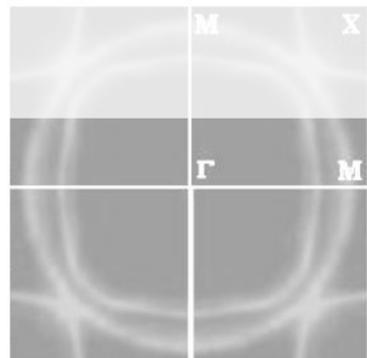
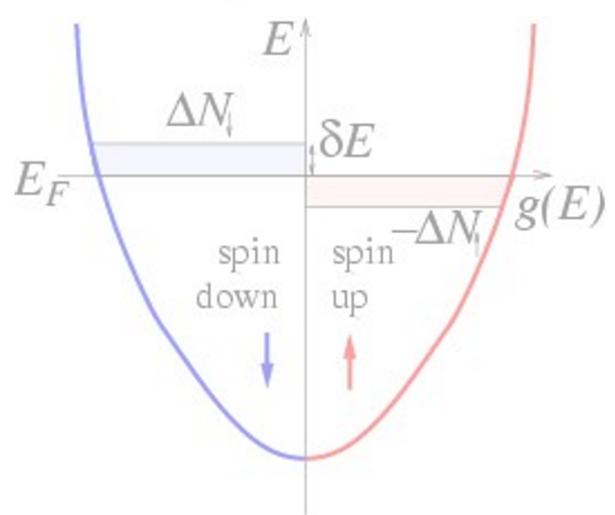
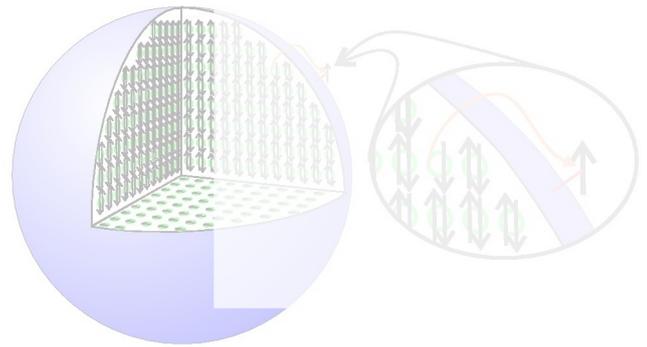
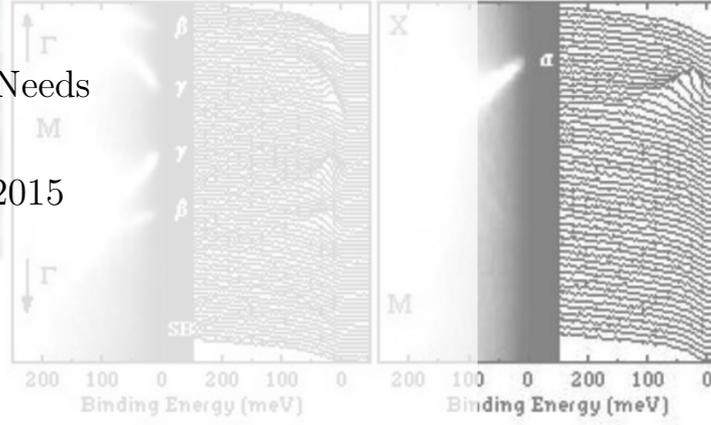
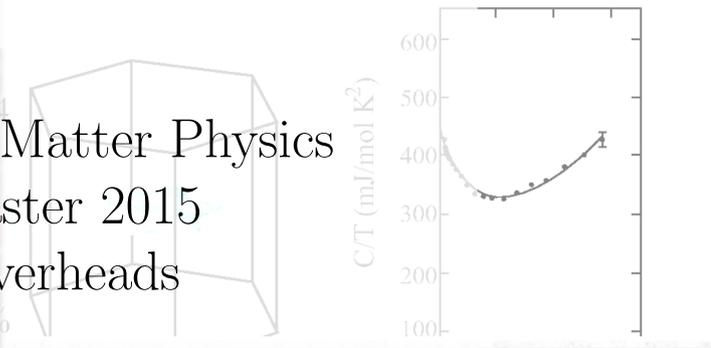


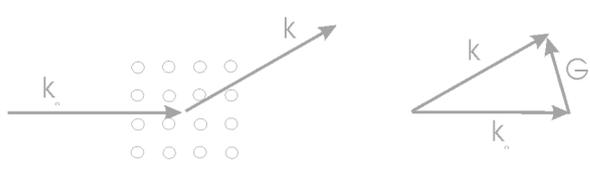
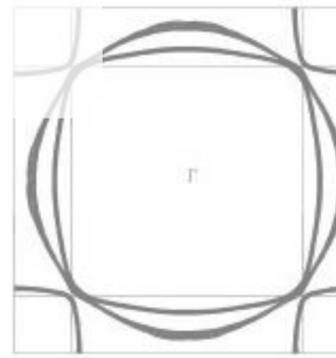
Quantum Condensed Matter Physics
 Part II Lent/Easter 2015
 Collection of overheads

Prof. Richard Needs

January 12, 2015



Sr_2EuO_4 cleaved at 180 K
 $T = 10$ K $h\nu = 28$ eV



Introductory remarks

“Could anything at first sight be more impractical than a body, which could only exist in vessels from which all but a minute fraction of the air has been extracted, which is so small that its mass is an insignificant fraction of the mass of an atom of hydrogen, which itself is so small that a crowd of these atoms equal in number to the population of the whole world would be too small to be detected by any means then known to science?” (*J. J. Thomson*)

The age of the electron

In an age of coal and steel, industrial sponsors might have taken a dim view of the experiments undertaken by J. J. Thomson and his contemporaries on the nature of the electron. Yet, being able to manipulate the motion of electrons, even if it required vacuum technology, led to a first generation of electronic devices that enabled radio technology and the cathode ray tube. A generation later, when an entire industry had grown around the use of vacuum tubes, few people would have seriously considered the prospects of replicating these devices in solids. However, as we will learn in this course, in sufficiently pure crystals the electrons exist as in an effective vacuum, subject to a periodic potential due to the lattice of atoms but otherwise free to travel over long distances without scattering. By choosing as the ‘vacuum replacement’ materials in which the density of mobile electrons is small – making it a semiconductor – the electrons could be controlled and manipulated to a previously unimagined degree, and out of this unprecedented control over matter our present electronics and computer industries could grow. These industries benefit from two key aspects of the electron: it is light and it is small, enabling speed and miniaturisation.

The electron also has other important properties: in metals, the density of mobile electrons can be very high. If we assign energy $\hbar^2 k^2 / 2m$ to plane wave states with wavevector k occupied by electrons with mass m , and we allow the electrons in a metal to fill these states according to the Pauli exclusion principle, we find that the most energetic electrons have an energy $\propto n^{2/3} / m$, where n is the particle density. This energy scale, called the Fermi energy, is of the order of several electron Volts in metals, corresponding to temperatures of the order of tens of thousands of Kelvin. This simple estimate has profound consequences: it means that, while we may get away with considering the electrons in a semiconductor as a gas of classical particles in the spirit of J. J. Thomson, electrons in metals form a quantum gas. They follow quantum statistics and present us with

manifestations of quantum mechanics ‘in the comfort of our living-room’, even at room temperature. The fact that electrons in metals form degenerate quantum gases under technologically attractive conditions results from their high density and low mass.

If we consider also that electrons interact strongly via the Coulomb interaction, the picture of a degenerate quantum gas is modified into one of an interacting quantum liquid. In semiconductors, the free electrons are usually too far apart for the screened Coulomb interaction between them to be more than a slight perturbation. In metals, however, the mutual interaction between the electrons can lead to a large variety of ordered states, such as magnetism, superconductivity, charge or orbital order. We are already surrounded by applications of magnetism and superconductivity, such as hard drives and their spin valve read/write heads, superconducting filters in mobile phone base stations, and superconducting MRI magnets. The future will reveal the devices and applications human ingenuity can produce from the growing number of unusual many-body quantum states which can form on the back of the electronic quantum liquid in metals.

Outline of the course

In this course, we will take a tentative first step towards working with electrons in solids. This requires skills you have acquired in other courses, in particular in electromagnetism, quantum mechanics and statistical physics. Maybe you will find this need for combining knowledge from different areas of physics on a daily basis disconcerting. It is a change from the closely-defined, self-contained courses you have been exposed to so far. This approach is not for the faint-hearted. It is necessary, however, to progress towards the frontier of knowledge, and you will find more courses of this type coming your way during Part III.

The course is structured as follows: roughly the first half of Lent term consists of a progression of more and more sophisticated models, each fixing deficiencies of its predecessor. We will start by considering electrons in insulators (Lorentz oscillator model) and metals (Drude model) by very intuitive classical approaches, which get quite a number of things right. We will then introduce quantum statistics (Sommerfeld model) to correct those things which go most spectacularly wrong in the classical approach. We will then introduce the crystalline lattice, which the Sommerfeld model does not take into account, and ponder its symmetry properties and its vibrations. Arguably the toughest point of the course is the introduction of Bloch’s theorem and the calculation of electronic energy levels (or band structure) in the presence of a periodic potential arising from the lattice atoms. This is done in two ways, (i) using the nearly free electron gas approach, which most people find a little harder to understand, and (ii) using linear combinations of atomic orbitals (or tight binding), which is technically easier. Having reached this point, it is downhill again, considering band structures of real materials and how band structures can be determined experimentally. Lent term will conclude with an introduction to how all of this can be applied to build semiconductor-based devices.

In Easter term, we will do a little more work on semiconductor devices and then have

a brief survey (five lectures) of electronic instabilities, or phase transitions of the electron liquid. We will focus on two examples, charge density waves and magnetism. Finally, we will be introduced to the standard model of interacting electron systems, Landau's Fermi liquid model, and where it may be seen to fail.

Books

There are many good books on solid state and condensed matter physics, but the subject is rich and diverse enough that each of these contains both much more and much less than the topics covered in this course. The two classic textbooks are Kittel, and Ashcroft and Mermin. These are both at the correct level of the course, and have the virtue of clear exposition, many examples, and lots of experimental data. Slightly more concise, though in places a little more formal is Ziman. Grosso and Parravicini has a somewhat wider coverage of material, but much of it goes well beyond the level of detail required for this course. Marder is at about the right level (though again with more detail than we shall need), and has a nice blend of quantum properties with statistical and classical properties. A well illustrated modern treatment of most topics in this course is also given by Ibach and Lüth. OUP have recently issued a series of short texts on condensed matter physics. One of these, **Singleton, matches this course quite closely**. You may find that it covers most key topics of our course at about the right level and without unnecessary detail.

- C. Kittel, *Introduction to Solid State Physics, 7th edition*, Wiley, NY, 1996.
- N.W. Ashcroft and N.D. Mermin, *Solid State Physics*, Holt-Saunders International Editions, 1976.
- J.M. Ziman, *Principles of the Theory of Solids*, CUP, Cambridge, 1972.
- H. Ibach and H. Lüth, *Solid State Physics*, Springer 1995.
- J. Singleton, *Band Theory and the Electronic Properties of Solids*, OUP 2001.
- M.P. Marder, *Condensed Matter Physics*, Wiley, NY, 2000. Covers both quantum matter and mechanical properties.
- G. Grosso and G.P. Parravicini, *Solid State Physics*, AP, NY, 2000. A wide coverage of material, very band structure oriented, very detailed.
- A very good book, though with a focus on statistical and “soft” condensed matter that makes it not so relevant for this course, is P.M. Chaikin and T. Lubensky, *Principles of Condensed Matter Physics*, CUP, Cambridge, 1995.

Handout and problem sets

This handout contains the overheads shown in the lectures. It will be accompanied by a set of notes, which may help to fill in the gaps left by the overheads. There are many good books on condensed matter physics, some of which are listed above. The handouts are not intended to form another book. Rather, they will help you assemble your own records of the course, complemented by the notes you will have taken during the lectures, and by the recommended text books.

Problems are provided on four separate problem sheets (three during Lent, and one during Easter term). They vary from the straightforward to the complex, and especially challenging problems are highlighted with an asterisk.

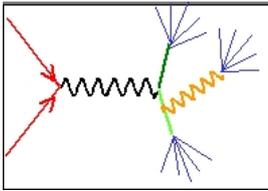
Lent term topics

- 1 Introduction
- 2 Electrodynamics of insulators and metals
- 3 Sommerfeld model
- 4 Bonding
- 5 Crystal lattice and lattice vibrations
- 6 Electronic structure in crystalline solids
- 7 Comments on band structure
- 8 Semiclassical model of electron dynamics
- 9 Probing the band structure and density of states
- 10 Semiconductors

Easter term topics

- 11 p - n junction based devices
- 12 Field effect transistor
- 13 Charge Density Waves
- 14 Magnetism
- 15 Fermi liquid theory
- 16 Heavy fermions
- 17 Beyond the standard model

Mystery of Matter

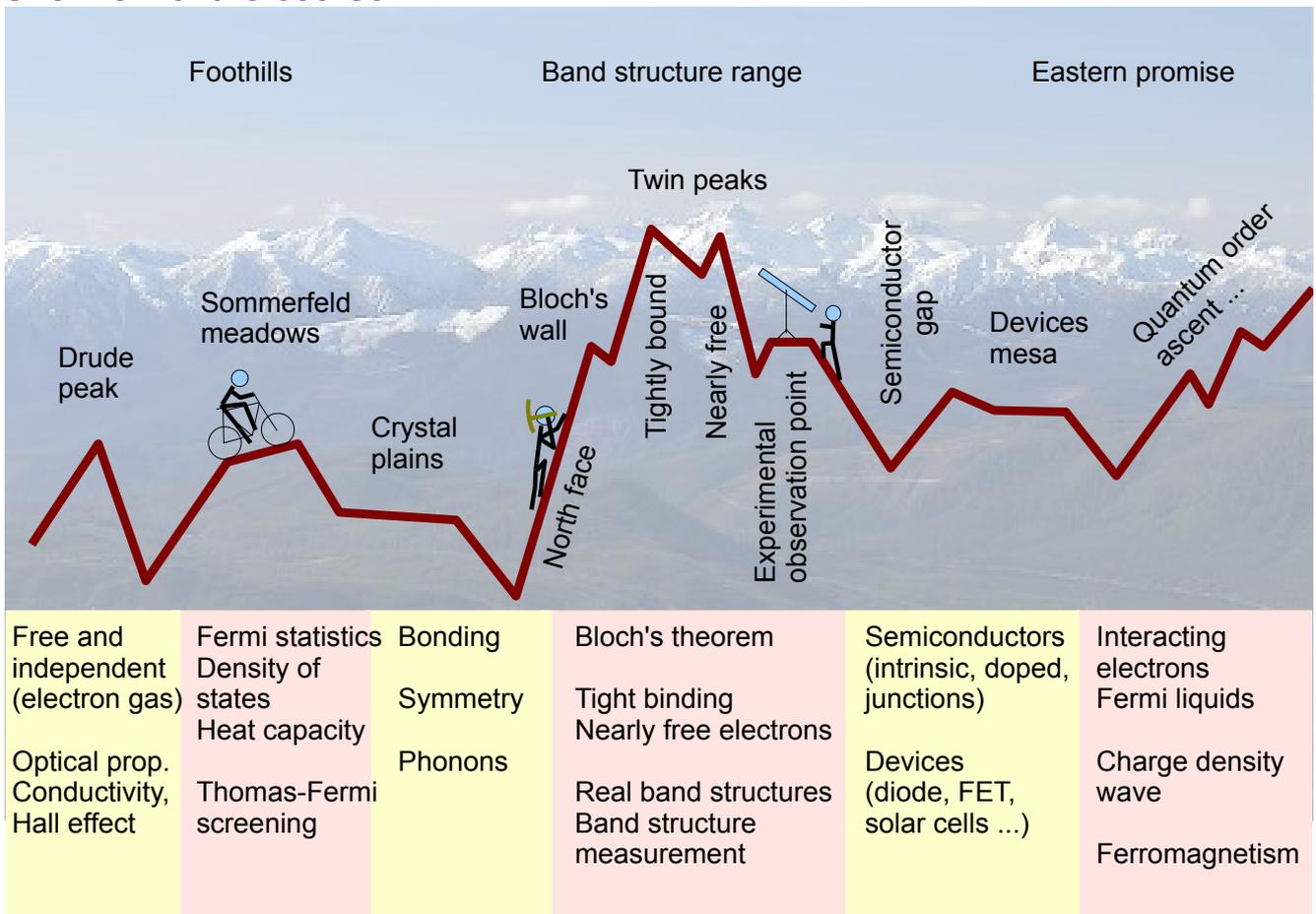


How do we get from the elementary particles to the

real world?

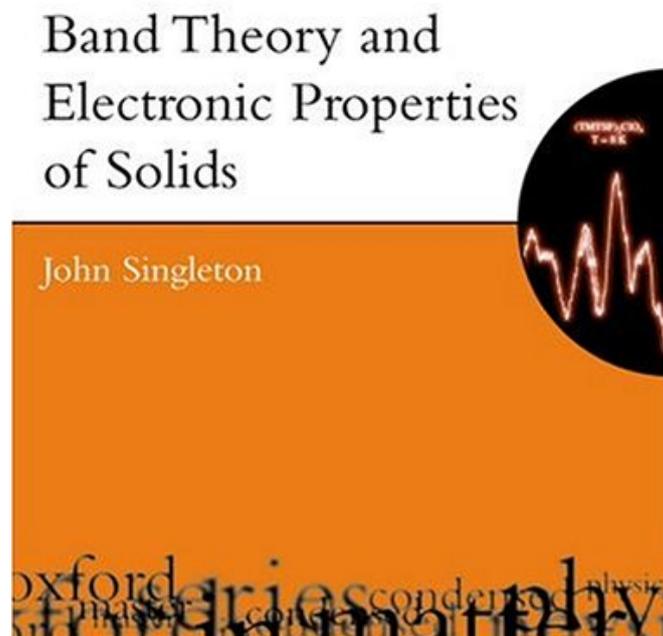


Overview of the course



A book recommendation: Singleton, OUP

[OXFORD MASTER SERIES IN CONDENSED MATTER PHYSICS]



Other books for background reading: Ashcroft&Mermin, Kittel

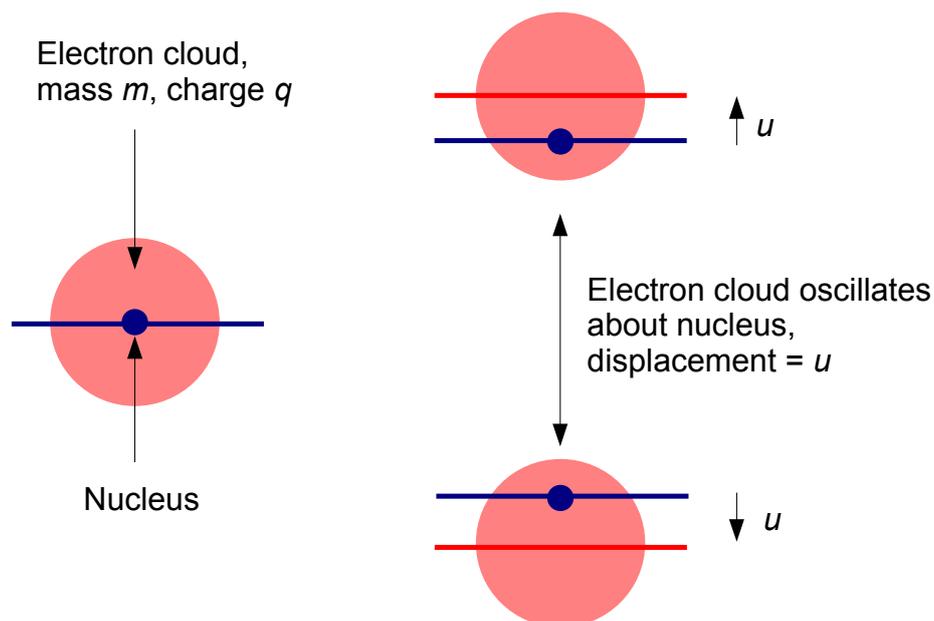
A warning

The slides are often complemented by blackboard work.
It is important to take copious notes in the lectures.
And: use the textbooks!

Optical properties of insulators

(Response to e-m waves, high-frequency electric field, wavelength long compared to interatomic spacing)

Optical properties of insulators, classical picture: Lorentz dipole oscillator model



- Model atoms as nucleus + electron cloud.
- Applied electric field causes displacement of electron cloud, u .
- Restoring force is proportional to displacement.

Lorentz oscillator model, frequency-dependent permittivity

- Electron cloud behaves as damped harmonic oscillator

$$m\ddot{u} + m\gamma\dot{u} + m\omega_T^2 u = qE$$

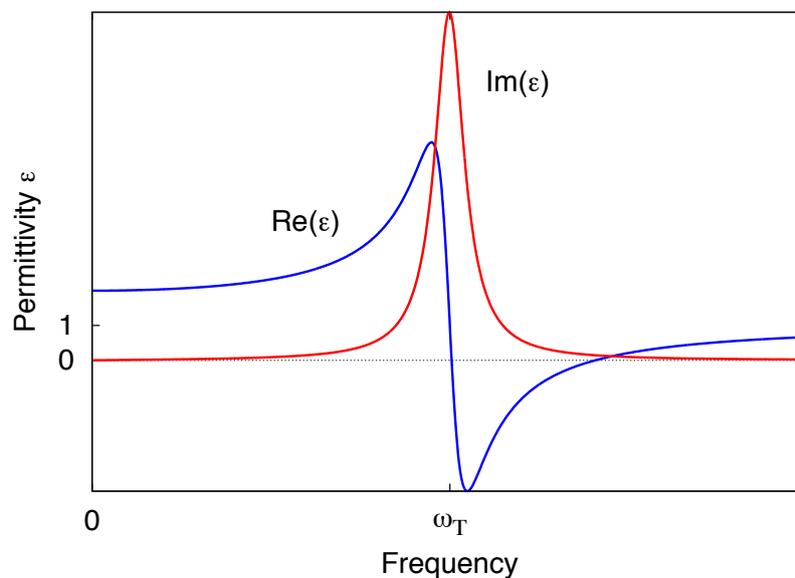
(ω_T = natural frequency, given by force constant and mass; γ = damping rate).

- Consider oscillating electric field $E(t) = E_\omega e^{-i\omega t}$, which induces oscillating displacement $u(t) = u_\omega e^{-i\omega t}$.
- Resulting dipole moment per atom at angular frequency ω : $p_\omega = qu_\omega$
- Polarisation = dipole moment density: $P_\omega = \epsilon_0 \chi_\omega E_\omega$, with

$$\chi_\omega = \frac{N}{V} \frac{q^2}{m\epsilon_0(\omega_T^2 - \omega^2 - i\omega\gamma)}$$

- Permittivity $\epsilon_\omega = 1 + \chi_\omega$.

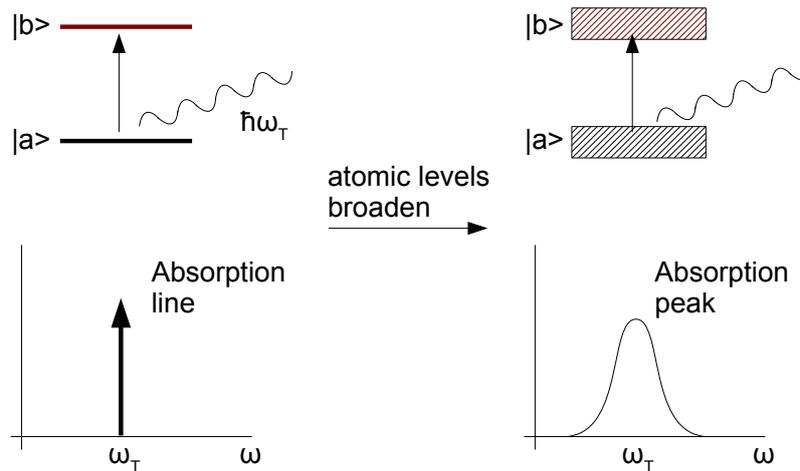
Lorentz oscillator model, absorption and reflection



- Work done per unit time and per volume (power absorption)
 $= \frac{1}{2} \omega \epsilon_0 |E_\omega|^2 \text{Im}(\epsilon_\omega)$
- At interfaces between medium 1 and 2, reflection coefficient $r = \frac{\sqrt{\epsilon_1} - \sqrt{\epsilon_2}}{\sqrt{\epsilon_1} + \sqrt{\epsilon_2}}$

Lorentz oscillator model, connection to quantum mechanics

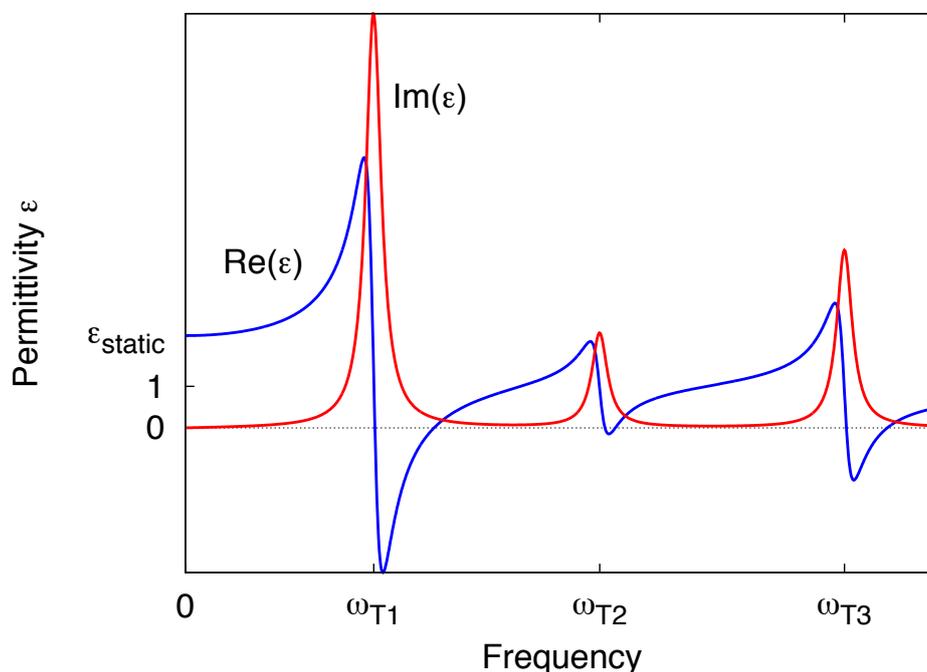
- Classical oscillator model cannot be the whole story.



- For two sharp levels, time-dependent perturbation theory gives $\chi_\omega \propto (E_b - E_a - \hbar\omega)^{-1} + i\delta(E_b - E_a - \hbar\omega)$
- As the energy levels broaden into bands, this becomes similar to the Lorentz model, at least close to the resonance frequency $\omega_T = E_b - E_a$.

Lorentz oscillator model, superposition of spectra

- May have a number of allowed transitions at energies $\hbar\omega_{T1}, \hbar\omega_{T2}, \dots, \hbar\omega_{Ti}, \dots$
- Usually, high frequency, at least optical range.
- Resulting frequency-dependent permittivity from adding responses associated with each transition: $\epsilon(\omega) = 1 + \sum \chi_i(\omega)$

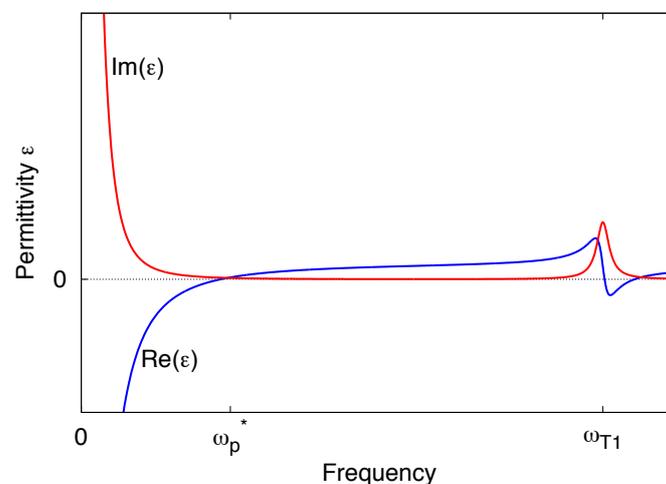


Optical and transport properties of metals

(Response to oscillating electric field, long wavelength)

Optical properties of metals: Drude model – cut the electrons free

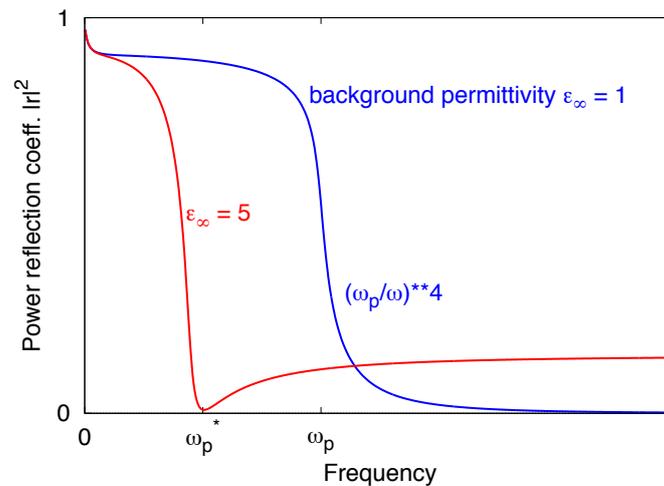
- Use Lorentz oscillator model for core electrons
- Conduction electrons = not bound to nucleus \implies restoring force = 0
 $\implies \omega_T = 0$.
- Obtain additional peak in $\text{Im}(\epsilon_\omega)$ at low frequency ('Drude peak'):



- $|\epsilon(\omega)|$ diverges for $\omega \rightarrow 0 \implies$ metals are highly reflecting at low frequency.
- $\epsilon(\omega)$ crosses through zero at high frequency $\omega_p^* \implies$ metals become transparent in the ultraviolet.

Reflectivity of metals in the Drude model

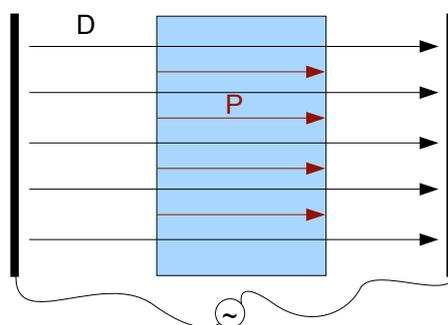
- Reflectivity at the interface between two media, if permeability is unchanged: $r = (\sqrt{\epsilon_1} - \sqrt{\epsilon_2}) / (\sqrt{\epsilon_1} + \sqrt{\epsilon_2})$
- Power reflection coefficient $R = |r|^2$.



- Plateau in the reflection coefficient R at low frequency, relates to conductivity of material.
- $R \propto \omega^{-4}$ at high frequency.
- If background permittivity ϵ_∞ (caused by polarisability of core electrons) is significant, R can go to zero at finite frequency.

Plasma oscillations

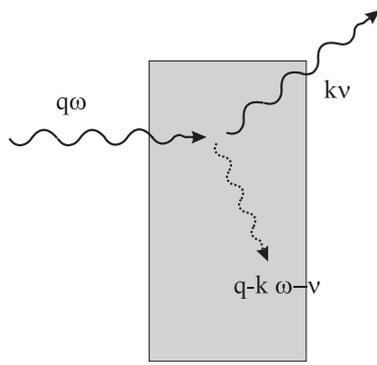
- 'Plasma'=electrons moving in a positively charged environment \implies model for metal.
- Oscillations? But we said $\omega_T \rightarrow 0$ in a metal!
Consider probing a slab of material by applying an oscillating field:



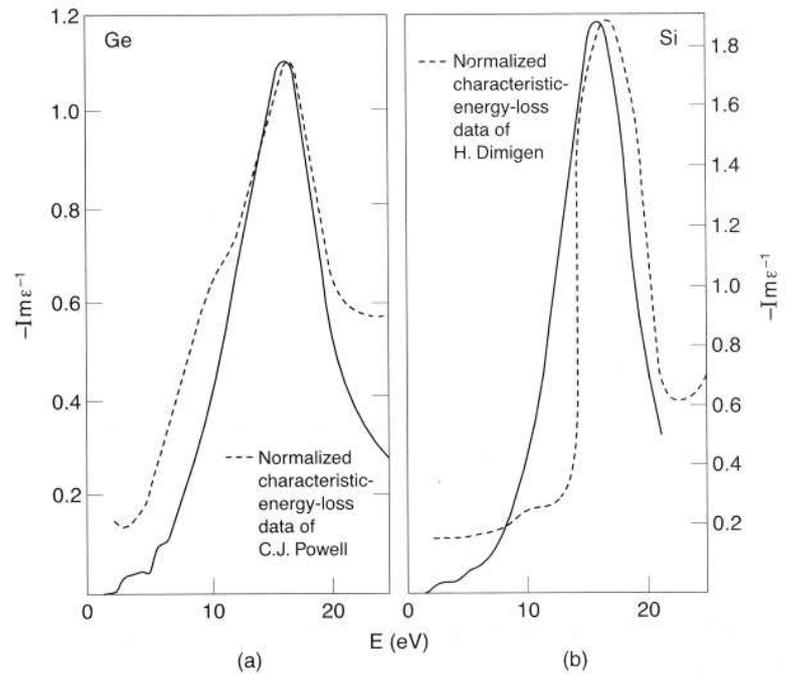
$$\epsilon_0 E = \epsilon^{-1} D$$

$$P = D(1 - \epsilon^{-1})$$

- $\epsilon(\omega_p) = 0$, where $\omega_p^2 = \frac{ne^2}{m\epsilon_0}$ (defining $n = N/V$), if background permittivity $\epsilon_\infty = 1$. In general, $\epsilon = 0$ at $\omega_p^* = \omega_p / \sqrt{\epsilon_\infty}$
- At ω_p^* ('Plasma frequency'), polarisation can oscillate without even applying a driving field \implies Plasma oscillations.
- Polarisation causes build-up of surface charge, which generates the restoring force driving the oscillations. The electrons slosh back and forth.



- Incoming electron at wavevector q , energy $\hbar\omega$. Outgoing electron at wavevector k , energy $\hbar\nu$. Plasmon generated with energy $\hbar(\omega - \nu)$.



- Response to oscillating applied D -field given by $\epsilon(\omega)^{-1} = \frac{\omega^2 + i\omega/\tau}{\omega^2 - \omega_p^2 + i\omega/\tau}$
- Resonance at plasma frequency $\omega_p^2 = \frac{ne^2}{m\epsilon_0}$, width τ^{-1} .

Connection to AC electrical conductivity

- Current density $j = \dot{u}(N/V)q$ (velocity \times density)
- But also, polarisation $P = (N/V)uq$.
- Hence, $j = \dot{P}$, if the polarisability of the core electrons is neglected. At angular frequency ω , this gives:

$$j_\omega = -i\omega\epsilon_0\chi_\omega E_\omega$$

- But, Ohm's law also gives $j_\omega = \sigma_\omega E_\omega$, hence:

$$\sigma(\omega) = -i\omega\epsilon_0(\epsilon(\omega) - 1)$$

- For the AC conductivity $\sigma(\omega)$, we find $\sigma(\omega) = \frac{ne^2\tau}{m(1-i\omega\tau)}$.
- Interpretation of τ : Charge carriers scatter occasionally from atoms, randomising their momentum. Relaxation time = 1/(damping rate): $\tau = 1/\gamma$.

• Equations of motion

$$(\partial_t + \tau^{-1})j_x = (q\rho/m)(E_x + Bv_y)$$

$$(\partial_t + \tau^{-1})j_y = (q\rho/m)(E_y - Bv_x)$$

(ρ charge density nq).

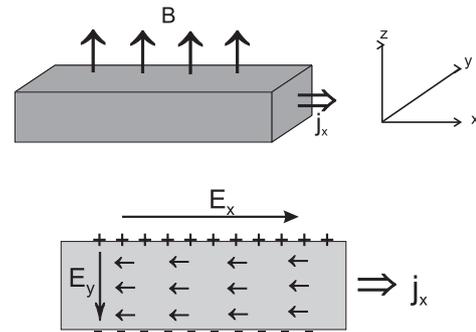
• Steady state, $\partial_t = d/dt = 0$

$$j_x = \frac{q\rho\tau}{m}(E_x + v_y B_z)$$

$$j_y = \frac{q\rho\tau}{m}(E_y - v_x B_z)$$

$$(\beta = \frac{eB}{m}\tau = \omega_c\tau = \mu B,$$

$$\omega_c = \text{cyclotron frequency})$$



- **Hall effect:** Current is confined to x-direction ($j_y = 0$) by transverse field E_y .

- **Hall coefficient**

$$R_H = \frac{E_y}{j_x B} = \frac{1}{nq}$$

- R_H gives carrier density and charge.

Key results in Drude theory

Plasma frequency

$$\omega_p^2 = \frac{ne^2}{\epsilon_0 m}$$

Taking into account susceptibility of atomic cores, $\chi_\infty = \epsilon_\infty - 1$ causes slight modifications:

$$\epsilon(\omega) = 1 - \frac{\omega_p^2}{\omega^2 + i\omega\gamma} \rightarrow \epsilon_\infty - \frac{\omega_p^2}{\omega^2 + i\omega\gamma}$$

$$\sigma(\omega) = -i\omega\epsilon_0(\epsilon(\omega) - 1) \rightarrow -i\omega\epsilon_0(\epsilon(\omega) - \epsilon_\infty)$$

Useful expressions for electrical conductivity and Hall coefficient:

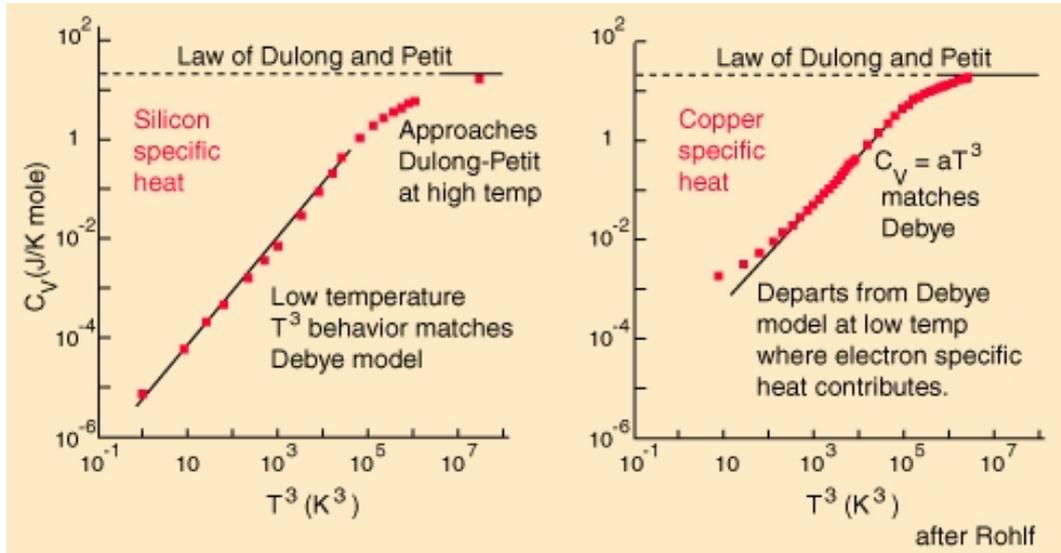
$$\sigma(\omega) = \frac{ne^2\tau}{m(1 - i\omega\tau)} \rightarrow \frac{ne^2\tau}{m}$$

$$R_H = \frac{1}{nq}$$

(q is carrier charge, n is carrier density, τ is relaxation time = $1/\gamma$)

The problems with Drude

- If the electrons are treated like an ideal gas – why is their heat capacity so low?
- Measured heat capacity falls far below that expected from equipartition theorem.

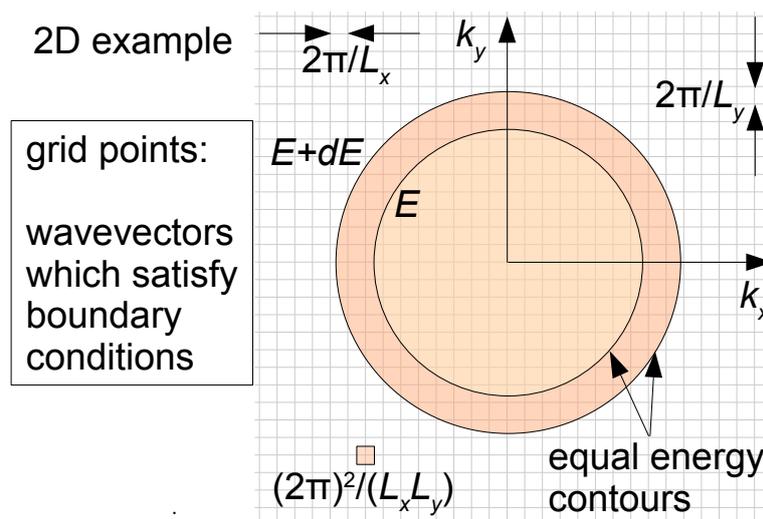


- Correct description: degenerate Fermi gas (cf. Stat. Phys. course).
- Interpret velocity \dot{u} in Drude model as *drift velocity*, averaged over many particles. Individual electrons travel at up to 1% of speed of light!

Sommerfeld model: degenerate Fermi gas in a uniform potential

(periodic boundary conditions, density of states, heat capacity: see Singleton book, Thomas-Fermi screening: handout)

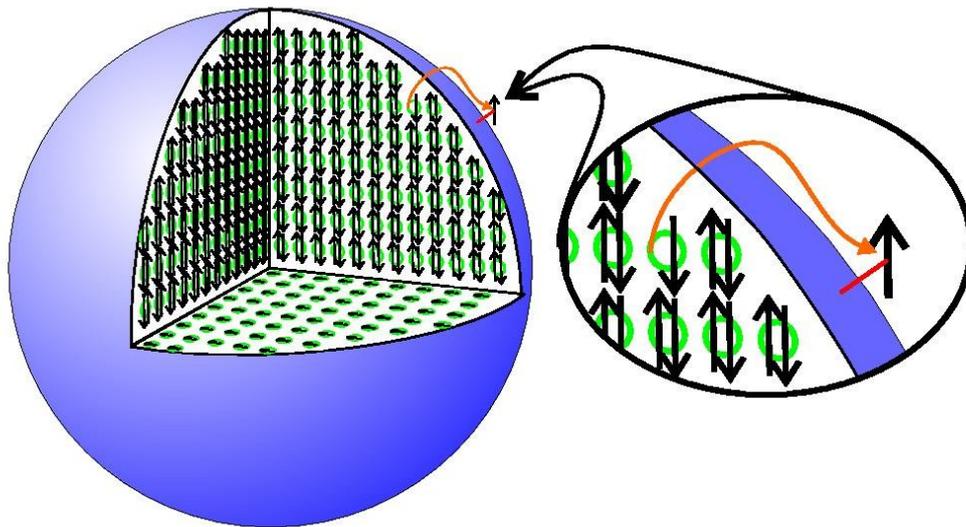
Consequence of periodic boundary conditions: discrete allowed states in k -space



- In 3D: density of allowed k -points $= \frac{1}{\Delta k^3} = \frac{\text{Volume}}{(2\pi)^3}$
- Number of allowed k -points between equal energy surfaces at E and $E + dE$:

$$g(E)dE = 4\pi k^2 dk \frac{\text{Volume}}{(2\pi)^3}$$

Free electron gas in 3D



Free electron **states**

Parabolic **dispersion**

Fermi surface at

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

$$\epsilon_{\mathbf{k}} = \frac{\hbar^2 |\mathbf{k}|^2}{2m}$$

$$k_F^3 = 3\pi^2 n$$

Heat capacity of electron gas

- The key result is:

$$C(T) = \frac{\pi^2}{3} k_B^2 T g(E_F) \propto T$$

($g(E_F)$ is the density of states at the Fermi level)

- For a parabolic band (free electrons), this corresponds to $C(T) = (\pi^2/2)(N/E_F)$, where N is the number of electrons.
- The value of $g(E_F)$ or of N depends on what quantity of material the heat capacity is calculated for (per volume, per mass, per mole?).
- **Simple argument:** electrons within range $k_B T$ of Fermi energy ϵ_F each contribute $(3/2)k_B T$ to internal energy by equipartition theorem. Their number is $g(\epsilon_F)k_B T$, and so the internal energy is $U = 3/2 k_B^2 T^2 g(E_F)$. Differentiation gives $C(T) \sim 3k_B^2 T g(E_F)$

Heat capacity of electron gas – calculation (details non-examinable)

- The detailed calculation is more cumbersome. It is not really important for the course, but given for completeness. There are many other ways to do this.
- We are looking for $C_N = \partial U / \partial T|_N = T \partial S / \partial T|_N$.
- This is difficult. Instead, first calculate

$$C_\mu = T \left. \frac{\partial S}{\partial T} \right|_\mu = \left. \frac{\partial(U - \mu N)}{\partial T} \right|_\mu$$

- U and N result from integrals over energy ϵ , including Fermi occupation numbers n_F and density of states $g(\epsilon)$:

$$U = \int_{-\infty}^{\infty} g(\epsilon) n_F(\epsilon) \epsilon d\epsilon$$

$$N = \int_{-\infty}^{\infty} g(\epsilon) n_F(\epsilon) d\epsilon$$

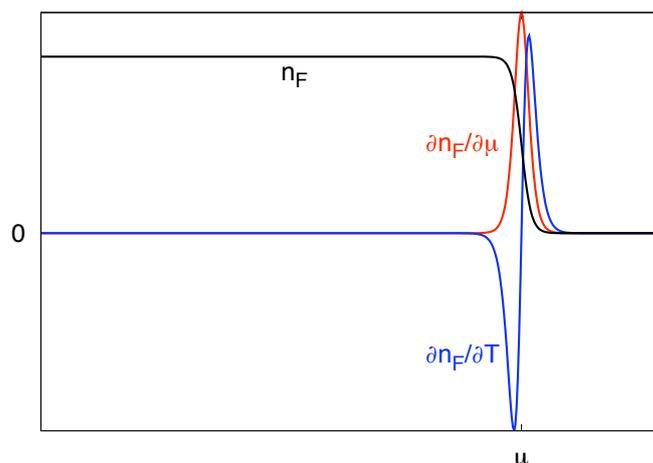
Heat capacity of electron gas – calculation step 2

- Hence,

$$C_\mu(T) = \int g(\epsilon) (\epsilon - \mu) \left. \frac{\partial n_F}{\partial T} \right|_\mu d\epsilon$$

$$n_F = \frac{1}{e^{(\epsilon - \mu)/k_B T} + 1}; \quad \frac{\partial n_F}{\partial \mu} = \frac{1}{k_B T} \frac{e^{(\epsilon - \mu)/k_B T}}{(e^{(\epsilon - \mu)/k_B T} + 1)^2}; \quad \frac{\partial n_F}{\partial T} = \frac{\epsilon - \mu}{T} \frac{\partial n_F}{\partial \mu}$$

- $\frac{\partial n_F}{\partial \mu}$ is even around μ , $\frac{\partial n_F}{\partial T}$ is odd around μ , both are $\neq 0$ only near μ :



Heat capacity of electron gas – calculation step 3

- Conveniently, we are looking for C_μ , i.e. μ is taken to be constant = ϵ_F (Fermi energy). Taylor expand $g(\epsilon)$ around ϵ_F :

$$g(\epsilon) = g_0 + g_1(\epsilon - \epsilon_F)$$

- The integral selects only the terms in $g(\epsilon)$ which are even around ϵ_F , in our case g_0 :

$$C_\mu(T) = \frac{1}{k_B T^2} g_0 \int_{-\infty}^{\infty} (\epsilon - \epsilon_F)^2 \frac{e^{(\epsilon - \epsilon_F)/(k_B T)}}{(e^{(\epsilon - \epsilon_F)/(k_B T)} + 1)^2} d\epsilon = g_0 k_B^2 T \frac{\pi^2}{3}$$

- To translate this into $C_N(T)$, use $dS = \partial S/\partial T|_\mu dT + \partial S/\partial \mu|_T d\mu$, together with the Maxwell relation $\partial S/\partial \mu|_T = \partial N/\partial T|_\mu$:

$$C_N(T) = C_\mu(T) + T \left. \frac{\partial S}{\partial \mu} \right|_T \left. \frac{\partial \mu}{\partial T} \right|_N = C_\mu(T) + T \left. \frac{\partial N}{\partial T} \right|_\mu \left. \frac{\partial \mu}{\partial T} \right|_N$$

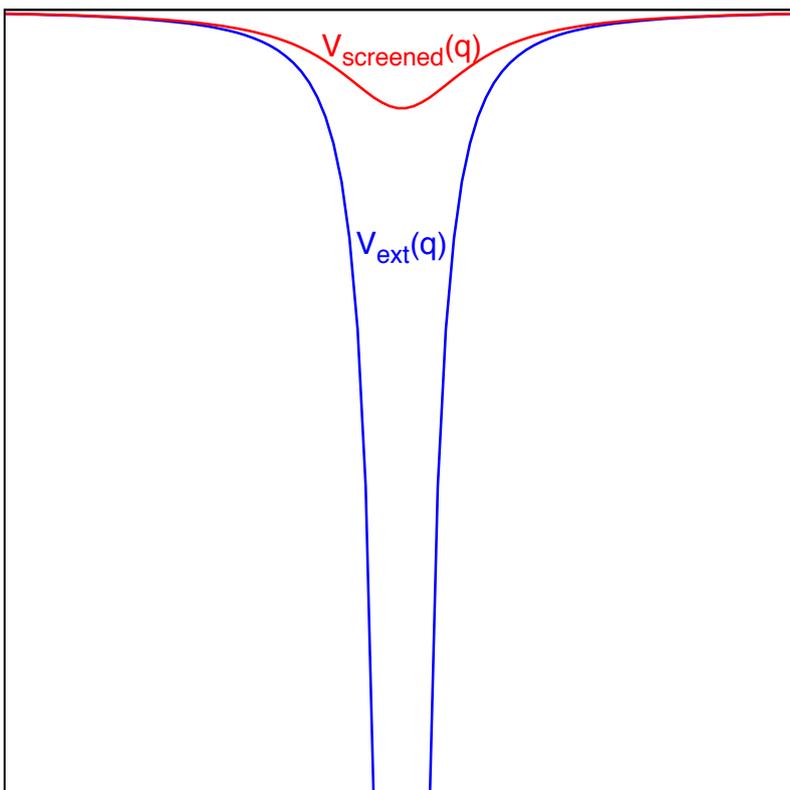
- Correction term $\propto T^3 \implies$ negligible at low T :

$$T \left. \frac{\partial N}{\partial T} \right|_\mu \left. \frac{\partial \mu}{\partial T} \right|_N \simeq \frac{g_1^2}{g_0} k_B^4 T^3 \frac{\pi^4}{9}$$

Screening in metals

(Electron gas responds to applied static potential, e.g. due to additional charges implanted in the material. This reduces the effect of the additional charge and screens the resulting electrostatic field at long distance.)

Screening in metals: Overview



- Insert external charge, causes Coulomb potential:

$$\nabla^2 V^{(ext)}(\mathbf{r}) = -\frac{\rho^{(ext)}(\mathbf{r})}{\epsilon_0},$$

$$\rho^{(ext)} = -en^{(ext)}$$

- Consider Fourier cpts:
 $V(\mathbf{r}) = V_{\mathbf{q}} e^{i\mathbf{q}\mathbf{r}}$, etc.

- Wavevector-dependence:

$$V_{\mathbf{q}}^{(ext)} = -\frac{e}{\epsilon_0 q^2} n_{\mathbf{q}}^{(ext)}$$

- In empty space: Full potential = $V_{\mathbf{q}}^{(tot)} = V_{\mathbf{q}}^{(ext)}$

- In metal: electrons move to screen the external potential

$$\rightarrow V_{\mathbf{q}}^{(tot)} = V_{\mathbf{q}}^{(ext)} + \delta V_{\mathbf{q}}$$

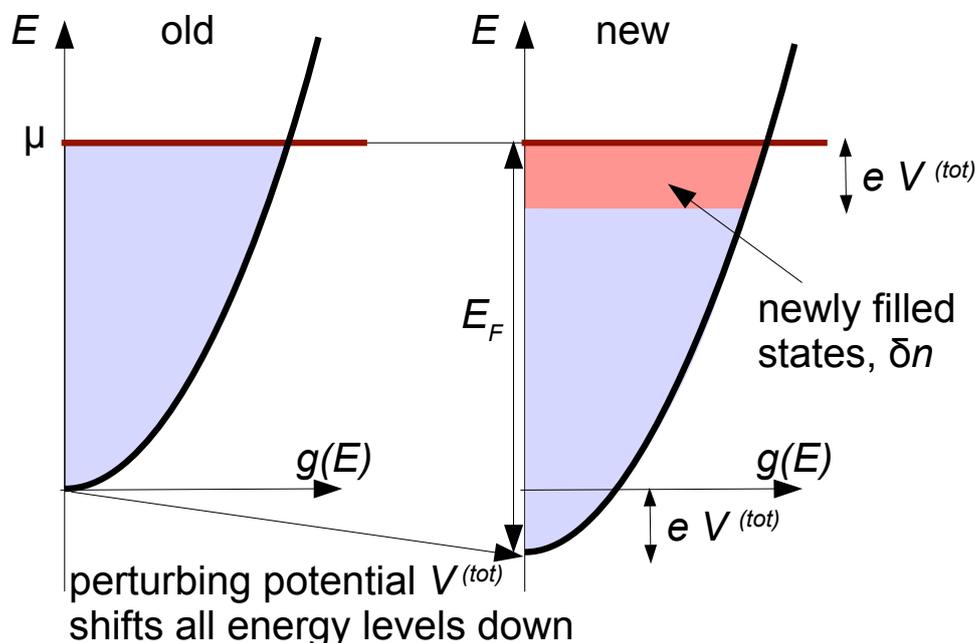
- Difficult to solve Schrödinger and Poisson equations self-consistently in presence of spatially varying external potential $V^{(tot)}$.
- Instead: **assume that spatial variation of potential is 'slow'**. We mean by that: characteristic length-scale is larger than wavelength of electronic states close to Fermi energy.
- Then, take potential $V^{(tot)}$ as constant over a small region of sample and use Fermi gas calculation with this changed, but uniform (only over small region) potential: **coarse-graining**.
- This is very doable, but we will find that the resulting screened potential **does vary** quite rapidly in space, which puts a question mark over the entire procedure.
- Nevertheless, it's the best we can do for now. More to follow in Part III Advanced Quantum Condensed Matter course.

Thomas-Fermi approximation: perturbing potential moves electronic energy levels

- Electronic energy levels shift in the presence of new potential $V^{(tot)}$

$$E_{\mathbf{k}} = E_{\mathbf{k}}^0 - eV^{(tot)}$$

($E_{\mathbf{k}}^0$ = energy of electron at wavevector \mathbf{k} , before perturbation was introduced).



Thomas-Fermi approximation: induced charge density from energy level shift

- Chemical potential μ remains constant \implies Fermi energy, as measured from bottom of the band, varies.

$$E_F = \mu + eV^{(tot)}$$

(E_F measured from bottom of band!)

- Additional local electron density ($g_V(E_F)$ is d.o.s. per unit volume at E_F)

$$\delta n \simeq e g_V(E_F) V^{(tot)}$$

- Poisson's equation

$$\nabla^2 \delta V = \frac{e}{\epsilon_0} \delta n = \frac{e^2}{\epsilon_0} g_V(E_F) (V^{(ext)} + \delta V)$$

- Induced potential

Thomas Fermi wavevector, $q_{TF}^2 = e^2 g_V(E_F) / \epsilon_0$

$$\delta V_{\mathbf{q}} = -\frac{q_{TF}^2}{q^2 + q_{TF}^2} V_{\mathbf{q}}^{(ext)}$$

Screening and Thomas-Fermi theory – a second look at the characters involved.

$$\nabla^2 V^{(ext)}(\mathbf{r}) = -\frac{\rho^{(ext)}}{\epsilon_0}$$

$$\rho_{tot}(\mathbf{r}) = \rho^{(ext)}(\mathbf{r}) + \delta\rho(\mathbf{r})$$

$$\nabla^2 V^{(tot)}(\mathbf{r}) = -\frac{1}{\epsilon_0} (\rho^{(ext)}(\mathbf{r}) + \delta\rho(\mathbf{r}))$$

$$\nabla^2 \delta V(\mathbf{r}) = -\frac{\delta\rho(\mathbf{r})}{\epsilon_0}$$

- Potential due to externally introduced charges
- causes charges to flow, inducing additional charge density $\delta\rho$,
- which determines full potential $V^{(tot)}$.
- Screening potential due to induced charges.

Screening and Thomas-Fermi theory – generalised permittivity and induced charge

$$\nabla V^{(ext)} = -\mathbf{D}/\epsilon_0, \quad \nabla V^{(tot)} = -\mathbf{E}$$

$$\mathbf{D}_{\mathbf{q}} = \epsilon_0 \epsilon(\mathbf{q}) \mathbf{E}_{\mathbf{q}}$$

$$i\mathbf{q} V_{\mathbf{q}}^{(ext)} = i\mathbf{q} \epsilon(\mathbf{q}) V_{\mathbf{q}}^{(tot)}$$

$$V_{\mathbf{q}}^{(ext)} = \epsilon(\mathbf{q}) V_{\mathbf{q}}^{(tot)}$$

- Free charges cause \mathbf{D} and $V^{(ext)}$, all charges cause \mathbf{E} and $V^{(tot)}$.
- Generalised wavevector dependent permittivity $\epsilon(\mathbf{q})$
- $\epsilon(\mathbf{q})$ links external and total potential.

$$\epsilon(\mathbf{q}) = 1 + \frac{q_{TF}^2}{q^2}$$

Note also: Total **induced charge = externally introduced charge**

$$\delta V_{\mathbf{q}} = -\frac{q_{TF}^2}{q^2 + q_{TF}^2} V_{\mathbf{q}}^{(ext)} \Rightarrow \delta n_{\mathbf{q}} = -\frac{q_{TF}^2}{q^2 + q_{TF}^2} n_{\mathbf{q}}^{(ext)}$$

$$\overline{\delta n} = \delta n(\mathbf{q} = 0) = -\overline{n^{(ext)}}$$

Fourier transforms in QCMP

(A mathematical excursion for your notes)

Finite sample volume: Fourier series

- $f(\mathbf{r})$ continuous function. Express as vector $|f\rangle$.
- First set of **basis functions**: sharp peak at position \mathbf{r} : $|\mathbf{r}\rangle$

$$f(\mathbf{r}) \equiv \langle \mathbf{r} | f \rangle$$

- Second set of basis functions: **plane wave** states with wavevector \mathbf{q} : $|\mathbf{q}\rangle$. $\langle \mathbf{r} | \mathbf{q} \rangle = \frac{1}{\sqrt{V}} e^{i\mathbf{q}\mathbf{r}}$.
- Periodic boundary condition: $\hat{T}_L |\mathbf{q}\rangle = |\mathbf{q}\rangle$. \Rightarrow allowed values $\mathbf{q} = 2\pi(n_x/L_x, n_y/L_y, n_z/L_z)$.

$$\Delta \mathbf{q}^3 = (2\pi)^3 / V$$

Inner product

$$\langle f | g \rangle \equiv \int_{\text{sample vol.}} f^*(\mathbf{r}) g(\mathbf{r}) d^3 \mathbf{r}$$

- **Orthonormal** basis: $\langle \mathbf{q}_1 | \mathbf{q}_2 \rangle = \delta_{\mathbf{q}_1, \mathbf{q}_2}$, $\hat{\mathbf{1}} = \sum_{\mathbf{q}} |\mathbf{q}\rangle \langle \mathbf{q}|$.
- **Fourier components**: projection onto basis vectors:

$$f_{\mathbf{q}} = \langle \mathbf{q} | f \rangle \equiv \frac{1}{\sqrt{V}} \int d^3 \mathbf{r} e^{-i\mathbf{q}\mathbf{r}} f(\mathbf{r})$$

Reverse:

$$f(\mathbf{r}) = \sum_{\mathbf{q}} \langle \mathbf{r} | \mathbf{q} \rangle \langle \mathbf{q} | f \rangle = \frac{1}{\sqrt{V}} \sum_{\mathbf{q}} f_{\mathbf{q}} e^{i\mathbf{q}\mathbf{r}}$$

Continuum limit: Fourier transform

- **Continuum limit:** $V \rightarrow \infty$.

$$\sum_{\mathbf{q}} \rightarrow \frac{1}{\Delta \mathbf{q}^3} \int d^3 \mathbf{q}$$

- The problem: how to get rid of V (which $\rightarrow \infty$) in $\Delta \mathbf{q}^3$?
- The solution: different basis function:

$$\begin{aligned} \langle \mathbf{r} | \mathbf{q} \rangle &= e^{i\mathbf{q}\mathbf{r}} \Rightarrow \\ | \mathbf{q}_{\text{continuous}} \rangle &= \sqrt{V} | \mathbf{q}_{\text{discrete}} \rangle. \end{aligned}$$

- Now

$$\hat{\mathbf{1}} = \int \frac{d^3 \mathbf{q}}{(2\pi)^3} | \mathbf{q} \rangle \langle \mathbf{q} |.$$

- Fourier components $f_{\mathbf{q}} \rightarrow$ **Fourier transform** $f(\mathbf{q})$.

$$f(\mathbf{q}) = \langle \mathbf{q} | f \rangle \equiv \int e^{-i\mathbf{q}\mathbf{r}} f(\mathbf{r}) d^3 \mathbf{r}$$

Reverse transform

$$f(\mathbf{r}) = \langle \mathbf{r} | \hat{\mathbf{1}} | f \rangle = \int \frac{d^3 \mathbf{q}}{(2\pi)^3} f(\mathbf{q}) e^{i\mathbf{q}\mathbf{r}}$$

- For $f(\mathbf{q}) = \delta(\mathbf{q})$, $f(\mathbf{r}) = 1/(2\pi)^3$. Hence **key integrals**

$$\begin{aligned} \int e^{-i\mathbf{q}\mathbf{r}} d^3 \mathbf{r} &= (2\pi)^3 \delta(\mathbf{q}) \\ \int e^{i\mathbf{q}\mathbf{r}} \frac{d^3 \mathbf{q}}{(2\pi)^3} &= \delta(\mathbf{r}) \end{aligned}$$

Chemical bonds give rise to solids

(Covalent, ionic, metallic, van der Waals)

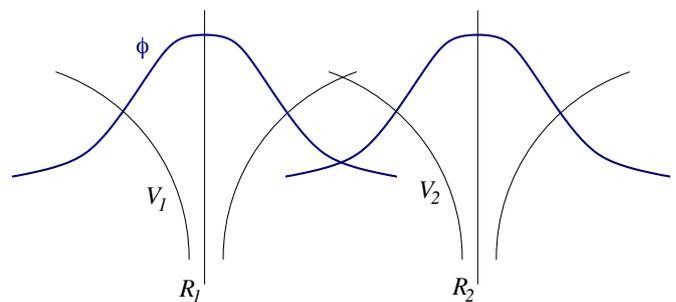
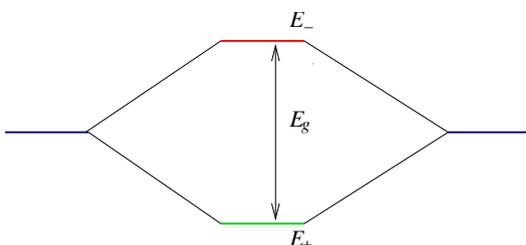
The electron glue: bonding

Covalent bonds, Hydrogen

- Overlapping orbitals on neighbouring atoms hybridise.
- Simple case: if \mathbf{H} symmetric, then ψ is even or odd.
- Atomic states: $\phi(\mathbf{r} - \mathbf{R})$ (nucleus at R) give

$$\psi_{\pm}(r) = \phi(\mathbf{r} - \mathbf{R}_a) \pm \phi(\mathbf{r} - \mathbf{R}_b)$$

- ψ_+ high between atoms, where ψ_- has a node.



- For attractive potential $E_+ < E_-$
- Two electrons in lower (**bonding**) state ψ_+ . **antibonding** state ψ_- separated by energy gap $E_g = E_- - E_+$, unfilled.
- Cohesive energy $\simeq E_g$

This is an example in degenerate perturbation theory; more details:

- Note that we are calculating **single-electron levels**. Electron-electron repulsion is neglected.
- Use Dirac notation: $\langle \mathbf{r} | a \rangle = \phi(\mathbf{r} - \mathbf{R}_a)$, $\langle \mathbf{r} | b \rangle = \phi(\mathbf{r} - \mathbf{R}_b)$.
- Look for energy eigenfunction within restricted subspace spanned by orthonormal basis functions, e.g. atomic orbitals: $|\psi\rangle = \alpha |a\rangle + \beta |b\rangle$
- Apply Hamiltonian \mathbf{H} :

$$\begin{aligned}\mathbf{H}|\psi\rangle &= E|\psi\rangle \\ \alpha\mathbf{H}|a\rangle + \beta\mathbf{H}|b\rangle &= \alpha E|a\rangle + \beta E|b\rangle\end{aligned}$$

- Left multiply with $|a\rangle$ and $|b\rangle$:

$$\begin{aligned}\alpha \langle a | \mathbf{H} | a \rangle + \beta \langle a | \mathbf{H} | b \rangle &= \alpha E \\ \alpha \langle b | \mathbf{H} | a \rangle + \beta \langle b | \mathbf{H} | b \rangle &= \beta E\end{aligned}$$

Covalent bonding calculation continued

- Obtain an eigenvector equation for the coefficients α, β , which only has non-trivial solutions if the determinant is zero:

$$\begin{vmatrix} H_{aa} - E & H_{ab} \\ H_{ab}^* & H_{bb} - E \end{vmatrix} = 0$$

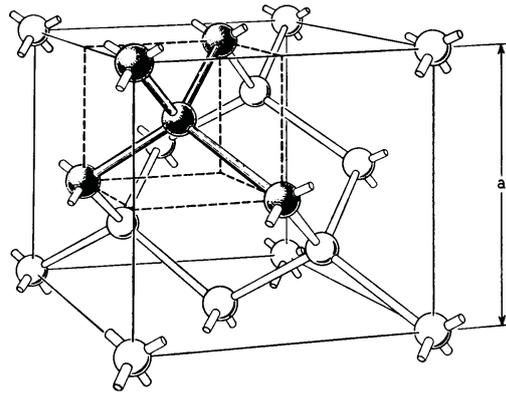
- Obtain energy eigenvalues E distributed around the average of the H_{aa} and H_{bb} :

$$E = \frac{H_{aa} + H_{bb}}{2} \pm \frac{\Delta E}{2}, \quad \frac{\Delta E}{2} = \left(\left(\frac{H_{aa} - H_{bb}}{2} \right)^2 + |H_{ab}|^2 \right)^{1/2}$$

- For $H_{aa} \simeq H_{bb}$, $\Delta E/2 = |H_{ab}|$: covalent bonding.
However, for $H_{aa} \ll H_{bb}$ (or the other way around): $E = H_{aa}$ or H_{bb} . H_{ab} irrelevant: ionic bonding.

Covalent semiconductors

- p, d orbitals → **directed** bonds. Low coordination numbers ($\simeq 4$)
- sp^3 hybrid orbitals in $C, Si,$ and Ge .
- Point in tetrahedral directions $(111), (\bar{1}\bar{1}1), (\bar{1}1\bar{1}), (1\bar{1}\bar{1})$. Each atom gives one electron.
- Open tetrahedral network = **diamond structure**.



Ionic semiconductors:

- GaAs and ZnS (“III-V”) satisfy octet rule.
- Tetrahedral structure, but atoms alternate → **zincblende** structure.
- Part ionic, part covalent.

IV → diamond, III-V → zincblende, II-VI → zincblende or wurtzite, I-VII → rocksalt.

Ionic crystals

Atoms close to filled shell → lose or gain electrons to fill shell.

- Energy for reaction $M \rightarrow M^+ + e^-$ in gas phase = **ionization energy I** .
- Energy for reaction $X + e^- \rightarrow X^-$ in gas phase = **electron affinity A** .
- Can overcome $I + A$ by electrostatic attraction, $e^2/(4\pi\epsilon_0 R)$
- Electrostatic interaction energy for diatomic crystal:

$$U_{\text{electrostatic}} = \frac{1}{2} \sum_i \sum_j U_{ij}$$

($U_{ij} = \pm q^2/(4\pi\epsilon_0 R_{ij})$ is sum of all Coulomb forces between ions.)

- On a regular lattice of lattice constant R :

$$U_{\text{electrostatic}} = -\frac{1}{2} N \frac{\alpha_M q^2}{4\pi\epsilon_0 R}$$

(Madelung constant $\alpha_M \sim 1$, depends on structure.)

- Also consider **short-range repulsion** (hard core) → different ionic sizes.
- Intermediate coordination numbers $\simeq 6 - 8$.

Inert gas atoms

- Filled shells, large ionisation energy
- Atoms neutral, interaction weak
- At large distance R :

van der Waals interaction

$$V(R) \propto -1/R^6$$

van der Waals

- Consider atom as oscillator
- Electrons fluctuate around nucleus
- Zero-point fluctuations cause dipole moment p

Induced interaction $\propto \langle p_1^2 \rangle > 0$, always attractive!



Induced interaction

- Atom 2 feels induced field $E(r_2) \propto p_1/R^3$
- $E(r_2)$ causes dipole $p_2 \propto \alpha p_1/R^3$ (α is atomic polarizability)
- p_2 induces $E(r_1) \propto p_2/R^3 \propto \alpha p_1/R^6$
- Energy due to interaction: $V(R) = \langle -p_1 \cdot E_1 \rangle \propto -\alpha \langle p_1^2 \rangle / R^6$

Inert gas and molecular solids

Short range (hard-core) **repulsion**

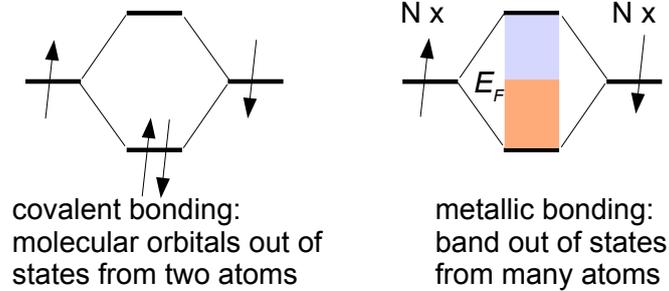
- Pauli exclusion principle: core electrons forced into **high energy states**.
- Energy grows rapidly with decreasing separation.
- Combine with long range van der Waals attraction:

$$U(R) = -\frac{A}{R^6} + \frac{B}{R^{12}}$$

(Lennard-Jones, empirical)

- Solids usually close-packed (fcc) and have high coordination numbers $\simeq 10 - 12$.

Metals



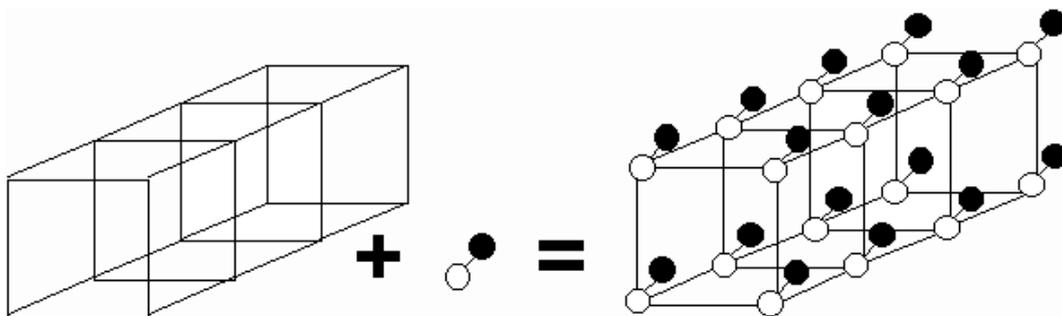
- **Band** forms from atomic states. Partially filled \rightarrow energy gain, generalisation of covalent bond to 'giant molecule'.
- Electrons in band states **delocalised**. Bonding is isotropic, like van der Waals.
- **Close packing**. to maximise density while keeping atomic cores far apart: fcc or hcp. High coordination numbers $\simeq 10 - 12$.
- **Screening by conduction electrons**. Screening length $\simeq 1 \text{ \AA}$.
- **Within a row** in periodic table: ion core potential grows. Density increases. Crossover to covalent, then molecular structures.
- **Transition metals**. d-electrons more localised, inside full s-orbital. Can be spin-polarised \rightarrow magnetism in 3d elements. 4d and 5d orbitals overlap \rightarrow high binding energy (e.g. W).

Crystal lattices

(Lattices and crystal symmetry: Singleton book, appendix. Lattice vibrations, phonons: last year's Solid State course.)

The lattice

- Ideal crystal = infinite **repetition** of structural **unit**.
- Repeating structure = **lattice**
- Group of atoms, which is repeated = **basis**



- **Bravais lattice:** built by combining translations.
- **Primitive** translation vectors \mathbf{a}_i , $i = 1, 2, 3$

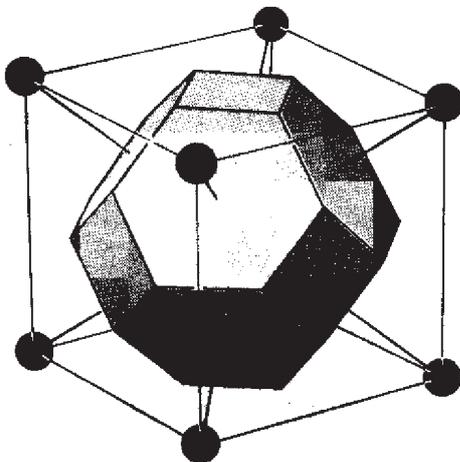
$$\mathbf{r}' = \mathbf{r} + \sum_i n_i \mathbf{a}_i \quad \forall \text{ integer } n_i .$$

- **Primitive unit cell:** formed by \mathbf{a}_i .
- Arbitrary lattice translation operation:

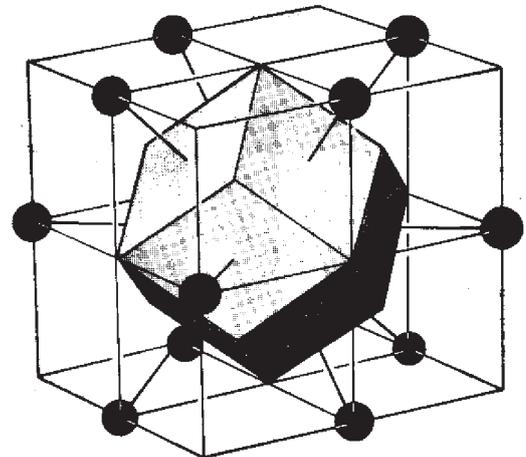
$$\mathbf{T} = \sum_i n_i \mathbf{a}_i$$

Wigner-Seitz cell

- Connect lattice point to its near neighbours.
- Draw planes normal to lines, through midpoints of lines.
- Smallest volume enclosed: **Wigner-Seitz primitive unit cell.**



bcc lattice, Wigner Seitz cell



fcc lattice, Wigner Seitz cell

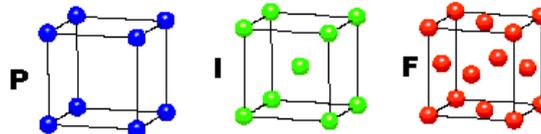
- Symmetry operations which map lattice onto itself → **Space group**.
- Map lattice onto itself, but keep one point fixed → **Point group**.
- Point group operations: reflections, inversions, rotations
- Seven point groups for Bravais lattices = **Seven crystal systems**
cubic, tetragonal, orthorhombic, monoclinic, triclinic, trigonal, hexagonal.
- Fourteen space groups for Bravais lattices
- **General crystal structures** (Bravais lattice + basis): 32 point groups, 230 space groups.

The Bravais lattice types

CUBIC

$$a = b = c$$

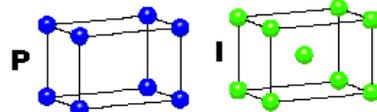
$$\alpha = \beta = \gamma = 90^\circ$$



TETRAGONAL

$$a = b \neq c$$

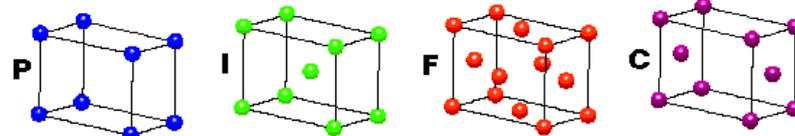
$$\alpha = \beta = \gamma = 90^\circ$$



ORTHORHOMBIC

$$a \neq b \neq c$$

$$\alpha = \beta = \gamma = 90^\circ$$

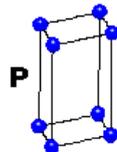


HEXAGONAL

$$a = b \neq c$$

$$\alpha = \beta = 90^\circ$$

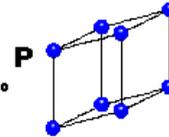
$$\gamma = 120^\circ$$



TRIGONAL

$$a = b = c$$

$$\alpha = \beta = \gamma \neq 90^\circ$$

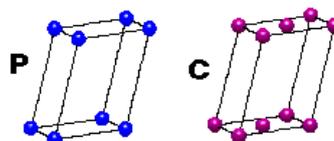


MONOCLINIC

$$a \neq b \neq c$$

$$\alpha = \gamma = 90^\circ$$

$$\beta \neq 120^\circ$$



TRICLINIC

$$a \neq b \neq c$$

$$\alpha \neq \beta \neq \gamma \neq 90^\circ$$



4 Types of Unit Cell

P = Primitive
I = Body-Centred
F = Face-Centred
C = Side-Centred

+

7 Crystal Classes
→ 14 Bravais Lattices

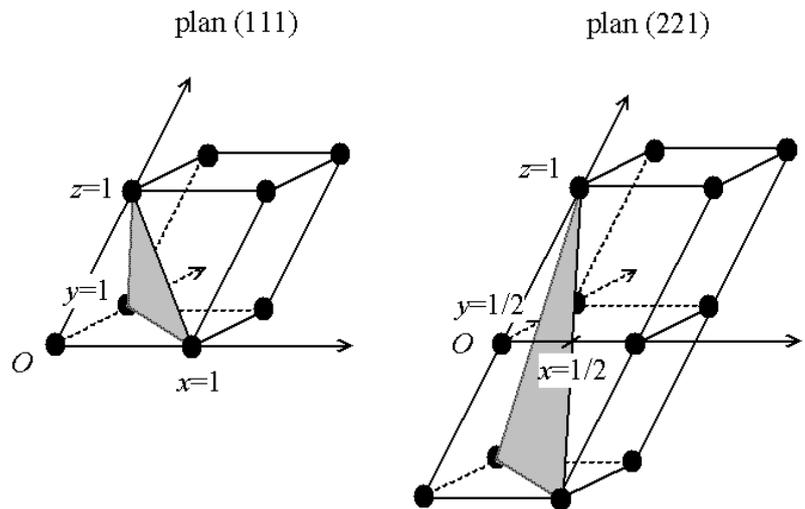
Index system for crystal planes

- **Label plane** by coordinates where it **cuts axes**.

$$\{\mathbf{r}_i\} = \{x\mathbf{a}_1, y\mathbf{a}_2, z\mathbf{a}_3\}$$

- (hkl) denotes plane which cuts at \mathbf{a}_1/h , \mathbf{a}_2/k and \mathbf{a}_3/l (or multiple thereof, so that $xh = yk = zl = \text{integer}$).

- (hkl) is **index** of the plane.
- Set of planes equivalent by symmetry: use $\{\}$. $\{100\}$ for a cubic crystal = equivalent symmetry planes (100) , (010) , (001) , $(\bar{1}00)$, $(0\bar{1}0)$, $(00\bar{1})$
- Overbar $\bar{1}$ denotes negation.



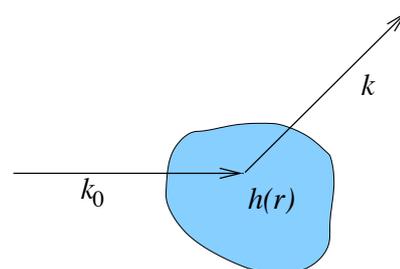
Diffraction from Bravais lattice

- Scattering theory: Waves incident on sample diffracted by periodic lattice.
- Incoming **wave-vector** \mathbf{k}_0 , outgoing \mathbf{k} , $|\mathbf{k}_0| = |\mathbf{k}|$, scattering amplitude $h(\mathbf{r})$.
- **Intensity** on screen (detector):

$$I(\mathbf{k}) = \left| \int h(\mathbf{r}) e^{i(\mathbf{k}_0 - \mathbf{k})\mathbf{r}} dV \right|^2$$

Fourier transform of $h(\mathbf{r})!$

Scattering geometry:



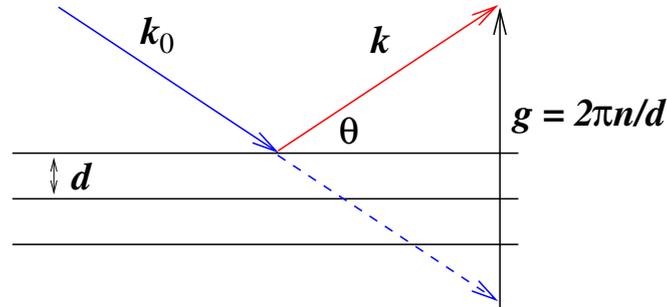
- Periodic lattice: peaks at $\mathbf{k} - \mathbf{k}_0 = \mathbf{g}$, where \mathbf{g} is reciprocal lattice vector.
- \mathbf{g} is such that $\exp(i\mathbf{g}\mathbf{R}) = 1$ ($\implies \mathbf{g}\mathbf{R} = 2\pi n$) for all \mathbf{R} in Bravais lattice.

Reciprocal lattice

- Primitive **reciprocal lattice** vectors:

$$\mathbf{b}_1 = 2\pi \frac{\mathbf{a}_2 \wedge \mathbf{a}_3}{\mathbf{a}_1 \cdot \mathbf{a}_2 \wedge \mathbf{a}_3} \quad \text{and cyclic permutations .}$$

- Diffraction peaks at $\mathbf{k} - \mathbf{k}_0 = \mathbf{g}$:



- Because \mathbf{g} is related to distance between planes, d , by $|\mathbf{g}| = 2\pi n/d$, this gives Bragg condition:

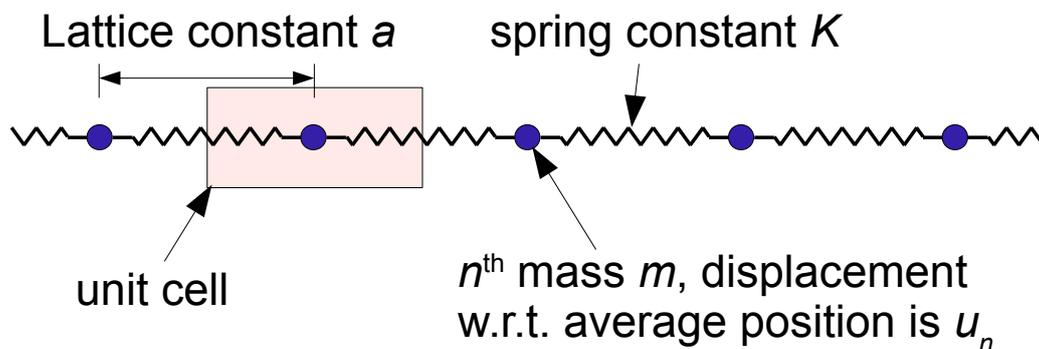
$$|k| \sin \theta = |g|/2 \implies 2d \sin \theta = n\lambda$$

- Define **Brillouin zone**: Wigner-Seitz cell in reciprocal space. Number of allowed k -points in BZ = N (number of unit cells in the sample).

Lattice vibrations

(Phonon dispersion. Diatomic chain (optical and acoustic modes). Heat capacity)

1D monatomic chain

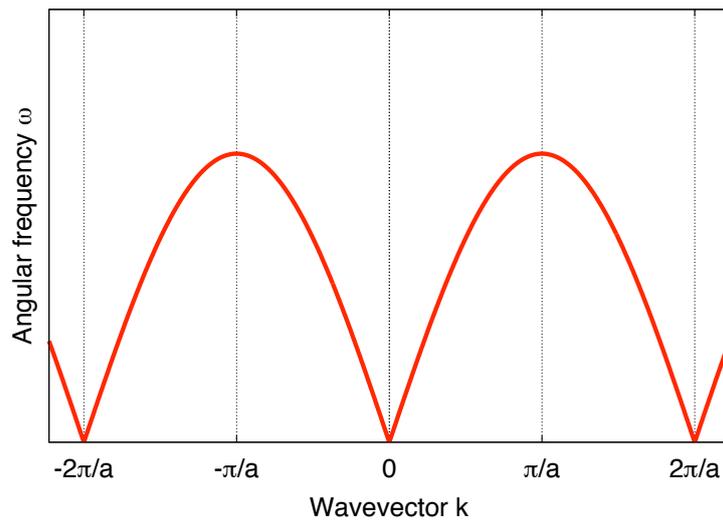


$$m\ddot{u} = K(u_{n+1} - u_n) + K(u_{n-1} - u_n)$$

- Plane wave solutions $u_n(t) = u_0 e^{ikR_n - \omega t}$
- Periodic boundary condition: $u_{N+n}(t) = u_n(t) \implies$ allowed wavenumbers = integer $\times \frac{2\pi}{L}$ (L = length of chain).

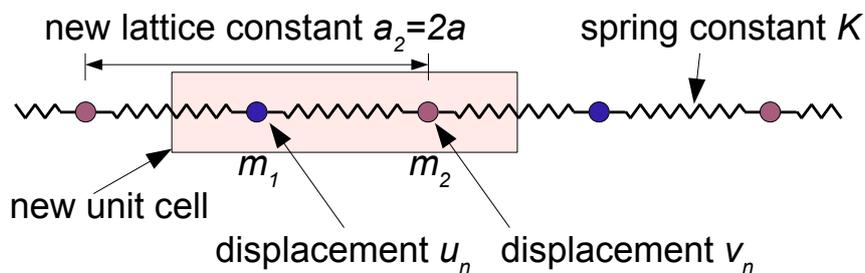
$$\omega(k) = 2(K/m)^{1/2} \left| \sin\left(\frac{ka}{2}\right) \right|$$

Dispersion of lattice vibrations in a monatomic chain

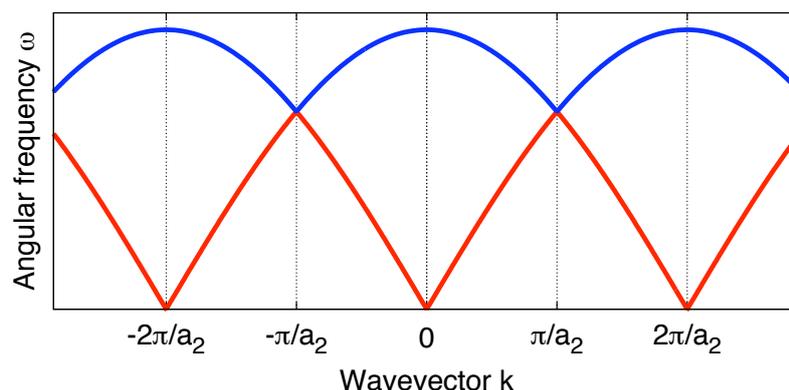


- Periodic in k with period $2\pi/a$ (=reciprocal lattice vector).
- Linear at low k : $\omega = vk$ like sound waves.
- Phase shift between neighbouring atoms is e^{ika} . At $k = \pi/a$ (Brillouin zone boundary), neighbouring atoms are in antiphase.

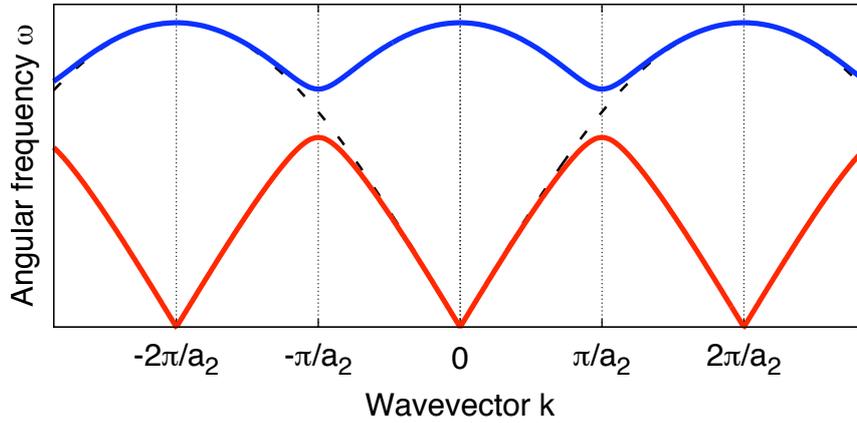
1D diatomic chain obtained by doubling the unit cell



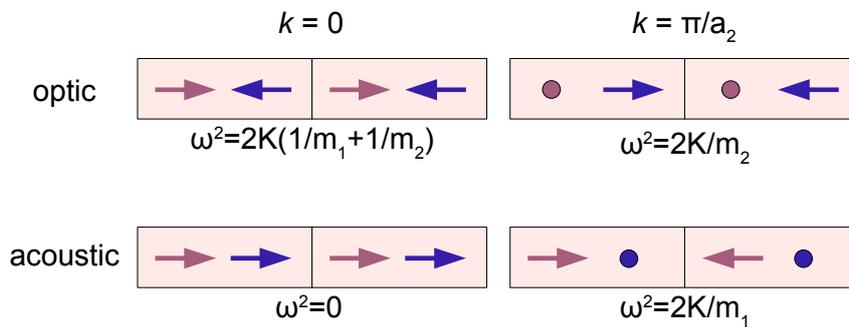
- What if $m_1 = m_2$? Dispersion relation should remain the same, but Brillouin zone has shrunk.
- A second branch appears in dispersion relation \rightarrow optical mode.



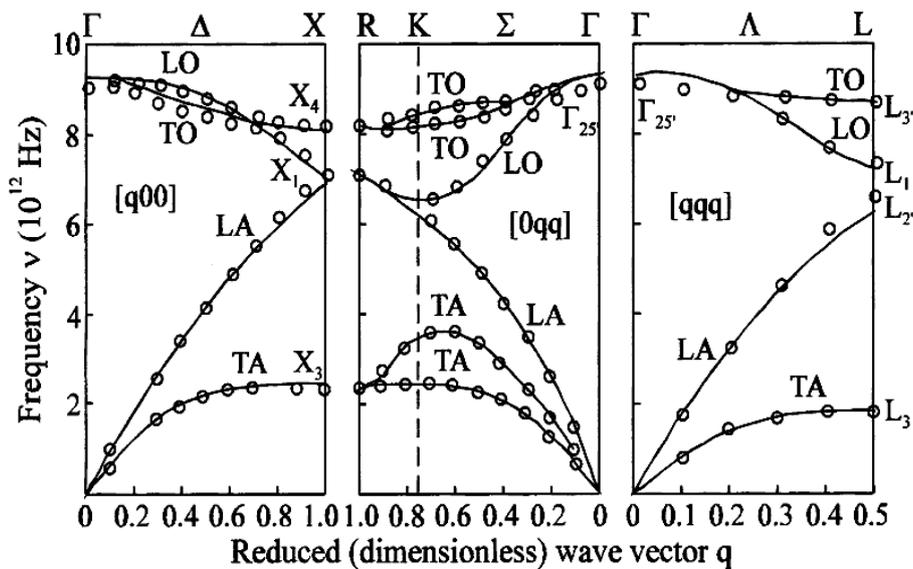
Dispersion of diatomic chain with different masses



- Different masses split degeneracy at $k = \pi/a_2 (= \pi/(2a))$.
- Note simple normal mode patterns at $k = 0$ and at $k = \pi/a_2$



Phonon dispersion in 3D crystal



[Phonon dispersion in Germanium. Diamond structure, 2 atoms/cell.]

- In 3D: one longitudinal (displacement $\parallel \mathbf{k}$) and two transverse modes for every atom in the unit cell.
- Three of these modes are acoustic, the rest are optical.

Heat capacity due to lattice vibrations

- Obtain internal energy due to lattice vibrations by summing phonon energies over all bands (polarisations, acoustic/optical) and all wavevectors, weighted with Bose factor.

$$U = \sum_{\text{band index } n} \sum_{\mathbf{k}} \hbar \omega_{\mathbf{k}}^{(n)} \frac{1}{e^{\hbar \omega_{\mathbf{k}}^{(n)} / k_B T} - 1}$$

where \mathbf{k} is summed over the first Brillouin zone.

- A complicated problem in general. But have simple asymptotic limits:

$$C_m \simeq \beta T^3$$

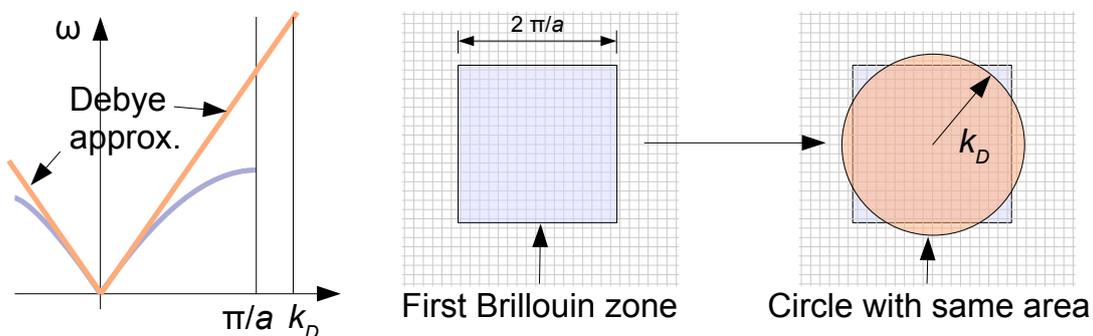
at low T and

$$C_m = 3R$$

at very high T .

Debye approximation

- Approximate the three acoustic branches by linear dispersion relation $\omega_{\mathbf{k}}^{(n)} = v^{(n)} |\mathbf{k}|$. $v^{(n)}$ are like speed of sound (at least for longitudinal mode).
- Instead of summing over Brillouin zone, sum over all modes $|\mathbf{k}| < k_D$, where k-space volume inside k_D is equal to that of Brillouin zone.



(Example in 2D. In 3D: sphere with radius k_D)

$$k_D^3 = 6\pi^2 N/V \quad ; \quad \omega_D = vk_D \quad ; \quad k_B \theta_D = \hbar \omega_D$$

θ_D is **Debye temperature**

Debye approximation – ctd

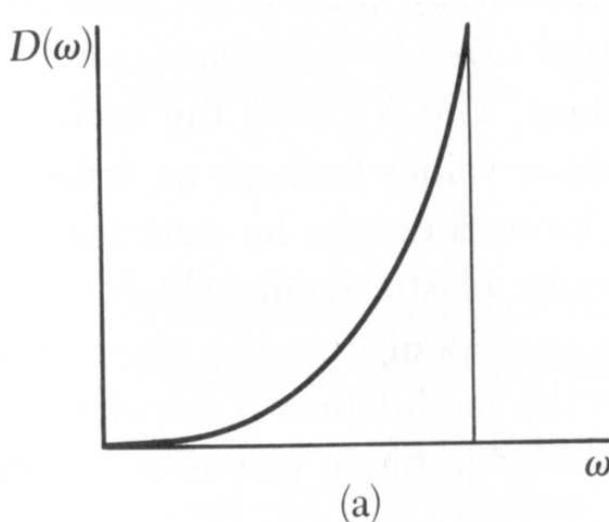
- **Freezing out** of normal modes. Consider $n_k = \frac{\hbar\omega}{k_B T} \frac{1}{\exp(\hbar\omega/(k_B T)) - 1}$:
- $n_k \rightarrow 0$ for $\hbar\omega > k_B T$
(normal mode freezes out, if temperature low compared to frequency).
- $n_k \rightarrow 1$ for $\hbar\omega < k_B T$
(normal mode is excited, if temperature is high compared to frequency).
- At low temperature, n_k determines range of the k -space integral. Using $k_{th} = k_B T / (\hbar v)$ to denote the thermal cut-off wavevector, above which the vibration modes are frozen out:

$$U = \int_0^{k_D} \frac{V}{(2\pi)^3} 4\pi k^2 dk (k_B T) n_k \sim \frac{V}{2\pi^2} k_B T k_{th}^3 = \frac{V}{2\pi^2} k_B T \left(\frac{k_B T}{\hbar v} \right)^3$$

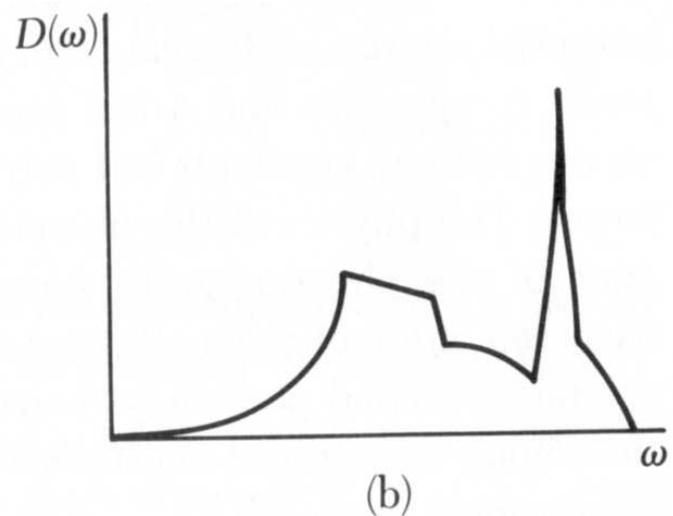
- Differentiating w.r.t. T , and doing the integral exactly, inserting Debye temperature, obtain:

$$C_m = 3R \left(\frac{T}{\theta_D} \right)^3 \frac{4\pi^4}{15}$$

Debye phonon density of states



Debye model for phonon d.o.s.



Phonon d.o.s. of a real material

- An alternative way to think about Debye theory: it approximates the density of states for lattice vibrations by a simple form, which gives the same energy dependence at low energy and the same total number of states.

Electrons in a periodic potential

(Finding single electron states in periodic potential by expanding in terms of plane wave states. Bloch's theorem. Chapter 2 in Singleton book.)

Schrödinger equation in a periodic potential – from Singleton book

- Looking for solutions to $\mathbf{H}|\psi\rangle = (\frac{\hat{p}^2}{2m} + V)|\psi\rangle = E|\psi\rangle$, where $V(\mathbf{r})$ is periodic.
- Because $V(\mathbf{r})$ has same periodicity as the lattice, can Fourier-expand it as: $V(\mathbf{r}) = \sum_{\mathbf{G}} V_{\mathbf{G}} e^{i\mathbf{G}\mathbf{r}}$, where $V_{\mathbf{G}}$ are Fourier components of V at reciprocal lattice vectors \mathbf{G} .
- For $\mathbf{G} = 0$, Fourier component $V_{\mathbf{G}} = V_0$ is average potential, set to zero.
- Build $|\psi\rangle$ from plane wave basis states $|\mathbf{k}\rangle$, defined such that $\langle \mathbf{r} | \mathbf{k} \rangle = e^{i\mathbf{k}\mathbf{r}}$.

$$|\psi\rangle = \sum_{\mathbf{k}} C_{\mathbf{k}} |\mathbf{k}\rangle$$

- Apply \mathbf{H} to this:

$$\sum_{\mathbf{k}} E_{\mathbf{k}}^0 C_{\mathbf{k}} e^{i\mathbf{k}\mathbf{r}} + \left[\sum_{\mathbf{G}} V_{\mathbf{G}} e^{i\mathbf{G}\mathbf{r}} \right] \left[\sum_{\mathbf{k}} C_{\mathbf{k}} e^{i\mathbf{k}\mathbf{r}} \right] = E \sum_{\mathbf{k}} C_{\mathbf{k}} e^{i\mathbf{k}\mathbf{r}}$$

(where $E_{\mathbf{k}}^0 = \frac{\hbar^2 k^2}{2m}$)

Schrödinger equation in a periodic potential – continued

- Rewrite this as

$$\sum_{\mathbf{k}} E_{\mathbf{k}}^0 C_{\mathbf{k}} |\mathbf{k}\rangle + \sum_{\mathbf{G}, \mathbf{k}} V_{\mathbf{G}} C_{\mathbf{k}} |\mathbf{G} + \mathbf{k}\rangle = E \sum_{\mathbf{k}} C_{\mathbf{k}} |\mathbf{k}\rangle$$

- Relabel the \mathbf{k} 's in the middle sum: $\mathbf{G} + \mathbf{k} \rightarrow \mathbf{k}$

$$\sum_{\mathbf{k}} E_{\mathbf{k}}^0 C_{\mathbf{k}} |\mathbf{k}\rangle + \sum_{\mathbf{G}, \mathbf{k}} V_{\mathbf{G}} C_{\mathbf{k}-\mathbf{G}} |\mathbf{k}\rangle = E \sum_{\mathbf{k}} C_{\mathbf{k}} |\mathbf{k}\rangle$$

- Left multiply by a single plane wave state to obtain eigenvalue equation

$$(E_{\mathbf{k}}^{(0)} - E) C_{\mathbf{k}} + \sum_{\mathbf{G}} V_{\mathbf{G}} C_{\mathbf{k}-\mathbf{G}} = 0$$

- Shift by reciprocal lattice vector \mathbf{G}' : $\mathbf{q} = \mathbf{k} + \mathbf{G}'$, where \mathbf{q} lies in first Brillouin zone. Relabel sum over \mathbf{G} .

$$\left[\left(\frac{\hbar^2}{2m} (\mathbf{q} - \mathbf{G}')^2 - E \right) C_{\mathbf{q}-\mathbf{G}'} + \sum_{\mathbf{G}''} V_{\mathbf{G}''-\mathbf{G}'} C_{\mathbf{q}-\mathbf{G}''} \right] = 0$$

Bloch's theorem follows from this (in an unintuitive way)

- For any wavevector from the first Brillouin zone, \mathbf{q} , we can in principle solve preceding eigenvector equation to find the set of coefficients $C_{\mathbf{q}-\mathbf{G}}$.
- This set of coefficients is a distinct sub-set of all $C_{\mathbf{k}}$. It allows us to find an eigenfunction of \mathbf{H} :

$$\psi_{\mathbf{q}}(\mathbf{r}) = \sum_{\mathbf{G}} C_{\mathbf{q}-\mathbf{G}} e^{i(\mathbf{q}-\mathbf{G})\mathbf{r}}$$

- By taking out a factor $e^{i\mathbf{q}\mathbf{r}}$, this can be rewritten as

$$\psi_{\mathbf{q}}(\mathbf{r}) = e^{i\mathbf{q}\mathbf{r}} \sum_{\mathbf{G}} C_{\mathbf{q}-\mathbf{G}} e^{-i\mathbf{G}\mathbf{r}} = e^{i\mathbf{q}\mathbf{r}} u_{j,\mathbf{q}}(\mathbf{r})$$

where $u_{j,\mathbf{q}}(\mathbf{r})$ is a function with the same periodicity as the lattice.

- This is Bloch's theorem:

Eigenstates of the one-electron Hamiltonian can be chosen to be a plane wave times a function with the periodicity of the Bravais lattice.

Bloch's theorem

(Translating an energy eigenstate by a lattice vector gives the same state times e^{ika} , or: the energy eigenstates are plane waves times a periodic function)

Using symmetry to derive Bloch's theorem

- Consider symmetry operator \mathbf{T} , e.g. translation $\langle \mathbf{r} | \mathbf{T} \psi \rangle = \psi(\mathbf{r} + \mathbf{a})$.
- Hamiltonian \mathbf{H} commutes with symmetry operator $\mathbf{T} \implies$ **\mathbf{T} maps one eigenstate of \mathbf{H} onto another with the same energy:**

$$\mathbf{H} | \mathbf{T} \psi \rangle = \mathbf{T} | \mathbf{H} \psi \rangle = E | \mathbf{T} \psi \rangle$$

- If non-degenerate: simple; there is only one eigenstate with this energy, and \mathbf{T} maps it onto itself.
- If degenerate: harder; degenerate eigenstates form subspace. \mathbf{T} maps states within the subspace. Because \mathbf{T} is unitary operator (symmetry operation leaves 'length' of ψ unchanged), can diagonalise associated matrix $T_{mn} = \langle \psi_m | \mathbf{T} \psi_n \rangle$. That means: we can find basis states within the degenerate subspace, which are eigenstates of \mathbf{T} .
- **We use the eigenvalue of \mathbf{T} to give an eigenstate of \mathbf{H} a meaningful label.**

For two commuting operators \mathbf{H} , \mathbf{T} , can choose simultaneous eigenstates of both \mathbf{H} and \mathbf{T} .

- In the lattice, \mathbf{H} commutes with translation operator $\mathbf{T}_{\mathbf{a}}$, where \mathbf{a} is a Bravais lattice vector.
- To find the possible eigenvalues of translation operator $\mathbf{T}_{\mathbf{a}}$, let it operate on plane wave states $|\mathbf{k}\rangle$, which form a complete basis set.

$$\mathbf{T}_{\mathbf{a}} |\mathbf{k}\rangle = e^{i\mathbf{k}\mathbf{a}} |\mathbf{k}\rangle$$

- Choose \mathbf{H} eigenstates $|\psi\rangle$ which are also eigenstates of \mathbf{T} :
 $\mathbf{H}|\psi\rangle = E|\psi\rangle \implies \mathbf{T}_{\mathbf{a}}|\psi\rangle = c_{\mathbf{a}}|\psi\rangle$, where $c_{\mathbf{a}}$ is an eigenvalue of $\mathbf{T}_{\mathbf{a}}$.
- $\mathbf{T}_{\mathbf{a}}$ -eigenvalue $c_{\mathbf{a}}$ must be of the form $e^{i\mathbf{k}\mathbf{a}}$, because these form a complete set of eigenvalues for \mathbf{T} .
- This leads directly to one form of Bloch's theorem:

$$\mathbf{T}_{\mathbf{a}} |\psi\rangle = e^{i\mathbf{k}\mathbf{a}} |\psi\rangle$$

- We use the \mathbf{k} in the exponent to label the energy eigenstate: $\psi \rightarrow \psi_{\mathbf{k}}$.

Bloch's theorem

- Electrons live in periodic potential:

$$\mathbf{H}\psi(\mathbf{r}) = \left[\frac{\hat{\mathbf{p}}^2}{2m} + V(\mathbf{r}) \right] \psi(\mathbf{r}) = E\psi(\mathbf{r}) ,$$

where $V(\mathbf{r} + \mathbf{R}) = V(\mathbf{r})$ for $\forall \mathbf{R}$ in a Bravais lattice.

- **Bloch's theorem:**

$$\psi_{\mathbf{k}}^{(n)}(\mathbf{r}) = e^{i\mathbf{k}\cdot\mathbf{r}} u_{n\mathbf{k}}(\mathbf{r}) , \text{ where } u_{\mathbf{k}}^{(n)}(\mathbf{r} + \mathbf{R}) = u_{\mathbf{k}}^{(n)}(\mathbf{r})$$

Or, alternatively:

$$\psi_{\mathbf{k}}^{(n)}(\mathbf{r} + \mathbf{R}) = e^{i\mathbf{k}\cdot\mathbf{R}} \psi_{\mathbf{k}}^{(n)}(\mathbf{r})$$

- Potential is periodic, but $\psi =$ **plane wave** \times periodic function.
- n is **band index**

Notes on Bloch's theorem: $|\psi_{\mathbf{k}}^{(n)}\rangle = |\psi_{\mathbf{k}}^{(m)}\rangle$. $E(\mathbf{k})$ is periodic

- Bloch states (plane wave \times periodic function) are similar to eigenstates of free electrons (just plane waves), but the choice of periodic function gives additional freedom in labelling states.
- Remember that $e^{i\mathbf{g}\mathbf{r}}$ is periodic with same periodicity as the Bravais lattice (follows from definition of reciprocal lattice vectors \mathbf{g}).
- We can use this to relabel a Bloch state \mathbf{k} with a different wavevector $\mathbf{k} - \mathbf{g}$ by introducing a different periodic function $u^{(n)} = e^{i\mathbf{g}\mathbf{r}} u^{(m)}$:

$$\psi_{\mathbf{k}}^{(m)}(\mathbf{r}) = e^{i\mathbf{k}\mathbf{r}} u_{\mathbf{k}}^{(m)}(\mathbf{r}) = e^{i\mathbf{k}\mathbf{r}} \left[e^{-i\mathbf{g}\mathbf{r}} u_{\mathbf{k}}^{(n)}(\mathbf{r}) \right] = e^{i(\mathbf{k}-\mathbf{g})\mathbf{r}} u_{\mathbf{k}}^{(n)}(\mathbf{r}) = \psi_{\mathbf{k}-\mathbf{g}}^{(n)}(\mathbf{r})$$

- The $^{(m)}$, $^{(n)}$ -labels are called **band indices**. In this case, there are two different states $|\psi_{\mathbf{k}}^{(m)}\rangle$, $|\psi_{\mathbf{k}}^{(n)}\rangle$ labelled with the same \mathbf{k} -vector, but belonging to different bands m, n . ($\psi_{\mathbf{k}}^{(m)}(\mathbf{r}) = e^{-i\mathbf{g}\mathbf{r}} \psi_{\mathbf{k}}^{(n)}(\mathbf{r})$).
- **For every state** labelled with a \mathbf{k} -vector outside the first Brillouin zone, **there is an identical state** which can be labelled with a vector $\mathbf{q} = \mathbf{k} - \mathbf{g}$ inside the first Brillouin zone.
- Corollary: any quantity that depends on the wavefunction, in particular **energy, is periodic in wavevector space**.

Nearly free electron approximation

(Finding approximate single electron states in periodic potential by hybridising nearly degenerate plane wave states. Chapter 3 in Singleton book.)

Nearly free electron approximation – connection to perturbation theory

- Recall that the single-electron state was obtained from plane wave expansion $|\psi_{\mathbf{k}}\rangle = \sum_{\mathbf{G}} c_{\mathbf{k}-\mathbf{G}} |\mathbf{k} - \mathbf{G}\rangle$.
- If lattice potential is weak, regard it as a perturbation. **Perturbation admixes excited states** $|\mathbf{k} - \mathbf{G}\rangle$ to the unperturbed ground state wavefunction.
- Energy-level shift due to admixing a particular state $|\mathbf{k} - \mathbf{G}\rangle$ in second order perturbation theory:

$$\Delta E_{\mathbf{k}} = \frac{|V_{\mathbf{G}}|^2}{E_{\mathbf{k}}^{(0)} - E_{\mathbf{k}-\mathbf{G}}^{(0)}}$$

(remember $V_{\mathbf{G}}$ is Fourier component of the lattice potential at reciprocal lattice wavevector \mathbf{G} . Because the potential is periodic, $V = \sum_{\mathbf{G}} V_{\mathbf{G}} e^{i\mathbf{G}\cdot\mathbf{r}}$.)

- **Energy shift is most pronounced, when $E_{\mathbf{k}}^{(0)} \simeq E_{\mathbf{k}-\mathbf{G}}^{(0)}$** , i.e. when there are several nearly degenerate states. Need to use degenerate perturbation theory in this case.

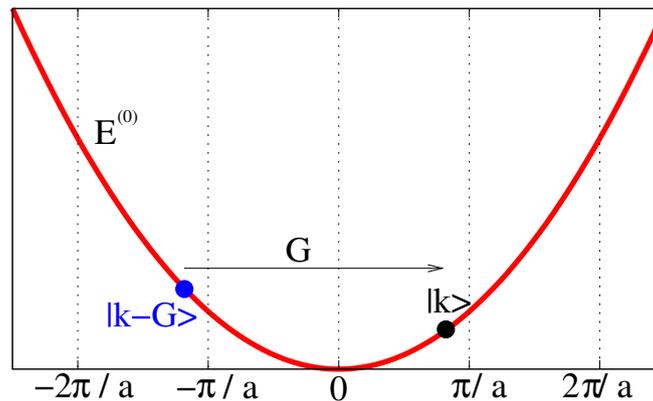
Nearly free electron approximation – connection to perturbation theory

- To work out energy levels in degenerate perturbation theory, we apply the general equation obtained earlier:

$$\left(E_{\mathbf{k}}^{(0)} - E_{\mathbf{k}-\mathbf{G}}^{(0)}\right) C_{\mathbf{k}} + \sum_{\mathbf{G}} V_{\mathbf{G}} C_{\mathbf{k}-\mathbf{G}} = 0$$

but **restrict the choice of \mathbf{G} -vectors to those which link together nearly degenerate states:** $E_{\mathbf{k}}^{(0)} \simeq E_{\mathbf{k}-\mathbf{G}}^{(0)}$.

- Example:** 1D case. Start with state $|\mathbf{k}\rangle$. Potential $V_{\mathbf{G}}$ admixes $|\mathbf{k}-\mathbf{G}\rangle$, which is close in energy. It also admixes other states, but their energies are more widely separated from that of $|\mathbf{k}\rangle$, so we concentrate on $|\mathbf{k}-\mathbf{G}\rangle$ for now.



Perturbation theory: Nearly Free Electrons – 1

- Apply \mathbf{H} to $|\psi\rangle$:**

$$|\psi\rangle = c_{\mathbf{k}} |\mathbf{k}\rangle + c_{\mathbf{k}-\mathbf{G}} |\mathbf{k}-\mathbf{G}\rangle$$

$$\mathbf{H} |\psi\rangle = E |\psi\rangle = c_{\mathbf{k}} \frac{p^2}{2m} |\mathbf{k}\rangle + c_{\mathbf{k}} V |\mathbf{k}\rangle + c_{\mathbf{k}-\mathbf{G}} \frac{p^2}{2m} |\mathbf{k}-\mathbf{G}\rangle + c_{\mathbf{k}-\mathbf{G}} V |\mathbf{k}-\mathbf{G}\rangle$$

- Left multiply with basis states $\langle \mathbf{k} |$ and $\langle \mathbf{k}-\mathbf{G} |$:**

$$c_{\mathbf{k}} E = c_{\mathbf{k}} E_{\mathbf{k}}^{(0)} + c_{\mathbf{k}} V_0 + c_{\mathbf{k}-\mathbf{G}} V_{\mathbf{G}}$$

$$c_{\mathbf{k}-\mathbf{G}} E = c_{\mathbf{k}} V_{-\mathbf{G}} + c_{\mathbf{k}-\mathbf{G}} V_0 + c_{\mathbf{k}-\mathbf{G}} E_{\mathbf{k}-\mathbf{G}}^{(0)}$$

(Note $E_{\mathbf{k}}^{(0)} = \hbar k^2 / 2m$, V_0 is set to zero, and $V_{-\mathbf{G}} = V_{\mathbf{G}}^*$).

- This is special case of general set of equations

$\left(E_{\mathbf{k}}^{(0)} - E\right) C_{\mathbf{k}} + \sum_{\mathbf{G}} V_{\mathbf{G}} C_{\mathbf{k}-\mathbf{G}} = 0$ (obtained earlier), in which we consider just one value of \mathbf{G} . If we wanted to consider the effect of more \mathbf{G} -vectors, we would have to solve more simultaneous equations.

- Obtain 2 perturbed energies E from roots of 2×2 determinant.**

Extended zone scheme: call one energy $E_{\mathbf{k}}$ and the other $E_{\mathbf{k}-\mathbf{G}}$.

Reduced zone scheme: call one energy $E_{\mathbf{k}}^{(1)}$ and the other $E_{\mathbf{k}}^{(2)}$.

- At Brillouin zone boundary ($k = \pi/a$), $E = E_{\pi/a}^{(0)} \pm |V_{\mathbf{G}}|$

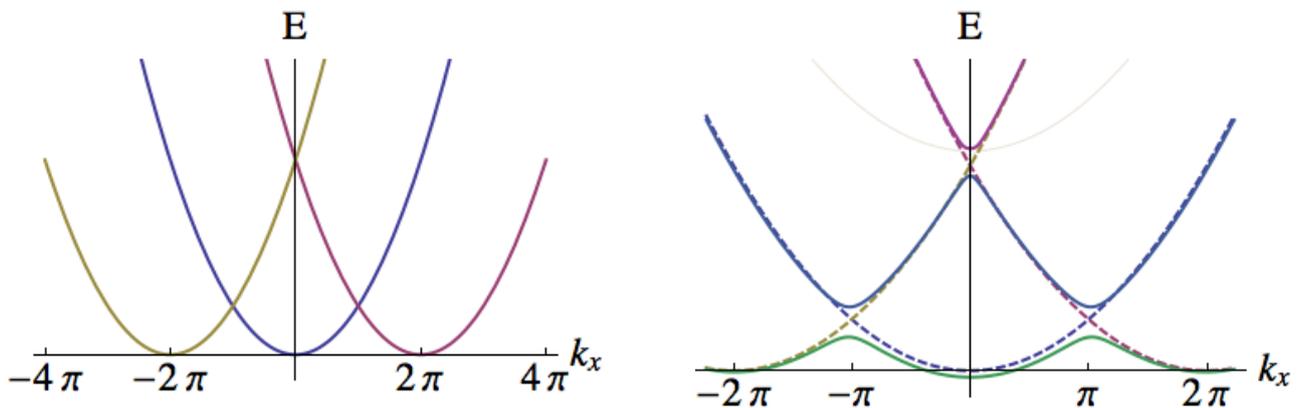
Perturbation theory: Nearly Free Electrons – 2

- Sometimes it is easier to use alternative form (derived earlier):

$$\left[\left(\frac{\hbar^2}{2m} (\mathbf{q} - \mathbf{G}')^2 - E \right) c_{\mathbf{q}-\mathbf{G}'} + \sum_{\mathbf{G}''} V_{\mathbf{G}''-\mathbf{G}'} c_{\mathbf{q}-\mathbf{G}''} \right] = 0$$

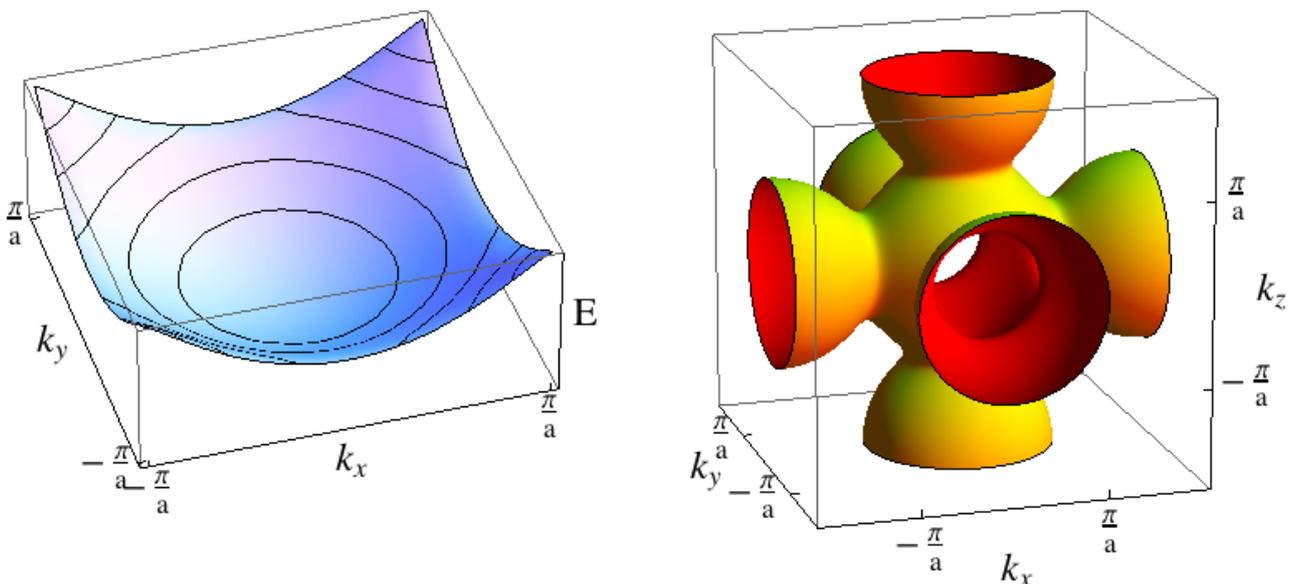
(\mathbf{q} is always in first BZ. It is obtained from \mathbf{k} , which might fall outside first BZ, by subtracting \mathbf{G}').

- Results of perturbation calculation:



Perturbation theory: Nearly Free Electrons – 3

- More examples: energy contours in 2D and isosurface in 3D.



- Because of Bloch's theorem, for every $|\psi_{\mathbf{k}+\mathbf{G}}^n\rangle$ there is an identical state $|\psi_{\mathbf{k}+\mathbf{G}}^m\rangle$. Therefore, $E_{\mathbf{k}}$ has the same periodicity as the reciprocal lattice.
- At BZ boundary, $|\mathbf{k}| = |\mathbf{k} - \mathbf{G}| \implies E_{\mathbf{k}}^{(0)} = E_{\mathbf{k}-\mathbf{G}}^{(0)}$. Band distortion is strongest here.

Tight binding approximation (Linear Combination of Atomic Orbitals, LCAO)

(Finding approximate single electron states by hybridising atomic orbitals.
Chapter 4 in Singleton book.)

Linear chain of atomic orbitals

- Remember **diatomic molecule**, formed molecular orbitals from atomic states

$$|\psi\rangle = \alpha|a\rangle + \beta|b\rangle$$

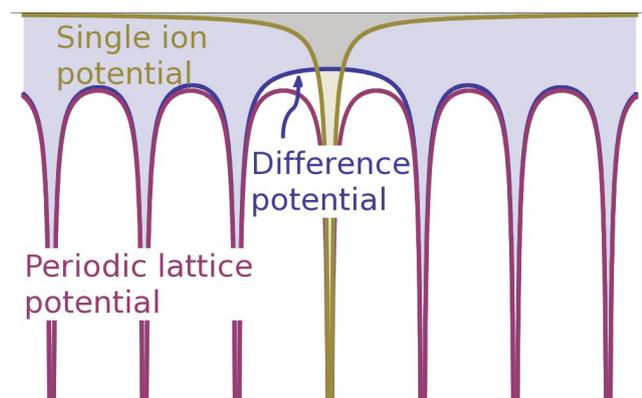
- Found coefficients α, β and energy levels from

$$\begin{pmatrix} \tilde{E}_0 - E & t \\ t^* & \tilde{E}_0 - E \end{pmatrix} \begin{pmatrix} \alpha \\ \beta \end{pmatrix} = 0$$

- Hopping** matrix element

$$t = H_{ab} = \langle a | \mathbf{H} | b \rangle$$

- Now **generalise** to ring of N atoms (periodic b.c.)



- Try

$$|\psi\rangle = \sum_n e^{i\mathbf{k}\mathbf{R}_n} |n\rangle, \quad ,$$

where \mathbf{R}_n = position of atom n ,
 $\mathbf{H}_n^{(0)} |n\rangle = E_0 |n\rangle$, \mathbf{H}_0 : single atom Hamiltonian,
 and $\mathbf{H} = \mathbf{H}_n^{(0)} + \text{difference potential}$.

The usual steps:

1 Check that $|\psi\rangle = \sum_n e^{ikR_n} |n\rangle$ **complies with Bloch's theorem:**

- ▶ Apply translation \mathbf{T}_a to $|\psi\rangle$: $\mathbf{T}_a\psi(\mathbf{r}) = \psi(\mathbf{r} + \mathbf{a})$.
- ▶ This maps an atomic orbital centred on atom n ($\phi(\mathbf{r} - \mathbf{R}_n)$) onto an orbital centred on atom m ($\phi(\mathbf{r} - \mathbf{R}_m)$).

$$\mathbf{T}_a\phi(\mathbf{r} - \mathbf{R}_n) = \phi(\mathbf{r} - (\mathbf{R}_n - \mathbf{a})) = \phi(\mathbf{r} - \mathbf{R}_m) \implies \mathbf{R}_n - \mathbf{a} = \mathbf{R}_m$$

$$\mathbf{T}_a|\psi\rangle = \mathbf{T}_a \sum_n e^{ikR_n} |n\rangle = \sum_m e^{ikR_n} |m\rangle = e^{ika} \sum_m e^{ikR_m} |m\rangle = e^{ika} |\psi\rangle$$

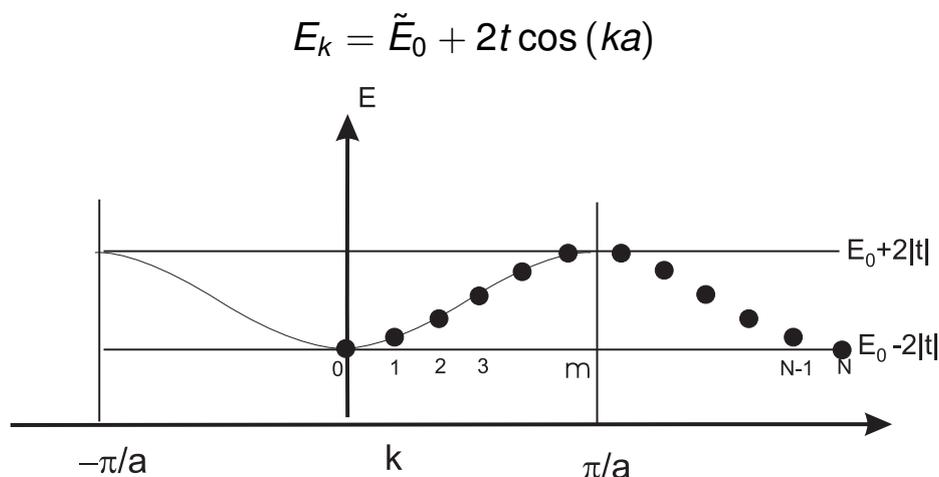
2 **Apply Hamiltonian:** $\mathbf{H}|\psi\rangle = E|\psi\rangle$

3 Assuming that the orbitals are orthogonal, **left multiply** with one of the **basis states**. It saves algebra to use the basis state $\langle 0|$, which is centred at the origin.

$$\langle 0|\mathbf{H}|\psi\rangle = E = \sum_n e^{ikR_n} \langle 0|\mathbf{H}|n\rangle$$

Example: chain of atoms with periodic boundary conditions

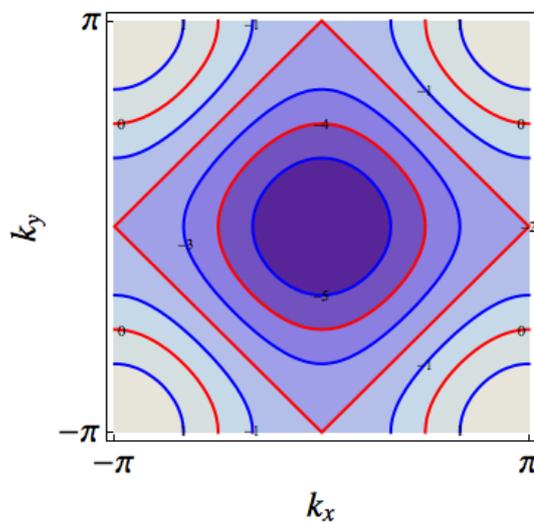
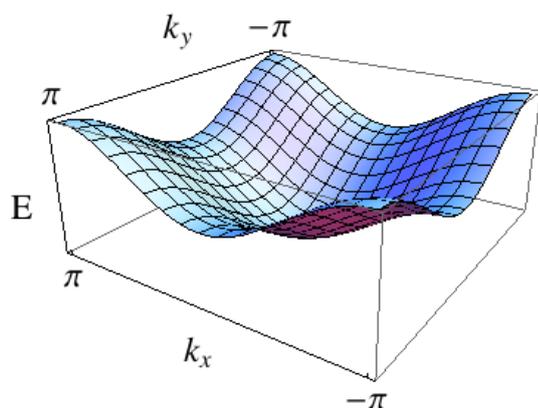
- Example: apply to linear chain, $t^* = t = \langle n|\mathbf{H}|n+1\rangle$ (nearest neighbour hopping only), and define $\tilde{E}_0 = \langle n|\mathbf{H}|n\rangle$



- **Note: ambiguity in defining t .** Some textbooks use a different definition of t , $t := -\langle n|\mathbf{H}|n+1\rangle$, in order to obtain $E_k = \tilde{E}_0 - 2t \cos(ka)$.
- Hopping element $t = \langle n|\mathbf{H}|n+1\rangle$ is < 0 between s-orbitals, giving the familiar free-electron like dispersion near $k = 0$.

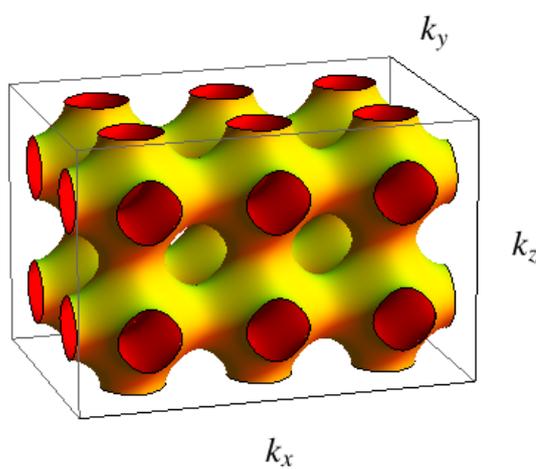
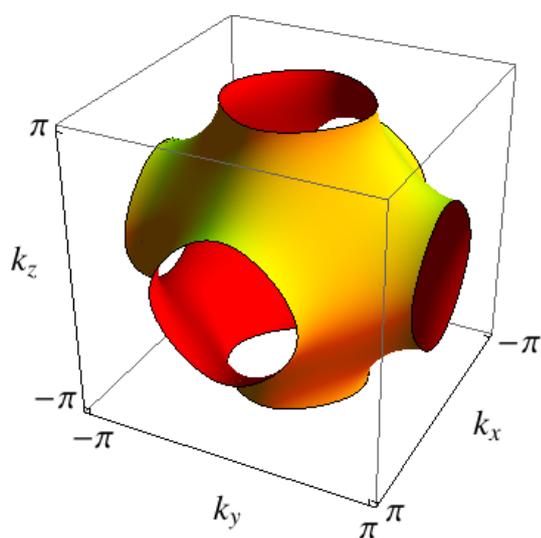
An example, using *Mathematica* – 1

$$E = E_0 + 2t(\cos(k_x a) + \cos(k_y a) + \cos(k_z a))$$



An example, using *Mathematica* – 2

$$E = E_0 + 2t(\cos(k_x a) + \cos(k_y a) + \cos(k_z a))$$



Tight binding vs. Nearly Free Electron approximation

- The two approximation schemes differ in the **choice of basis states** for expanding the single-electron wavefunction.
- Both give the **same results** in principle, because they form a complete set of basis functions.
- **Nearly free electron** approximation will be more efficient, if the lattice potential is very smooth, because only few Fourier coefficients of $V(\mathbf{r})$ are significant then.
- **Tight binding** will be more efficient approximation, if the lattice potential is strongly modulated, so that in NFE scheme many plane wave states would be mixed in by lattice potential.

General points about band structure

(Consequences of formation of energy bands, semiclassical description of electron dynamics, Chapter 5 in Singleton book.)

Bands and Brillouin zones

- **Brillouin zones:**

Gap = splitting of degeneracy due to scattering from Fourier component of $V(r)$:

Degeneracies occur at Brillouin zone boundaries, because there $\mathbf{k}^2 = (\mathbf{k} - \mathbf{g})^2$

- **Electronic bands:** Energy eigenstates form **bands** $E^{(n)}(\mathbf{k})$. Functions of momentum $\hbar\mathbf{k}$, labelled by **band index** n .

Energy dispersion is periodic:
 $E^{(n)}(\mathbf{k} + \mathbf{G}) = E^{(n)}(\mathbf{k})$

- **Fermi surface:** Energy isosurface in wavevector space which encloses all the filled \mathbf{k} -states.

Fermi surface usually cuts Brillouin zone boundary at right angles

Bands and Brillouin zones – 2

- **Counting states:** \mathbf{k} -points discrete but closely spaced. Each occupies a volume

$$(\Delta \mathbf{k})^3 = \frac{(2\pi)^3}{V}$$

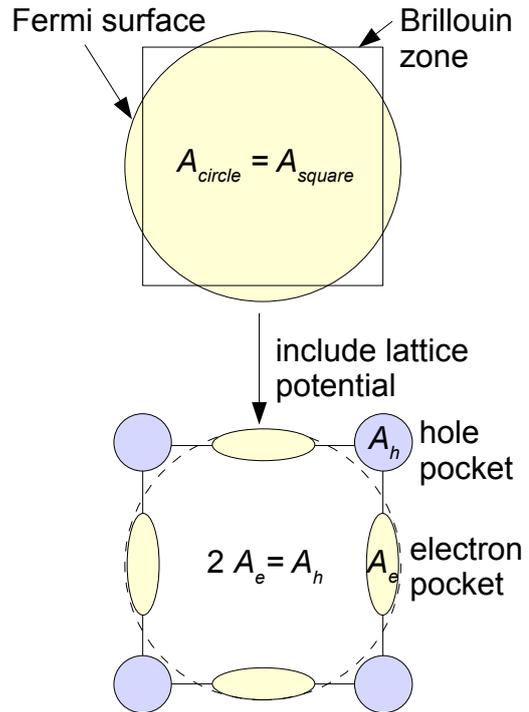
Primitive unit cell (= Brillouin zone) contains N \mathbf{k} -values.

- **Even number rule.**

Two electrons per real space unit cell fill a Brillouin zone.

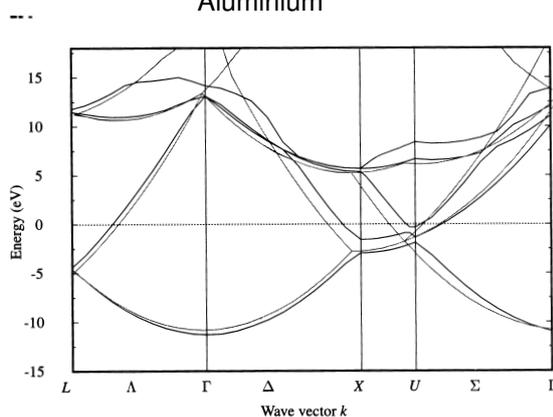
Even number of electrons \rightarrow
may be insulator.
 Otherwise \rightarrow metal (usually).

- 2D example: 2 e^- per unit cell in square lattice.

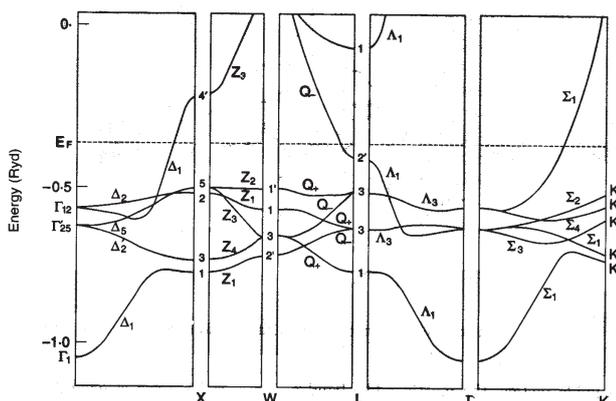


Examples of band structures: Metals

Aluminium

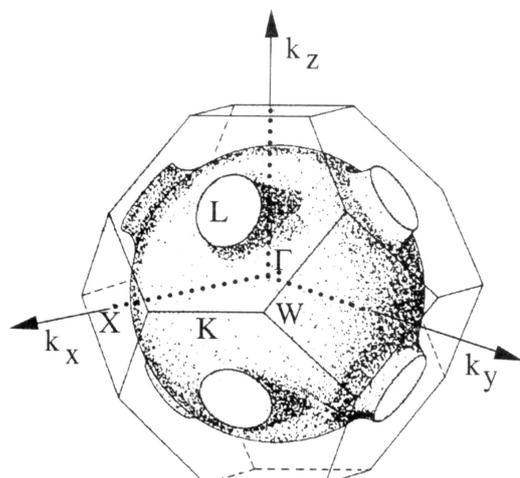


Copper



- **Notation:**

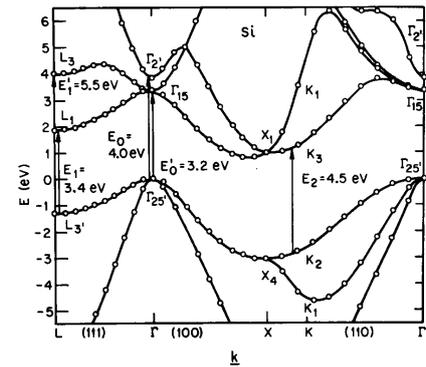
$\Gamma = (0, 0, 0)$ = zone centre.
 X is on zone boundary along (100) , Y along (010) , Z along (001)
 L is on zone boundary along (111) , K along (110)



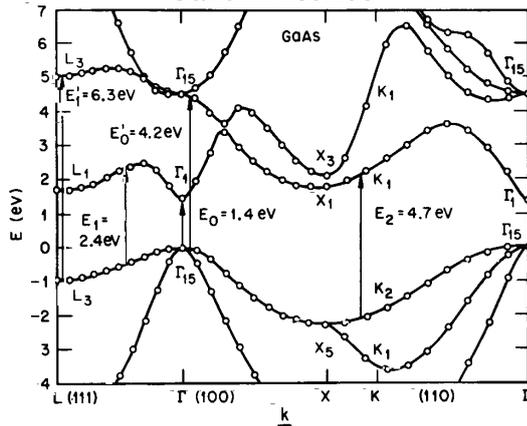
Examples of band structures: Semiconductors and insulators

- Filled bands separated from empty bands by **energy gap**.
- In **group IV** *C*, *Si* and *Ge*, in **III-V** compounds *GaAs* and *AlAs*.
- Valence band maxima at Γ . *Si* and *Ge* = **indirect gap** materials, because conduction band minima not at Γ .

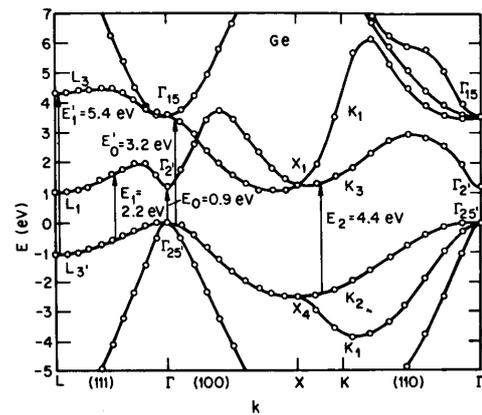
Silicon



Gallium Arsenide



Germanium



Semiclassical model of electron dynamics

(Modelling electrons in metals as particles subject to forces: wavepackets, crystal momentum, effective mass, electrons and holes, transport properties. Singleton book chapter 5.2)

Wavepackets and equations of motion: semiclassical model

- Treat particles as **wave-packets**. (superposition of $|\psi_{\mathbf{k}}\rangle$)
- **Group velocity** $v_g = d\omega/dk$ in 1D. In general:

$$\dot{\mathbf{r}} = \mathbf{v}_g = \hbar^{-1} \nabla_{\mathbf{k}} \epsilon(\mathbf{k})$$

- Effects of lattice potential contained in dispersion $\epsilon(\mathbf{k})$.
- **Force F** on electron:

$$d\epsilon/dt = \mathbf{F} \cdot \mathbf{v} = \dot{\mathbf{k}} \cdot \nabla_{\mathbf{k}} \epsilon(\mathbf{k})$$

$$\Rightarrow \mathbf{F} = \hbar \dot{\mathbf{k}}$$

Crystal momentum $\hbar\mathbf{k}$.

- $\hbar\mathbf{k}$ enters **conservation laws**.

Example: electron absorbs phonon momentum $\hbar\mathbf{q}$; final state: $\mathbf{k}' = \mathbf{k} + \mathbf{q} + \mathbf{G}$. \mathbf{G} = reciprocal lattice vector necessary to keep \mathbf{k}' inside Brillouin zone.

Physical momentum transferred to lattice in units of $\hbar\mathbf{G}$.

- Also: effective mass from $\epsilon(\mathbf{k}) = \epsilon(\mathbf{k}_0) + \frac{1}{2}(\hbar(\mathbf{k} - \mathbf{k}_0))\mathbf{m}^{-1}(\hbar(\mathbf{k} - \mathbf{k}_0))$:

$$\mathbf{m}_{ij}^{-1} = \frac{1}{\hbar^2} \nabla_{k_i} \nabla_{k_j} \epsilon(\mathbf{k})$$

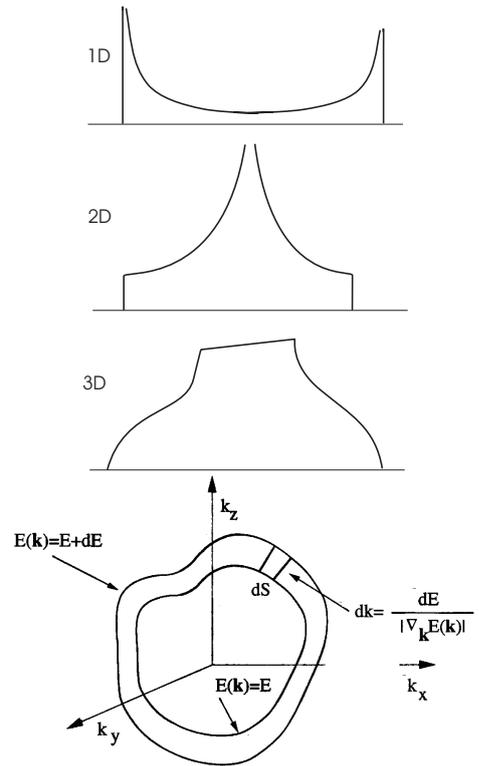
Approximates parabolic energy dispersion near bottom or top of band.

- Near minima E_{min} : **quadratic dispersion**

$$g(E \gtrsim E_{min}) = \frac{V}{\pi^2} \frac{m^*}{\hbar^2} \left(\frac{2m^*(E - E_{min})}{\hbar^2} \right)^{\frac{1}{2}}$$

with effective mass $m^* = (m_x^* m_y^* m_z^*)^{1/3}$

- Near band maxima: $g(E) \propto (E_{max} - E)^{\frac{1}{2}}$.
- Flat bands \rightarrow large effective mass, large density of states
- Can have **saddle points**: points where bands are flat but curvature is of opposite sign in different directions.



Accelerated electron – Bloch oscillations

Force on electron in electric, magnetic field:

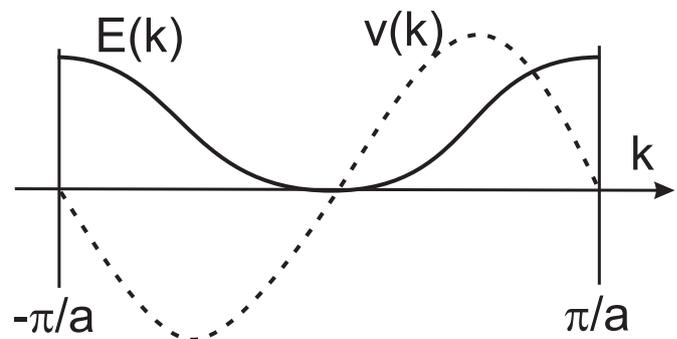
$$\hbar \frac{d\mathbf{k}}{dt} = \mathbf{F} = -e(\mathbf{E} + \mathbf{v} \wedge \mathbf{B}) = -e(\mathbf{E} + \hbar^{-1} \nabla_{\mathbf{k}} \epsilon(\mathbf{k}) \wedge \mathbf{B})$$

Bloch oscillations

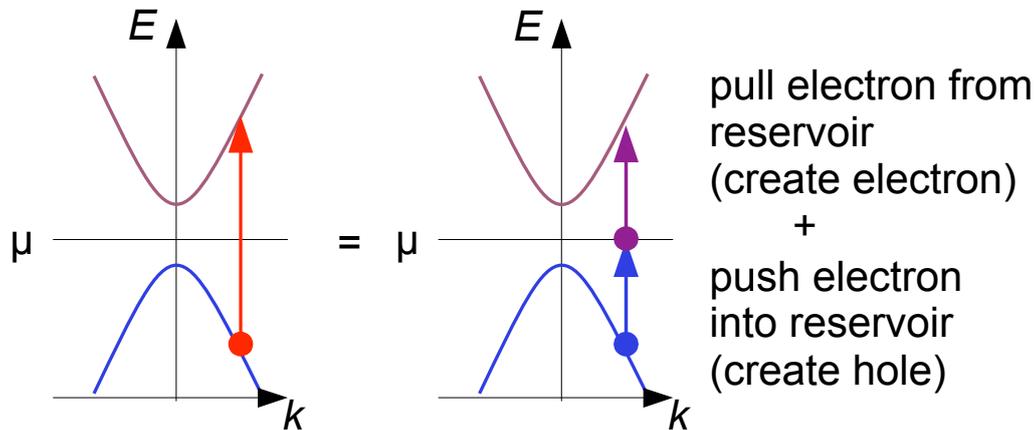
- Electron velocity $v(k)$ alternates.
- Electron in constant electric field

$$k(t) = k(0) - \frac{eEt}{\hbar}$$

- Group velocity **oscillates**



Electrons and holes



Electron from valence to conduction band
= creating electron-hole pair

- Promoting an electron to a higher band could be seen as a two-step process:
 - 1 Promote electron from lower band to chemical potential, let it drain away to reservoir: **create a hole**
 - 2 Pull an electron from chemical potential, promote it to the upper band: **create an electron**

The shadowy mirror-world of the holes

- Regard the result of process 1, a 'hole', as a particle in its own right.
- It takes energy $E_h(\mathbf{k}) = \mu - E_e^{(valence)}(\mathbf{k})$ to create a hole. Referred to μ its energy is $(-1) \times$ that of the electron state from which it derives.
- Hole appears **like an antiparticle** to the electron. The hole band structure is like the electron band structure, inverted around μ .
- Full band has no momentum
- Hole = one e^- missing
- Hole momentum
- Hole velocity
- Hole effective mass: near band bottom/top $\epsilon = \epsilon_0 + \frac{\hbar^2 k^2}{2m^*} \Rightarrow m_h^* = -m_e^*$
- Hole charge $q_h = -q_e > 0$

Scattering and electrical conductivity of metals

- Equation of motion

$$\hbar \frac{d\mathbf{k}}{dt} = \mathbf{F} - \hbar \frac{\mathbf{k}}{\tau} = -e(\mathbf{E} + \mathbf{v} \wedge \mathbf{B}) - \hbar \frac{\mathbf{k}}{\tau}$$

- Electric field $E \rightarrow$ Fermi sea shifts by $\delta\mathbf{k} = -eE\tau/\hbar$

- Velocity changes by $\delta\mathbf{v} = \hbar\delta\mathbf{k}/m^*$

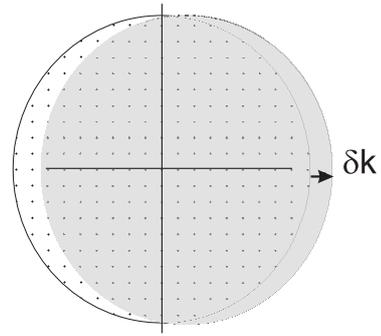
- Resulting current density

$$\mathbf{j} = -ne\delta\mathbf{v} = \frac{ne^2\tau}{m^*} \mathbf{E}$$

- Compare to Ohm's law $\mathbf{j} = \sigma\mathbf{E} \Rightarrow$

$$\sigma = ne\mu = \frac{ne^2\tau}{m^*}$$

- (defines **mobility** $\mu = e\tau/m^*$)
- $\delta k \ll k_F \rightarrow$ **tiny shift** of Fermi volume.



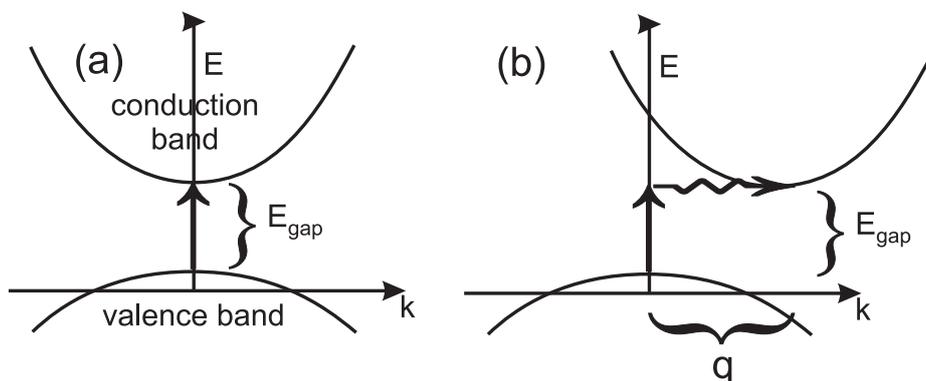
- Electrons **near Fermi surface** determine conductivity.
- **Thermal conductivity** analogous, $K \propto \sigma T$.
- **Hall effect** calculation carries over from Drude model approach, but now carrier charge can be positive (hole pockets) or negative (electron pockets).

Band structure probes

(Probing the band structure via: optical spectroscopy, photoemission spectroscopy, tunneling, quantum oscillations (de Haas van Alphen effect. Singleton book chapter 8.)

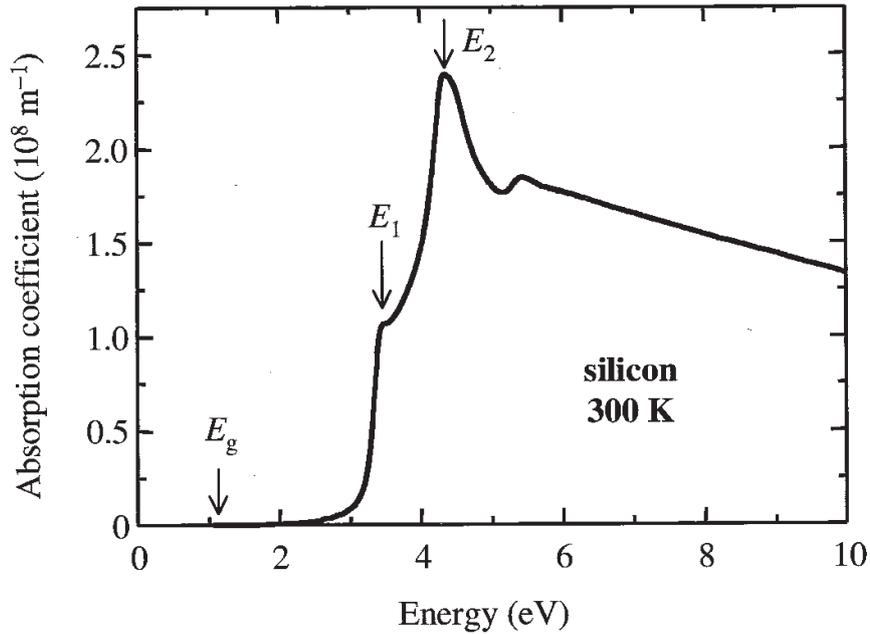
Optical spectroscopy

- Absorption peaks correspond to energy spacings between filled and unfilled bands.
- Details of band dispersion are important, e.g. direct vs. indirect gaps:



- **Direct gap:** Valence band maximum lines up with conduction band minimum.
- Strong absorption for photon energies in excess of gap energy.
- **Indirect gap:** Optical transitions between flat portions of band require additional momentum transfer due to phonons.
- Much less likely \implies smaller absorption coefficient.

Silicon, interband absorption spectrum

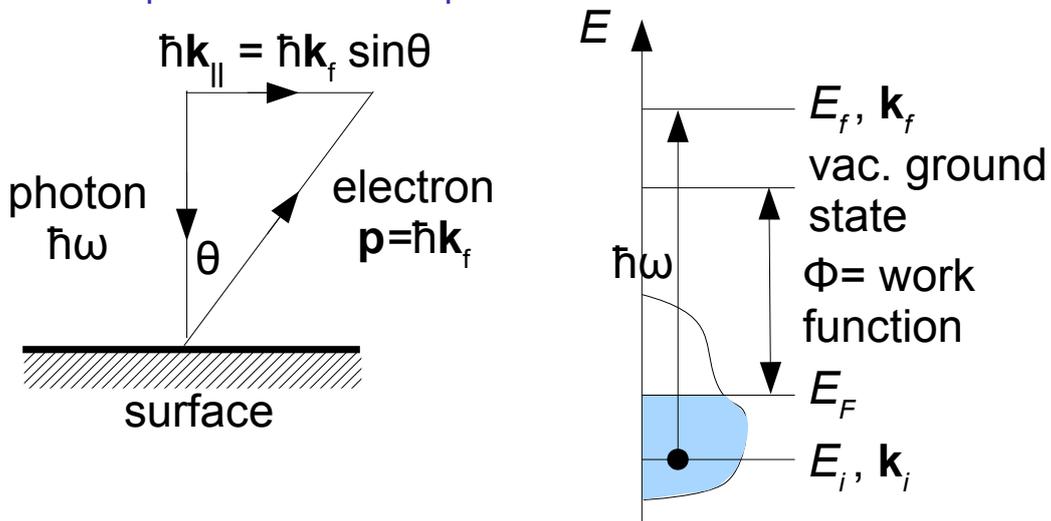


Threshold at indirect gap $E_g \approx 1.1$ eV.

Involves a phonon and is very weak.

E_1 and E_2 : conduction and valence bands parallel \rightarrow absorption is direct

Schematics of a photoemission experiment

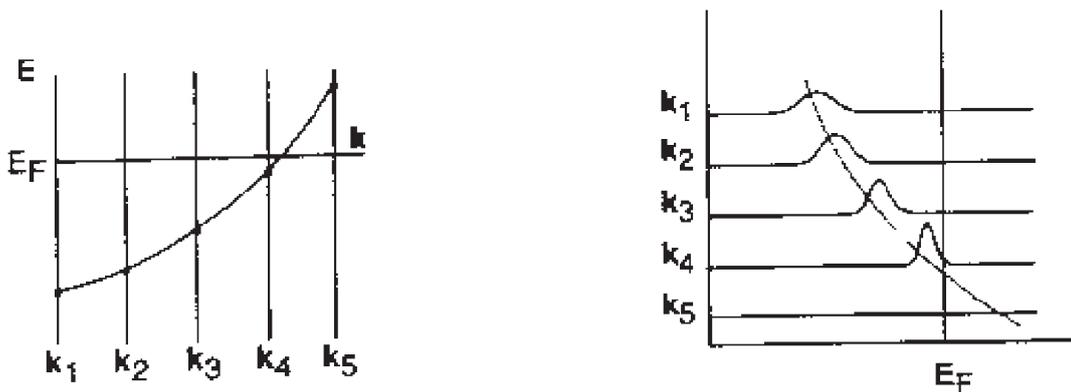


$$E_f = \frac{\hbar^2 k_f^2}{2m} = E_i + \hbar\omega - \phi \quad k_{f||} = k_{i||}$$

(E_i is referenced to E_F , whereas E_f is referenced to vac. ground state energy)

- Momentum parallel to surface is **conserved**.
- Detector angle θ gives $k_{||}$.

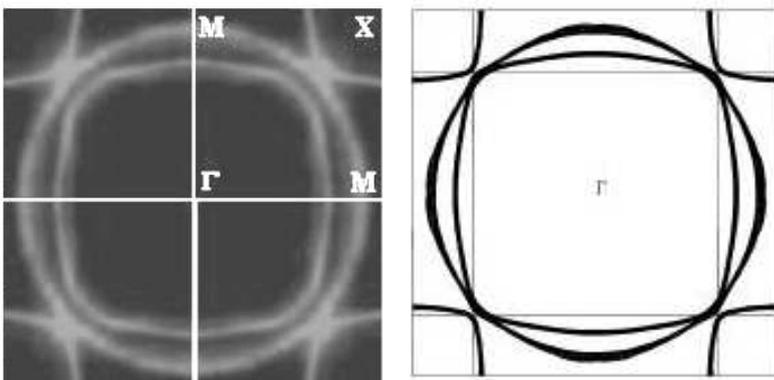
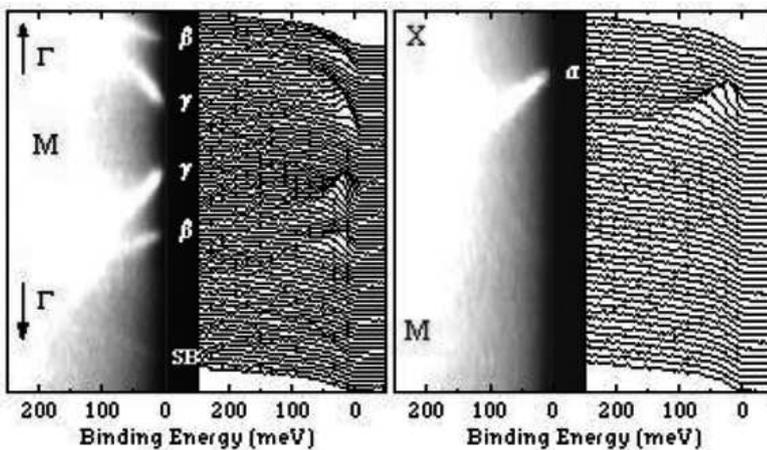
Idealised results from a photoemission experiment:



- At each $k_{||}$, a peak is observed at the band energy.
- Peak disappears, when the band crosses the Fermi energy (no more electrons to excite).

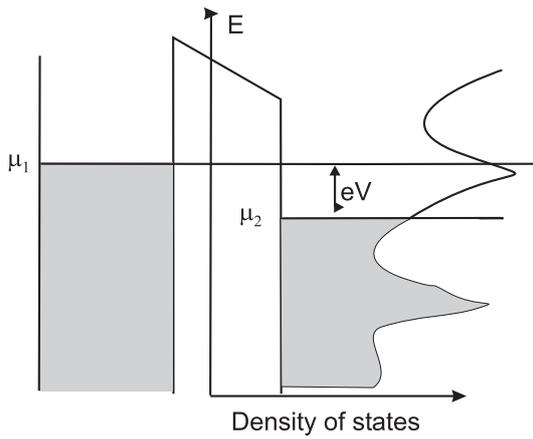
Photoemission

Layered metal Sr_2RuO_4 :



- Bands nearly two-dimensional. Angle \rightarrow in-plane momentum.
- Upper panels = energy scans.
- Several bands cross the Fermi energy
- Left hand lower panel = peak positions as function of momentum E_F
- Calculated Fermi surface on lower right.

Tunnelling

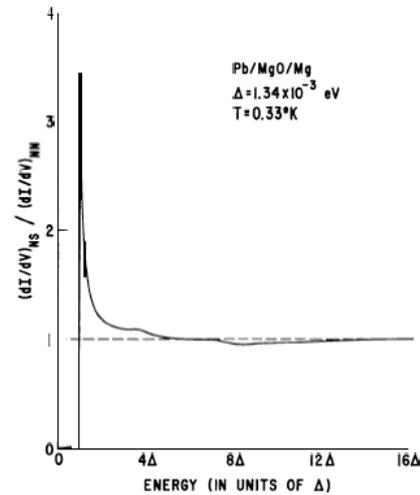


$$I \propto \int_{\mu_1 - eV}^{\mu_1} g_L(\omega) g_R(\omega) T(\omega) d\omega$$

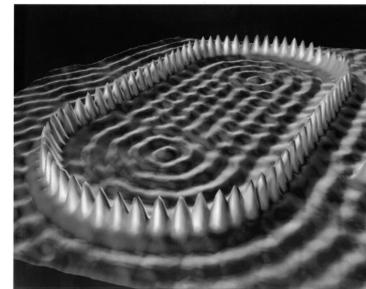
T is the transmission through the barrier for an electron of energy ω ; g_L and g_R are the densities of states.

$$dI/dV \propto g(\mu_1 - eV)$$

Tunnelling reveals gap in DOS of superconductor



Fe atoms on Cu surface of Cu, imaged by STM



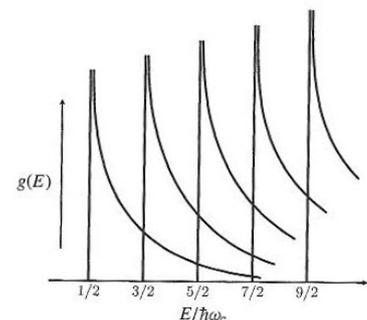
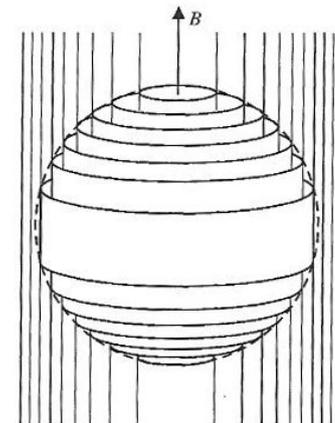
Quantum Oscillations – rough overview (cf. Singleton book)

- In strong magnetic fields $B \parallel z$, **electron energies are quantised**.

$$E = \frac{\hbar^2 k_z^2}{2m} + (l + 1/2)\hbar\omega_c$$

with $\omega_c = eB/m^* =$ cyclotron frequency.

- This can be observed only if **relaxation time τ is long** enough, so that $\omega_c > 2\pi/\tau$
- **Density of states** acquires **strongly peaked** energy dependence.
- With increasing magnetic field, the **peaks shift through the chemical potential**, causing all thermodynamic properties of the metal to **oscillate as functions of B^{-1}** .



Quantum Oscillations – orbit quantisation (semi-classical treatment)

- We are going to show that the cross-sectional area of a Landau tube in k -space is proportional to the magnetic field times a half-integer number.
- Semi-classical approach. Use Bohr-Sommerfeld quantisation condition (e.g. Kittel ch. 9):

$$\oint \mathbf{p} d\mathbf{r} = \left(n + \frac{1}{2}\right) h$$

\mathbf{p} = **canonical momentum** = $m\mathbf{v}$ - momentum + field momentum $q\mathbf{A}$.

- Lorentz force: $m\dot{\mathbf{v}} = q\dot{\mathbf{r}} \times \mathbf{B} \Rightarrow$.

$$\oint \mathbf{p} d\mathbf{r} = q \oint \mathbf{r} \times \mathbf{B} d\mathbf{r} + q\Phi = -q\Phi$$

flux threading the real space orbit is quantised:

$$\Phi_n = \mathbf{A}_r^{(n)} \mathbf{B} = \left(n + \frac{1}{2}\right) \frac{h}{e}$$

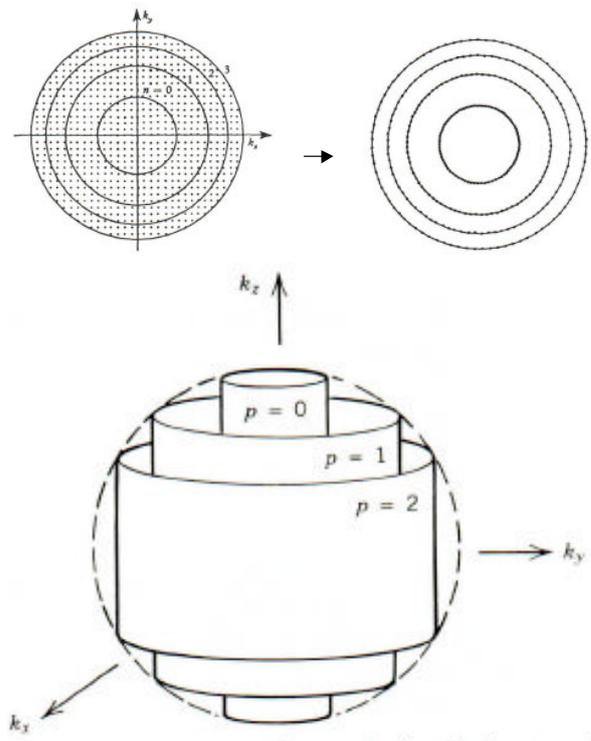
Quantum Oscillations – k -space orbits

- From Lorentz force
 $m\mathbf{v}_\perp = \hbar\mathbf{k}_\perp = q\mathbf{r} \times \mathbf{B}$:
 \mathbf{k} -space orbit = real space orbit,
 turned by 90 degrees, stretched
 by Bq/\hbar .
- Area of \mathbf{k} -space orbit A_k :

$$A_k = \left(\frac{e}{\hbar}\right)^2 B^2 A_r$$

- Combining with flux quantisation gives:

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



Landau tubes

Electrons in high magnetic fields – μ oscillations

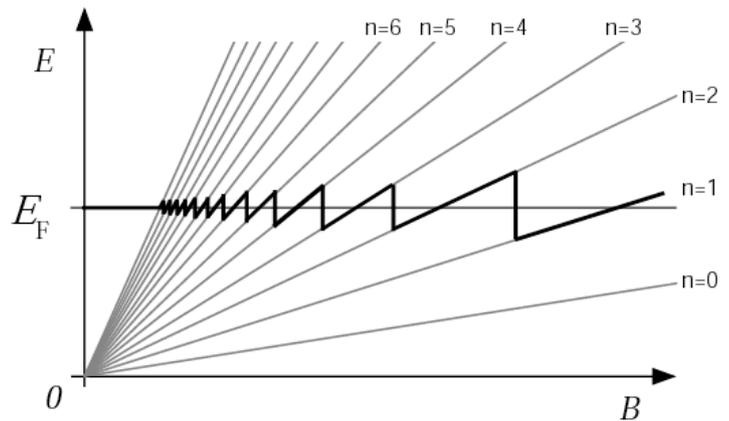
- Orbit area quantised:

$$A_k = \frac{2\pi e}{\hbar} B \left(n + \frac{1}{2} \right)$$
- \Rightarrow inverse field \sim inverse of orbit area.

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

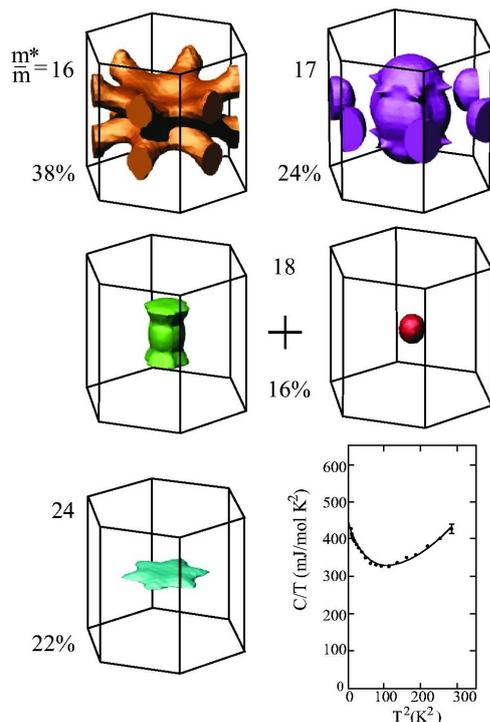
- Onsager relation** for cross-section area of **extremal orbits**

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



DOS and chemical potential oscillations, **periodic in $1/B$** .

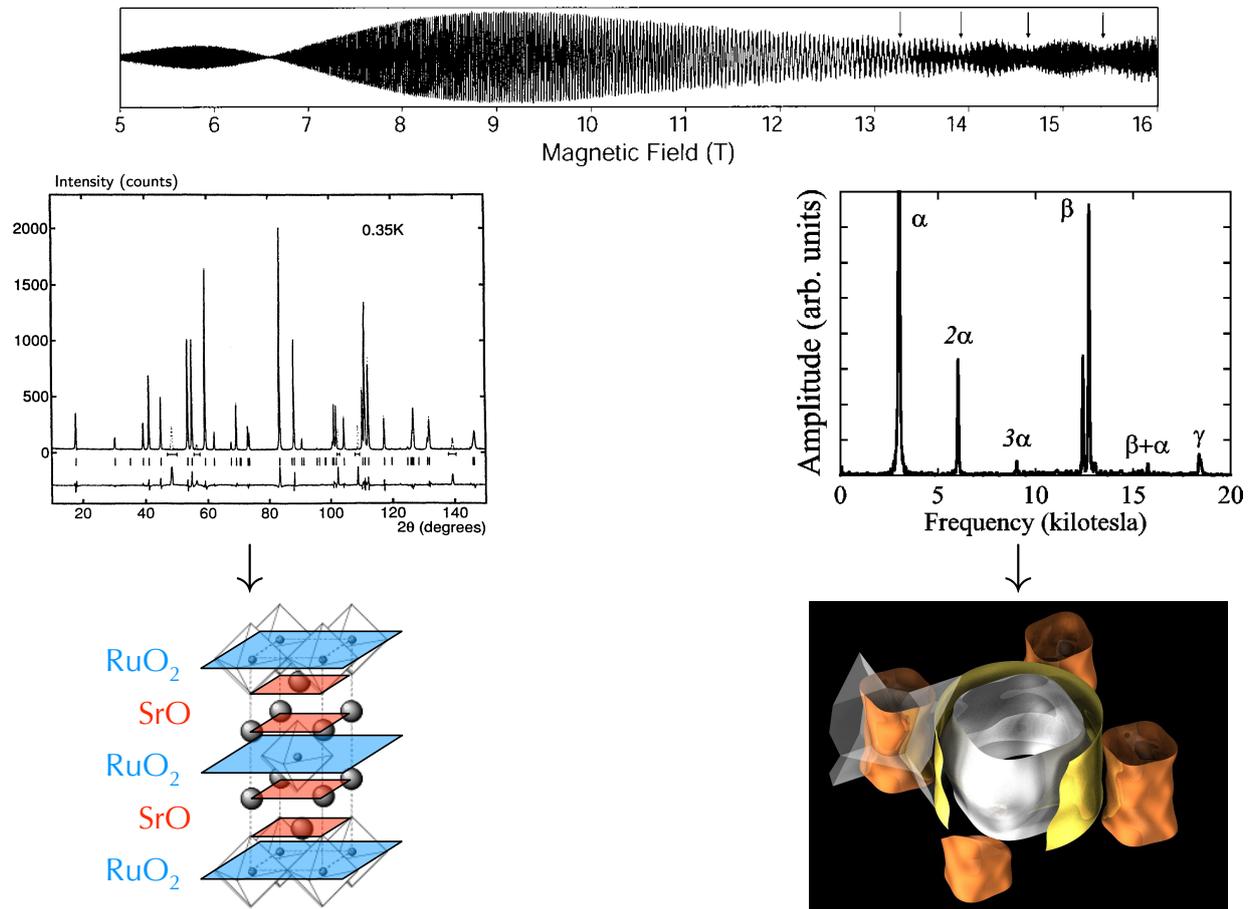
Quasiparticles detected in de Haas-van Alphen experiments



UPt₃ [Taillefer and Lonzarich, Phys. Rev. Lett. **60** 1570 (1988)]

- Magnetic susceptibility (or resistivity, or heat capacity, or ...) **oscillates** as function of **magnetic field**
- Reveal several **Fermi surface sheets**
- Temperature dependence of oscillation amplitude \rightarrow **effective mass**.
- Measured effective masses consistent with **heat capacity results**.

Quantum oscillation measurements reveal electronic structure



Semiconductors

(Semiconductor band structure. Temperature dependence of carrier numbers in intrinsic semiconductors. Law of mass action. Doping. Singleton book chapter 6.)

Intrinsic carrier concentration

- Thermal excitation across gap \rightarrow **intrinsic** carrier concentration.

- **Parabolic** conduction and valence bands.

$$E_c(k) = E_c + \frac{\hbar^2 k^2}{2m_e^*} ; E_v(k) = E_v - \frac{\hbar^2 k^2}{2m_h^*}$$

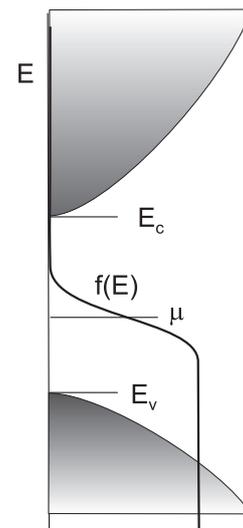
- **Densities of states**

$$g_{c,v}(E) = \frac{1}{2\pi^2} \left(\frac{2m_{c,v}^*}{\hbar^2} \right)^{3/2} |E - E_{c,v}|^{1/2}$$

- **Carrier density:** electron concentration

$$n = \int_{E_c}^{\infty} dE g_e(E) f(E), \text{ where}$$

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



$$n \approx 2 \left(\frac{m_e^* k_B T}{2\pi \hbar^2} \right)^{3/2} e^{-\frac{E_c - \mu}{k_B T}}, \quad p \approx 2 \left(\frac{m_h^* k_B T}{2\pi \hbar^2} \right)^{3/2} e^{-\frac{\mu - E_v}{k_B T}}$$

$$n \approx 2 \left(\frac{m_e^* k_B T}{2\pi \hbar^2} \right)^{3/2} e^{-\frac{E_c - \mu}{k_B T}}, \quad p \approx 2 \left(\frac{m_h^* k_B T}{2\pi \hbar^2} \right)^{3/2} e^{-\frac{\mu - E_v}{k_B T}}$$

- Product np **independent of** chemical potential μ .
- Intrinsic semiconductor: $n = p$ (charge neutral).

$$n_i = p_i = 2 \left(\frac{k_B T}{2\pi \hbar^2} \right)^{3/2} (m_e^* m_h^*)^{3/4} e^{-\frac{E_{gap}}{2k_B T}}$$

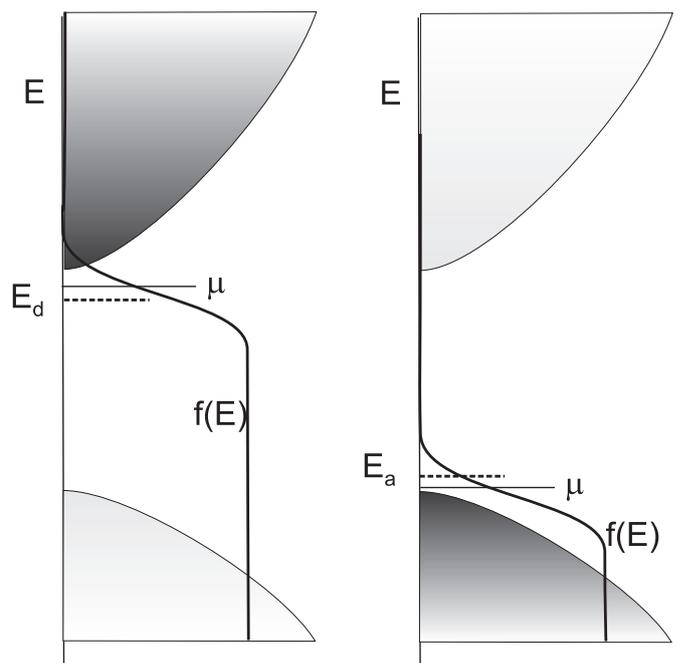
- This gives the chemical potential:

$$\mu = \frac{1}{2}(E_c + E_v) + \frac{3}{4}k_B T \log(m_h^*/m_e^*)$$

- Chemical potential in **middle of gap** at $T = 0$. Activation energy = $E_g/2$

Extrinsic semiconductors

- Create carriers by **doping**
- **Donor levels:** e.g. group V element (As, P). One extra electron.
- Hydrogen-like problem. But: $\epsilon \gg 1$ in semiconductor, and $m_e^* \ll m_e$.
- Resulting binding energy $\Delta_d = \frac{m_e^*/m_e}{\epsilon^2} \times 13.6 \text{ eV} \ll \text{bandgap}$
- $\Delta_d \sim k_B T$, electrons promoted to conduction band.
- **Acceptor levels:** e.g. group III element (B, Ga). One extra hole. Analogous situation.



- Donor atoms dominate → **n-type**, acceptors dominate → **p-type**. Distinguish by Hall effect ($R_H = \frac{1}{nq}$)
- Thermally activated **impurity ionisation**.

For donors only:

- **At low T :**

$$n = (n_c N_d)^{1/2} e^{-\frac{\Delta_d}{2k_B T}}$$

N_d = donor density.

$n_c = 2(m_e^* k_B T / 2\pi \hbar^2)^{3/2}$ is the effective density of electrons, within $k_B T$ of band edge.

- **At intermediate T ,** $\Delta_d < 2k_B T < E_g$: All donors are ionised. $n \approx N_d$.
- **At high T :** intrinsic carrier generation.
- Acceptors only: analogous.
- Both acceptors and donors: usually one species dominates, e.g. $N_d^{eff} = N_d - N_a$
- Note **law of mass action:**

$$np = const.$$

More donors than acceptors → increases n and decreases p .

More to follow in Easter Term

Six more lectures over two weeks to look into

- more on semiconductor devices
- electronic instabilities such as (i) Peierls transition or more generally charge density wave order, and (ii) ferromagnetism
- the Fermi liquid picture for interacting electrons in metals

The story so far

Structure of the Lent term part of the course:

- 1 **Classical models of electrons in solids:** Lorentz oscillator model for optical response of insulators, Drude model for optical and transport properties of metals.
- 2 **Minimal quantum model of electrons:** Fermi gas (Sommerfeld) model for electrons in metals → Fermi surface = sphere, linear temperature dependence of heat capacity. Thomas-Fermi theory of screening.
- 3 **Introducing the lattice:** Bravais lattice, basis, unit cells, symmetry properties, diffraction, reciprocal space, Brillouin zone, lattice vibrations.
- 4 **Quantum states of electrons in a lattice:** Bloch's theorem, approximation methods – nearly free electrons versus tight binding (linear combination of atomic orbitals). Even number rule ($2 e^-$ per unit cell can fill a band). Holes are electron anti-particles. Probes of the electronic band structure – optical spectroscopy, photoemission spectroscopy (ARPES), quantum oscillations, tunneling.
- 5 **Semiconductors:** Intrinsic carrier density. Effects of doping. Extrinsic carrier density.

Now for the fun part

Six lectures in Easter:

- 1 ***p-n*-junction-based semiconductor devices:** rectifying diodes, light emitting diodes, solar cells.
- 2 **Field effect transistors and band-gap engineering:** Operation and fabrication of modern devices; 2-D electron gases and quantum wells.
- 3 **Electronically driven phase transitions – Charge:** Peierls distortions and charge density waves.
- 4 **Electronically driven phase transitions – Spin:** Origin of spin-spin (exchange) interaction, local moment magnets, magnetism in metals.
- 5 **Standard model of interacting electrons in solids:** Fermi liquid theory in a nutshell.
- 6 **Beyond the standard model:** survey of more exotic states of condensed matter – heavy fermions, non-Fermi liquids, skyrmion lattice, spin ice.

p-n junctions

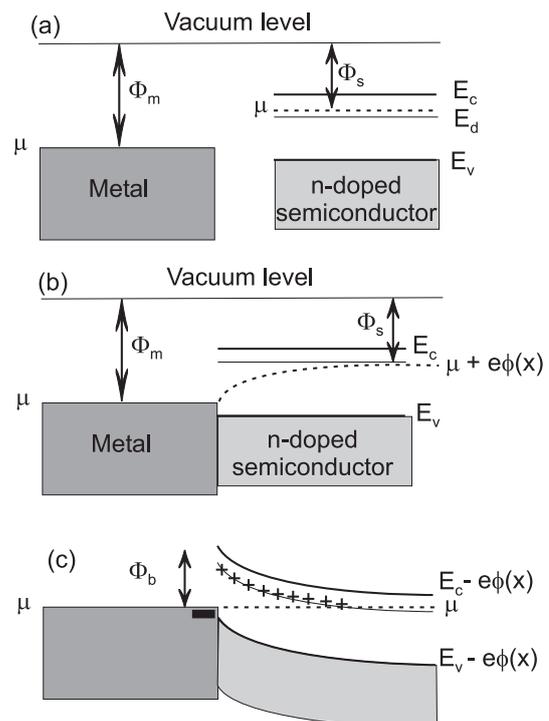
(Principles of operation of key semiconductor devices I: p-n junction diode.)

Let's start with a metal - semiconductor contact (Schottky barrier)

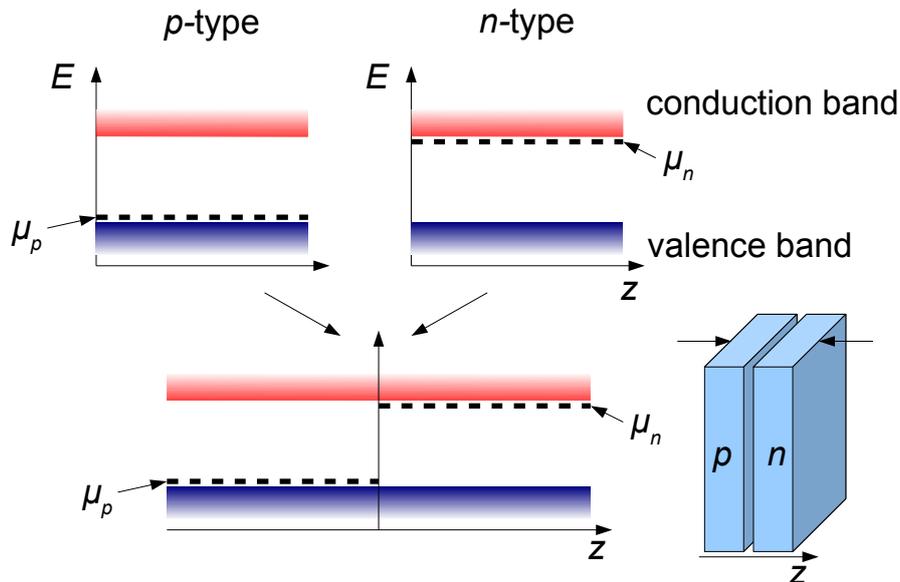
- **Work function**
 $\Phi = E_{vac}(\mathbf{k} = 0) - \mu$.
- Bring together materials with different $\Phi_{1,2} \rightarrow \mu_{1,2}$ differ, \rightarrow **charge flows**, internal potential ϕ develops.
- Electrostatic **potential modifies Hamiltonian**

$$H = E_n(\mathbf{k}) - e\phi(\mathbf{r})$$

- **Energy levels shift** by $-e\phi(\mathbf{r})$.
- End result: μ **constant** across both materials, charge redistribution. **Depletion layer** in semiconductor.

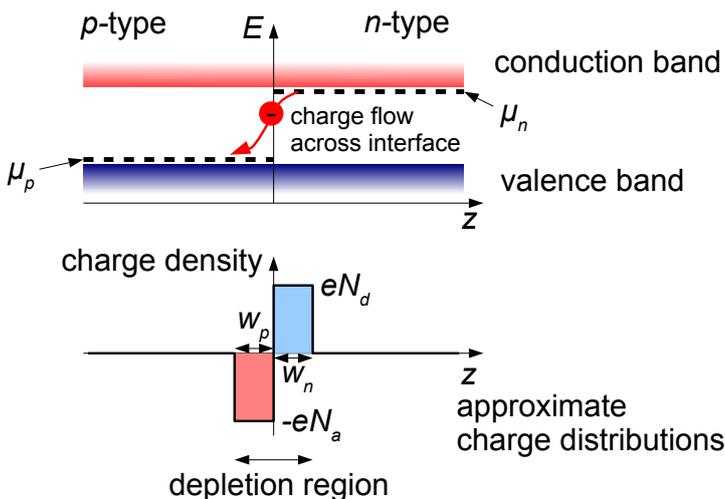


p-n junction: Consider joining two differently doped semiconductors



- p-type: chemical potential μ close to top of valence band. n-type, μ close to bottom of conduction band.
- On joining the two types, obtain step in μ at junction.
- In practice, junction is produced by **inhomogeneous doping**, producing n-type layer next to p-type layer.

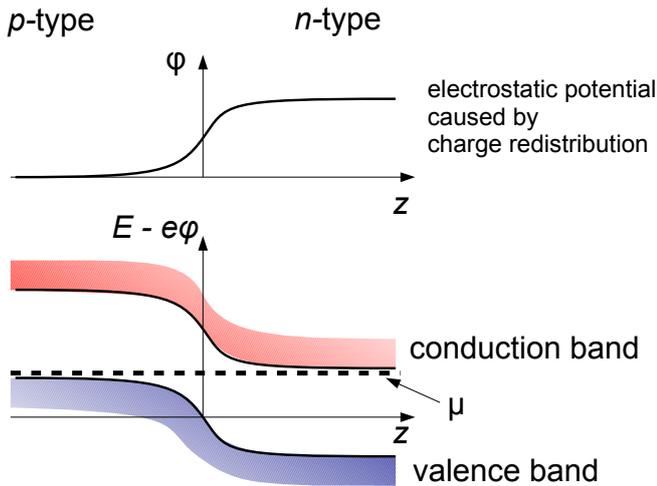
p-n junction: charge redistribution, depletion region



- Imbalance in chemical potential causes **charge flow**.
- Electrons from n-side fill holes on p-side. To rough approximation, no mobile charges left within a zone around the junction called **depletion region**.
- Remaining negatively charged acceptor sites (p-side) and positively charged donor sites (n-side) give rise to new **charge distribution**.

- Charge neutrality gives $N_a w_p = N_d w_n$.

p-n junction: band bending due to electrostatic potential

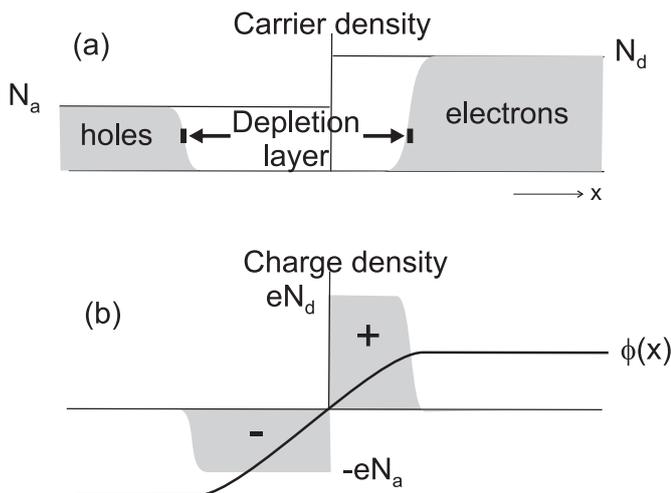


- By Poisson's law: charge distribution causes electrostatic potential ϕ .
- All energy levels shift as $E \rightarrow E - e\phi(z)$. Far away from junction, μ still aligns with top (for p) or bottom (for n).
- Charge will flow, until the energy levels have shifted sufficiently for μ to line up across the junction \rightarrow equilibrium is reached. Junction potential $e\phi_j = \mu_n - \mu_p \simeq E_g$.

- Charge neutrality and solving Poisson's equation give

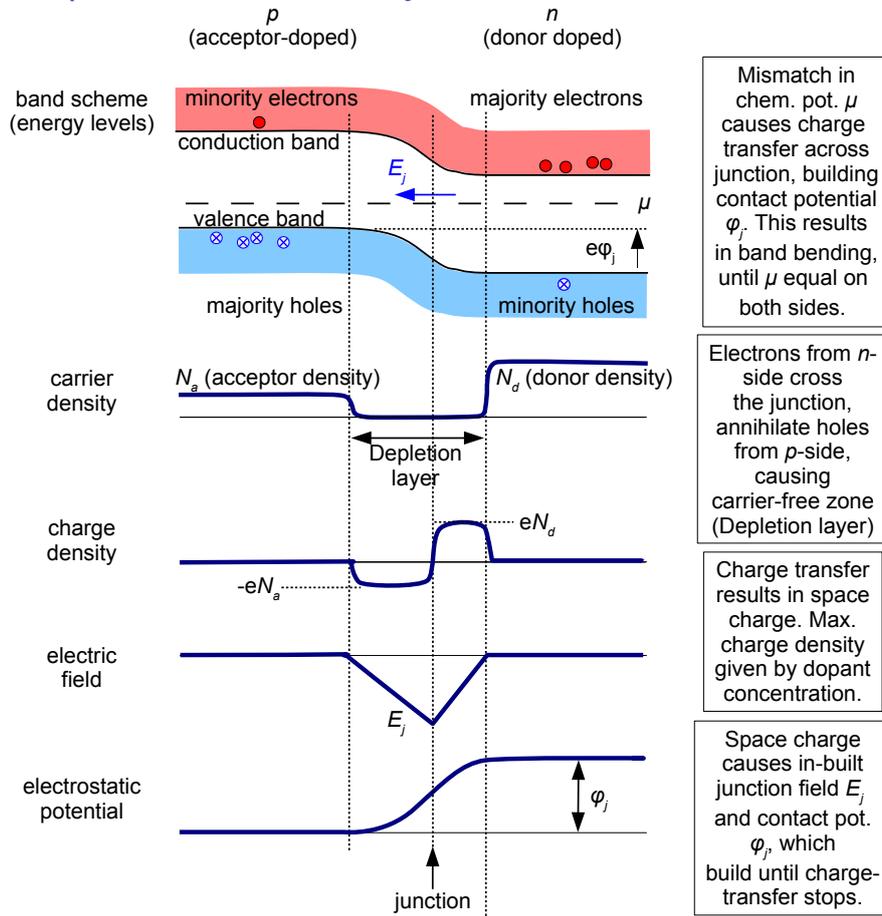
$$N_{(a,d)} w_{(p,n)} = \left(\frac{2\epsilon_0\epsilon\phi_j}{e} \frac{1}{N_a^{-1} + N_d^{-1}} \right)^{1/2}, \text{ and } w_p + w_n = \left(\frac{2\epsilon_0\epsilon\phi_j}{e} \frac{N_a + N_d}{N_a N_d} \right)^{1/2}$$

p-n junction in equilibrium – carrier density vs. charge density

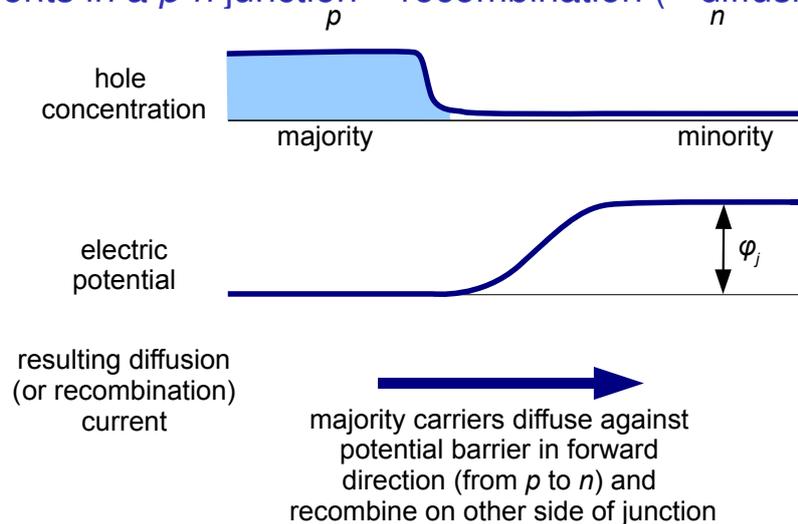


- At low T : where bottom of conduction band or top of valence band pull away from μ , the **carrier density changes abruptly**.
- **Carriers depleted** near interface. No mobile carriers here!
- However, **charge density** due to ionic background is large near junction: eN_d (n side), $-eN_a$ (p side).
- This **charge density causes potential** $\phi(x)$,
- Potential $\phi(x)$ in turn determines charge flow **selfconsistently**.

p-n junction in equilibrium – summary



Balance of currents in a p-n junction – recombination (= diffusion) current

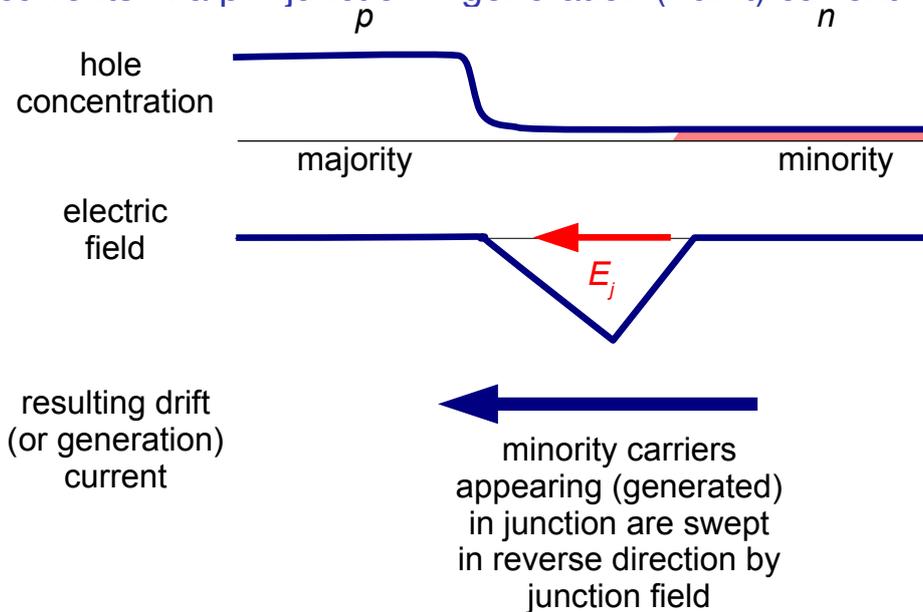


- Holes diffuse from p to n side and recombine with electrons there. Electrons do the same in opposite direction. Currents add.
- Hole **recombination current** $J_{rec}^{(h)}$: probability that holes **climb the potential barrier** is $\propto e^{-e\phi_j/(k_B T)}$, which suggests

$$J_{rec}^{(h)} = J_0^{(h)} e^{-e\phi_j/(k_B T)}$$

($J_0^{(h)}$ is just a constant of proportionality)

Balance of currents in a p-n junction – generation (=drift) current



- Small number of minority holes (remember $np = n_i^2$) generated on n -side, drift to p -side under influence of in-built field. Electrons do the same in opposite direction. Currents add.
- Resulting hole **generation current** $J_{gen}^{(h)}$ depends on temperature and details of the band structure and of the doping level.
- In equilibrium: $J_{tot}^{(h)} = J_{rec}^{(h)} - J_{gen}^{(h)} = 0$.

Voltage biased p-n junction – rectification

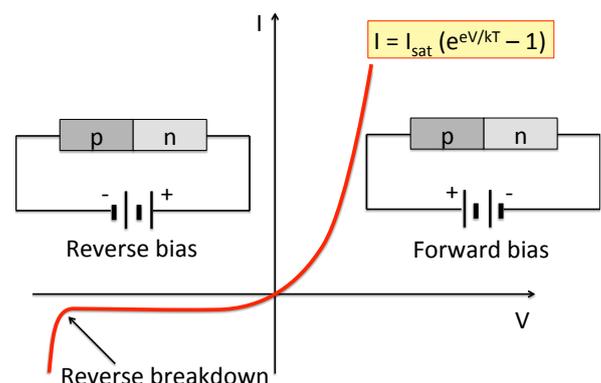
- Bias voltage (positive on p -side) **modifies effective junction potential:**

$$\phi_j^{eff} = \phi_j - V$$
- This changes the diffusion current (because the barrier height changes), but leaves the generation current unchanged (because the minority carrier number on either side remains the same).
- Forward bias: $J_{rec}^{(h)} = J_{gen}^{(h)} e^{eV/k_B T}$ **outstrips** generation current **exponentially** → diode action.
- Reverse bias: $J_{rec}^{(h)} \rightarrow 0$, $J^{(h)} \rightarrow -J_{gen}^{(h)}$, **saturates** at low level.
- **Saturation current** $I_{sat} = J_{gen}^{(h)} + J_{gen}^{(e)} \propto n_i^2 \propto e^{-E_g/k_B T}$

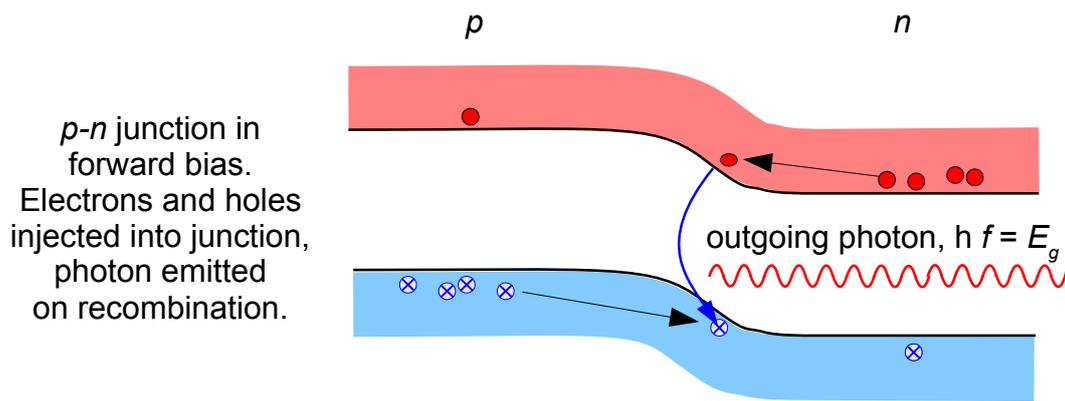
- From this, obtain **diode equation**

$$I = I_{sat} (e^{eV/k_B T} - 1)$$

- **Note: reverse breakdown** when reverse bias gets too large! Mechanism e.g. tunneling of majority carriers across depletion zone.

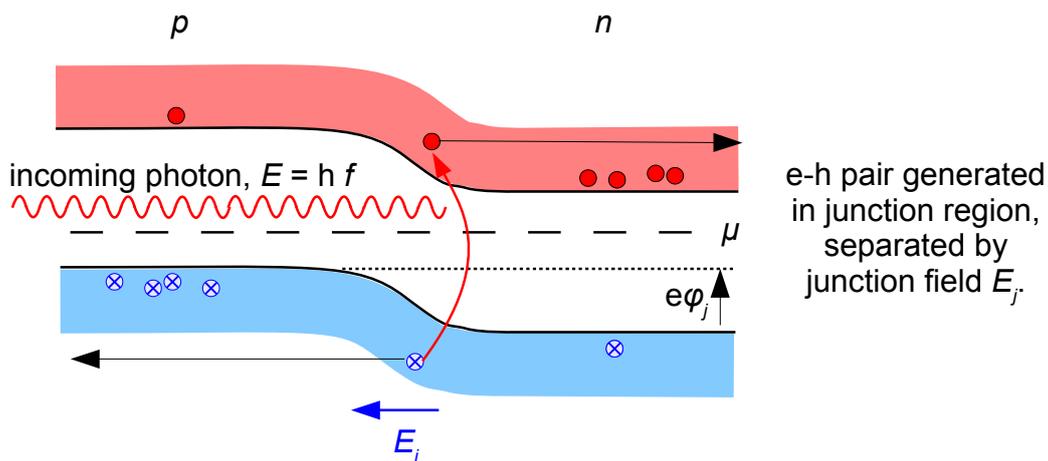


Light emitting diodes



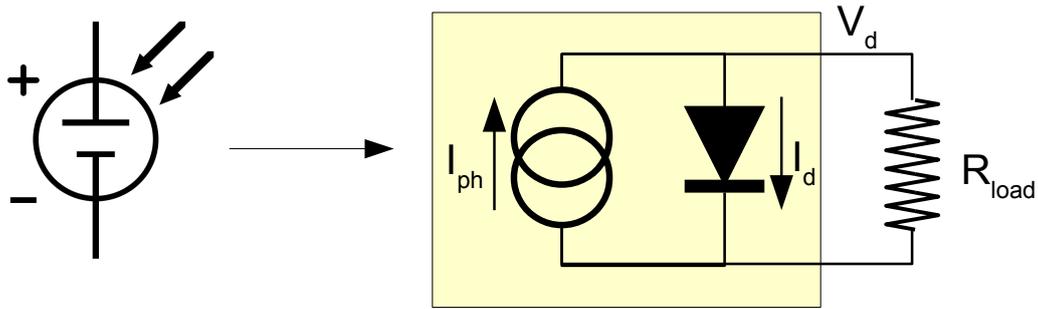
- Large bias eV produces **current**.
- Electrons and holes recombine in junction \rightarrow photons.
- Photon energy \simeq band gap.
- More efficient for **direct-gap** materials (III-V or II-VI) than for Si or Ge (indirect gap).
- **Organic LED's**

How do solar cells work?



- Illuminate p-n junction: absorbed photons set free **electron-hole pairs**.
- In-built electric **field** in junction **separates electrons and holes**.
- Electrons flow towards n -side, holes towards p -side. Equivalent to increasing the generation current. Remember that this flows in reverse direction (n to p).

Solar cells – equivalent circuit

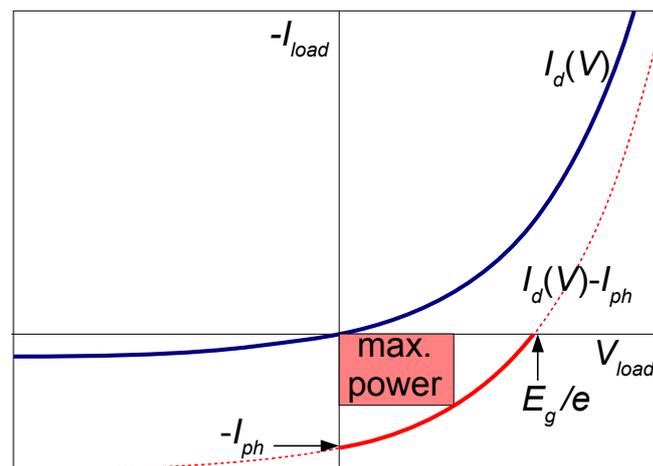


solar cell equivalent circuit

- Model solar cell as $p - n$ diode with a current source in parallel, which produces photocurrent.
- Photocurrent I_{ph} adds to standard $I - V$ characteristic of $p - n$ junction, but flows in reverse direction:

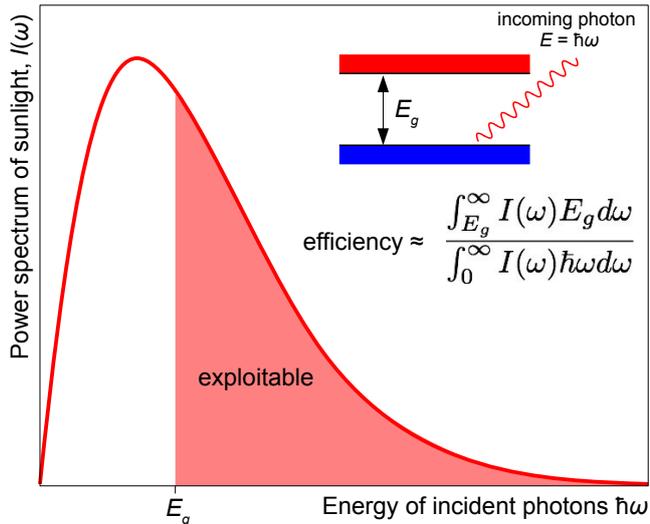
$$I_{load} = I_{ph} - I_d(V_d)$$

Efficiency of solar cells



- Case 1: $R_{load} = 0$ (short circuit). $I_{load} = I_{ph}$, but $V_{load} = V_d = 0$, no power is extracted.
- Case 2: $R_{load} \rightarrow \infty$ (open circuit). $I_{load} = 0$, so again no power. But what is open circuit V_d ? Upper limit is given by band gap E_g , because if V_d exceed $\phi_j (\sim E_g/e)$, then the in-built junction field vanishes and photo-generated carriers are no longer swept out of the junction area.
- Ideal load is in between, extracted power $\propto I_{ph} E_g/e$

Efficiency of solar cells – Shockley-Queisser limit



- Optimise solar cells by tuning gap energy E_g to match intensity spectrum of sunlight.
- Low E_g : benefit from large part of sun's spectrum, but open circuit voltage drops.
- High E_g : high open circuit voltage, but that only few photons energetic enough to promote electrons across gap.

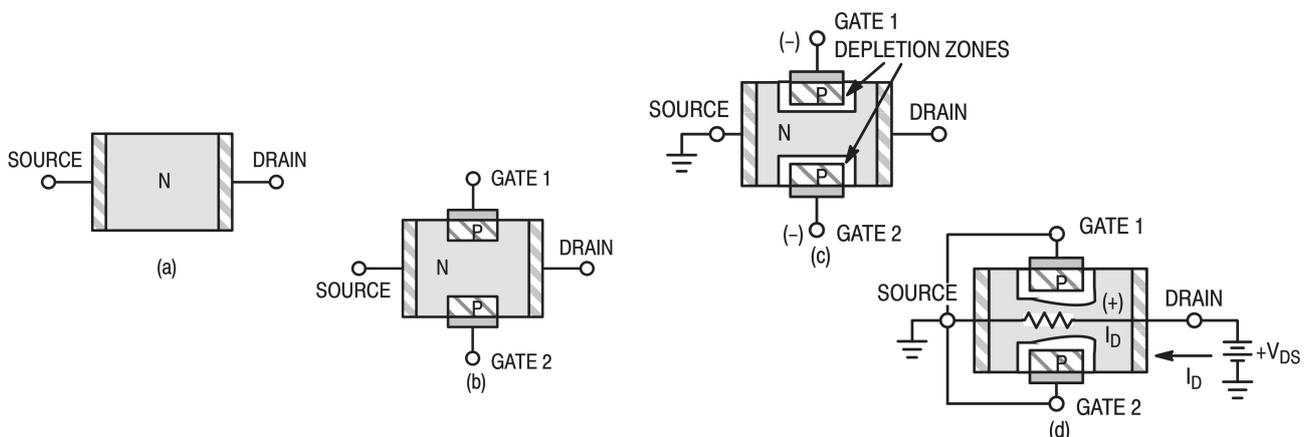
- Full treatment [Shockley and Queisser, J. Appl. Phys. **32**, 510 (1961)] takes into account additional complications.
- Arrive at max. possible efficiency of $\simeq 33\%$ for single junction with band gap $E_g \simeq 1.2\text{eV}$

Field effect transistors

(See also excellent review in http://www.freescale.com/files/rf_if/doc/app_note/AN211A.pdf band gap engineering, quantum wells.)

Junction field effect transistor: JFET

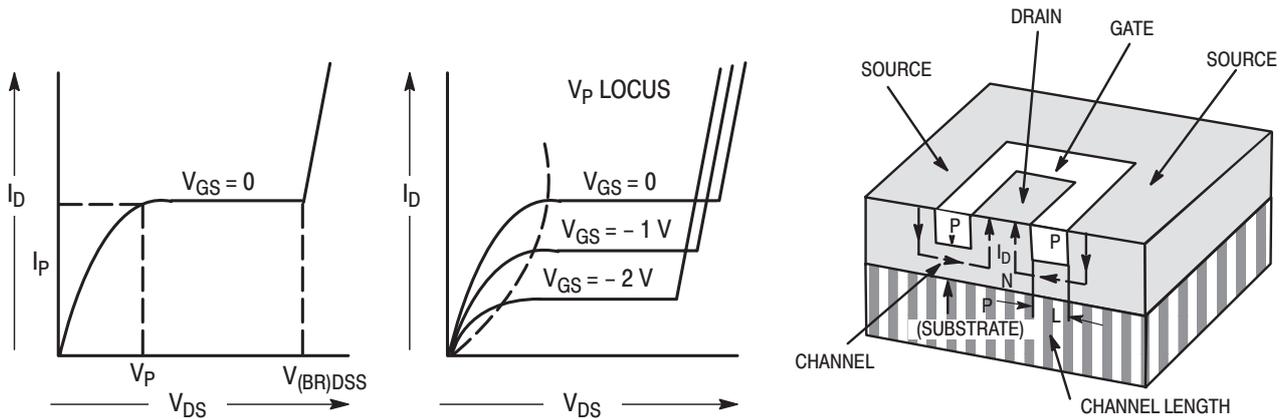
- Vary the current through a doped semiconductor by **changing the size of the conducting channel**.



- a) **Metallic current contacts** on n -doped semiconductor (source, drain).
- b) p -doped **gate contacts** in between source and drain.
- c) **Depletion zones** surround the $p - n$ junctions.
- d) Biasing the gates **changes width of depletion zones**. This changes the width of the remaining current-carrying channel in between the gates.

JFET: I-V characteristics, pinch-off, fabrication

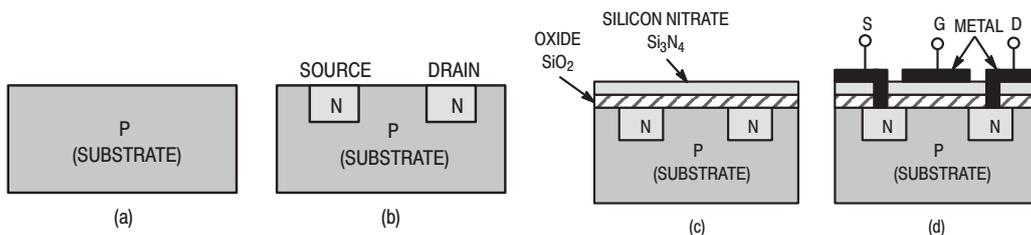
- Vary the resistance of a doped semiconductor by changing the size of the conducting channel.



- Very important: **Pinch-off!** At high drain-source voltages, depleted zones widen on drain-side of gate, eventually pinching off the conducting channel.
- Pinch-off results in **saturation of drain-source current** for high drain-source voltages. This is a good thing – it's the basis for operating the device as an **amplifier**: drain-source saturation current depends on the gate-source voltage.

Metal-oxide-semiconductor field effect transistor: MOSFET

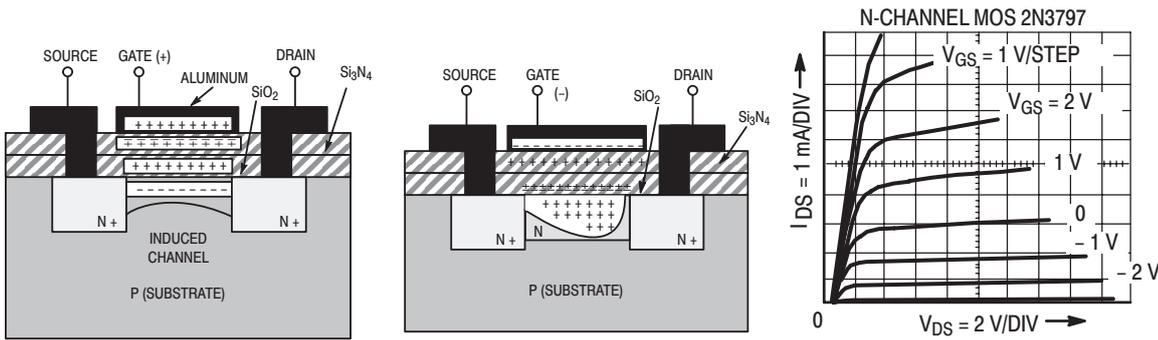
- Gate electrode separated from conducting channel by insulating layers.



- This is an enhancement-mode *n*-channel MOSFET.
 - p*-doped substrate,
 - n*-doped **source and drain contacts**. Depletion zone around contacts produce very high resistance.
 - insulating layers (silicon nitride guards against sodium diffusing in).
 - Metallic contacts to source and drain through holes etched into insulator, metallic gate electrode insulated from substrate.

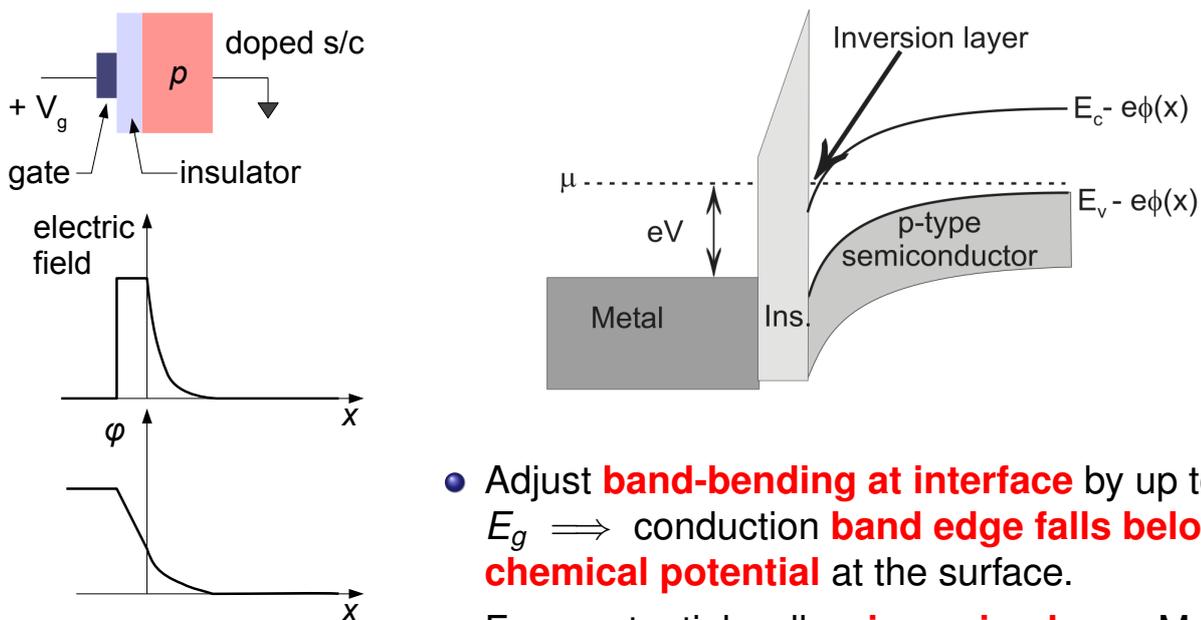
MOSFET – principle of operation

- Applying a gate voltage will redistribute minority carriers in source-drain channel.



- Left: enhancement mode MOSFET: positive voltage pulls minority carriers (electrons) towards the surface, forming a high-conductivity channel, also called **inversion layer**.
- Centre: depletion-enhancement mode MOSFET: negative voltage depletes conducting channel, increasing the resistance, positive voltage reduces the resistance
- Right: typical I-V characteristic for a depletion-enhancement mode MOSFET. Note pinch-off at high drain-source voltage.

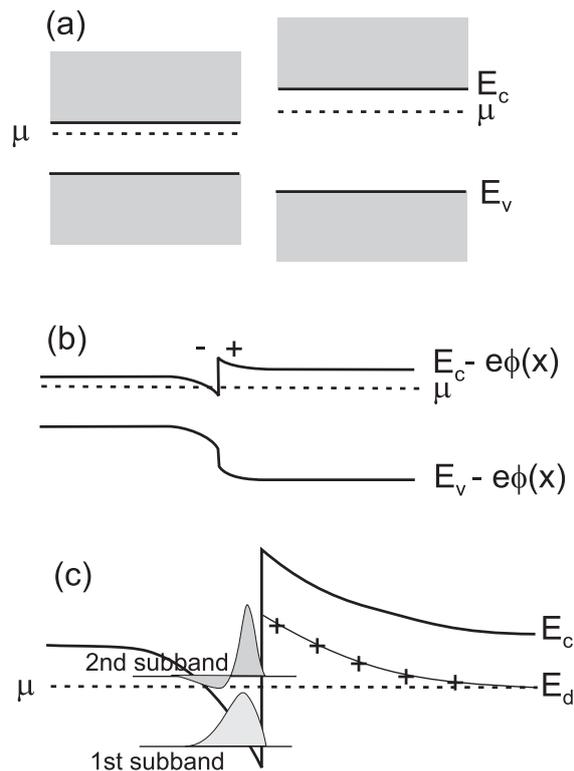
Band bending in the MOSFET – formation of inversion layer



- Adjust **band-bending at interface** by up to $E_g \Rightarrow$ conduction **band edge falls below chemical potential** at the surface.
- Form potential well \rightarrow **inversion layer**. May have quantisation inside well.
- Modulate conductivity** by changing voltage applied at metallic gate, which varies size of conducting channel.

Bandstructure engineering

- Vary gap and band edges by **finely controlled doping** in $\text{Al}_{1-x}\text{Ga}_x\text{As}$ (or others)
- **Modulation doping** by epitaxial (layer-by-layer) growth: interface region free from dopants.
- **Internal potential** arises in equilibrium, to line up μ .
- Can form **high mobility 2D electron gas** at interface.
- Further control by **gate electrodes**.
- **Quantisation** in potential well.



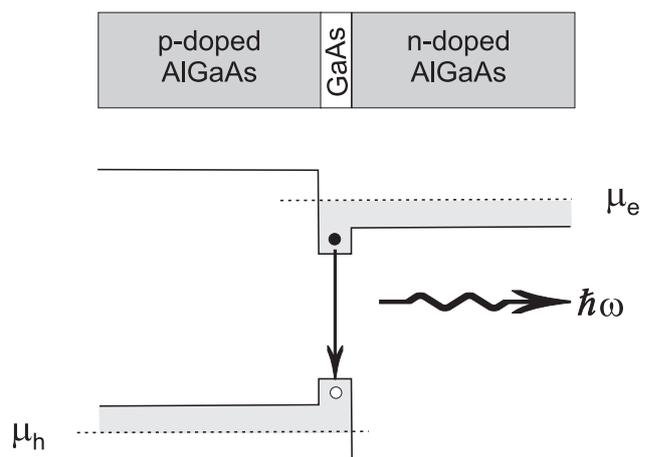
Quantum well laser

Laser requires

- efficient luminescent electron-hole recombination \rightarrow need **direct gap** semiconductor.
- **inversion**, meaning that the average electron (hole) occupancy in the luminescing states exceeds $1/2$.

Double heterojunction laser:

- Quantum well traps both electrons and holes, from either side of well.
- Like diode, but far from equilibrium $\rightarrow \mu_h \neq \mu_e$.

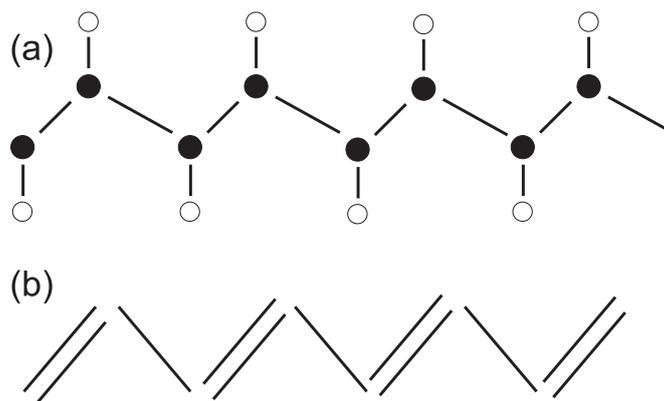


Peierls distortion and charge density waves

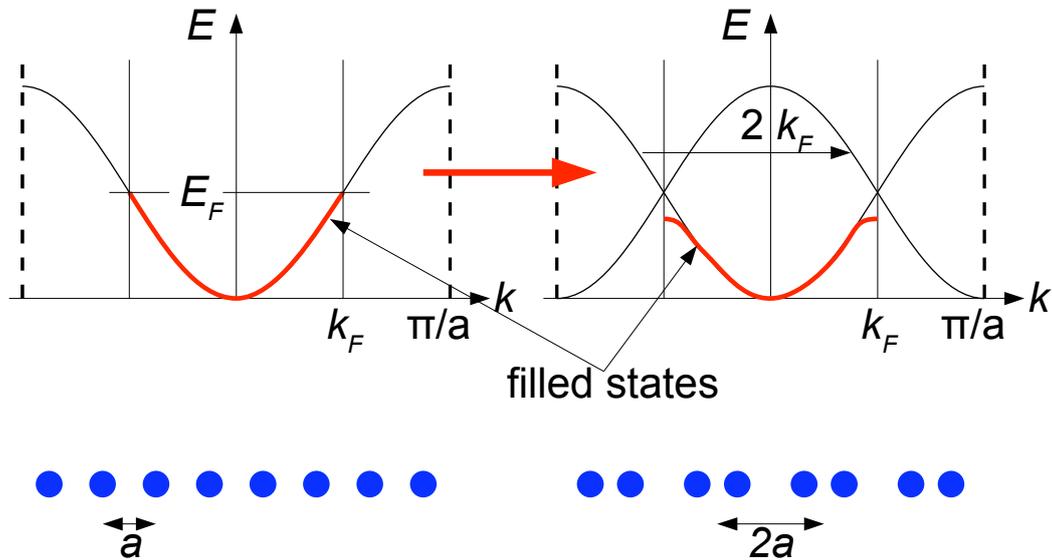
(An electronically driven structural phase transition in '1D' materials. Generalisation to CDW. Some interesting associated phenomena.)

Peierls transition – 1D metal unstable to periodic lattice distortion

- Consider a **chain of atoms**, in which one electron per atom goes into conduction band.
- Example: **Polyacetylene** $(\text{CH})^n$
- **sp^2 hybridised** orbitals bond covalently with neighbouring H, C atoms, taking up three e^- per C.
- One p_z orbital, one remaining e^- per C \rightarrow hybridisation between neighbouring p_z orbitals produces **half-filled** conduction band.
- **Conjugated bonds**: Unstable towards **dimerisation** and associated lattice distortion \rightarrow **Peierls** mechanism.



Origin of Peierls transition



- If there was an external **modulated potential**, wavevector $Q = 2k_F$, it would produce a gap at E_F .
- Same effect: potential due to spontaneous **periodic lattice distortion** ($R_n = na + u_o \cos(Qna)$)
- **Lowers energy** of occupied states. At k_F : $\Delta E(k_F-) = |V_{-Q}| = g_Q u_o$

Peierls distortion – considering the electronic energy

- Linearising the dispersion close to k_F , the extra lattice potential mixes states at energy $E^{(0)}(k_F) + \hbar v_F(k - k_F)$ and $E^{(0)}(k_F) - \hbar v_F(k - k_F)$.
- Filled states are at

$$E = E^{(0)} - \left((\hbar v_F(k - k_F))^2 + (g_Q u_o)^2 \right)^{1/2}$$

- The change in electronic energy is (approximately, writing $\delta k = k - k_F$, and noting that there are two e^- per state and a state at $-k$ for every state at $+k$):

$$\begin{aligned} \Delta E_{\text{electronic}} &\simeq -4 \int_{-k_F}^0 \frac{d\delta k}{2\pi} \left[\left((\hbar v_F \delta k)^2 + (g_Q u_o)^2 \right)^{1/2} + \hbar v_F \delta k \right] \\ &= -4 \int_0^{k_F} \frac{d\delta k}{2\pi} \left[\left((\hbar v_F \delta k)^2 + (g_Q u_o)^2 \right)^{1/2} - \hbar v_F \delta k \right] \end{aligned}$$

- Adding up the electronic energy shifts and using $k_F = \pi/(2a)$:

$$\Delta E_{\text{electronic}} \simeq A(u_o/a)^2 \ln |u_o/a|$$

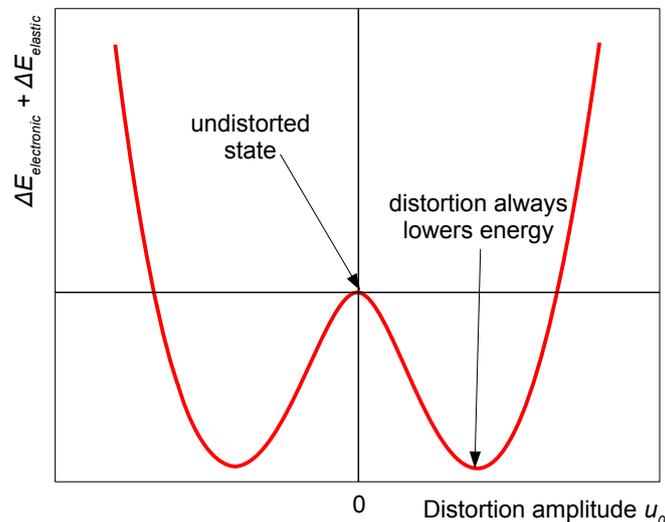
Peierls distortion – electronic vs. lattice energy

- Distortion with amplitude u_0 **lowers the energy**:

$$\Delta E_{\text{electronic}} = A(u_0/a)^2 \ln |u_0/a|$$

- Elastic lattice deformation, by contrast, increases the energy:

$$\Delta E_{\text{elastic}} = K(u_0/a)^2$$



- Sum of both terms **always** has **minimum** at finite u_0 .

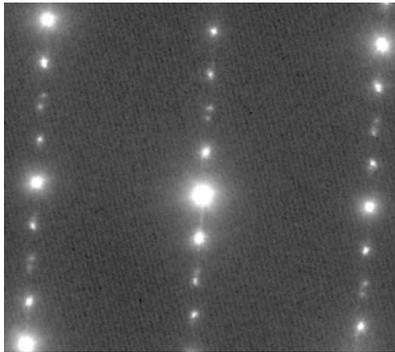
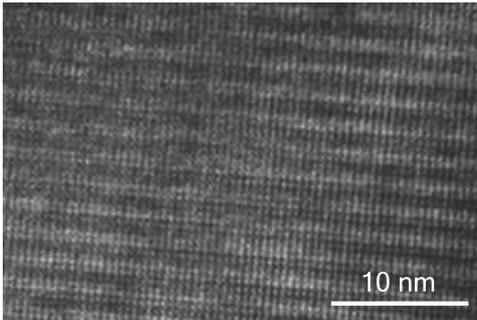
More generally ...

- Periodic lattice distortion causes **charge modulation** (remember question 1 on problem sheet 2).
- A periodic modulation of the charge density $n(\mathbf{r})$ is called **charge density wave** (CDW).
- The CDW (Peierls transition is special case) formed, because the distortion modifies the energy level scheme such that **the filled states move down**, while the empty states move up. Consequently, the chemical potential falls into an energy gap (generally, a dip in the density of states).
- Fundamental principle of bonding:

Arrange energy levels such that μ falls near a minimum in the density of states \rightarrow energy of occupied states is lowered.

- Charge density wave transitions can happen in all kinds of materials – generally, they don't have to feature 1D chains. Also, for arbitrary band filling, the ordering wavevector $Q = 2k_F$ can be incommensurate with the lattice.

Microscopic evidence for charge density waves

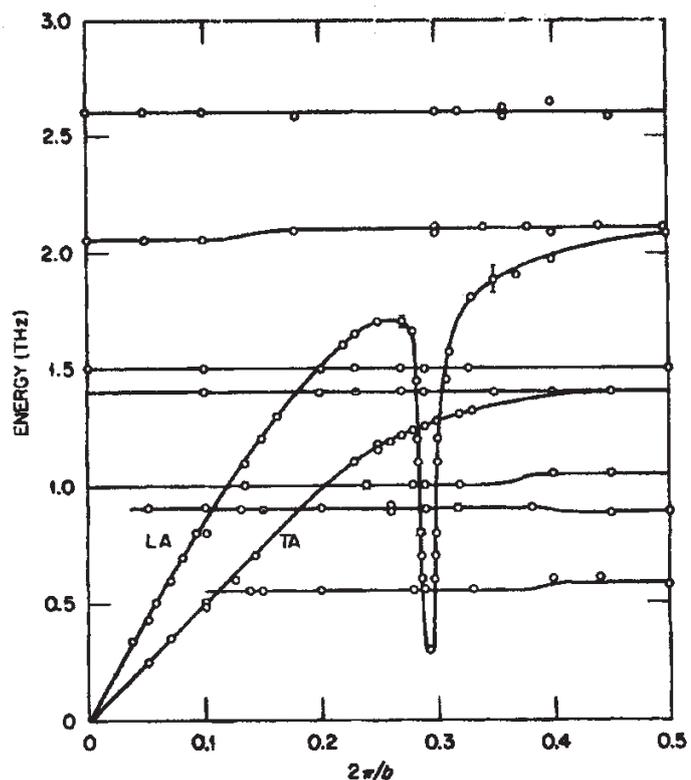


$\text{La}_{0.29}\text{Ca}_{0.71}\text{MnO}_3$

- Real space picture (scanning probe microscopy)
- Long wavelength modulation visible (roughly vertical on picture) on top of narrow grid represented by individual atoms.
- Diffraction image (electron diffraction)
- Bright spots come from undistorted structure.
- Additional (satellite) spots caused by superposed structural modulation.

Microscopic evidence for charge density waves

- If the transition happens at finite temperature T_{CDW} , then for higher temperature, there is no static distortion.
- However, the lattice vibrations show precursor effect of the transition even at $T > T_{CDW}$: **phonon frequency dips** for wavevectors close to ordering wavevector Q .
- A phonon mode whose frequency has been decreased in this way is called a **soft mode**. The phenomenon is called **phonon softening**.



Phonon dispersion curves in TTF-TCNQ

Magnetism

(Origin of spin-spin interaction. Types of exchange interaction. Magnetism in metals.)

Dipole vs. exchange interaction

Origin of magnetic interaction?

- **Dipole interaction**

too weak:

$$E_{dip} \sim \mu_0 \frac{\mu_B^2}{4\pi r^3} \sim 3\mu\text{eV} \sim k_B \cdot 0.03 \text{ K}$$

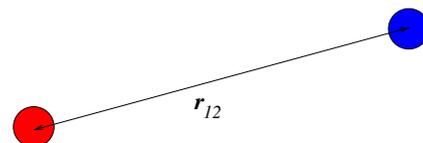
[for $r = 2.5 \text{ \AA}$ (e.g. Fe)]

Much too small to explain ferromagnetism at 1000 K!

- **Coulomb interaction**

independent of spin:

$$V(\mathbf{r}_1, \sigma_1; \mathbf{r}_2, \sigma_2) = \frac{e^2}{4\pi\epsilon_0 |\mathbf{r}_1 - \mathbf{r}_2|}$$



Charge-charge interaction depends only on distance!

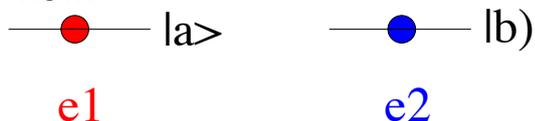
So where does magnetism come from?!

Spin-dependent interactions

(Origin of spin-spin interaction. Singlet-triplet splitting. Heisenberg Hamiltonian. Types of exchange interaction.)

Two-electron system

- Need a quantum-mechanical **model system**.
- **Simplest case**: 2 e^- in 2 orbitals, $|a\rangle$, $|b\rangle$. Forget about spin for now.



- Full state of system \simeq **product**

$$\Psi(\mathbf{r}_1, \mathbf{r}_2) = |a\rangle \otimes |b\rangle$$

[$|\dots\rangle$ denotes first e^- , $|\dots\rangle$ is second e^-]

- **Energy** = expectation value of Hamiltonian:

$$E = \langle \Psi | \mathbf{H} | \Psi \rangle$$

$$\mathbf{H} = \mathbf{H}_1 + \mathbf{H}_2 + \mathbf{H}_{1,2}$$

$$\mathbf{H}_1 |a\rangle = E_a |a\rangle, \quad \mathbf{H}_2 |a\rangle = E_a |a\rangle$$

[\mathbf{H}_1 and H_2 operate only on first/second electron, $|a\rangle$ and $|b\rangle$ are eigenstates of \mathbf{H}_1 , $|a\rangle$ and $|b\rangle$ are eigenstates of \mathbf{H}_2 . $\mathbf{H}_{1,2}$ is $e^- - e^-$ interaction (Coulomb)]

- Careful! e^- **indistinguishable**.
 $\Psi(\mathbf{r}_1, \mathbf{r}_2) = -\Psi(\mathbf{r}_2, \mathbf{r}_1)$.
- Antisymmetric** product wavefunction:

$$\Psi(\mathbf{r}_1, \mathbf{r}_2) = \frac{1}{\sqrt{2}} (|a\rangle|b\rangle - |b\rangle|a\rangle)$$

$$\left(\begin{array}{c} \uparrow \\ \text{---} \\ e1 \end{array} |a\rangle \quad \begin{array}{c} \uparrow \\ \text{---} \\ e2 \end{array} |b\rangle \right) - \left(\begin{array}{c} \uparrow \\ \text{---} \\ e2 \end{array} |a\rangle \quad \begin{array}{c} \uparrow \\ \text{---} \\ e1 \end{array} |b\rangle \right)$$

[$e^- 1$ in state a, $e^- 2$ in state b, **minus** $e^- 1$ in state b, $e^- 2$ in state a]

- Now consider **spin**, as well.
- Antisymmetrised products:
spin-singlet \times **symmetric spatial part**

$$\frac{1}{2} (|ab\rangle + |ba\rangle) (|\uparrow\downarrow\rangle - |\downarrow\uparrow\rangle)$$

spin-triplet \times **antisymmetric spatial part**

$$\frac{1}{2} (|ab\rangle - |ba\rangle) \begin{pmatrix} |\uparrow\uparrow\rangle \\ |\uparrow\downarrow\rangle + |\downarrow\uparrow\rangle \\ |\downarrow\downarrow\rangle \end{pmatrix}$$

Singlet-triplet splitting – 1

Calculate energy of **singlet vs. triplet** state:

- Shorthand:

$$\begin{aligned} |ab\rangle &\equiv |a\rangle|b\rangle, |ba\rangle \equiv |b\rangle|a\rangle \\ E_0 &\equiv \langle ab|\mathbf{H}|ab\rangle = E_a + E_b + E_{Coul} \\ E_{Coul} &\equiv \langle ab|\mathbf{H}_{1,2}|ab\rangle \\ &= \int d^3\mathbf{r}_1 d^3\mathbf{r}_2 |\psi_a(\mathbf{r}_1)|^2 |\psi_b(\mathbf{r}_2)|^2 V(\mathbf{r}_1 - \mathbf{r}_2) \\ E_{ex} &\equiv \langle ba|\mathbf{H}_{1,2}|ab\rangle \\ &= \int d^3\mathbf{r}_1 d^3\mathbf{r}_2 \psi_b^*(\mathbf{r}_1) \psi_a(\mathbf{r}_1) \psi_a^*(\mathbf{r}_2) \psi_b(\mathbf{r}_2) V(\mathbf{r}_1 - \mathbf{r}_2) \end{aligned}$$

- E_{Coul} looks like **Coulomb repulsion** between charge densities.
 E_{ex} has electrons trading places \Rightarrow **exchange**.
 $E_{Coul} = E_{ex}$ for short range interaction $V = \delta(\mathbf{r}_1 - \mathbf{r}_2)$.

Singlet-triplet splitting – 2

- Energy of **singlet** state:

$$\begin{aligned} E_{\text{singlet}} &= \frac{1}{2} (\langle ab + ba | \mathbf{H} | ab + ba \rangle) \\ &= E_0 + E_{\text{ex}} \end{aligned}$$

- Energy of **triplet** state:

$$\begin{aligned} E_{\text{triplet}} &= \frac{1}{2} (\langle ab - ba | \mathbf{H} | ab - ba \rangle) \\ &= E_0 - E_{\text{ex}} \end{aligned}$$

- Spin-aligned (triplet) state has lower energy!
- Using $S^2 = (\mathbf{S}_1 + \mathbf{S}_2)^2 = S_1^2 + S_2^2 + 2\mathbf{S}_1 \cdot \mathbf{S}_2$, and $\langle S^2 \rangle = 2\hbar^2, 0$ for triplet/singlet, this leads to a simplified Hamiltonian:

$$\mathbf{H} = E_0 + \frac{1}{2} E_{\text{ex}} - \frac{E_{\text{ex}}}{\hbar^2} \hat{\mathbf{S}}_1 \cdot \hat{\mathbf{S}}_2$$

- Spin-dependent **effective interaction**. Originates from Coulomb interaction by constraining the system to a low-energy subspace (only spin changes were allowed, movement of the electrons into other spatial states were not considered).

Spin-dependent effective interactions – 1

Couple spins on neighbouring sites
Heisenberg Hamiltonian

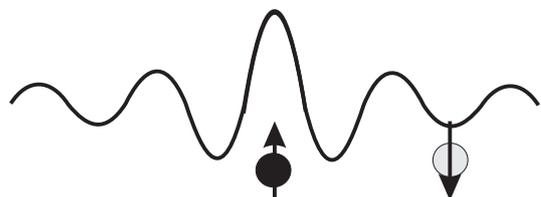
$$H_{\text{spin}} = - \sum_{ij} J_{ij} \mathbf{S}_i \cdot \mathbf{S}_j$$

Different **origins for J** :

- **Direct exchange**: as discussed. Interactions between overlapping orbitals.
- Spins align ($J > 0$) for orthogonal orbitals. Orbital overlap can make spins anti-align ($J < 0$, e.g. covalent bonds)

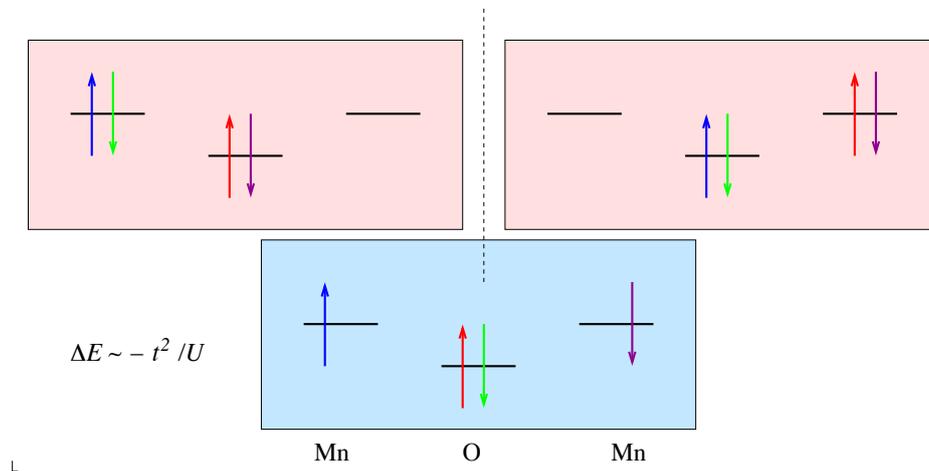
- **Indirect exchange** in metals, RKKY
- Localised f -electrons (“local moments”) interact with itinerant s, p, d electrons.
- Itinerant electrons mediate interaction between local moments.

$$H_{\text{RKKY}} = - \sum_{ij} J^2 \chi_{\sigma}(\mathbf{R}_{ij}) \mathbf{S}(\mathbf{R}_i) \cdot \mathbf{S}(\mathbf{R}_j)$$



Superexchange in insulators → antiferromagnets

- Two magnetic moments **separated by non-magnetic ion** (O^{2-}).
- Ground state energy lowered by **admixmapg** states with **double occupancy**. Only possible for anti-aligned spins:
- Hence effective $J \sim -t^2/U < 0$, favours **antiferromagnetism**

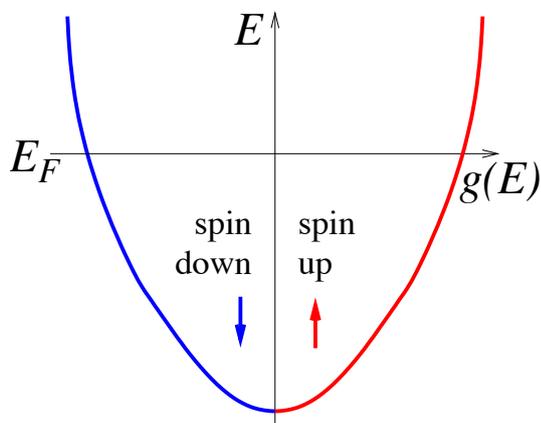


Magnetism in metals

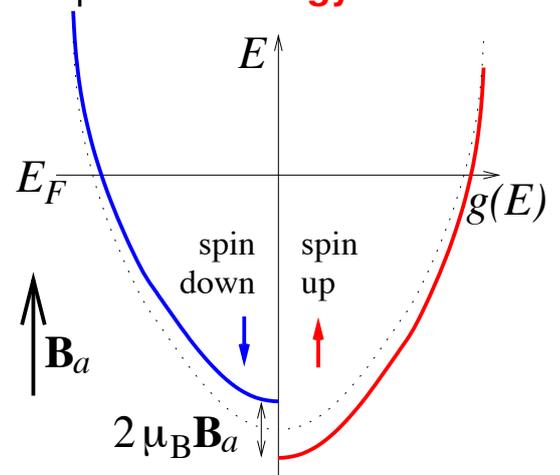
(Pauli paramagnetism. Stoner picture for metallic ferromagnetism.)

Pauli paramagnetism – 1

- Central quantity: **density of states** at E_F , $g(E_F)$.
- Magnetic **field off**: Up and down spins have **equal energy**.

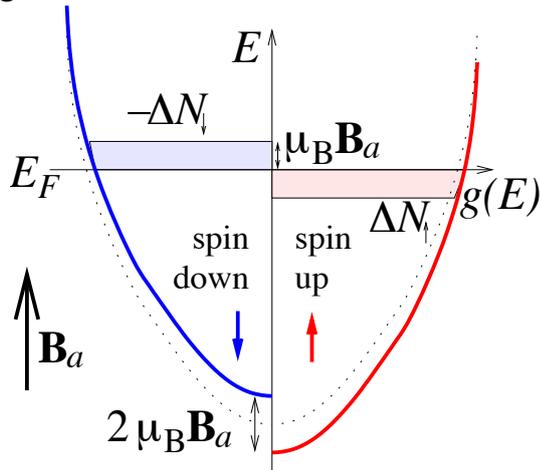


- Magnetic **field on**: spin-dependent **energy shift**.



- Total no. of electrons (per unit volume): $N = N_{\uparrow} + N_{\downarrow}$
- Magnetisation: $M = \mu_B(N_{\uparrow} - N_{\downarrow})$

Magnetisation in finite field:



- Resulting **magnetisation**:

$$M = \mu_B^2 g(E_F) B$$

$$= \mu_B^2 g(E_F) \mu_0 H$$

- Paramagnetic metal:
Pauli susceptibility

$$\chi_P = \frac{dM}{dH}$$

$$= \mu_0 \mu_B^2 g(E_F)$$

Note $g(E_F) \sim \frac{N}{\sqrt{E_F}}$

- Spin-up electrons get more:
 $\Delta N_\uparrow = \frac{1}{2} \mu_B B g(E_F)$
- Spin-down electrons get fewer:
 $\Delta N_\downarrow = -\frac{1}{2} \mu_B B g(E_F)$

- Compare to insulator:
local moment susceptibil.

$$\chi = \frac{1}{3} \frac{N}{V} \mu_0 \mu^2 \frac{1}{k_B T}$$

Band ferromagnetism – 1

Weiss molecular field

- Equation of state** for noninteracting paramagnet:

$$H = \chi_P^{-1} M + \dots$$

- Exchange molecular field** in metals.

$$H_{mol} = \lambda M = \lambda \mu_B (N_\uparrow - N_\downarrow)$$

- Equation of state **including exchange field**

$$H + \lambda M = \chi_P^{-1} M + \dots \Rightarrow$$

$$H = (\chi_P^{-1} - \lambda) M + \dots$$

- Instability**, if $\mu_0 \lambda > \chi_P^{-1}$, or

$$\mu_0 \mu_B^2 \lambda g(E_F) > 1$$

Band ferromagnetism – 2

Microscopic origin of molecular field.

- **Stoner-Hubbard** model: Interaction term $\mathbf{H}_{int} = Un_{\uparrow}n_{\downarrow}$. General treatment difficult.
- **Decoupling:** $n_{\uparrow}n_{\downarrow} \simeq n_{\uparrow}\bar{n}_{\downarrow} + n_{\downarrow}\bar{n}_{\uparrow} - \bar{n}_{\uparrow}\bar{n}_{\downarrow}$
- Single-electron **states shift:**

$$\epsilon_{\mathbf{k}\uparrow,\downarrow} = \epsilon_{\mathbf{k}} + U\bar{n}_{\downarrow,\uparrow}$$

- $U\bar{n}_{\uparrow}, U\bar{n}_{\downarrow}$ act like magnetic field \rightarrow **Weiss molecular field**.
- Find that $\mu_0\mu_B^2\lambda = U/2$
- **Ferromagnetism** favourable, if:

Stoner criterion

$$Ug(E_F)/2 > 1$$

- The spirit of the Stoner criterion: **high density of states combined with strong electronic interactions leads to a phase transition** can be generalised to many other forms of electronic order, e.g. spin and charge density waves and even superconductivity.

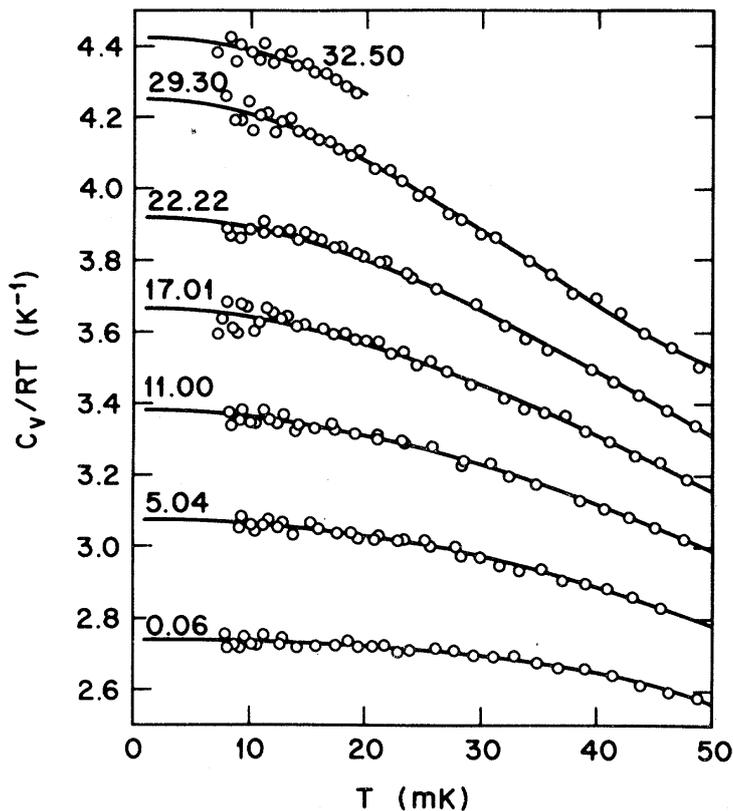
Introduction to Fermi liquid theory – the standard model of electrons in solids

(Why treating interacting electron systems using single-electron states can work, and what is really happening. Adiabatic continuity. Landau expansion of total energy. Resonances near the Fermi level.)

The problem with the single electron picture

- All the band structure arguments were based on calculating eigenstates of a **single-particle** Hamiltonian (subject to periodic lattice potential).
- We know, however, that the **electrons interact with each other**. The Coulomb repulsion is very strong. Could we treat this as a perturbation? We may say that the interaction is weak, because it is screened by the movement of the electrons themselves (remember Thomas-Fermi). But this implies that the electrons **correlate their motion**. Such **correlations are not contained in a single-particle description**.
- The success of the band structure approach so far suggests that it is **not altogether wrong**.
- Can we reconcile these conceptual difficulties with the success of the single-particle approach?

The extreme case of liquid helium 3, which behaves 'like' a Fermi gas!



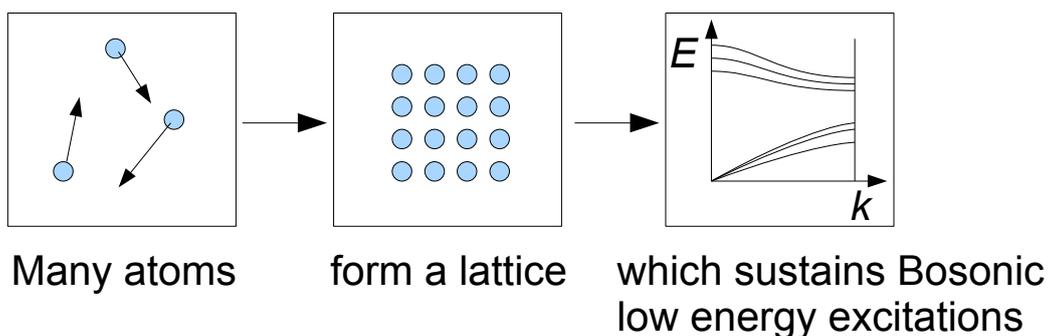
- Helium atoms are like hard spheres, closely packed.
- Experimental data: molar heat capacity C_m/T of ^3He .
- Degenerate Fermi gas: $C_m/T \rightarrow \text{const.}$ at low T .

$$C_m/T \simeq \frac{\pi^2}{2} \frac{R}{T_F}$$

We visualise liquid ^3He as a pool full of billiard balls, yet it is described by a model of free particles (Fermi gas)?!

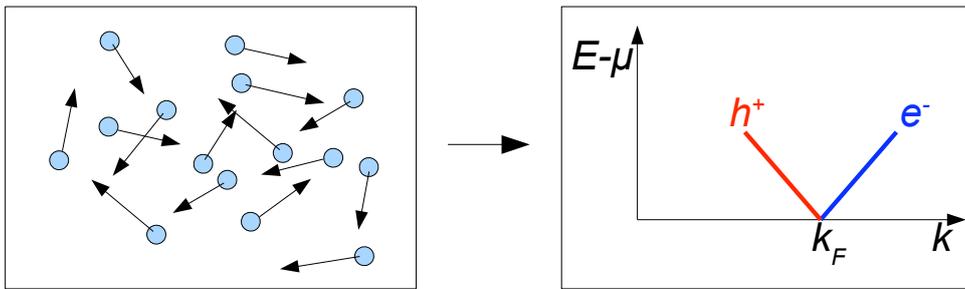
[Greywall, Phys. Rev. B **27**, 2747 (1983)]

Collective excitations – remember phonons



- **Vibrations of a harmonic lattice** = quantum harmonic oscillator. Creation and annihilation operators → exciting the lattice is thought of as 'creating a phonon'.
- Because of how the creation and annihilation operators commute, (which allows multiple excitation of the same k -state), the phonons follow Bose statistics.
- So, a collection of atoms (which themselves may be Fermions **or** Bosons!) can form a lattice, and the **low energy excitations of the lattice can behave like a Bose gas.**

Collective excitations in a Fermi liquid

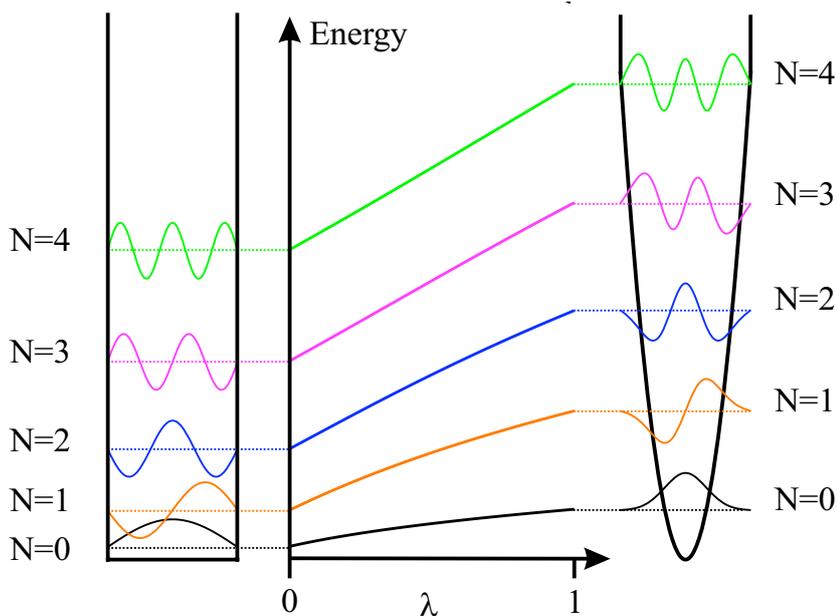


Many interacting Fermions form a liquid

which sustains Fermionic low energy excitations

- Maybe something analogous happens, when a collection of Fermions forms a liquid: could **the low energy excitations** of a 'liquid' formed from strongly interacting Fermions (e.g. electrons) **behave** like a gas of weakly interacting Fermions?
- This would explain why a single-particle description works so well in many materials. In many cases, the properties of the electrons making up the Fermi liquid carry over with only slight modification to the properties of the fermionic excitations of the Fermi liquid.

Adiabatic continuity – state labels may survive, although energy levels shift

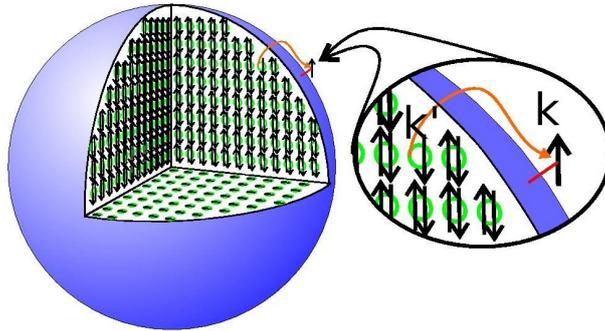
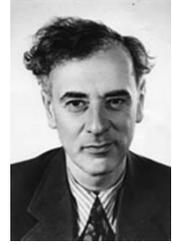


[from Schofield, Contemporary Physics **40**, 95 (1999)]

- Energy eigenstates shift, as system is tuned.
- Labels remain useful (provided the states don't cross over).
- We could view our Fermi liquid similarly:
- Turning on the interaction between particles, the energy levels of the starting description (Fermi gas) shift, but the state labels remain the same.

Landau Fermi liquid theory: expansion of total energy

Lev Landau: label excited states of interacting system with quantum numbers of non-interacting system (\mathbf{k} , spin, band index, ...)



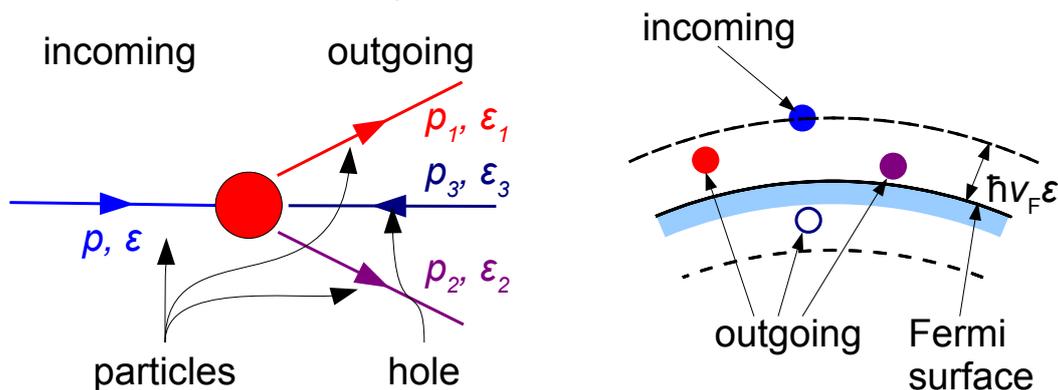
Expand total energy in terms of occupation numbers:

$$E[n_{\mathbf{k}}] = \sum_{\mathbf{k}} \epsilon(\mathbf{k}) n(\mathbf{k}) + \frac{1}{2} \sum_{\mathbf{k}\mathbf{k}'} f(\mathbf{k}, \mathbf{k}') n(\mathbf{k}) n(\mathbf{k}')$$

Second-order term accounts for interactions between excited states (which are called **quasiparticles**).

Landau Fermi liquid: energy dependence of quasiparticle scattering rate

Quasiparticle scatters by creating electron-hole pair (particle with energy ϵ , momentum p comes in, two particles and one hole come out).

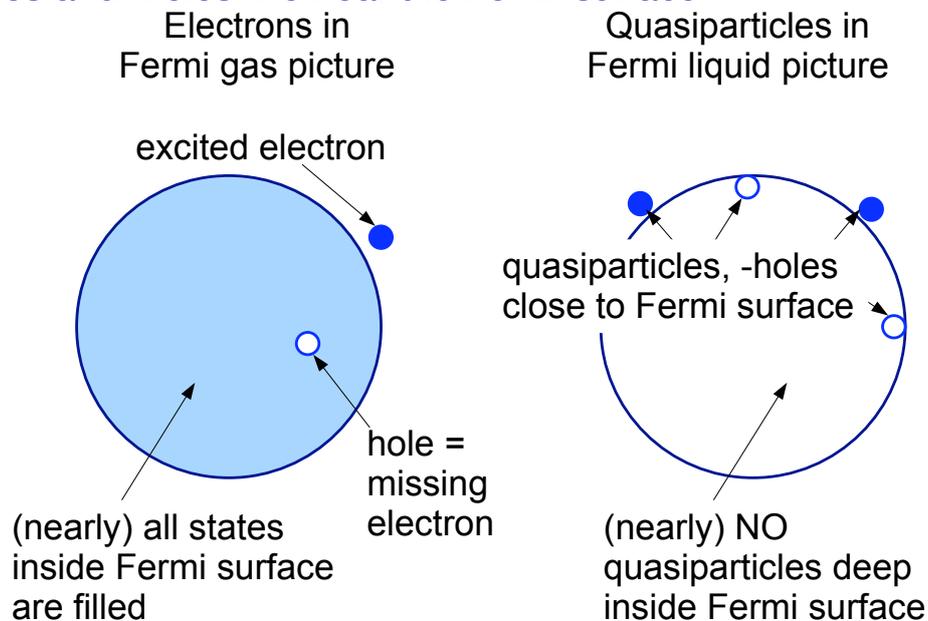


- By **Pauli exclusion principle**: all the outgoing particles must have energy (referenced to E_F) > 0 . Remember that the hole energy $= -\epsilon_3$.
- By **conservation of energy**: $\epsilon = \epsilon_1 + \epsilon_2 - \epsilon_3$ is fixed.
- ϵ_1 and ϵ_2 can be chosen freely from the range $[0, \epsilon]$, and this fixes ϵ_3 . Hence, the **number of available final states** for the scattering event rises with increasing incident quasiparticle energy as $\propto \epsilon^2$.

Scattering rate $\sim \epsilon^2$

- A key result. It means that quasiparticles **close to the Fermi surface** are **long-lived**.
- With increasing $\epsilon = E - E_F$, the scattering rate grows more quickly than ϵ . When the scattering rate exceeds ϵ/\hbar , the **quasiparticles are no longer well-defined**, because they scatter before their wavefunction can undergo a full oscillation (overdamped).
- Landau's Fermi liquid approach can only apply to **low energy** excitations. It will only work well at low temperature, so that $k_B T \ll E_F$, but in most metals E_F corresponds to 1000's of Kelvin.

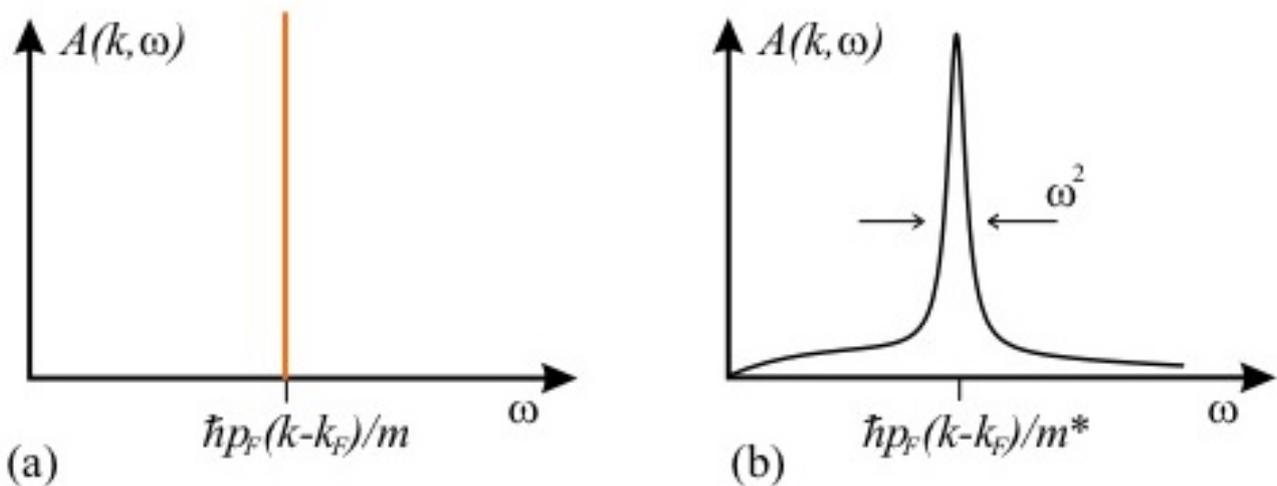
Quasiparticles and -holes live near the Fermi surface



- Because the quasiparticles can only be defined close to the Fermi surface, we cannot have a filled Fermi sphere of quasiparticles, as in the Fermi gas picture.
- Rather, there is an unusual 'vacuum' ground state, from which the low energy excitations are Fermionic particles and holes which sit on either side of a boundary surface in momentum space.

Analogy with damped harmonic oscillator – spectral function

- The spectral function $A(k, \omega)$ (where $\hbar\omega = \epsilon$, used before) describes how an electron with wavevector k resonates in the interacting electron system.
- For a non-interacting system (left), A has zero width \implies no damping. Analogy with harmonic oscillator: quality factor = ∞ .



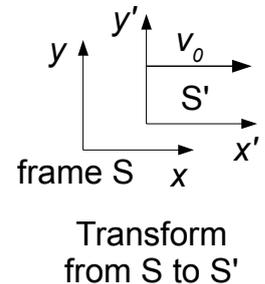
- For an interacting system (right), A has width = $2 \times$ (scattering rate) $\propto \epsilon^2$. The **quality factor** $\propto \epsilon/\epsilon^2$ **diverges for $\epsilon \rightarrow 0$** . Quasiparticles are overdamped at high energies, but well-defined for $E \rightarrow E_F$.

Quasiparticle properties

- The interaction term $\frac{1}{2} \sum_{\mathbf{k}\mathbf{k}'} f(\mathbf{k}, \mathbf{k}') n(\mathbf{k}) n(\mathbf{k}')$ in the Landau expansion for the total energy causes **various quasiparticle properties to be changed w.r.t. the free electron value**. Most importantly: **the effective mass m^*** can be orders of magnitude larger than the bare electron mass.
- The quasiparticle interaction $f(\mathbf{k}, \mathbf{k}')$ can be completely different from the Coulomb repulsion, which acts on the underlying electrons.
- In particular, $f(\mathbf{k}, \mathbf{k}')$ can be spin-dependent.
- This is an example of the **tunability** of correlated electron systems: although the underlying Coulomb interaction is fixed, the **effective interaction** in the low energy model is highly dependent on details of the system, and can therefore be tuned over a wide range by changing, for example, magnetic field, pressure or doping.

Backflow (strictly for enthusiasts) – 1

- The structure of the Fermi liquid 'vacuum state' is quite complex: for example, the movement of a single quasiparticle causes backflow within the electron system, which modifies the expression for particle flux.
- Intuitively, we expect particle flux = $\frac{1}{\text{Vol.}} \sum_n \mathbf{v}_n$.
- Consider **inertial frame S'**, moving w.r.t. S with $\mathbf{v}_0 = \hbar \mathbf{q} / m$,
- A particle with momentum \mathbf{p} in S, has mtm. $\mathbf{p} - \hbar \mathbf{q}$ in S'
- Kinetic energy of each particle is changed by $-\hbar \mathbf{q} \mathbf{p}_n / m + \hbar^2 \mathbf{q}^2 / (2m)$.



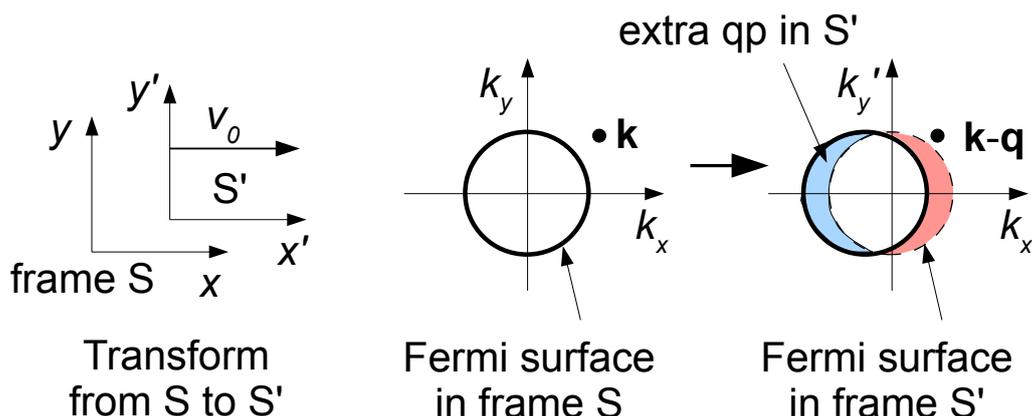
- From this, find **general expression for particle flux:**

$$\mathbf{J} = -\frac{1}{\text{Vol.}} \frac{1}{\hbar} \nabla_{\mathbf{q}} \Big|_{\mathbf{q}=0} E(\mathbf{q})$$

where $E(\mathbf{q})$ is the energy computed in S'.

Backflow (strictly for enthusiasts) – 2

- For a single quasiparticle in state \mathbf{k} :

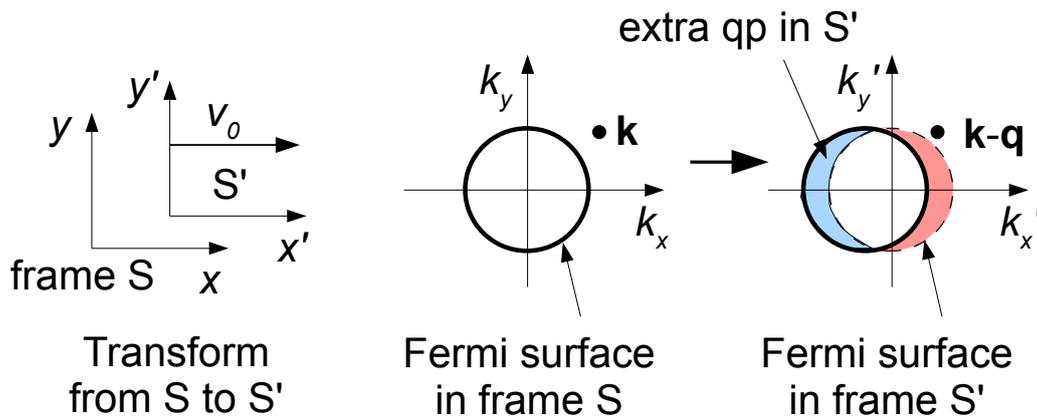


- Energy of the system in S is simply $E_0 = \epsilon_{\mathbf{k}}$, as there is only one quasiparticle $\rightarrow f(\mathbf{k}, \mathbf{k}')$ -sum in energy expansion is zero.
- In S', **quasiparticles and -holes appear**, as the Fermi surface in S' does not coincide with the shifted Fermi surface from S $\implies f(\mathbf{k}, \mathbf{k}')$ -sum **contributes to energy!**

$$E(\mathbf{q}) = \epsilon(\mathbf{k} - \mathbf{q}) + \sum_{\mathbf{k}'} f(\mathbf{k} - \mathbf{q}, \mathbf{k}' - \mathbf{q}) n(\mathbf{k}' - \mathbf{q})$$

Backflow (strictly for enthusiasts) – 3

$$E(\mathbf{q}) = \epsilon(\mathbf{k} - \mathbf{q}) + \sum_{\mathbf{k}'} f(\mathbf{k} - \mathbf{q}, \mathbf{k}' - \mathbf{q}) n(\mathbf{k}' - \mathbf{q})$$



- Taking the gradient w.r.t. \mathbf{q} gives $\mathbf{J} = \frac{1}{\text{Vol}} \mathbf{v}_{\mathbf{k}} + \text{interaction term}$
- Particle flux due to single qp. is given by qp. velocity + general commotion in the system (**'backflow'**).
- What is more: because f function can be spin dependent, **spin current can differ from charge current!**

Heavy Fermions

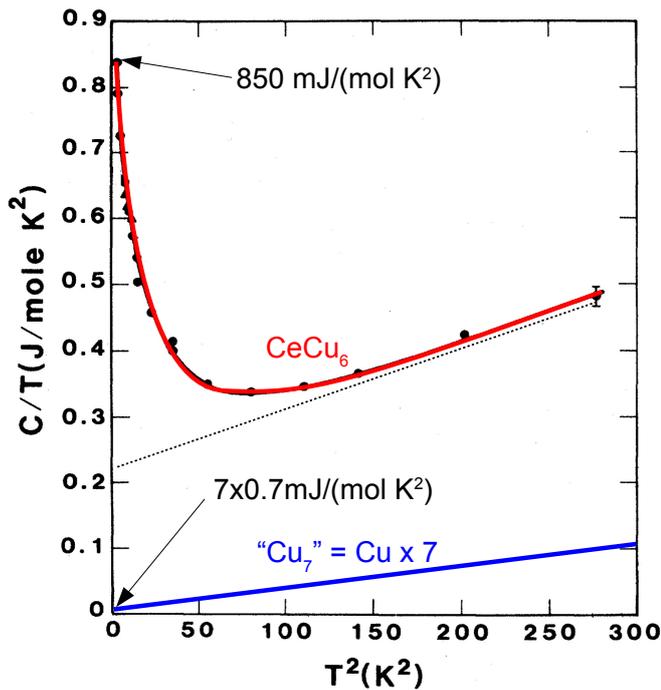
– Fermi liquid at the limit

(Strong interactions and narrow bands result in high effective masses. Heavy quasiparticles in quantum oscillation measurements. Superconductivity.)

What are heavy Fermions?

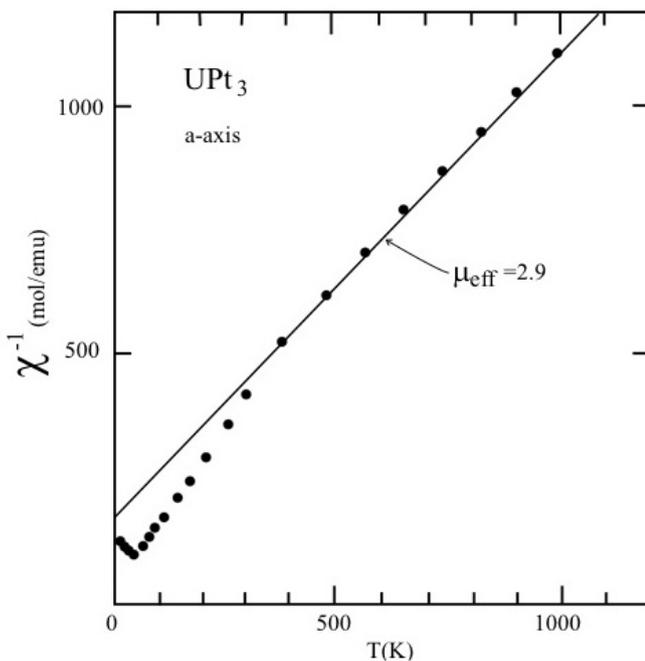
- In Fermi liquid theory, quasiparticle mass differs from bare electron mass.
- **Strong interactions can cause high effective masses.**
- **Heavy Fermion** materials (at very low temperature) have very high Sommerfeld coefficient of the heat capacity $C/T \sim 1 \text{ J}/(\text{molK})$, and high, weakly temperature-dependent magnetic susceptibility.
- This suggests they follow Fermi liquid theory, but the effective quasiparticle masses are strongly enhanced: in some cases up to **1000 times** m_e .
- Usually, heavy Fermion materials contain Cerium, Ytterbium or Uranium, which contribute **partially filled f-orbitals** to the band structure.
- These highly localised states are important, because in a lattice, they lead to very narrow bands. The strong Coulomb repulsion prevents double occupancy of these states.
- There are **hundreds of heavy Fermion materials**. Examples: CeCu_2Si_2 , CeCu_6 , CeCoIn_5 , YbCu_2Si_2 , UPt_3 .

Colossal heat capacity → “Heavy Fermions”



- Remember $C/T \simeq \gamma + \beta T^2$, where β -term comes from phonons, and $\gamma \propto$ **density of states**.
- Replacing 14% of Cu by Ce, to produce CeCu_6 , **increases γ by $> \times 150$** .
- All else being equal, 150 times **higher effective mass of Landau quasiparticles**.
($g(E_F) \propto 1/v_F$, $m^* v_F = \hbar k_F \sim \text{const.}$)
 $\implies m^* \propto g(E_F)$)
- Note strong upturn in C/T at low T : heavy fermion state develops fully only at low temperature.

High T: “local moments”, low T: Fermi liquid



- High temperature** magnetic susceptibility:

$$\chi^{-1} \propto T$$

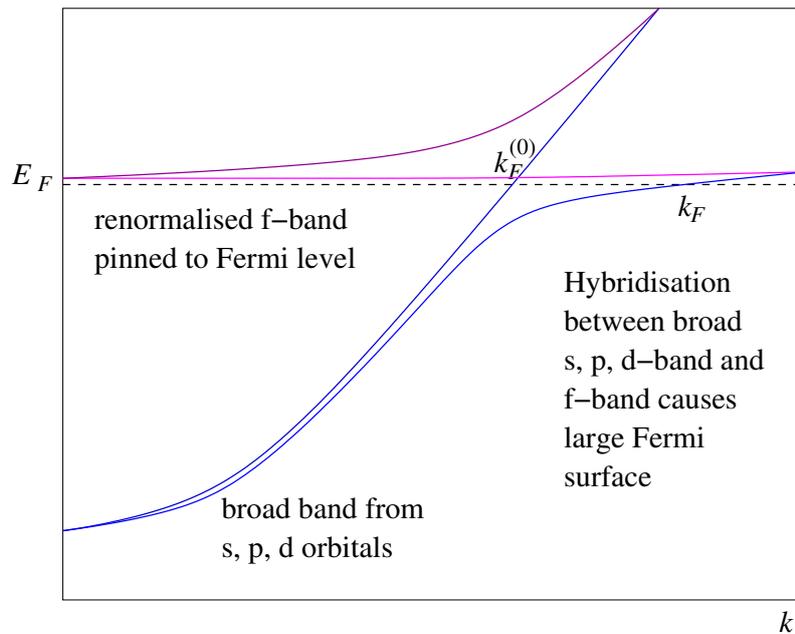
(Curie law for isolated **local moments**, with magn. moment consistent with electronic configuration of Uranium ions.)

- Low temperature** magnetic susceptibility:

$$\chi^{-1} \propto \text{const.}$$

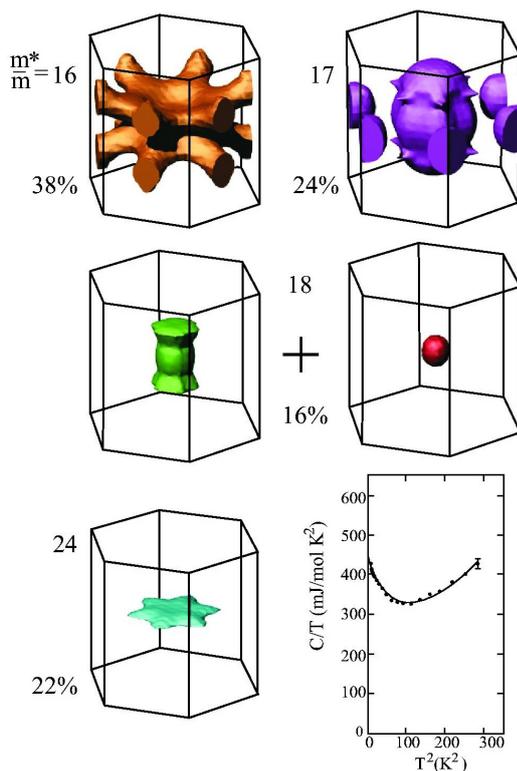
(Like Pauli susceptibility of **Fermi liquid**, but enhanced value).

Renormalised band picture for heavy fermion systems



Remember band structure of copper question (s-d hybridisation)? This is almost the same, but f-band is pinned to E_F so that each f-level contains exactly one electron.

Quasiparticles detected in de Haas-Alphen experiments



- **Quantum oscillation** studies
- High **magnetic field**
- Several **Fermi surface sheets**
- Temperature dependence of oscillation amplitude → **effective mass**.
- Measured effective masses consistent with **heat capacity results**.

f-electrons included in Fermi surface volume!

Quantum oscillation results in UPt₃

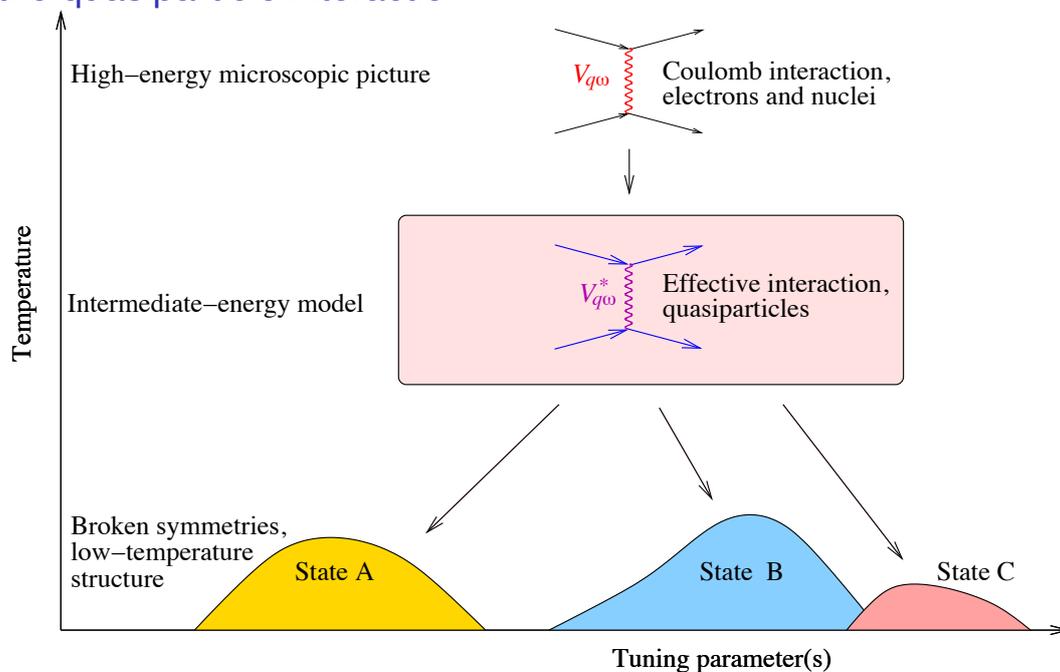
Heavy Fermion materials – summary

- Usually 4f (Ce, Yb) or 5f (U) intermetallic compounds, such as UPt_3 or CeCu_2Si_2 .
- Low temperature properties consistent with Fermi liquid theory, but very high effective carrier masses.
- What is the role of electrons in partially filled f-orbitals? Do they behave like local moments or like conduction electrons? Where quantum oscillation studies have been successful, they indicate that the electrons contribute to the Fermi surface, like in a normal metal.
- Because $g(E_F)$ is so high in these materials, they tend to order magnetically or even become superconducting. There are many different ordered low temperature states in these metals, some simple, some very exotic.
- There is an increasing number of materials (e.g. YbRh_2Si_2), which do not follow Fermi liquid theory at low T . Are they 'non-Fermi' liquids? Do the f-electrons remain as local moments down to absolute 0 in this case, not contributing to the Fermi surface? This is being investigated at the moment.

Beyond the standard model

(Fermi liquid breakdown at quantum phase transitions. Tunability of quantum matter. Topological quantum matter – skyrmion lattice, monopoles in spin ice.)

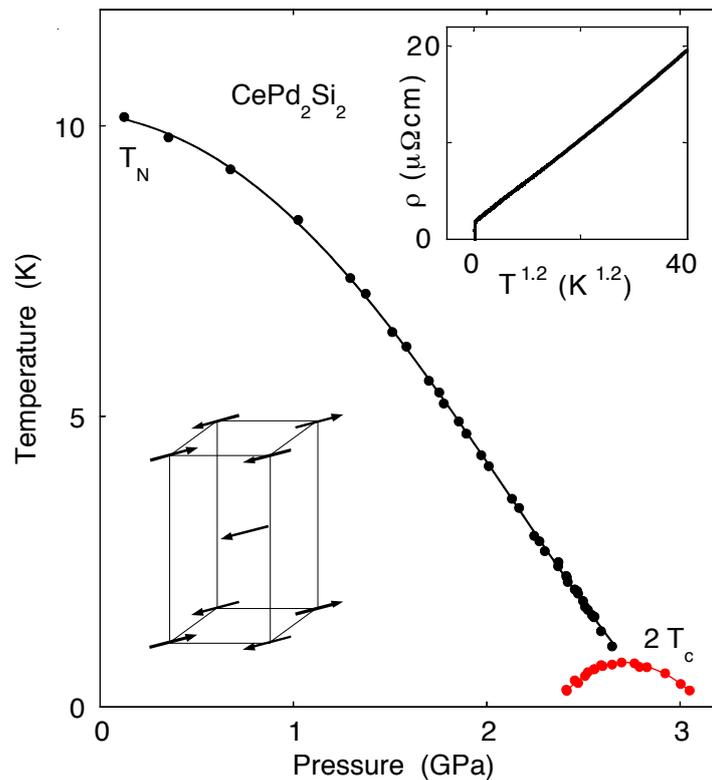
Tuning the quasiparticle interaction



- We cannot tune the Coulomb interaction – but the **effective interaction**, which governs the behaviour of a system at low temperatures, depends on many details and is thereby **highly tunable**.
- By varying the effective interaction, we **can select different ground states** (magnetism, superconductivity, etc.).

CePd₂Si₂: heavy-fermion magnet to unconventional superconductor

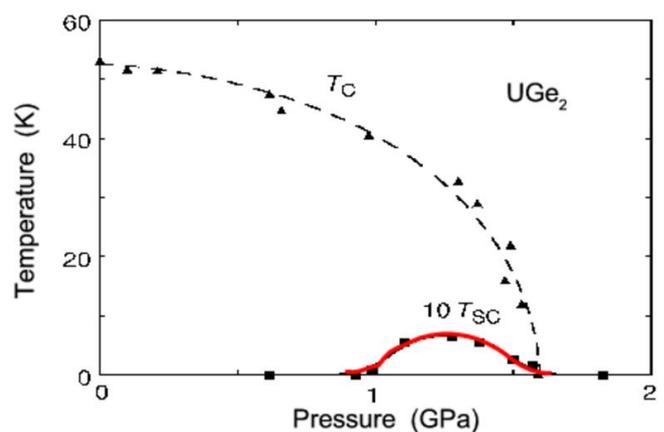
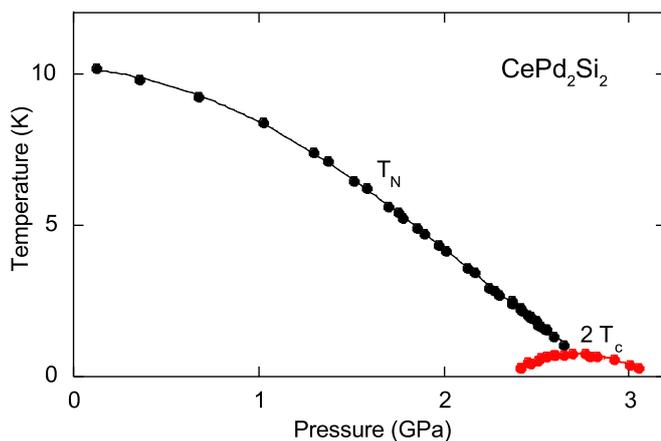
- Antiferromagnet below $T_N \simeq 10$ K.
- T_N depends on pressure.
- Magnetism suppressed near 2.8 GPa.
- Anomalous resistivity T -dependence.
- Quantum phase transition: cross phase boundary at low T , using control parameter other than temperature.



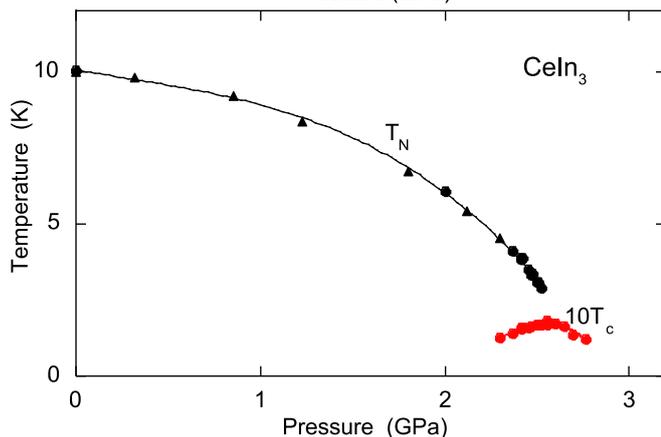
[Mathur *et al.*, Nature **394** (1998) 39]

Superconductivity and anomalous normal state.

Example: superconductivity and magnetism in heavy fermion materials

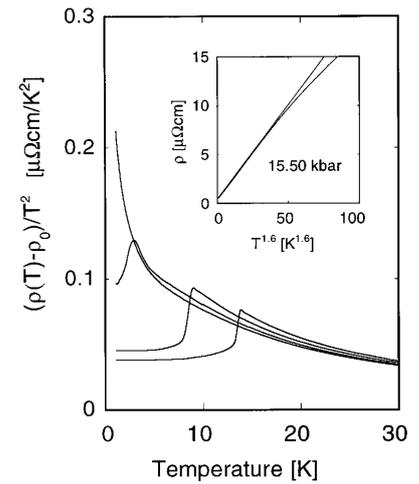
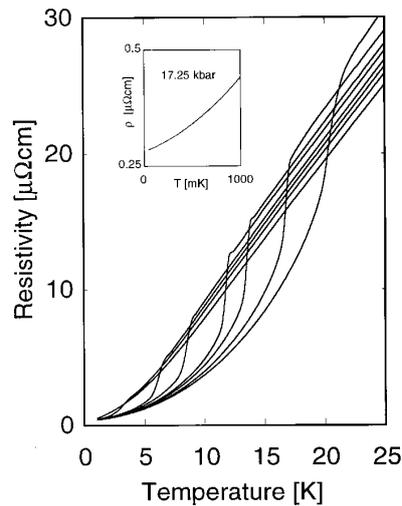
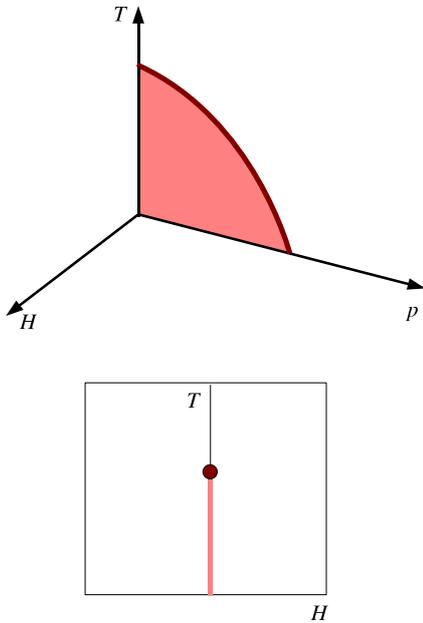


[S. S. Saxena, Nature **406** 587 (2000)]



- T_N : magnetic, T_C : superconducting transition temperature.
- Further examples:
CeCu₂Si₂, CeNi₂Ge₂, CeRh₂Si₂,
 CeCu₂, CeCu₅Au, CeIrIn₅,
 URhGe, ...

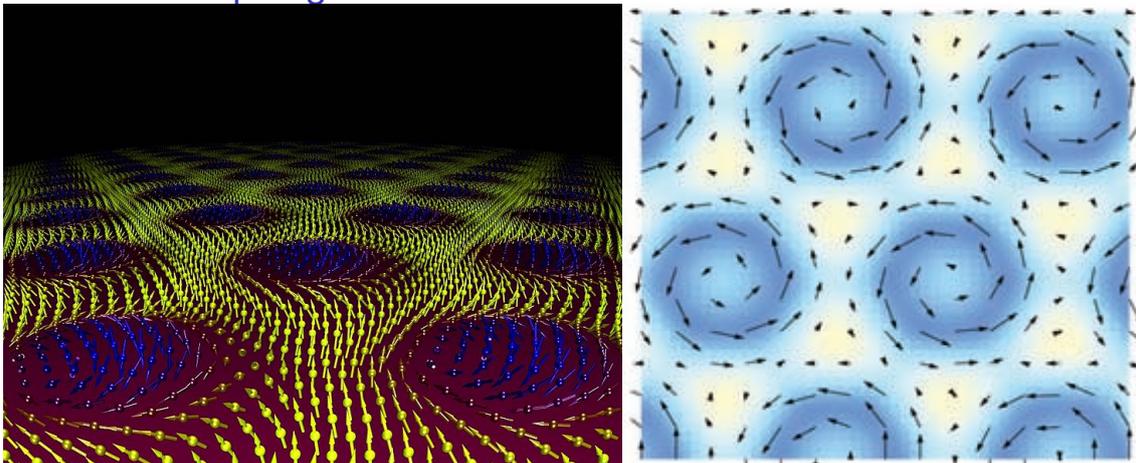
Quantum criticality on the border of ferromagnetism



[MnSi: Pfeleiderer *et al.* PRB **55** 8330 (1997)]

- Pressure **tunes transition** temperature.
- Ferromagnetism **disappears.**
- Scattering cross-section **diverges.**
- T – dependence of the resistivity ($\propto T^{3/2}$) violates Fermi liquid theory.

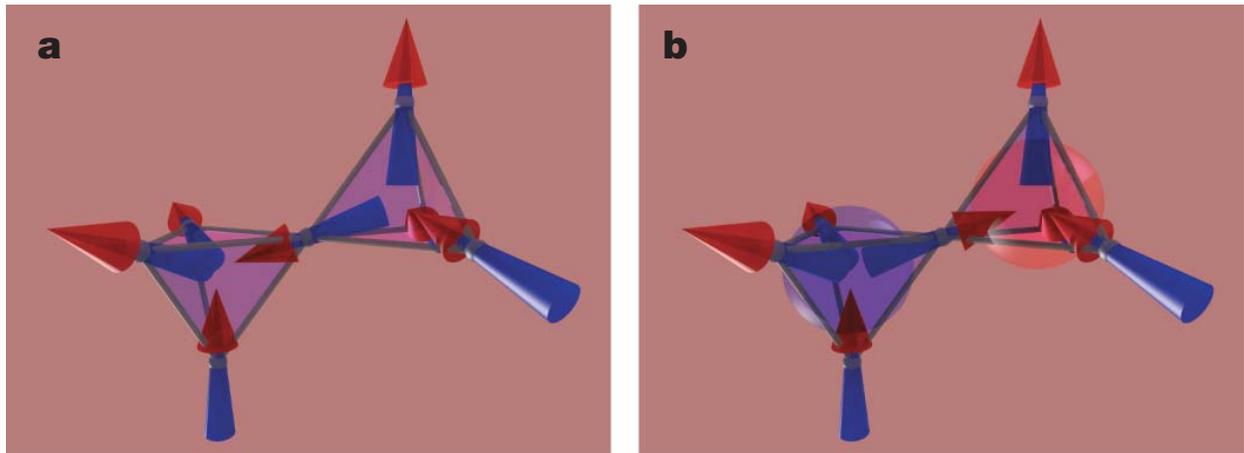
Skyrmion lattice: topological defects in MnSi – and elsewhere



[Mühlbauer *et al.* Science **323**, 915 (2009)]

- When investigating magnetic order in MnSi using neutron scattering, Pfeleiderer & Co. discovered **lattice of vortex-like topological defects** of the magnetisation in a narrow range of field and temperature: the **Skyrmion lattice.**
- Within a few months, this has been observed in a number of **other materials.**
- Skyrmions have been found to interact with electrical current \implies spintronic devices?

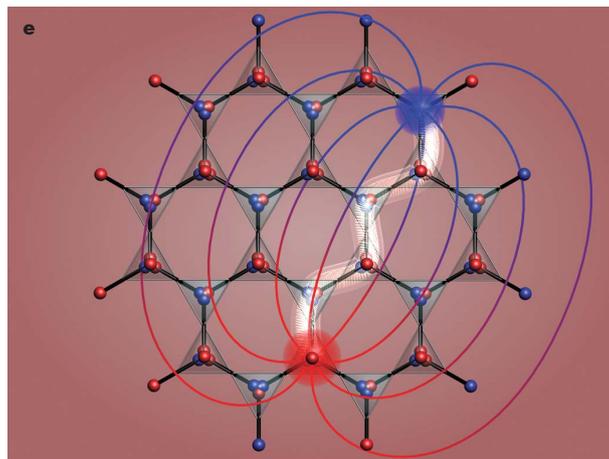
Monopoles in spin ice – another example of topological defects in magnetic systems



[Castelnovo, Moessner and Sondhi, Nature **451**, 42 (2007)]

- In some insulating local moment magnets (e.g. $\text{Ho}_2\text{Ti}_2\text{O}_7$), no magnetic order forms at low T because of constraints imposed by lattice structure and crystal field.
- The spins within a tetrahedral structural unit obey the Pauling ice-rule: two point in, two point out (left), but there is no long-range order.
- A deviation from the ice rule produces two neighbouring tetrahedra with magnetic 'charge' (one N, one S, right) \implies **monopoles**.

Monopoles in spin ice can travel and have $1/r$ potential

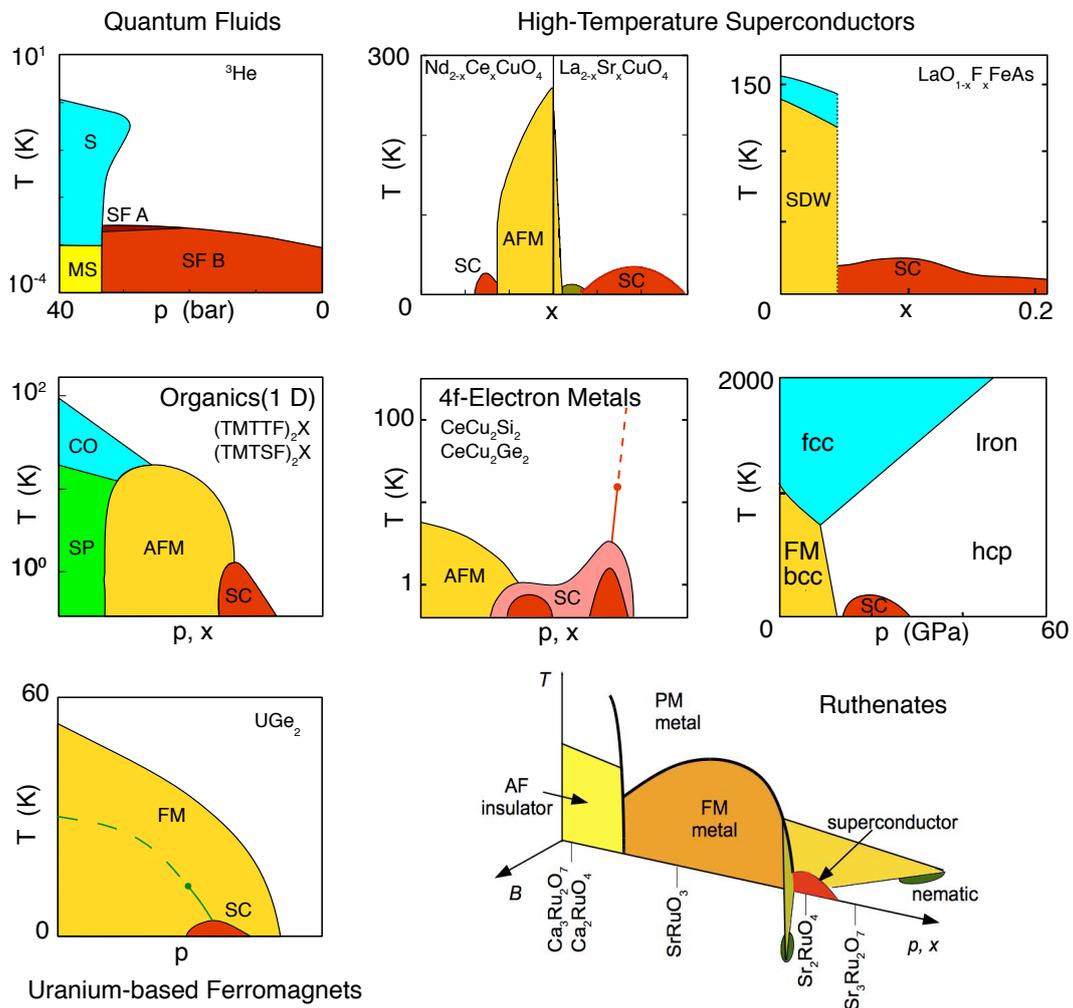


[Castelnovo, Moessner and Sondhi, Nature **451**, 42 (2007)]

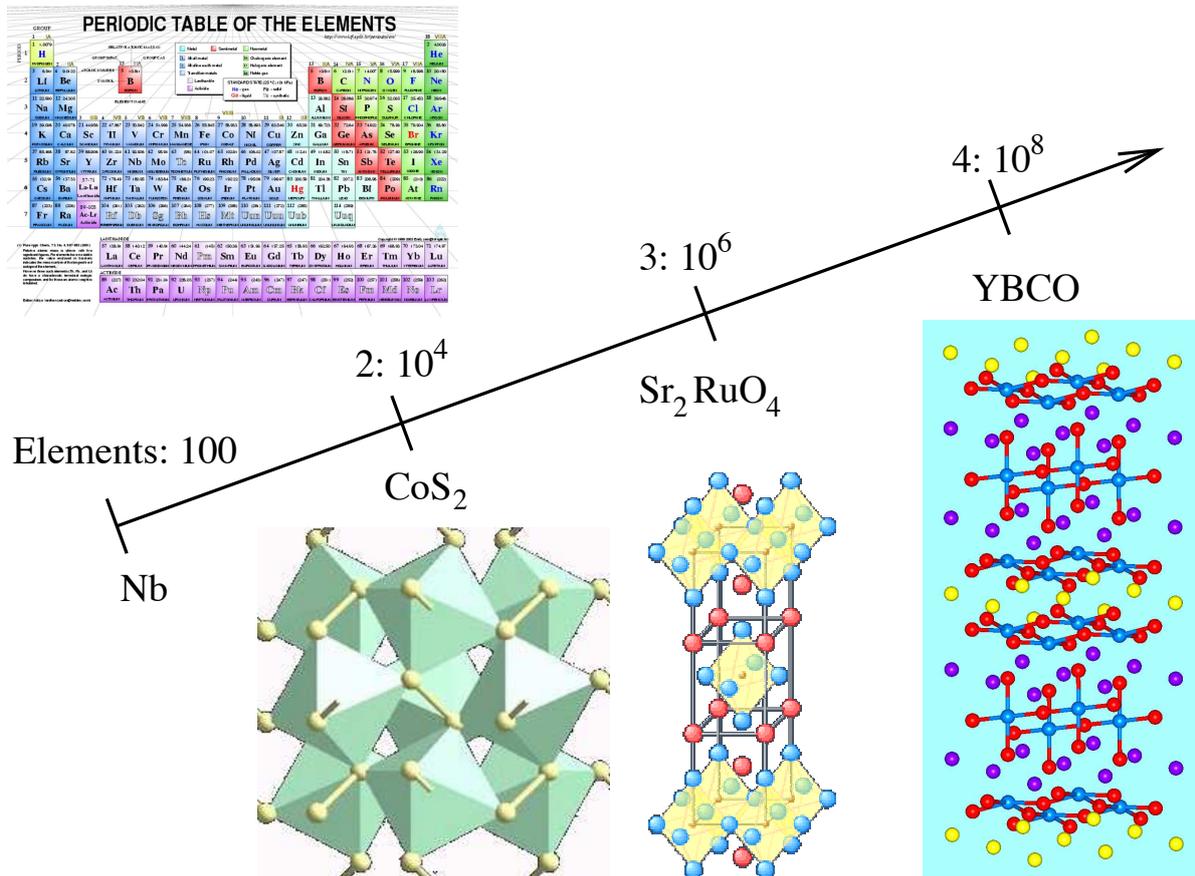
- By further spin-flips, the monopoles can travel at little energy cost.
- The energy required to separate 'monopoles' decays as $1/r$, as in Coulomb potential.
- Various detailed experimental studies in recent years, mostly involving neutron scattering.

Outlook

(Diversity of ordered states in correlated systems. Plenty of room in materials space. Devices and applications.)



Plenty of room in materials space



Reasons to do Advanced Quantum Condensed Matter Physics and Quantum Condensed Matter Field Theory in Part III

- Dense electronic matter such as electrons in metals offers plenty of opportunities for electrons to self-organise.
- Superconductivity, magnetism, charge density waves are just some examples – many more states (e.g. topological order) have been postulated and found.
- Ability to manipulate many-particle quantum order will lead to new devices and applications.

Any new discovery contains the germ of a new industry.

J. J. Thomson