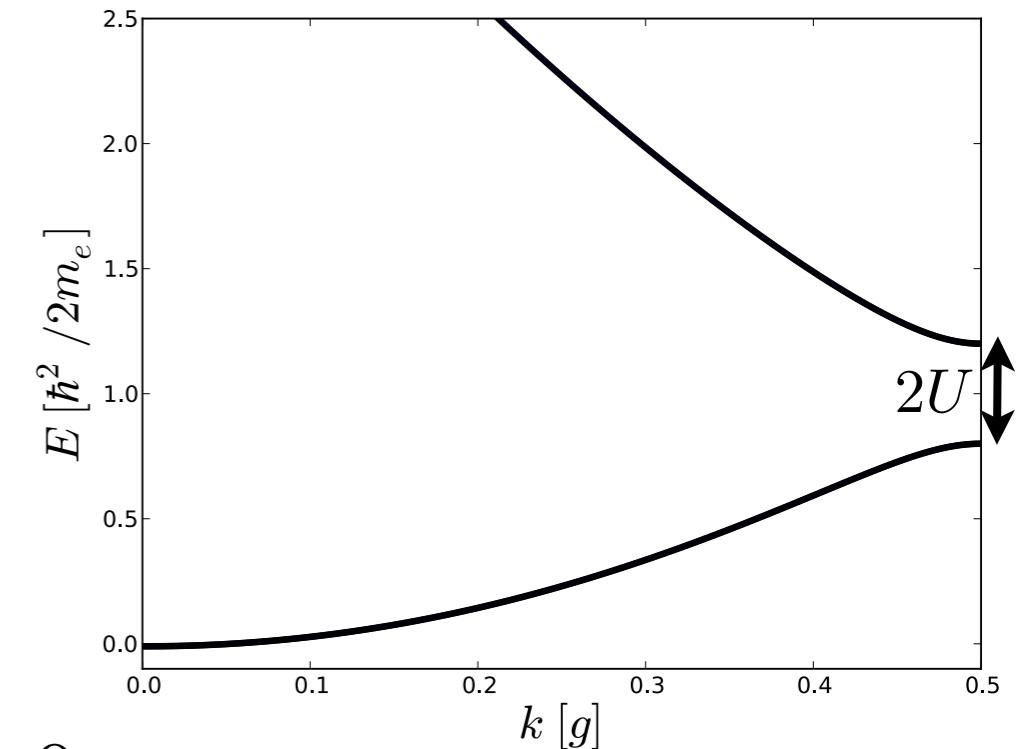
$u_{\mathbf{k}}(\mathbf{r})$  is just a function  
which has the  
periodicity of the  
lattice

$$U(\mathbf{r}) = \sum_{\mathbf{G}} U_{\mathbf{G}} e^{i\mathbf{G} \cdot \mathbf{r}}$$

Simplest potential :

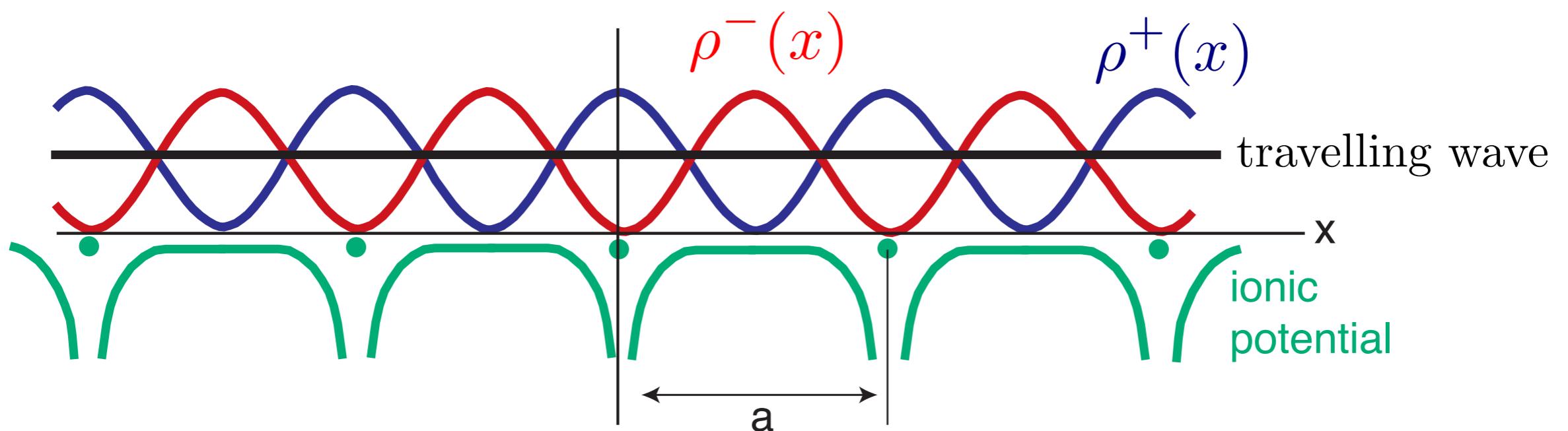
$$\begin{aligned} U(x) &= U(e^{-i2\pi x/a} + e^{i2\pi x/a}) \\ () &= 2U \cos(2\pi x/a) \end{aligned}$$

$$\begin{pmatrix} \frac{\hbar^2(-g/2)^2}{2m_e} - E & U \\ U & \frac{\hbar^2(g/2)^2}{2m_e} - E \end{pmatrix} \begin{pmatrix} c_{-g/2} \\ c_{g/2} \end{pmatrix} = 0$$



probability  
density

$$\psi_{g/2}(x) = c_{g/2} \left( e^{igx/2} \pm e^{-igx/2} \right)$$



## 2.5.7 Crystal Momentum is Not Momentum

When we considered free electrons, their wavefunctions were simple plane waves :

$$\psi(\mathbf{r}) = \frac{1}{\sqrt{V}} e^{i\mathbf{k}\cdot\mathbf{r}}$$

The momentum is obtained through the application of the operator :

$$\begin{aligned}\hat{\mathbf{p}}\psi(\mathbf{r}) &= -i\hbar\nabla\psi(\mathbf{r}) \\ &= -i\hbar i\mathbf{k} \frac{1}{\sqrt{V}} e^{i\mathbf{k}\cdot\mathbf{r}} \\ &= \hbar\mathbf{k}\psi(\mathbf{r})\end{aligned}$$

Thus for free electrons, the (plane) wavefunctions are simultaneous eigenstates of the Hamiltonian and the momentum operator. Is this be true for Bloch electrons? Let's see...

$$\begin{aligned}
\hat{\mathbf{p}}\psi_k(\mathbf{r}) &= -i\hbar\nabla(e^{i\mathbf{k}\cdot\mathbf{r}}u_{\mathbf{k}}(\mathbf{r})) \\
&= -i\hbar i\mathbf{k}u_{\mathbf{k}}(\mathbf{r})e^{i\mathbf{k}\cdot\mathbf{r}} - i\hbar e^{i\mathbf{k}\cdot\mathbf{r}}\nabla u_{\mathbf{k}}(\mathbf{r}) \\
&= \hbar\mathbf{k}\psi_k(\mathbf{r}) - i\hbar e^{i\mathbf{k}\cdot\mathbf{r}}\nabla u_{\mathbf{k}}(\mathbf{r})
\end{aligned}$$

This is only the same as before if  $u_{\mathbf{k}}(\mathbf{r})$  is a constant (i.e. when the Bloch wave reduces to a free-electron plane wave).

We call  $\hbar\mathbf{k}$  the *crystal momentum*, and it is a conserved quantity in the periodic, translationally invariant environment of a crystal, just as real momentum  $\mathbf{p}$  is a conserved quantity in the greater rotationally invariant symmetry of free space.

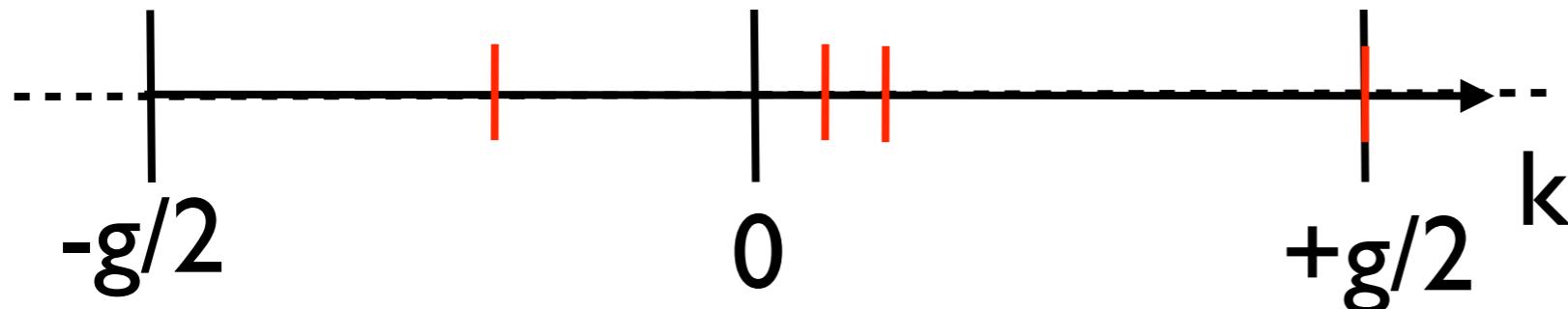
These Bloch states are *not* simultaneous eigenstates of the Hamiltonian and the momentum operator, but rather of the Hamiltonian and the translation operator :

$$\hat{T}\psi(\mathbf{r}) = \psi(\mathbf{r} + \mathbf{R})$$

## 2.6 Orbital Counting and Band filling

Let's examine the relationship between the number of different primitive unit cells, and the number of independent k-points in a band. We'll do this in one-dimension as it's easier to understand, but the generalisation to three-dimensions is straightforward. We start with our one-dimensional crystal of length  $L$  with an even number of atoms  $N$  and a lattice spacing of  $a$ . The allowed values of  $k$  are :

$$k = 0; k = \pm 2\pi/L; k = \pm 4\pi/L; \dots; k = N\pi/L$$

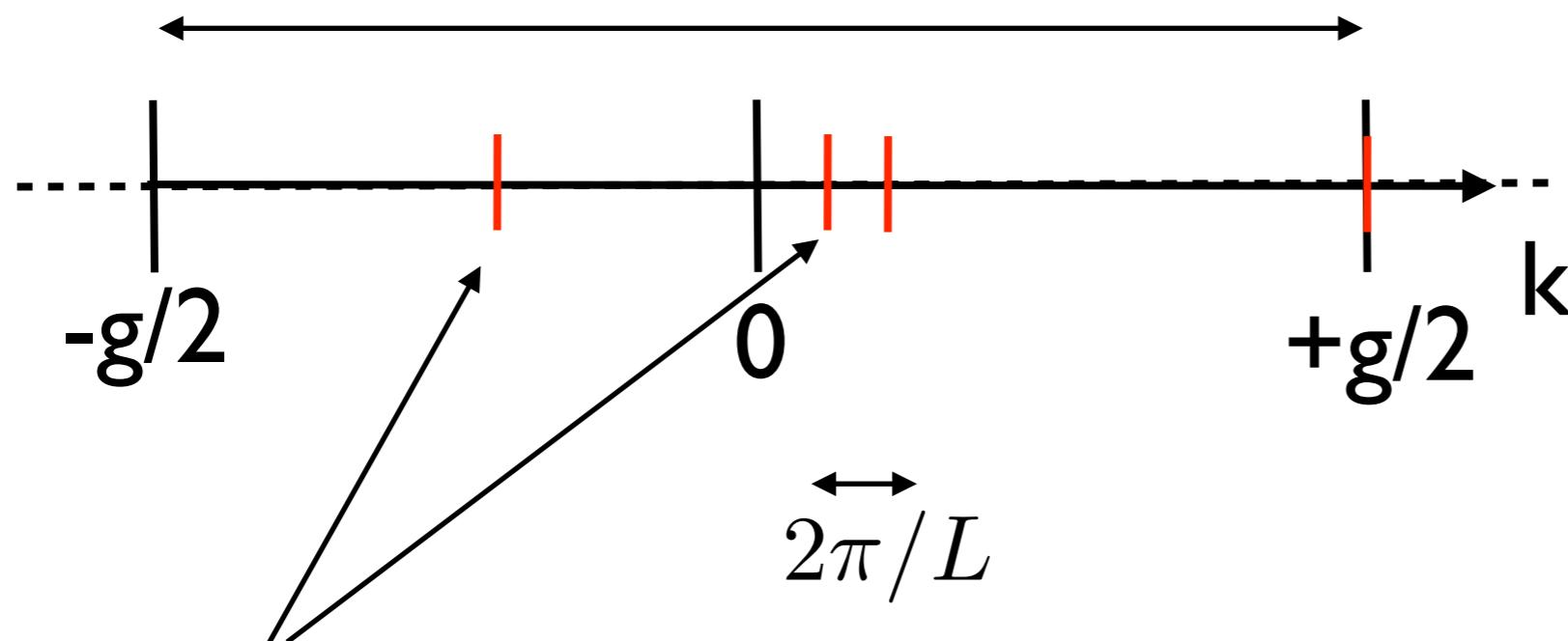


We don't include  $-N\pi/L$  as this point can be connected to  $+N\pi/L$  by a reciprocal lattice vector i.e. both points are on the zone boundary

We also know that  $L=Na$  (length of crystal = no. atoms  $\times$  spacing). Therefore, there are  $N$  independent values of  $k$ . That is, **each primitive cell contributes exactly one independent value of  $k$  to each energy band.**

Another way of seeing this :

$$\begin{aligned}\text{Number of levels} &= \frac{2\pi/a}{2\pi/L} \\ &= L/a \\ &= N\end{aligned}$$



allowed values of  $k$

There are the same number of these |  
as there are primitive cells

This result is also true in two and three dimensions.

Further, if we take into account *spin*, then each band can contain  $2N$  independent orbitals. This is perhaps more usefully expressed as **each band can contain two electrons per primitive unit cell** (\*).

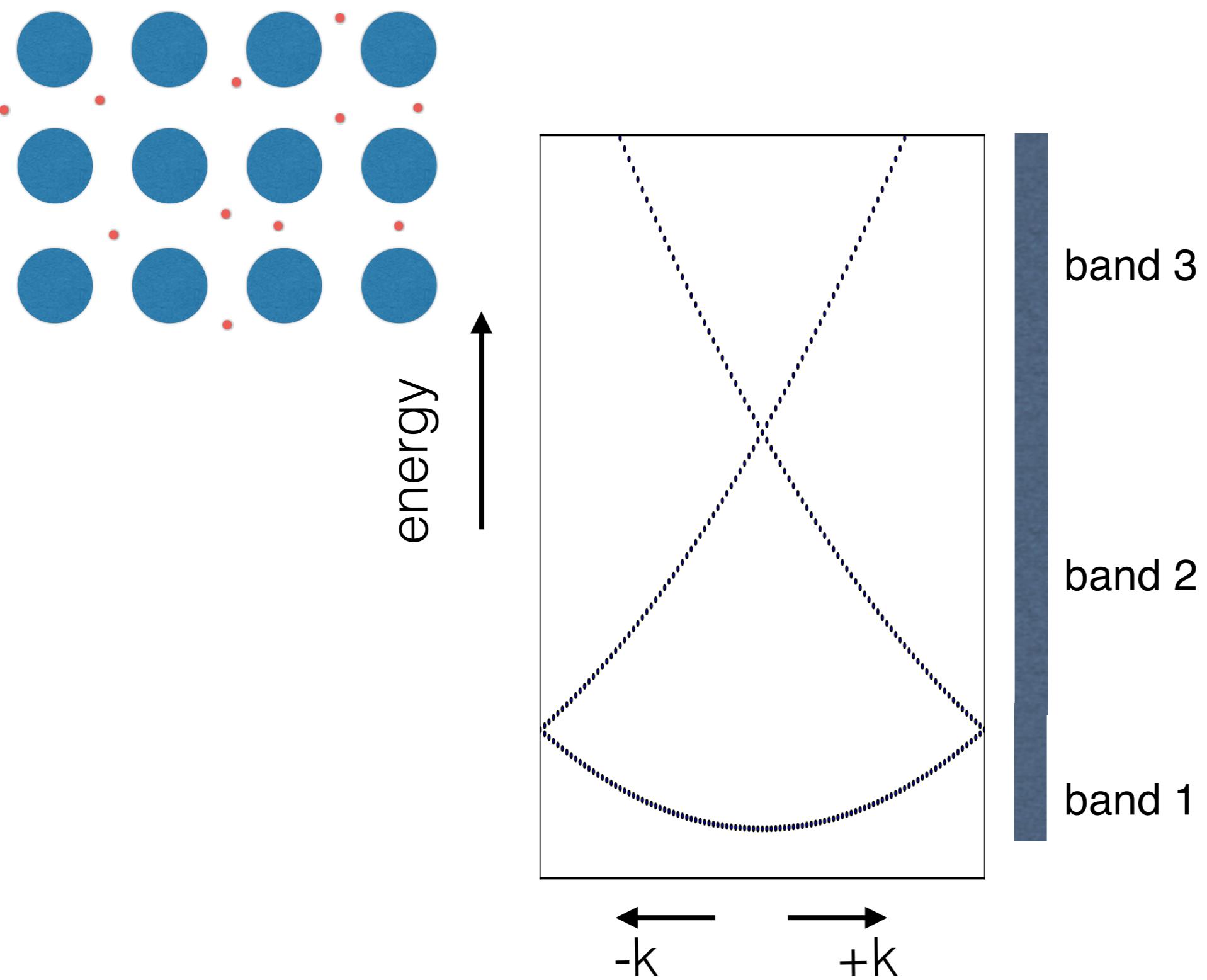
If an atom contributes a single electron per primitive cell (e.g. Na), we have enough electrons to only half-fill a band (half the number of independent k-points are occupied).

If an atom contributes two electrons per primitive cell, then we have enough electrons to completely fill a band (all independent k-points are occupied).

\* In later courses, when you start to consider magnetism, you will discover that the bands for spin-up and spin-down electrons can have different energies. So perhaps a better statement would be that each band can contain one electron per primitive unit cell per spin.

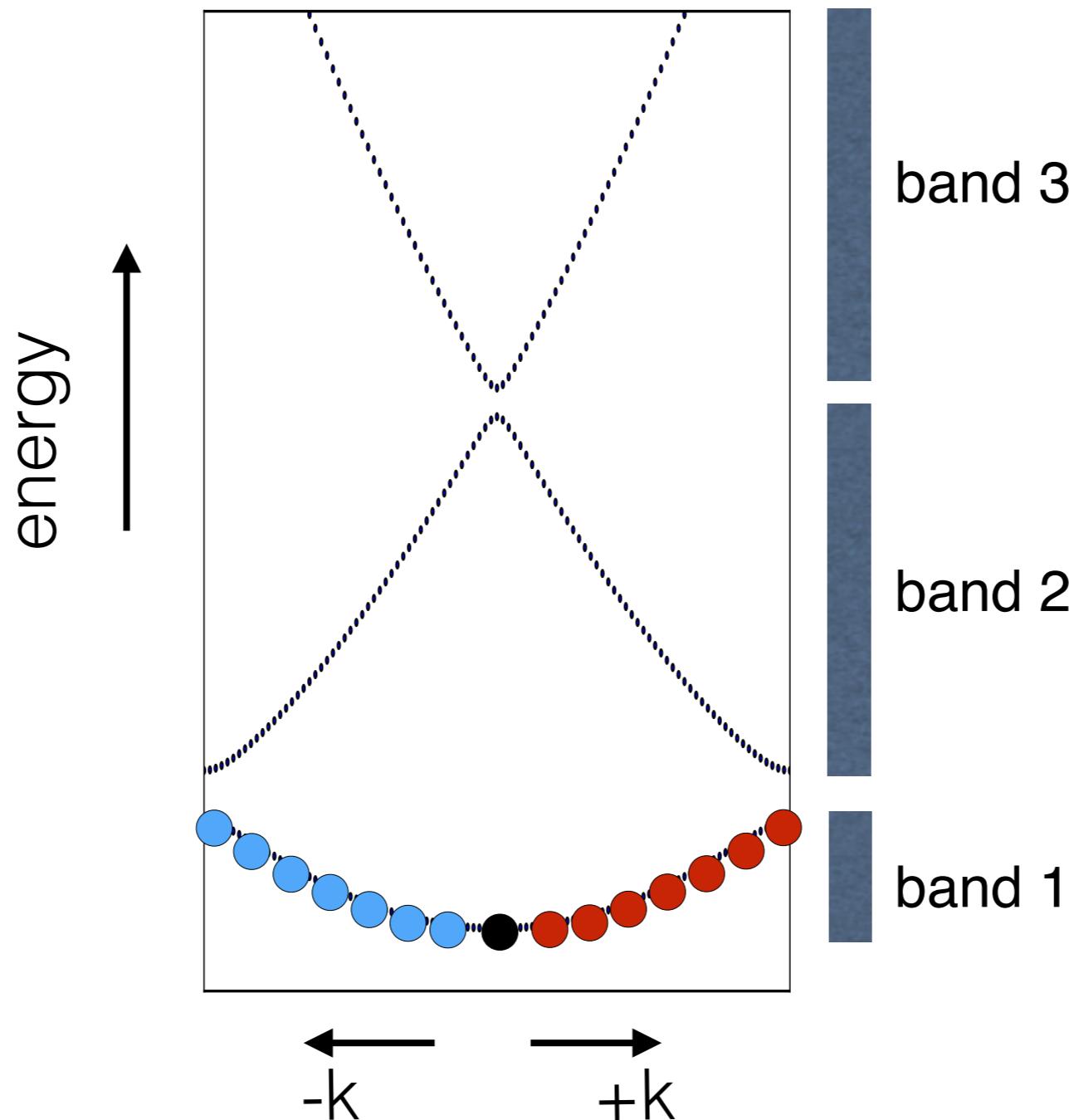
## 2.7 Metals and Insulators

Why does it matter if a band is full or not? Let's think about what happens when we want to drive a current through the solid by applying an electric field - we're going to need to change the velocity (and hence wavevector) of an electron. The electron's options for finding a state to scatter into are limited by the Pauli principle - it has to be an *empty* state, and it has to be within an infinitesimally small energy jump of where it came from. If a band is completely full, then we have just seen that there is likely to be an energy gap between the top of that band and the bottom of the next, so it will be impossible for the electron to change its wavevector - it therefore can't carry a current and we have an *insulator*. If the gap is there, but very small, then there may be enough thermal energy in the system for electrons to jump across the gap to find an unoccupied state, and then we have an *intrinsic semiconductor*.

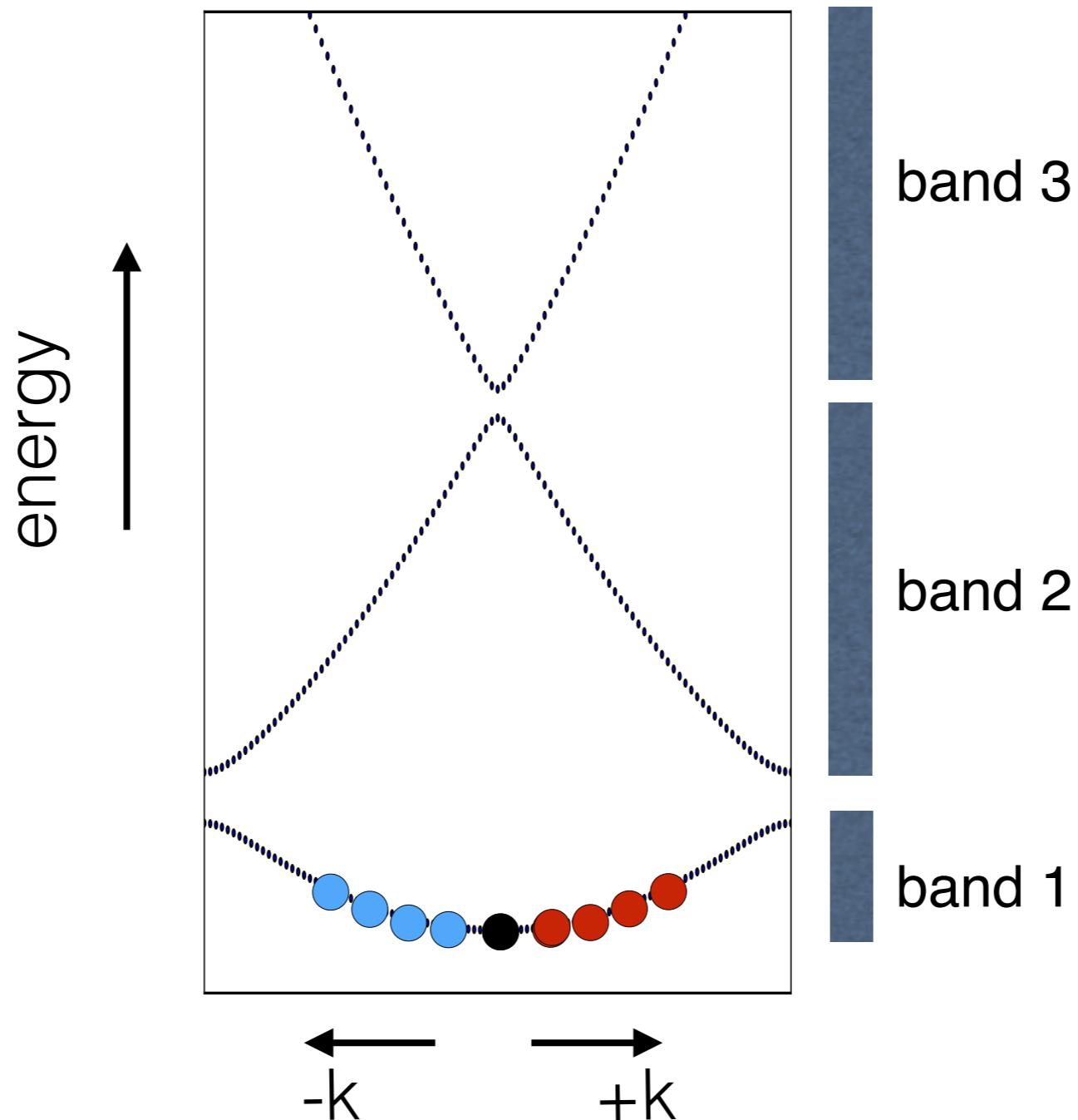


Turn the interaction between the electrons and the ions back on

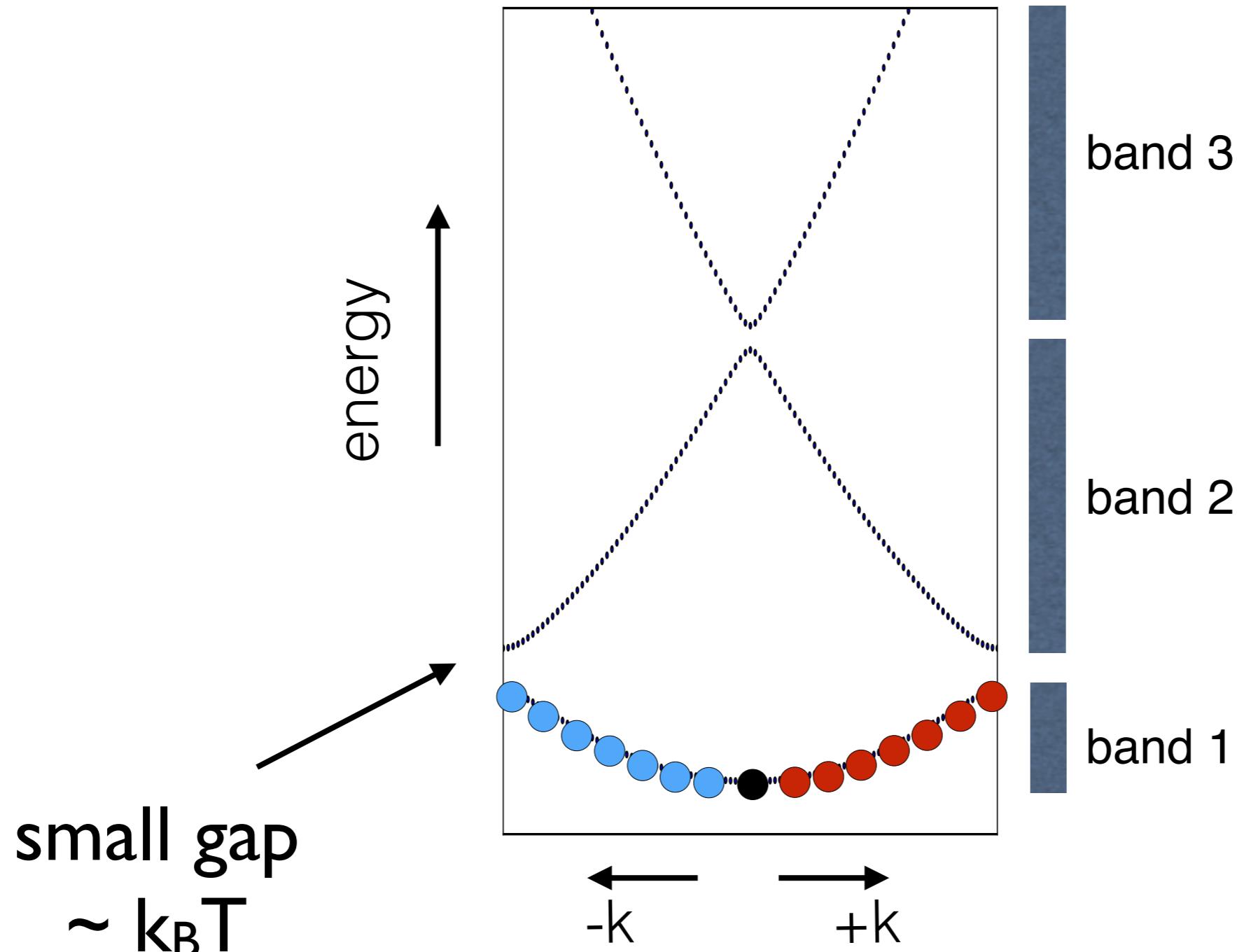
# Insulator - full band



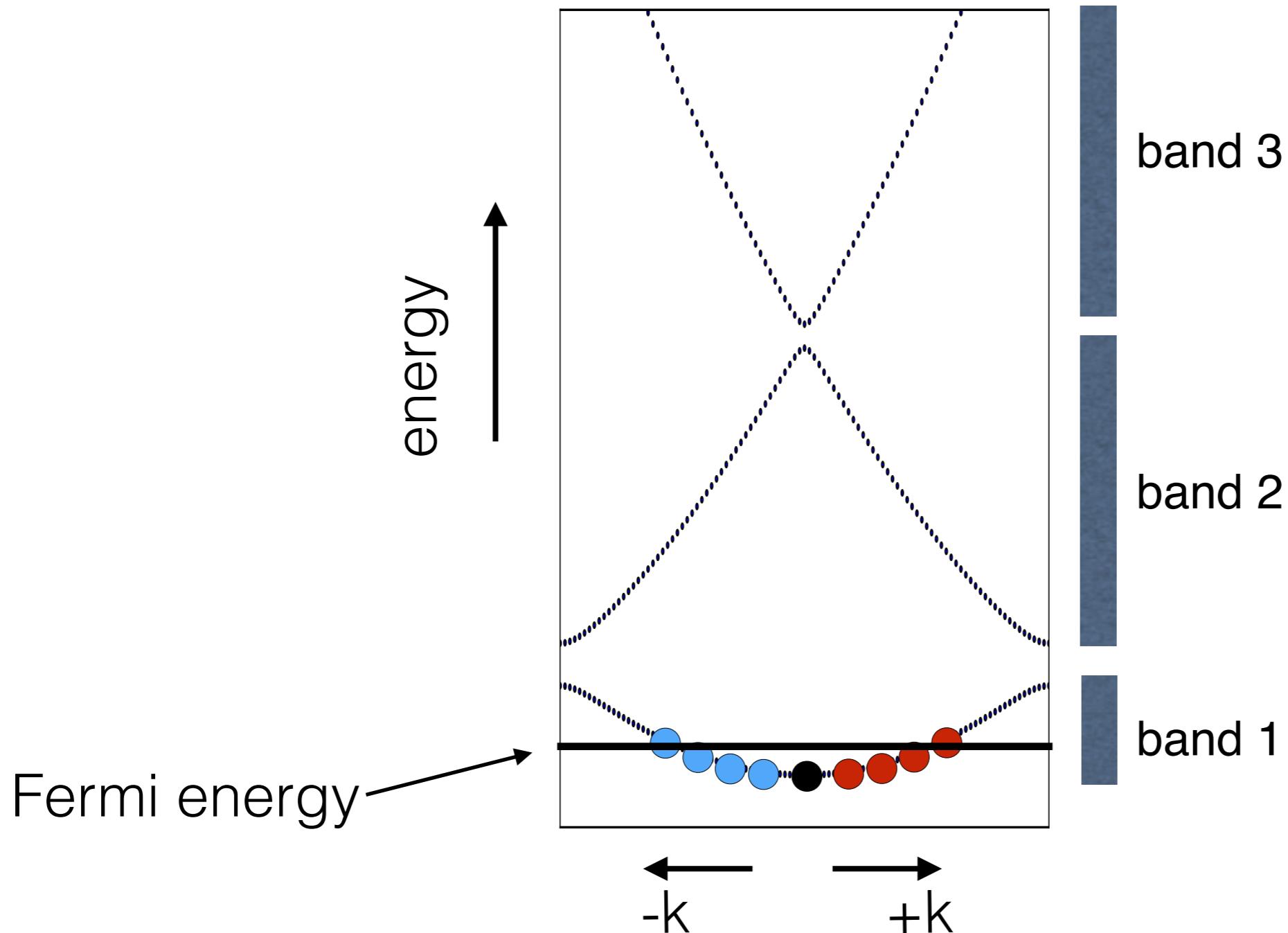
# Metal - partially filled band



# Semiconductor



# Metal - partially filled band



Let's return to the band filling again. We've just argued that substances with an even *number* of valence electrons contain just the right number of electrons to fill up an integer number of bands. It's tempting to argue then, that if there is an even number of valence electrons we should have an *insulator* and if we have an odd number (giving a half-filled band), a *metal*.

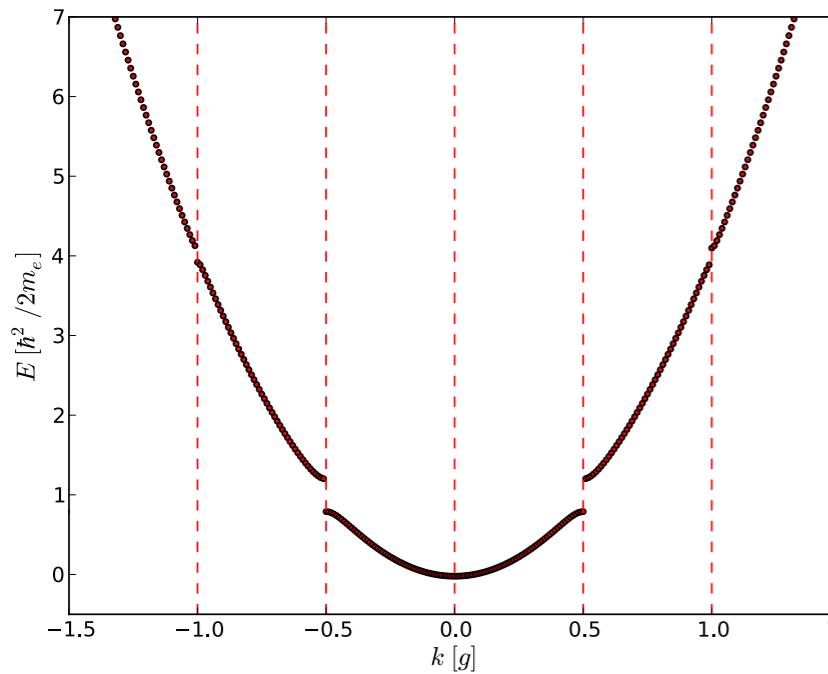
In reality it's a bit more complicated than that, because bands can overlap in energy, meaning that you can have several partially occupied bands crossing the Fermi energy (giving a metal), even if the total number of occupied states is equivalent to an integer number of full bands.

## 2.8 Reduced, Repeated and Extended Zone Schemes

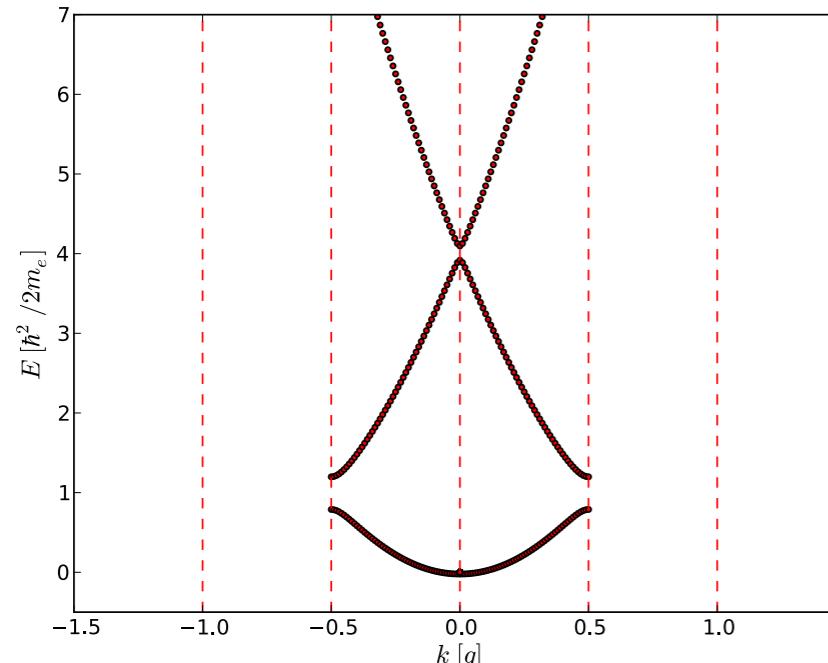
Earlier we saw that the translational invariance of the Bloch states means that :

$$E_{\mathbf{k}} = E_{\mathbf{k} + \mathbf{G'}}$$

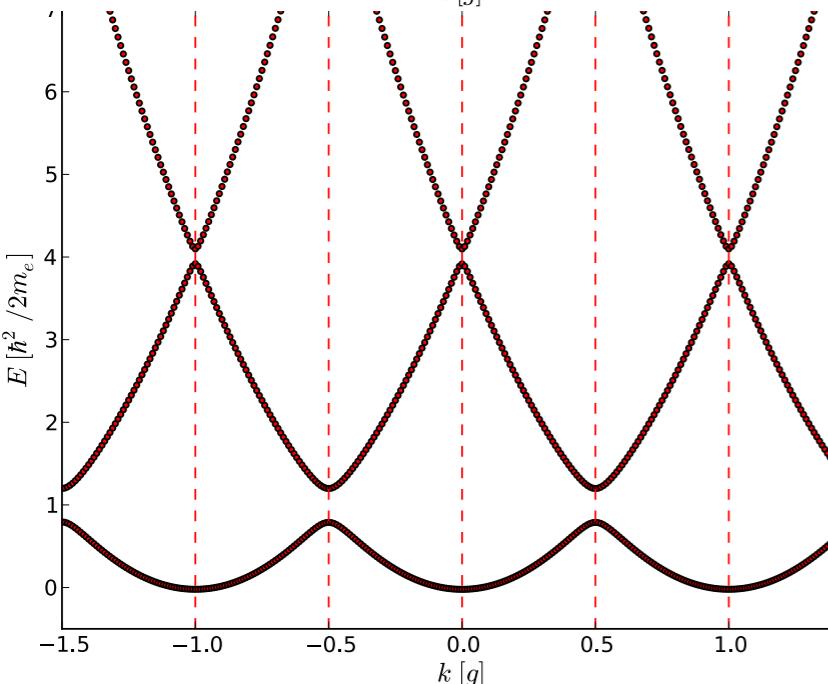
Therefore, if we know what the energy eigenvalues are in the first Brillouin zone, then we know them everywhere. Normally, therefore, we only ever calculate and plot the bands within the first Brillouin zone. This is called the *reduced zone scheme*. In the *extended zone scheme* we plot each band in a separate zone, while in the *repeated zone scheme*, we simply plot all bands in all zones!



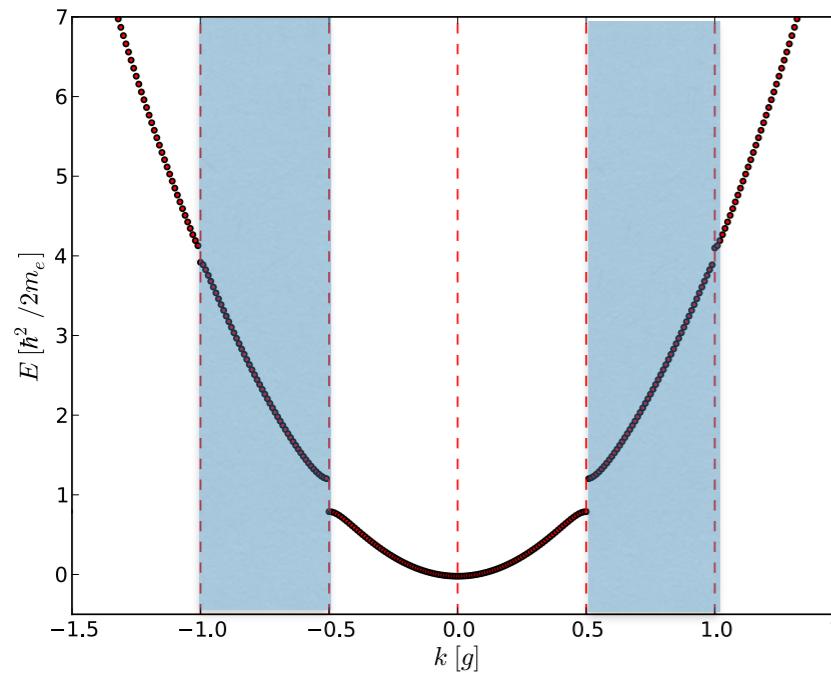
Extended Zone Scheme



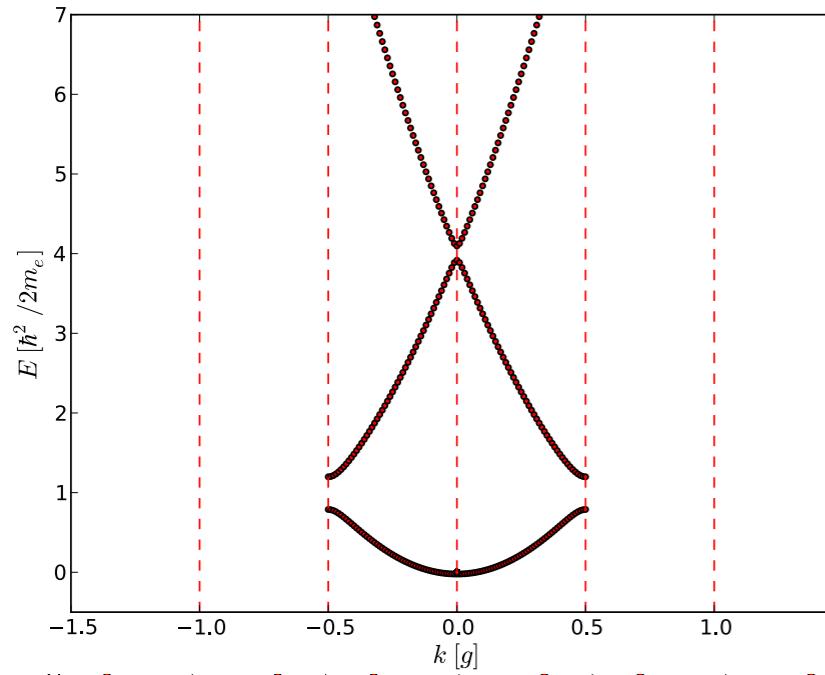
Reduced Zone Scheme



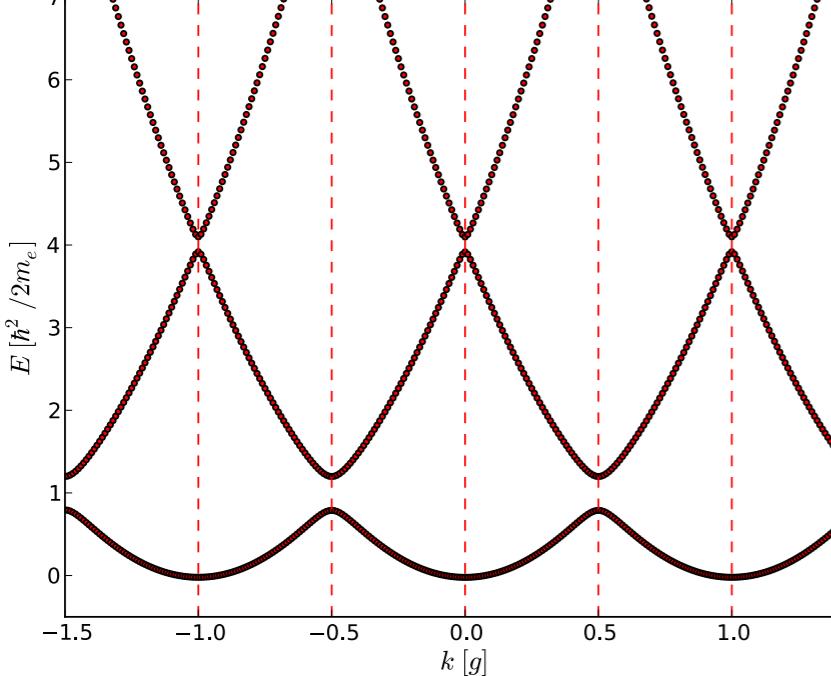
Repeated Zone Scheme



Extended Zone Scheme



2nd Brillouin zone



Repeated Zone Scheme

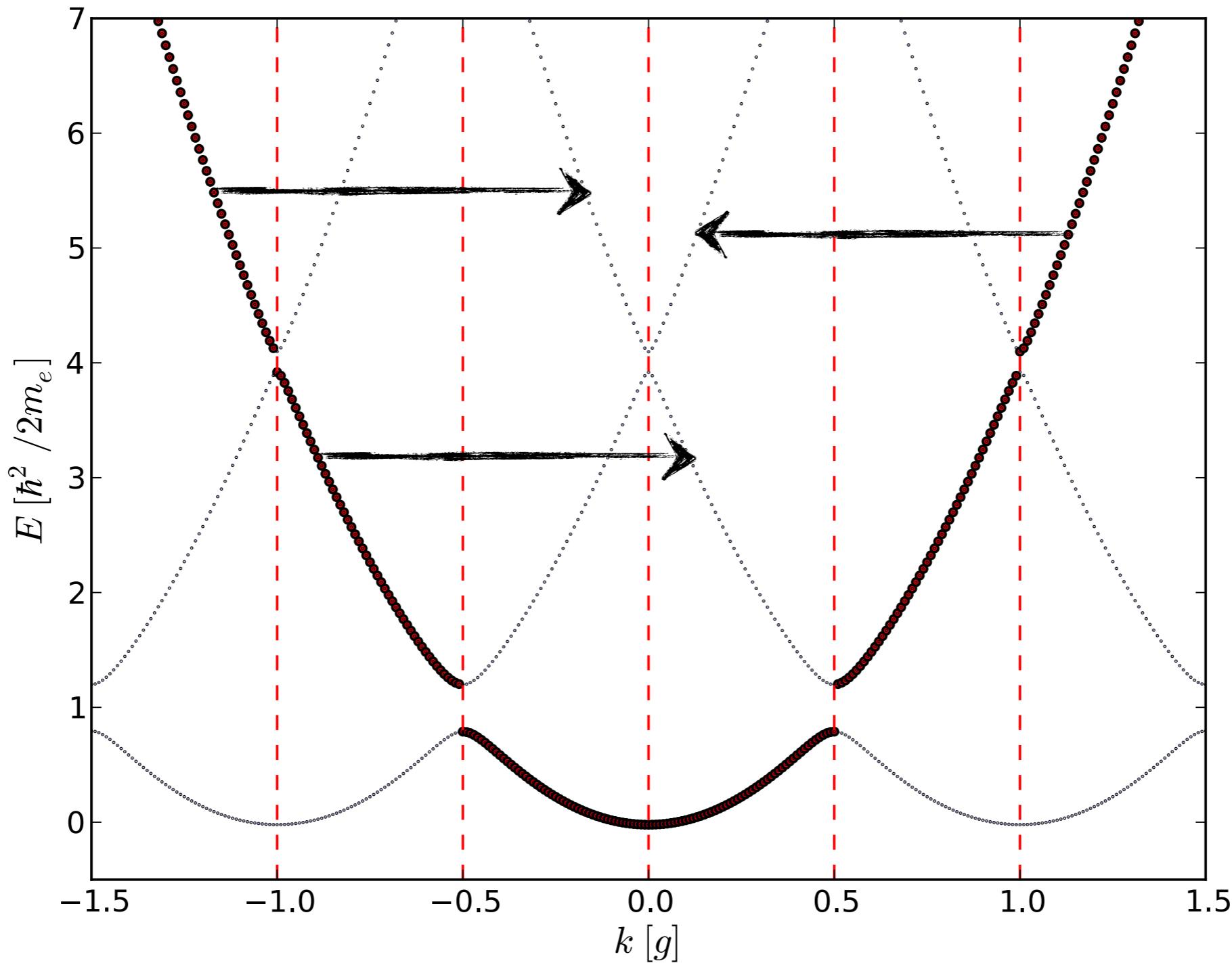


Illustration of how bands in the extended zone scheme (heavy lines) can be brought back into the first Brillouin zone by translating them by a reciprocal lattice vector ( $g$ ,  $2g$ ,  $16g$  etc., in this case the arrows are of length  $g$ ) to obtain the reduced zone scheme plot.

## 2.9 The Tight-Binding Approximation

In its spirit, the tight-binding approximation starts from the opposite limit to that of the nearly-free electron approach. We imagine that the wavefunctions of electrons are going to most closely resemble those of free atoms (in which the electrons are completely localised on the atomic sites, and whose wavefunctions and energies we know how to calculate), and then let these wavefunctions start to interact with each other. We start by assuming that a good approximation to the true wavefunction can be obtained by making a linear combination of the atomic wavefunctions (which to a first approximation, do not overlap) :

$$\psi_{\mathbf{k}}(\mathbf{r}) = \frac{1}{\sqrt{N}} \sum_{n=1}^N e^{i\mathbf{k} \cdot \mathbf{r}_n} \phi_i(\mathbf{r} - \mathbf{r}_n)$$

number of atoms in  
our crystal is  $N$

normalised isolated free atomic  
wavefunction (hence the  $i$ )  
which is centred at position  $\mathbf{r}_n$   
in the crystal

Let's begin by checking that this Bloch state is properly normalised :

$$\begin{aligned}
 \int_V \psi_{\mathbf{k}}^*(\mathbf{r}) \psi_{\mathbf{k}}(\mathbf{r}) dV &= \frac{1}{N} \int_V \sum_{m=1}^N \sum_{n=1}^N e^{-i\mathbf{k}\cdot\mathbf{r}_m} \phi_i^*(\mathbf{r} - \mathbf{r}_m) e^{i\mathbf{k}\cdot\mathbf{r}_n} \phi_i(\mathbf{r} - \mathbf{r}_n) dV \\
 &= \frac{1}{N} \int_V \sum_{m=1}^N \sum_{n=1}^N e^{i\mathbf{k}\cdot(\mathbf{r}_n - \mathbf{r}_m)} \phi_i^*(\mathbf{r} - \mathbf{r}_m) \phi_i(\mathbf{r} - \mathbf{r}_n) dV \\
 &= \frac{1}{N} \sum_{m=1}^N \sum_{n=1}^N \delta_{mn} \\
 &= 1
 \end{aligned}$$



This part of the integrand is describing the overlap between wavefunctions in two sites labelled by  $m$  and  $n$ , and our starting point in this theory is that **to a first approximation** they do not overlap. Hence we only have a contribution when  $m=n$  (i.e. our two wavefunctions are on the same site), and as they are themselves normalised we get an integral of 1

Good - our Bloch function is, to a first approximation in which the wavefunctions on neighbouring sites do not overlap, normalised. When doing the energy calculation, because this normalisation is an approximation (albeit a good one), I should probably write “ $\approx$ ” rather than “ $=$ ”, but I won’t.

The Hamiltonian in the crystal can be written as :

$$\hat{H} = \frac{-\hbar^2 \nabla^2}{2m_e} + V_i(\mathbf{r} - \mathbf{r}_n) + \sum_{m \neq n} V_i(\mathbf{r} - \mathbf{r}_m)$$



Hamiltonian of  
isolated atom



small perturbation potential  
coming from other atoms

which we can write as :

$$\hat{H} = \hat{H}_i + v(\mathbf{r} - \mathbf{r}_n)$$

Therefore we can now proceed to calculate the energies...

$$\begin{aligned} E_{\mathbf{k}} &= \int_V \psi_{\mathbf{k}}^*(\mathbf{r}) (\hat{H}_i + v(\mathbf{r} - \mathbf{r}_n)) \psi_{\mathbf{k}}(\mathbf{r}) dV \\ &= \frac{1}{N} \int_V \sum_{m=1}^N \sum_{n=1}^N e^{i\mathbf{k} \cdot (\mathbf{r}_n - \mathbf{r}_m)} \phi_i^*(\mathbf{r} - \mathbf{r}_m) (\hat{H}_i + v(\mathbf{r} - \mathbf{r}_n)) \phi_i(\mathbf{r} - \mathbf{r}_n) dV \\ &= E_i - A - B \sum_m e^{i\mathbf{k} \cdot (\mathbf{r}_n - \mathbf{r}_m)} \end{aligned}$$

sum should only include contributions when  
n and m are nearest neighbours, so we are just  
summing over m nearest neighbours

where

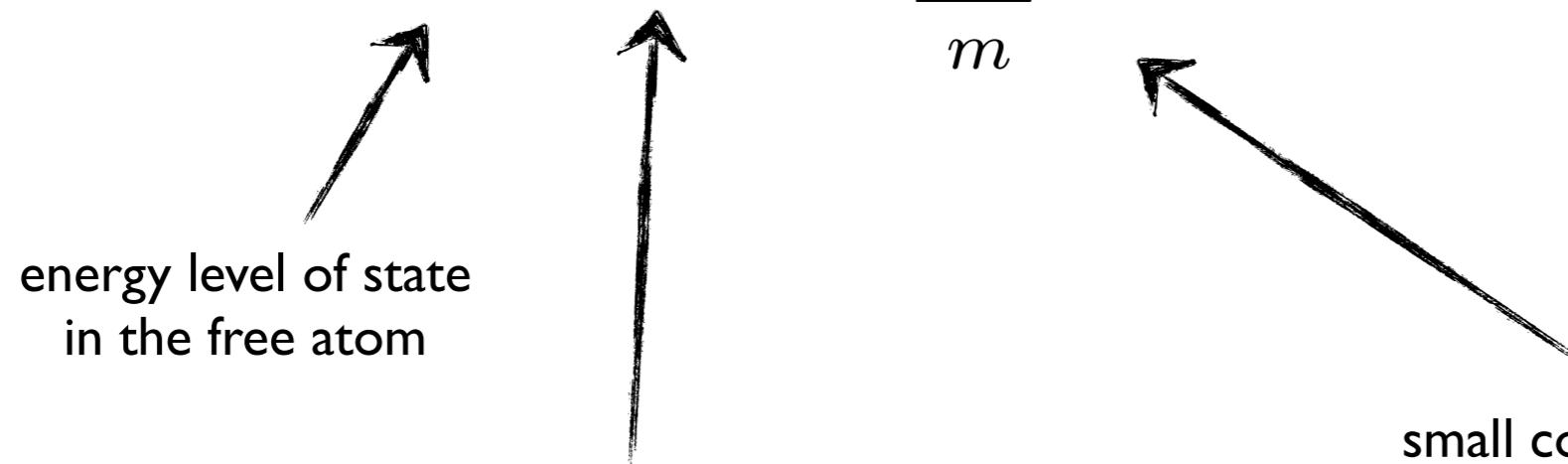
$$A = - \int_V \phi_i^*(\mathbf{r} - \mathbf{r}_n) v(\mathbf{r} - \mathbf{r}_n) \phi_i(\mathbf{r} - \mathbf{r}_n) dV$$

$$B = - \int_V \phi_i^*(\mathbf{r} - \mathbf{r}_m) v(\mathbf{r} - \mathbf{r}_n) \phi_i(\mathbf{r} - \mathbf{r}_n) dV$$

and  $E_i$  is the energy level in the free atom (just a number). Note that since  $v$  is negative (attractive),  $A$  is a positive number.

Let's examine this a bit more closely.

$$E_{\mathbf{k}} = E_i - A - B \sum_m e^{i\mathbf{k}\cdot(\mathbf{r}_n - \mathbf{r}_m)}$$



correction to free atom  
energy level due to  
perturbation

small correction ( $B$  is small)  
to free atom  
energy level due to  
overlapping wavefunctions

It's the third term involving the  $B$  that leads to band formation.  $B$  is called a *transfer integral*, or sometimes a *hopping integral*. It represents the probability of an electron hopping from site  $m$  to site  $n$ . Let's look at an example (one dimensional, to keep things simple) to see how this works.

We can set the lattice constant equal to  $a$ , and we'll allow nearest neighbour hopping only:

$$E_k = E_i - A - B \sum_m e^{ik(r_n - r_m)}$$

$r_n - r_m = \pm a$  (nearest neighbours *only*), and therefore :

$$\begin{aligned} E_k &= E_i - A - Be^{ik(-a)} - Be^{ik(+a)} \\ &= E_i - A - 2B \cos(ka) \end{aligned}$$

# Atoms, orbitals and electron configuration

Schrödinger equation for hydrogenic atom : note :  $\psi = \psi(r, \theta, \phi)$

$$\frac{1}{r^2} \frac{\partial}{\partial r} \left( r^2 \frac{\partial \psi}{\partial r} \right) + \frac{1}{r^2 \sin \theta} \frac{\partial}{\partial \theta} \left( \sin \theta \frac{\partial \psi}{\partial \theta} \right) + \frac{1}{r^2 \sin^2 \theta} \frac{\partial^2 \psi}{\partial \phi^2} + \frac{2m}{\hbar^2} (E - U) \psi = 0$$

Separation of variables gives radial part  $R_{nl}(r)$  and an angular part

$$R_{10} = 2 \left( \frac{Z}{a_0} \right)^{\frac{3}{2}} e^{-Zr/a_0}$$

Bohr radius :  $a_0 = \frac{\hbar}{\alpha mc}$

$$R_{21} = \frac{1}{2\sqrt{6}} \left( \frac{Z}{a_0} \right)^{\frac{3}{2}} \left( \frac{Zr}{a_0} \right) e^{-Zr/2a_0}$$

$$R_{20} = \frac{1}{\sqrt{2}} \left( \frac{Z}{a_0} \right)^{\frac{3}{2}} \left( 1 - \frac{1}{2} \frac{Zr}{a_0} \right) e^{-Zr/2a_0}$$

$$R_{32} = \frac{1}{9\sqrt{30}} \left( \frac{Z}{a_0} \right)^{\frac{3}{2}} \left( \frac{2Zr}{3a_0} \right)^2 e^{-Zr/3a_0}$$

$$R_{31} = \frac{2\sqrt{2}}{9\sqrt{3}} \left( \frac{Z}{a_0} \right)^{\frac{3}{2}} \left( \frac{2Zr}{3a_0} \right) \left( 1 - \frac{1}{4} \frac{2Zr}{3a_0} \right) e^{-Zr/3a_0}$$

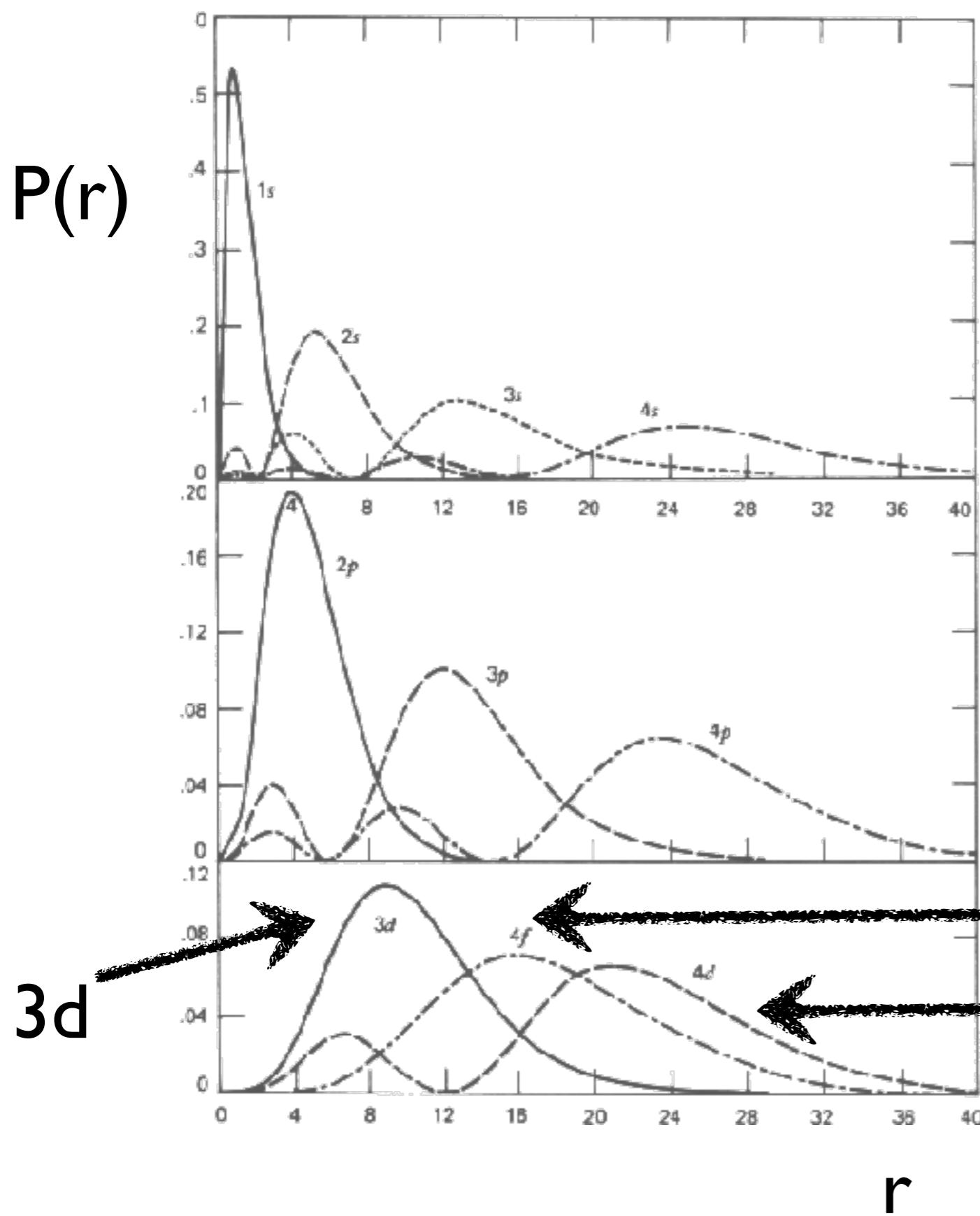
$$R_{30} = \frac{2}{3\sqrt{3}} \left( \frac{Z}{a_0} \right)^{\frac{3}{2}} \left( 1 - \frac{2Zr}{3a_0} + \frac{1}{6} \left( \frac{2Zr}{3a_0} \right)^2 \right) e^{-Zr/3a_0}$$

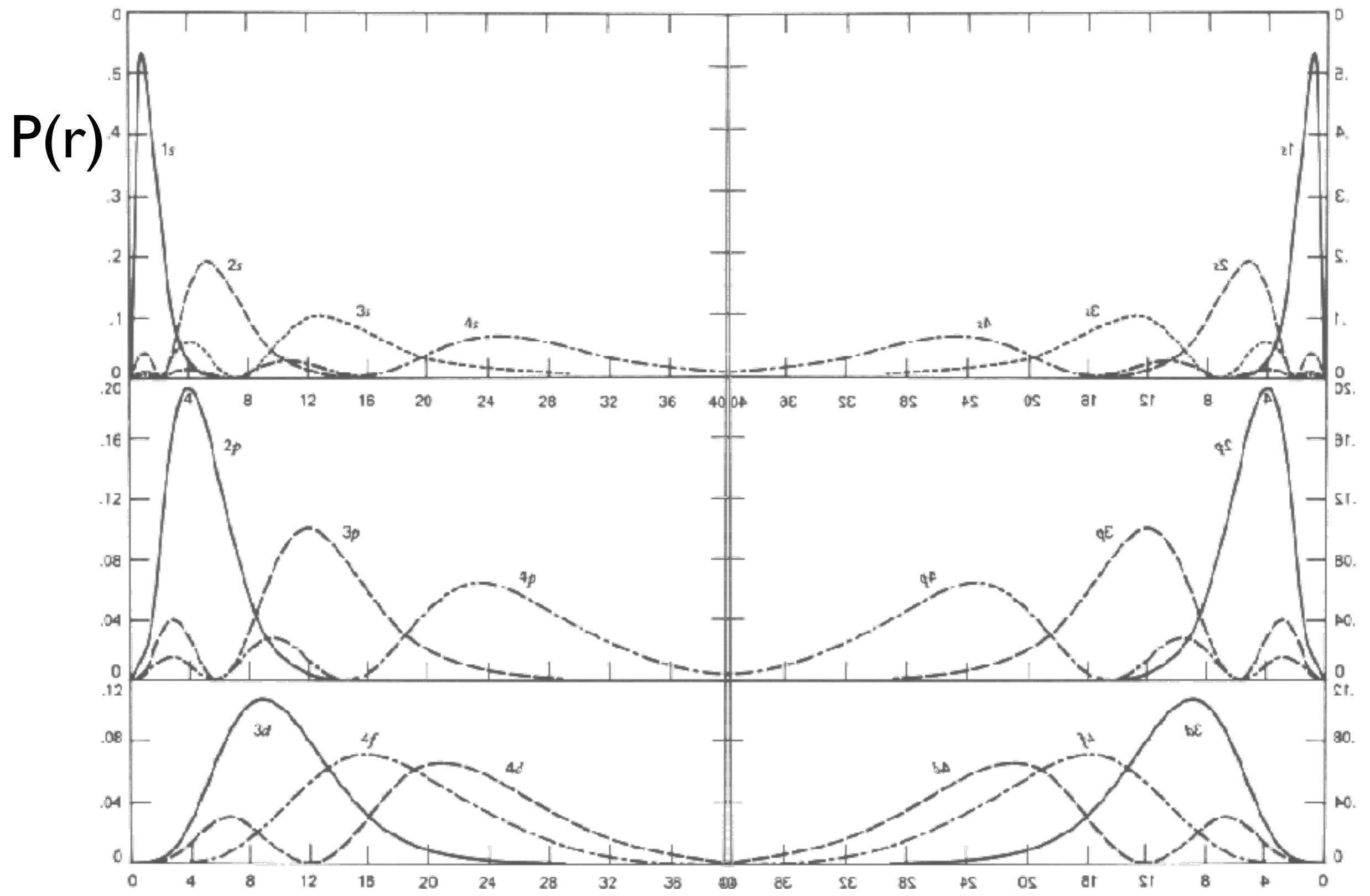
$$\psi_{nlm}(r, \theta, \phi) = R_{nl}(r) Y_{lm}(\theta, \phi)$$



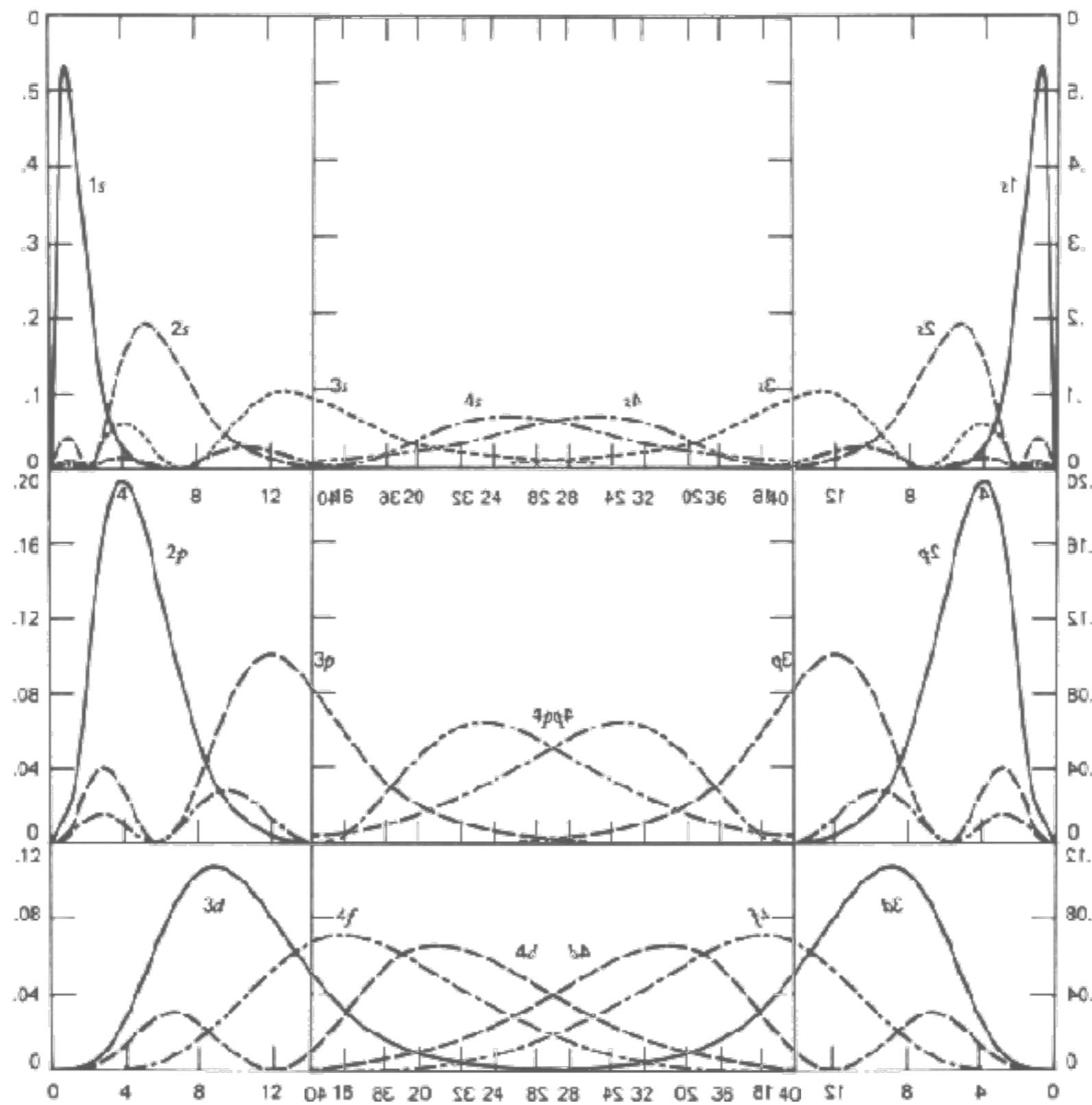
these are the spherical harmonics

$$P(r) = \psi^*(r)\psi(r)$$



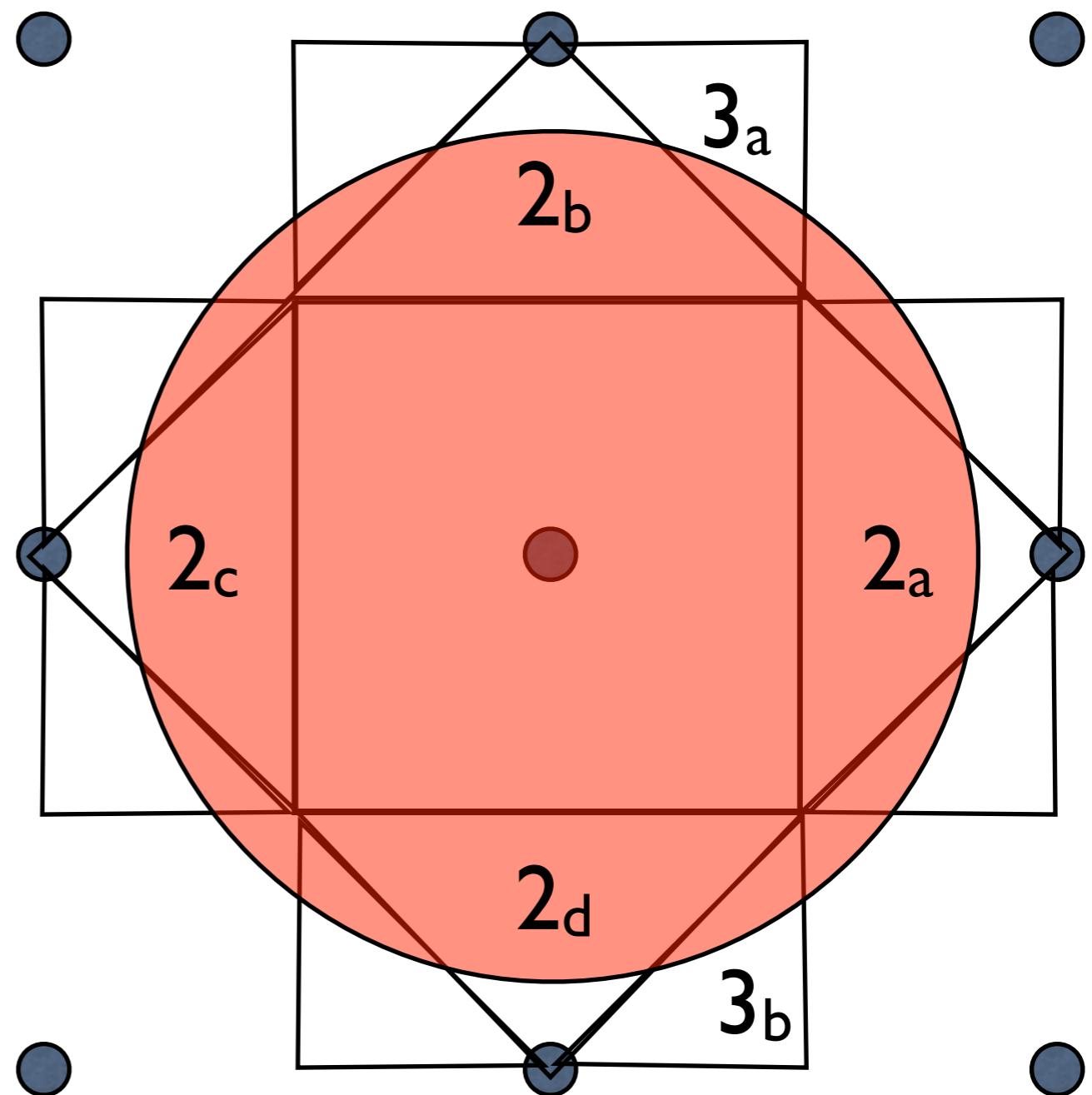
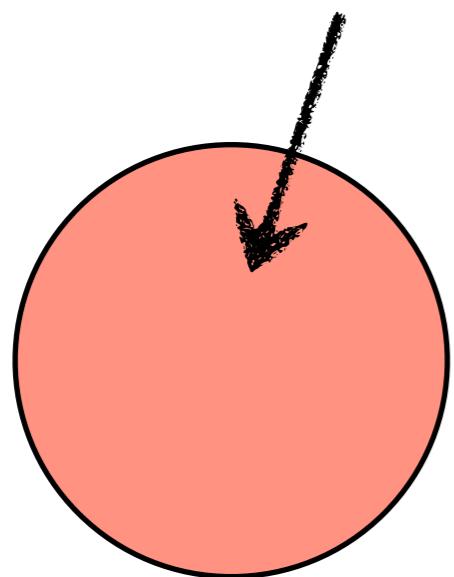


$P(r)$

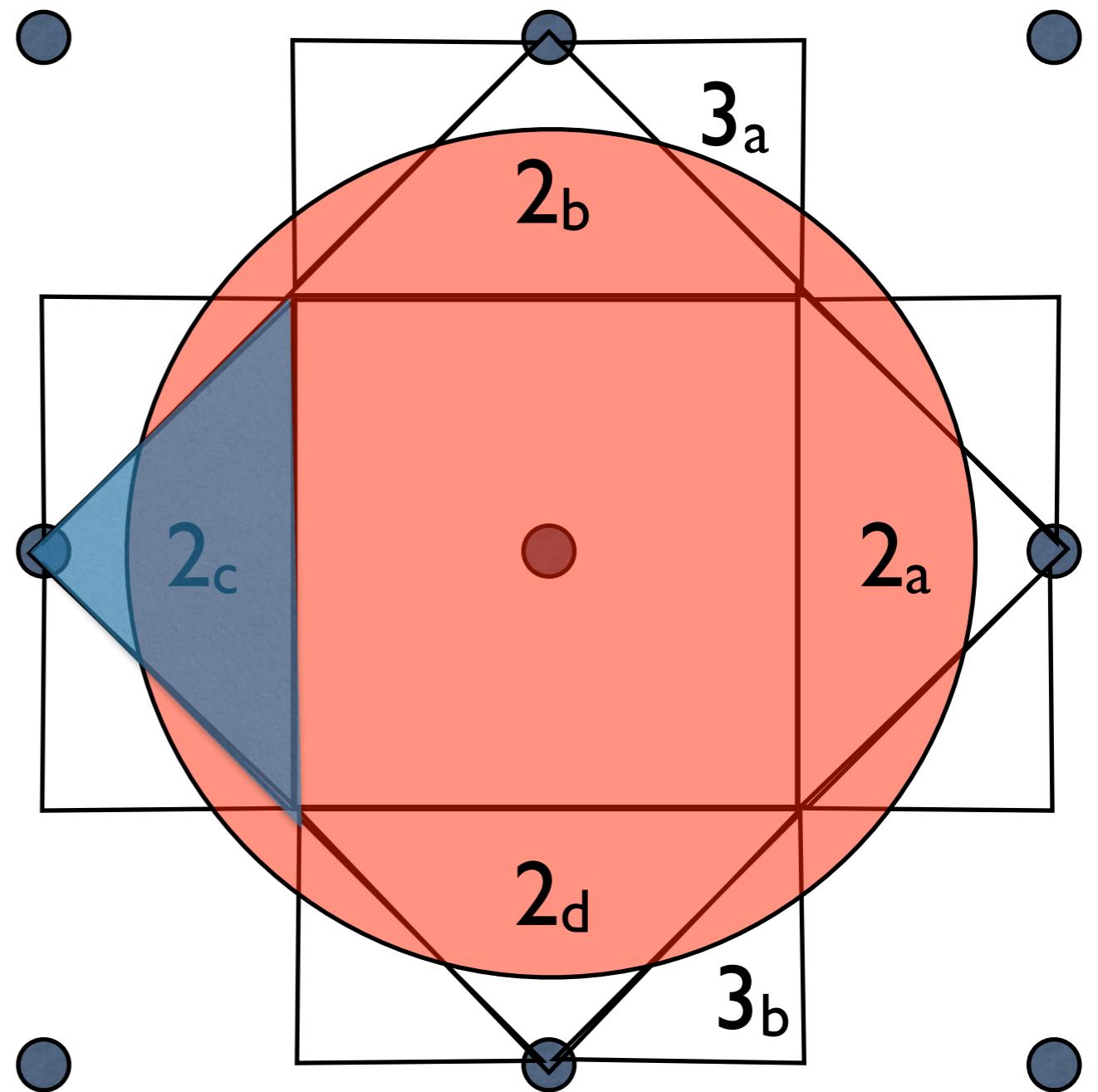


## 2.10 Construction of Fermi surfaces

Free-electron Fermi surface  
containing occupied states

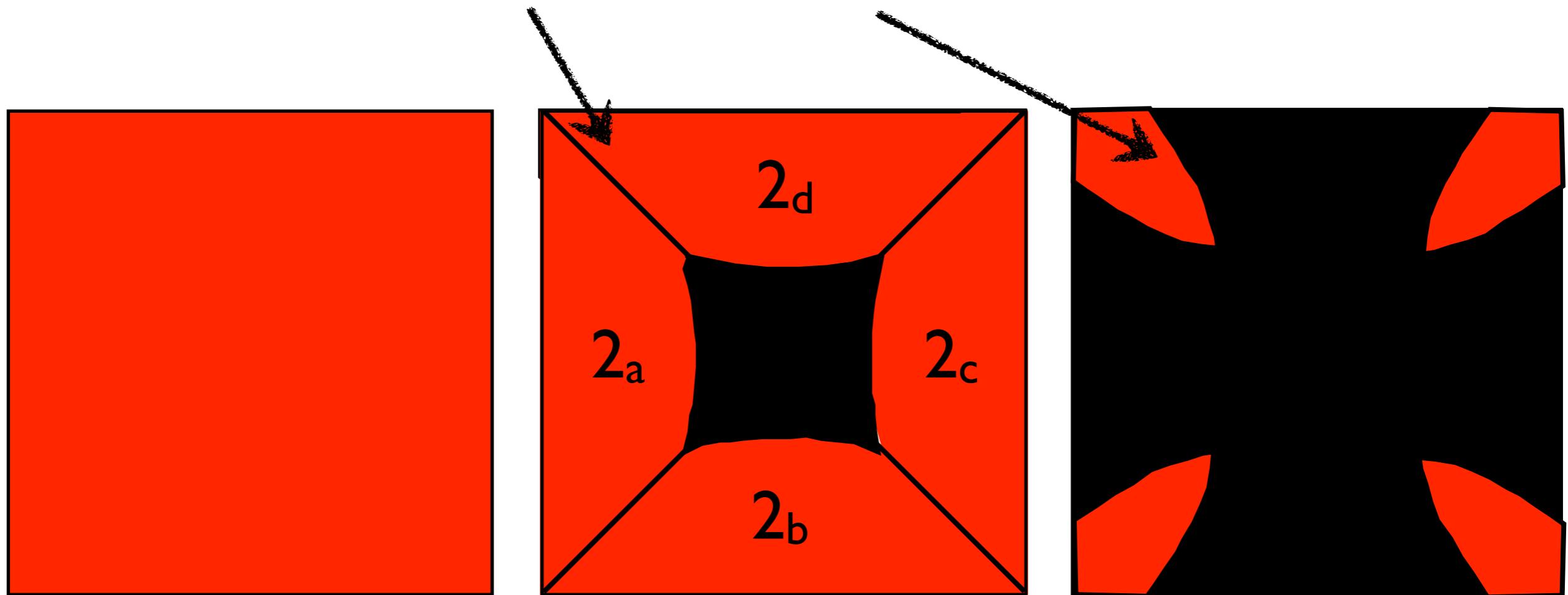


## 2.10 Construction of Fermi surfaces



How would this look in the Reduced Zone Scheme? Let's translate the pieces of each zone separately by an appropriate **G** vector ...

Notice how the overlapping bits of the Second zone look like the third zone Fermi surface - see the "Harrison Construction" on Problem Sheet 3



First  
Brillouin Zone

First zone is full - no Fermi surface in first zone!

Second  
Brillouin Zone

We have a Fermi surface in the second zone...

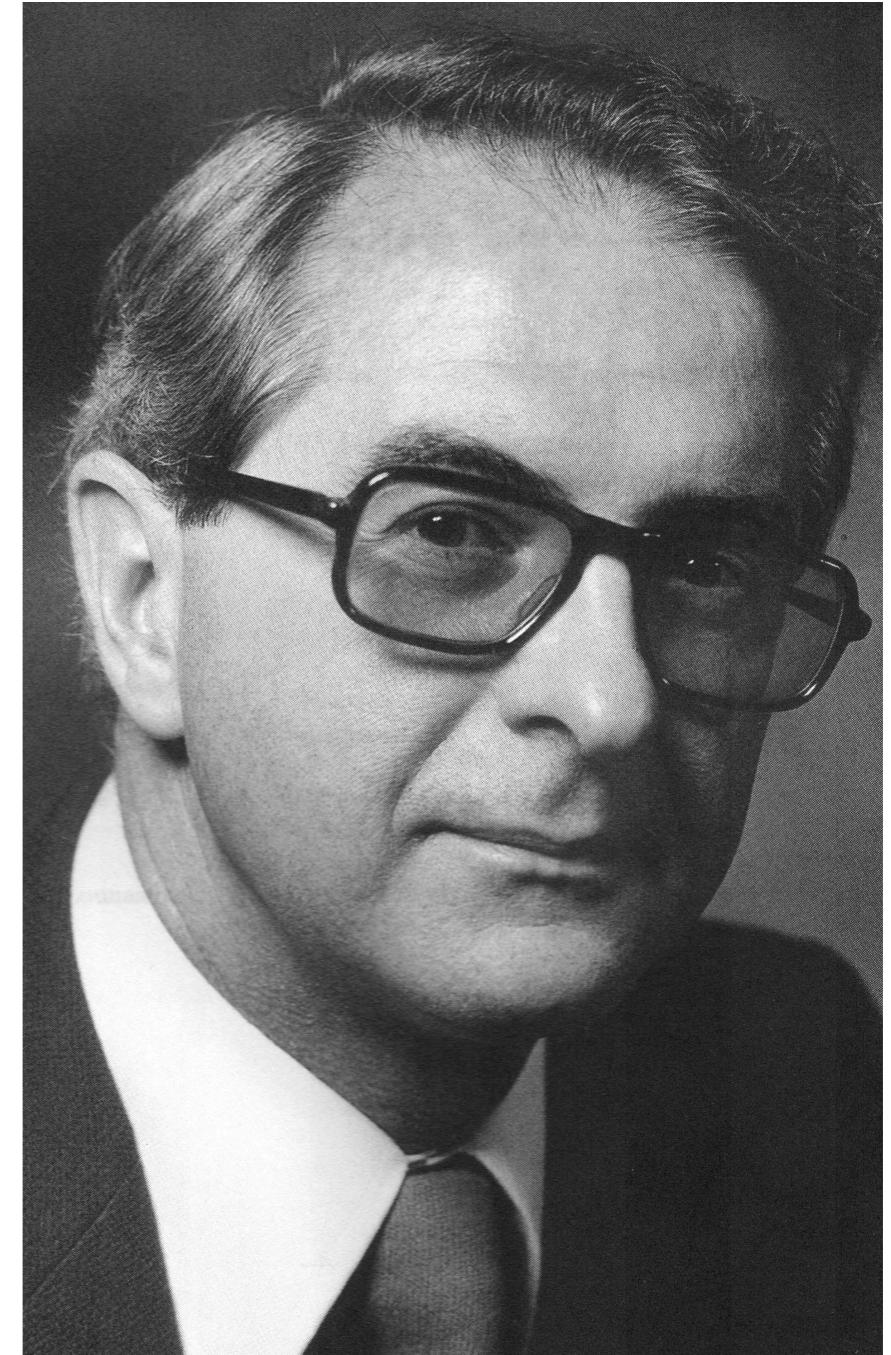
Third  
Brillouin Zone

and in the third zone... (and fourth, which is not shown)

## 2.11 The Electronic Structure of Real Metals

“Few people would define a metal as ‘*a solid with a Fermi surface*’. This may nevertheless be the most meaningful definition of a metal one can give today.”

“The Fermi Surface of Metals”, Scientific American **209**, 110 (1963)



Allan R Mackintosh  
(Image: Det Kongelige Danske Videnskabernes Selskab)

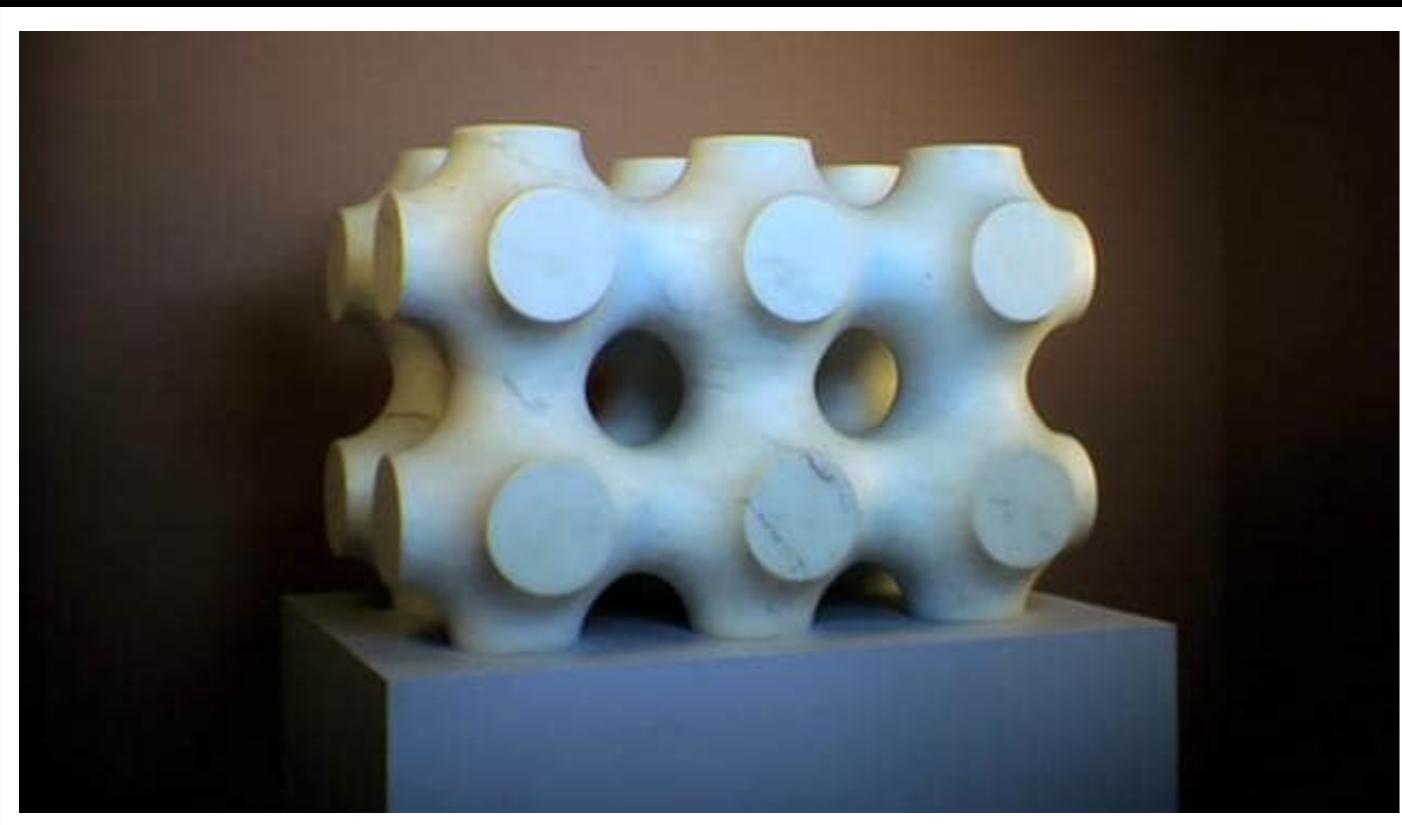
### 3. Application.

In the previous section we have found the expression for the coefficient B in terms of certain integrals. These integrals may be reduced, by a standard method, to integrations over the surface of the Fermi distribution. In applying our formulæ it is thus advantageous that we select a metal whose Fermi surface has a particularly simple form. Blochinzev and Nordheim (*loc. cit.*) concluded from the consideration of a simple cubic lattice that the Fermi surface of a monavalent metal is of a rather complicated nature, the surface touching the six faces of the cube across which the energy is discontinuous. Now all monovalent metals have either a face or body centred structure. In such a structure the lattice perturbation is much more symmetrical than in a simple cubic lattice, and so it is to be expected that the surface of the Fermi distribution is here simpler than in the simple cubic structure. We show below that this surface is, in fact, nearly spherical, at least in the case of lithium.

## First use of term “Fermi surface”?

*The Theory of the Change in Resistance in a Magnetic Field.*

By H. JONES and C. ZENER, Wills Physics Laboratory, University of Bristol.



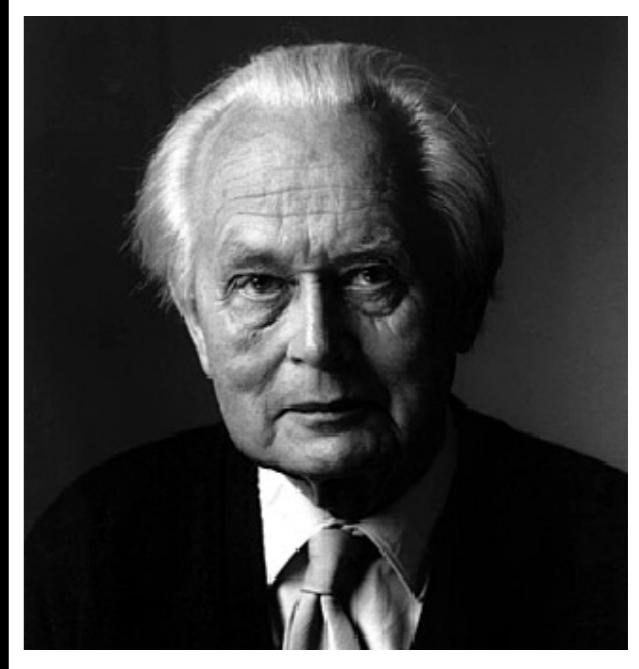
“*Fermi*” (Tony Smith, 1973)  
Costa Mesa (California)



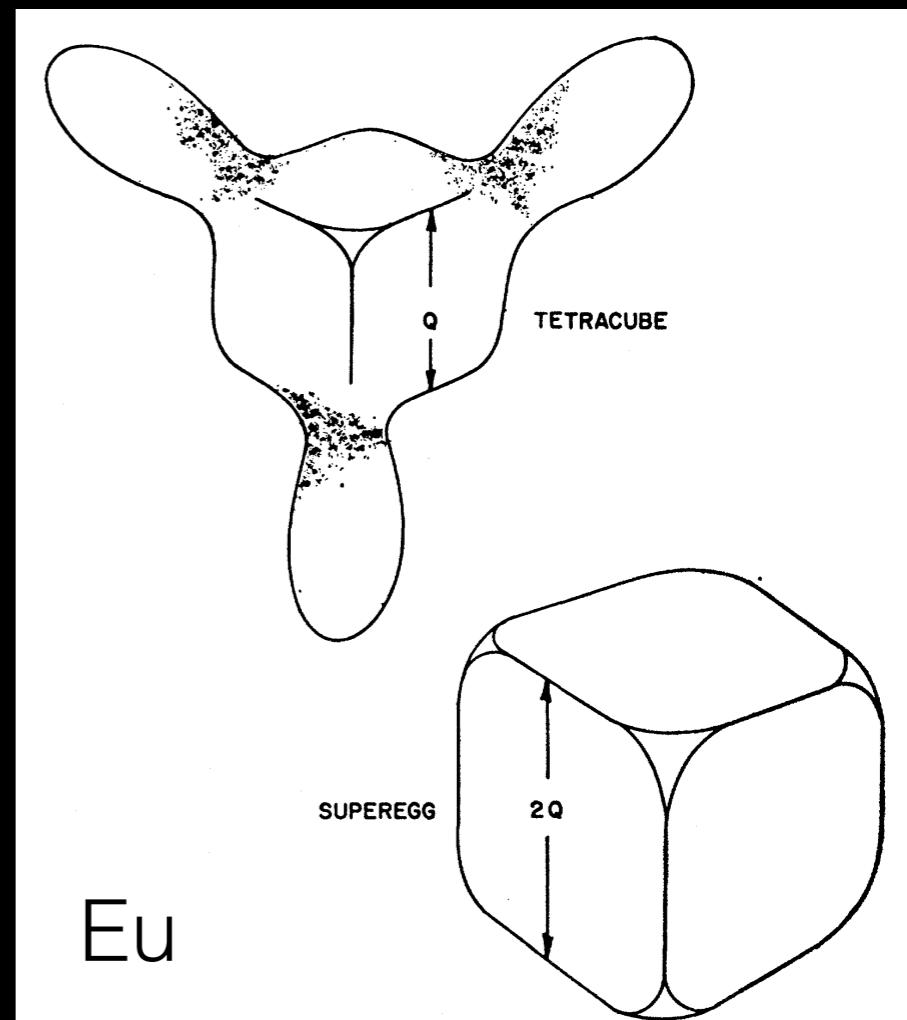
“*For Dolores*”  
or  
“*Flores para los muertos*”  
(Tony Smith, 1973)  
Nasher Sculpture Centre (Dallas)



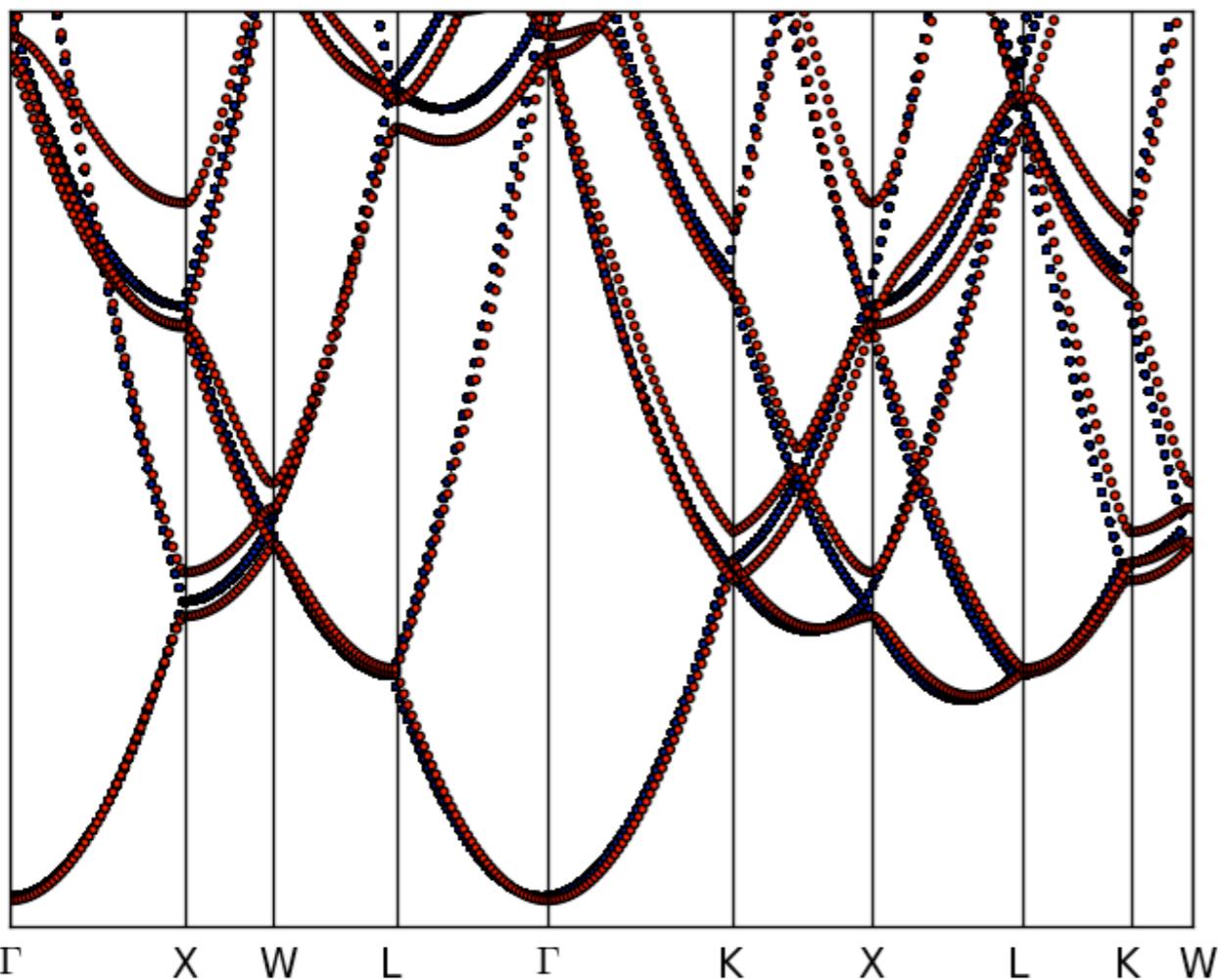
*Piet Hein's super-egg made of stainless steel is also known as the "anti-stress egg". Its soft curves combined with the cold steel make it perfect for de-stressing play and fidgeting. Delivered in a grey leather bag.*



<sup>32</sup> We have chosen the name “superegg” because of the similarity between our rounded-off cube and the “super-egg” designed by Piet Hien, the Danish writer and inventor. In many design applications he has used simple and pleasing shapes which mediate between the round and the rectangular; in two dimensions the curves are called super-ellipses, and in three dimensions he has chosen to call them super-eggs. One family of these surfaces can be described by the equation  $x^n + y^n + z^n = \text{const}$ . If  $n$  is infinite, this reduces to a cube, and if  $n=2$ , it is the equation for a sphere. For intermediate values of  $n$ , the equation describes a family of surfaces ranging between these two. We found that  $n=13/4$  gives a good fit to our Fermi surface except near the corners, where the spin-orbit splitting with the tetracube is important. Literature on the super-egg can be obtained from The Super-Egg World Center, Skjern, Denmark.

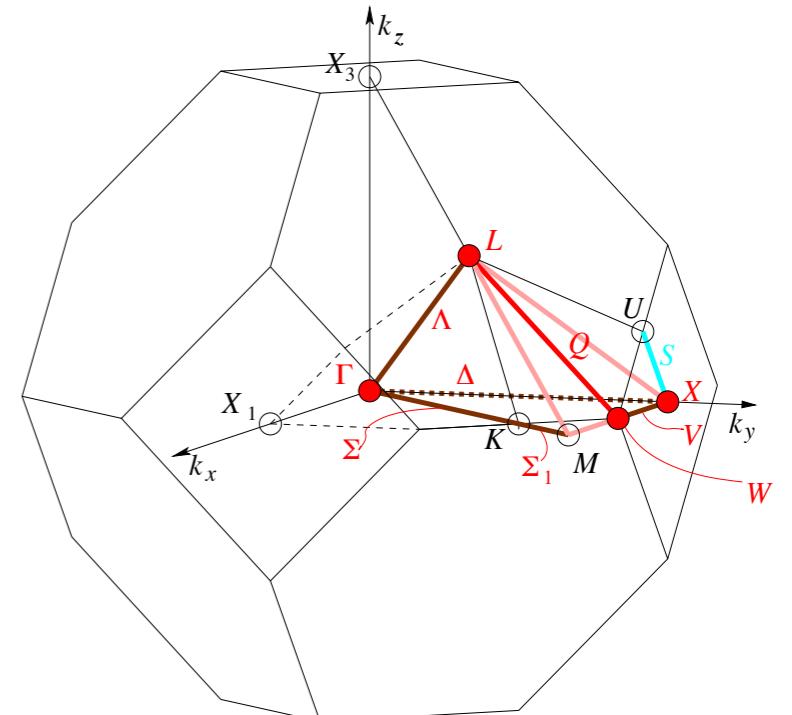


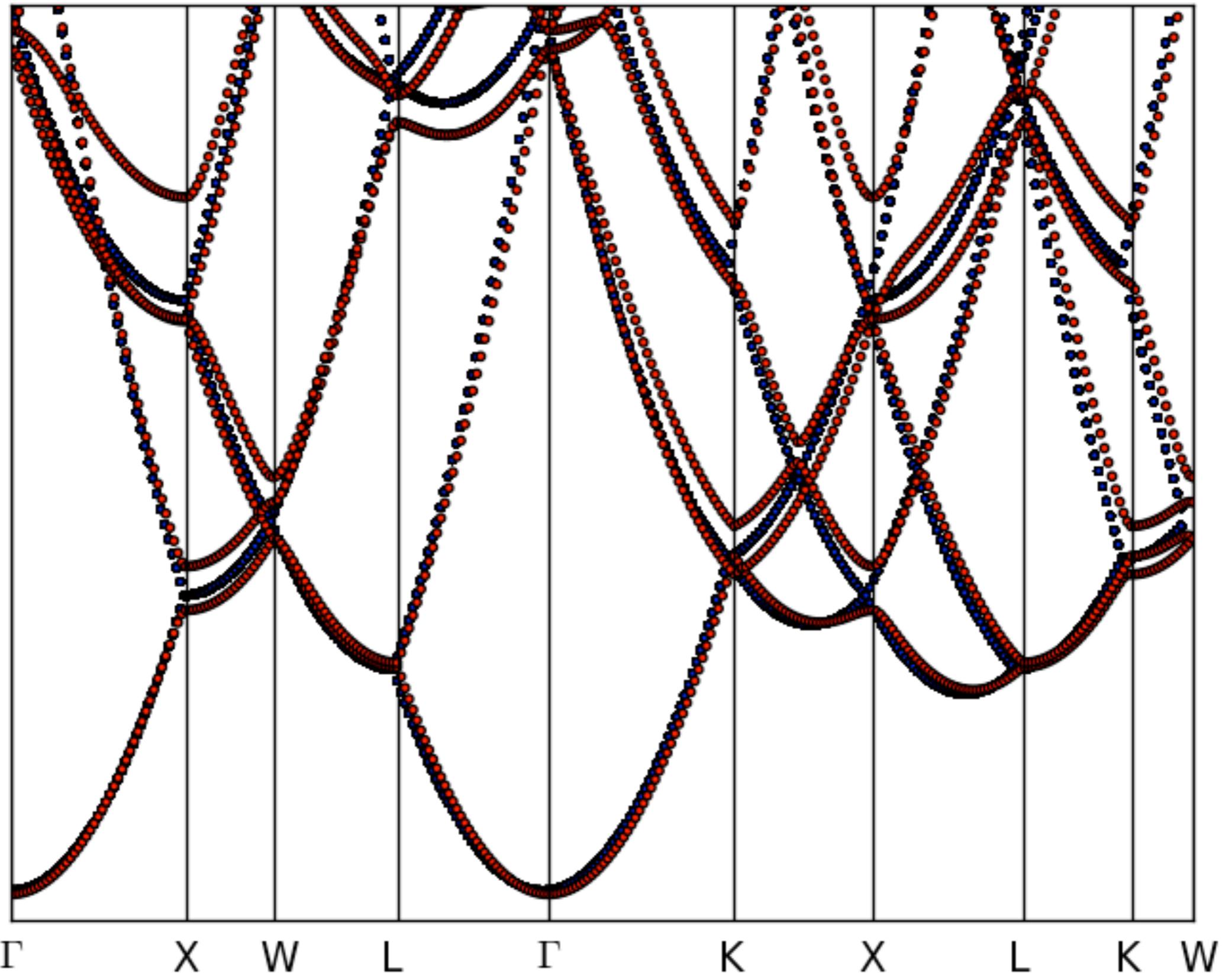
Shortly, we will look at ways of measuring the Fermi surface (and even band structure) of real materials, but first it is instructive to see just how well our simple models work, and see what we can understand in plots of the band structures of real materials. These plots have come from state-of-the-art all-electron band structure calculations (you can download them, e.g. ELK <http://elk.sourceforge.net/> ).



Band structure of Al. Red symbols are from a “proper” calculation, and the black is just the empty lattice (§2.5.4) approximation (pretty good, except for the missing gaps)

The black symbols are coming from free electron parabolas centred on many reciprocal lattice points. This “band structure” may look complex, but it is astonishing how closely a state-of-the-art calculation resembles these simple free electron parabolas.





Band structure of Al. Red symbols are from a “proper” calculation,  
and the black is just the empty lattice (§2.5.4) approximation  
(pretty good, except for the missing gaps)

# Periodic Table of Chemical Elements

	1 IA	2s																		18 VIIIA		
1	1 H Hydrogen 1.0079																	2 He Helium 4.0025				
2	3 Li Lithium 6.941	4 Be Beryllium 9.0122																				
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7	87 Fr Francium 223	88 Ra Radium 226	89-103 Ac-Lr Actinide 261	104 Rf Rutherfordium 261	105 Db Dubnium 262	106 Sg Seaborgium 266	107 Bk Bohrium 264	108 Hs Hassium 277	109 Mt Meitnerium 268	110 Ds Darmstadtium 281	111 Rg Roentgenium 280	112 Uub Ununbium 285	113 Uut Ununtrium 284	114 Uuq Ununquadium 289	115 Uup Ununpentium 293	116 Uuh Ununhexium 293	117 Uus Ununseptium 292	118 Uuo Ununoctium 294				

- █ Alkali Metal
- █ Alkaline Earth Metal
- █ Metal
- █ Metalloid
- █ Non-metal
- █ Halogen
- █ Noble Gas
- █ Lanthanide/Actinide

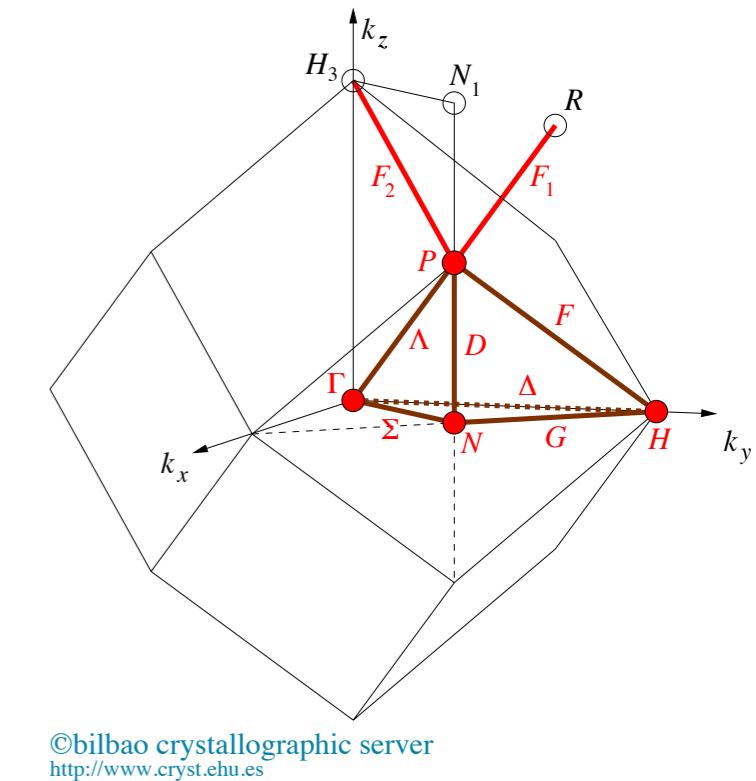
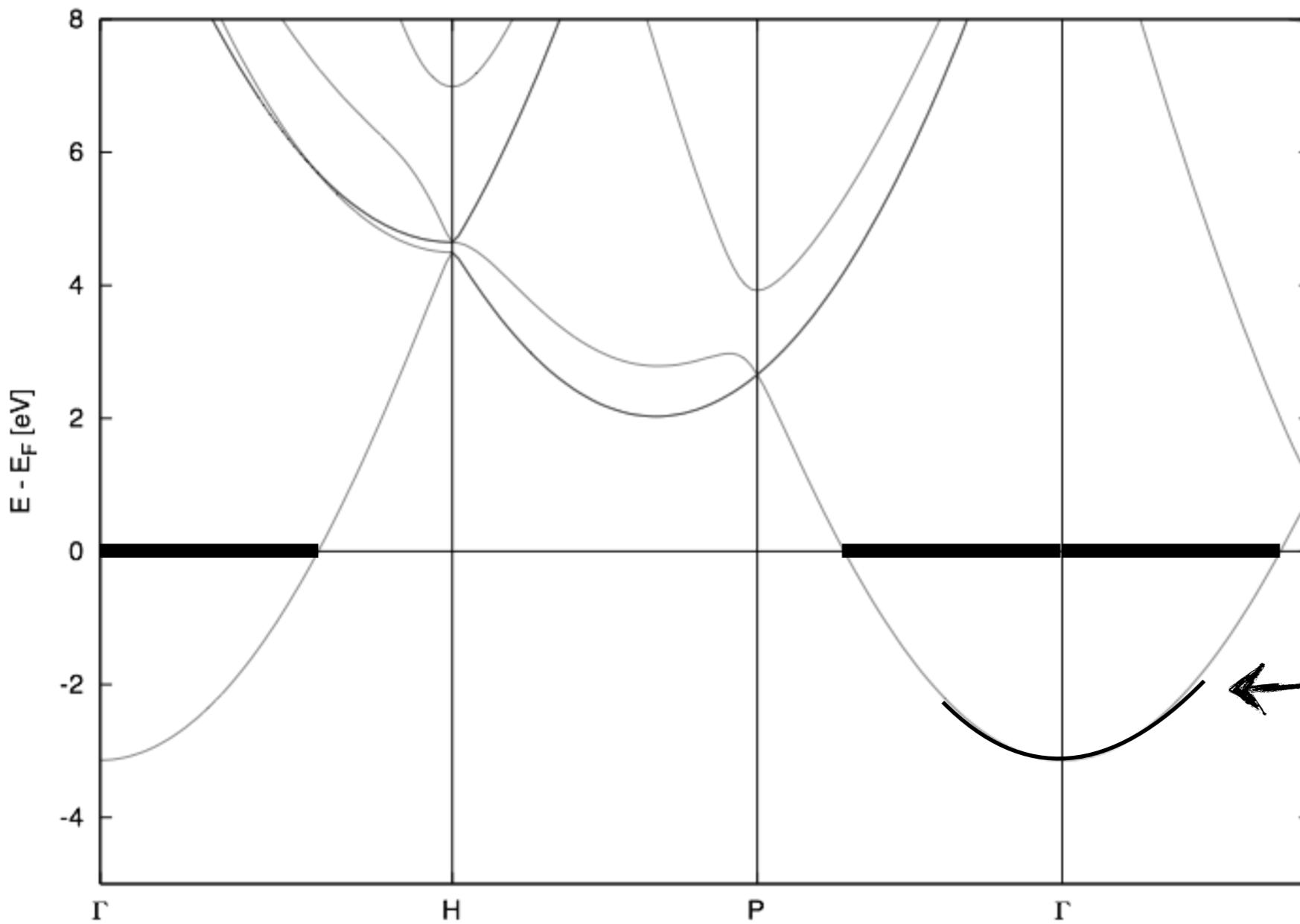
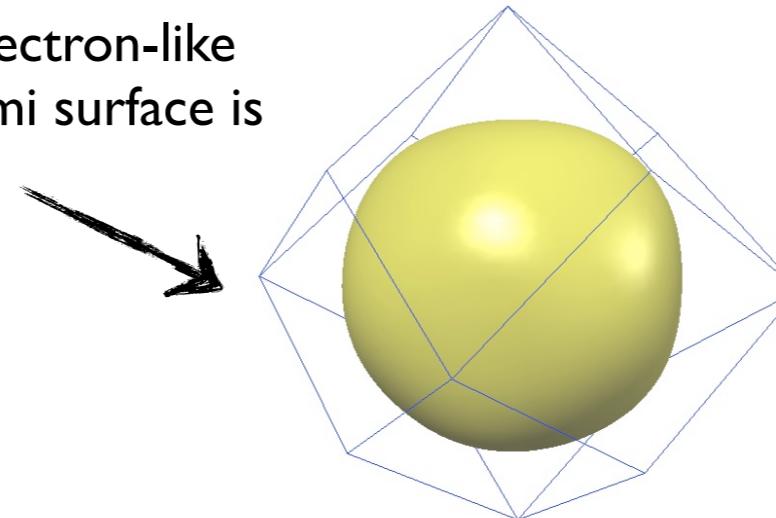
z <b>Symbol</b>	mass	man-made
Name		

57 La Lanthanum	58 Ce Cerium	59 Pr Praseodymium	60 Nd Neodymium	61 Pm Promethium	62 Sm Samarium	63 Eu Europium	64 Gd Gadolinium	65 Tb Terbium	66 Dy Dysprosium	67 Ho Holmium	68 Er Erbium	69 Tm Thulium	70 Yb Ytterbium	71 Lu Lutetium
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89 Ac Actinium	90 Th Thorium	91 Pa Protactinium	92 U Uranium	93 Np Neptunium	94 Pu Plutonium	95 Am Americium	96 Cm Curium	97 Bk Berkelium	98 Cf Californium	99 Es Einsteinium	100 Fm Fermium	101 Md Mendelevium	102 No Nobelium	103 Lr Lawrencium
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**Na**

Note how free-electron-like  
(spherical) the Fermi surface is



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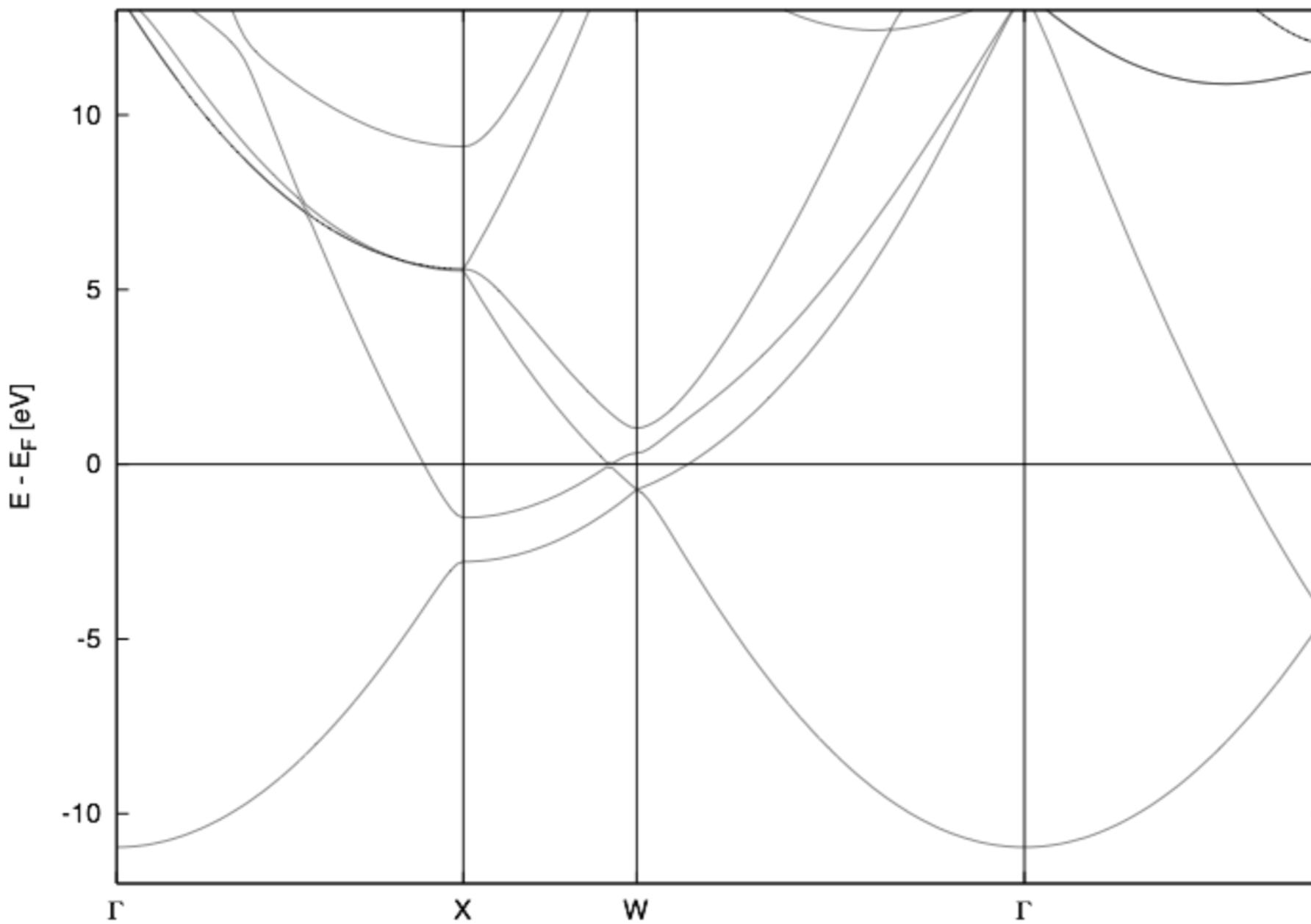
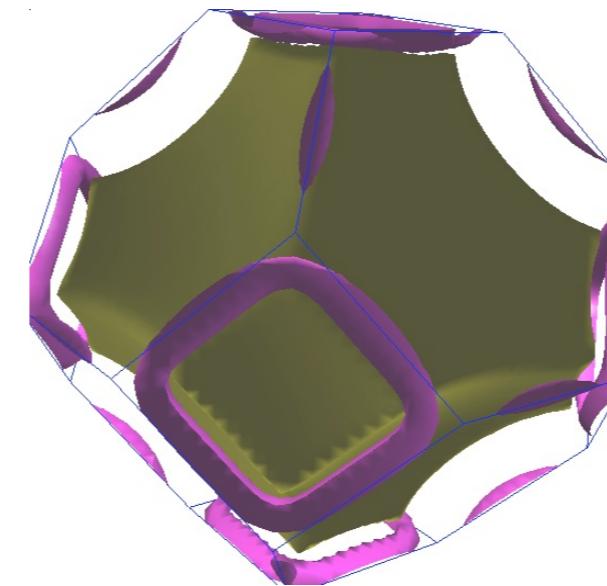
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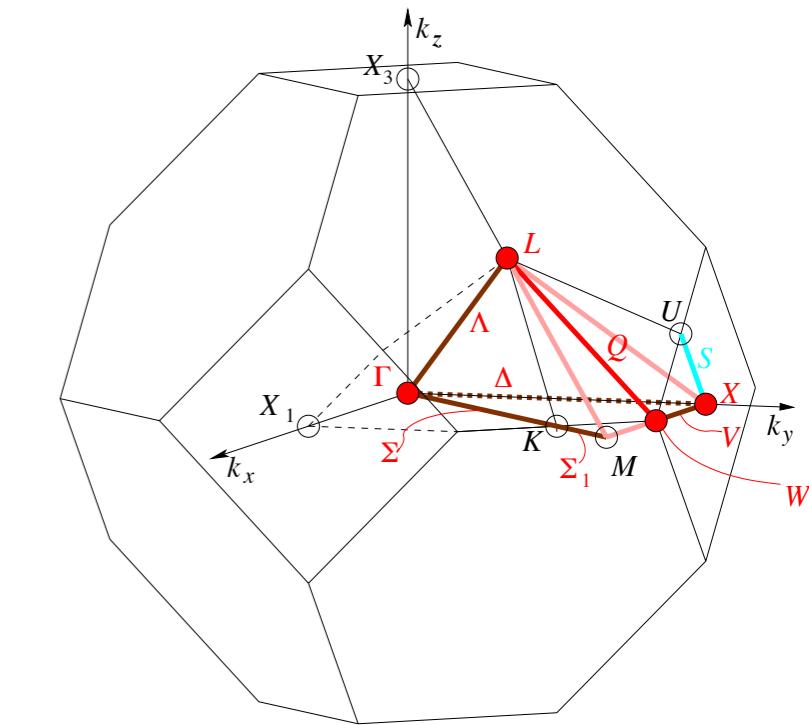
Al

Two bands cross the Fermi energy, so we have two sheets of Fermi surface



©bilbao crystallographic server  
<http://www.cryst.ehu.es>

Fermi level is now in the  $p$ -bands



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6	55 Cs Caesium 132.91	56 Ba Barium 137.33	57-71 La-Lu Lanthanide 178.49	72 Hf Hafnium 180.95	73 Ta Tantalum 183.84	74 W Tungsten 186.21	75 Re Rhenium 190.23	76 Os Osmium 192.22	77 Ir Iridium 195.08	78 Pt Platinum 196.97	79 Au Gold 200.59	80 Hg Mercury 204.38	81 Tl Thallium 207.2	82 Pb Lead 208.98	83 Bi Bismuth 209	84 Po Polonium 210	85 At Astatine 210	86 Rn Radon 222				
7	87 Fr Francium 223	88 Ra Radium 226	89-103 Ac-Lr Actinide 261	104 Rf Rutherfordium 261	105 Db Dubnium 262	106 Sg Seaborgium 266	107 Bk Bohrium 264	108 Hs Hassium 277	109 Mt Meitnerium 268	110 Ds Darmstadtium 281	111 Rg Roentgenium 280	112 Uub Ununbium 285	113 Uut Ununtrium 284	114 Uuq Ununquadium 289	115 Uup Ununpentium 293	116 Uuh Ununhexium 293	117 Uus Ununseptium 292	118 Uuo Ununoctium 294				

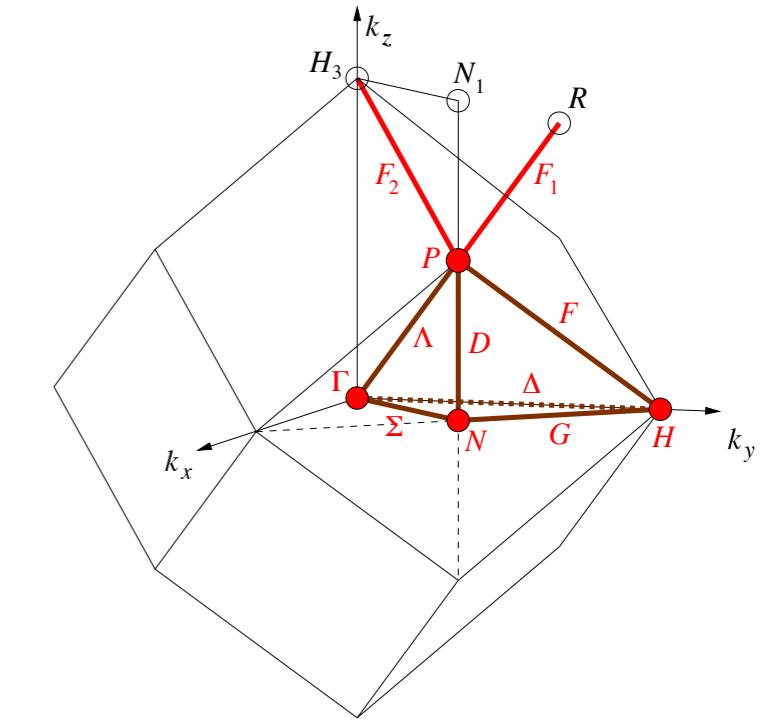
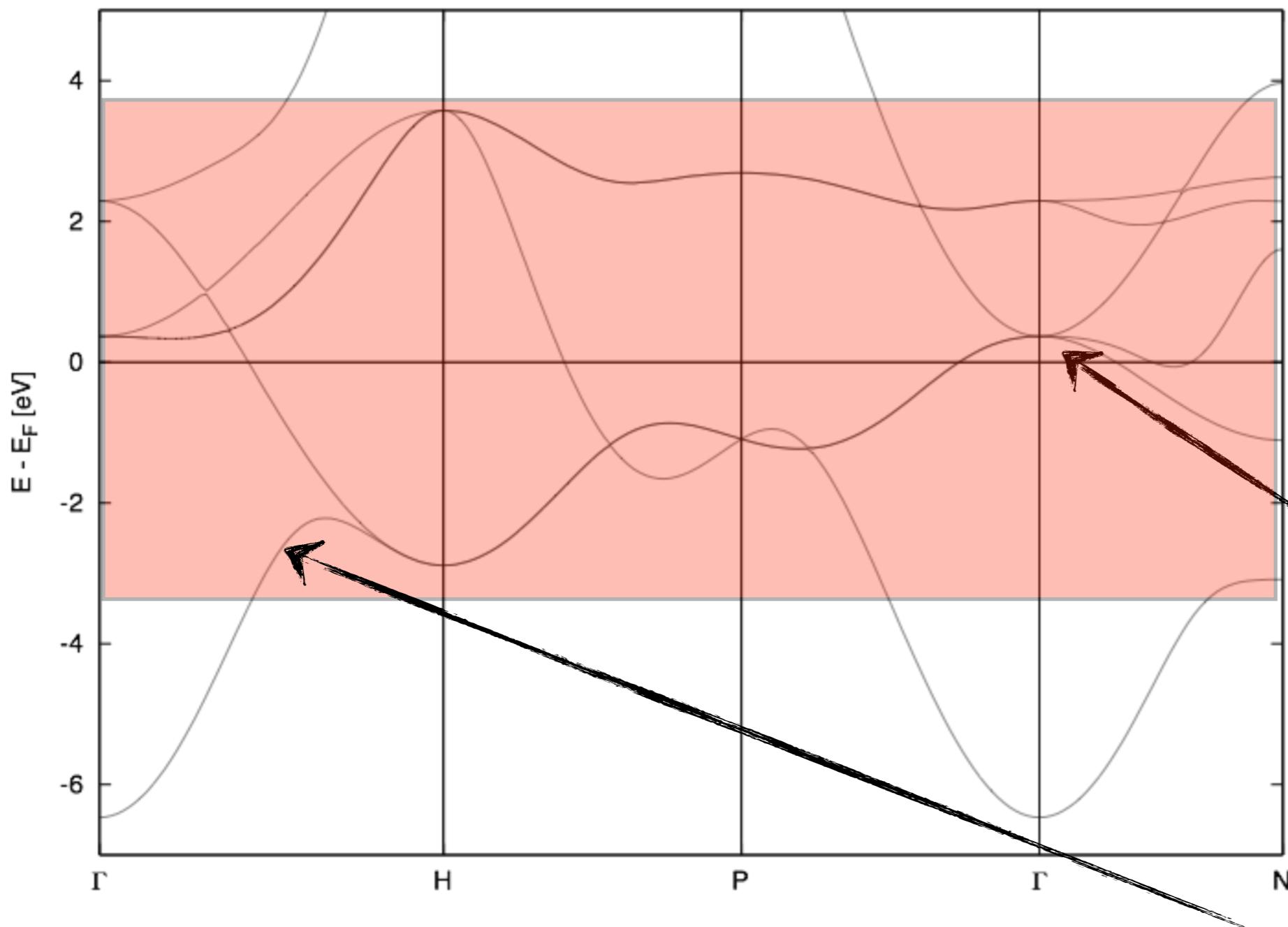
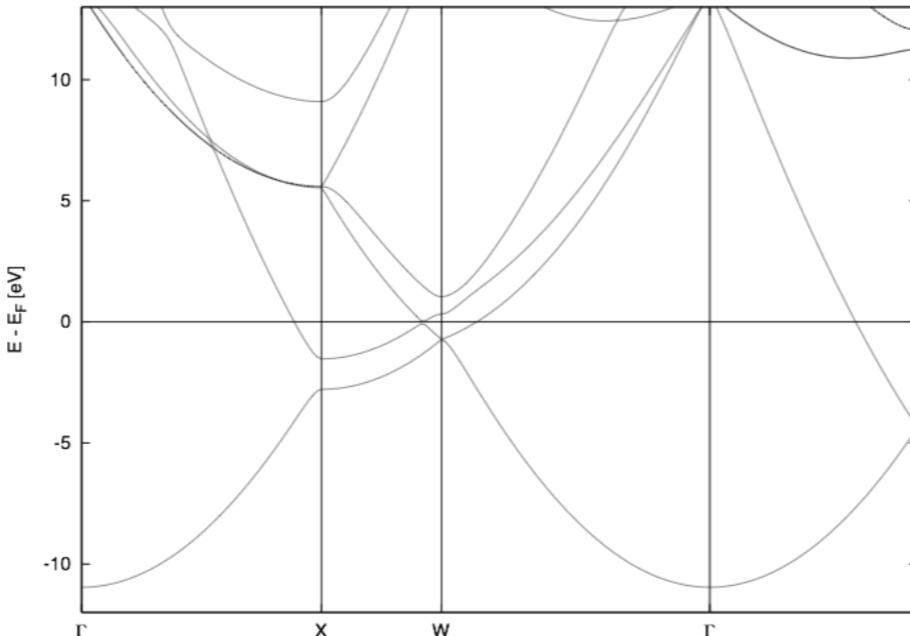
- █ Alkali Metal
- █ Alkaline Earth Metal
- █ Metal
- █ Metalloid
- █ Non-metal
- █ Halogen
- █ Noble Gas
- █ Lanthanide/Actinide

z <b>Symbol</b>	mass	man-made
Name		

57 La Lanthanum	58 Ce Cerium	59 Pr Praseodymium	60 Nd Neodymium	61 Pm Promethium	62 Sm Samarium	63 Eu Europium	64 Gd Gadolinium	65 Tb Terbium	66 Dy Dysprosium	67 Ho Holmium	68 Er Erbium	69 Tm Thulium	70 Yb Ytterbium	71 Lu Lutetium
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89 Ac Actinium	90 Th Thorium	91 Pa Protactinium	92 U Uranium	93 Np Neptunium	94 Pu Plutonium	95 Am Americium	96 Cm Curium	97 Bk Berkelium	98 Cf Californium	99 Es Einsteinium	100 Fm Fermium	101 Md Mendelevium	102 No Nobelium	103 Lr Lawrencium
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V



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Fermi level is now in the 3d bands

Look how flat the d-bands are - this is because the 3d electrons are very much more tightly bound than the s electrons.

Look how the 4s band hybridises with the 3d bands

## Periodic Table of Chemical Elements

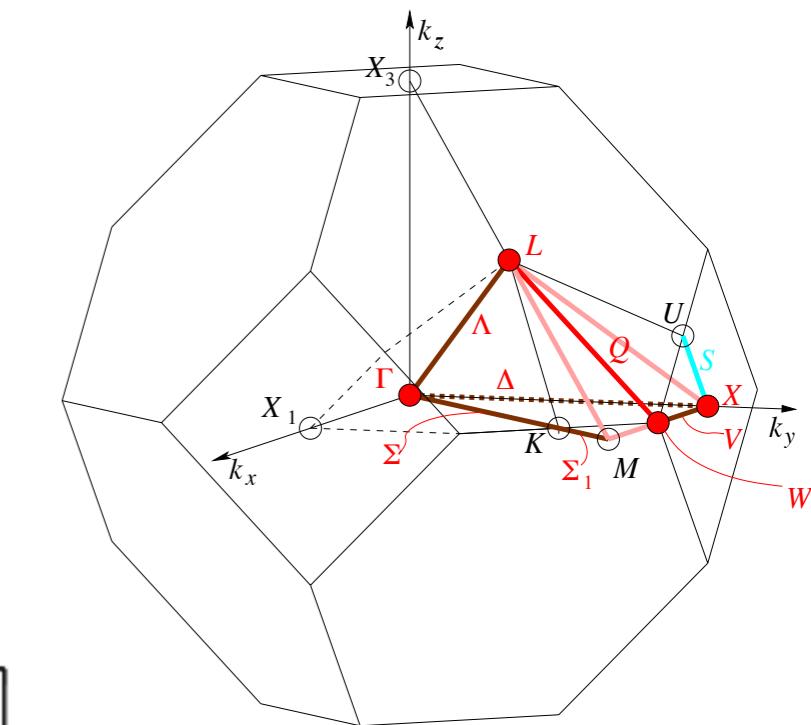
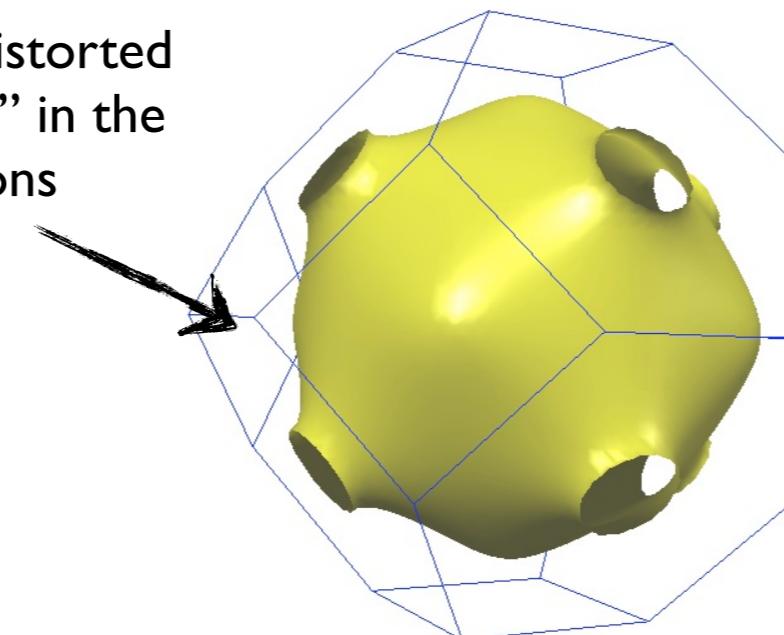
1 IA		Periodic Table of Chemical Elements																		18 VIIIA															
1 H Hydrogen	2 He Helium	2 IIA		3 IIIA		4 IVB		5 VB		6 VIB		7 VIIIB		8 VIIIIB		9 VIIIB		10 VIIIB		11 IB		12 IIB		13 IIIA		14 IVA		15 VA		16 VIA		17 VIIA			
3 Li Lithium	4 Be Beryllium	5 B Boron	6 C Carbon	7 N Nitrogen	8 O Oxygen	9 F Flourine	10 Ne Neon	11 Na Sodium	12 Mg Magnesium	13 Al Aluminium	14 Si Silicon	15 P Phosphorus	16 S Sulphur	17 Cl Chlorine	18 Ar Argon	19 K Potassium	20 Ca Calcium	21 Sc Scandium	22 Ti Titanium	23 V Vanadium	24 Cr Chromium	25 Mn Manganese	26 Fe Iron	27 Co Cobalt	28 Ni Nickel	29 Cu Copper	30 Zn Zinc	31 Ga Gallium	32 Ge Germanium	33 As Arsenic	34 Se Selenium	35 Br Bromine	36 Kr Krypton		
37 Rb Rubidium	38 Sr Strontium	39 Y Yttrium	40 Zr Zirconium	41 Nb Niobium	42 Mo Molybdenum	43 Tc Technetium	44 Ru Ruthenium	45 Rh Rhodium	46 Pd Palladium	47 Ag Silver	48 Cd Cadmium	49 In Indium	50 Sn Tin	51 Sb Antimony	52 Te Tellurium	53 I Iodine	54 Xe Xenon	55 Cs Caesium	56 Ba Barium	57-71 La-Lu Lanthanide	72 Hf Hafnium	73 Ta Tantalum	74 W Tungsten	75 Re Rhenium	76 Os Osmium	77 Ir Iridium	78 Pt Platinum	79 Au Gold	80 Hg Mercury	81 Tl Thallium	82 Pb Lead	83 Bi Bismuth	84 Po Polonium	85 At Astatine	86 Rn Radon
87 Fr Francium	88 Ra Radium	89-103 Ac-Lr Actinide	104 Rf Rutherfordium	105 Db Dubnium	106 Sg Seaborgium	107 Bh Bohrium	108 Hs Hassium	109 Mt Meitnerium	110 Ds Darmstadtium	111 Rg Roentgenium	112 Uub Ununbiunium	113 Uut Ununtrium	114 Uuq Ununquadium	115 Uup Ununpentium	116 Uuh Ununhexium	117 Uus Ununseptium	118 Uuo Ununoctium	119 Unk Unknown	120 Unq Ununquadium	121 Unp Ununpentium	122 Unh Ununhexium	123 Uns Ununseptium	124 Uno Ununoctium												
1 H Hydrogen	2 He Helium	2 IIA		3 IIIA		4 IVB		5 VB		6 VIB		7 VIIIB		8 VIIIIB		9 VIIIB		10 VIIIB		11 IB		12 IIB		13 IIIA		14 IVA		15 VA		16 VIA		17 VIIA			
3 Li Lithium	4 Be Beryllium	5 B Boron	6 C Carbon	7 N Nitrogen	8 O Oxygen	9 F Flourine	10 Ne Neon	11 Na Sodium	12 Mg Magnesium	13 Al Aluminium	14 Si Silicon	15 P Phosphorus	16 S Sulphur	17 Cl Chlorine	18 Ar Argon	19 K Potassium	20 Ca Calcium	21 Sc Scandium	22 Ti Titanium	23 V Vanadium	24 Cr Chromium	25 Mn Manganese	26 Fe Iron	27 Co Cobalt	28 Ni Nickel	29 Cu Copper	30 Zn Zinc	31 Ga Gallium	32 Ge Germanium	33 As Arsenic	34 Se Selenium	35 Br Bromine	36 Kr Krypton		
37 Rb Rubidium	38 Sr Strontium	39 Y Yttrium	40 Zr Zirconium	41 Nb Niobium	42 Mo Molybdenum	43 Tc Technetium	44 Ru Ruthenium	45 Rh Rhodium	46 Pd Palladium	47 Ag Silver	48 Cd Cadmium	49 In Indium	50 Sn Tin	51 Sb Antimony	52 Te Tellurium	53 I Iodine	54 Xe Xenon	55 Cs Caesium	56 Ba Barium	57-71 La-Lu Lanthanide	72 Hf Hafnium	73 Ta Tantalum	74 W Tungsten	75 Re Rhenium	76 Os Osmium	77 Ir Iridium	78 Pt Platinum	79 Au Gold	80 Hg Mercury	81 Tl Thallium	82 Pb Lead	83 Bi Bismuth	84 Po Polonium	85 At Astatine	86 Rn Radon
87 Fr Francium	88 Ra Radium	89-103 Ac-Lr Actinide	104 Rf Rutherfordium	105 Db Dubnium	106 Sg Seaborgium	107 Bh Bohrium	108 Hs Hassium	109 Mt Meitnerium	110 Ds Darmstadtium	111 Rg Roentgenium	112 Uub Ununbiunium	113 Uut Ununtrium	114 Uuq Ununquadium	115 Uup Ununpentium	116 Uuh Ununhexium	117 Uus Ununseptium	118 Uuo Ununoctium	119 Unk Unknown	120 Unq Ununquadium	121 Unp Ununpentium	122 Unh Ununhexium	123 Uns Ununseptium	124 Uno Ununoctium	125 Unp Ununpentium	126 Unh Ununhexium	127 Uns Ununseptium	128 Uno Ununoctium	129 Unp Ununpentium	130 Unh Ununhexium	131 Uns Ununseptium	132 Uno Ununoctium				

- [Blue square] Alkali Metal
- [Purple square] Alkaline Earth Metal
- [Light Blue square] Metal
- [Orange square] Metalloid
- [Light Green square] Non-metal
- [Green square] Halogen
- [Dark Green square] Noble Gas
- [Pink square] Lanthanide/Actinide

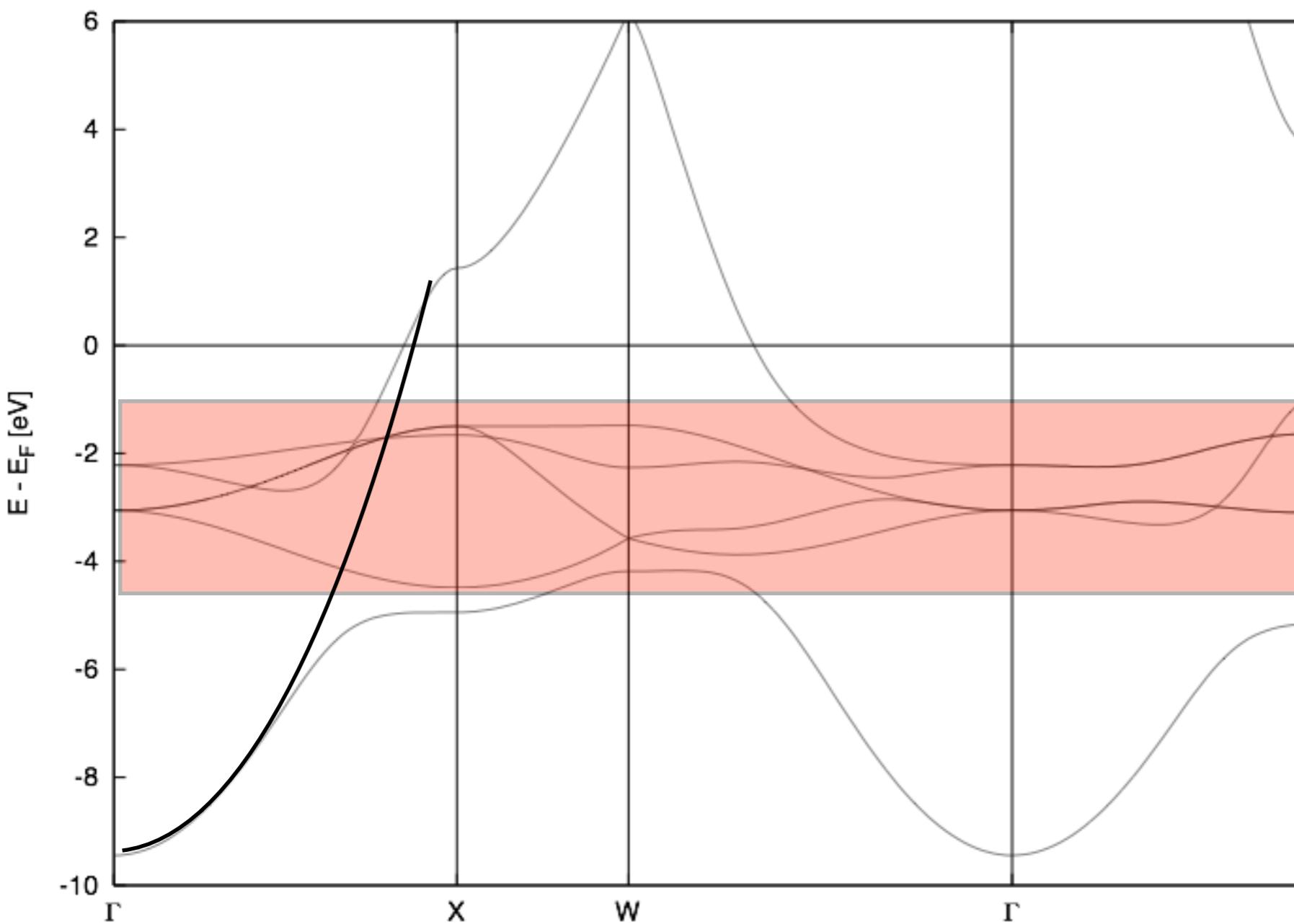
Z	mass
<b>Symbol</b>	man-made
Name	

# Cu

Fermi surface is a distorted sphere, with “necks” in the  $\langle 111 \rangle$  directions



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Fermi level is now above the 3d bands

# Chapter 3 - Probing the Fermi Surfaces of Real Metals

*“It was a revelation to me that quantum mechanics could penetrate into the business of the metals industry”*

NF Mott, reminiscing about Bristol in the 1930s (Mott 1986 *A Life in Science*)

### 3.1 Quantisation of Orbits in Magnetic Fields

When we apply a magnetic field, there is going to be an additional force (Lorentz) on the charged particles (electrons, but we'll keep it general for now, and just say they have charge  $q$ ) which will cause them to execute orbits in both real space and in reciprocal space. However, these orbits will be restricted, that is to say quantised :

$$\oint d\mathbf{r} \cdot \mathbf{p} = \left(n + \frac{1}{2}\right) h \quad \xleftarrow{\text{Bohr-Sommerfeld quantisation condition}}$$

where  $n=0,1,2\dots$  and  $\mathbf{p}$  is the so-called canonical momentum,

$$\mathbf{p} = \hbar\mathbf{k} + q\mathbf{A} \quad \xleftarrow{\text{you're just going to have to accept this as true}}$$

where  $\mathbf{A}$  is the magnetic vector potential (recall  $\mathbf{B} = \nabla \times \mathbf{A}$ ).

Substituting for  $\mathbf{p}$  in the Bohr-Sommerfeld condition, we get :

$$\oint d\mathbf{r} \cdot \mathbf{p} = \hbar \oint d\mathbf{r} \cdot \mathbf{k} + q \oint d\mathbf{r} \cdot \mathbf{A}$$

Let's look at the second term first. We note that

$$\begin{aligned}\oint d\mathbf{r} \cdot \mathbf{A} &= \int_S d\mathbf{S} \cdot \nabla \times \mathbf{A} && \xleftarrow{\text{by Stokes' Theorem}} \\ &= \int_S d\mathbf{S} \cdot \mathbf{B} \\ &= \Phi && \xleftarrow{\text{i.e. the magnetic flux}}\end{aligned}$$

And now we can tackle the first term. First, we can write down the Lorentz force on a particle in a constant magnetic field as :

$$\frac{d(\hbar\mathbf{k})}{dt} = q \frac{d\mathbf{r}}{dt} \times \mathbf{B}$$

force is rate of change of momentum

there is no term involving the vector potential on the left hand side because it is constant, so its time derivative is zero

We can therefore write :

$$\mathbf{k} = \frac{q}{\hbar} \mathbf{r} \times \mathbf{B}$$

there will be an integration constant here, but it is irrelevant to the result, so we ignore it

Therefore the first term becomes :

$$\begin{aligned}\hbar \oint d\mathbf{r} \cdot \mathbf{k} &= q \oint d\mathbf{r} \cdot (\mathbf{r} \times \mathbf{B}) \\ &= q \mathbf{B} \cdot \oint d\mathbf{r} \times \mathbf{r} \\ &= -q \mathbf{B} \cdot \oint \mathbf{r} \times d\mathbf{r} \\ &= -q B (2A_r) \\ &= -2q \Phi\end{aligned}$$

i.e.  $A_r$  is the area enclosed by the orbit in real space :

$$\text{Area} = \frac{1}{2} \oint \mathbf{r} \times d\mathbf{r}$$

the  $r$  here is to remind us that this is an area in *real space*

Putting this back together with the second term, we get ...

$$\oint d\mathbf{r} \cdot \mathbf{p} = -2q\Phi + q\Phi = -q\Phi$$

$$= \left(n + \frac{1}{2}\right) h$$

And putting  $q=-e$  (for the electron), we have :

$$\Phi_n = \left(n + \frac{1}{2}\right) \frac{h}{e}$$

which means that the quantisation condition on the allowed orbits in a magnetic field is actually a quantisation condition on the enclosed magnetic flux. Since  $\Phi_n = BA_n$ , the quantisation of the allowed orbits in *real space* is given by :

$$A_n = \left(n + \frac{1}{2}\right) \frac{h}{eB}$$

I don't want to have too many subscripts, so I'm no longer reminding us that this is an area in real space.  $A_n$  is area of  $n^{\text{th}}$  allowed level

Ultimately, we would like to be working in reciprocal space, but fortunately there is a simple relationship between the area in  $k$ -space (reciprocal space) and the area in real space. Earlier we had

$$\frac{d(\hbar\mathbf{k})}{dt} = q \frac{d\mathbf{r}}{dt} \times \mathbf{B}$$

and so we can argue that a line element  $\Delta r$  traced out in the plane normal the the  $\mathbf{B}$  field is related to a line element in reciprocal space  $\Delta k$ , by

$$\Delta k = \left( \frac{qB}{\hbar} \right) \Delta r$$

Therefore the areas in real space and reciprocal space are connected by a factor

$$\frac{\Delta k^2}{\Delta r^2} = \left( \frac{qB}{\hbar} \right)^2$$

Hence the quantised areas in reciprocal space (let's call them  $S_n$ ) are related to those in real space ( $A_n$ ) by :

$$A_n = \left( \frac{\hbar}{eB} \right)^2 S_n$$

where we are once again being specific about the charge being the electronic charge. It directly follows that

$$\Phi_n = \left( \frac{\hbar}{e} \right)^2 \frac{1}{B} S_n = \left( n + \frac{1}{2} \right) \frac{h}{e}$$

or, in other words, the area of an orbit in reciprocal space must satisfy :

$$S_n = \left( n + \frac{1}{2} \right) \frac{2\pi e}{\hbar} B$$

# [ Some extra working to help understand the next slide

Let two successive levels ( $n$  and  $n+1$ ) have the same area  $S$ . Obviously the magnetic field will be different, and we can imagine changing the magnetic field until the next Landau level has the same area as the previous one did.

$$S = \left(n + \frac{1}{2}\right) \frac{2\pi e}{\hbar} B_n$$

$$S = \left(n + 1 + \frac{1}{2}\right) \frac{2\pi e}{\hbar} B_{n+1}$$

$$\frac{S}{B_n} = \left(n + \frac{1}{2}\right) \frac{2\pi e}{\hbar}$$

$$\frac{S}{B_{n+1}} = \left(n + 1 + \frac{1}{2}\right) \frac{2\pi e}{\hbar}$$

$$S \left( \frac{1}{B_{n+1}} - \frac{1}{B_n} \right) = \frac{2\pi e}{\hbar}$$

]

We can now see that for two successive orbits (let's call them  $n$  and  $n+1$ ) to have the same area in  $k$ -space,  $S$ , we must have :

$$S \left( \frac{1}{B_{n+1}} - \frac{1}{B_n} \right) = \frac{2\pi e}{\hbar}$$

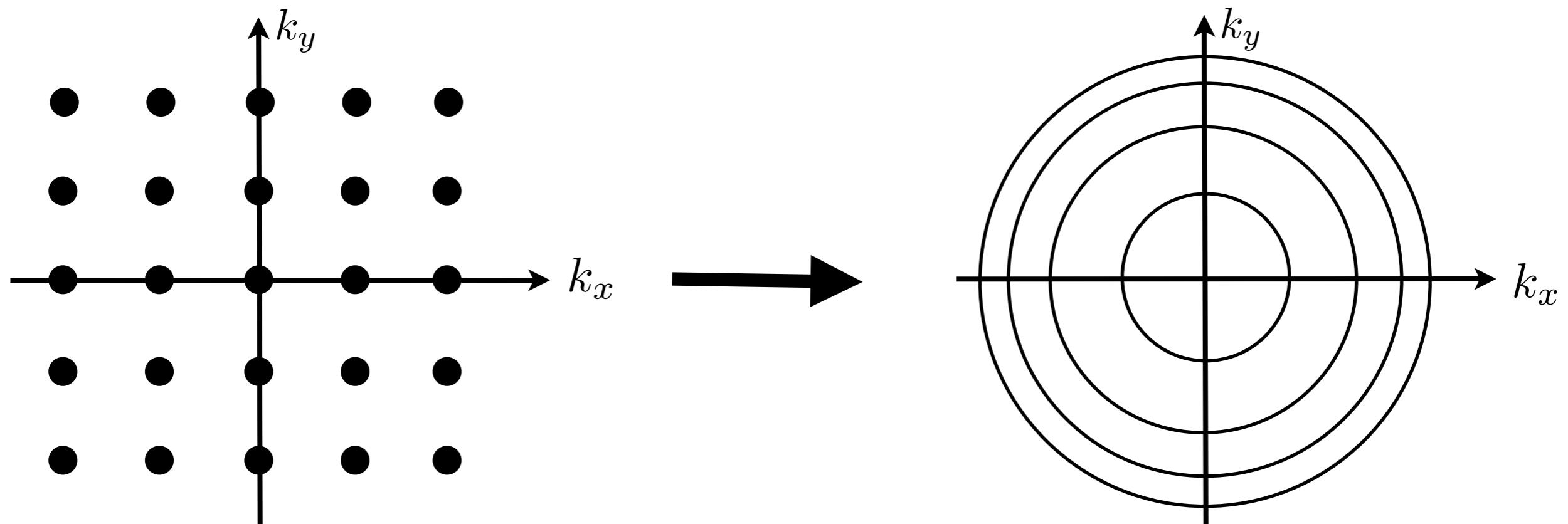
i.e. equal increments of  $1/B$  produce orbits of the same area. We can express this as :

$$\Delta \left( \frac{1}{B} \right) = \frac{2\pi e}{\hbar S}$$

Let's recap where we are. We've argued that in the presence of a magnetic field, electrons will execute orbits in the plane perpendicular to the magnetic field, and that those orbits are quantised. Finally, we've argued that if we change the field such that the successive quantum levels have the same area, then this is periodic in  $1/B$ . We now have to understand how this is useful for measuring the Fermi surface!

## 3.2 Landau Levels, Quantum Oscillations and the Fermi Surface

By turning on the magnetic field, the allowed values of  $\mathbf{k}$  in the  $k_x$ - $k_y$  plane (the plane perpendicular to the direction of  $\mathbf{B}$ ) have become confined to circles - these are called *Landau levels*.



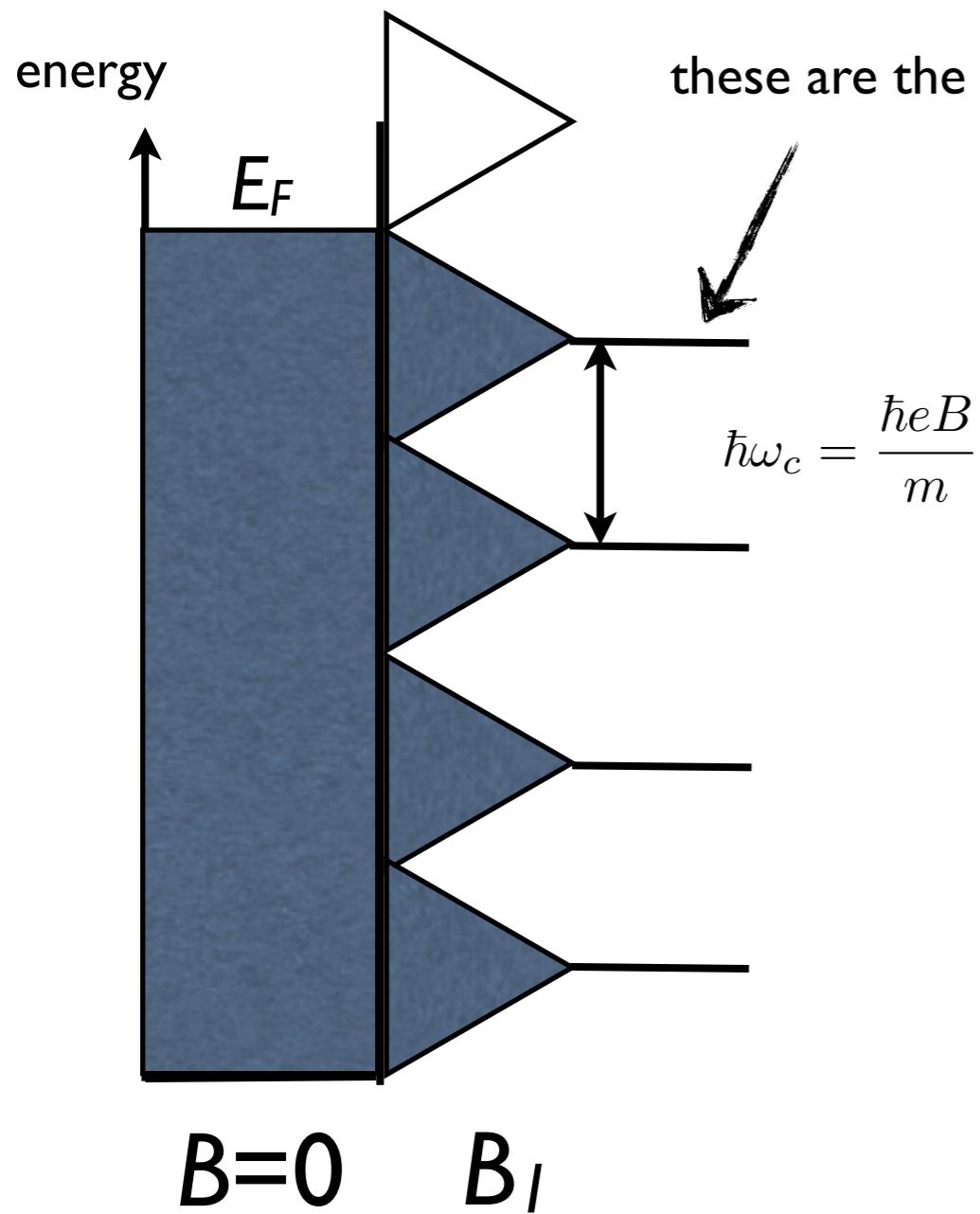
Allowed levels with no magnetic field

Allowed levels when magnetic field  
applied in direction  
perpendicular to this plane

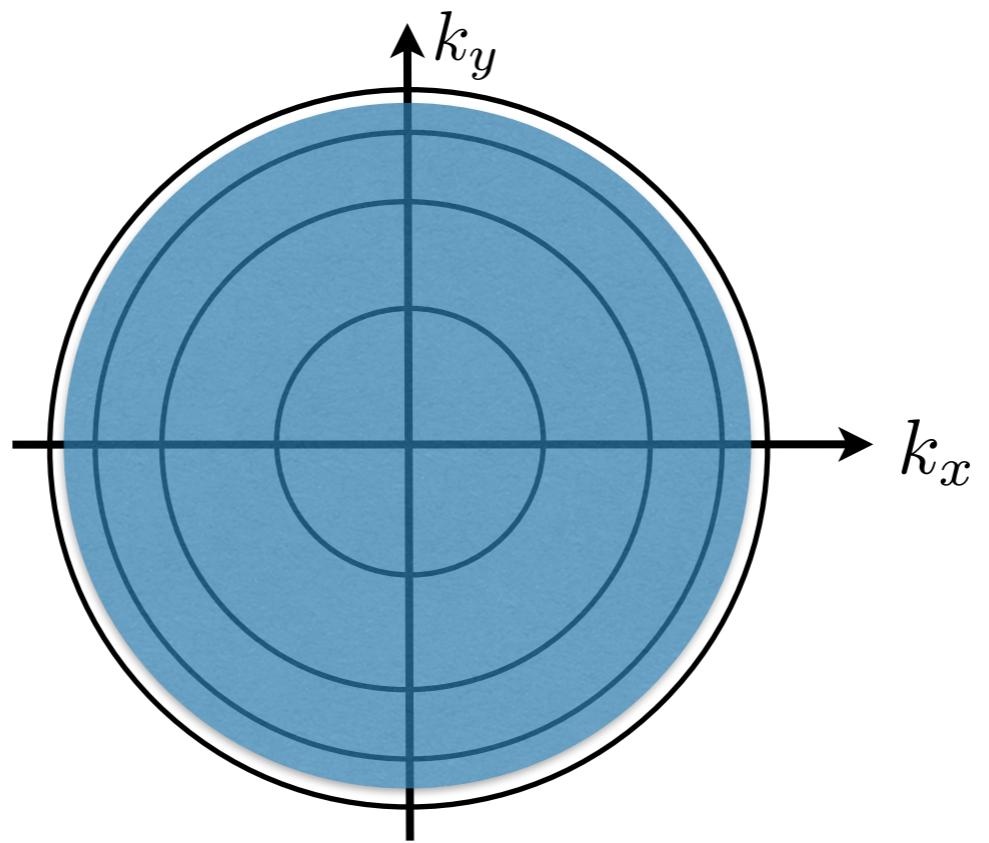
The separation of these levels in energy is just

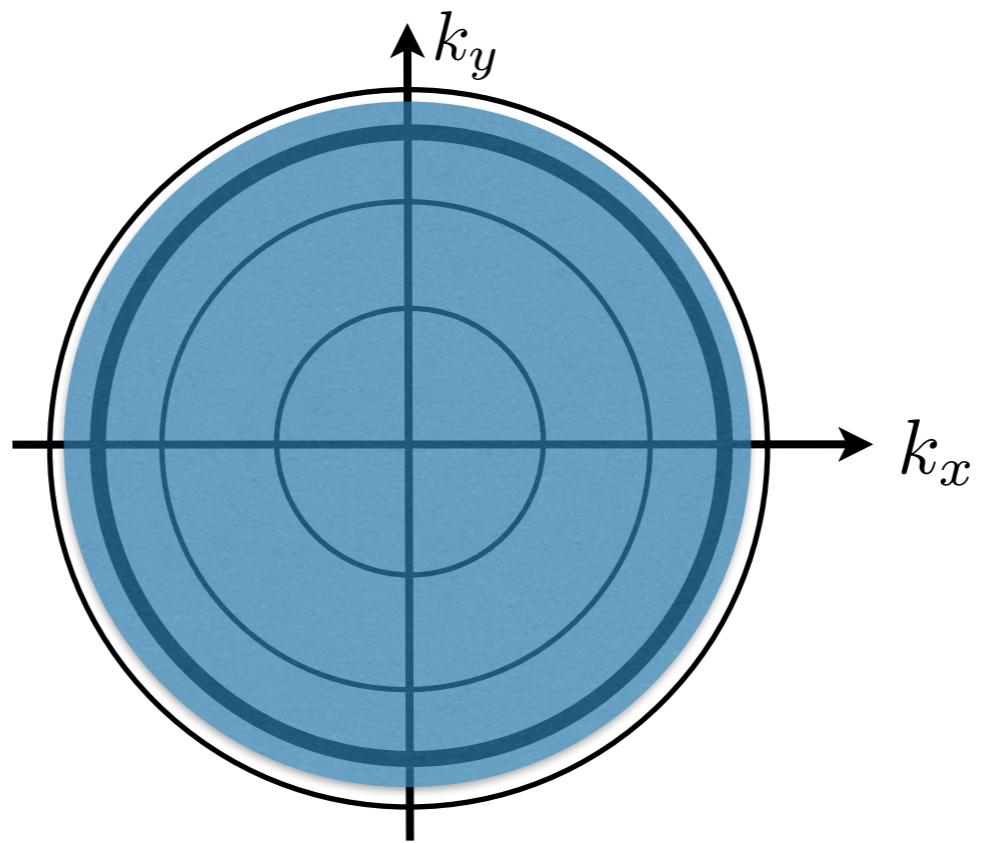
$$\Delta E = \hbar\omega_c = \frac{\hbar e B}{m}$$

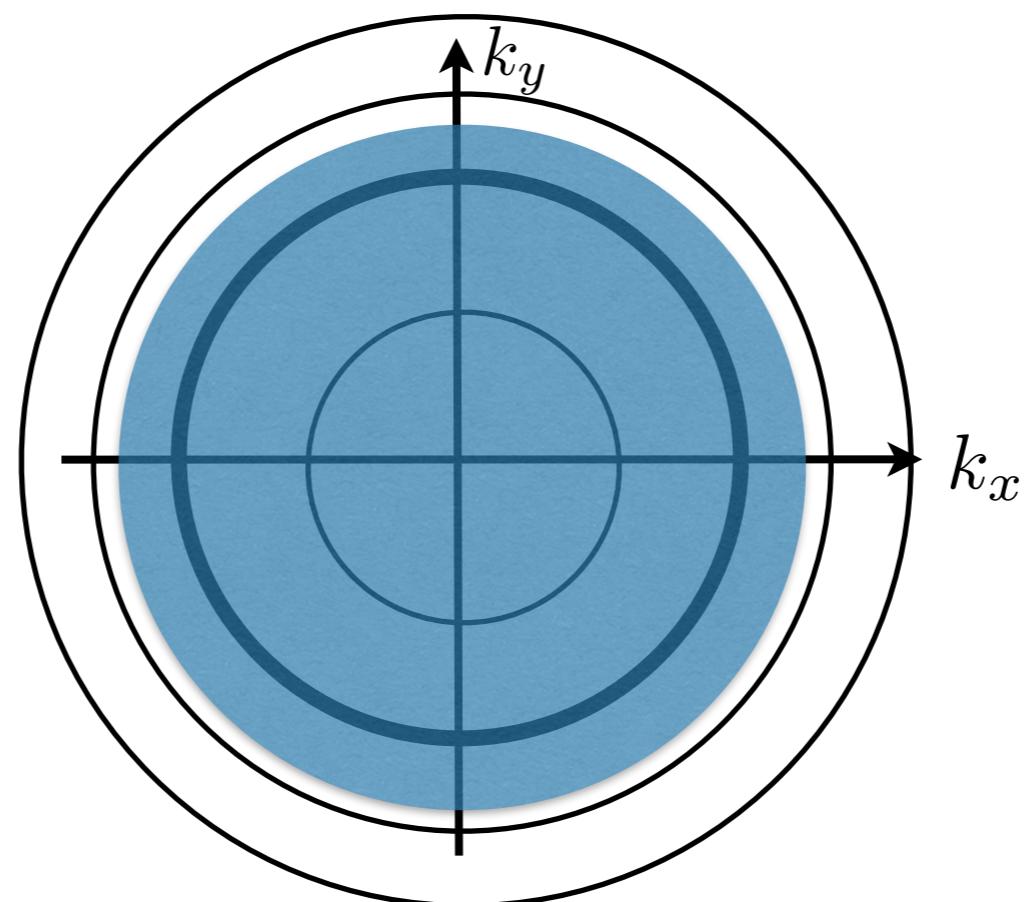
For our purposes here,  $m$  is the electron mass. It is really, however, the effective mass (which you will encounter in subsequent courses). That's why I've not put  $m_e$ .



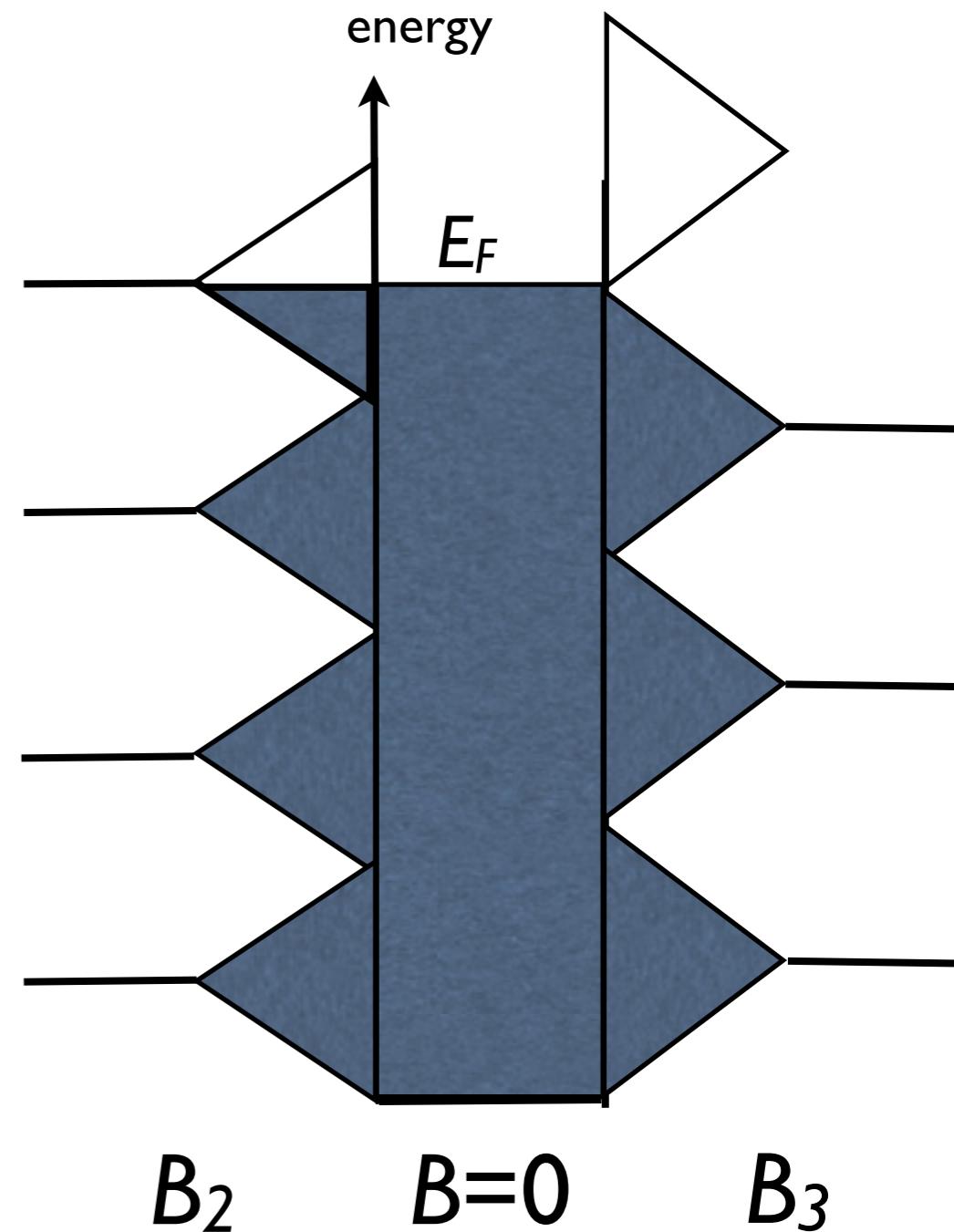
As the field is switched on (goes from zero to some value  $B_I$ ), and the allowed states coalesce onto the Landau levels, as is schematically illustrated in the diagram. For this particular value of  $B$ , as many electrons have gone up in energy as have gone down, and hence the total energy has not changed.







Let's increase the field to  $B_2$ . Now the total energy has increased, because electrons just below the original Fermi energy have had their energy raised. Let's increase the field a little more to  $B_3$ . Now one of the Landau levels has passed through the Fermi energy, but in terms of the total energy it is the same as it was for  $B_1$  (and in the absence of a field). So as we change  $B$ , the total energy changes. This means that any quantity which depends on the total energy will change, and therefore as  $B$  is swept up in value or down, there will be oscillations in these thermodynamic quantities.

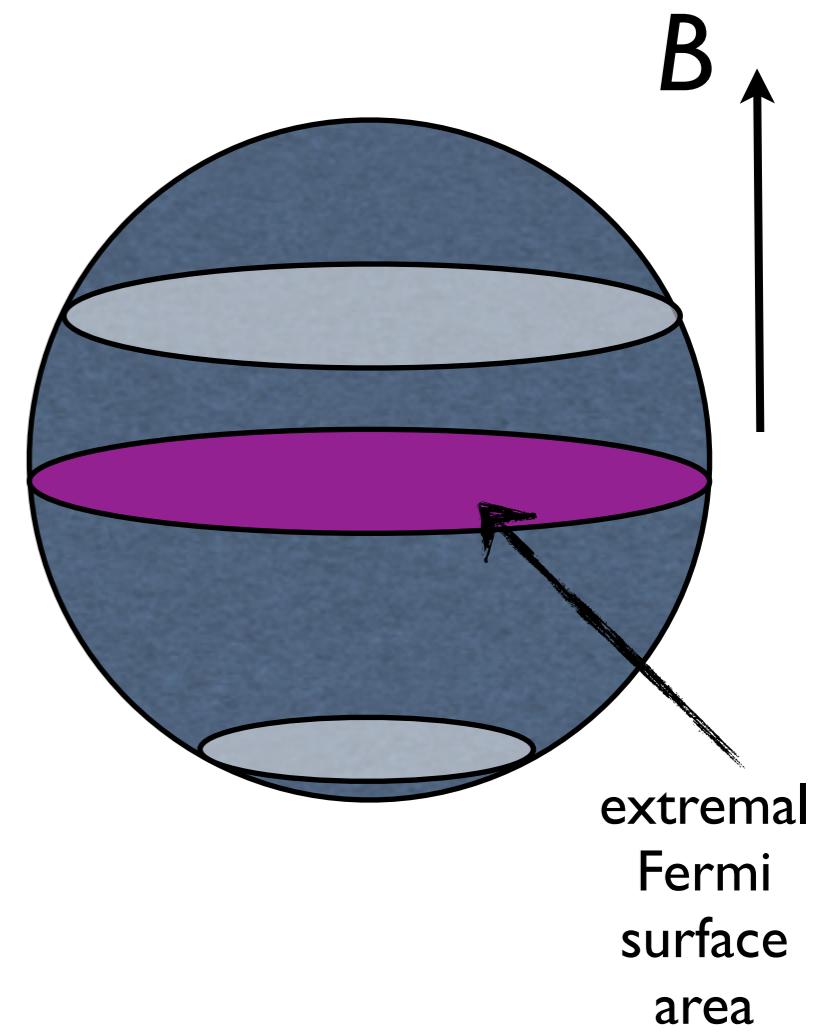


These are generically called *quantum oscillations* and they can be experimentally observed. They have different names depending on what you are looking at. If it is oscillations in the magnetisation of your sample then you call it the *de Haas-van Alphen effect*, if it is oscillations in the resistivity then they are called *Shubnikov-de Haas oscillations*, and if it is oscillations in the length of your sample (yes, the sample will change in length), then it is called *magnetostriiction*. If you can measure the period of these oscillations as a function of  $(I/B)$  (*n.b.* the oscillations are periodic in inverse field), then you can measure the Fermi surface area ( $S$ ) using the formula we derived earlier.

$$\Delta \left( \frac{1}{B} \right) = \frac{2\pi e}{\hbar S}$$

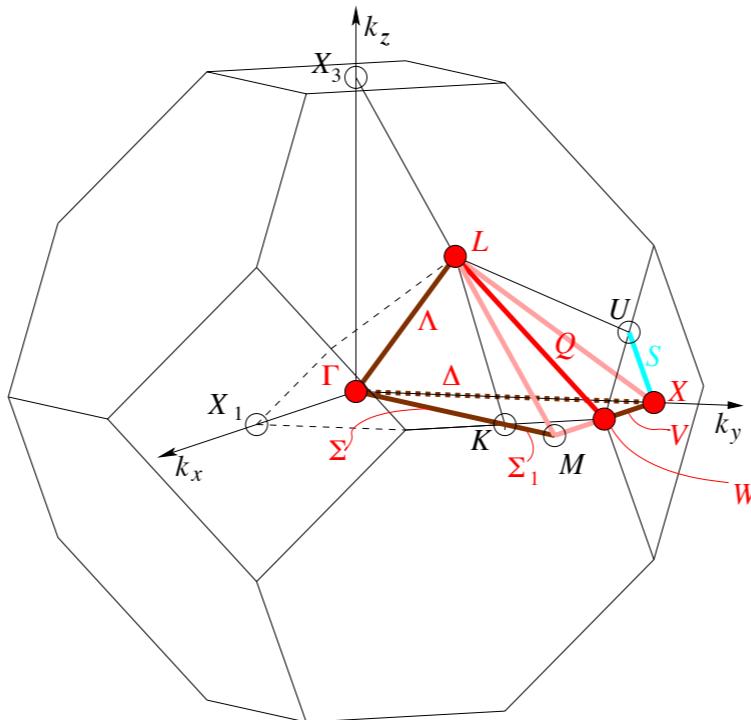
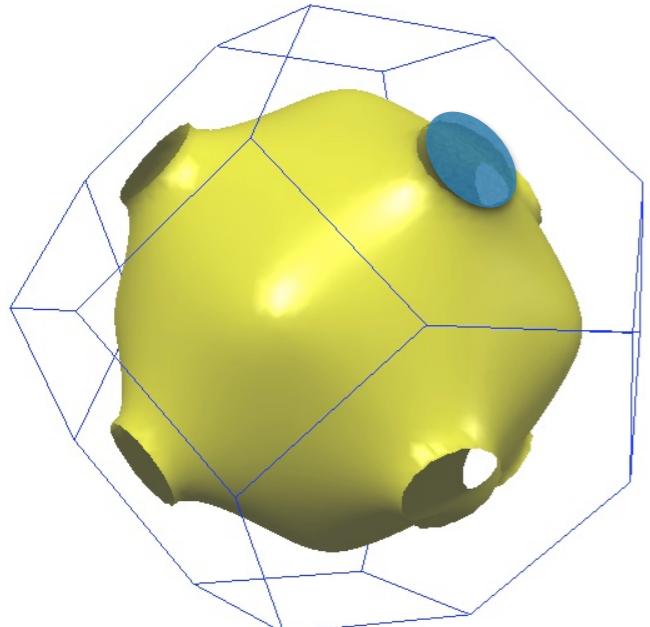
There are some subtleties. So far we've argued that from the quantisation of the semi-classical electron orbits, we can infer the “size” of the Fermi surface. That's ok in two dimensions, but Fermi surfaces are three dimensional. Imagine a simple spherical Fermi surface with the field applied in the direction shown.

There are lots of “areas” which are perpendicular to  $B$  - a few are shown - so which one do we measure? It turns out that the experimental signal is completely dominated by orbits which are *extremal* (that is maximal or minimal, the largest or smallest orbits in the planes perpendicular to the direction of the applied field). The reason for this is that there is phase cancellation such that contributions from different non-extremal cancel out.

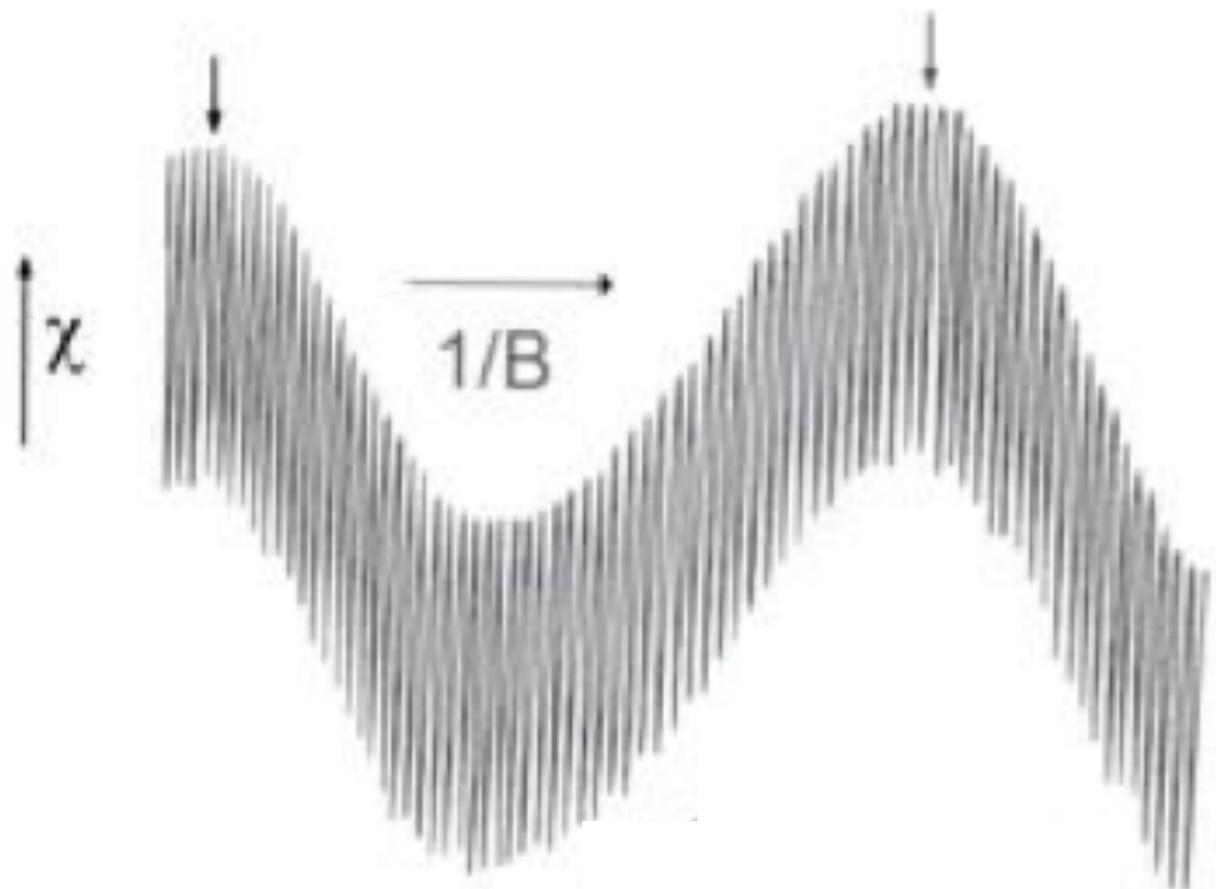


In summary, by applying a magnetic field in some particular direction with respect to the crystallographic axes (and thus with respect to the reciprocal lattice - let's say parallel to  $k_z$ ), the allowed states for electrons in k-space coalesce onto cylinders (often called *Landau tubes* - in 2D we had circles, but there is no further restriction in the  $k_z$  direction so our circles in 2D become cylinders in 3D). As we change  $B$ , these Landau levels pass through the Fermi surface and as they do the total energy of the system will change. Thus any quantity which depends on the total energy will change, and in fact there will be oscillations which are periodic in inverse magnetic field. Further, the oscillation period can be used to calculate the *extremal* Fermi surface areas perpendicular to  $k_z$ . If there is more than one extremal area, we'll get a superposition of frequencies, and we can identify the different ones by taking a Fourier Transform. Finally, by rotating the crystal we can look at how these extremal areas change, and hence we can map out the Fermi surface.

But there are some restrictions! First, we need low temperature. This is because at higher temperatures (i) the Fermi function will smear out the Fermi surface and thus smear out the oscillations, (ii) there will be increased disorder (more lattice vibrations i.e. phonons) which will scatter electrons. If electrons are scattered before they can complete orbits, then the original quantisation condition is irrelevant, so no oscillations are seen. Finally, and along the same lines, if there is disorder coming from substitutional impurities (e.g. in an alloy) then again the electronic mean-free-path will be shortened, making it difficult for the electrons to complete orbits without being scattered. In general then, one needs high-quality samples, very low temperatures (mK if possible) and high magnetic fields (tens of tesla). When it does work, it can provide extremely precise information about the Fermi surface topology (shape).

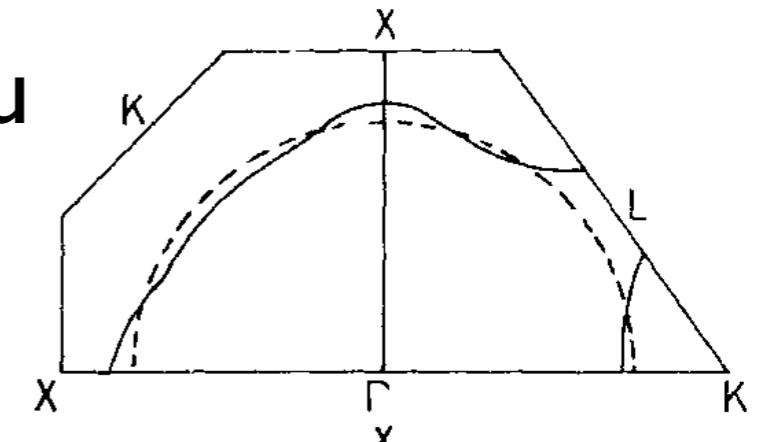


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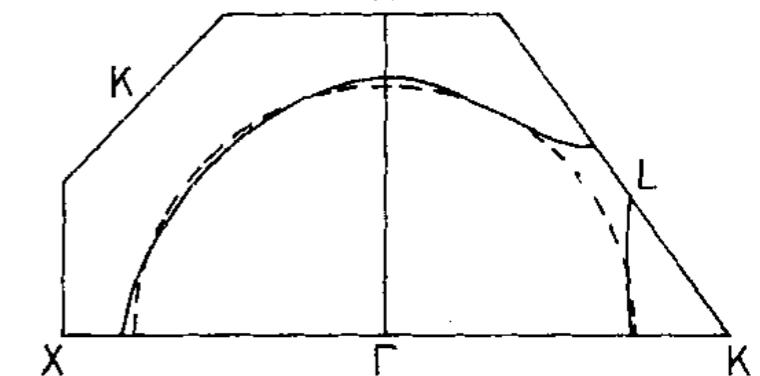


de Haas-van Alphen oscillations in Ag with field along  
 $\langle 111 \rangle$  directions

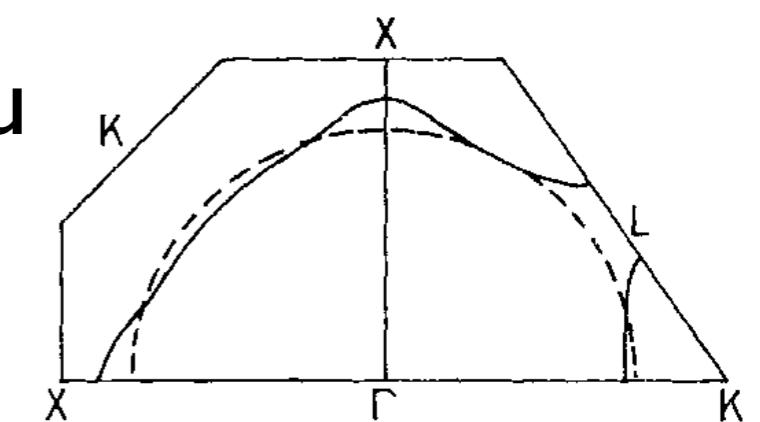
**Cu**



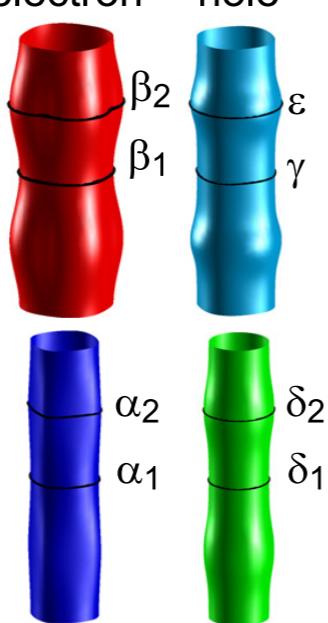
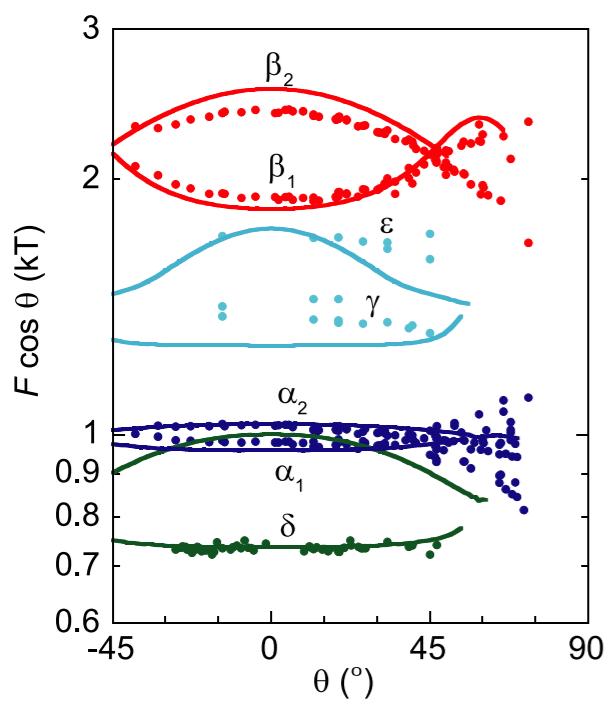
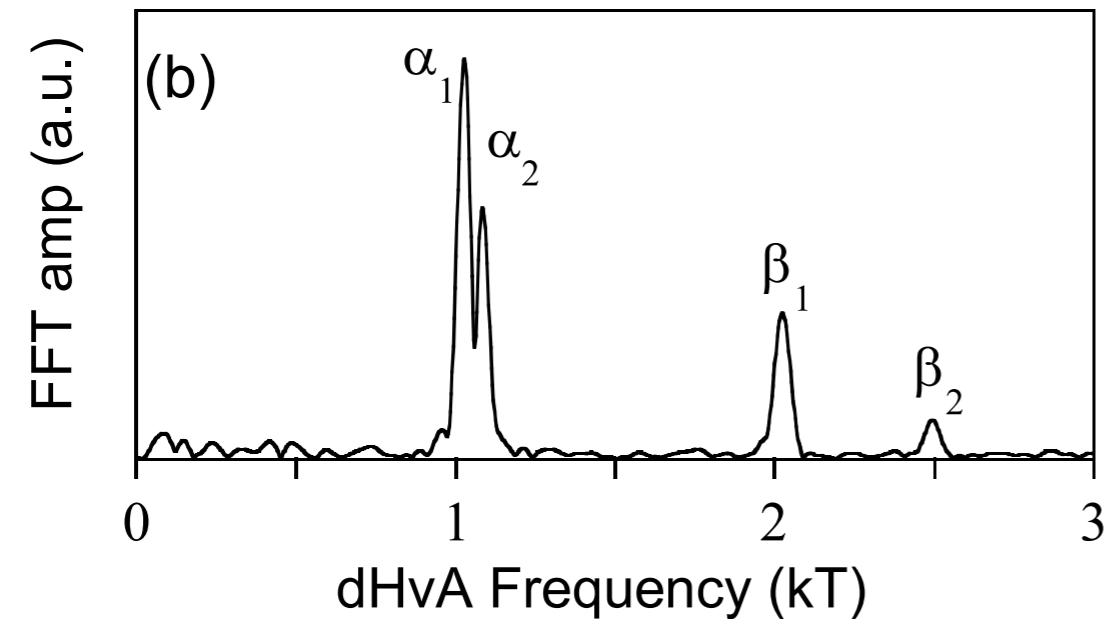
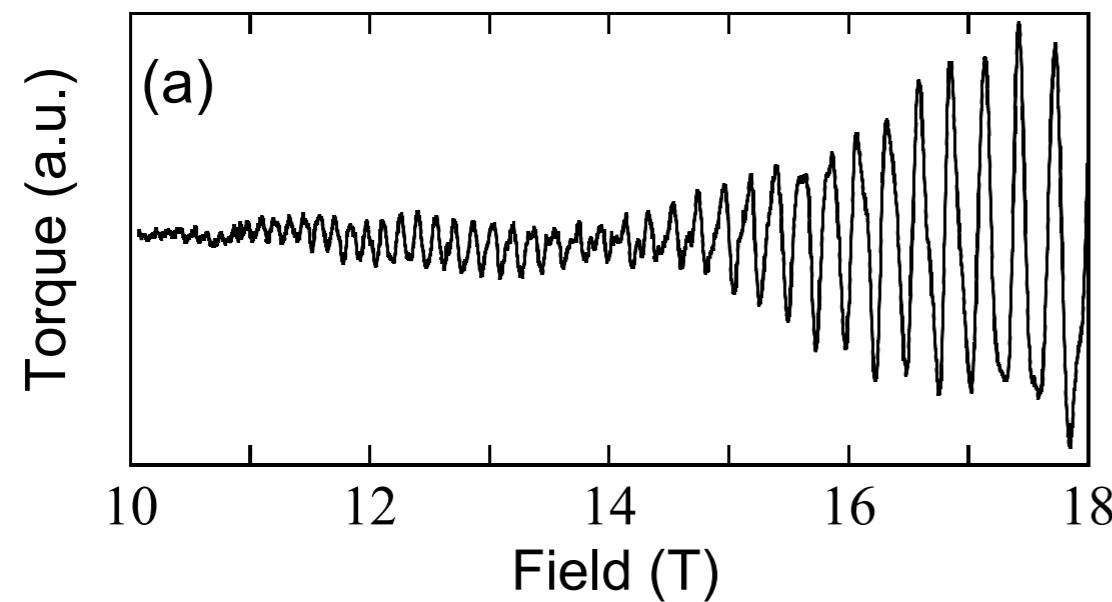
**Ag**



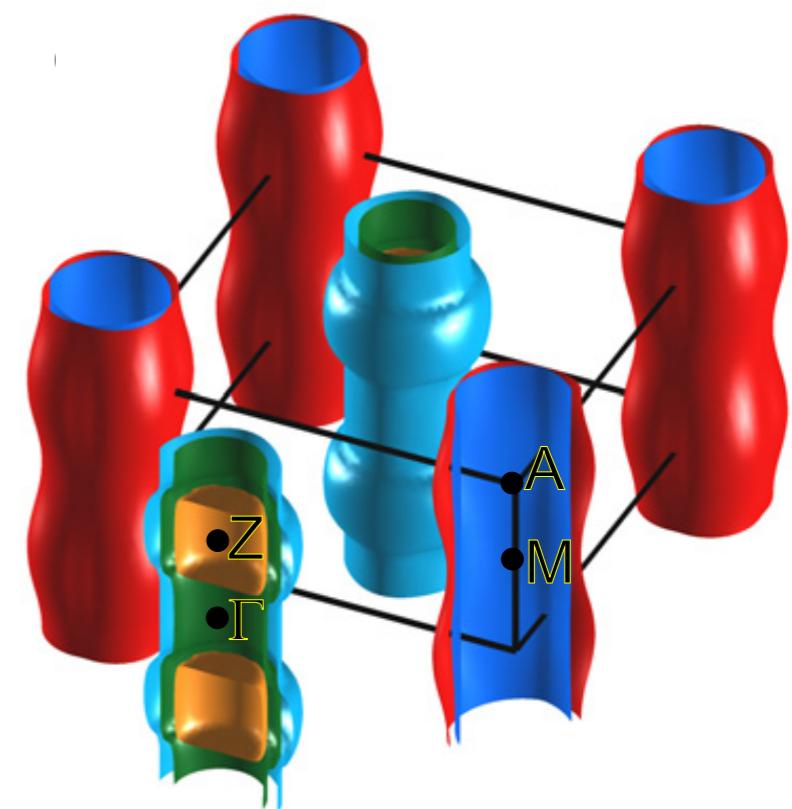
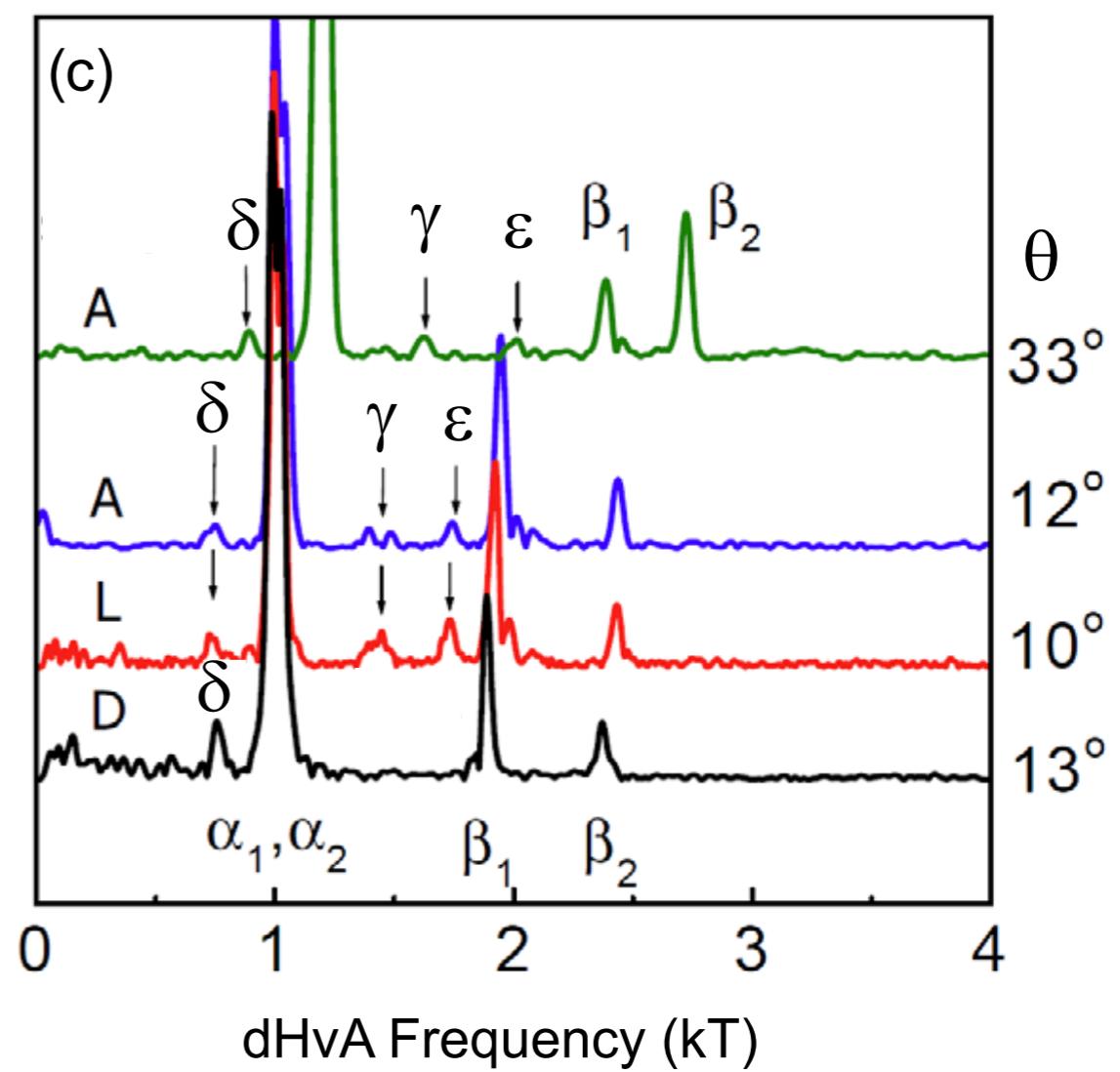
**Au**



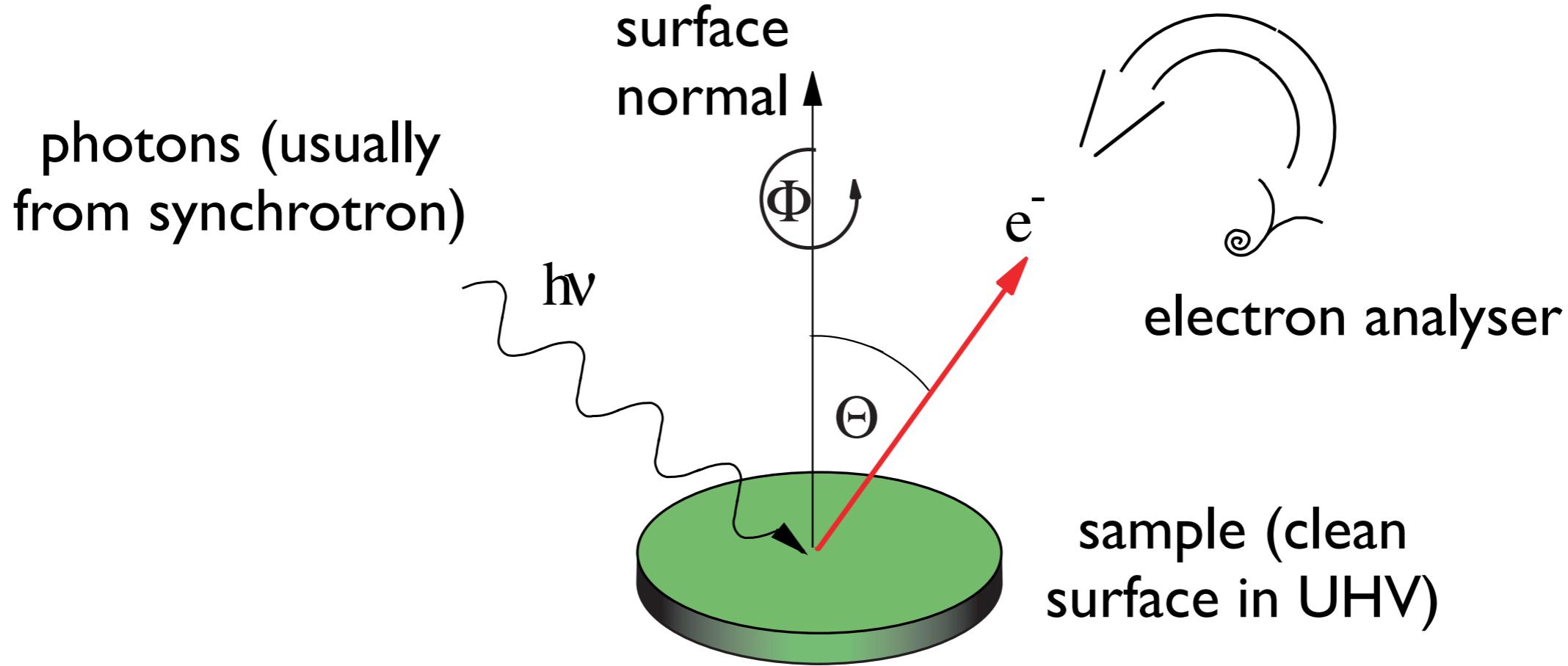
Fermi surfaces of Cu, Ag, Au,  
showing the effect of the  
distortion from free electron  
sphere (taken from Roaf, Phil.  
Trans. R. Soc. **255** 135 (1962))



Quantum oscillations  
measure the Fermi  
surface of LaFePO  
(taken from Carrington,  
Rep. Prog. Phys. **74**  
124507 (2011))



### 3.3 Angle-Resolved Photoemission (ARPES)



Photons (UV), typically from a synchrotron source, impinge on the sample being studied. The sample itself is in UHV (ultra-high vacuum) and has been cleaved (*in-situ*) to reveal a clean surface. Photoelectrons are emitted and they have their energy and angle analysed. It can be shown that the energy and angle measured at the analyser can be related to the energy and wavevector of the electron which was photoemitted.

Let's call the wavevector of the photoelectron  $K$  and the wavevector of the electron before it is ejected  $k$ .

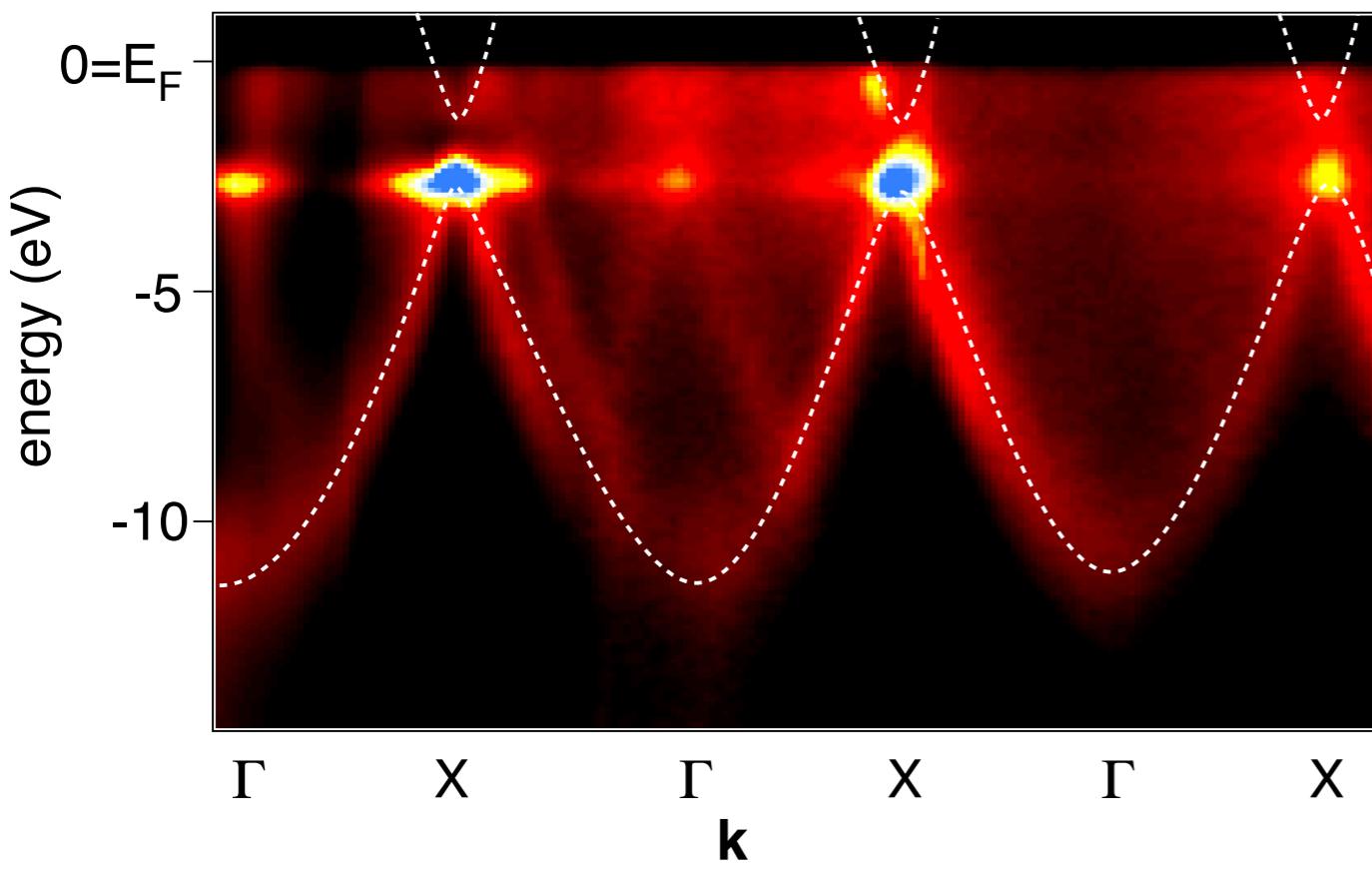
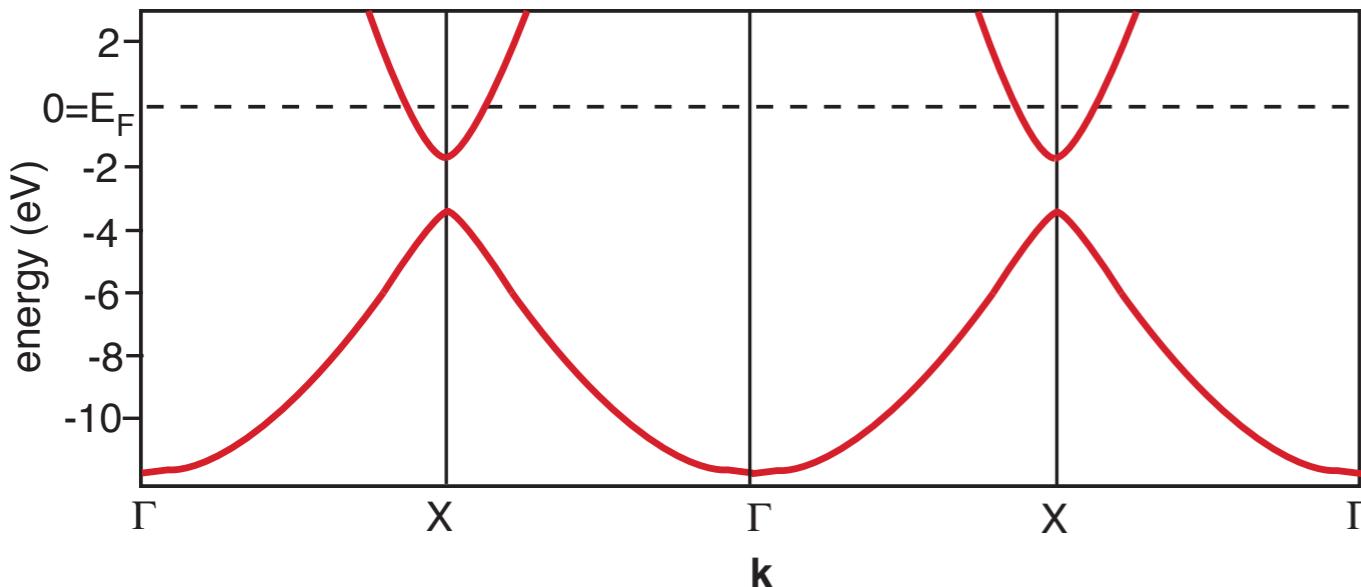
If  $k_z$  is in the direction normal to the sample and therefore  $k_x$  and  $k_y$  are the (crystal) momentum of the electron in the plane of the sample, then only  $k_z$  is not conserved (the electron has to cross the surface - think about the work function).

$$K_{\parallel} = k_{\parallel} \quad \xleftarrow{\text{measure } K \text{ of photoelectron outside, get } k \text{ of electron inside}}$$
$$K_{\perp} \neq k_{\perp}$$

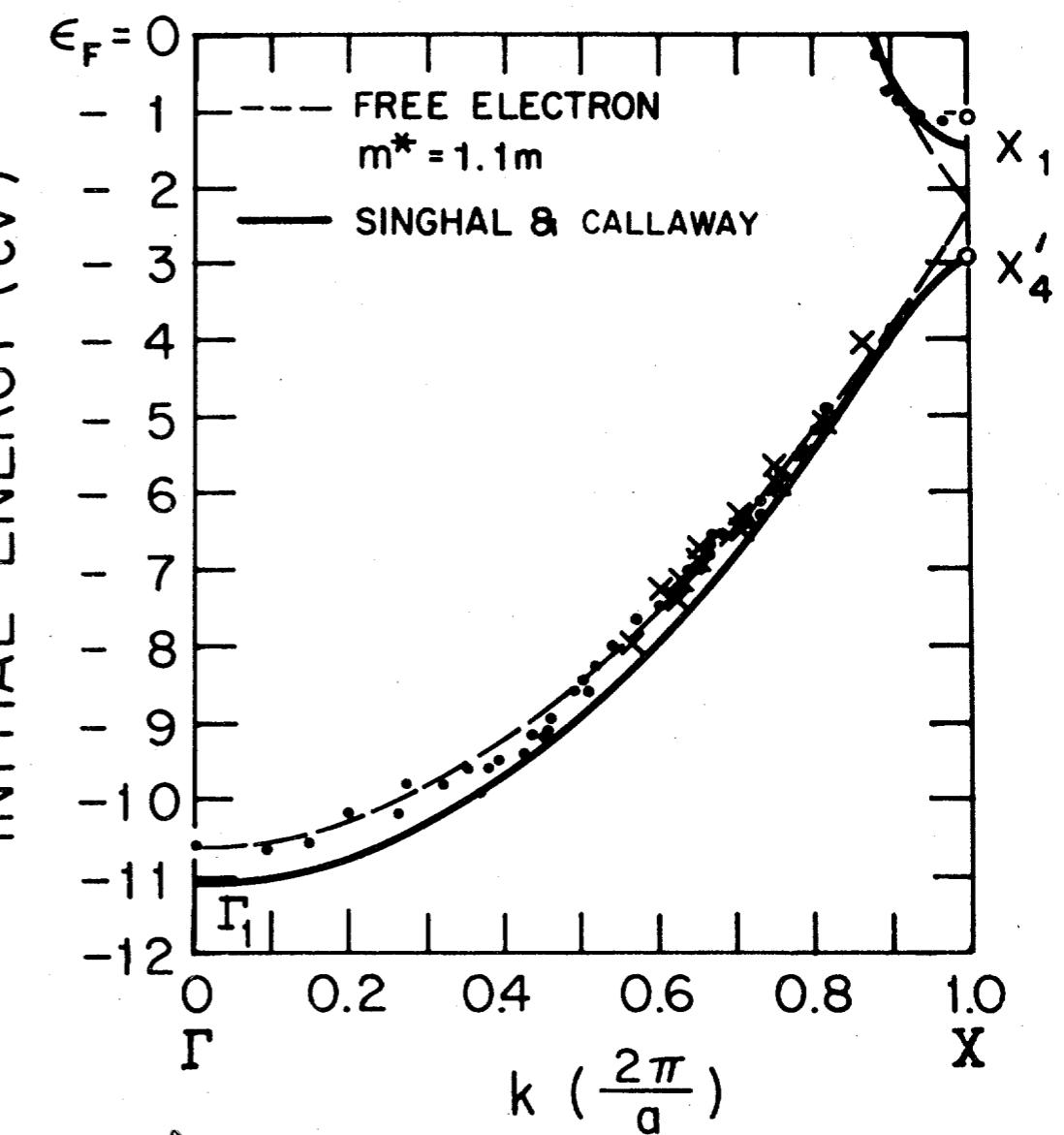
Experiments are analysed in the so-called sudden approximation; we don't worry about the fact that there is going to be some interesting many-body physics going on between the ejected electron and the hole it leaves behind.

Really good surfaces are needed, the samples normally being cleaved within the sample chamber under UHV conditions.

# Band structure of Al

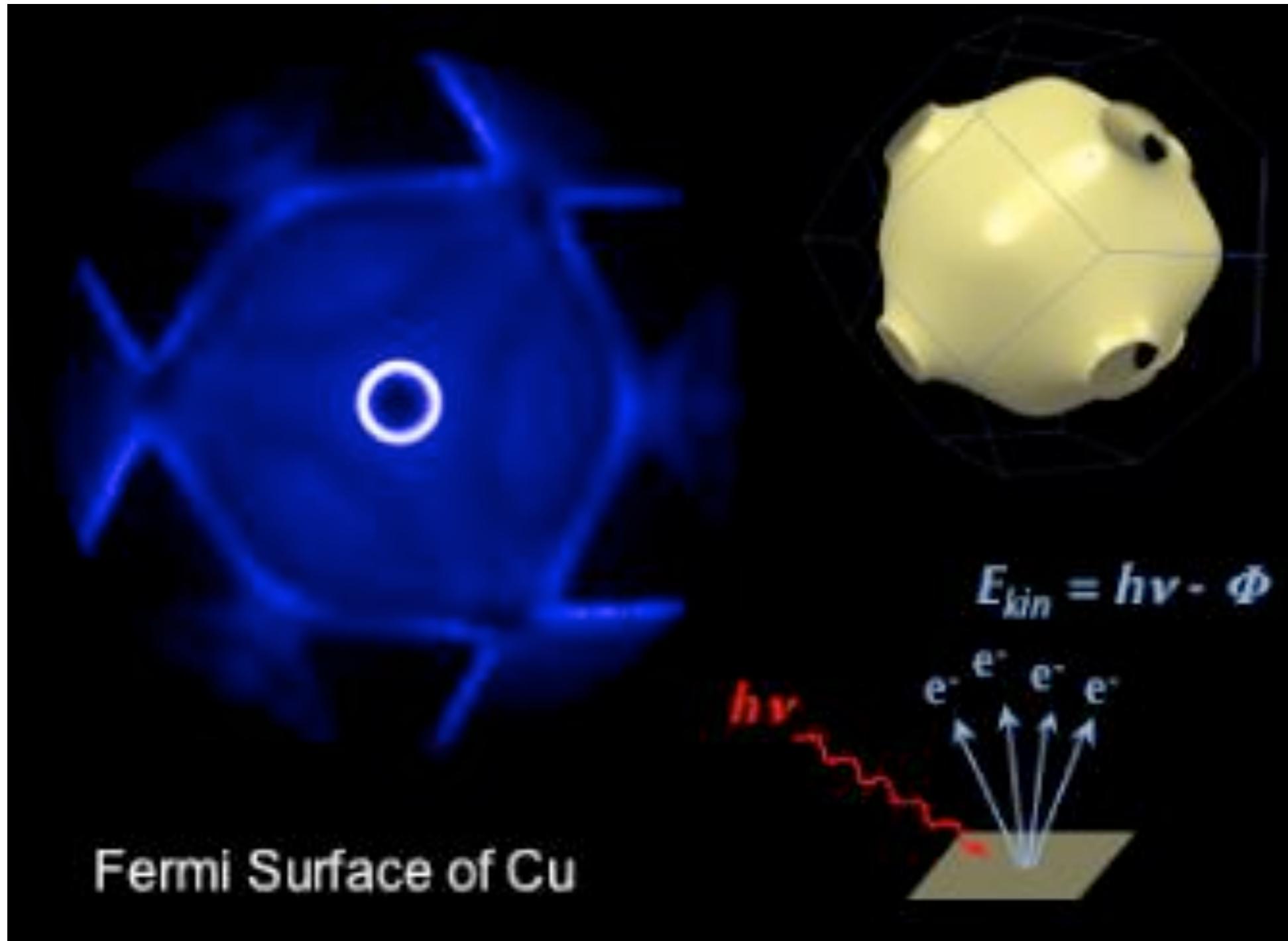


$\Gamma$ X DISPERSION

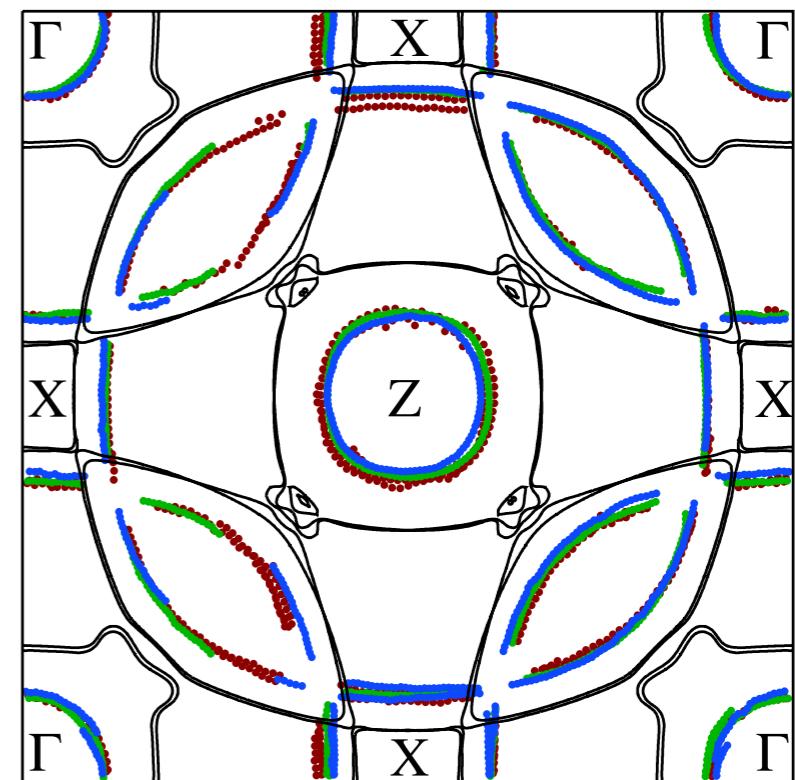
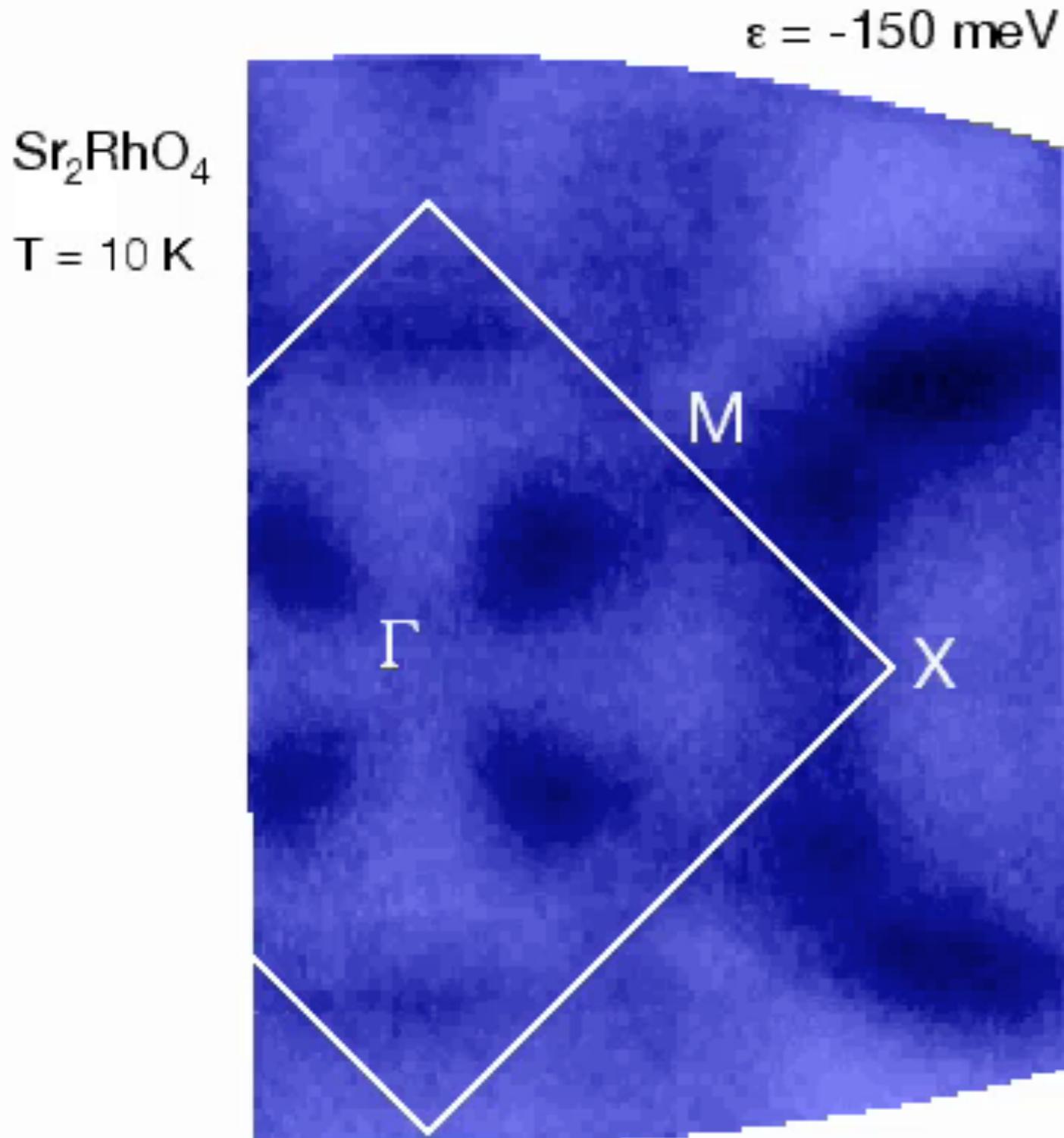


Dispersion in Al measured by  
ARPES (taken from Levinson et  
al., Phys. Rev. B **27** 727 (1983))

The technique has  
developed fast over the  
last 30 years



<http://www.st-andrews.ac.uk/physics/condmat/arpes/research.html>



Theoretical calculation of the Fermi surface of  $\text{Sr}_2\text{RhO}_4$  (taken from Baumberger et al., Phys. Rev. Lett. **96** 246402 (2006) )

F. Baumberger R. Perry, A.P. Mackenzie and Z.-X. Shen

<http://www.st-andrews.ac.uk/physics/condmat/arpes/research.html>

## **Strengths:**

- (i) Provides direct visualisation of Fermi surfaces and band dispersions.
- (ii) Energy resolution good enough to probe superconducting gaps (see subsequent courses).
- (iii) Electron mean-free path doesn't matter.

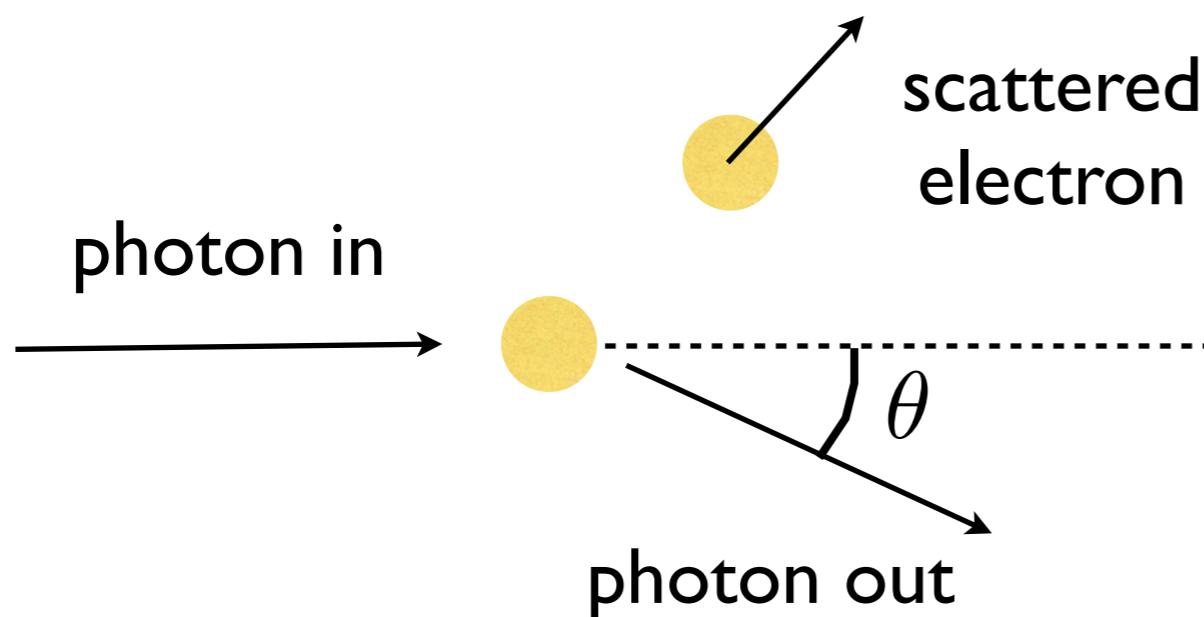
## **Weaknesses :**

- (i) Surface sensitive - need good clean surfaces (not everything cleaves), plus is the surface representative of the bulk?
- (ii) Works best in 2D systems (remember  $K_z$  is not conserved).
- (iii) Need to be careful about matrix elements of photoemission process (might some transitions be forbidden?)

### 3.4 Positron Annihilation and Compton Scattering

These two techniques have a very similar theoretical background because they are both routes to measuring the Fermi surface via the *momentum distribution* of electrons.

Basic idea is that an electronic state can only contribute to the momentum distribution if it is occupied. In the case of positron annihilation it contributes by being annihilated by a positron. For Compton scattering it contributes by scattering an incoming X-ray photon. We'll start with the **Compton scattering** of a photon by a stationary electron.



$$\Delta\lambda = \frac{h}{m_e c} (1 - \cos \theta)$$

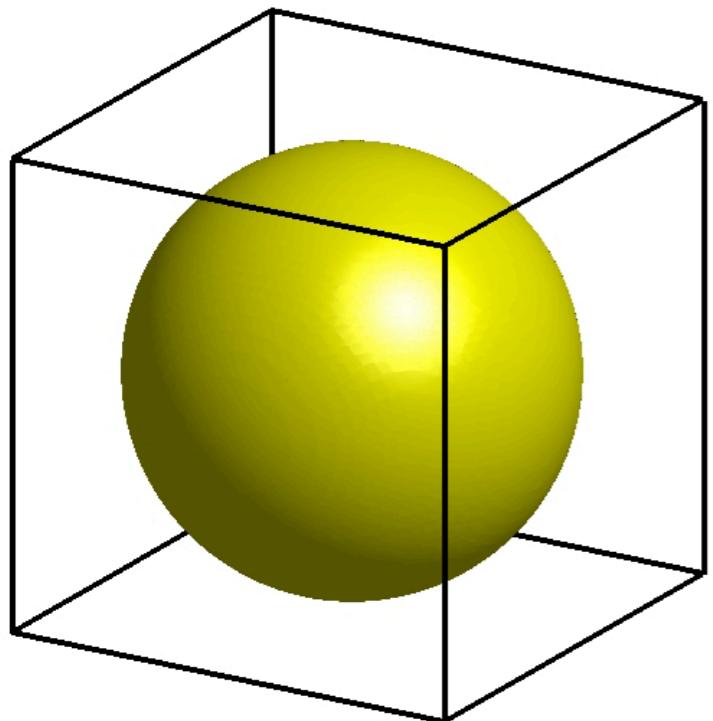
If we measure the energy of the photon at a fixed angle, then we should find that its energy has changed, according to the Compton formula.

What if the electron isn't stationary?

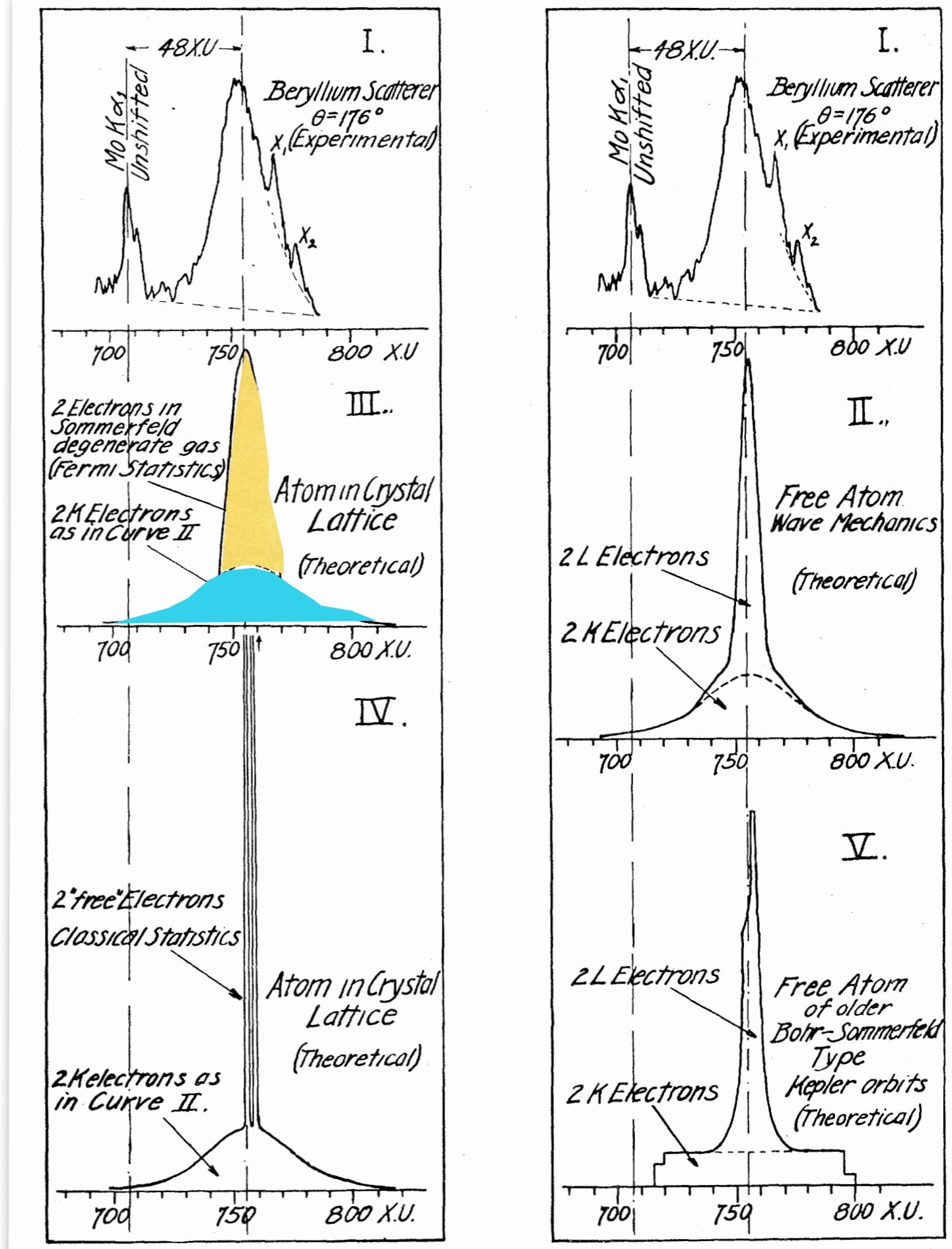
Then we should see a Doppler broadening of this energy, and the amount of broadening being related to the momentum of the electron. Measuring the spread of photon energies (which will be centred on the Compton energy) is equivalent to measuring the momentum distribution of the electrons (the probability distribution in momentum space). Clearly a given momentum state can only scatter if it is occupied by an electron, so encoded in this momentum distribution is information about the occupied states and hence about the Fermi surface. What is actually measured is a *Compton profile* :

$$J(p_z) = \int \int \rho(p_x, p_y, p_z) dp_x dp_y$$


the momentum density is  
just the probability  
density in momentum  
space i.e.  $\psi^*(\mathbf{p})\psi(\mathbf{p})$



# Historical note : validation of quantum Fermi- Dirac statistics via Compton scattering

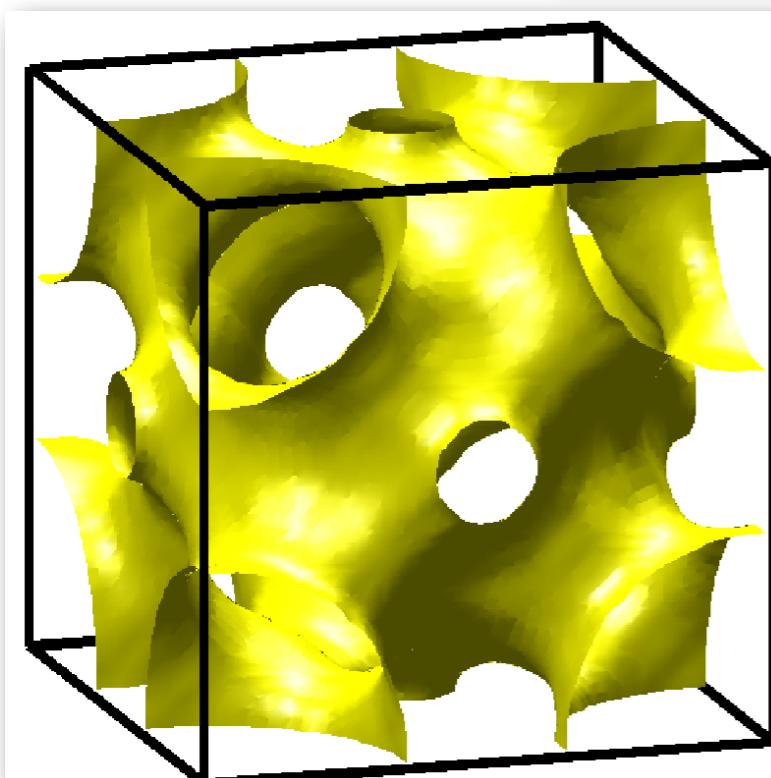
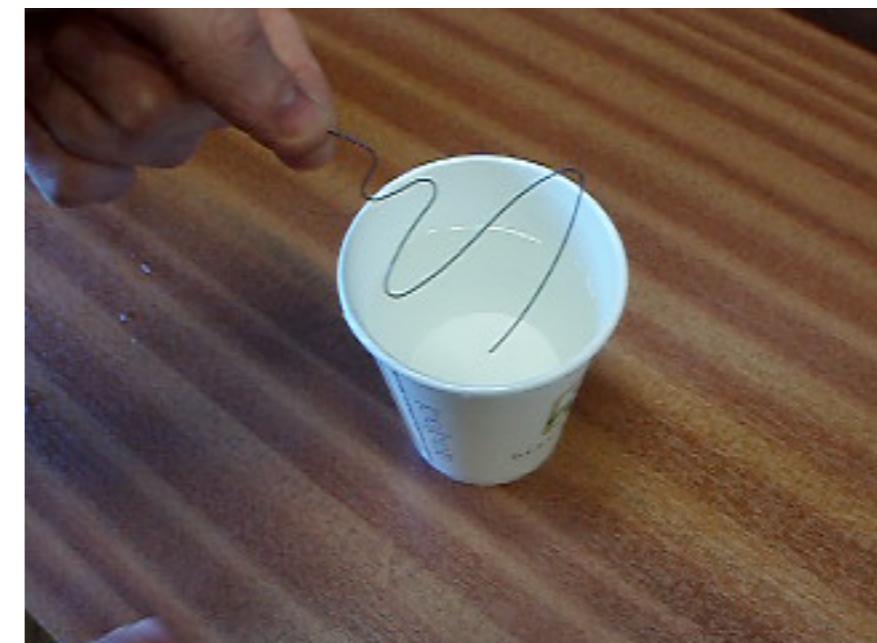


**Observation of a Strongly Nested Fermi Surface in the Shape-Memory Alloy  $\text{Ni}_{0.62}\text{Al}_{0.38}$** 

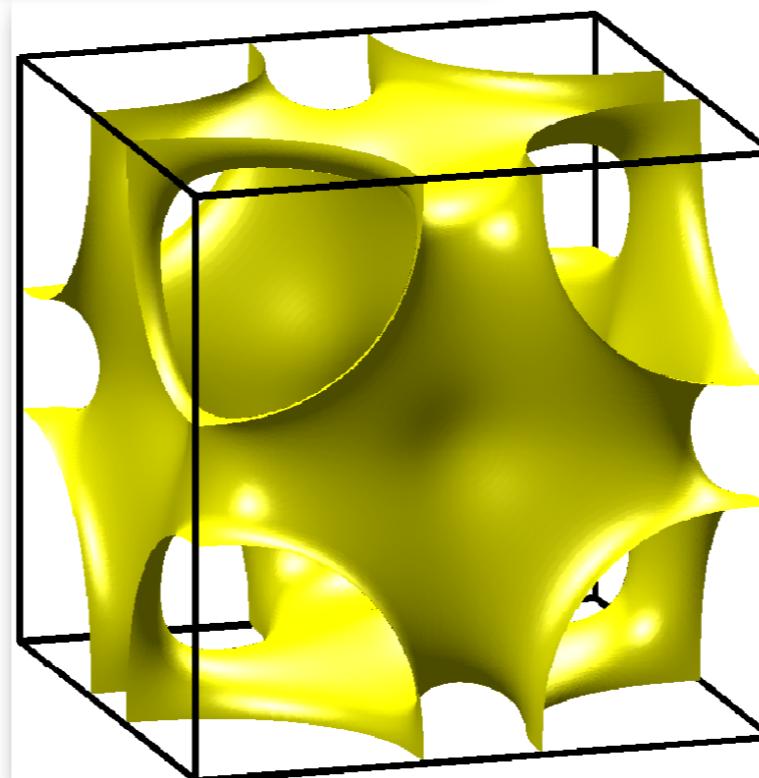
3D electronic  
structure



ID to 3D  
reconstruction  
from 24 Compton  
profiles



experiment



theory

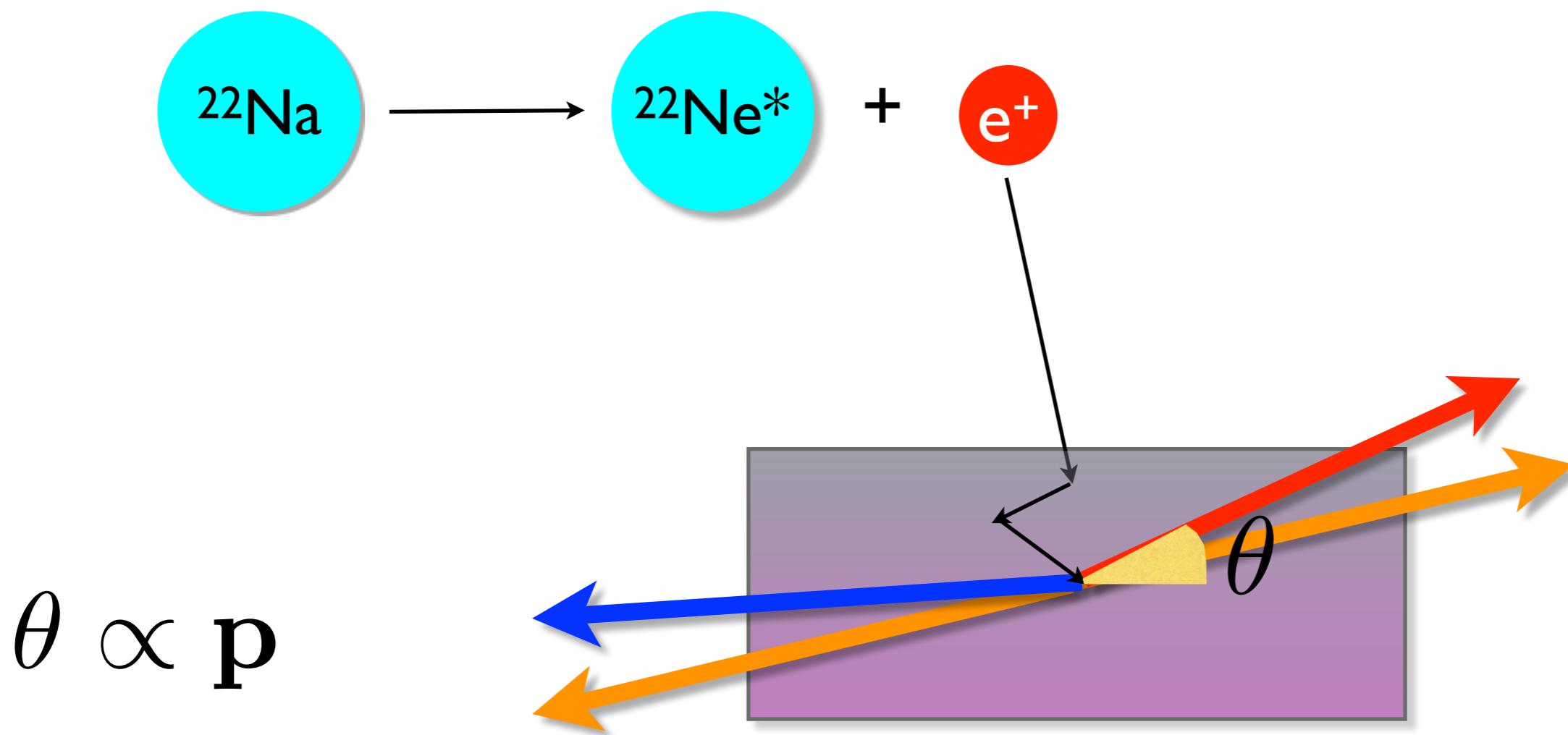
## **Strengths:**

- (i) Provides direct visualisation of Fermi surfaces (in 3D)
- (ii) Electron mean-free path doesn't matter

## **Weaknesses :**

- (i) Momentum resolution not as good as some other techniques
- (ii) Comparatively slow measurement as you need to measure lots of profiles to go from 1D to 3D
- (iii) Need a synchrotron

# Positron Annihilation

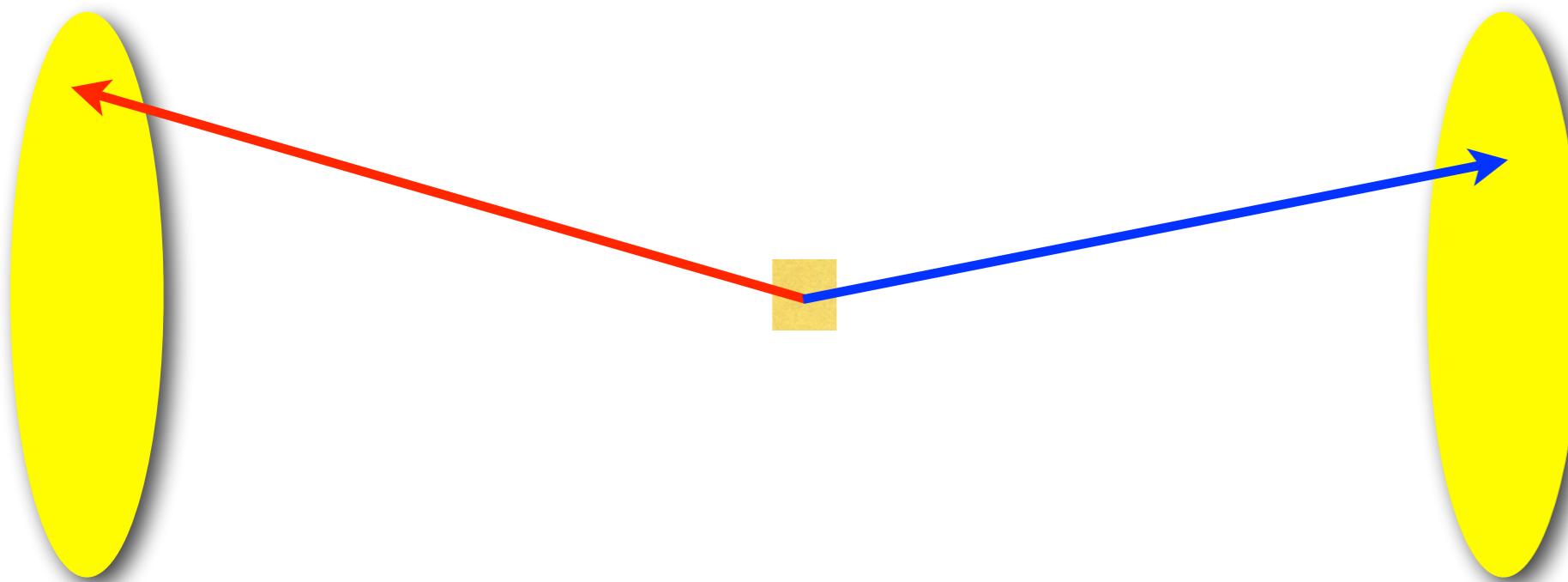


Low Temperature Physics 40 328 (2014)

Physica Status Solidi C-Current Topics in Solid State Physics 4, 3851-3856 (2007)

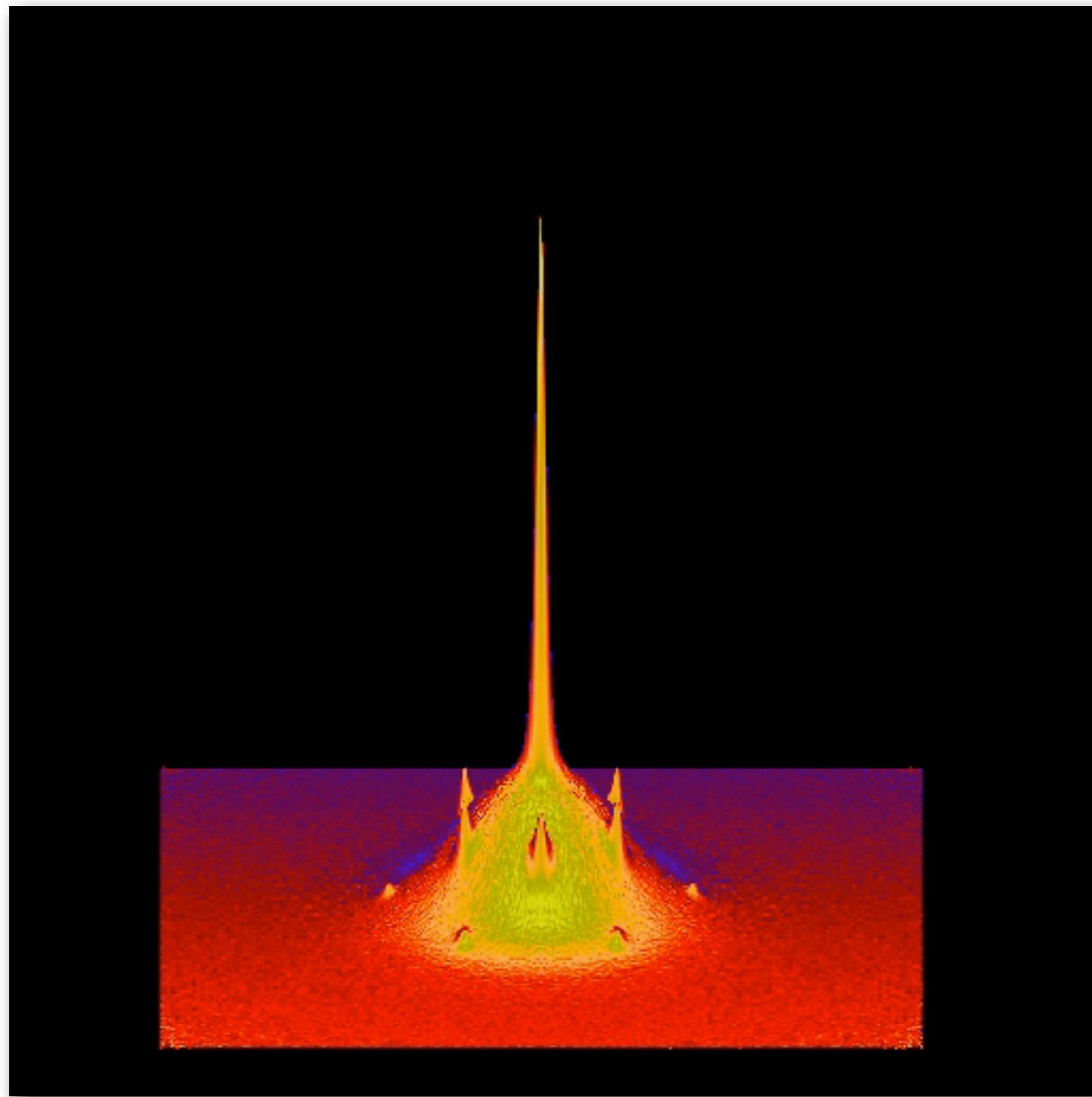


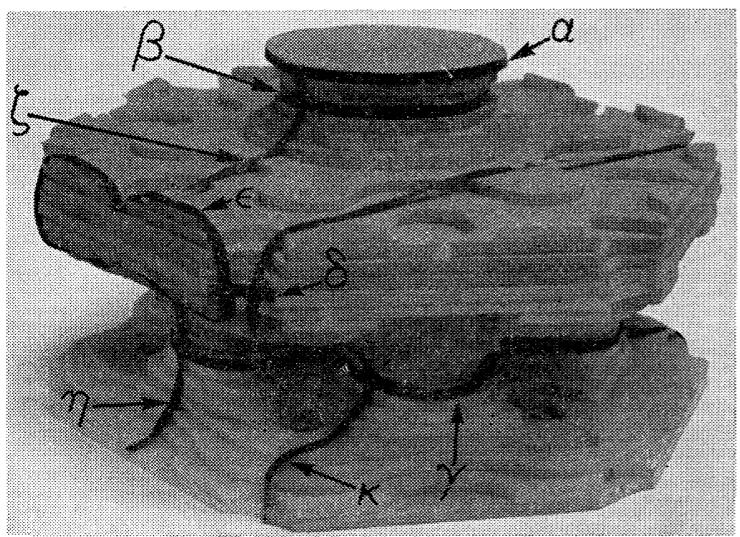
Bristol 2D-ACAR Spectrometer  
(using Anger Cameras as  
position-sensitive detectors)



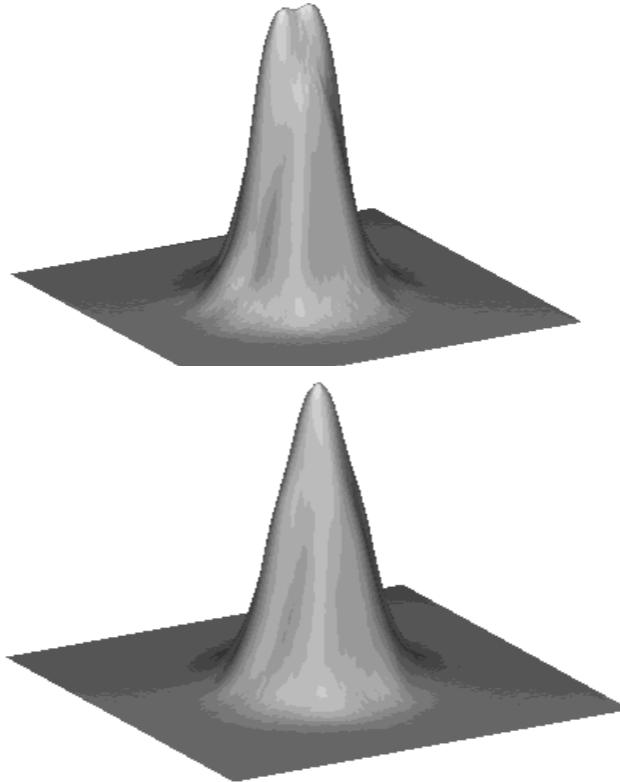
Schematic, showing how positions of two gamma rays can be measured and hence angle between them recorded

# Positronium in a Bloch state in alpha-quartz





Calculation (Loucks, Phys. Rev.  
**144** 504 (1966))



Positron experiment

VOLUME 79, NUMBER 5

PHYSICAL REVIEW LETTERS

4 AUGUST 1997

## Direct Observation and Calipering of the “Webbing” Fermi Surface of Yttrium

S. B. Dugdale, H. M. Fretwell, and M. A. Alam

*H.H. Wills Physics Laboratory, University of Bristol, Tyndall Avenue, Bristol, BS8 1TL, United Kingdom*

G. Kontrym-Sznajd

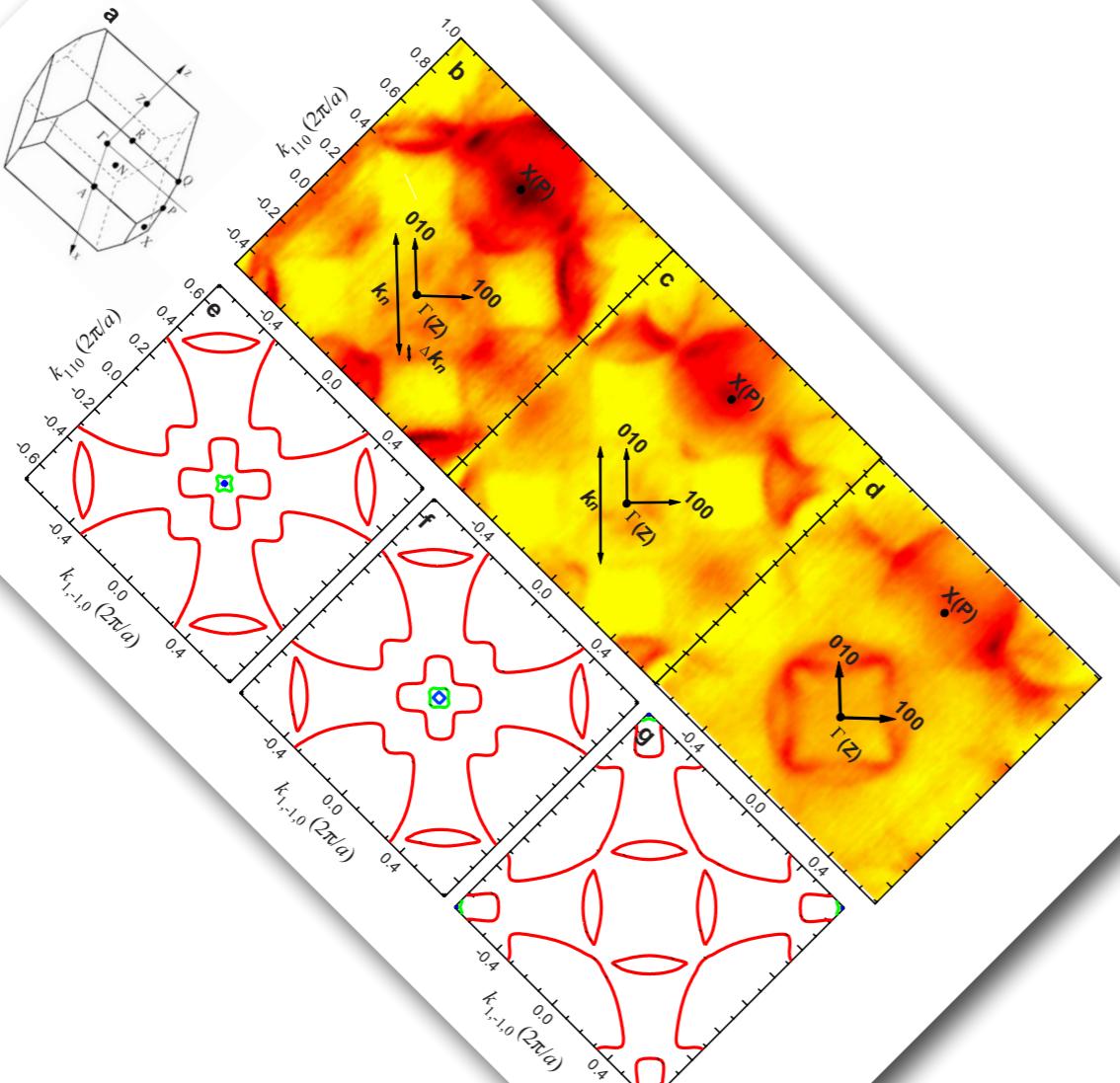
*Polish Academy of Sciences, W. Trzebiatowski Institute of Low Temperature and Structure Research,  
50-950 Wrocław 2, P.O. Box 937, Poland*

R. N. West and S. Badrzadeh

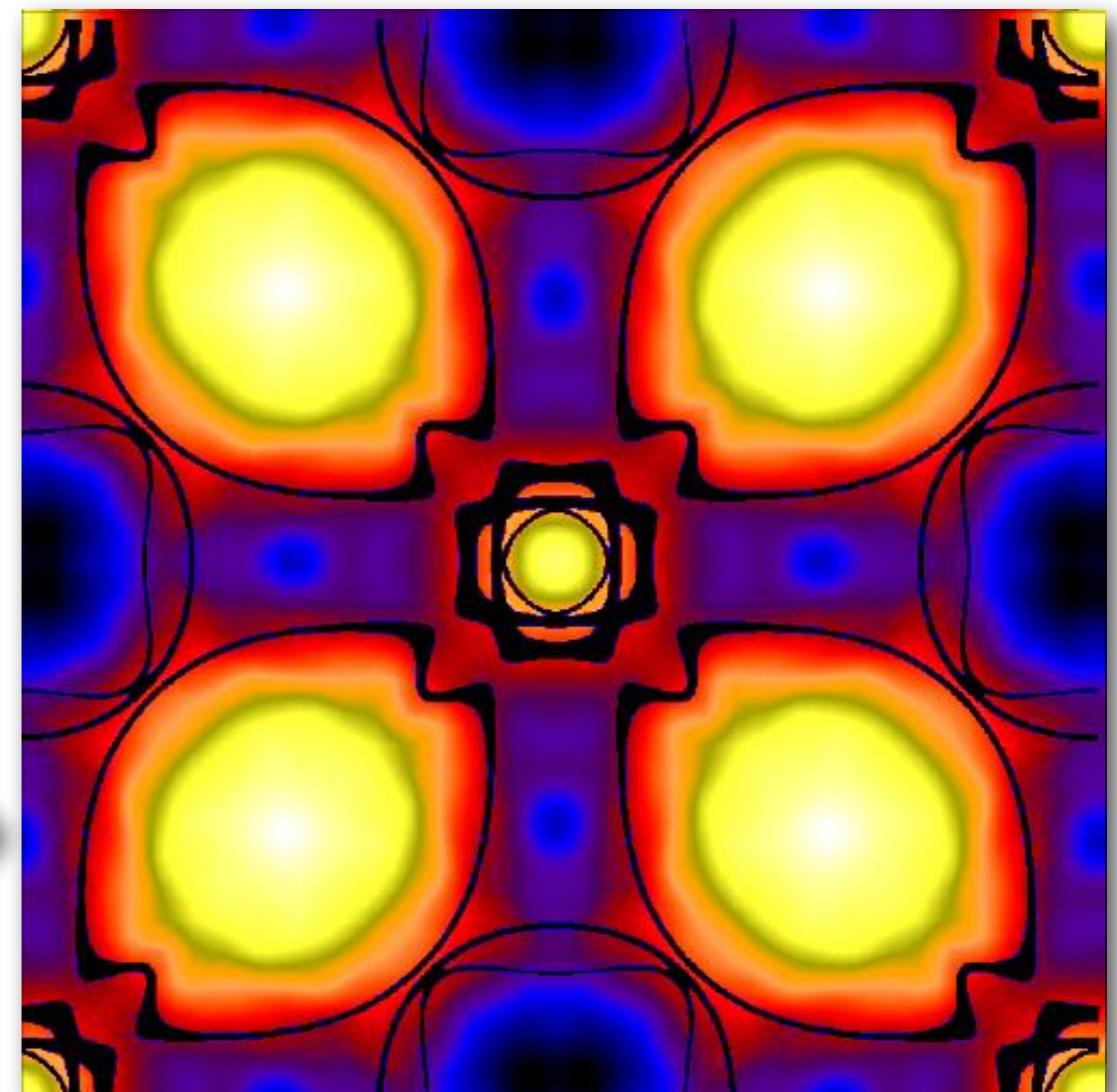
*Department of Physics, University of Texas at Arlington, P.O. Box 19059, Arlington, Texas 76019*

(Received 6 January 1997)

# $\text{LuNi}_2\text{B}_2\text{C}$ - borocarbide superconductor



ARPES



Positron

Phys. Rev. Lett. **83**, 4824 (1999)  
Supercond. Sci. Technol. **22** (2009) 014002  
STAROWICZ *et al.* PHYSICAL REVIEW B **77**, 134520 (2008)

## **Weaknesses :**

- (i) Positron can sometimes prevent measurement (presence of vacancy-type defects trap the positron, or positron may not sample the electrons you want it to)
- (ii) Resolution better than Compton scattering, but not as good as ARPES or quantum oscillations
- (iii) Comparatively slow measurement

## **Strengths :**

- (i) Provides direct visualisation of Fermi surfaces (in 3D)
- (ii) Electron mean-free-path doesn't matter



## Probing the Fermi surface by positron annihilation and Compton scattering

S. B. Dugdale<sup>a)</sup>

*H.H. Wills Physics Laboratory, University of Bristol, Tyndall Avenue, Bristol BS8 1TL, United Kingdom*

(Submitted December 2, 2013)

Fiz. Nizk. Temp. **40**, 426–438 (April 2014)

Positron annihilation and Compton scattering are important probes of the Fermi surface. Relying on conservation of energy and momentum, being bulk sensitive and not limited by short electronic mean-free-paths, they can provide unique information in circumstances when other methods fail. Using a variety of examples, their contribution to knowledge about the electronic structure of a wide range of materials is demonstrated. © 2014 AIP Publishing LLC.

[<http://dx.doi.org/10.1063/1.4869588>]

Download here : <http://dx.doi.org/10.1063/1.4869588>

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[doi:10.1088/0031-8949/91/5/053009](https://doi.org/10.1088/0031-8949/91/5/053009)

**Invited Comment**

**Life on the edge: a beginner's guide to the Fermi surface**

**S B Dugdale**

H.H. Wills Physics Laboratory, University of Bristol, Tyndall Avenue, Bristol BS8 1TL, UK