

L1 AQCMP - Concepts in Solid-State Physics

L2 AQCMP - Independent-Electron Theory

What is solid-state physics
The need for phenomenological models
The role of experiments
Elementary Excitations
Energy Scales
Questions

What is solid-state physics

- Provides framework to understand chemical, structural, electrical, optical and magnetic properties of materials.
- Is essentially hardcore quantum mechanics, can be viewed as solving the hamiltonian:

$$\hat{H} = \sum_{i=1}^N \frac{\hat{p}_i^2}{2m_i} + \sum_{i=1}^M \frac{\hat{P}_i^2}{2M_i} - \sum_{i=1}^N \sum_{j=1}^M \frac{Z_j e^2}{4\pi\epsilon_0 |\vec{r}_i - \vec{R}_j|} + \sum_{i=1}^N \sum_{j < i} \frac{e^2}{4\pi\epsilon_0 |\vec{r}_i - \vec{r}_j|} + \sum_{i=1}^M \sum_{j < i} \frac{Z_i Z_j e^2}{4\pi\epsilon_0 |\vec{r}_i - \vec{R}_j|}$$

- Here, \hat{p}_i , \vec{r}_i and m_i are the momentum, position and mass of the i^{th} electron, \hat{P}_i , \vec{R}_i and M_i are the momentum, position and mass of the i^{th} ion and N and M are the number of electrons and ions respectively.

The need for phenomenological models

- To solve these systems reasonably, approximations are required. This course will focus on
 - Independent-Electron approximation
 - Hartree-Fock method
 - Density Functional Theory
 - Fermi Liquid Theory
- Other methods include
 - Configuration interaction and coupled cluster methods
 - Dynamical mean field theory
 - Quantum monte carlo methods
 - Analytic solutions
- Phenomenological models based on observations can give good insight, this is particularly useful given that solutions to Schrödinger's equation can be difficult to interpret. Examples include:
 - The Heisenberg Hamiltonian for (anti)ferromagnetism
 - Bardeen-Cooper-Schrieffer (BCS) Hamiltonian for superconductivity

$$\hat{H} = - \sum_{n,m} J_{n,m} \vec{S}_n \cdot \vec{S}_m$$

- Bardeen-Cooper-Schrieffer (BCS) Hamiltonian for superconductivity

$$\hat{H} = \sum_{\vec{k}, \lambda} \epsilon_{\vec{k}} c_{\vec{k}, \lambda}^\dagger c_{\vec{k}, \lambda} - \gamma^2 \sum_{\vec{k}, \lambda, \vec{k}', \lambda', \vec{q}} c_{\vec{k}' + \vec{q}, \lambda'}^\dagger c_{\vec{k} - \vec{q}, \lambda}^\dagger c_{\vec{k}, \lambda} c_{\vec{k}', \lambda'}$$

The role of experiments

- Experiments provide clues on how to construct the right model by identifying key principles for emergent phenomena. E.g. Superconductivity (below)
- However, often theoretical frameworks are too complicated to predict even simple properties, so discovery depends on both experiment and theory.
 - The characteristic energy gap $\Delta(\vec{k})$ in a semiconductor excitation spectrum can be used as the order parameter for superconductivity.
 - This gap is related to the formation of bound Cooper pairs. These form from two electrons with opposite wavevector and spin (k, \uparrow) and $(-k, \downarrow)$.
 - Conventional superconductors, such as those in elemental metals, have isotropic energy gaps, and are s-wave (c.f. s-orbital wavefunctions, no angular dependence). If doped, then the superconducting order parameter can be locally suppressed.

- By analysing the spatial distribution of the suppression of the gap, it can be seen that the order parameter must have d-wave symmetry with

$$\Delta(\vec{k}) = \frac{\Delta_0}{2} (\cos(k_x a) - \cos(k_y a))$$

- Experiments tend to probe the response of a system to a stimulus, so often probe excited states rather than the ground state.
 - Linear response theory is used to interpret these experiments, with excited states understood in terms of elementary excitations.

Elementary Excitations

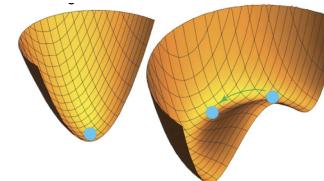
- Elementary excitations are excitations of a many-particle system that cannot be thought of as combinations of lower energy excitations.

Quasiparticles

- Fermionic quasiparticles follow Fermi-liquid theory.
- First, consider a fermi system with a fermi sphere + one extra particle with momentum p .
 - Then slowly turn on the Coulomb interaction. As the system still has total momentum p , it may be considered as a Fermi sphere + one quasiparticle of momentum p .
 - If there is a one-to-one correspondence between states of the non-interacting system and the states of the interacting system, then the quasiparticle can be considered as a non-interacting particle with a modified energy-momentum dispersion relation, such as a quasihole or quasielectron.
- Some elementary excitations are difficult to describe with quasiparticles, such as the response of a solid to an acoustic stimulus.
 - In these cases, it is easier to consider collective excitations involving a macroscopic number of degrees of freedom. Phonons are an example of a collective excitation.
 - Magnons can represent spin waves in a ferromagnet, representing wave-like small deviations of all spins from their perfectly aligned state.
 - Palasmons can represent the longitudinal electron density oscillations in response to a stimulus, such as an optical excitation or bombardment with high energy electrons.

Collective Excitations

- In some cases, a low-symmetry ground state is not the true ground state, but only a metastable state. In these cases, the true ground state is a coherent superposition of degenerate states.
 - This explains why ferromagnets have rotational symmetry about only one axis despite the fact that the ground state should be isotropic.
 - These "broken symmetry" states must undergo phase transition as temperature increases, with entropy driving return to a symmetry disordered state.
 - As this process cannot occur spontaneously, a critical temperate is seen T_C .
- Elementary excitations weaken the broken symmetry state below the critical temperature and eventually reduce the order parameter to zero at T_C .
- If a continuous global symmetry is broken, then the system must have long-wavelength collective excitations with vanishingly small energy - massless Goldstone bosons.



Klein-Gordon model, Spontaneous symmetry breaking: At high energy (left) the ball settles in the centre – the system and the state are symmetric. At low energy (right), the ball settles at an arbitrary point on the minimum – the system is symmetric but not the state.

Energy Scales

- 1 eV per atom: Optical absorption energies, Bonding energies, Plasmon energies

- 10–100 meV per atom: Optical phonon energies, Exchange energy in ferromagnets, Activation energy for dopants in semiconductors
 - 1–10 meV per atom: Acoustic phonons, Exchange energies in more weakly coupled magnetic systems, Energy of the excitation gap in high - T_C superconductors
 - < 1 meV per atom: Energy gap in conventional superconductors.
 - This therefore sets the temperature scales where phenomenon occur; $k_B T = 25$ meV at room temperature and $k_B T = 0.3$ meV at 4K.
 - Similarly to before, it is also possible to write down a hamiltonian for interactions

$$\hat{H} = \underbrace{\sum_{i=1}^N \frac{1}{2m} \left(-ih\nabla_{\vec{r}_i} + e\vec{A}(\vec{r}_i, t) \right)^2}_{\text{Electron-Photon interactions}} - \underbrace{\sum_{j=1}^M \frac{\hbar^2}{2M_j} \nabla_{\vec{R}_j}^2 + \frac{1}{2} \sum_{j=1}^M \frac{Z_j Ze^2}{4\pi\epsilon_0 |\vec{R}_j - \vec{R}_i|}}_{\text{Many-Phonon system}} - \underbrace{\sum_{i,j=1}^{N,M} \frac{Z_j Ze^2}{4\pi\epsilon_0 |\vec{r}_i - \vec{R}_j|}}_{\text{Electron-Photon interactions}} + \underbrace{\frac{1}{2} \sum_{i\neq j=1}^N \frac{e^2}{4\pi\epsilon_0 |\vec{r}_i - \vec{r}_j|}}_{\text{Electron-Electron interactions}}$$

Questions

- How to find the irreps of a point group?

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L1 AQCMP - Concepts in Solid-State Physics

The Reciprocal Lattice

The Independent-Electron Approximation

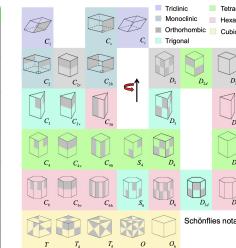
Bloch's Theorem

Bandstructure

Hund's rule In a two-electron two-site system

Crystalline Systems

Basis lattice	Parameters	Simple (P)	Values contained	Base contained	Per contained
Triclinic	$\alpha_1 \neq \beta_2 \neq \gamma_3$		$\alpha_1, \beta_2, \gamma_3$	a_1, b_2, c_3	$\alpha_1, \beta_2, \gamma_3$
	$\alpha_1 = \beta_2 \neq \gamma_3$		$\alpha_1, \beta_2, \gamma_3$	a_1, b_2, c_3	$\alpha_1, \beta_2, \gamma_3$
Monoclinic	$\alpha_1 = \beta_2 \neq \gamma_3$		$\alpha_1, \beta_2, \gamma_3$	a_1, b_2, c_3	$\alpha_1, \beta_2, \gamma_3$
	$\alpha_1 = \beta_2 = \gamma_3$		$\alpha_1, \beta_2, \gamma_3$	a_1, b_2, c_3	$\alpha_1, \beta_2, \gamma_3$
Orthorhombic	$\alpha_1 = \beta_2 \neq \gamma_3$		$\alpha_1, \beta_2, \gamma_3$	a_1, b_2, c_3	$\alpha_1, \beta_2, \gamma_3$
	$\alpha_1 = \beta_2 = \gamma_3$		$\alpha_1, \beta_2, \gamma_3$	a_1, b_2, c_3	$\alpha_1, \beta_2, \gamma_3$
Tetragonal	$\alpha_1 = \beta_2 \neq \gamma_3$		$\alpha_1, \beta_2, \gamma_3$	a_1, b_2, c_3	$\alpha_1, \beta_2, \gamma_3$
	$\alpha_1 = \beta_2 = \gamma_3$		$\alpha_1, \beta_2, \gamma_3$	a_1, b_2, c_3	$\alpha_1, \beta_2, \gamma_3$
Trigonal	$\alpha_1 = \beta_2 \neq \gamma_3$		$\alpha_1, \beta_2, \gamma_3$	a_1, b_2, c_3	$\alpha_1, \beta_2, \gamma_3$
	$\alpha_1 = \beta_2 = \gamma_3$		$\alpha_1, \beta_2, \gamma_3$	a_1, b_2, c_3	$\alpha_1, \beta_2, \gamma_3$
Hexagonal	$\alpha_1 = \beta_2 \neq \gamma_3$		$\alpha_1, \beta_2, \gamma_3$	a_1, b_2, c_3	$\alpha_1, \beta_2, \gamma_3$
	$\alpha_1 = \beta_2 = \gamma_3$		$\alpha_1, \beta_2, \gamma_3$	a_1, b_2, c_3	$\alpha_1, \beta_2, \gamma_3$
Cubic	$\alpha_1 = \beta_2 = \gamma_3$		$\alpha_1, \beta_2, \gamma_3$	a_1, b_2, c_3	$\alpha_1, \beta_2, \gamma_3$



- C₁** – inversion symmetry.
- C_n** – reflection symmetry.
- C_{nh}** – has an n-fold rotation axis.
- C_{nv}** = C_n + a mirror plane perpendicular to the axis of rotation.
- C_{nhv}** = C_{nv} + mirror planes parallel to the axis of rotation.
- S_{2n}** – contains only a 2n-fold rotation-reflection axis.
- D_n** – has an n-fold rotation axis plus two-fold axes perpendicular to that axis.
- D_{nh}** = D_n + a mirror plane perpendicular to the n-fold axis.
- D_{nd}** = D_n + mirror planes parallel to the n-fold axis.
- T_d** – chiral tetrahedral symmetry.
- T_{dh}** – full tetrahedral symmetry.
- T_g** – pyrithohedral symmetry.
- O** – chiral octahedral symmetry.
- O_h** – full octahedral symmetry.

- A specific lattice point within the lattice can be specified as

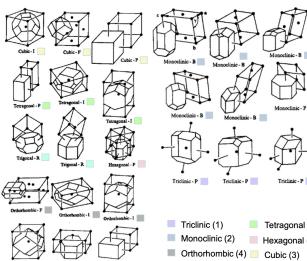
$$\vec{R}_0 = n_1 \vec{a}_1 + n_2 \vec{a}_2 + n_3 \vec{a}_3$$
 - Each crystal has an associated point group symmetry. Only 32 point groups can maintain 3D translational symmetry. These can be labelled using Schönflies notation:
 - C_n - Cyclic group, symmetry around a single axis
 - D_n - Dihedral group, symmetry around a single axis with additional perpendicular mirror planes
 - S_n - Improper rotation group, including a rotation followed by a reflection
 - T - Tetrahedral symmetry
 - O - Octahedral symmetry
 - Modifiers:
 - h - Horizontal mirror plane
 - v - Vertical mirror plane
 - d - Diagonal mirror plan
 - The space group of a crystal is a set of symmetry operations which leave it unchanged.
 - A space group consists of a set of translational symmetry operations, specified by the Bravais lattice (14) combined with a set of rotational and reflection symmetries defined by the crystallographic point group (32).
 - These combine to give 230 (not 14×32) different space groups for 3D crystal structures, which are labelled by Hermann-Mauguin symbols.
 - Bi_3Se_2 should be an insulator due to anticrossing giving a band gap at the Fermi surface. However, the broken symmetry associated with the surface causes a metallic surface state to appear. This is a topological insulator.

The Reciprocal Lattice

- For a given Bravais lattice, its reciprocal lattice is the set of wavevectors \vec{G} that have the same periodicity as the Bravais lattice; $e^{i\vec{G}\cdot\vec{r}} = e^{i\vec{G}\cdot(\vec{r} + \vec{R})} \implies e^{i\vec{G}\cdot\vec{R}} = 1$
 - Reciprocal lattice vectors are then given by

$$\begin{aligned}\vec{b}_1 &= 2\pi \frac{\vec{a}_2 \times \vec{a}_3}{\vec{a}_1 \cdot (\vec{a}_2 \times \vec{a}_3)}, \\ \vec{b}_2 &= 2\pi \frac{\vec{a}_3 \times \vec{a}_1}{\vec{a}_2 \cdot (\vec{a}_3 \times \vec{a}_1)}, \\ \vec{b}_3 &= 2\pi \frac{\vec{a}_1 \times \vec{a}_2}{\vec{a}_3 \cdot (\vec{a}_1 \times \vec{a}_2)}.\end{aligned}$$

Real Space	Reciprocal Space
Cubic	Cubic
FCC	BCC
BCC	FCC
Hexagonal	Hexagonal



High symmetry points

Symbol	Description
Γ	Center of the Brillouin zone
Simple cube	
M	Center of an edge
R	Corner point
X	Center of a face
Face-centered cubic (real space)	
K	Middle of an edge joining two hexagonal faces
L	Center of a hexagonal face
U	Middle of an edge joining a hexagonal and a square face
W	Corner point
X	Center of a square face
Body-centered cubic (real space)	
H	Corner point joining four edges
N	Center of a face
P	Corner point joining three edges
Hexagonal	
A	Lower hexagonal face
H	Corner point
K	Middle of an edge joining two rectangular faces
L	Middle of an edge joining a hexagonal and a rectangular face
M	Center of a rectangular face

P Simple, **I** Volume Centred, **B** Base Centred, **F** Face Centred, **R** Rhombohedral.

- The Wigner-Seitz unit cell around a lattice point is the locus of points in space that are closer to that point than any other lattice point.

It is a primitive cell spanning the entire Bravais lattice with no gaps.

For each of the Bravais lattices, there is at least one Wigner-Seitz cell (24 if different ratios of axes considered).

The Wigner Seitz cell of the reciprocal lattice is called the First Brillouin zone

The Independent-Electron Approximation

$$\hat{H} = \sum_{i=1}^N \frac{\vec{p}_i^2}{2m} + \sum_{i=1}^M \frac{\vec{p}_i^2}{2M_i} - \sum_{i=1}^N \sum_{j=1}^M \frac{Z_j e^2}{4\pi\epsilon_0 |\vec{r}_i - \vec{R}_j|} + \sum_{i=1}^N \sum_{j < i} \frac{e^2}{4\pi\epsilon_0 |\vec{r}_i - \vec{r}_j|} + \sum_{i=1}^M \sum_{j < i} \frac{Z_i Z_j e^2}{4\pi\epsilon_0 |\vec{R}_i - \vec{R}_j|}$$

- The above is the general hamiltonian for a solid. Using the Born-Oppenheimer approximation (nucleus is much more massive than the electrons, so is assumed to be approximately stationary), this simplifies to:

$$\hat{H}_{el} = \sum_{i=1}^N \left(\frac{\vec{p}_i^2}{2m} + \sum_{k=1}^M \frac{Ze^2}{4\pi\epsilon_0 |\vec{r}_i - \vec{R}_k|} \right) + \frac{1}{2} \sum_{i,j=1}^N \frac{e^2}{4\pi\epsilon_0 |\vec{r}_i - \vec{r}_j|},$$

- The independent-electron approximation assumes that electrons do not interact and move within an effective potential $V(\vec{r})$, which has the symmetry of the underlying lattice; $V(\vec{r} + \vec{R}_i) = V(\vec{r}) \forall i \in Z$;

$$\hat{H}_{el-cl} = \frac{\vec{p}^2}{2m} + V(\vec{r}).$$

Bloch's Theorem

- The eigenstates of the Schrödinger equation for a crystal lattice are Bloch states;

$$\psi_{n,\vec{k}}(\vec{r}) = \frac{1}{\sqrt{V}} e^{i\vec{k} \cdot \vec{r}} U_{n,\vec{k}}(\vec{r}) \quad \text{with} \quad U_{n,\vec{k}}(\vec{r} + \vec{R}) = U_{n,\vec{k}}(\vec{r}) \quad (1)$$

$$\psi_{n,\vec{k}}(\vec{r} + \vec{R}) = e^{i\vec{k} \cdot \vec{R}} \psi_{n,\vec{k}}(\vec{r}) \quad (2)$$

- \vec{k} is then a quantum number that defines the eigenstates of the translation operators with $T_{\vec{R}} \psi_{n,\vec{k}}(\vec{r}) = \psi_{n,\vec{k}}(\vec{r} + \vec{R}) = e^{i\vec{k} \cdot \vec{R}} \psi_{n,\vec{k}}(\vec{r})$.

Note that here $\hbar\vec{k}$, the crystal momentum, is not the same as momentum; \vec{p} is not an eigenvalue of $\psi_{n,\vec{k}}(\vec{r})$.

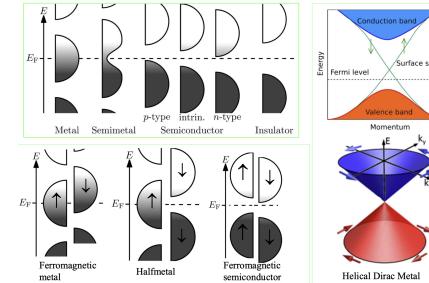
- Written in Fourier form with \vec{G} and \vec{K} reciprocal lattice vectors,

$$\begin{aligned}\psi_{n,\vec{k}}(\vec{r}) &= e^{i\vec{k} \cdot \vec{r}} \left(\sum_{\vec{K}} c_{n,\vec{k}-\vec{K}} e^{-i\vec{K} \cdot \vec{r}} \right) = \sum_{\vec{K}} c_{n,\vec{k}+\vec{G}-\vec{K}} e^{i(\vec{k}+\vec{G}-\vec{K}) \cdot \vec{r}} = \psi_{n,\vec{k}+\vec{G}-\vec{K}}(\vec{r}) \\ V(\vec{r}) &= \sum_{\vec{G}} V_{\vec{G}} e^{i\vec{G} \cdot \vec{r}}\end{aligned}$$

Bandstructure

- There are many eigenvalues for each \vec{k} , each labelled by a band index.
- Inserting the Bloch function into the Schrödinger equation gives a Hermitian eigenvalue problem for $U_{n,\vec{k}}(\vec{r})$. The eigenvalues are discrete due to the symmetry conditions for Bloch's theorem (eq 1).
- Capital Greek letters denote directions in the Brillouin Zone, and subscripts denote the number of irreps of the group at each high symmetry point.
- If a crystal has N unit cells, then each energy band $E_n(\vec{k})$ can accommodate up to $2N$ electrons (spin up and down).

In a metal, the energy of the highest filled energy level at $T = 0$ is the Fermi energy E_F .



(Image above), the properties of conductors and magnets can be interpreted by analysing the density of states at the Fermi energy.

Breakdown of the Independent-Electron Approximation

- This is all nice, but electron-electron interactions are observed experimentally, such as:
 - Hund's rules - filling single-electron states in an atomic shell with as many as possible spin aligned in ground state
 - Magnetism - a collective phenomenon due to electron-electron interactions
 - Plasmons - collective longitudinal density oscillations of the electron gas
 - Screening - rearrangement of the charge density of electron gas in response to the presence of a local charge
 - Heavy fermions - very strong electron-electron interactions with a partially filled f-shell of a lanthanide (4f) or actinide (5f) atom
 - Gives a strong drop in resistivity to $\propto T^2$ at low T
 - Laughlin Liquid - interacting electrons in a one-dimensional system have low energy elementary excitations that are charge and spin density waves
 - Insulator to metal transition in Sr doped La₂CuO₄
- To model these interactions we undo some of the simplifications made earlier, and could also add in relativistic effect through the spin-orbit interaction, giving
 - Hamiltonian:

$$\hat{H}_{cl} = \sum_{i=1}^N \left(-\frac{\hbar^2}{2m} \nabla_i^2 + U_{e-ion}(\vec{r}_i) \right) + \frac{1}{2} \sum_{i,j=1}^N \frac{e^2}{4\pi\epsilon_0 |\vec{r}_i - \vec{r}_j|} - g(|\vec{r}_i - \vec{r}_j|) \cdot 0, \text{ Two-particle operator}$$

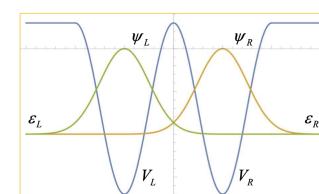
Spin-Orbit would add

$$\hat{H}_{SO} = \frac{1}{2mc^2} \vec{r} \frac{\partial V}{\partial \vec{r}} \cdot \hat{\vec{L}} \cdot \hat{\vec{S}} = \hat{\vec{L}} \cdot \hat{\vec{S}}$$

Attempting to then solve the Schrödinger equation; $\hat{H}_1 \Psi(\vec{r}_1, \sigma_1; \vec{r}_2, \sigma_2; \dots; \vec{r}_N, \sigma_N) = E\Psi(\vec{r}_1, \sigma_1; \vec{r}_2, \sigma_2; \dots; \vec{r}_N, \sigma_N)$ is then difficult, as the wavefunction is not separable because it would not satisfy the Pauli principle.

Hund's rule in a two-electron two-site system

- The two-electron two-site system has four single-particle basis states; combinations of two spatial states and spin up or down states, giving the usual singlet and triplet states.
 - Finding the eigenenergies of these states then reveals both Hartree and Exchange contributions.
 - Hence, although the Hamiltonian is spin-independent, the Pauli principle has produced a spin-dependent energy, which is the origin of magnetism (Hund's rule).
- The Pauli principle states that the wavefunction changes sign on particle exchange. Hence, the wavefunction of an N-electron system may be written as a linear combination of Slater determinants formed from a complete set of orthonormal single-particle wavefunctions.



$$\begin{aligned}\Psi(\vec{x}_1, \vec{x}_2, \dots, \vec{x}_N) &= \sum_{i_1, i_2, \dots, i_N=1}^{\infty} a_{i_1, i_2, \dots, i_N} \Phi_{i_1, i_2, \dots, i_N}(\vec{x}_1, \vec{x}_2, \dots, \vec{x}_N), \quad \text{where } \vec{x}_i = \{\vec{r}_i, \sigma_i\} \text{ and} \\ \Phi_{i_1, i_2, \dots, i_N}(\vec{x}_1, \vec{x}_2, \dots, \vec{x}_N) &= \frac{1}{\sqrt{N!}} \begin{vmatrix} \psi_{i_1}(\vec{x}_1) & \psi_{i_1}(\vec{x}_2) & \dots & \psi_{i_1}(\vec{x}_N) \\ \psi_{i_2}(\vec{x}_1) & \psi_{i_2}(\vec{x}_2) & \dots & \psi_{i_2}(\vec{x}_N) \\ \vdots & \vdots & \ddots & \vdots \\ \psi_{i_N}(\vec{x}_1) & \psi_{i_N}(\vec{x}_2) & \dots & \psi_{i_N}(\vec{x}_N) \end{vmatrix} = A \{ \psi_{i_1}(\vec{x}_1) \psi_{i_2}(\vec{x}_2) \dots \psi_{i_N}(\vec{x}_N) \} \text{ with} \\ A &= \frac{1}{\sqrt{N!}} \sum_{i=1}^N (-1)^i P_i \quad \text{and} \quad \psi_i(\vec{x}_j) = \phi_i(\vec{r}_j) \chi_s(\sigma_j)\end{aligned}$$

- Here, P_i denotes the i th permutation of the subscripts $i_1, i_2 \dots i_N$ to produce the antisymmetrisation operator A .
- Finally, it can then be seen that $\psi_i(\vec{r}_j) = \phi_i(\vec{r}_j)\chi_s(\sigma_j)$, where χ represents the spin part of the wavefunction for particle i in configuration j .
 - If all electrons have the same spin and position, then $\Phi = 0$.

L3 AQCMP - Hartree-Fock Theory

[L2 AQCMP - Independent-Electron Theory](#)

Hartree-Fock Theory
 The Hartree-Fock Equation
 Solving the Hartree-Fock Equation
 Interpretation
 Homogeneous Electron Gas
 The Interacting Electron Gas
 Electron Correlations: The Exchange-Correlation Hole

[L4 AQCMP - Density Functional Theory](#)

Hartree-Fock Theory

- The many-electron Hamiltonian

$$\hat{H}_{el} = \sum_{i=1}^N \left(-\frac{\hbar^2}{2m} \nabla_i^2 + U_{e-ion}(\vec{r}_i) \right) + \frac{1}{2} \sum_{\substack{i,j=1 \\ i \neq j}}^N \underbrace{\frac{e^2}{4\pi\epsilon_0 |\vec{r}_i - \vec{r}_j|}}_{h(r_i), \text{Single-particle operator}} = \sum_{i=1}^N g(|\vec{r}_i - \vec{r}_j|) \quad \text{where } U_{e-ion}(\vec{r}_i) = -\sum_{k=1}^M \frac{Ze^2}{4\pi\epsilon_0 |\vec{r}_i - \vec{R}_k|}$$

- Has eigenstates

$$\Psi(\vec{x}_1, \vec{x}_2, \dots, \vec{x}_N) = \sum_{i_1, i_2, \dots, i_N=1}^{\infty} \alpha_{i_1, i_2, \dots, i_N} \Phi_{i_1, i_2, \dots, i_N}(\vec{x}_1, \vec{x}_2, \dots, \vec{x}_N), \quad \text{where } \vec{x}_i = \{\vec{r}_i, \sigma_i\} \quad \text{and}$$

$$\Phi_{i_1, i_2, \dots, i_N}(\vec{x}_1, \vec{x}_2, \dots, \vec{x}_N) = \frac{1}{\sqrt{N!}} \begin{vmatrix} \psi_{i_1}(\vec{x}_1) & \psi_{i_1}(\vec{x}_2) & \dots & \psi_{i_1}(\vec{x}_N) \\ \psi_{i_2}(\vec{x}_1) & \psi_{i_2}(\vec{x}_2) & \dots & \psi_{i_2}(\vec{x}_N) \\ \vdots & \vdots & \ddots & \vdots \\ \psi_{i_N}(\vec{x}_1) & \psi_{i_N}(\vec{x}_2) & \dots & \psi_{i_N}(\vec{x}_N) \end{vmatrix} = A \{ \psi_{i_1}(\vec{x}_1) \psi_{i_2}(\vec{x}_2) \dots \psi_{i_N}(\vec{x}_N) \} \quad \text{with}$$

$$A = \frac{1}{\sqrt{N!}} \sum_{i=1}^{N!} (-1)^i P_i \quad \text{and} \quad \psi_i(\vec{r}_j) = \phi_i(\vec{r}_j)\chi_s(\sigma_j)$$

- The Hartree-Fock approximation assumes that the ground-state wavefunction can be approximated by a single slater determinant () such that

$$\Psi_0(\vec{x}_1, \vec{x}_2, \dots, \vec{x}_N) = \Phi_{1,2,\dots,N}(\vec{x}_1, \vec{x}_2, \dots, \vec{x}_N) = A \{ \psi_1(\vec{x}_1) \psi_2(\vec{x}_2) \dots \psi_N(\vec{x}_N) \},$$

$$= \frac{1}{\sqrt{N!}} \sum_{i=1}^{N!} (-1)^i P_i (\psi_1(\vec{x}_1) \psi_2(\vec{x}_2) \dots \psi_N(\vec{x}_N)).$$

- Using variational calculus to minimise the Hartree-Fock estimate of the ground-state energy $E_0 = E_0(\{\psi_n\}) = \langle \psi_0 | \hat{H} | \psi_0 \rangle$, the best fit functions $\psi_i(\vec{x}_j)$ may be found.

- Note that $\vec{x}_1 = \begin{pmatrix} 1 \\ 0 \end{pmatrix}$ and $\vec{x}_1 = \begin{pmatrix} 0 \\ 1 \end{pmatrix}$.

- Substituting to find the ground state energy considering only the single-particle term,

HF Energy Derivation Summary

$$\langle \Psi_0 | \sum_{i=1}^N h(\vec{x}_i) | \Psi_0 \rangle = \int d\vec{x}_1 \dots d\vec{x}_N \left(\frac{1}{\sqrt{N!}} \sum_{i=1}^{N!} (-1)^{P_i} P_i (\psi_1^{\dagger}(\vec{x}_1) \psi_2^{\dagger}(\vec{x}_2) \dots \psi_N^{\dagger}(\vec{x}_N)) \right) \sum_{i=1}^N h(\vec{x}_i) \left(\frac{1}{\sqrt{N!}} \sum_{m=1}^{N!} (-1)^{P_m} P_m (\psi_1(\vec{x}_1) \psi_2(\vec{x}_2) \dots \psi_N(\vec{x}_N)) \right)$$

$$= \frac{1}{N!} \sum_{i=1}^N \sum_{l=1}^{N!} \sum_{m=1}^{N!} \int d\vec{x}_1 \dots d\vec{x}_N (-1)^{P_l} P_l (\psi_1^{\dagger}(\vec{x}_1) \psi_2^{\dagger}(\vec{x}_2) \dots \psi_N^{\dagger}(\vec{x}_N)) h(\vec{x}_i) (-1)^{P_m} P_m (\psi_1(\vec{x}_1) \psi_2(\vec{x}_2) \dots \psi_N(\vec{x}_N))$$

- Also, note that $\int d\vec{x} f(\vec{x}) = \sum_{\sigma=1,2} \int d^3\vec{r} f(\vec{r}, \sigma)$.

- This gives two possibilities; either $P_l = P_m$ or $P_l \neq P_m$. In the first case, simple forms of the integrals can be found and in the second case, all integrals are zero.

- With $P_l = P_m$, and where the set $\{p_i\}$ is defined by the permutation P_l , the integral becomes

$$I = \int d\vec{x}_1 \psi_{P_l}^{\dagger}(\vec{x}_1) \psi_{P_l}(\vec{x}_1) \cdot \int d\vec{x}_2 \psi_{P_l}^{\dagger}(\vec{x}_2) \psi_{P_l}(\vec{x}_2) \cdots \int d\vec{x}_i \psi_{P_l}^{\dagger}(\vec{x}_i) h(\vec{x}_i) \psi_{P_l}(\vec{x}_i) \cdots \int d\vec{x}_N \psi_{P_l}^{\dagger}(\vec{x}_N) \psi_{P_l}(\vec{x}_N)$$

$$= 1 \cdot 1 \cdots \int d\vec{x}_i \psi_{P_l}^{\dagger}(\vec{x}_i) h(\vec{x}_i) \psi_{P_l}(\vec{x}_i) \cdots 1$$

$$= \int d\vec{x}_i \psi_{P_l}^{\dagger}(\vec{x}_i) h(\vec{x}_i) \psi_{P_l}(\vec{x}_i).$$

- Where $P_l \neq P_m$, noting that the two permutations are different, so at least two of the p_i and q_i must be different, meaning at least one of the integrals zero.

$$I = (-1)^{\delta_{P_l, P_m}} \int d\vec{x}_1 \psi_{P_l}^{\dagger}(\vec{x}_1) \psi_{P_m}(\vec{x}_1) \cdot \int d\vec{x}_2 \psi_{P_l}^{\dagger}(\vec{x}_2) \psi_{P_m}(\vec{x}_2) \cdots \int d\vec{x}_i \psi_{P_l}^{\dagger}(\vec{x}_i) \psi_{P_m}(\vec{x}_i) \cdots \int d\vec{x}_N \psi_{P_l}^{\dagger}(\vec{x}_N) \psi_{P_m}(\vec{x}_N)$$

$$= (-1)^{\delta_{P_l, P_m}} 1 \cdot 1 \cdots \int d\vec{x}_i \psi_{P_l}^{\dagger}(\vec{x}_i) h(\vec{x}_i) \psi_{P_m}(\vec{x}_i) \cdots 0 \cdots$$

$$= 0.$$

- Hence, where p_i^l is the value of the i^{th} index for the l^{th} permutation, and noting that there are N possible values for p_i^l and each appears $(N - 1)!$ times, and that integrating over \vec{x}_i is the same as integrating over a dummy variable \vec{z} .

$$\begin{aligned} \sum_{i=1}^N \langle \psi_0 | h(\vec{x}_i) | \psi_0 \rangle &= \sum_{i=1}^N \frac{1}{N!} \sum_{l=1}^{N!} \int d\vec{x}_i \psi_{p_i^l}^\dagger(\vec{x}_i) h(\vec{x}_i) \psi_{p_i^l}(\vec{x}_i) \\ &= \sum_{i=1}^N \frac{1}{N!} \sum_{n=1}^N (N-1)! \int d\vec{x}_i \psi_n^\dagger(\vec{x}_i) h(\vec{x}_i) \psi_n(\vec{x}_i) \\ &= \sum_{n=1}^N \int d\vec{x} \psi_n^\dagger(\vec{x}) h(\vec{x}) \psi_n(\vec{x}) \\ &= \sum_{n=1}^N [\psi_n^\dagger \psi_n | h] \end{aligned}$$

- Where integral notation has been used in the last step.

- Now considering the two-particle (Coulomb) term.

$$\frac{1}{2} \sum_{i \neq j=1}^N \langle \Psi_0 | g | \Psi_0 \rangle = \frac{1}{2} \sum_{i \neq j=1}^N \sum_{l=1}^{N!} \frac{1}{N!} \sum_{m=1}^{N!} \frac{1}{\sqrt{N!}} \int d\vec{x}_i \cdots d\vec{x}_N (-1)^n P_l(\psi_1^\dagger(\vec{x}_1) \psi_2^\dagger(\vec{x}_2) \cdots \psi_N^\dagger(\vec{x}_N)) g(|\vec{x}_i - \vec{x}_j|) \\ \times (-1)^{p_m} P_m(\psi_1(\vec{x}_1) \psi_2(\vec{x}_2) \cdots \psi_N(\vec{x}_N)).$$

- This is non-zero when $P_m = P_l$ and where $P_m = P_l P_{i+j}$

- In the $P_m = P_l$ case (the Hartree energy term), noting that $(N-2)!$ permutations contain the terms $\psi_n(\vec{x}_i)$ and $\psi_m(\vec{x}_j)$.

$$\begin{aligned} \frac{1}{2} \sum_{i \neq j=1}^N \langle \Psi_0 | g | \Psi_0 \rangle &= \frac{1}{2} \sum_{i \neq j=1}^N \frac{1}{N!} \sum_{n \neq m=1}^N (N-2)! \int d\vec{x}_i d\vec{x}_j \psi_n^\dagger(\vec{x}_i) \psi_m^\dagger(\vec{x}_j) g(|\vec{x}_i - \vec{x}_j|) \psi_n(\vec{x}_i) \psi_m(\vec{x}_j) \\ &= \frac{1}{2} \sum_{n \neq m=1}^N \int d\vec{x} d\vec{y} \psi_n^\dagger(\vec{x}) \psi_m(\vec{x}) g(|\vec{x} - \vec{y}|) \psi_m^\dagger(\vec{y}) \psi_n(\vec{y}) \\ &= \frac{1}{2} \sum_{n \neq m=1}^N [\psi_n^\dagger \psi_n | g | \psi_m^\dagger \psi_m] \text{ (change of notation)} \end{aligned}$$

- In the $P_m = P_l P_{i+j}$ case (the Exchange energy term)

$$\begin{aligned} \frac{1}{2} \sum_{i \neq j=1}^N \langle \Psi_0 | g | \Psi_0 \rangle &= -\frac{1}{2} \sum_{i \neq j=1}^N \frac{1}{N!} \sum_{n \neq m=1}^N (N-2)! \int d\vec{x}_i d\vec{x}_j \psi_n^\dagger(\vec{x}_i) \psi_m^\dagger(\vec{x}_j) g(|\vec{x}_i - \vec{x}_j|) \psi_n(\vec{x}_i) \psi_m(\vec{x}_j) \\ &= -\frac{1}{2} \sum_{n \neq m=1}^N \int d\vec{x} d\vec{y} \psi_n^\dagger(\vec{x}) \psi_m(\vec{x}) g(|\vec{x} - \vec{y}|) \psi_m^\dagger(\vec{y}) \psi_n(\vec{y}) \\ &= -\frac{1}{2} \sum_{n \neq m=1}^N [\psi_n^\dagger \psi_m | g | \psi_m^\dagger \psi_n]. \end{aligned}$$

- Finally, collecting all of these terms together gives (note that for $n = m$ the Hartree and Exchange terms cancel, so the sum condition can be removed).

$$E_0[\{\psi_n\}] = \sum_{n=1}^N [\psi_n^\dagger \psi_n | h] + \underbrace{\frac{1}{2} \sum_{n,m=1}^N ([\psi_n^\dagger \psi_n | g | \psi_m^\dagger \psi_m] - [\psi_n^\dagger \psi_m | g | \psi_m^\dagger \psi_n])}_{\text{Coulomb term}}$$

- It can also be seen from this that the Coulomb term is positive.
- The Hartree term is also always positive and is also spin independent.

$$\begin{aligned} [\psi_n^\dagger \psi_n | g | \psi_m] &= \iint d^3\vec{r} d^3\vec{r}' \varphi_n^\dagger(\vec{r}) \varphi_n(\vec{r}') \frac{e^2}{4\pi\epsilon_0 |\vec{r} - \vec{r}'|} \varphi_m^\dagger(\vec{r}') \varphi_m(\vec{r}') \times \sum_{\sigma=1,2} \chi_{s_n}^\dagger(\sigma) \chi_{s_n}(\sigma) \sum_{\sigma'=1,2} \chi_{s_m}^\dagger(\sigma') \chi_{s_m}(\sigma'), \\ &= \iint d^3\vec{r} d^3\vec{r}' |\varphi_n(\vec{r})|^2 \frac{e^2}{4\pi\epsilon_0 |\vec{r} - \vec{r}'|} |\varphi_m(\vec{r}')|^2 \cdot 1 \cdot 1 \\ &= \iint d^3\vec{r} d^3\vec{r}' e |\varphi_n(\vec{r})|^2 \frac{e}{4\pi\epsilon_0 |\vec{r} - \vec{r}'|} e |\varphi_m(\vec{r}')|^2 \\ &= \iint d^3\vec{r} d^3\vec{r}' \frac{\rho_n(\vec{r}) \rho_m(\vec{r}')}{4\pi\epsilon_0} \frac{1}{|\vec{r} - \vec{r}'|} > 0. \end{aligned}$$

- It turns out this is just the classical Coulomb energy between two charge distributions. This is the energy required to put two electrons into the same quantum state n with opposite spin and is known as the "Hubbard U".

$$U_n = \iint d^3\vec{r} d^3\vec{r}' \frac{\rho_n(\vec{r}) \rho_m(\vec{r}')}{4\pi\epsilon_0 |\vec{r} - \vec{r}'|}$$

- The exchange integral can also be analysed

- Noting that

$$\frac{1}{4\pi |\vec{r} - \vec{r}'|} = \frac{1}{(2\pi)^3} \int d^3\vec{k} \frac{1}{k^2} e^{i\vec{k} \cdot (\vec{r} - \vec{r}')}.$$

- It can then be seen that

$$\begin{aligned} [\psi_n^\dagger \psi_m | g | \psi_n^\dagger \psi_m] &= \iint d^3\vec{r} d^3\vec{r}' \varphi_n^\dagger(\vec{r}) \varphi_m(\vec{r}) \frac{e^2}{4\pi\epsilon_0 |\vec{r} - \vec{r}'|} \varphi_m^\dagger(\vec{r}') \varphi_n(\vec{r}') \sum_{\sigma=1,2} \chi_{s_n}^\dagger(\sigma) \chi_{s_n}(\sigma) \sum_{\sigma'=1,2} \chi_{s_m}^\dagger(\sigma') \chi_{s_m}(\sigma') \\ &= \frac{e^2}{\epsilon_0 (2\pi)^3} \int d^3\vec{k} \frac{1}{k^2} \iint d^3\vec{r} d^3\vec{r}' \varphi_n^\dagger(\vec{r}) \varphi_m(\vec{r}) \varphi_m^\dagger(\vec{r}') \varphi_n(\vec{r}') e^{i\vec{k} \cdot (\vec{r} - \vec{r}')} \varphi_m^\dagger(\vec{r}') \varphi_n(\vec{r}') \delta_{s_n, s_m} \delta_{s_n, s_m} \\ &= \frac{e^2}{\epsilon_0 (2\pi)^3} \int d^3\vec{k} \frac{1}{k^2} \int d^3\vec{r} \varphi_n^\dagger(\vec{r}) \varphi_m(\vec{r}) e^{i\vec{k} \cdot \vec{r}} \int d^3\vec{r}' \varphi_m^\dagger(\vec{r}') \varphi_n(\vec{r}') e^{-i\vec{k} \cdot \vec{r}'} \delta_{s_n, s_m} \\ &= \frac{e^2}{\epsilon_0 (2\pi)^3} \int d^3\vec{k} \frac{1}{k^2} \left| \int d^3\vec{r} \varphi_n^\dagger(\vec{r}) \varphi_m(\vec{r}) e^{i\vec{k} \cdot \vec{r}} \right|^2 \delta_{s_n, s_m} > 0. \end{aligned}$$

- Hence, the exchange energy is either positive for states of identical spin, or is zero for states of opposite spin.
- As the Coulomb energy, Hartree energy and the Exchange energies are all positive, we must have $E_H > E_E$.
- Typically, E_H is an order of magnitude larger than E_E .
- The exchange interaction therefore reduces the quantum Coulomb energy below the classical Coulomb energy.
- This occurs, as electrons of equal spin are kept apart in real space.

The Hartree-Fock Equation

- We wish to minimise the ground-state energy subject to constraint that the $\{\psi_n\}$ form an orthonormal set; $\int d\vec{x} \psi_n^\dagger \psi_m = [\psi_n^\dagger \psi_m] = \delta_{n,m}$.
- We introduce N^2 Lagrange multipliers $\epsilon_{n,m}$ and minimise

$$L[\{\psi_n\}] = E_0[\{\psi_n\}] - \sum_{n,m=1}^N \epsilon_{n,m} [\psi_n^\dagger \psi_m] - \delta_{n,m}.$$

- Assuming the states are already orthogonal and that the lagrange multipliers $\epsilon_{n,n}$ are real (this can be done WLOG), the above simplifies to

$$L[\{\psi_n\}] = E_0[\{\psi_n\}] - \sum_{n=1}^N \epsilon_n [\psi_n^\dagger \psi_n] - 1.$$

- Varying the functions $\{\psi_n\}$ to find $\delta L[\{\psi_n\}]$, using the previous result for E_0 and rearranging gives

$$\delta L[\{\psi_n\}] = \left(\sum_{n=1}^N [\delta \psi_n^\dagger \psi_n] h \right) + \sum_{n,m=1}^N \left([\delta \psi_n^\dagger \psi_n | g | \psi_m^\dagger \psi_m] - [\delta \psi_n^\dagger \psi_m | g | \psi_m^\dagger \psi_n] - \sum_{n=1}^N \epsilon_n [\delta \psi_n^\dagger \psi_n] \right) + (\text{hermitian conjugate}),$$

- This can be simplified by introducing:

$$\begin{aligned} \text{The local Hartree operator } J_m(\vec{x}) f(\vec{x}) &= \left(\int d\vec{y} \psi_m^\dagger(\vec{y}) g(\vec{x} - \vec{y}) \psi_m(\vec{y}) \right) f(\vec{x}) \\ \text{And the non-local Exchange operator } \hat{K}_m(\vec{x}) f(\vec{x}) &= \left(\int d\vec{y} \psi_m^\dagger(\vec{y}) g(\vec{x} - \vec{y}) f(\vec{y}) \right) \psi_m(\vec{x}) \\ \text{Therefore, } L[\{\psi_n\}] \text{ is minimised if} & \end{aligned}$$

$$0 = \delta L[\{\psi_n\}] = \sum_{n=1}^N \int d\vec{x} \delta \psi_n^\dagger \left(h(\vec{x}) \psi_n(\vec{x}) + \sum_{m=1}^N \left(J_m(\vec{x}) - K_m(\vec{x}) \right) \psi_n(\vec{x}) - \epsilon_n \psi_n(\vec{x}) \right) + \sum_{n=1}^N \int d\vec{x} \delta \psi_n \text{ (hermitian conjugate).}$$

- The condition to meet the above requirement is the Hartree-Fock equation, which is an eigensystem equation;

$$\begin{aligned} \left(h(\vec{x}) + \sum_{m=1}^N \left(J_m(\vec{x}) - K_m(\vec{x}) \right) \right) \psi_n(\vec{x}) &= \hat{H} \psi_n(\vec{x}) = \epsilon_n \psi_n(\vec{x}) \quad \text{where} \\ \hat{H} = h(\vec{x}) + \sum_{m=1}^N \hat{J}_m(\vec{x}) - \sum_{m=1}^N \hat{K}_m(\vec{x}) &= -\frac{\hbar^2}{2m} \vec{\nabla}_r^2 + U_{\text{ion}}(\vec{r}) + \hat{U}_H(\vec{x}) - \hat{U}_E(\vec{x}) \quad \text{with} \\ &= -\frac{\hbar^2}{2m} \vec{\nabla}_r^2 + \hat{U}_{\text{Effective}}(\vec{x}) \end{aligned}$$

Solving the Hartree-Fock Equation

- This is difficult to solve, as the potential operators are themselves functions of the eigenfunctions. One method is the self-consistent iterative technique

- Find initial values for the $\psi_n(\vec{x})$ by solving the single-particle problem $h(\vec{x}) \psi_n^{(0)}(\vec{x}) = \epsilon_n \psi_n^{(0)}(\vec{x})$ numerically using basis states appropriate to the symmetry.

- Use the resulting eigenfunctions and the definitions of \hat{U}_H and \hat{U}_E to express \hat{H} as a matrix (the Fock matrix) using the same basis states.

- Diagonalise this matrix and find the eigenfunctions.

- Repeat steps 2 and 3 until the eigenfunctions are the same on each iteration (convergence).

- Using only a small fraction of the eigenfunctions calculated in each iteration, this process can be made more stable. That is letting

$$\phi_n^{(N)}(\vec{x}) = (1 - \alpha) \psi_n^{N-1}(\vec{x}) + \alpha \psi_n(\text{morestuff})$$

Interpretation

- The Hartree-Fock ground state energy, $E_0 > E^{\text{Exact}}$.
 - The difference between the Hartree-Fock and exact ground state energies is the correlation energy.
 - The Lagrange multipliers ϵ_i are addition energies.

- Koopmans theorem gives the energy required to take one electron out (assuming wavefunctions are unchanged) is

$$\Delta E = \langle \Psi_0^{(N)} | \hat{H} | \Psi_0^{(N)} \rangle - \langle \Psi_0^{(N-1)} | \hat{H} | \Psi_0^{(N-1)} \rangle = \epsilon_i.$$

- Hartree-Fock theorem accounts for exchange interactions from the Pauli principle., but electrons of opposite spin remain uncorrelated.

Homogenous Electron Gas

- The properties of an independent-electron gas are given by the classical Fermi-Dirac analysis using electron wavefunctions

$$\psi_{k,\lambda}(\vec{r}, \sigma) = \frac{1}{\sqrt{V}} e^{i\vec{k}\cdot\vec{r}} \chi_\lambda(\sigma)$$

- Jellium is homogeneous interacting electron gas, a model of interacting electrons in a uniform background of positive charge. Exact solutions to the Hartree-Fock approximation can be found using the above electron wavefunction and the below Hamiltonian.

$$\left(-\frac{\hbar^2}{2m} \nabla_r^2 + U_{e-\text{ion}}(\vec{r}) + \hat{U}_H(\vec{r}) - \hat{U}_E(\vec{r}) \right) \Psi_{k,\lambda}(\vec{r}) = \epsilon_{k,\lambda} \Psi_{k,\lambda}(\vec{r})$$

- Inspecting the Kinetic energy term

$$\begin{aligned} -\frac{\hbar^2}{2m} \nabla_r^2 \psi_{k,\lambda}(\vec{r}, \sigma) &= -\frac{\hbar^2}{2m} \nabla_r^2 \left(\frac{1}{\sqrt{V}} e^{i\vec{k}\cdot\vec{r}} \chi_\lambda(\sigma) \right), \\ &= \frac{\hbar^2}{2m} |\vec{k}|^2 \frac{1}{\sqrt{V}} e^{i\vec{k}\cdot\vec{r}} \chi_\lambda(\sigma), \\ &= \frac{\hbar^2}{2m} |\vec{k}|^2 \psi_{k,\lambda}(\vec{r}, \sigma). \end{aligned}$$

- The Hartree term (not quite sure what happens with the factor of 2 here)

$$\begin{aligned} \hat{U}_H(\vec{r}) \psi_{k,\lambda}(\vec{r}) &= \sum_{\substack{|\vec{k}'| \leq k_F \\ \lambda' = \pm 1}} J_{\vec{k}',\lambda'}(\vec{r}) \psi_{\vec{k}',\lambda'}(\vec{r}), \\ &= \left(\sum_{\substack{|\vec{k}'| \leq k_F \\ \lambda' = \pm 1}} \int d^3 \vec{r}' \psi_{\vec{k}',\lambda'}^\dagger(\vec{r}') \frac{e^2}{4\pi\epsilon_0 |\vec{r} - \vec{r}'|} \psi_{\vec{k}',\lambda'}(\vec{r}') \right) \psi_{k,\lambda}(\vec{r}), \\ &= \left(\sum_{\substack{|\vec{k}'| \leq k_F \\ \lambda' = \pm 1 \\ \sigma' = -1}} \sum_{\lambda'' = \pm 1} \int d^3 \vec{r}' \frac{1}{\sqrt{V}} e^{-i\vec{k}' \cdot \vec{r}'} \chi_{\lambda'}^\dagger(\sigma') \frac{e^2}{4\pi\epsilon_0 |\vec{r} - \vec{r}'|} \frac{1}{\sqrt{V}} e^{i\vec{k}' \cdot \vec{r}'} \chi_{\lambda''}(\sigma') \right) \psi_{k,\lambda}(\vec{r}), \\ &= \frac{1}{V} \sum_{\substack{|\vec{k}'| \leq k_F \\ \lambda' = \pm 1}} \left(\int d^3 \vec{r}' \frac{e^2}{4\pi\epsilon_0 |\vec{r} - \vec{r}'|} \right) \psi_{k,\lambda}(\vec{r}), \\ &= \frac{N}{V} \left(\int d^3 \vec{z} \frac{e^2}{4\pi\epsilon_0 |\vec{z}|} \right) \psi_{k,\lambda}(\vec{r}). \end{aligned}$$

- The Ion term, assuming the density of ions is N/V , giving neutral Jellium, and that each ion is assumed to be spread evenly over the whole volume.

- Notably, the Hartree term and Ion terms cancel under these conditions.

$$\begin{aligned} U_{e-\text{ion}}(\vec{r}) \psi_{k,\lambda}(\vec{r}) &= - \sum_{i=1}^N \left(\frac{1}{V} \int d^3 \vec{R}_i \frac{e^2}{4\pi\epsilon_0 |\vec{r} - \vec{R}_i|} \right) \psi_{k,\lambda}(\vec{r}) \\ &= - \frac{N}{V} \left(\int d^3 \vec{z} \frac{e^2}{4\pi\epsilon_0 |\vec{z}|} \right) \psi_{k,\lambda}(\vec{r}). \end{aligned}$$

- The Exchange term can also be evaluated analytically, giving

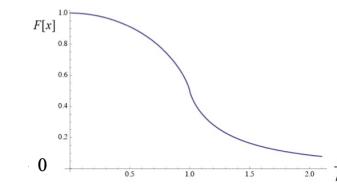
$$-\hat{U}_E(\vec{r}) \cdot \psi_{k,\lambda}(\vec{r}) = -\frac{e^2}{\epsilon_0} S(\vec{k}) \psi_{k,\lambda}(\vec{r}) \quad \text{with}$$

$$S(\vec{k}) = \int_{|\vec{k}'| \leq k_F} \frac{d^3 \vec{k}'}{(2\pi)^3 |\vec{k} - \vec{k}'|^2} = \frac{1}{2\pi} k_F F\left(\frac{k}{k_F}\right) \quad \text{where}$$

After polar integration

- Here, $F(x)$ is the Lindhard function. Note this function is continuous, its first derivative has a discontinuity and the second derivative has a singularity.

$$F(x) = \frac{1}{2} + \frac{1-x^2}{4x} \ln \left| \frac{1+x}{1-x} \right|$$



- Hence, the Hartree-Fock jellium addition energy dispersion is of the form

$$\epsilon_{k,\lambda}(\vec{k}) = \frac{\hbar^2 k^2}{2m} - \frac{e^2}{\epsilon_0} \frac{1}{2\pi^2} k_F F\left(\frac{k}{k_F}\right)$$

- Note, this describes ionisation energies, not a dispersion relation.

- The exchange energy provides a negative contribution to the ground-state energy, contributing to the binding energy of metals.
 - When considering metals, it can be useful to add the ion-ion term to the ground state energy, such that the ground-state energy zero is zero.
 - The Wigner-Seitz radius (r_s) is the radius of the sphere that on average contains one electron; $\frac{1}{n} = \frac{4\pi}{3} (r_s a_B)^3$.
 - Have another look at slide I-26.

The Interacting Electron Gas

- With high electron density (small r_s), the kinetic energy is dominant and an electron gas behaves as an almost ideal non-interacting Fermi gas.
- With intermediate electron density, the exchange energy causes full ferromagnetic alignment of electron spins with lower energy than the normal fluid ($75 < r_s < 100$).
- With low electron density ($r_s > 100$), electrons are trapped in the Coulomb potential of other electrons, become localised to minimise their Coulomb repulsion, and the system undergoes a metal-insulator transition (a Mott insulator).
 - In this regime, the free electron gas crystallises on a regular BCC lattice.
 - The energy of a classical electron crystal is given by

$$E_0 = \frac{1}{2} \sum_{i,j=1}^N \frac{e^2}{4\pi\epsilon_0 |\vec{R}_i - \vec{r}_j|} - \sum_{i=1}^N \int d^3 \vec{R} \frac{ne^2}{4\pi\epsilon_0 |\vec{R} - \vec{r}_i|} + \frac{1}{2} \int d^3 \vec{R} \int d^3 \vec{R}' \frac{n^2 e^2}{4\pi\epsilon_0 |\vec{R} - \vec{R}'|}.$$

- Consider the Wigner crystal as an infinite repetition of spherical unit cells, each containing a uniform positive charge with a single electron at its centre.
 - Finding the potential for each sphere and calculating $E_0 = N U_{\text{cell}}$ using $U_{\text{sphere}} = \frac{1}{2} \int_{r < r_{\text{c}} a_B} d^3 \vec{r} \rho(r) V_{\text{sphere}}(r)$ allows for the total energy of the cell to be found as $\frac{E_0}{N} = U_{\text{cell}} = -e V_{\text{sphere}}(0) + U_{\text{sphere}} = -\frac{1}{r_s} R_Y$
 - Notably, $\frac{E_0}{N} < \frac{E_{\text{kin}}}{N}$, so the variational principle guarantees a phase transition to the Wigner state as $r_s \rightarrow \infty$. Note HEG denotes homogeneous electron gas, discussed before).

- A Mott insulator is a material which according to conventional band theory, should be metallic, due to its partially filled electronic bands. However, it behave as an insulator due to strong electron-electron interactions.
 - In other words, is a material with sufficiently large on-site Coulomb repulsion and relative small electronic bandwidth. An example is NiO.

Electron Correlations: The Exchange-Correlation Hole

- For two non-interacting electrons with the same spin in plane-wave states, their antisymmetrised real-space wavefunction is

$$\psi_{k,k'}(\vec{r}_1, \vec{r}_2) = \frac{1}{\sqrt{2V}} (e^{i\vec{k}_1 \cdot \vec{r}_1} e^{i\vec{k}_2 \cdot \vec{r}_2} - e^{i\vec{k}_1 \cdot \vec{r}_2} e^{i\vec{k}_2 \cdot \vec{r}_1})$$

- Hence, the probability of finding one electron in volume $d^3 r_1$ and the other in $d^3 r_2$ is

$$\int |\Psi_{k,k'}(\vec{r}_1, \vec{r}_2)|^2 d^3 \vec{r}_1 d^3 \vec{r}_2 = \frac{1}{V^2} (1 - \cos((\vec{k}_1 - \vec{k}_2) \cdot (\vec{r}_1 - \vec{r}_2))) d^3 \vec{r}_1 d^3 \vec{r}_2$$

= 0 for $\vec{r}_1 = \vec{r}_2$

- This demonstrates that equal spin electrons avoid each other - this has an impact on screening.

- For a Hartree-Fock gas, the exchange term gives (see slide 23)

$$\begin{aligned} -U_E(\vec{r}) \psi_{k,\lambda}(\vec{r}) &= - \left[\frac{1}{V} \sum_{\vec{k}' < k_F} \int d^3 \vec{r}' e^{-i(\vec{k}-\vec{k}') \cdot (\vec{r}-\vec{r}')} \frac{e^2}{4\pi\epsilon_0 |\vec{r} - \vec{r}'|} \right] \psi_{k,\lambda}(\vec{r}) \\ &= - \left[\int d^3 \vec{r}' \frac{-e \rho_k^{HF}(\vec{r} - \vec{r}')}{4\pi\epsilon_0 |\vec{r} - \vec{r}'|} \right] \psi_{k,\lambda}(\vec{r}). \end{aligned}$$

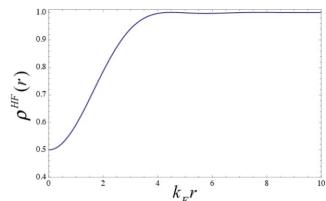
- This defines an exchange charge density - the extra charge density seen by a particular electron at \vec{r} as a result of its exchange interaction with other electrons at \vec{r}'

$$\rho_k^{HF}(\vec{r} - \vec{r}') = -\frac{e}{V} \sum_{\vec{k}' < k_F} e^{-i(\vec{k}-\vec{k}') \cdot (\vec{r}-\vec{r}')}$$

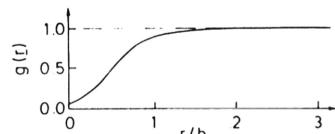
- Converting this to a k-space integral and performing the integral allows for calculation of an average exchange charge density over occupied states in the Fermi sphere. By adding this to the uniform Coulomb charge density, the total average charge density seen by a HF electron is found as

$$\rho_{\text{tot}}^{\text{HF}}(\vec{r}) = -e \frac{N}{V} \left(1 - \frac{9}{2} \frac{(\sin k_F r - k_F r \cos k_F r)^2}{(k_F r)^6} \right)$$

- This reduced concentration of electrons with equal spin in the vicinity of an electron is the Exchange-Correlation hole.
- HF does not include correlations for electrons with antiparallel spin.
More advanced techniques such as Density Functional Theory do.



Pair distribution function of jellium in the Hartree-Fock approximation.



Pair distribution function of jellium in density functional theory (b - bond length).

L4 AQCMP - Density Functional Theory

[L3 AQCMP - Hartree-Fock Theory](#)

[L5 AQCMP - Electronic Response Theory](#)

Density Functional Theory
Thomas-Fermi Model
Hohenberg-Kohn Theorems
Kohn-Sham
Local Density Approximation
Molecular Simulation

Density Functional Theory

- Use the same many-particle Hamiltonian as Hartree-Fock theory, where $V_{\text{Ne}}(\vec{r}_i) = U_{\text{e-ion}}(\vec{r}_i)$ is the potential energy due to the ion background;

$$\hat{H} = \sum_{i=1}^N \frac{\hat{p}_i^2}{2m} + \sum_{i=1}^N V_{\text{Ne}}(\vec{r}_i) + \frac{1}{2} \sum_{\substack{i=1 \\ i \neq j}}^N \frac{e^2}{4\pi\epsilon_0 |\vec{r}_i - \vec{r}_j|}$$

- Concentrate on electron density rather than the wavefunction;

$$n(\vec{r}) = \left\langle \Psi_0 \left| \left[\sum_{i=1}^N \delta(\vec{r} - \vec{r}_i) \right] \right| \Psi_0 \right\rangle = \int d^3\vec{x}_1 \dots d^3\vec{x}_N \Psi_0^\dagger(\vec{x}_1, \dots, \vec{x}_N) \left[\sum_{i=1}^N \delta(\vec{r} - \vec{r}_i) \right] \Psi_0(\vec{x}_1, \dots, \vec{x}_N)$$

- The electron density obeys $n(\vec{r}) \geq 0 \forall \vec{r}$, $\lim_{|\vec{r}| \rightarrow \infty} n(\vec{r}) = 0$, $\int d^3\vec{r} n(\vec{r}) = N$.

Thomas-Fermi Model

- In a homogeneous electron gas, $n = 2 \frac{1}{(2\pi)^3} \frac{k^3}{3\pi^2} = \frac{k^3}{3\pi^2}$, which implies $n(\vec{r}) = \frac{k(\vec{r})^3}{3\pi^2}$.
- This is used to approximate the kinetic energy of a many-particle system as a functional (map of a function to a real number) of electron density;

$$\begin{aligned} T[n] &\approx T_{TF}[n(\vec{r})], \\ &= \frac{1}{V} \int d^3\vec{r} \left[\sum_{\vec{k} \in k_F, \lambda=\uparrow,\downarrow} \frac{\hbar^2 |\vec{k}(\vec{r})|^2}{2m^*} \right], \\ &= \frac{\hbar^2}{m^*} \frac{3}{10} (3\pi^2)^{2/3} \int d^3\vec{r} n^{5/3}(\vec{r}). \end{aligned}$$

- This then allows for approximation of the ground state energy by minimising $E_0[n(\vec{r})]$ subject to the constraints of an electron density;

$$E_0[n(\vec{r})] \approx T_{TF}[n(\vec{r})] - \int d^3\vec{r} \sum_{i=1}^M \frac{en(\vec{r})Ze}{4\pi\epsilon_0 |\vec{r} - \vec{R}_i|} + \frac{1}{2} \iint d^3\vec{r} d^3\vec{r}' \frac{e^2 n(\vec{r}) n(\vec{r}')}{4\pi\epsilon_0 |\vec{r} - \vec{r}'|}.$$

Hohenberg-Kohn Theorems

- The first Hohenberg-Kohn theorem states that: For a system of N interacting electrons, the external potential $V_{\text{Ne}}(\vec{r})$ is a unique functional of the ground-state electron density $n(\vec{r})$, apart from a trivial additive constant; $V_{\text{Ne}} = V_{\text{Ne}}[n(\vec{r})]$.
 - As $V_{\text{Ne}}(\vec{r})$ determines \hat{H} , all properties of the many-particle ground state are unique functionals of $n(\vec{r})$.
 - Here, we assume a non-degenerate ground state. Where this is problematic, breaking the symmetry of the Hamiltonian will remove degeneracy.
 - The first Hohenberg-Kohn theorem may be proven by assuming there are two external potentials differing by more than a constant, each giving the same $n(\vec{r})$ in the ground state. Evaluating the energies of these systems with trial wavefunctions leads to a contradiction, hence there cannot be two different external potentials that give rise to the same electron density, so $V_{\text{Ne}}(\vec{r})$ is a unique functional of $n(\vec{r})$.
 - Hence, we may write

$$E_0[n] = T[n] + E_{Ne}[n] + E_{ee}[n] \quad (1)$$

$$= \int d^3\vec{r} n(\vec{r}) V_{Ne}(\vec{r}) + F_{HK}[n] \quad (2)$$

- Here, $F_{HK}[n] = T[n] + E_{ee}[n]$ is the Hohenberg-Kohn density functional.
- The second Hohenberg-Kohn theorem states that: The ground-state energy functional $E_0[\hat{n}]$ has its global minimum at the exact ground-state density.
- Hence, for any trial density, the energy obtained from $E_0[\hat{n}] = \int d^3\vec{r} \hat{n}(\vec{r}) V_{Ne}(\vec{r}) + F_{HK}[\hat{n}]$ is an upper bound on the true ground-state energy.
- The proof for this follows from the variational principle and the fact that any trial density defines its own Hamiltonian and hence its own ground-state wavefunction.

Kohn-Sham

- The largest contribution to $E_{ee}[n]$ will be the classical Coulomb energy $J[n]$. Separating this from $E_{ee}[n]$ gives

$$E_{ee}[n] = \frac{1}{2} \iint d^3\vec{r} d^3\vec{r}' \frac{e^2}{4\pi\epsilon_0} \frac{n(\vec{r})n(\vec{r}')}{|\vec{r} - \vec{r}'|} + E_{NCI}[n], \quad (3)$$

$$= J[n] + E_{NCI}[n]. \quad (4)$$

- Here, E_{NCI} is the Non-Classical contribution to the electron-electron interaction, including exchange and high-order corrections.
 - The self-interaction term is also included and cancels with that in $J[n]$.
- $T[n]$ may be split into $T_S[n]$ and a smaller part that can only be estimated.
 - Taking $T_S[n]$ as the exact kinetic energy of a non-interacting reference system with the same density as the interacting system;

$$n_S(\vec{r}) = \sum_{i=1}^N |\phi_i(\vec{r})|^2 = n(\vec{r}), \quad (5)$$

$$T_S = \sum_{i=1}^N \int d^3\vec{x} \psi_i^\dagger(\vec{x}) \frac{\vec{p}^2}{2m} \psi_i(\vec{x}), \quad (6)$$

- Now writing $F_{HK}[n] = T_S[n] + J[n] + E_{XC}[n]$ where E_{XC} is the exchange-correlation energy containing everything that is unknown;

$$E_{XC}[n] \equiv (T[n] - T_S[n]) + (E_{ee}[n] - J[n]).$$

- Combining the above, the ground state functional may be written in terms of the previously (lecture 2) defined h and g as (including self-interactions)

$$\begin{aligned} E_0[n] &= \int d^3\vec{r} n(\vec{r}) V_{Ne}(\vec{r}) + T_S[n] + \frac{1}{2} \iint d^3\vec{r} d^3\vec{r}' \frac{e^2}{4\pi\epsilon_0} \frac{n(\vec{r})n(\vec{r}')}{|\vec{r} - \vec{r}'|} + E_{XC}[n], \\ &= \sum_{i=1}^N \int d^3\vec{r} \phi_i^\dagger(\vec{r}) \left(-\frac{\hbar^2}{2m} \nabla_r^2 + V_{Ne}(\vec{r}) \right) \phi_i(\vec{r}) + \frac{1}{2} \sum_{i,j=1}^N \iint d^3\vec{r} d^3\vec{r}' |\phi_i(\vec{r})|^2 \frac{e^2}{4\pi\epsilon_0} \frac{1}{|\vec{r} - \vec{r}'|} |\phi_j(\vec{r}')|^2 + E_{XC}[n], \\ &= \sum_{i=1}^N [\psi_i^\dagger \psi_i | h] + \frac{1}{2} \sum_{i,j=1}^N [\psi_i^\dagger \psi_i | g | \psi_j^\dagger \psi_j] + E_{XC}[n]. \end{aligned}$$

- Again using calculus of variations to minimise this energy with the constraint that the wavefunctions form an orthonormal set, assuming they are already orthogonal and that the Lagrange multipliers $\epsilon_{i,i} = \epsilon_i$ are real, then we must minimise the following, either with respect to n or the ψ_i .

$$L[\{\psi_i\}] = E_0[\{\psi_i\}] - \sum_{i=1}^N \epsilon_i (\psi_i^\dagger \psi_i - 1).$$

- Recalling that $\hat{U}_H = \left(\sum_{m=1}^N \int d\vec{y} \psi_m^\dagger(\vec{y}) g(\vec{x} - \vec{y}) \psi_m(\vec{y}) \right)$, L is minimised if

$$\begin{aligned} 0 = \delta L[\{\psi_i\}] &= \sum_{i=1}^N \int d\vec{x} \delta \psi_i^\dagger \left(h(\vec{x}) \psi_i(\vec{x}) + \hat{U}_H \psi_i(\vec{x}) + \frac{\delta E_{XC}}{\delta n(\vec{r})} \psi_i(\vec{x}) - \epsilon_i \psi_i(\vec{x}) \right) \\ &+ \sum_{i=1}^N \int d\vec{x} \delta \psi_i \text{ (hermitian conjugate).} \end{aligned}$$

- Note that here,

$$\delta E_{XC} = E_{XC}[n + \delta n] - E_{XC}[n] = \int d^3\vec{r} \delta n(\vec{r}) \frac{\delta E_{XC}}{\delta n(\vec{r})}, \quad (7)$$

$$= \int d^3\vec{r} \sum_{i=1}^N \delta \psi_i^\dagger \psi_i \frac{\delta E_{XC}}{\delta n(\vec{r})}, \quad (8)$$

$$= \sum_{i=1}^N \int d\vec{x} \delta \psi_i^\dagger \frac{\delta E_{XC}}{\delta n(\vec{r})} \psi_i(\vec{x}) + \sum_{i=1}^N \int d\vec{x} \text{ (hermitian conjugate).} \quad (9)$$

- Finally, requiring the brackets to be zero gives (with $V_{XC}(\vec{r}) = \frac{\delta E_{XC}}{\delta n(\vec{r})}$)

$$\left(-\frac{\hbar^2}{2m} \nabla^2 + V_{Ne}(\vec{r}) + U_H(\vec{r}) + V_{XC}(\vec{r}) \right) \psi_i(\vec{x}) = \epsilon_i \psi_i(\vec{x}).$$

- These are the Kohn-Sham equations, and must be solved iteratively.

- This can be solved by first setting the Hartree and Exchange potentials to zero, giving an initial set of Kohn-Sham orbitals. Iteration between the above $\hat{U}_H(\vec{r})$ and $V_{XC}(\vec{r})$ allows stable solutions to be found.
- Calculating the sum of the Kohn-Sham eigenvalues shows that they do not have significance as single-particle energies. However, the orbitals and energies do prove to give reasonable descriptions of band structures and bonding characteristics if treated naively. The reason why is not fully understood.

Local Density Approximation

- For regions of slowly varying charge density, we can approximate the exchange correlation energy at any point E_{XC} with the value for a locally uniform electron gas of the same charge density; $E_{XC}[n] = \int \epsilon_{XC}(n) n(\vec{r}) d^3\vec{r}$.
 - The local spin density approximation is a variation of this where $E_{XC}[n_\uparrow, n_\downarrow] = \int \epsilon_{XC}(n_\uparrow, n_\downarrow) n(\vec{r}) d^3\vec{r}$.
 - These approximations work reasonably well even in systems with rapidly varying charge density. However, tend to under-predict atomic ground state energies and ionisation energies, while over-predicting binding energies.
 - Attempts have been made to incorporate gradients - but with tradeoffs; $E_{XC}[n_\uparrow, n_\downarrow] = \int \epsilon_{XC}(n_\uparrow, n_\downarrow, \nabla_r n_\uparrow, \nabla_r n_\downarrow) n(\vec{r}) d^3\vec{r}$.
 - Quantum Monte-Carlo techniques can also be used.

Molecular Simulation

- Use the Born-Oppenheimer approximation, and treating the motion of nuclear classically with

$$M_I \ddot{\vec{R}}_I = -\nabla_I \left(\underbrace{E_0(\vec{R}_1, \dots, \vec{R}_N)}_{\text{DFT}} + \underbrace{V_{NN}(\vec{R}_1, \dots, \vec{R}_N)}_{\text{Nuclear-nuclear Coulomb repulsion}} \right)$$

- By minimising the Kohn-Sham energy functional for the nuclear configuration at each time step, forces are found.
- It is also possible to incorporate temperature effects.

L5 AQCMP - Electronic Response Theory

L4 AQCMP - Density Functional Theory

Excitations of the Electron Gas
 Response Theory
 Kramers-Krönig Relations
 Kramers-Krönig proof
 Longitudinal Response Function of the Electron Gas
 Lindhard Dielectric Function of the Homogeneous Electron Gas
 Static Dielectric Screening in Metals
 Correlation Functions
 CSG Units

Excitations of the Electron Gas

- An exciton is a bound electron-hole pair in a sea of other electrons.
- Plasmons are longitudinal charge density oscillations induced by the Coulomb interactions between electrons.
- Response theory describes the response of a system to stimuli, such as a perturbing electromagnetic field, which may then generate excitations.

Response Theory

- For weak perturbations, a linear response theory may be used, otherwise non-linear response theory is required.
- The linear response of a dynamical system property Ψ to a perturbing force \vec{F} is

$$\Psi_i(\vec{x}, t) = \int d^3 \vec{x}' \int dt' \sum_{j=1}^3 \chi_{i,j}(\vec{x}, \vec{x}', t, t') F_j(\vec{x}', t').$$

- Here, the (real) dynamic response function (susceptibility) $\chi_{i,j}(\vec{x}, \vec{x}', t, t')$ describes the response of the field component Ψ_i at location \vec{x} and time t to a perturbing force applied at \vec{x}' at earlier time t' .

- By causality,

$$\chi_{i,j}(\vec{x}, \vec{x}', t, t') = \begin{cases} \text{finite} & \text{for } t > t' \\ 0 & \text{for } t < t' \end{cases}$$

- If the system is translationally invariant then $\chi_{i,j}$ depends only on the relative coordinate $\vec{x} - \vec{x}'$. If also in an equilibrium state, then it will depend only on the relative time $t - t'$.
- Here, we define (weirdly) the Fourier transform and the inverse Fourier transform in both space and time as:

$$\begin{aligned} \chi(\vec{q}, \omega) &= \int d^3 \vec{x} \int dt \chi(\vec{x}, t) e^{-i\vec{q}\cdot\vec{x}} e^{i\omega t}, \\ \chi(\vec{x}, t) &= \frac{1}{(2\pi)^3} \int d^3 \vec{q} \frac{1}{2\pi} \int d\omega \chi(\vec{q}, \omega) e^{i\vec{q}\cdot\vec{x}} e^{-i\omega t}. \end{aligned}$$

- Scalar fields are denoted:

$$\Psi(\vec{x}, t) = \int d^3 \vec{x}' \int dt' \chi(\vec{x} - \vec{x}', t - t') F(\vec{x}', t').$$

- Hence, the FT of such a scalar field is given by convolution as:

$$\Psi(\vec{q}, \omega) = \chi(\vec{q}, \omega) F(\vec{q}, \omega)$$

Kramers-Krönig Relations

- Assuming a perturbing field varies with time, but is constant in space,

$$\begin{aligned} \psi(t) &= \int_{-\infty}^{\infty} \chi(t - t') F(t') dt' \\ \Psi(\omega) &= \chi(\omega) F(\omega) \end{aligned}$$

- The Kramers-Krönig relations show that the causality condition on χ causes the real $\chi_1(\omega)$ and imaginary $\chi_2(\omega)$ parts of $\chi(\omega) = \chi_1(\omega) + i\chi_2(\omega)$ to become dependent on each other. The proof now follows:

Kramers-Krönig proof

- Write $\chi(t) = \Theta(t)\nu(t)$ where $\Theta(t)$ is the Heaviside step-function and $\nu(t)$ is real and antisymmetric with respect to $t \rightarrow \pm\infty$. Hence,

$$\begin{aligned} \chi(t) &= \Theta(t)\nu(t), \\ &= \int \Theta(\eta) e^{-i\eta t} \frac{d\eta}{2\pi} \int \nu(\omega') e^{-i\omega' t} \frac{d\omega'}{2\pi}, \\ \text{set } \eta &= \omega - \omega' \text{ so that } d\eta = d\omega, \\ &= \iint \Theta(\omega - \omega') \nu(\omega') e^{-i(\omega - \omega')t} e^{-i\omega' t} \frac{d\omega d\omega'}{2\pi \cdot 2\pi}, \\ &= \int \left(\int \Theta(\omega - \omega') \nu(\omega') \frac{d\omega'}{2\pi} \right) e^{-i\omega t} \frac{d\omega}{2\pi}. \end{aligned}$$

- From here, taking the inverse FT of both sides gives

$$\chi(\omega) = \int_{-\infty}^{\infty} \Theta(\omega - \omega') \eta(\omega') \frac{d\omega'}{2\pi}$$

- As $\nu(t)$ is real and antisymmetric in time, its FT, $\nu(\omega)$ is purely imaginary.

- The FT of a Heaviside step function is

$$\begin{aligned} \Theta(\omega) &= \int_{-\infty}^{\infty} \Theta(t) e^{i\omega t} dt \\ &= \lim_{\epsilon \rightarrow 0} \int_0^{\infty} e^{i\omega t - \epsilon t} dt, \\ &= \lim_{\epsilon \rightarrow 0} \frac{1}{\epsilon - i\omega}, \\ &= \lim_{\epsilon \rightarrow 0} \left(\frac{\epsilon}{\epsilon^2 + \omega^2} + i \frac{\omega}{\epsilon^2 + \omega^2} \right), \\ &= \pi\delta(\omega) + \mathcal{P} \frac{i}{\omega}, \end{aligned}$$

- Here, \mathcal{P} is a Cauchy principal value;

$$\mathcal{P} \int_a^b f(x) dx = \lim_{\epsilon \rightarrow 0^+} \left[\int_a^{c-\epsilon} f(x) dx + \int_{c+\epsilon}^b f(x) dx \right]$$

- The frequency-dependent linear response function is therefore

$$\chi(\omega) = \chi_1(\omega) + i\chi_2(\omega) = \int_{-\infty}^{\infty} \left(\pi\delta(\omega - \omega') + \mathcal{P} \frac{i}{\omega - \omega'} \right) \nu(\omega') \frac{d\omega'}{2\pi}.$$

- Comparing imaginary parts gives $i\chi_2(\omega) = \nu(\omega)/2$, as $\nu(\omega)$ is purely imaginary.

- Comparing the real parts then gives the first Kramers-Krönig relation,

$$\chi_1(\omega) = \mathcal{P} \int_{\infty}^{\infty} \frac{\chi_2(\omega')}{\omega' - \omega} \frac{d\omega'}{\pi}$$

- Conducting a similar analysis using a real symmetric $\nu(t) = \nu(-t)$ gives the second Kramers-Krönig relation,

$$\chi_2(\omega) = -\mathcal{P} \int_{-\infty}^{\infty} \frac{\chi_1(\omega') d\omega'}{\omega' - \omega / \pi}$$

- $\chi_1(\omega)$ can be determined from the spectral dependence of $\chi_2(\omega)$ and vice versa. However, the real or imaginary part of the response function must be known at all positive frequencies.

- As $\chi(t) = \chi^*(-\omega)$, rewriting the fourier transform it is seen that

$$\chi(\omega) = \int dt' \chi(t') e^{i\omega t'} = \chi^*(-\omega)$$

- Therefore, using that $\chi_i(\omega) = \chi_i^*(\omega)$

$$\chi_1(\omega) + i\chi_2(\omega) = \chi_1(-\omega) - i\chi_2(-\omega)$$

- Hence, $\chi_1(\omega) = \chi_1(-\omega)$, ie is an even function and $\chi_2(\omega) = -\chi_2(-\omega)$ ie is an odd function.

- Exploiting the properties of odd and even functions it can then be seen that $\chi_1(\omega)$ and $\chi_2(\omega)$ need only be known for positive ω , as

$$\begin{aligned}\chi_1(\omega) &= \frac{1}{\pi} \mathcal{P} \int_{-\infty}^{\infty} \frac{\chi_2(\omega') \omega' + \omega}{\omega' - \omega} \frac{d\omega'}{\omega' + \omega}, \\ &= \frac{1}{\pi} \mathcal{P} \int_{-\infty}^{\infty} \frac{\chi_2(\omega') \omega'}{(\omega')^2 - \omega^2} d\omega' + \frac{\omega}{\pi} \mathcal{P} \int_{-\infty}^{\infty} \frac{\chi_2(\omega')}{(\omega')^2 - \omega^2} d\omega', \\ &= \frac{2}{\pi} \mathcal{P} \int_0^{\infty} \frac{\chi_2(\omega') \omega'}{(\omega')^2 - \omega^2} d\omega',\end{aligned}$$

Similarly,

$$\chi_2(\omega) = -\frac{2\omega}{\pi} \mathcal{P} \int_0^{\infty} \frac{\chi_1(\omega')}{(\omega')^2 - \omega^2} d\omega'.$$

Longitudinal Response Function of the Electron Gas

- Consider the response of an electron gas to a longitudinal plane wave perturbation potential.
- Consider a system with one-electron hamiltonian $\hat{H}_0 = -\frac{\hbar^2}{2m} \vec{\nabla}^2 + V(\vec{r})$ with eigenvalues and eigenvectors E_α and $\psi_\alpha(\vec{r})$.

- Applying a time-dependent perturbation potential with the form of a plane wave with wavevector \vec{q} , $U(\vec{r}, t) = A_0(\vec{q}, \omega) e^{i(\vec{q} \cdot \vec{r} - \omega t)} + \text{c.c.}$ gives

$$\hat{H} = -\frac{\hbar^2}{2m} \nabla^2 + V(\vec{r}) + A_0 e^{i(\vec{q} \cdot \vec{r} - \omega t)} + A_0^* e^{-i(\vec{q} \cdot \vec{r} - \omega t)}$$

- The corresponding electric field is then longitudinal ($\vec{E} \parallel \vec{q}$), as

$$\begin{aligned}\vec{E}(\vec{r}, t) &= -\nabla \left(\frac{U(\vec{r}, t)}{-e} \right) \\ &= \frac{iqA_0}{e} \frac{\vec{q}}{q} e^{i(\vec{q} \cdot \vec{r} - \omega t)} + \text{c.c.} \\ &= \vec{E}_0 e^{i(\vec{q} \cdot \vec{r} - \omega t)} + \text{c.c.}\end{aligned}$$

$$\text{where } E_0 = \frac{iqA_0}{e} \quad \text{and} \quad \vec{e} = \frac{\vec{q}}{q}$$

- The perturbation induces transitions between eigenstates of H_0 through absorption or emission of energies $\hbar\omega$. For transitions from state $\alpha \rightarrow \beta$ and $\beta \rightarrow \alpha$, the number of transitions per unit time are given by Fermi's golden rule as;

$$\text{Absorption} \quad W_{\alpha \rightarrow \beta} = \frac{2\pi}{\hbar} \left| \langle \psi_\beta | A_0 e^{i\vec{q} \cdot \vec{r}} | \psi_\alpha \rangle \right|^2 \delta(E_\beta - E_\alpha - \hbar\omega) f(E_\alpha)(1 - f(E_\beta))$$

$$\text{Emission} \quad W_{\beta \rightarrow \alpha} = \frac{2\pi}{\hbar} \left| \langle \psi_\alpha | A_0^* e^{-i\vec{q} \cdot \vec{r}} | \psi_\beta \rangle \right|^2 \delta(E_\alpha + \hbar\omega - E_\beta) f(E_\beta)(1 - f(E_\alpha))$$

- Hence, the total power in a volume is found by multiplying the number of transitions by the energy per transition;

$$\begin{aligned}P(\vec{q}, \omega) &= \hbar\omega W(\vec{q}, \omega) = 2\hbar\omega \sum_{\alpha, \beta} (W_{\alpha \rightarrow \beta} - W_{\beta \rightarrow \alpha}) \quad (\text{factor of 2 for spin}) \\ &= 2\hbar\omega \frac{2\pi}{\hbar} \sum_{\alpha, \beta} \left| \langle \psi_\beta | A_0 e^{i\vec{q} \cdot \vec{r}} | \psi_\alpha \rangle \right|^2 \delta(E_\beta - E_\alpha - \hbar\omega) (f(E_\alpha) - f(E_\beta))\end{aligned}$$

- It is then possible to relate this and the dielectric response function $\epsilon(\vec{q}, \omega)$ by considering Joule heating.

- Using Ohm's law, $J(\vec{q}, \omega) = \sigma(\vec{q}, \omega) E(\vec{q}, \omega)$ with $\sigma(\vec{q}, \omega) = \sigma_1 + i\sigma_2$ is the complex conductivity.
- Substituting for \vec{E} gives $J(\vec{r}, t) = \sigma(\vec{q}, \omega) E_0 \vec{e} e^{i(\vec{q} \cdot \vec{r} - \omega t)} + \text{c.c.}$
- Hence, the power dissipated (note that only terms at frequency ω survive) is

$$\begin{aligned}P(\vec{q}, \omega) &= \int_V d^3 r \vec{J} \cdot \vec{E} \\ &= \int_V d^3 r \left(\sigma(\vec{q}, \omega) E_0 \vec{e} e^{i(\vec{q} \cdot \vec{r} - \omega t)} + \text{c.c.} \right) \left(E_0 e^{i(\vec{q} \cdot \vec{r} - \omega t)} + \text{c.c.} \right) \\ &= \sigma(\vec{q}, \omega) |E_0|^2 V + \text{c.c.} \\ &= 2\sigma_1(\vec{q}, \omega) \frac{q^2}{e^2} |A_0|^2 V\end{aligned}$$

- Comparing the classical and QM results then gives

$$P(\vec{q}, \omega) = 2\sigma_1(\vec{q}, \omega) \frac{q^2}{e^2} |A_0|^2 V = \hbar\omega W(\vec{q}, \omega)$$

- Rearranging gives

$$\sigma_1 = \Re(\sigma) = \frac{1}{2} \frac{e^2}{q^2} \frac{\hbar\omega W(\vec{q}, \omega)}{|A_0|^2 V}$$

- It is also possible to relate σ and ϵ using Maxwell's Laws

$$\nabla \times \vec{H} = \vec{J} + \frac{\partial \vec{D}_{\text{free}}}{\partial t} \quad (1)$$

$$\vec{J} = \sigma \vec{E} \quad (\text{for free electrons}) \quad (2)$$

$$\vec{D}_{\text{free}} = \epsilon_0 \vec{E} \quad (\text{for free space}) \quad (3)$$

- Substituting (2) and (3) into (1) gives $\vec{\nabla} \times \vec{H} = \sigma \vec{E} + \epsilon_0 \frac{\partial \vec{E}}{\partial t}$. Then assuming plane wave solutions of $\vec{E} = \vec{E}_0 \exp(-i\omega t)$ and $\vec{H} = \vec{H}_0 \exp(-i\omega t)$ gives;

$$\vec{\nabla} \times \vec{H}_0 = \sigma \vec{E}_0 - i\omega \epsilon_0 \vec{E}_0$$

- The dielectric response function is then properly defined as

$$\vec{D} = \epsilon_0 \epsilon \vec{E}$$

$$\vec{\nabla} \times \vec{H}_0 = -i\omega \epsilon_0 \epsilon \vec{E}_0$$

- Combining the above gives $-i\omega \epsilon \epsilon_0 = -i\omega \epsilon_0 + \sigma$, so

$$\epsilon = 1 + \frac{i\sigma}{\epsilon_0 \omega}$$

- Where $\epsilon = \epsilon_1 + i\epsilon_2$, taking the imaginary part gives

$$\epsilon_2(\vec{q}, \omega) = \frac{1}{\epsilon_0 \omega} \sigma_1(\vec{q}, \omega)$$

- Note that $\epsilon = 1 + \chi$ implies that $\epsilon_1 = 1 + \chi_1$ but $\epsilon_2 = \chi_2$.

$$\epsilon_2(\vec{q}, \omega) = \frac{1}{\epsilon_0 \omega} \sigma_1(\vec{q}, \omega)$$

$$\sigma_1 = \Re(\sigma) = \frac{1}{2} \frac{e^2}{q^2} \frac{\hbar \omega W(\vec{q}, \omega)}{|A_0|^2 V}$$

$$\begin{aligned} P(\vec{q}, \omega) &= \hbar \omega W(\vec{q}, \omega) = 2 \hbar \omega \sum_{\alpha, \beta} (W_{\alpha \rightarrow \beta} - W_{\beta \rightarrow \alpha}) \quad (\text{factor of 2 for spin}) \\ &= 2 \hbar \omega \frac{2\pi}{\hbar} \sum_{\alpha, \beta} |\langle \psi_\beta | A_0 e^{i\vec{q} \cdot \vec{r}} | \psi_\alpha \rangle|^2 \delta(E_\beta - E_\alpha - \hbar \omega) (f(E_\alpha) - f(E_\beta)) \end{aligned}$$

- The three above equations can then be combined to find

$$\begin{aligned} \epsilon_2(\vec{q}, \omega) &= \frac{1}{\epsilon_0 \omega} \frac{1}{2q^2} \frac{e^2}{|A_0|^2 V} \cdot \hbar \omega \cdot \frac{2\pi}{\hbar} \sum_{\alpha, \beta} |\langle \psi_\beta | A_0 e^{i\vec{q} \cdot \vec{r}} | \psi_\alpha \rangle|^2 \delta(E_\beta - E_\alpha - \hbar \omega) (f(E_\alpha) - f(E_\beta)) \\ &= \frac{2\pi e^2}{\epsilon_0 q^2} \frac{1}{V} \sum_{\alpha, \beta} |\langle \psi_\beta | e^{i\vec{q} \cdot \vec{r}} | \psi_\alpha \rangle|^2 \delta(E_\beta - E_\alpha - \hbar \omega) (f(E_\alpha) - f(E_\beta)). \end{aligned}$$

- Remembering that $\epsilon = 1 + \chi$ implies that $\epsilon_1 = 1 + \chi_1$ but $\epsilon_2 = \chi_2$, using the Kramers-Krönig relationships for χ give

$$\begin{aligned} \epsilon_1(\vec{q}, \omega) &= 1 + \frac{1}{\pi} \mathcal{P} \int_{-\infty}^{\infty} \frac{\epsilon_2(\vec{q}, \omega') d\omega'}{\omega' - \omega} \\ &= 1 + \frac{1}{\pi} \mathcal{P} \int_{-\infty}^{\infty} \frac{1}{\omega' - \omega} \cdot \frac{2\pi e^2}{\epsilon_0 |\vec{q}|^2 V} \sum_{\alpha, \beta} |\langle \psi_\beta | e^{i\vec{q} \cdot \vec{r}} | \psi_\alpha \rangle|^2 \delta(E_\beta - E_\alpha - \hbar \omega') (f(E_\alpha) - f(E_\beta)) d\omega' \\ &= 1 + \frac{2e^2 \hbar}{\epsilon_0 |\vec{q}|^2 V} \sum_{\alpha, \beta} |\langle \psi_\beta | e^{i\vec{q} \cdot \vec{r}} | \psi_\alpha \rangle|^2 \frac{f(E_\alpha) - f(E_\beta)}{E_\beta - E_\alpha - \hbar \omega}. \end{aligned}$$

- This can also be expressed compactly (real and imaginary parts) as

$$\epsilon(\vec{q}, \omega) = \lim_{\eta \rightarrow 0^+} \left(1 + \frac{2e^2}{\epsilon_0 |\vec{q}|^2 V} \sum_{\alpha, \beta} |\langle \psi_\beta | e^{i\vec{q} \cdot \vec{r}} | \psi_\alpha \rangle|^2 \frac{f(E_\alpha) - f(E_\beta)}{E_\beta - E_\alpha - \hbar \omega - i\eta} \right).$$

- Where we have used that

$$\lim_{\eta \rightarrow 0^+} \frac{1}{x - i\eta} = \lim_{\eta \rightarrow 0^+} \left(\frac{x}{x^2 + \eta^2} + i\pi \frac{\eta}{\pi x^2 + \eta^2} \right) = \mathcal{P} \frac{1}{x} + i\pi \delta(x).$$

- Elementary excitations of an electron system from an occupied state α to unoccupied state β with an $\hbar \omega$ energy difference result in singularities in the response function at $E_\beta - E_\alpha - \hbar \omega = 0$.

$$\epsilon_2(\vec{q}, \omega) = \frac{1}{\epsilon_0 \omega} \sigma_1(\vec{q}, \omega)$$

$$\begin{aligned} P(\vec{q}, \omega) &= \int_V d^3 \vec{r} \cdot \vec{J} \cdot \vec{E} \\ &= \int_V d^3 \vec{r} \left(\sigma(\vec{q}, \omega) E_0 \vec{e} e^{i(\vec{q} \cdot \vec{r} - \omega t)} + \text{c.c.} \right) (E_0 e^{i(\vec{q} \cdot \vec{r} - \omega t)} + \text{c.c.}) \\ &= \sigma(\vec{q}, \omega) |E_0|^2 V + \text{c.c.} \\ &= 2\sigma_1(\vec{q}, \omega) \frac{q^2}{e^2} |A_0|^2 V \end{aligned}$$

- Combining the above two equations gives that

$$P(\vec{q}, \omega) = \left[2\epsilon_0 \omega \frac{|\vec{q}|^2}{e^2} |A_0|^2 V \right] \chi_2(\vec{q}, \omega)$$

- This is in fact a generally valid relationship; the dissipated energy P of a perturbing field E is proportional to the imaginary part of the response function of the system χ_2 .

Lindhard Dielectric Function of the Homogeneous Electron Gas

- In the case of the homogeneous electron gas with plane wave eigenstates $\psi_\alpha = \frac{1}{\sqrt{V}} e^{i\vec{k} \cdot \vec{r}}$ and $\psi_\beta = \frac{1}{\sqrt{V}} e^{i\vec{k}' \cdot \vec{r}}$, $\langle \psi_\beta | e^{i\vec{q} \cdot \vec{r}} | \psi_\alpha \rangle = \frac{1}{V} \int d^3 \vec{r} \exp(i(\vec{k} - \vec{q} + \vec{k}') \cdot \vec{r}) = \delta_{\vec{k}, \vec{k}' + \vec{q}}$

- Therefore, the dielectric function simplifies to (where $\lim_{\eta \rightarrow 0^+}$ is implicit),

$$\epsilon(\vec{q}, \omega) = 1 + \frac{2e^2}{\epsilon_0 |\vec{q}|^2} \frac{1}{V} \sum_{\vec{k}} \frac{f(E_{\vec{k}}) - f(E_{\vec{k} + \vec{q}})}{E(\vec{k} + \vec{q}) - E(\vec{k}) - \hbar \omega - i\eta}.$$

- Writing this out more explicitly, and substituting $\vec{k}' = \vec{k} + \vec{q}$ gives

$$\epsilon(\vec{q}, \omega) = 1 + \frac{2e^2}{\epsilon_0 q^2} \lim_{\eta \rightarrow 0^+} \left(\underbrace{\int \frac{d^3 \vec{k}}{(2\pi)^3} \frac{f(E_{\vec{k}})}{E_{\vec{k} + \vec{q}} - E_{\vec{k}} - \hbar \omega - i\eta} + \int \frac{d^3 \vec{k}}{(2\pi)^3} \frac{f(E_{\vec{k}})}{E_{\vec{k} - \vec{q}} - E_{\vec{k}} + \hbar \omega + i\eta} \right).$$

- Taking the limit where $T \rightarrow 0$, so the Fermi-Dirac function $f(E)$ is a step function,

$$S_1 = \frac{2e^2}{\epsilon_0 q^2} \frac{1}{(2\pi)^3} \int_{k \leq k_F} d^3 \vec{k} \frac{2m}{\hbar^2} \frac{1}{2\vec{q} \cdot \vec{k} + q^2 - \tilde{\omega}},$$

with $\tilde{\omega} = \frac{2m}{\hbar} \omega + i\tilde{\eta}$, $\tilde{\eta} = \frac{2m}{\hbar^2} \eta$, in the limit $\tilde{\eta} \rightarrow 0^+$.

- Then, converting to spherical polar coordinates, substituting $x = \cos \theta$ and assuming \vec{q} is along z wlog, and where $k_{TF}^2 = \frac{me^2 k_F}{\epsilon_0 \pi^2 \hbar^2}$ gives

$$\begin{aligned} S_1 &= \frac{k_{TF}^2}{k_F q^2} \int_0^{k_F} k^2 dk \int_0^\pi \frac{\sin \theta d\theta}{2qk \cos \theta + q^2 - \tilde{\omega}} \\ &= \frac{k_{TF}^2}{k_F q^2} \int_0^{k_F} \frac{k^2}{2qk} \ln \left| \frac{2qk + q^2 - \tilde{\omega}}{-2qk + q^2 - \tilde{\omega}} \right| dk \\ &= \frac{k_{TF}^2}{2k_F q^3} \left(\frac{q^2 - \tilde{\omega}}{2q} k_F + \frac{1}{2} k_F^2 - \frac{(q^2 - \tilde{\omega})^2}{4q^2} \right) \ln \left| \frac{2qk_F + q^2 - \tilde{\omega}}{-2qk_F + q^2 - \tilde{\omega}} \right|. \end{aligned}$$

- A similar method can be used for S_2 , eventually giving

$$\begin{aligned} \epsilon(\vec{q}, \omega) &= 1 + \frac{k_{TF}^2}{2q^2} + \frac{k_{TF}^2}{4k_F q^3} \left(k_F^2 - \left(\frac{q}{2} - \frac{\tilde{\omega}}{2q} \right)^2 \right) \ln \left| \frac{2qk_F + q^2 - \tilde{\omega}}{-2qk_F + q^2 - \tilde{\omega}} \right| \\ &\quad + \frac{k_{TF}^2}{4k_F q^3} \left(k_F^2 - \left(\frac{q}{2} + \frac{\tilde{\omega}}{2q} \right)^2 \right) \ln \left| \frac{2qk_F + q^2 + \tilde{\omega}}{-2qk_F + q^2 + \tilde{\omega}} \right|. \end{aligned}$$

- Taking the real part of ϵ by taking the limit $\text{Im}(\tilde{\omega}) = \eta \rightarrow 0^+$ gives

$$\begin{aligned}\epsilon_1(\vec{q}, \omega) &= 1 + \frac{k_{TF}^2}{2q^2} + \frac{k_{TF}^2}{4k_F q^3} \left(k_F^2 - \left(\frac{q}{2} - \frac{m\omega}{\hbar q} \right)^2 \right) \ln \left| \frac{2qk_F + q^2 - 2m\omega/\hbar}{-2qk_F + q^2 - 2m\omega/\hbar} \right| \\ &\quad + \frac{k_{TF}^2}{4k_F q^3} \left(k_F^2 - \left(\frac{q}{2} + \frac{m\omega}{\hbar q} \right)^2 \right) \ln \left| \frac{2qk_F + q^2 + 2m\omega/\hbar}{-2qk_F + q^2 + 2m\omega/\hbar} \right|.\end{aligned}$$

- Finally, in the static limit with $\omega \rightarrow 0$, we obtain the Lindhard dielectric function

$$\begin{aligned}\epsilon_1(\vec{q}, 0) &= 1 + \frac{k_{TF}^2}{2q^2} + \frac{k_{TF}^2}{2k_F q^3} \left(k_F^2 - \left(\frac{q}{2} \right)^2 \right) \ln \left| \frac{2k_F + q}{2k_F - q} \right| \\ &= 1 + \frac{k_{TF}^2}{q^2} F \left(\frac{q}{2k_F} \right)\end{aligned}$$

- It can also be shown that $\epsilon_2(\vec{q}, 0) = 0$.

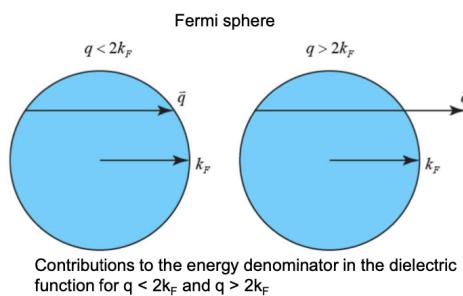
- Note that $F(x) = \frac{1}{2} + \frac{1-x^2}{4x} \ln \left| \frac{1+x}{1-x} \right|$.

- Hence, with $q \ll k_F$, $\epsilon_1(q, 0) = 1 + \frac{k_{TF}^2}{q^2}$, which is the Thomas-Fermi result.

- With $q \gg k_F$, $\lim_{x \rightarrow \infty} F(x) = \frac{1}{3x^2} + \dots \Rightarrow \epsilon_1(q, 0) = 1 + \frac{k_{TF}^2}{q^2}$.

- With $q \approx 2k_F$, $\epsilon_1(1, 0) \approx \epsilon_1(2k_F, 0) + \frac{k_{TF}^2}{16k_F^3} (q - 2k_F) \ln \left| \frac{q - 2k_F}{4k_F} \right|$ is continuous, but there is a logarithmic singularity in its derivative at $q = 2k_F$.

- This singularity is responsible for the Friedel oscillations in the charge density.
- For $q < 2k_F$, transitions between an occupied and unoccupied state with the same energies $E(k+q) = E(k)$ may contribute to the energy denominator. These transitions are not possible for $q > 2k_F$.
- This gives an abrupt drop to the dielectric function at $q = 2k_F$.



Static Dielectric Screening in Metals

- Converting the Coulomb potential to the Fourier domain gives

$$U_{\text{ext}}(\vec{r}) = -\frac{Ze^2}{4\pi\epsilon_0 r} = -\frac{1}{(2\pi)^3} \int d^3\vec{q} \frac{Ze^2}{\epsilon_0 q^2} e^{i\vec{q}\cdot\vec{r}}.$$

- In direct analogy, the dielectric screening response gives

$$U(\vec{r}) = -\frac{1}{(2\pi)^3} \int d^3\vec{q} \frac{1}{\epsilon_1(\vec{q}, 0)} \frac{Ze^2}{\epsilon_0 q^2} e^{i\vec{q}\cdot\vec{r}}.$$

- The difference between these determines the induced charge density of the electron gas in the vicinity of the point charge;

$$-\nabla^2 \frac{U(\vec{r}) - U_{\text{ext}}(\vec{r})}{(-e)} = \frac{\rho_{\text{ind}}(\vec{r})}{\epsilon_0}.$$

- Hence,

$$\begin{aligned}\rho_{\text{ind}}(\vec{r}) &= -\frac{Ze}{(2\pi)^3} \int d^3\vec{q} \frac{1}{q^2} \left(\frac{1}{\epsilon_1(\vec{q}, 0)} - 1 \right) \nabla^2 e^{i\vec{q}\cdot\vec{r}}, \\ &= \frac{Ze}{(2\pi)^3} \int d^3\vec{q} \left(\frac{1}{\epsilon_1(\vec{q}, 0)} - 1 \right) e^{i\vec{q}\cdot\vec{r}}, \\ &= \frac{Ze}{(2\pi)^3} \int dq d\theta d\phi q^2 \sin \theta \left(\frac{1}{\epsilon_1(\vec{q}, 0)} - 1 \right) e^{iqr \cos \theta}, \\ &= -\frac{Ze}{r} \int_0^\infty dq g(q) \sin qr, \\ \text{where } g(q) &= \frac{q}{2\pi^2} \left(\frac{\epsilon_1(\vec{q}, 0) - 1}{\epsilon_1(\vec{q}, 0)} \right).\end{aligned}$$

- With $q = 2k_F$, $\frac{dg(q)}{dq} \rightarrow C \ln |q - 2k_F|$ for a constant C .

- Also, the total screened electron charge around the point charge is $-Ze$, perfectly screening the charge. This follows from noting that $\epsilon_1(0, 0)$ is infinite in metals;

$$\begin{aligned}Q_S &= \int d^3\vec{r} \rho_{\text{ind}}(\vec{r}), \\ &= \frac{Ze}{(2\pi)^3} \int d^3\vec{r} \int d^3\vec{q} \left(\frac{1}{\epsilon_1(\vec{q}, 0)} - 1 \right) e^{i\vec{q}\cdot\vec{r}}, \\ &= \frac{Ze}{(2\pi)^3} \int d^3\vec{q} \left(\frac{1}{\epsilon_1(\vec{q}, 0)} - 1 \right) (2\pi)^3 \delta(\vec{q}), \\ &= -Ze.\end{aligned}$$

- Integrating by parts twice, it can be shown that

$$\rho_{\text{ind}}(\vec{r}) = \frac{Ze}{r^3} \int_0^\infty dq \frac{d^2g(q)}{dq^2} \sin qr$$

- At large distances from the point charge, rapid oscillations result in the integral being dominated by the interval $\pm \Delta$ around $q = 2k_F$. Hence,

$$\begin{aligned}\rho_{\text{ind}}(\vec{r}) &\approx \frac{ZeC}{r^3} \int_{2k_F - \Delta}^{2k_F + \Delta} dq \frac{1}{q - 2k_F} \sin qr \\ &\approx \pi \frac{ZeC \cos 2k_F r}{r^3}\end{aligned}$$

- These oscillations are called Friedel oscillations. Analogous oscillations in spin density occur around a magnetic moment, giving RKKY exchange coupling between magnetic ions.

- In 1D, the dielectric function diverges, implying the metallic state is unstable (Peierls transition).

Correlation Functions

- The density correlation function is

$$C_\rho(\vec{x}, \vec{x}', t, t') = \langle \hat{\rho}(\vec{x}, t) \hat{\rho}(\vec{x}', t') \rangle.$$

- The density fluctuation correlation function is

$$\begin{aligned} S_\rho(\vec{x}, \vec{x}', t, t') &= (\langle \hat{\rho}(\vec{x}, t) - \langle \hat{\rho}(\vec{x}, t) \rangle \rangle) (\langle \hat{\rho}(\vec{x}', t') - \langle \hat{\rho}(\vec{x}', t') \rangle \rangle) \\ &= C_\rho(\vec{x}, \vec{x}', t, t') - \langle \hat{\rho}(\vec{x}, t) \rangle^2. \end{aligned}$$

- These describe the correlation between the charge density of a system at one location and time with that at another location and time.
 - Hence, in a crystal there is a peak if $\vec{x} - \vec{x}'$ is a direct lattice vector.
- The structure factor is the Fourier transform in both space and time of the density correlation function;

$$C_\rho(\vec{q}, \omega) = \frac{1}{V} \int d^3\vec{x} d^3\vec{x}' \int dt C_\rho(\vec{x}, \vec{x}', t) e^{-i\vec{q} \cdot (\vec{x} - \vec{x}')} e^{i\omega t}.$$

- With a huge amount of work, it can be shown that the structure factor is proportional to the cross section for the scattering of an incoming particle with \vec{k} and $E_{\vec{k}}$ into an outgoing particle with $\vec{k}' = \vec{k} + \vec{q}$ and energy $E_{\vec{k}'} = E_{\vec{k}} + \hbar\omega$;

$$C_\rho(\vec{q}, \omega) \propto \frac{d^2\sigma}{d\Omega d\omega}$$

- This is a realisation of the fluctuation-dissipation theorem.
- Using linear response theory, it can be shown that the density fluctuation correlation function S_ρ of an electron gas is related to the dissipation in the electron gas χ_2 by the **fluctuation dissipation theorem**;

$$S_\rho(\vec{q}, \omega) = \frac{2k_B T}{\omega} \chi_2(\vec{q}, \omega)$$

- Relationships between response functions, energy loss and structure factors are generally valid for any response function irrespective of whether interactions are present or not.
- The density response functions are often relatively easy to probe, giving good experimental insight.

CSG Units

Unit system	ϵ_0	μ_0	\vec{D}, \vec{H}	Maxwell equations	Lorentz force
CGS	1	1	$\vec{D} = \vec{E} + 4\pi\vec{P}$ $\vec{H} = \vec{B} - 4\pi\vec{M}$	$\vec{\nabla} \cdot \vec{D} = 4\pi\rho$ $\vec{\nabla} \times \vec{H} = \frac{4\pi}{c} \vec{J} + \frac{1}{c} \frac{\partial \vec{D}}{\partial t}$ $\vec{\nabla} \times \vec{E} = -\frac{1}{c} \frac{\partial \vec{B}}{\partial t}$ $\vec{\nabla} \cdot \vec{B} = 0$	$\vec{F} = e \left(\vec{E} + \frac{\vec{v}}{c} \times \vec{B} \right)$
SI	$\frac{10^7}{4\pi c^2} = 8.854 \times 10^{-12}$ Farad/m	$4\pi \times 10^{-7}$ Henry/m	$\vec{D} = \epsilon_0 \vec{E} + \vec{P}$ $\vec{B} = \mu_0 (\vec{H} + \vec{M})$	$\vec{\nabla} \cdot \vec{D} = \rho$ $\vec{\nabla} \times \vec{H} = \vec{J} + \frac{\partial \vec{D}}{\partial t}$ $\vec{\nabla} \times \vec{E} = -\frac{\partial \vec{B}}{\partial t}$ $\vec{\nabla} \cdot \vec{B} = 0$	$\vec{F} = e \left(\vec{E} + \vec{v} \times \vec{B} \right)$

L6 AQCMP - Quasiparticles

L5 AQCMP - Electronic Response Theory

Landau's Fermi Liquid Theory
 Normal Fermi Liquids
 Quasiparticles
 Quasiparticle Lifetime
 Landau Fermi Liquid Theory
 Second Quantisation - Fermions
 Jellium in Second Quantisation
 Hartree-Fock in Second Quantisation

L7 AQCMP - Magnetism Fundamentals

Landau's Fermi Liquid Theory

- Curiously, independent-particle models describe some many-Fermion metallic systems even when their inter-particle interactions are very strong. These are "Normal Fermi Liquids".
 - For example, at low temperature, the heat capacity of 3He is linear with a gradient determined by an enhanced particle mass that depends on the density; the same behaviour as with the independent-particle model.

Normal Fermi Liquids

- Consider a system of non-interacting Fermions with single-particle states $\psi_1, \dots, \psi_\infty$, giving many-particle (Slater determinant) states.

$$|\psi_{i_1, \dots, i_N}\rangle(\vec{x}_1, \dots, \vec{x}_N) = A\{\psi_{i_1}(\vec{x}_1), \dots, \psi_{i_N}(\vec{x}_N)\}$$

- Here, $\{i_1, \dots, i_N\}$ are the quantum numbers of the occupied single-particle states.
- Labelling many-particle states by occupation numbers of single-particle states gives (where $n_i = 0, 1$ is the occupation number of state i),

$$|\psi_{i_1, \dots, i_N}\rangle = |n_1, n_2, n_3, \dots\rangle_0,$$

- Assuming no phase transition occurs, taking a non-interacting many-particle state and switching on the inter-particle interactions produces a state representing many interacting particles. If the same is also true in reverse, then there is a one-to-one correspondence, ie the properties of $|\psi_{i_1, \dots, i_N}\rangle$ determine those of $|\psi\rangle$.
 - Hence, an interacting system $|\psi\rangle$ is defined by the same occupation numbers;

$$|\psi\rangle = |n_1, \dots, n_\infty\rangle$$

- Fermi systems exhibiting this one-to-one correspondence are normal Fermi liquids.

Quasiparticles

- If the ground-state of a many-Fermion system is $|n_1, \dots, n_p, \dots, n_\infty\rangle$, then $|n_1, \dots, n_p + 1, \dots, n_\infty\rangle$ in a non-interacting system represents adding a single particle to state \vec{p} , whereas in an interacting system it represents adding a quasiparticle to state \vec{p} .
 - A quasiparticle is a bare particle, together with the distortion it causes to the fermion distribution as interactions are slowly turned on.
 - Where E_0 is ground-state energy, the energy of the interacting many-particle system is $E_0 + \epsilon_\lambda(\vec{p})$, defining the quasiparticle energy $\epsilon_\lambda(\vec{p})$.
- For a filled Fermi sphere of non-interacting particles and one extra particle of momentum \vec{p} , where $p > p_F$, $|p - p_F| \ll p_F$ and $v_F = \frac{p_F}{m}$,

$$\begin{aligned}\epsilon_\lambda(\vec{p}) - \mu &= \frac{\vec{p}^2}{2m} - \mu \\ &= \frac{1}{2m}(p + p_F)(p - p_F), \\ &\approx \frac{p_F}{m}(p - p_F) = v_F(p - p_F),\end{aligned}$$

- Turning on the interaction, total momentum is conserved, and the extra particle evolves into a quasiparticle of momentum \vec{p}' .
 - Given the one-to-one relationship in the states, we expect the quasiparticle excitation energy $\epsilon_\lambda(\vec{p}) - \mu$ to have the same \vec{p} dependence as the non-interacting system, but modified by a scaling factor.
 - This scaling is provided by the effective mass m^* (qualitatively different from the band effective mass).
 - Quasiparticle excitation energy is therefore

$$\epsilon_\lambda(\vec{p}) - \mu = v_F(p - p_F)$$

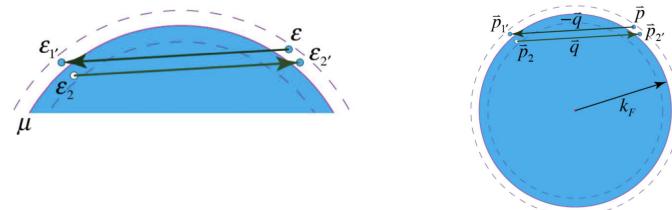
- Here, $v_F = \frac{p_F}{m}$ is the quasiparticle group velocity on the Fermi surface.

- In anisotropic systems, m^* is quite artificial, and it can be more useful to use the quasiparticle density of states, which at low temperatures, dictates all physical properties;

$$g_V(\epsilon) = \frac{1}{V} \sum_{\vec{p}, \lambda} \delta(\epsilon_\lambda(\vec{p}) - \mu - \epsilon)$$

Quasiparticle Lifetime

- The dominant low-temperature scattering mechanics consists of a quasiparticle of energy $\epsilon \geq \mu$ scattering with a quasiparticle of energy $\epsilon_2 \leq \mu$, generating a new quasiparticle-quasihole pair with quasiparticle energy $\epsilon_{2'} \geq \mu$ and quasi-hole energy $\epsilon_2 \leq \mu$, leaving the original quasiparticle with energy $\epsilon_{1'} \geq \mu$. This is depicted below.



- This must conserve total energy, momentum and spin, so, where $\vec{p} - \vec{q} = \vec{p}'_1$ and $\vec{p}_2 + \vec{q} = \vec{p}'_2$,

$$\begin{aligned}\epsilon + \epsilon_2 - \epsilon_{1'} - \epsilon_{2'} &= 0 \\ \vec{p} + \vec{p}_2 - \vec{p}'_1 - \vec{p}'_2 &= 0 \\ \lambda + \lambda_2 - \lambda_{1'} - \lambda_{2'} &= 0\end{aligned}$$

- At zero temperature, $\mu \rightarrow E_F$, so combining these with the conditions $\epsilon_2 \leq E_F$, $\epsilon_{2'} \geq E_F$ and $\epsilon_{1'} \geq E_F$ gives that for a particle initially on the Fermi-Surface, $\epsilon_2 = E_F$ and hence,

$$\epsilon_{2'} + \epsilon_{1'} = 2E_F \implies \epsilon_{2'} = \epsilon_{1'} = E_F$$

- Therefore, the lifetime of a quasiparticle on the Fermi surface of a normal Fermi liquid at zero temperature is infinite, regardless of the interaction strength.

- Quasiparticle scattering rate $\tau(\vec{p})$ is:

$$\frac{1}{\tau(\vec{p})} = \sum_{\vec{p}_2, \vec{p}'_1, \vec{p}'_2, \lambda_2, \lambda'_1, \lambda'_2} W(\vec{p}, \lambda, \vec{p}_2, \lambda_2, \vec{p}'_1, \lambda'_1, \vec{p}'_2, \lambda'_2) n_2(1 - n'_1)(1 - n'_2) \times \delta(\epsilon + \epsilon_2 - \epsilon'_1 - \epsilon'_2) \delta(\vec{p} + \vec{p}_2 - \vec{p}'_1 - \vec{p}'_2) \delta_{\lambda + \lambda_2, \lambda'_1 + \lambda'_2}$$

- Where W is scattering amplitude, n_i is the quasiparticle distribution function - giving the probability state \vec{p}_i , λ_i is occupied, and $1 - n_i$ is the probability that state is unoccupied.

- Swapping to polar coordinates and treating the plane containing \vec{p}_2 and \vec{p} separately to that containing \vec{p}'_2 and \vec{p}'_1 , then using

$$n_\lambda(\vec{p}) \approx \frac{1}{1 + e^{-\beta(\mu - \epsilon_\lambda(\vec{p}))}}$$

- We eventually find that

$$\frac{1}{\tau(\vec{p})} = \frac{(m^*)^3}{16\pi^4 \hbar^6} \left\langle \frac{W(\theta, \phi)}{\cos(\theta/2)} \right\rangle \frac{\pi^2 (k_B T)^2 + (\epsilon(\vec{p}) - \mu)^2}{1 + \exp((\mu - \epsilon(\vec{p}))/k_B T)}.$$

- This is rigorous where $|\epsilon(\vec{p}) - \mu| \ll \mu$.

- Where $|\epsilon(\vec{p}) - \mu| \ll k_B T$, elementary excitations exist within an energy range $\pm k_B T$ with a scattering rate $\frac{1}{\tau(\vec{p})} \propto T^2$.
- Where $\epsilon(\vec{p}) - \mu \ll -k_B T$ the system is in the ground-state regime and scattering rate $\rightarrow 0$.
- Where $\epsilon(\vec{p}) - \mu \gg k_B T$, thermal broadening plays no role.

Landau Fermi Liquid Theory

- Turning on the interaction adiabatically, we obtain an eigenstate of the real system where $n_\lambda(\vec{p})$ represents the distribution of quasiparticles.
- The level of excitation in the system is defined by the quasiparticle excitation distribution

$$\delta n_\lambda(\vec{p}) = n_\lambda(\vec{p}) - n_\lambda^0(\vec{p})$$

- Here, $n_\lambda^0(\vec{p}) = n^{(0)}(\epsilon_\lambda(\vec{p}) - \mu)$ is the ground-state distribution function and $n^{(0)}(x)$ is a step function in x .

- At low temperatures, quasiparticles and quasiholes are excited near the Fermi surface.

- Fermi liquid theory assumes that the system is in contact with a reservoir with chemical potential μ , allowing N to deviate from the ground-state value.
- The free energy $F = U - \mu N$ is used to allow the formalism to be framed in terms of excitations from the ground state. It may be approximated well below the Fermi temperature $T_F = E_F/k_B$ by a Taylor expansion in $\delta n_\lambda(\vec{p})$:

$$F = F_0 + \sum_{\vec{p}, \lambda} (\epsilon_\lambda(\vec{p}) - \mu) \delta n_\lambda(\vec{p}) + \frac{1}{2V} \sum_{\vec{p}, \vec{p}'} \sum_{\lambda, \lambda'} f_{\lambda, \lambda'}(\vec{p}, \vec{p}') \delta n_\lambda(\vec{p}) \delta n_{\lambda'}(\vec{p}')$$

- The first order coefficient $\epsilon_\lambda(\vec{p}) - \mu$ is the quasiparticle excitation energy.

- The second order coefficient $f_{\lambda, \lambda'}(\vec{p}, \vec{p}')$ is the quasiparticle-quasiparticle interaction energy.

- The spin-dependence on the quasiparticle-quasiparticle interaction energy arises from relativistic (spin-spin and spin-orbit) interactions as well as the exchange interaction.
 - The exchange interaction is typically an order of magnitude larger than these other effect in metals.
 - If only accounting for the exchange interaction, then for a system with time-reversal and inversion symmetries, we may parameterise its coefficient in spherical polars as

$$f_{\lambda,\lambda'}(\vec{p}, \vec{p}') = f^{(s)}(\cos \xi) + \gamma_{\lambda,\lambda'} f^{(a)}(\cos \xi).$$

- Here, $\vec{p} \cdot \vec{p}' = pp' \cos \xi$ with $\cos \xi = \cos \theta \cos \theta' + \sin \theta \sin \theta' \cos(\phi - \phi')$ and $\gamma_{\lambda,\lambda'} = 1$ if $\lambda = \lambda'$ and $\gamma_{\lambda,\lambda'} = -1$ if $\lambda \neq \lambda'$.

- Writing $f^{(s)}$ and $f^{(a)}$ in terms of Legendre polynomials

$$f^{(a)}(\cos \xi) = \sum_{l=0}^{\infty} f_l^{(a)} P_l(\cos \xi),$$

- Where the coefficients of the expansion define the Landau Parameters;

$$F_l^{(a)} = g_V(0) f_l^{(a)} = \frac{m^* p_F}{\pi^2 \hbar^3} f_l^{(a)}.$$

- Using the addition theorem;

$$P_l(\cos \xi) = \frac{4\pi}{2l+1} \sum_{m=-l}^l Y_{l,m}(\theta, \phi) Y_{l,m}^*(\theta', \phi').$$

- It is then possible to write the contributions to the quasiparticle-quasiparticle interaction energy, $f^{(s)}$ and $f^{(a)}$ as

$$f^{(a)}(\cos \xi) = \sum_{l=0}^{\infty} \sum_{m=-l}^l \frac{4\pi}{2l+1} f_l^{(a)} Y_{l,m}(\theta, \phi) Y_{l,m}^*(\theta', \phi'). \quad (1)$$

- When adding an additional quasiparticle of momentum \vec{p} to a normal Fermi liquid with quasiparticle excitation distribution $\delta n_{\lambda}(\vec{p})$, the free energy of the additional particle, $\tilde{\epsilon}_{\lambda}(\vec{p}) - \mu$ is given by the first variational derivative of F

$$\implies \tilde{\epsilon}_{\lambda}(\vec{p}) - \mu = \frac{\delta F}{\delta n_{\lambda}(\vec{p})} = (\epsilon_{\lambda}(\vec{p}) - \mu) + \frac{1}{V} \sum_{\vec{p}', \lambda'} f_{\lambda, \lambda'}(\vec{p}, \vec{p}') \delta n_{\lambda'}(\vec{p}'). \quad (2)$$

- Therefore, the free energy of a quasiparticle is determined by its interaction with other excited quasiparticles.
- This result holds when the system is inhomogeneous and the deviation from equilibrium is position dependent; $\delta n_{\lambda}(\vec{p}; \vec{r})$. Hence, $\tilde{\epsilon}_{\lambda}(\vec{p}) - \mu$ is referred to as the local quasiparticle excitation energy.
- The gradient of $\tilde{\epsilon}_{\lambda}(\vec{p}) - \mu$ in ordinary space can be interpreted as an average force exerted by the surrounding medium on the quasiparticle \vec{p} :

$$\nabla_{\vec{r}} \tilde{\epsilon}_{\lambda}(\vec{p}; \vec{r}) = \nabla_{\vec{r}} \left(\frac{1}{2V} \sum_{\vec{p}', \lambda'} f_{\lambda, \lambda'}(\vec{p}, \vec{p}') \delta n_{\lambda'}(\vec{p}') \right).$$

- It is also possible to define the local quasiparticle excitation distribution as

$$\delta \tilde{n}_{\lambda}(\vec{p}) = n_{\lambda}(\vec{p}) - \tilde{n}_{\lambda}^0(\vec{p}) \quad \text{where} \quad \tilde{n}_{\lambda}^0(\vec{p}) = n^{(0)}(\tilde{\epsilon}_{\lambda}(\vec{p}) - \mu)$$

- This quantifies the departure from local equilibrium in a Fermi liquid.
- Therefore, the total current density J arising from a distribution of excited quasiparticles $\delta n_{\lambda}(\vec{p})$ is directly related to $\delta \tilde{n}_{\lambda}(\vec{p})$ and not $\delta n_{\lambda}(\vec{p})$ via (proof in Pines and Nozieres)

$$J = \frac{1}{V} \sum_{\vec{p}, \lambda} v_{\vec{p}} \delta \tilde{n}_{\lambda}(\vec{p}) \quad \text{where} \quad v_{\vec{p}} = \nabla_{\vec{p}} \epsilon_{\lambda}(\vec{p})$$

- Combining equation (2) with the definitions for $\delta \tilde{n}_{\lambda}(\vec{p})$ and $\delta n_{\lambda}(\vec{p})$ allows the latter two to be related;

$$\delta \tilde{n}_{\lambda}(\vec{p}) = \delta n_{\lambda}(\vec{p}) - \frac{\partial n^{(0)}}{\partial \epsilon_{\lambda}(\vec{p})} \frac{1}{V} \sum_{\vec{p}', \lambda'} f_{\lambda, \lambda'}(\vec{p}, \vec{p}') \delta n_{\lambda'}(\vec{p}'). \quad (3)$$

- This can be greatly simplified for an isotropic system at zero temperature by splitting $\delta \tilde{n}_{\lambda}$ and δn_{λ} into spin symmetric and antisymmetric parts, such as

$$\delta n_{\lambda}(\vec{p}) = \delta n^{(s)}(\vec{p}) + \eta_{\lambda} \delta n^{(a)}(\vec{p})$$

- Here, $\eta_{\lambda} = \pm 1$ for $\lambda = \uparrow, \downarrow$ respectively. The same can be done for $\delta \tilde{n}_{\lambda}$.

- Substituting this into the above equation for $\delta \tilde{n}_{\lambda}(\vec{p})$, using $\epsilon_{\lambda}(\vec{p}) = \epsilon(\vec{p})$, expanding on the Fermi surface as a series of normalised spherical harmonics, substituting this into equation (1) and using the zero temperature result that $\frac{\partial n^{(0)}}{\partial \epsilon(\vec{p})} = -\delta(\epsilon(\vec{p}) - \mu)$ gives

$$\delta \tilde{n}^{(\alpha)}(\vec{p}) = \delta(\epsilon(\vec{p}) - \mu) \sum_{l,m} \left(1 + \frac{F_l^{(\alpha)}}{2l+1} \right) \delta n_{l,m}^{(\alpha)} Y_{l,m}(\theta, \phi),$$

- This implies that

$$\delta \tilde{n}_{l,m}^{(\alpha)} = \left(1 + \frac{F_l^{(\alpha)}}{2l+1} \right) \delta n_{l,m}^{(\alpha)}$$

- Substituting (3) into J allows for the quasiparticle effective mass to be found, giving

$$\begin{aligned} J &= \frac{1}{V} \sum_{\vec{p}, \lambda} v_{\vec{p}, \lambda} \left(\delta n_{\lambda}(\vec{p}) - \frac{\partial n^{(0)}}{\partial \epsilon_{\lambda}(\vec{p})} \frac{1}{V} \sum_{\vec{p}', \lambda'} f_{\lambda, \lambda'}(\vec{p}, \vec{p}') \delta n_{\lambda'}(\vec{p}') \right) \\ &= \frac{1}{V} \sum_{\vec{p}, \lambda} v_{\vec{p}, \lambda} \delta n_{\lambda}(\vec{p}) - \frac{1}{V} \sum_{\vec{p}, \lambda} v_{\vec{p}, \lambda} \frac{\partial n^{(0)}}{\partial \epsilon_{\lambda}(\vec{p})} \frac{1}{V} \sum_{\vec{p}', \lambda'} f_{\lambda, \lambda'}(\vec{p}, \vec{p}') \delta n_{\lambda'}(\vec{p}') \\ &\quad (\text{swapping dummy variables}) \\ &= \frac{1}{V} \sum_{\vec{p}, \lambda} v_{\vec{p}, \lambda} \delta n_{\lambda}(\vec{p}) - \frac{1}{V} \sum_{\vec{p}', \lambda'} \sum_{\vec{p}, \lambda} v_{\vec{p}', \lambda'} \frac{\partial n^{(0)}}{\partial \epsilon_{\lambda'}(\vec{p}')} \frac{1}{V} f_{\lambda, \lambda'}(\vec{p}', \vec{p}) \delta n_{\lambda}(\vec{p}) \\ &\quad (\text{using the symmetries of } f_{\lambda, \lambda'}(\vec{p}, \vec{p}')) \\ &= \frac{1}{V} \sum_{\vec{p}, \lambda} \left(v_{\vec{p}, \lambda} - \frac{1}{V} \sum_{\vec{p}', \lambda'} v_{\vec{p}', \lambda'} \frac{\partial n^{(0)}}{\partial \epsilon_{\lambda'}(\vec{p}')} f_{\lambda, \lambda'}(\vec{p}, \vec{p}') \right) \delta n_{\lambda}(\vec{p}) \\ &= \frac{1}{V} \sum_{\vec{p}, \lambda} j_{\vec{p}, \lambda} \delta n_{\lambda}(\vec{p}) \end{aligned}$$

- $j_{\vec{p}, \lambda}$ is the quasiparticle current density. Then substituting for the quasiparticle current density $j_{\vec{p}, \lambda} = \frac{\vec{p}}{m^*}$ and using the definition $v_{\vec{p}, \lambda} = \frac{\vec{p}}{m^*}$, taking the dot product with \vec{p} , using $p = p' = p_F$ and performing the spin sum assuming spin degeneracy gives (note the density of states $g_V(0)$)

$$\begin{aligned} \frac{1}{m} &= \frac{1}{m^*} + \frac{2}{V} \sum_{\vec{p}'} \frac{1}{m^*} \delta(\epsilon(\vec{p}') - \mu) \sum_{l=0}^{\infty} f_l^{(s)} P_l(\cos \xi) P_1(\cos \xi), \\ &= \frac{1}{m^*} + \frac{1}{m^*} \frac{1}{4\pi} g_V(0) \sum_{l=0}^{\infty} f_l^{(s)} \int dS P_l(\cos \xi) P_1(\cos \xi), \\ &= \frac{1}{m^*} + \frac{1}{m^*} \frac{1}{4\pi} g_V(0) \sum_{l=0}^{\infty} f_l^{(s)} \frac{4\pi}{2l+1} \delta_{l,1} \quad (\text{using an identity}), \\ &= \frac{1}{m^*} + \frac{1}{m^*} \frac{F_1^{(s)}}{3}. \end{aligned}$$

- Therefore, $m^* = \left(1 + \frac{F^{(s)}}{3}\right) m$.

- At finite temperature, the free energy to add a single quasiparticle to a Fermi liquid is given by the local quasiparticle energy $\tilde{\epsilon}_\lambda(\vec{p}) - \mu$. Hence, the equilibrium quasiparticle distribution is given by

$$n_{\vec{p},\lambda}^0(T, \mu) = (1 + \exp(\beta(\tilde{\epsilon}_\lambda(\vec{p}) - \mu)))^{-1}$$

- Combining the previously derived expressions for $\tilde{\epsilon}_\lambda(\vec{p}) - \mu$ and $f_l^{(a)}(\cos(\zeta))$ gives

$$\begin{aligned} \tilde{\epsilon}_\lambda(\vec{p}) - \mu &= \epsilon_\lambda(\vec{p}) - \mu + \frac{4\pi}{2l+1} \sum_{l=0}^{\infty} \sum_{m=-l}^l (f_1^{(s)} + f_l^{(a)}) Y_{l,m}(\theta, \phi) \frac{1}{V} \sum_{\vec{p}'} Y_{l,m}^*(\theta', \phi') \delta n_\lambda(\vec{p}') \\ &\quad + \frac{4\pi}{2l+1} \sum_{l=0}^{\infty} \sum_{m=-l}^l (f_1^{(s)} - f_l^{(a)}) Y_{l,m}(\theta, \phi) \frac{1}{V} \sum_{\vec{p}'} Y_{l,m}^*(\theta', \phi') \delta n_\lambda(\vec{p}') \end{aligned}$$

- Here, INCLUDE THE LOGIC FOR δ

$$\begin{aligned} \frac{1}{V} \sum_{\vec{p}} Y_{l,m}^*(\theta, \phi') \delta n^{(a)}(\vec{p}) &= \frac{1}{(2\pi)^3} \sum_{l',m'} \int dS Y_{l,m}^*(\theta, \phi) Y_{l',m'}^*(\theta, \phi) \int p^2 dp \frac{\partial n^0}{\partial \epsilon(\vec{p})} \delta n^{(a)}(\vec{p}) \\ &= \int_{-\infty}^{\infty} H(\epsilon) \delta n_\lambda(\vec{p}) d\epsilon \end{aligned}$$

- The Sommerfeld integral is:

$$\int_{-\infty}^{\infty} H(\epsilon) \delta n_\lambda(\vec{p}) d\epsilon = \frac{\pi^2}{6} (k_B T)^2 \frac{dH(\epsilon)}{d\epsilon} \Big|_{\epsilon=\mu} + O(T^4),$$

- Combining this with the expression above implies each of the interaction terms in $\tilde{\epsilon}_\lambda(\vec{p}) - \mu$ is $\mathcal{O}(T^2)$, so can be neglected relative to $\epsilon_\lambda(\vec{p}) - \mu \sim k_B T$.

- Hence, we may instead write the distribution function as

$$n_{\vec{p},\lambda}^0(T, \mu) \approx \frac{1}{1 + \exp((\epsilon_\lambda(\vec{p}) - \mu)/k_B T)}.$$

- The free energy therefore has temperature dependence (using the same method as before, but now on F itself, gives

$$\begin{aligned} F &= F_0 + \sum_{\vec{p},\lambda} (\epsilon_\lambda(\vec{p}) - \mu) \delta n_\lambda(\vec{p}) \\ &\quad + \frac{1}{2V} \sum_{\vec{p},\vec{p}',\lambda,\lambda'} f_{\lambda,\lambda'}(\vec{p}, \vec{p}') \delta n_\lambda(\vec{p}) \delta n_{\lambda'}(\vec{p}') \\ &= F_0 + \sum_{\vec{p},\lambda} (\epsilon_\lambda(\vec{p}) - \mu) \delta n_\lambda(\vec{p}) \\ &\quad + \frac{1}{2V} \sum_{\lambda,\lambda'} \frac{4\pi}{2l+1} \sum_{l=0}^{\infty} \sum_{m=-l}^l (f_l^{(s)} + \lambda \lambda' f_l^{(a)}) \\ &\quad \times \sum_{\vec{p}} Y_{l,m}(\theta, \phi) \delta n_\lambda(\vec{p}) \sum_{\vec{p}'} Y_{l,m}^*(\theta', \phi') \delta n_{\lambda'}(\vec{p}'), \\ &= F_0 + \sum_{\vec{p},\lambda} (\epsilon_\lambda(\vec{p}) - \mu) \delta n_\lambda(\vec{p}) + O(T^4). \end{aligned}$$

- Hence, any thermodynamic quantity that depends only on F is not affected by quasiparticle interactions. This is the case for heat capacity, but not bulk compressibility or spin susceptibility.

- Evaluating $C_V = \frac{\partial U}{\partial T} \Big|_N = \frac{\partial F}{\partial T} \Big|_\mu$ with the above, $\epsilon = \frac{p^2}{2m}$ and the Sommerfeld integral, we find that

$$F = F_0 + V \frac{m^* p_F}{6\hbar^3} (k_B T)^2 + \mathcal{O}(T^4)$$

- Hence, taking the derivative,

$$C_V = V \frac{m^* p_F}{3\hbar^2} k_B^2 T + \mathcal{O}(T^3)$$

- Where the quasiparticle interactions only contribute to the $\mathcal{O}(T^3)$ part.

- Changes in the linearity of a heat capacity at low temperatures can be accounted for within Fermi-liquid theory by a change in the effective mass m^* resulting from inter-particle interactions.

Second Quantisation - Fermions

- Second quantisation provides a short hand notation to write the Hamiltonian for many-particle systems, allowing understanding non-Fermi Liquid behaviour.
- Again, writing many-particle Slater determinant states of a non-interacting system where $n_i = 0, 1$ is the occupation number of state i as

$$|\psi_{i_1, \dots, i_N}\rangle = |n_1, n_2, \dots\rangle$$

- The general wavefunction for an interacting many-electron system can be written as a linear combination of these Slater determinant states;

$$|\Psi(t)\rangle = \sum_{n_1, \dots, n_\infty=0}^1 f(n_1, \dots, n_\infty; t) |n_1, \dots, n_\infty\rangle$$

- Defining creation and annihilation operators c_i^\dagger and c_i respectively which add and remove single electrons from the particle state i , it is then seen that where $S_i = n_1 + n_2 + \dots + n_i$

$$\begin{aligned} |n_1, \dots, n_\infty\rangle &= (c_1^\dagger)^{n_1} (c_2^\dagger)^{n_2} \dots (c_\infty^\dagger)^{n_\infty} |0, 0, \dots, 0\rangle \\ c_i^\dagger | \dots n_i \dots \rangle &= \begin{cases} (-1)^{S_i} (n_i)^{1/2} | \dots n_i - 1 \dots \rangle & \text{for } n_i = 1 \\ 0 & \text{for } n_i = 0 \end{cases} \\ c_i^\dagger | \dots n_i \dots \rangle &= \begin{cases} (-1)^{S_i} (n_i + 1)^{1/2} | \dots n_i + 1 \dots \rangle & \text{for } n_i = 0 \\ 0 & \text{for } n_i = 1 \end{cases} \\ c_i^\dagger c_i | \dots n_i \dots \rangle &= n_i | \dots n_i \dots \rangle \end{aligned}$$

- These can all be derived using the anti-commutation rules $\{c_i, c_j^\dagger\} = \delta_{ij}$ and $\{c_i, c_j\} = \{c_i^\dagger, c_j^\dagger\} = 0$ with $\{a, b\} \equiv ab + ba$.

- These commutation rules themselves derive from the Fermion symmetry requirement on a two-particle state; (note this gives normal-commutation relations for Bosons)

$$c_i^\dagger c_j^\dagger |\vec{0}\rangle = \pm c_j^\dagger c_i^\dagger |\vec{0}\rangle$$

- It is therefore possible to derive the form of the Schrödinger equation in the occupation-number basis;
 - First considering an additive single-particle operator K (such as kinetic energy or momentum). Suppose $|k_i\rangle$ are eigenstates of this operator, the eigenvalue of the multiparticle operator \mathcal{K} will then be $\sum_i n_i k_i$. Hence we may write

$$\mathcal{K} = \sum_i k_i N_i = \sum_i k_i c_i^\dagger c_i$$

- If the single-particle states are specified in an inconvenient basis $|l_j\rangle$, then using completeness,

$$|k_i\rangle = \sum_j |l_j\rangle \langle l_j |k_i\rangle$$

- Then postulating that, where b_j^\dagger and b_j create and annihilate particles in single-particle states $|l_j\rangle$,

$$c_i^\dagger = \sum_j b_j^\dagger \langle l_j |k_i\rangle \quad (\implies c_i = \sum_j \langle k_i |l_j\rangle b_j)$$

- Hence, we may rewrite \mathcal{K} as

$$\begin{aligned} \mathcal{K} &= \sum_i k_i \sum_{mn} b_m^\dagger \langle l_m |k_i\rangle \langle k_i |l_n\rangle b_n \\ &= \sum_{mn} b_m^\dagger b_n \sum_i \langle l_m |k_i\rangle k_i \langle k_i |l_n\rangle \\ &= \sum_{mn} b_m^\dagger b_n \langle l_m | \left[K \sum_i |k_i\rangle \langle k_i| \right] |l_n\rangle \\ &= \sum_{mn} b_m^\dagger b_n \langle l_m | K |l_n\rangle \end{aligned}$$

- Where two-particle interactions between $|k_i\rangle$ and $|k_j\rangle$ are represented by the operator V_{ij} , many-particle interactions are represented by

$$\begin{aligned} V &= \frac{1}{2} \sum_{i \neq j} V_{ij} N_i N_j + \frac{1}{2} \sum_i V_{ii} N_i (N_i - 1) \\ &= \frac{1}{2} \sum_{ij} V_{ij} (N_i N_j - N_i \delta_{ij}) \\ &= \frac{1}{2} \sum_{mnpq} \langle mn | V | pq \rangle b_m^\dagger b_n^\dagger b_q b_p \end{aligned}$$

- Hence, finally relabelling $b \rightarrow c$ to convert from Sakurai's notation gives

$$\hat{H} = \sum_{i,j} \langle \psi_i | h | \psi_j \rangle c_i^\dagger c_j + \frac{1}{2} \sum_{i,j,k,l} \langle \psi_i |_1 \langle \psi_j |_2 | g | \psi_k \rangle_2 | \psi_l \rangle_1 c_i^\dagger c_j^\dagger c_l c_k$$

Jellium in Second Quantisation

- Using the Jellium Hamiltonian of the form

$$\begin{aligned} \hat{H} &= \sum_{i=1}^N \frac{\hat{p}_i^2}{2m^*} + \frac{1}{2} \sum_{\substack{i,j=1 \\ i \neq j}}^N \frac{e^2}{4\pi\epsilon_0} e^{-\mu|\vec{r}_i - \vec{r}_j|} \frac{1}{|\vec{r}_i - \vec{r}_j|} + \hat{H}_{\text{e-ion}} + \hat{H}_{\text{ion-ion}} \\ \hat{H}_{\text{ion-ion}} &= \frac{1}{2} \frac{e^2}{4\pi\epsilon_0} \int d^3 r \int d^3 r' e^{-\mu|\vec{r} - \vec{r}'|} \frac{n(\vec{r})n(\vec{r}')}{|\vec{r} - \vec{r}'|} \\ \text{where } \hat{H}_{\text{e-ion}} &= -\frac{e^2}{4\pi\epsilon_0} \sum_{i=1}^N \int d^3 r n(\vec{r}) e^{-\mu|\vec{r} - \vec{r}_i|} \frac{1}{|\vec{r} - \vec{r}_i|}. \end{aligned}$$

- Here, m^* is the band effective mass, and the exponential factors have been introduced with the intention to later take the limit $\mu \rightarrow 0$, so that $e^{-\mu|\vec{r} - \vec{r}_i|} \rightarrow 1$.

- The single-particle term

$$\hat{H}_s = \sum_{\vec{k}_1, \lambda_1} \sum_{\vec{k}_2, \lambda_2} \langle \psi_{\vec{k}_1, \lambda_1} | \hat{h} | \psi_{\vec{k}_2, \lambda_2} \rangle c_{\vec{k}_1, \lambda_1}^\dagger c_{\vec{k}_2, \lambda_2}$$

where $\hat{h} = \frac{\hbar^2}{2m^*} \nabla^2$ and $\psi_{\vec{k}, \lambda} = \frac{1}{\sqrt{V}} e^{i\vec{k} \cdot \vec{r}} \chi_\lambda$

o Hence,

$$\begin{aligned} \left\langle \vec{k}_1, \lambda_1 \left| \frac{\hbar^2}{2m^*} \nabla^2 \right| \vec{k}_2, \lambda_2 \right\rangle &= \int d^3 \vec{r} \frac{1}{\sqrt{V}} e^{-i\vec{k}_1 \cdot \vec{r}} \chi_{\lambda_1}^\dagger \frac{\hbar^2}{2m^*} \nabla^2 \frac{1}{\sqrt{V}} e^{i\vec{k}_2 \cdot \vec{r}} \chi_{\lambda_2} \\ &= \frac{1}{V} \int d^3 \vec{r} e^{i(\vec{k}_2 - \vec{k}_1) \cdot \vec{r}} \frac{\hbar^2 |\vec{k}_2|^2}{2m^*} \delta_{\lambda_1, \lambda_2} \\ &= \delta_{\vec{k}_1, \vec{k}_2} \frac{\hbar^2 |\vec{k}_2|^2}{2m^*} \delta_{\lambda_1, \lambda_2} \end{aligned}$$

o Therefore,

$$\hat{H}_s = \sum_{\vec{k}, \lambda} \frac{\hbar^2 k^2}{2m^*} c_{\vec{k}, \lambda}^\dagger c_{\vec{k}, \lambda}$$

- For the background term $H_{\text{ion-ion}}$, noting that for Jellium $n(\vec{r}) = N/V$ is a const;

$$\begin{aligned} \hat{H}_{\text{ion-ion}} &= \frac{1}{2} \frac{e^2}{4\pi\epsilon_0} \frac{N^2}{V^2} \int d\vec{r} \int d\vec{r}' \frac{e^{-\mu|\vec{r}-\vec{r}'|}}{|\vec{r}-\vec{r}'|} \quad \text{let } \vec{z} = \vec{r}' - \vec{r} \\ &= \frac{1}{2} \frac{e^2}{4\pi\epsilon_0} \frac{N^2}{V^2} V \int dz \frac{e^{-\mu z}}{z} \\ &= \frac{1}{2} \frac{e^2}{4\pi\epsilon_0} \frac{N^2}{V} \frac{4\pi}{\mu^2} \end{aligned}$$

- For the electron background term $\hat{H}_{\text{e-ion}}$, using the same assumption,

$$\begin{aligned} \hat{H}_{\text{e-ion}} &= -\frac{e^2}{4\pi\epsilon_0} \frac{N}{V} \sum_{i=1}^N \int d\vec{r} e^{-\mu|\vec{r}-\vec{r}_i|} \frac{1}{|\vec{r}-\vec{r}_i|} \\ &= -\frac{e^2}{4\pi\epsilon_0} \frac{N}{V} \sum_{i=1}^N \int dz \frac{e^{-\mu z}}{z} \\ &= -\frac{e^2}{4\pi\epsilon_0} \frac{N^2}{V} \frac{4\pi}{\mu^2} \end{aligned}$$

- Considering the Coulomb interaction term, where the electrons 1 and 2 are denoted (1) and (2). Also where $\vec{x} = \vec{r}_2$, $\vec{y} = \vec{r}_1 - \vec{r}_2$ and hence $\vec{r}_1 = \vec{x} + \vec{y}$,

$$\begin{aligned} \left\langle \vec{k}_1, \lambda_1 \left| \left\langle \vec{k}_2, \lambda_2 \left| g \right| \vec{k}_3, \lambda_3 \right\rangle \right| \vec{k}_4, \lambda_4 \right\rangle_2 &= \frac{1}{2} \frac{e^2}{4\pi\epsilon_0} \int d^3 \vec{r}_1 \int d^3 \vec{r}_2 \frac{1}{\sqrt{V}} e^{-i\vec{k}_1 \cdot \vec{r}_1} \chi_{\lambda_1}^\dagger(1) \frac{1}{\sqrt{V}} e^{-i\vec{k}_2 \cdot \vec{r}_2} \chi_{\lambda_2}^\dagger(2) \\ &\times e^{-\mu|\vec{r}_1 - \vec{r}_2|} \frac{1}{|\vec{r}_1 - \vec{r}_2|} \frac{1}{\sqrt{V}} e^{i\vec{k}_3 \cdot \vec{r}_1} \chi_{\lambda_3}(1) \frac{1}{\sqrt{V}} e^{i\vec{k}_4 \cdot \vec{r}_2} \chi_{\lambda_4}(2) \\ &= \frac{1}{2} \frac{e^2}{4\pi\epsilon_0} \frac{1}{V^2} \int d\vec{x} \int d\vec{y} e^{-i\vec{k}_1 \cdot \vec{x}} e^{-i\vec{k}_2 \cdot (\vec{x} + \vec{y})} \frac{e^{-\mu y}}{y} e^{i\vec{k}_3 \cdot (\vec{x} + \vec{y})} e^{i\vec{k}_4 \cdot \vec{x}} \delta_{\lambda_1, \lambda_3} \delta_{\lambda_2, \lambda_4}, \\ &= \frac{1}{2} \frac{e^2}{4\pi\epsilon_0} \frac{1}{V^2} \int d\vec{x} e^{-i(\vec{k}_1 + \vec{k}_2 - \vec{k}_3 - \vec{k}_4) \cdot \vec{x}} \int d\vec{y} \frac{e^{i(\vec{k}_3 - \vec{k}_1) \cdot \vec{y}} e^{-\mu y}}{y} \delta_{\lambda_1, \lambda_3} \delta_{\lambda_2, \lambda_4}, \\ &= \frac{1}{2} \frac{e^2}{4\pi\epsilon_0} \frac{1}{V^2} V \delta_{\vec{k}_1 + \vec{k}_2, \vec{k}_3 + \vec{k}_4} \frac{4\pi}{|\vec{k}_3 - \vec{k}_1|^2 + \mu^2} \delta_{\lambda_1, \lambda_3} \delta_{\lambda_2, \lambda_4}. \end{aligned}$$

- Then defining $\vec{k}_1 = \vec{k} + \vec{q}$, $\vec{k}_2 = \vec{p} - \vec{q}$, $\vec{k}_3 = \vec{k}$ and $\vec{k}_4 = \vec{p}$, such that $\vec{k}_1 + \vec{k}_2 = \vec{k}_3 + \vec{k}_4 = \vec{k} + \vec{p}$ and using the properties of the number states used to derive the Coulomb term, as well as the identity

$$c_{\vec{k}, \lambda_1}^\dagger c_{\vec{p}, \lambda_2}^\dagger \delta_{\vec{k}, \vec{p}} \delta_{\lambda_1, \lambda_2} = c_{\vec{k}, \lambda_1}^\dagger c_{\vec{k}, \lambda_1} c_{\vec{p}, \lambda_2}^\dagger \delta_{\lambda_1, \lambda_2}$$

$$\begin{aligned} \hat{H}_{\text{el-el}} &= \frac{1}{2} \sum_{i,j,k,l} \langle \psi_i | \langle \psi_j | g | \psi_k \rangle_2 | \psi_l \rangle_2 c_i^\dagger c_j^\dagger c_k c_l \\ &= \frac{1}{2} \frac{e^2}{4\pi\epsilon_0} \frac{1}{V} \sum_{\substack{i,j,q \\ q \neq 0}} \sum_{\substack{\lambda_1, \lambda_2 \\ \lambda_1 + \lambda_2 = q}} \frac{4\pi}{q^2 + \mu^2} c_{\vec{k}+q, \lambda_1}^\dagger c_{\vec{p}-q, \lambda_2}^\dagger c_{\vec{p}, \lambda_2} c_{\vec{k}, \lambda_1} + \frac{1}{2} \frac{e^2}{4\pi\epsilon_0} \frac{1}{V} \frac{4\pi}{\mu^2} (N^2 - N). \end{aligned}$$

- Finally, collecting all terms together and taking the limit $V \rightarrow \infty$ (hence also $N \rightarrow \infty$) followed by $\mu \rightarrow 0$, keeping $\mu^{-1} \ll V^{1/3}$ gives the form the Jellium hamiltonian in second quantisaiton:

$$\hat{H} = \sum_{\vec{k}, \lambda} \frac{\hbar^2 |\vec{k}|^2}{2m^*} c_{\vec{k}, \lambda}^\dagger c_{\vec{k}, \lambda} + \frac{1}{2} \frac{e^2}{4\pi\epsilon_0} \frac{1}{V} \sum_{\substack{i,j,k \\ i+j=k}} \sum_{\substack{\lambda_1, \lambda_2 \\ \lambda_1 + \lambda_2 = q}} \frac{4\pi}{q^2} c_{\vec{k}+q, \lambda_1}^\dagger c_{\vec{p}-q, \lambda_2}^\dagger c_{\vec{p}, \lambda_2} c_{\vec{k}, \lambda_1}$$

Hartree-Fock in Second Quantisation

- A similar method can be used with the Hartree-Fock Hamiltonian (see slide 29 of lecture 6 for derivation), giving

$$\hat{H} = \sum_{i,j} \left(\langle \psi_i | h | \psi_j \rangle + \sum_{m=1}^N \langle \psi_i | \langle \psi_m | g | \psi_m \rangle_2 | \psi_j \rangle_1 - \sum_{m=1}^N \langle \psi_i | \langle \psi_m | g | \psi_j \rangle_2 | \psi_m \rangle_1 \right) c_i^\dagger c_j.$$

- The Hartree-Fock approximation may also be derived in second quantisation using the mean field approximation (Wick's theorem);

$$\begin{aligned} c_i^\dagger c_j^\dagger c_k c_l &= \langle c_i^\dagger c_i \rangle \langle c_j^\dagger c_k \rangle - \langle c_i^\dagger c_k \rangle \langle c_j^\dagger c_l \rangle + c_i^\dagger c_l \langle c_j^\dagger c_k \rangle - \langle c_i^\dagger c_l \rangle \langle c_j^\dagger c_k \rangle \\ &- \langle c_i^\dagger c_k \rangle c_j^\dagger c_l + \langle c_j^\dagger c_k \rangle c_i^\dagger c_l + \langle c_i^\dagger c_k \rangle \langle c_j^\dagger c_l \rangle. \end{aligned}$$

L7 AQCMP - Magnetism Fundamentals

L6 AQCMP - Quasiparticles

Hubbard Model
 Hubbard Model with two Electrons on Two Sites
 Heisenberg Model
 Heitler-London Model
 The Origin of Magnetic Exchange Interactions
 Ferromagnetic Ordering in Mean Field Theory
 Elementary Excitations of Ferromagnets - Magnons

Hubbard Model

- Ferromagnetism and antiferromagnetism cannot be understood in the independent-electron approximation, as the spontaneous ordering involved is a result of collective ordering of all particles in a solid, so is intrinsically a many-body effect.
- Writing the single-particle Hamiltonian for a lattice of atoms in terms of fermionic creation and annihilation operators $c_\lambda^\dagger(\vec{R}_i)$ and $c_\lambda(\vec{R}_i)$ which add or remove a single electron of spin λ to a site \vec{R}_i :

$$\hat{H}_S = \sum_{i,\lambda} \epsilon_i n_\lambda(\vec{R}_i) = \sum_{i,\lambda} \epsilon_i c_\lambda^\dagger(\vec{R}_i) c_\lambda(\vec{R}_i)$$

- Allowing electrons to hop to other sites introduces a hopping energy term, where $t_{i,j}$ are integrals that depend on wavefunction overlap (second term is required to make this Hermitian);

$$\hat{H}_h = - \sum_{i \neq j, \lambda} t_{i,j} (c_\lambda^\dagger(\vec{R}_i) c_\lambda(\vec{R}_j) + c_\lambda^\dagger(\vec{R}_j) c_\lambda(\vec{R}_i))$$

- If both a spin up and spin down electron are at site \vec{R}_i , then there is an intra-site Coulomb interaction given by the Hubbard U:

$$U_n = \iint d^3\vec{r} d^3\vec{r}' \frac{\rho_n(\vec{r})\rho_n(\vec{r}')}{4\pi\epsilon_0|\vec{r}-\vec{r}'|}.$$

- This takes an approximate form in the Hamiltonian as;

$$\begin{aligned} \hat{H}_C &= U \sum_i n_\uparrow(\vec{R}_i) n_\downarrow(\vec{R}_i) \\ &= U \sum_i c_\uparrow^\dagger(\vec{R}_i) c_\uparrow(\vec{R}_i) c_\downarrow^\dagger(\vec{R}_i) c_\downarrow(\vec{R}_i) \end{aligned}$$

- Combining the above terms gives an approximate many-body Hamiltonian for the full system;

$$\hat{H} = \sum_{i,\lambda} \epsilon_i c_\lambda^\dagger(\vec{R}_i) c_\lambda(\vec{R}_i) - \sum_{< i,j >, \lambda} t_{i,j} (c_\lambda^\dagger(\vec{R}_i) c_\lambda(\vec{r}_j) + c_\lambda^\dagger(\vec{R}-j) c_\lambda(\vec{R}_i)) + U \sum_i n_\uparrow(\vec{R}_i) n_\downarrow(\vec{R}_i)$$

- In the case where $< i,j >$ denotes summing over nearest neighbours only, then this is the Hubbard Hamiltonian.

Hubbard Model with two Electrons on Two Sites

- Considering the single-particle Hamiltonian for a two-site system

$$\begin{aligned} \hat{H}_{LR} &= \frac{p^2}{2m^*} + V_L + V_R \\ \text{with } \hat{H}_{L/R} &= \frac{p^2}{2m^*} + V_{L/R} \end{aligned}$$

- We then wish to evaluate the many-body Hubbard Hamiltonian.

$$\hat{H} = \sum_{i,j} \langle \psi_i | h | \psi_j \rangle c_i^\dagger c_j$$

- To evaluate the off-diagonal elements;

$$\begin{aligned} \langle \psi_R | \hat{H}_{LR} | \psi_L \rangle &= \langle \psi_L | \hat{H}_{LR} | \psi_R \rangle, \\ &= \left\langle \psi_L \left| H_L + H_R - \frac{p^2}{2m^*} \right| \psi_R \right\rangle, \\ &= (\epsilon_L + \epsilon_R) \langle \psi_L | \psi_R \rangle - \left\langle \psi_L \left| \frac{p^2}{2m^*} \right| \psi_R \right\rangle, \\ &\approx - \left\langle \psi_L \left| \frac{p^2}{2m^*} \right| \psi_R \right\rangle = -t_{LR}. \end{aligned}$$

- To evaluate the diagonal elements,

$$\begin{aligned} \langle \psi_R | \hat{H}_{LR} | \psi_R \rangle &= \left\langle \psi_R \left| \frac{p^2}{2m^*} + V_L + V_R \right| \psi_R \right\rangle, \\ &= \epsilon_R + \langle \psi_R | V_L | \psi_R \rangle \\ &\approx \epsilon_R. \\ \langle \psi_L | \hat{H}_{LR} | \psi_L \rangle &\approx \epsilon_L. \end{aligned}$$

- Finally, setting $\epsilon_L = \epsilon_R = \epsilon$, the two-particle Hubbard Hamiltonian is

$$\hat{H} = \sum_{\lambda=\uparrow,\downarrow} \left[\epsilon (c_{L,\lambda}^\dagger c_{L,\lambda} + c_{R,\lambda}^\dagger c_{R,\lambda}) - t_{LR} (c_{L,\lambda}^\dagger c_{R,\lambda} + c_{R,\lambda}^\dagger c_{L,\lambda}) \right] + U n_{L,\uparrow} n_{L,\downarrow} + U n_{R,\uparrow} n_{R,\downarrow},$$

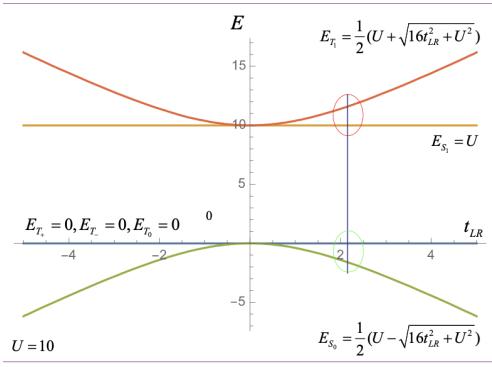
- It is then sensible to convert to a number basis using single-particle states such that the complete set of basis states $|n_{L,\uparrow}, n_{L,\downarrow}, n_{R,\uparrow}, n_{R,\downarrow}\rangle$ is;

$$\begin{aligned} |\uparrow, \uparrow\rangle &= c_{L,\uparrow}^\dagger c_{R,\uparrow}^\dagger |0,0,0,0\rangle = |1,0,1,0\rangle, \\ |\uparrow, \downarrow\rangle &= c_{L,\uparrow}^\dagger c_{R,\downarrow}^\dagger |0,0,0,0\rangle = |1,0,0,1\rangle, \\ |\downarrow, \uparrow\rangle &= c_{L,\downarrow}^\dagger c_{R,\uparrow}^\dagger |0,0,0,0\rangle = |0,1,1,0\rangle, \\ |\downarrow, \downarrow\rangle &= c_{L,\downarrow}^\dagger c_{R,\downarrow}^\dagger |0,0,0,0\rangle = |0,1,0,1\rangle, \\ |\uparrow\downarrow, 0\rangle &= c_{L,\uparrow}^\dagger c_{L,\downarrow}^\dagger |0,0,0,0\rangle = |1,1,0,0\rangle, \\ |0, \uparrow\downarrow\rangle &= c_{R,\uparrow}^\dagger c_{R,\downarrow}^\dagger |0,0,0,0\rangle = |0,0,1,1\rangle. \end{aligned}$$

- Now setting $\epsilon = 0$ for convenience and evaluating the inner products to find the matrix representation of the hamiltonian, we find

$$\hat{H} = \begin{pmatrix} 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & -t_{LR} & -t_{LR} \\ 0 & 0 & 0 & 0 & t_{LR} & t_{LR} \\ 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & -t_{LR} & t_{LR} & 0 & U & 0 \\ 0 & -t_{LR} & t_{LR} & 0 & 0 & U \end{pmatrix}.$$

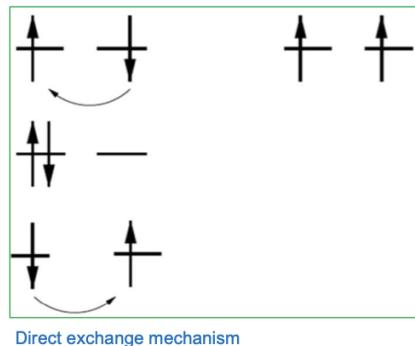
- Finding the eigenvectors and eigenvalues, we see that there are four low-energy states $|v_{T_+}\rangle$, $|v_{T_0}\rangle$, $|v_{T_-}\rangle$ and $|v_{S_0}\rangle$, as well as two higher energy states $|v_{S_1}\rangle$ and $|v_{T_1}\rangle$.



- Solutions to the time-dependent Schrödinger equation therefore have the form

$$|\psi\rangle = Ae^{-iE_{T_+}t/\hbar}|v_{T_+}\rangle + Be^{-iE_{T_-}t/\hbar}|v_{T_-}\rangle + Ce^{-iE_{T_0}t/\hbar}|v_{T_0}\rangle + De^{-iE_{S_0}t/\hbar}|v_{S_0}\rangle + Ee^{-iE_{S_1}t/\hbar}|v_{S_1}\rangle + Fe^{-iE_{T_1}t/\hbar}|v_{T_1}\rangle.$$

- A system initially in state $|\downarrow, \uparrow\rangle$, is therefore seen to oscillate between $|\downarrow, \uparrow\rangle$ and $|\uparrow, \downarrow\rangle$ via the doubly occupied states $|\uparrow\downarrow, 0\rangle$ and $|0, \uparrow\downarrow\rangle$.
 - This is the direct exchange mechanism.
- Triplet states $|\uparrow, \uparrow\rangle$ and $|\downarrow, \downarrow\rangle$ are eigenstates, so do not change. Both of these mechanisms are depicted in the figure below.



Heisenberg Model

- In the limit where $U \gg t$, the eigenvalues and eigenstates reduce to the form:

Eigenvalue	Eigenstate	
0	$ \uparrow, \uparrow\rangle$	T_+
0	$\frac{1}{\sqrt{2}}(\uparrow, \downarrow\rangle + \downarrow, \uparrow\rangle)$	
0	$ \downarrow, \downarrow\rangle$	
$-4\frac{t_{LR}^2}{U}$	$\frac{1}{\sqrt{2}}(\uparrow, \downarrow\rangle - \downarrow, \uparrow\rangle)$	$S_b \}$ Singlet
U	$\frac{1}{\sqrt{2}}(\uparrow\downarrow, 0\rangle + 0, \uparrow\downarrow\rangle)$	
U	$\frac{1}{\sqrt{2}}(\uparrow\downarrow, 0\rangle - 0, \uparrow\downarrow\rangle)$	$T_i \}$ Double occupation

- In this limit, the two states with energy U may be neglected if the system is close to its ground state.
- Hence, we are left with the typical triplet states and the singlet state with an exchange energy, $J \approx -4\frac{t_{LR}}{U}$.
- Note that J is negative, making the Singlet state the ground state.

- Constructing an approximate matrix of eigenvectors (S) and eigenvalues (D)

$$S = \begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & \frac{1}{\sqrt{2}} & 0 & \frac{1}{\sqrt{2}} \\ 0 & \frac{1}{\sqrt{2}} & 0 & -\frac{1}{\sqrt{2}} \\ 0 & 0 & 1 & 0 \end{pmatrix}, \quad D = \begin{pmatrix} 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & -\frac{4t_{LR}^2}{U} \end{pmatrix}$$

- Hence, $\hat{H}_A S = SD$, such that, where $\hat{S}^{(i)} = \frac{1}{2}(\hat{\sigma}_x^{(i)}, \hat{\sigma}_y^{(i)}, \hat{\sigma}_z^{(i)})$ are vectors of Pauli matrices and i denotes the particle number and J is the exchange energy,

$$\begin{aligned} \hat{H}_A &= SDS^{-1} \\ &= SDS^\dagger \\ &= \frac{t_{LR}^2}{U} \begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & -1 & 2 & 0 \\ 0 & 2 & -1 & 0 \\ 0 & 0 & 0 & 1 \end{pmatrix} - \frac{t_{LR}^2}{U} \begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 1 \end{pmatrix} \\ &= \frac{4t_{LR}^2}{U} \left(\hat{S}_L^{(1)} \cdot \hat{S}_R^{(2)} - \frac{1}{4} \right) \\ &= -JS_L^{(1)} \cdot \hat{S}_R^{(2)} + \text{const} \end{aligned}$$

◦ \hat{H}_A is the Heisenberg Hamiltonian, and adaptations of it allow for quantifying all magnetic phenomena.

- To properly deal with systems with localised spin we need to consider the half-filled Hubbard model for an arbitrary number of sites in 3D. This can be done using the t-J model:

$$\hat{H} = -t \sum_{\langle i,j \rangle, \lambda} (c_{i,\lambda}^\dagger c_{j,\lambda} + c_{j,\lambda}^\dagger c_{i,\lambda}) - J \sum_{\langle i,j \rangle} \left(\hat{S}_i \cdot \hat{S}_j - \frac{n_i n_j}{4} \right)$$

- By considering both intra and inter (see next section) - site Coulomb interactions J may be either positive or negative.
- With $J > 0$, the ground-state is ferromagnetic, whereas if $J < 0$, it is antiferromagnetic.

Heitler-London Model

- The key parameter determining the sign of J is the overlap between adjacent site orbitals,

$$I = \int d\vec{r} \psi_L^*(\vec{r}) \psi_R(\vec{r})$$

- With $|I| \geq 0$, the spatial wavefunctions for the singlet (S) and triplet (T) states are

$$\psi_{S,T}(r_1, r_2) = \frac{1}{\sqrt{2(1 \pm |t|)}} (\psi_L(r_1)\psi_R(r_2) \pm \psi_L(r_2)\psi_R(r_1))$$

- Hence, the two-particle Hamiltonian, \hat{H} ,

$$\hat{H} = \sum_{i=1,2} \left(\frac{\hat{p}_i^2}{2m} + V_L(\vec{r}_i) + V_R(\vec{r}_i) \right) + \frac{e^2}{4\pi\epsilon_0 |\vec{r}_1 - \vec{r}_2|} = \hat{h}(\vec{r}_1) + \hat{h}(\vec{r}_2) + g(\vec{r}_1, \vec{r}_2)$$

- Has singlet and triplet energies

$$E_{S,T} = \int d\vec{r}_1 d\vec{r}_2 \psi_{S,T}^*(\vec{r}_1, \vec{r}_2) \hat{H} \psi_{S,T}(\vec{r}_1, \vec{r}_2)$$

- Performing the calculations, we find that $J = E_S - E_T$ is;

$$J = \frac{2}{(1-I^2)} (U_E - 2It - I^2 (U_H - (\epsilon_L + \epsilon_R) + \Delta\epsilon_L + \Delta\epsilon_R))$$

$$\text{where } \Delta\epsilon_L = \int d\vec{r} \psi_L^*(\vec{r}) V_R(\vec{r}) \psi_L(\vec{r}), \quad \Delta\epsilon_R = \int d\vec{r} \psi_R^*(\vec{r}) V_L(\vec{r}) \psi_R(\vec{r})$$

- As their integrands involve $\frac{1}{|\vec{r}_1 - \vec{r}_2|}$, U_H and U_E are the largest energies, and $U_H > U_E$ from the Cauchy-Schwarz inequality.

- We also have that $\epsilon_1 + \epsilon_2 > t \gg \delta\epsilon_1 + \delta\epsilon_2$ where $\psi_L(r)$ and $\psi_R(r)$ can be used as a sufficiently complete single-particle basis.
- Hence, typically, $U_H \gg U_E > \epsilon_L + \epsilon_R > t \gg \Delta\epsilon_L + \Delta\epsilon_R$.

- As I increases from 0 to 1, the ground state will change from the triplet state to the ground state.

- With $I \rightarrow 0$, the triplet state is the ground state and $J = E_S - E_T \approx 2U_\epsilon > 0$
- With $I \rightarrow 1$, the singlet state is the ground state and $J = E_S - E_T \approx \frac{2}{(1-I^2)} (U_E - U_H) < 0$.

The Origin of Magnetic Exchange Interactions

- Atomic exchange: For two electrons in different orbitals which are nearly orthogonal, exchange energy J is positive, so the triplet state is the ground state.
 - Hence, a ferromagnetic alignment requires $J > 0$. here, the triplet spatial state keeps the two electrons separate, minimising Coulomb repulsion.
- Molecular exchange: When two electrons occupy two different orbitals which overlap, J can be negative, giving a lower energy singlet state than triplet state.
 - Antiferromagnetic alignment therefore requires $J < 0$, which may occur by forming lower energy, delocalised molecular orbitals.

Ferromagnetic Ordering in Mean Field Theory

- In the presence of an external magnetic field, B , the Heisenberg Hamiltonian takes the form

$$\hat{H} = -J \sum_{<i,j>} \hat{S}_i \cdot \hat{S}_j - g\mu_B \sum_i \hat{S}_i \cdot \vec{B}$$

- The mean field theory approximation is to treat each spin as if it is subject to an effective molecular field \vec{B}_{mf} generated by the other spins; where $\langle \hat{S}_j \rangle$ is the expectation value of \hat{S}_j ,

$$-J \sum_{<i,j>} \hat{S}_i \cdot \langle \hat{S}_j \rangle = -g\mu_B \sum_i \hat{S}_i \cdot \vec{B}_{mf}$$

- Hence, the Hamiltonian may be rewritten as (implicitly assume spin up to be majority spin);

$$\begin{aligned} \hat{H}_{mf} &= -g\mu_B \sum_i \hat{S}_i \cdot (\vec{B} + \vec{B}_{mf}) \\ &= -g\mu_B \sum_i \hat{S}_i \cdot \vec{B}_{eff} \end{aligned}$$

- If there are ν nearest neighbours, then the effective molecular field is given by

$$\vec{B}_{mf} = \frac{1}{g\mu_B J} \sum_{<j>} \langle \hat{S}_j \rangle \approx \frac{1}{g\mu_B} J \nu \langle \hat{S}_j \rangle$$

- We also assume that \vec{B}_{mf} is proportional to the magnetisation, $\vec{B}_{mf} = \lambda \vec{M}$.

- Using the partition function, assuming the effective magnetic field is aligned with z , the microstate energies are

$$E_{S_i} = -g\mu_B S_i B_{eff}$$

- The partition function is therefore

$$Z = \sum_{S_z=-S}^S \exp \left(-\frac{E_{S_z}}{k_B T} \right)$$

- The magnetisation can then be found via (see Thermo)

$$\begin{aligned} M &= -\frac{1}{V} \left. \frac{\partial F}{\partial B_{eff}} \right|_{T,V} \\ &= nk_B T \left. \frac{\partial \ln Z}{\partial B_{eff}} \right|_{T,V}, \\ &= nk_B T \frac{\sum_{S_z=-S}^S \frac{g\mu_B}{k_B T} S_z \exp \left(-\frac{g\mu_B}{k_B T} S_z B_{eff} \right)}{\sum_{S_z=-S}^S \exp \left(-\frac{g\mu_B}{k_B T} S_z B_{eff} \right)}. \end{aligned}$$

- Eventually it is found that

$$\begin{aligned} M &= M_s B_s(y) \\ y &= \frac{g\mu_B S(B + \lambda M)}{k_B T} \\ \text{where } B_s(y) &= \frac{2S+1}{2S} \coth \left(\frac{2S+1}{2S} y \right) - \frac{1}{2S} \coth \frac{y}{2S} \end{aligned}$$

- In the case where $B = 0$, the solutions to the above equations are shown to the right.

- Where $T > T_C$, there is no simultaneous solutions with $\vec{M} > 0$.

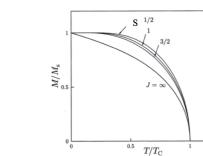
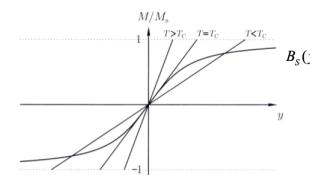


Fig: Spontaneous magnetization curve in a ferromagnet.

- By equating the gradients of both lines for small y , it can then be shown that

$$T_c = \frac{g\mu_B (S+1)\lambda M_s}{3k_B} \quad \text{where } M_s = ng\mu_B S$$

- The phase transition at T_c is second order, as the magnetisation is continuous, but its gradient is not - hence there is discontinuity in the second derivative of free energy.

- Noting that for small y , $\coth(y) \approx \frac{1}{y} + \frac{1}{3}y - \frac{1}{45}y^2$, for $B > 0$ and $y \ll 1$, we get

$$\begin{aligned}\frac{M}{M_s} &\approx \frac{S+1}{3S}y \\ &= \frac{(S+1)g\mu_B S(B+\lambda M)}{3Sk_B T} \\ &= \frac{T_c(B+\lambda M)}{\lambda M_s T}\end{aligned}$$

- Rearranging gives

$$M = \frac{1}{\lambda} \frac{T_c}{T-T_c} B \quad \text{alternatively written} \quad \frac{M}{M_s} \left(1 - \frac{T_c}{T}\right) = \frac{T_c B}{\lambda M_s T}$$

- From here, defining magnetic susceptibility χ of a ferromagnet in the paramagnetic region above the Curie point as $\chi = \lim_{B \rightarrow 0} \frac{\mu_0 M}{B}$, we derive the Curie-Weiss law:

$$\chi = \frac{\mu_0}{\lambda} \frac{T_c}{T-T_c}$$

- Finally, using that $(B_{mf})_{max} = \frac{1}{g\mu_B} J \nu S$, $M_s = g\mu_B n S$ and $(B_{mf})_{max} = \lambda M$ gives

$$\lambda = \frac{\nu J}{n(g\mu_B)^2} \quad \text{and} \quad T_c = \frac{S(S+1)\nu J}{3k_B}$$

- For very large λ values, T_c becomes very large ($> 1000 K$).

- It is possible to measure magnetic ordering using Neutron scattering, as the thermal neutrons from a nuclear reactor have de-Broglie wavelengths similar to atomic spacings.
 - The magnetic measurements are made possible by the fact that the neutrons are neutral **spin 1/2** particles.
 - Therefore, coupling of the magnetic moment of the atoms to the neutrons produces new peaks in the neutron diffraction pattern after magnetic ordering. An example is MnO.

Elementary Excitations of Ferromagnets - Magnons

- As the ferromagnetic ground state breaks the continuous global rotation symmetry of the Heisenberg Hamiltonian, we expect low-energy collective excitations without a gap in their energy spectrum at small wavevectors which reduce the magnetisation of the system from the remanent magnetisation. These are spin waves or magnons.
- Consider a one-dimensional chain of Heisenberg spins with only nearest neighbours interactions,

$$\begin{aligned}\hat{H} &= -2J \sum_i \hat{S}_i \cdot \hat{S}_{i+1}, \\ &= -2J \sum_i (S_i^z S_{i+1}^z + S_i^x S_{i+1}^x + S_i^y S_{i+1}^y), \\ &= -2J \sum_i \left(S_i^z S_{i+1}^z + \frac{1}{2} (S_i^+ S_{i+1}^- + S_i^- S_{i+1}^+) \right).\end{aligned}$$

- We may construct eigenstates of this by delocalising a flipped spin over all sites, such that relative to the $T=0$ ground state, Φ in which all spins are aligned, the wavefunction of a magnon with wavevector \vec{q} is;

$$|\vec{q}\rangle = \frac{1}{\sqrt{N}} \sum_j e^{i\vec{q} \cdot \vec{R}_j} |j\rangle \quad \text{where} \quad |j\rangle = S_j^- |\Phi\rangle$$

- Substituting this into the Schrödinger equation gives

$$\begin{aligned}\hat{H} |\vec{q}\rangle &= -2J \sum_i \left(S_i^z S_{i+1}^z + \frac{1}{2} (S_i^+ S_{i+1}^- + S_i^- S_{i+1}^+) \right) \frac{1}{\sqrt{N}} \sum_j e^{i\vec{q} \cdot \vec{R}_j} |j\rangle, \\ &= \frac{1}{\sqrt{N}} \sum_j e^{i\vec{q} \cdot \vec{R}_j} \left(-2J \left(\frac{N}{4} - 1 \right) |j\rangle - J |j+1\rangle - J |j-1\rangle \right), \\ &= -2J \left(\frac{N}{4} - 1 \right) |\vec{q}\rangle - J e^{-i\vec{q} \cdot \vec{a}} \frac{1}{\sqrt{N}} \sum_j e^{i\vec{q} \cdot (\vec{R}_j + \vec{a})} |j+1\rangle - J e^{i\vec{q} \cdot \vec{a}} \frac{1}{\sqrt{N}} \sum_j e^{i\vec{q} \cdot (\vec{R}_j - \vec{a})} |j-1\rangle, \\ &= -2J \left(\frac{N}{4} - 1 \right) |\vec{q}\rangle - J e^{-i\vec{q} \cdot \vec{a}} |\vec{q}\rangle - J e^{i\vec{q} \cdot \vec{a}} |\vec{q}\rangle, \\ &= -2J \left(\left(\frac{N}{4} - 1 \right) + \cos \vec{q} \cdot \vec{a} \right) |\vec{q}\rangle.\end{aligned}$$

- Hence, the energy of these states is

$$\begin{aligned}E(\vec{q}) &= -2J \left(\left(\frac{N}{4} - 1 \right) + \cos \vec{q} \cdot \vec{a} \right), \\ &= -2J \left(\frac{N}{4} - (1 - \cos \vec{q} \cdot \vec{a}) \right), \\ &= E_0 + 2J(1 - \cos \vec{q} \cdot \vec{a}).\end{aligned}$$

- For small \vec{q} , these excitations therefore have arbitrarily small energy at sufficiently long wavelengths, as Goldstone bosons should have. Hence, we get $E(\vec{q}) \approx 2J \frac{\vec{q} \cdot \vec{q}'}{2} \propto q^2$.

- It can also be seen from this analysis that magnons are bosons with spin 1, as they lower the total spin of the system by 1 from the ground state.

- Extending this calculation to 3D it is seen that

$$E(\vec{q}) = \hbar\omega = SJz(1 - \gamma(\vec{q})) \quad \text{where} \quad \gamma(\vec{q}) = \frac{1}{z} \sum_{i \in \vec{t}_i} e^{-i\vec{q} \cdot \vec{t}_i}$$

- This again gives that for small q , $\omega \propto q^2$.

- We may therefore calculate the density of state of magnons;

$$\begin{aligned}g(\omega)d\omega &\propto 4\pi q^2 dq = 4\pi q^2 \frac{dq}{d\omega} d\omega \\ &\propto \omega^{1/2} d\omega\end{aligned}$$

- Using Bose statistics, we then find that

$$\begin{aligned}n_{magnon} &= \int_0^\infty \frac{g(\omega)d\omega}{\exp(\hbar\omega/k_B T) - 1} \\ &= \left(\frac{k_B T}{\hbar} \right)^{3/2} \int_0^\infty \frac{\sqrt{x}}{e^x - 1} dx \\ &\propto T^{3/2}\end{aligned}$$

- As each magnon reduces spin by 1, the magnetisation at low temperature therefore follows (where a is a material-dependent constant),

$$M(T) = (1 - aT^{3/2})M(0)$$

- Similarly, the total energy due to magnons may be calculated

$$E_{magnon} = \int_0^\infty \frac{\hbar\omega g(\omega)d\omega}{\exp(\hbar\omega/k_B T) - 1} \propto T^{5/2}$$

- Hence, the heat capacity, $C_V \propto T^{3/2}$.

- In 1D and 2D, the number of magnons in the Heisenberg model diverges, implying that at any finite temperature, magnetisation is reduced to zero by excited magnons.
- Therefore, the isotropic Heisenberg model in 1D and 2D does not exhibit magnetic order at finite temperatures - the Mermin-Wagner-Berezinskii theorem.
- This is a result of the continuous symmetry in the isotropic ferromagnet; the same idea in Goldstone excitations. Therefore, this theorem does not apply in anisotropic systems
- Anisotropy can arise from spin-orbit coupling, producing an easy axis of magnetisation, or from shape anisotropy where magnetisation prefers to lie in the plane of a film parallel to an interface.

L8 AQCMP - Magnetism: Exchange Effects

[L7 AQCMP - Magnetism Fundamentals](#)

Magnetic Interactions
 Superexchange
 Itinerant Ferromagnetism
 RKKY Exchange Interaction
 Magnetoresistance
 Giant Magnetoresistance (GMR)
 Double Exchange
 Colossal Magnetoresistance
 Kondo Effect: Resonant Spin Scattering

[L9 AQCMP - Weak Electron-Photon Interactions](#)

Magnetic Interactions

- Direct magnetostatic coupling energy is only of order a few K, so cannot explain ferromagnetism which may persist above 1000K, however do play a role in establishing domain structure.
- Direct exchange is only important where there is a sufficient degree of wavefunction overlap between neighbouring magnetic ions.
 - This effect is negligible in many magnetic materials, as 4f and 3d orbitals do not extend far enough from the nucleus to give significant exchange coupling.
 - In these cases, indirect exchange is responsible for the magnetic behaviour.
 - Superexchange, itinerant ferromagnetism, the RKKY interaction and double exchange are all examples of this.

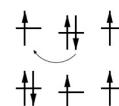
Superexchange

- Consider the interaction between the two singly-occupied spin-degenerate d-orbitals of two Mn^{2+} ions separated by an O^{2-} ion with a doubly occupied p-orbital.
- The superexchange Hamiltonian is an adaptation of the Hubbard model with 4 electrons in 6 single-particle states;

$$\hat{H}_{s-exc} = \epsilon_d \sum_{i=1,2} \sum_{\lambda=\uparrow,\downarrow} n_{i,\lambda} + \epsilon_p \sum_{\lambda=\uparrow,\downarrow} n_{p,\lambda} - t_{pd} \sum_{i=1,2} \sum_{\lambda=\uparrow,\downarrow} (c_{i,\lambda}^\dagger c_{p,\lambda} + c_{p,\lambda}^\dagger c_{i,\lambda}) + U_d \sum_{i=1,2} n_{i,\uparrow} n_{i,\downarrow}$$

- Here, ϵ_d and ϵ_p denote the orbital single-particle energies, U_d is the on-site Coulomb interaction of the d-orbitals and $t_{p,d}$ are the hopping integrals between the p and d orbitals.
- Representing the hamiltonian using a six-single particle state basis $d_{1\uparrow}, d_{1\downarrow}, p_{\uparrow}, p_{\downarrow}, d_{2\uparrow}$ and $d_{2\downarrow}$ and noting that there are four electrons in the model gives ${}^6C_4 = 15$ number basis states. Fortunately, it is sufficient to consider only two cases; where the d-spins are parallel / when they are antiparallel.

- The three possible basis states where both d-spins are pointing up are



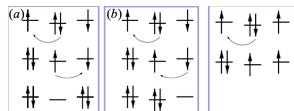
1. $c_{2\uparrow}^\dagger c_{p\uparrow}^\dagger c_{p\downarrow}^\dagger c_{1\uparrow}^\dagger |0\rangle$
2. $c_{2\uparrow}^\dagger c_{p\uparrow}^\dagger c_{1\downarrow}^\dagger c_{1\uparrow}^\dagger |0\rangle$
3. $c_{2\downarrow}^\dagger c_{2\uparrow}^\dagger c_{p\downarrow}^\dagger c_{1\uparrow}^\dagger |0\rangle$

- Here, one p-spin on the O^{2-} site can hop to one of the d-sites, but the other p-spin is then blocked from hopping to the other d-site by the Pauli principle. Hence, there is no coupling between the two

Mn^{2+} d-sites for the parallel spin case.

- Where the d-spins are anti-aligned, there are four possible basis states;

1. $c_{2\downarrow}^\dagger c_{2\uparrow}^\dagger c_{p\downarrow}^\dagger c_{p\uparrow}^\dagger |0\rangle$
2. $c_{2\downarrow}^\dagger c_{2\uparrow}^\dagger c_{p\downarrow}^\dagger c_{p\uparrow}^\dagger |0\rangle$
3. $c_{2\downarrow}^\dagger c_{2\uparrow}^\dagger c_{p\downarrow}^\dagger c_{p\uparrow}^\dagger |0\rangle$
4. $c_{2\downarrow}^\dagger c_{2\uparrow}^\dagger c_{1\downarrow}^\dagger c_{1\uparrow}^\dagger |0\rangle$



- Here, the effective exchange coupling between the two d-spins is known as superexchange. Through analogy with direct exchange, we represent it with an effective Heisenberg interaction;

$$\hat{H} = -J \vec{S}_1 \cdot \vec{S}_2$$

$$\text{where } J = -\frac{4t_{pd}^4}{(U_d + \Delta_{pd})^2} \left(\frac{1}{U_d + \Delta_{pd}} + \frac{1}{U_d} \right)$$

- Here the factor of t_{pd}^4 in J reflects the fact that four hopping processes are required for superexchange. The processes in (a) and (b) are responsible for the first and second terms in brackets respectively.

Itinerant Ferromagnetism

- This acts in transition metals with partially filled d-bands, such that the electrons are free to move and their interaction gives rise to itinerant band magnetism. Considering the Hubbard interaction,

$$\begin{aligned} \hat{H}_{\text{int}} &= U \sum_{i=1}^N c_{i,\uparrow}^\dagger c_{i,\uparrow} c_{i,\downarrow}^\dagger c_{i,\downarrow} \\ &= \frac{U}{2} \sum_{i=1}^N (c_{i,\uparrow}^\dagger c_{i,\uparrow} c_{i,\downarrow} c_{i,\downarrow} + c_{i,\downarrow}^\dagger c_{i,\uparrow} c_{i,\downarrow} c_{i,\uparrow}) \\ &= \frac{U}{2} \sum_{i=1}^N \sum_{\lambda,\lambda'} c_{i,\lambda}^\dagger c_{i,\lambda'}^\dagger c_{i,\lambda} c_{i,\lambda'} \end{aligned}$$

- Assuming these metals are homogenous and therefore writing the annihilation operators in Bloch form:

$$c_{i,\lambda} = \frac{1}{\sqrt{N}} \sum_{\vec{k}} e^{i\vec{k}\cdot\vec{R}_i} c_{\vec{k},\lambda}$$

- We can therefore rewrite, where we use in the last step that $\sum_{i=1}^N e^{-i(\vec{k}_1+\vec{k}_2+\vec{k}_3-\vec{k}_4)\cdot\vec{R}_i} = N\delta_{\vec{k}_1+\vec{k}_2-\vec{k}_3-\vec{k}_4}$;

$$\begin{aligned} \hat{H}_{\text{int}} &= \frac{U}{2} \sum_{i=1}^N \sum_{\lambda,\lambda'} \frac{1}{N} \sum_{\vec{k}_1} e^{-i\vec{k}_1\cdot\vec{R}_i} c_{\vec{k}_1,\lambda}^\dagger \frac{1}{\sqrt{N}} \sum_{\vec{k}_2} e^{-i\vec{k}_2\cdot\vec{R}_i} c_{\vec{k}_2,\lambda}^\dagger \frac{1}{\sqrt{N}} \sum_{\vec{k}_3} e^{-i\vec{k}_3\cdot\vec{R}_i} c_{\vec{k}_3,\lambda}^\dagger \frac{1}{\sqrt{N}} \sum_{\vec{k}_4} e^{-i\vec{k}_4\cdot\vec{R}_i} c_{\vec{k}_4,\lambda'}^\dagger, \\ &= \frac{U}{2N^2} \sum_{i=1}^N \sum_{\lambda,\lambda'} \sum_{\vec{k}_1, \vec{k}_2, \vec{k}_3, \vec{k}_4} e^{-i(\vec{k}_1+\vec{k}_2-\vec{k}_3-\vec{k}_4)\cdot\vec{R}_i} c_{\vec{k}_1,\lambda}^\dagger c_{\vec{k}_2,\lambda}^\dagger c_{\vec{k}_3,\lambda}^\dagger c_{\vec{k}_4,\lambda'}, \\ &= \frac{U}{2N} \sum_{\vec{k}, \vec{k}', \lambda, \lambda'} c_{\vec{k}+\vec{q}, \lambda}^\dagger c_{\vec{k}'-\vec{q}, \lambda}^\dagger c_{\vec{k}', \lambda'}^\dagger c_{\vec{k}, \lambda'}^\dagger \end{aligned}$$

- Hence, the Hubbard interaction potential has no wavevector dependence.

- Using the Hartree-Fock approximation in the form

$$\begin{aligned} c_i^\dagger c_j^\dagger c_k c_l &= \langle c_i^\dagger c_i \rangle \langle c_j^\dagger c_k \rangle - \langle c_i^\dagger c_k \rangle \langle c_j^\dagger c_l \rangle + c_i^\dagger c_l \langle c_j^\dagger c_k \rangle - \langle c_i^\dagger c_l \rangle \langle c_j^\dagger c_k \rangle \\ &\quad - \langle c_i^\dagger c_k \rangle c_l^\dagger c_l + \langle c_j^\dagger c_k \rangle c_l^\dagger c_l + \langle c_i^\dagger c_k \rangle \langle c_j^\dagger c_l \rangle. \end{aligned}$$

- It is then possible to show that (see slide 12)

$$\hat{H}_{\text{int}} \approx \sum_{\vec{k}, \lambda} U \bar{n}_\lambda c_{\vec{k}, \lambda}^\dagger c_{\vec{k}, \lambda} - UN \bar{n}_\uparrow \bar{n}_\downarrow$$

$$\text{where } \bar{n}_\lambda = \frac{1}{N} \sum_{\vec{k}} n_{\vec{k}, \lambda} \text{ and } \lambda = \uparrow \implies \bar{\lambda} = \downarrow$$

- Therefore, within the Hartree-Fock approximation, \hat{H}_{int} is represented by a spin-dependent single-particle Hamiltonian.

- The Stoner Hamiltonian for a metal in the Hartree-Fock approximation is

$$\begin{aligned} \hat{H}_{\text{Stoner}} &= \sum_{\vec{k}, \lambda} \epsilon_{\vec{k}} c_{\vec{k}, \lambda}^\dagger c_{\vec{k}, \lambda} + \hat{H}_{\text{int}} \\ &= \sum_{\vec{k}, \lambda} (\epsilon_{\vec{k}} + U \bar{n}_\lambda) c_{\vec{k}, \lambda}^\dagger c_{\vec{k}, \lambda} - UN \bar{n}_\uparrow \bar{n}_\downarrow \end{aligned}$$

- The ground state energy is therefore, where Θ is the Heavyside step function, effectively acting as a filter to only include \vec{k} values within the Fermi sphere,

$$\begin{aligned} E &= \langle \hat{H}_{\text{Stoner}} \rangle = \sum_{\vec{k}, \lambda} (\epsilon_{\vec{k}} + U \bar{n}_\lambda) \langle c_{\vec{k}, \lambda}^\dagger c_{\vec{k}, \lambda} \rangle - UN \bar{n}_\uparrow \bar{n}_\downarrow, \\ &= \sum_{\vec{k}, \lambda} (\epsilon_{\vec{k}} + U \bar{n}_\lambda) \Theta \left(E_F - \frac{\hbar^2 k^2}{2m} \right) - UN \bar{n}_\uparrow \bar{n}_\downarrow, \\ &= \frac{V}{(2\pi)^3} 4\pi \sum_{\lambda} \int_0^{k_{F\lambda}} dk k^2 (\epsilon_{\vec{k}} + U \bar{n}_\lambda) - UN \bar{n}_\uparrow \bar{n}_\downarrow, \\ &= \frac{4\pi V}{(2\pi)^3} \sum_{\lambda} \left(\frac{\hbar^2 k_{F\lambda}^5}{2m \cdot 5} + U \bar{n}_\lambda \frac{k_{F\lambda}^3}{3} \right) - UN \bar{n}_\uparrow \bar{n}_\downarrow. \end{aligned}$$

- Now, noticing that

$$\bar{n}_\lambda = \frac{1}{N} \sum_{\vec{k}} n_{\vec{k}, \lambda} = \frac{1}{N} \frac{V}{(2\pi)^3} \frac{4\pi k_{F\lambda}^3}{3} \implies k_{F\lambda} = \left(3\bar{n}_\lambda \left(\frac{(2\pi)^3 N}{4\pi V} \right) \right)^{1/3}$$

- Gives

$$\begin{aligned} E &= \frac{4\pi V}{(2\pi)^3} \frac{\hbar^2 k_{F\perp}^5}{2m \cdot 5} + \frac{4\pi V}{(2\pi)^3} \frac{k_{F\perp}^5}{5} + UN \bar{n}_\uparrow \bar{n}_\downarrow, \\ &= \frac{4\pi V}{(2\pi)^3} \frac{\hbar^2}{2m \cdot 5} \left(3 \left(\frac{(2\pi)^3 N}{4\pi V} \right)^{5/3} \left(\bar{n}_\downarrow^{5/3} + \bar{n}_\uparrow^{5/3} \right) \right) + UN \bar{n}_\uparrow \bar{n}_\downarrow. \end{aligned}$$

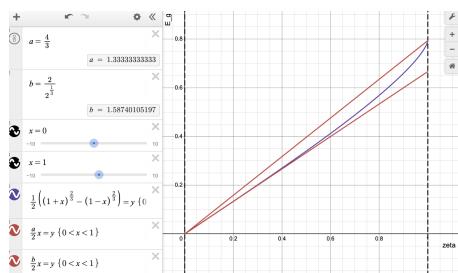
- Now performing a change of variables

$$\begin{aligned} n &= \bar{n}_\uparrow + \bar{n}_\downarrow, \quad \zeta = \frac{\bar{n}_\uparrow - \bar{n}_\downarrow}{n}, \quad \gamma = \left(\frac{2m}{\hbar^2} n^{1/3} \frac{1}{(3\pi^2)^{2/3}} \left(\frac{V}{N} \right)^{2/3} \right) U \\ &\text{such that } \frac{\bar{n}_\uparrow}{n} = \frac{1+\zeta}{2} \text{ and } \frac{\bar{n}_\downarrow}{n} = \frac{1-\zeta}{2} \\ \text{gives } E_g &= \gamma \frac{E}{UN n^2} \left((1+\zeta)^{5/3} + (1-\zeta)^{5/3} \right) - \frac{\gamma}{4} (\zeta^2 - 1) \end{aligned}$$

- Minimising gives

$$\frac{dE_g}{d\zeta} = \frac{1}{2} \left((1 + \zeta)^{2/3} - (1 - \zeta)^{2/3} \right) - \frac{\gamma}{2} \zeta = 0$$

- Which has bounding solutions for $0 \leq \zeta \leq 1$ of $\gamma = 4/3$ and $\gamma = 2^{2/3}$, as seen below, (I DISAGREE WITH HANDOUT HERE WATCH OUT)



- For $\gamma \leq 4/3$, the minimum of E_g is at $\zeta = 0$, so $\bar{n}_\uparrow = \bar{n}_\downarrow$ ie this is a paramagnetic state. $\gamma = 4/3$ is therefore the Stoner criterion for the onset of Ferromagnetism.
- For $4/3 < \gamma < 2^{2/3}$, the ground state is partially spin-polarised.
- For $\gamma > 2^{2/3}$, the state is fully polarised, ie ferromagnetic.

RKKY Exchange Interaction

- Indirect coupling between magnetic ions can be mediated by a polarisable sea of conduction electrons. For this, the Hamiltonian below applies, where s_i is the electron spin operator for electron i and S_n is the impurity spin operator for ion n ;

$$\hat{H} = \sum_{i=1}^N \frac{\vec{p}_i^2}{2m^*} - \sum_{i=1}^N \sum_{n=1}^M J(|\vec{r}_i - \vec{R}_n|) \vec{s}_i \cdot \vec{S}_n$$

where $J(r) \propto \frac{\sin(2k_F r)}{(2k_F r)^4} - \frac{\cos(2k_F r)}{(2k_F r)^3}$

- Rudermann-Kittel-Kasuya-Yosida exchange (also referred to as itinerant exchange) works as;

- Local magnetic moments spin-polarise conduction electrons, which then couple to neighbouring localised magnetic moments a (potentially far) distance r away.
- The sign of the exchange parameter varies with distance, so itinerant exchange response varies from ferromagnetism to antiferromagnetism and back with distance.
- Consider a gas of independent free electrons subject to a perturbation by a magnetic which is spatially varying with wavevector \vec{q} ; $H(\vec{r}) = H(\vec{q}) \cos \vec{q} \cdot \vec{r}$. The Hamiltonian is then

$$\hat{H}_{\text{mag}} = -\vec{\mu} \cdot \vec{B} = \frac{\lambda}{2} g \mu_B \mu_0 H(\vec{q}) \cos(\vec{q} \cdot \vec{r})$$

- Here, $\lambda = \pm 1$; $(+)$ for electrons with spin parallel (antiparallel) to H and $g \sim 2$ is the Lande g-factor.
- Using first order perturbation theory, the wavefunctions of the perturbed system are

$$\begin{aligned} \psi_{\vec{k},\lambda}(\vec{r}) &= \frac{1}{\sqrt{V}} e^{i\vec{k} \cdot \vec{r}} \chi_\lambda + \sum_{\vec{k}'} \frac{\langle \vec{k}' | \hat{H}_{\text{mag}} | \vec{k} \rangle}{E(\vec{k}) - E(\vec{k}')} \frac{1}{\sqrt{V}} e^{i\vec{k}' \cdot \vec{r}} \chi_{\lambda}, \\ &= \frac{1}{\sqrt{V}} e^{i\vec{k} \cdot \vec{r}} \chi_\lambda + \frac{\lambda}{2} g \mu_B \mu_0 H(\vec{q}) \frac{1}{V} \sum_{\vec{k}'} \int d^3 r e^{-i\vec{k}' \cdot \vec{r}} \cos(\vec{q} \cdot \vec{r}) \frac{1}{E(\vec{k}) - E(\vec{k}')} \frac{1}{\sqrt{V}} e^{i\vec{k}' \cdot \vec{r}} \chi_\lambda, \\ &= \frac{1}{\sqrt{V}} e^{i\vec{k} \cdot \vec{r}} \chi_\lambda + \frac{\lambda g \mu_B \mu_0 H(\vec{q})}{4\sqrt{V}} \sum_{\vec{k}'} \left(\frac{e^{i(\vec{k}+\vec{q}) \cdot \vec{r}}}{E(\vec{k}) - E(\vec{k} + \vec{q})} + \frac{e^{i(\vec{k}-\vec{q}) \cdot \vec{r}}}{E(\vec{k}) - E(\vec{k} - \vec{q})} \right) \chi_\lambda. \end{aligned}$$

- The difference in numbers of spin-up and spin-down electron wavefunctions results in a contribution to the magnetisation. Keeping leading orders of H and using $E(\vec{k}) = \hbar^2 k^2 / 2m^*$,

$$|\psi_{\vec{k},\lambda}(\vec{r})|^2 \approx \frac{1}{V} \left(1 + \lambda g \mu_B \mu_0 H(\vec{q}) \frac{m^*}{\hbar^2} \left(\frac{1}{k^2 - (\vec{k} + \vec{q})^2} + \frac{1}{k^2 - (\vec{k} - \vec{q})^2} \right) \cos(\vec{q} \cdot \vec{r}) \right)$$

- Hence, evaluating the magnetisation

$$\begin{aligned} M(\vec{r}) &= \frac{g\mu_B}{2} \sum_{\vec{k} \leq k_F} \left(|\psi_{\vec{k},\uparrow}(\vec{r})|^2 - |\psi_{\vec{k},\downarrow}(\vec{r})|^2 \right), \\ &= g^2 \mu_B^2 \mu_0 H(\vec{q}) \frac{m^*}{\hbar^2} \frac{1}{V} \sum_{\vec{k} \leq k_F} \left(\frac{1}{(\vec{k} + \vec{q})^2 - \vec{k}^2} + \frac{1}{(\vec{k} - \vec{q})^2 - \vec{k}^2} \right) \cos(\vec{q} \cdot \vec{r}), \\ &= g^2 \mu_B^2 \mu_0 H(\vec{q}) \frac{m^*}{\hbar^2} \frac{1}{(2\pi)^3} \int_{\vec{k} \leq k_F} d^3 \vec{k} \left(\frac{1}{(\vec{k} + \vec{q})^2 - \vec{k}^2} + \frac{1}{(\vec{k} - \vec{q})^2 - \vec{k}^2} \right) \cos(\vec{q} \cdot \vec{r}), \\ &= g^2 \mu_B^2 \mu_0 H(\vec{q}) \frac{m^*}{\hbar^2} \frac{1}{(2\pi)^3} \pi k_F \left[1 + \frac{4k_F^2 - q^2}{4k_F q} \ln \left| \frac{q + 2k_F}{q - 2k_F} \right| \right] \cos(\vec{q} \cdot \vec{r}), \\ &= M(\vec{q}) \cos(\vec{q} \cdot \vec{r}). \end{aligned}$$

- Paramagnetic susceptibility $\chi(\vec{q})$ is defined below. χ_p is then the Pauli spin susceptibility and $F(x)$ is the again the Lindhard function.

$$\begin{aligned} \chi(\vec{q}) &= \frac{M(\vec{q})}{H(\vec{q})}, \\ &= g^2 \mu_B^2 \mu_0 \frac{m^*}{\hbar^2} \frac{1}{(2\pi)^3} \pi k_F \left(1 + \frac{4k_F^2 - q^2}{4k_F q} \ln \left| \frac{q + 2k_F}{q - 2k_F} \right| \right), \\ &= \chi_p F\left(\frac{q}{2k_F}\right), \\ \text{where } F(x) &= \frac{1}{2} \left(1 + \frac{1 - x^2}{2x} \ln \left| \frac{1 + x}{1 - x} \right| \right) \quad \text{and} \quad \chi_p = \frac{1}{(2\pi)^2} g^2 \mu_B^2 \mu_0 \frac{m}{\hbar^2} k_F \end{aligned}$$

- Note the logarithmic singularity at $q = 2k_F$ which is responsible for the oscillatory RKKY coupling between two magnetic moments. Also note the divergence at $q = 2k_F$ in 1D, showing instability to those spin-density waves.

- As magnetisation at a point r is given by $M(\vec{r}) = \int d^3 \vec{r}' \delta(\vec{r} - \vec{r}') H(\vec{r}')$ and the magnetic field from a magnetic ion can be approximated as $H(\vec{r}) = \delta(\vec{r}) H_0$, we see that $M(\vec{r}) = \chi(\vec{r}) H_0$.

- Using the response function from the electron gas then gives

$$\begin{aligned} \chi(\vec{r}) &= \frac{1}{(2\pi)^3} \int d^3 \vec{q} \chi(\vec{q}) e^{i\vec{q} \cdot \vec{r}}, \\ &= \frac{\chi_p}{(2\pi)^3} \int d^3 \vec{q} F\left(\frac{q}{2k_F}\right) e^{i\vec{q} \cdot \vec{r}}, \\ &= \frac{\chi_p}{(2\pi)^3} \int q^2 F\left(\frac{q}{2k_F}\right) e^{iqr \cos \theta} \sin \theta d\theta d\phi dq, \\ &= \frac{\chi_p}{(2\pi)^2} \int_0^\infty q^2 F\left(\frac{q}{2k_F}\right) \left(\frac{2 \sin qr}{qr} \right) dq. \end{aligned}$$

- Hence, after integrating using the change of variables $2k_F x = q$, we get that the magnetisation of the electron gas around a localised magnetic moment is

$$M(r) = \frac{2\chi_p k_F^3}{\pi} H_0 \left(\frac{\sin(2k_F r)}{(2k_F r)^4} - \frac{\cos(2k_F r)}{(2k_F r)^3} \right)$$

- At large distances,

$$\chi(\vec{r}) \approx \frac{2k_F^3 \chi_p}{\pi} \frac{\cos(2k_F r)}{(2k_F r)^3} \implies J_{RKKY}(r) \propto \frac{\cos(2k_F r)}{r^3}$$

Magnetoresistance

- Magnetoresistance is defined as

$$R_M = \frac{R(0) - R(B)}{R(0)}$$

- Where $R(B)$ is the resistance of a sample in magnetic field B and $R(0)$ is the resistance in zero field.
- Magnetoresistance is defined to be positive when $R(B) < R(0)$.

- In magnetic materials, resistivity varies with the angle ϕ between the magnetisation and the current;

$$\rho = \rho_\perp + (\rho_\parallel - \rho_\perp) \cos^2 \phi, \quad (\rho_\parallel > \rho_\perp)$$

Giant Magnetoresistance (GMR)

- A significant (~50%) positive magnetoresistance is observed in thin-film structures with alternating ferromagnetic and non-magnetic conductive layers. This is GMR.

- The overall resistance is relatively high for antiparallel alignment of the adjacent ferromagnetic layers ($B = 0$) and is relatively low for parallel alignment ($B > 0$).
- The effect here is based on the dependence of electron scattering to spin orientation in the ferromagnetic layers.
- Depending on the thickness t of the non-magnetic layer, the zero-field RKKY coupling between the magnetic layers is either parallel or antiparallel. Large magnetoresistance is observed when t is such as to make the couplings anti-ferromagnetic.
- Integrating over all magnetic ions at the two surfaces of the non-magnetic layer, the interlayer coupling is

$$J(t) \propto \cos(2k_F t)/t^2$$

- Notably, the denominator is now t^2 rather than t^3 .
- The expected periodicity with $\lambda_F/2$ is not generally observed due to interface and finite thickness effects.

- The way in which scattering occurs depends on the spin;

- When the spin of an electron flips on scattering, we can model the scatter with the absorption of a magnon by the electron.
 - This is typically how spin-orbit scattering with heavy impurities occurs.
 - In systems with strong spin-flip scattering, no GMR is observed.
- Scattering processes in which the spin of the electron remains unchanged have spin-dependent cross-sections.
 - It is these interactions which cause GMR.

- The Mott two-current model proposes that in transition metals, conduction is due to two channels; one for the majority spin-up electrons with spin parallel to the magnetisation direction, and another for the minority spin-down electrons with spin antiparallel to the magnetisation.

- This neglects the relatively weak spin-flip scattering.

- In transition metals, the dominant scattering process is from the s conduction band into the more localised d-states with density $g_V^{(d)}(E_F, \lambda)$

- For example, in Co, the majority spin d-band is full, so there is no scattering for spin-up s-electrons into spin-up d states at E_F . However, spin-down electrons are strongly scattered into minority spin d-states, so $\rho_{\uparrow}^{Co} \ll \rho_{\downarrow}^{Co}$.

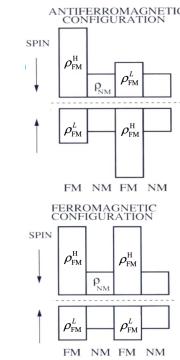
- Consider a case in which the current flows along the interfaces and the minority spin channel has higher resistance.

- We can assign resistivities to each layer, as depicted right.

- Here, ρ_{FM}^H is the resistivity of the ferromagnetic layer for minority carriers (this resistivity is high), ρ_{FM}^L is the resistivity of the ferromagnetic layer for the majority spin (low) and ρ_{NM} is the resistivity of the non-magnetic layer.

- In an ordinary clean metal, the mean free path of an electron will be shorter than the layer thickness, so scattering prevents electrons from crossing layers. Hence, the resistance is just that of conventional resistors in parallel.

- In ultra-pure metals, the mean free path is $> t$, so can approximate total resistivity by using a weighted average of resistivities.



- Using this approach, where L is the width and length of each layer, and t_1 is the thickness of a FM layer and t_2 is the thickness of a NM layer, the spin-up and spin-down resistances of one period for ferromagnetic alignment are:

$$R_{\uparrow} = \bar{\rho}_{\uparrow} \frac{L}{(2t_1 + 2t_2)L} = \frac{2t_1 \rho_{FM}^L + 2t_2 \rho_{NM}}{2t_1 + 2t_2} \frac{L}{(2t_1 + 2t_2)L} = \frac{t_1 \rho_{FM}^L + t_2 \rho_{NM}}{2(t_1 + t_2)^2},$$

$$R_{\downarrow} = \bar{\rho}_{\downarrow} \frac{L}{(2t_1 + 2t_2)L} = \frac{2t_1 \rho_{FM}^H + 2t_2 \rho_{NM}}{2t_1 + 2t_2} \frac{L}{(2t_1 + 2t_2)L} = \frac{t_1 \rho_{FM}^H + t_2 \rho_{NM}}{2(t_1 + t_2)^2}.$$

- Hence, the two-channel resistance in ferromagnetic alignment is

$$\left(\frac{1}{R}\right)_{\uparrow\downarrow} = \left(\frac{1}{R_{\uparrow}} + \frac{1}{R_{\downarrow}}\right)_{\uparrow\downarrow} = 2(t_1 + t_2)^2 \left(\frac{1}{t_1 \rho_{FM}^L + t_2 \rho_{NM}} + \frac{1}{t_1 \rho_{FM}^H + t_2 \rho_{NM}} \right)$$

- For antiferromagnetic alignment, the spin-up and spin-down resistances are the same;

$$R_{\uparrow} = R_{\downarrow} = \bar{\rho} \frac{L}{(2t_1 + 2t_2)L} = \frac{t_1 \rho_{FM}^L + t_1 \rho_{FM}^H + 2t_2 \rho_{NM}}{2t_1 + 2t_2} \frac{L}{(2t_1 + 2t_2)L} = \frac{t_1 \rho_{FM}^L + t_1 \rho_{FM}^H + 2t_2 \rho_{NM}}{4(t_1 + t_2)^2}$$

- Therefore, the two-channel resistance in antiferromagnetic alignment is

$$\left(\frac{1}{R}\right)_{\uparrow\downarrow} = \left(\frac{1}{R_{\uparrow}} + \frac{1}{R_{\downarrow}}\right)_{\uparrow\downarrow} = \frac{8(t_1 + t_2)^2}{t_1 \rho_{FM}^L + t_1 \rho_{FM}^H + 2t_2 \rho_{NM}}$$

- Therefore, the magnetoresistance of a GMR device is

$$GMR = \frac{R_{\uparrow\downarrow} - R_{\uparrow\uparrow}}{R_{\uparrow\uparrow}} = \frac{(\rho_{FM}^H - \rho_{FM}^L)^2 t_1^2}{4(\rho_{FM}^H t_1 + \rho_{NM} t_2)(\rho_{FM}^L t_1 + \rho_{NM} t_2)}$$

- Therefore, for a good GMR, a large value of $\frac{\rho_{FM}^H}{\rho_{FM}^L}$ is required.

Double Exchange

- For double exchange, an electron may hop from one ion to another, e.g. Mn^{3+} to Mn^{4+} in an Mn-O-Mn bridge.

- As the electron maintains its spin when moving, it can only hop from one ion to the next if the two ionic spins are not antiparallel.
- This hopping lowers the ground state energy, as the carriers are then able to participate in binding, hence giving a lower energy for ferromagnetic configurations.

- A simplified Hamiltonian for this double exchange is

$$\hat{H} = \sum_{\vec{k}, \lambda} \epsilon_{\vec{k}, \lambda} c_{\vec{k}, \lambda}^\dagger c_{\vec{k}, \lambda} + U \sum_i n_{i,\uparrow} n_{i,\downarrow} - J \sum_i \vec{s}_i \cdot \vec{S}_i$$

- The first two terms give rise to itinerant ferromagnetism if the Stoner Criterion is satisfied.
- The third term represented a ferromagnetic exchange interaction between conduction electrons \vec{s}_i and localised spins \vec{S}_i on each atomic site i .
- J is positive to be consistent with Hund's rules. In fact, double exchange occurs most easily when spin direction doesn't need to change because of conformance to Hund's rules.

Colossal Magnetoresistance

- Especially around the Curie temperature, very high positive magnetoresistance (up to 120,000%) has been observed.
- In some of these structures, the system lowers its symmetry by a tetragonal deformation of an O_6 octahedra, stabilising a different orbital. This is the Jahn-Teller effect.
- Near the Curie temperature, fluctuations in spin alignment lead to a rapid increase in resistivity, and above T_c , the material behaves as a paramagnetic insulator.

Kondo Effect: Resonant Spin Scattering

- Introducing a very small concentration of magnetic impurities into a metal (e.g. Fe into Cu) can change the low-temperature material behaviour from having a low-temperature residual resistivity to displaying a logarithmic increase in resistivity as $T \rightarrow 0$.
- The local exchange interaction between a set of magnetic impurity spins at R_i with spin S_i and metal conduction electrons with spin $\hat{s}(\vec{r})$ is

$$\begin{aligned} \hat{V}_K &= \sum_i \hat{V}_{K,i} \\ &= J \sum_i \hat{\vec{S}}_i \cdot \hat{\vec{s}}(\vec{r}) \delta(\vec{r} - \vec{R}_i), \\ &= J \sum_i \left(\hat{S}_i^z \hat{s}^z(\vec{r}) + \frac{1}{2} \left(\hat{S}_i^+ \hat{s}^- (\vec{r}) + \hat{S}_i^- \hat{s}^+ (\vec{r}) \right) \right) \delta(\vec{r} - \vec{R}_i), \\ &= J \frac{\hbar}{2V} \sum_{\vec{k}, \vec{k}', i} \left(\hat{S}_i^z \left(c_{\vec{k}, \uparrow}^\dagger c_{\vec{k}', \uparrow} - c_{\vec{k}, \downarrow}^\dagger c_{\vec{k}', \downarrow} \right) + \hat{S}_i^+ c_{\vec{k}, \downarrow}^\dagger c_{\vec{k}', \uparrow} + \hat{S}_i^- c_{\vec{k}, \uparrow}^\dagger c_{\vec{k}', \downarrow} \right) e^{-i(\vec{k} - \vec{k}') \cdot \vec{R}_i} \end{aligned}$$

- The final two terms here show that scattering of conduction electrons is accompanied by a spin flip of the impurity atoms.
- Close to the Fermi energy, there is a resonance process which greatly enhances the scattering probability to

$$W(\vec{k}, \vec{k}') \approx J^2 S(S+1) \left(1 + 2Jg_V(\epsilon_F) \ln \left| \frac{D}{\epsilon_{\vec{k}} - \epsilon_F} \right| + \dots \right)$$

- Using Boltzmann transport theory (lectures 12-13), the conduction electron scattering rate $1/\tau(\epsilon_i)$ and the conductivity $\sigma(T)$ may be found;

$$\begin{aligned} \frac{1}{\tau(\epsilon_{\vec{k}})} &= \frac{J^2 S(S+1)}{\hbar} g_V(\epsilon_F) \left(1 + 2Jg_V(\epsilon_F) \ln \left| \frac{D}{\epsilon_{\vec{k}} - \epsilon_F} \right| + \dots \right), \\ \sigma(T) &= \frac{e^2 n}{2m} J^2 S(S+1) \left(1 - 2Jg_V(\epsilon_F) \ln \left| \frac{D}{k_B T} \right| + \dots \right) \end{aligned}$$

- The logarithmic divergence in $\sigma(T)$ gives the observed logarithmic increase in resistivity as $T \rightarrow 0$.

L9 AQCMP - Weak Electron-Photon Interactions

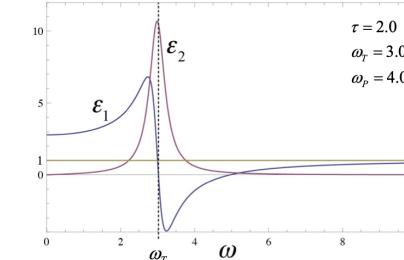
L8 AQCMP - Magnetism: Exchange Effects

Electron-Photon Interactions
 Lorentz Oscillator
 Relationship of susceptibility to optical properties
 Electron-Photon Interaction in Quantum Theory
 Transverse Dielectric Response
 Optical Absorption
 Transverse Dielectric Response in Semiconductors
 Joint Density of States
 Indirect Bandgap Semiconductors

L10/11 AQCMP - Strong Electron-Photon Interactions - Excitons

$$\epsilon(\omega) = 1 + \underbrace{\frac{\omega_p^2(\omega_T^2 - \omega^2)}{(\omega_T^2 - \omega^2)^2 + \omega^2/\tau^2}}_{\epsilon_1} + i \left(\underbrace{\frac{\omega_p^2\omega/\tau}{(\omega_T^2 - \omega^2)^2 + \omega^2/\tau^2}}_{\epsilon_2} \right)$$

- This provides a qualitative understanding for how optical constants of a material vary at energies close to the photon-induced transition between occupied and empty quantum states.



Electron-Photon Interactions

- With low light intensities, photons may probe the quantum ground and excited states of solids. In this (weak-coupling) regime, it can be assumed that the transitions do not modify the quantum states themselves.
- In the strong light intensity (strong-coupling) regime, the strength of the electric field incoming radiation becomes comparable with the electric field between electrons and ions in the crystal.
 - Here, we expect quantum states of the solid to be modified, leading to a regime where non-linear optical effects occur.

Lorentz Oscillator

- Using the equation for the electric field forcing damped harmonic motion of electrons within an ion potential, where y is electron displacement, τ is the damping constant and ω_T is the ion resonant frequency;

$$m^* \frac{d^2y}{dt^2} + \frac{m^*}{\tau} \frac{dy}{dt} + m^* \omega_T^2 y = -eE(t)$$

- Finding steady-state solutions where $E = E_0 \exp(-i\omega t)$ and $y(t) = y(\omega) \exp(-i\omega t)$ gives

$$y(\omega) = \frac{-eE_0/m^*}{\omega_T^2 - \omega^2 - i\omega/\tau}$$

- This displacement of the electron results in a periodic polarisation of the medium, which is also proportional to electron density n ;

$$P(\omega) = -ney(\omega) = \chi(\omega)\epsilon_0 E(\omega)$$

- Hence, the polarisation susceptibility,

$$\begin{aligned} \chi(\omega) &= -\frac{ney(\omega)}{\epsilon_0 E_0} \\ &= \frac{ne}{\epsilon_0} \frac{e/m^*}{\omega_T^2 - \omega^2 - i\omega/\tau} \\ &= \frac{\omega_p^2}{\omega_T^2 - \omega^2 - i\omega/\tau} \end{aligned}$$

where plasma frequency, $\omega_p^2 = \frac{ne^2}{\epsilon_0 m^*}$

- As $P = -ney = \epsilon_0 \epsilon E - \epsilon_0 E = \epsilon_0(\epsilon - 1)E$, $\chi(\omega) = \epsilon(\omega) - 1$, defining the dielectric function.

- It can therefore be found that

Relationship of susceptibility to optical properties

- Defining complex refractive index as $N(\omega) = n(\omega) + i\kappa(\omega)$ with $N = \sqrt{\epsilon}$ means that $\epsilon_1 = n^2 - \kappa^2$ and $\epsilon_2 = 2n\kappa$. Therefore,

$$\begin{aligned} n &= \sqrt{\frac{1}{2} \left(\epsilon_1 + \sqrt{\epsilon_1^2 + \epsilon_2^2} \right)} \\ \kappa &= \sqrt{\frac{1}{2} \left(-\epsilon_1 + \sqrt{\epsilon_1^2 + \epsilon_2^2} \right)} \end{aligned}$$

- Considering continuity of parallel components of E and H at an interface, and writing in the form $E(z) = E e^{ikz}$ with $k = (\omega/c)N$, it is found that $E_i - E_r = NE_t$ at an interface.

The associated reflection coefficient is $R = \frac{(1-n)^2 + \kappa^2}{(1+n)^2 + \kappa^2}$.

Applying Beer's law $k = \frac{\omega}{c}(n + i\kappa)$ here then also implies that for an intensity

$$\begin{aligned} I &= I_{z=0} e^{-\alpha z} \propto |E_t e^{ikz}|^2 = |E_t|^2 \exp(-2\frac{\omega}{c}\kappa z) \\ \implies \alpha &= 2\frac{\omega}{c}\kappa = \frac{\omega}{cn}\epsilon_2(\omega) \implies \boxed{\epsilon_2 = 2n\kappa} \end{aligned}$$

- Applying the Kramers-Krönig relations to $\chi(\omega)$ gives,

$$\begin{aligned} \epsilon_1(\omega) &= 1 + \frac{1}{\pi} \mathcal{P} \int_{-\infty}^{\infty} \frac{\epsilon_2(\omega')}{\omega' - \omega} d\omega' \\ \epsilon_2(\omega) &= -\frac{1}{\pi} \mathcal{P} \int_{-\infty}^{\infty} \frac{\epsilon_1(\omega') - 1}{\omega' - \omega} d\omega' \end{aligned}$$

Using the Kramers-Krönig relationships we also find that

$$\begin{aligned} n(\omega) &= 1 + \frac{1}{\pi} \mathcal{P} \int_{-\infty}^{\infty} \frac{\kappa(\omega')}{\omega' - \omega} d\omega' \\ \kappa(\omega) &= -\frac{1}{\pi} \mathcal{P} \int_{-\infty}^{\infty} \frac{n(\omega') - 1}{\omega' - \omega} d\omega' \end{aligned}$$

- Hence, absorption at one frequency results in dispersion at all other frequencies. Also, knowledge of an absorptions spectrum can be used to calculate the refractive index.
- Absorption, κ of a dielectric increases dramatically as light energy approaches a band edge.
 - Kramers-Krönig suggests the real part will peak just before the resonance.
 - Just above an absorption peak, n drops while κ falls more slowly, resulting in a peak of reflectivity.

Electron-Photon Interaction in Quantum Theory

Transverse Dielectric Response

- For a solid with effective potential $V(r)$ subject to an electromagnetic wave,

$$\begin{aligned}\hat{H} &= \frac{1}{2m} \left(\vec{p} + e\vec{A}(\vec{r}, t) \right)^2 + V(\vec{r}), \\ &= \frac{1}{2m} \left(\vec{p}^2 + e \left(\vec{p} \cdot \vec{A} + \vec{A} \cdot \vec{p} \right) + e^2 \vec{A}^2 \right) + V(\vec{r}) \\ &= \underbrace{\frac{\vec{p}^2}{2m} + V(\vec{r})}_{\hat{H}_0} + \underbrace{\frac{e}{2m} \left(\vec{p} \cdot \vec{A} + \vec{A} \cdot \vec{p} \right)}_{\hat{H}_1} + O(A^2)\end{aligned}$$

- Using the Coulomb gauge, $\nabla \cdot \vec{A} = 0$, $[\vec{p}, \vec{A}] = 0$, so $\hat{H}_1 \approx \frac{e}{m} \vec{A} \cdot \vec{p}$.
- Then to represent a transverse EM wave, where \vec{a} is a unit vector in the direction of \vec{A} perpendicular to \vec{q} , using

$$\vec{A}(\vec{r}, t) = A_0 \vec{a} \left(e^{i(\vec{q} \cdot \vec{r} - \omega t)} + e^{-i(\vec{q} \cdot \vec{r} - \omega t)} \right)$$

- Gives that

$$\hat{H}_1 = \frac{e}{m} A_0 \left(e^{i(\vec{q} \cdot \vec{r} - \omega t)} \vec{a} \cdot \vec{p} + e^{-i(\vec{q} \cdot \vec{r} - \omega t)} \vec{a} \cdot \vec{p} \right)$$

- Here, the first term includes transitions from an initial state $|\psi_i\rangle$ to $|\psi_f\rangle$ via the absorption of a photon and the second term includes transitions from $|\psi_f\rangle$ to $|\psi_i\rangle$ via the emission of a photon. These have rates given by Fermi's golden rule and stimulated emission as below. Note that the terms involving Fermi distributions ensure the resulting state is unoccupied and the starting state occupied before transition.

$$\begin{aligned}W_{i \rightarrow f} &= \frac{2\pi e^2 A_0^2}{\hbar m^2} |\langle \psi_f | e^{i\vec{q} \cdot \vec{r}} \vec{a} \cdot \vec{p} | \psi_i \rangle|^2 \delta(E_f - E_i - \hbar\omega) f(E_i) (1 - f(E_f)) \\ W_{f \rightarrow i} &= \frac{2\pi e^2 A_0^2}{\hbar m^2} |\langle \psi_i | e^{-i\vec{q} \cdot \vec{r}} \vec{a} \cdot \vec{p} | \psi_f \rangle|^2 \delta(E_i - E_f + \hbar\omega) f(E_f) (1 - f(E_i))\end{aligned}$$

- Using the above, we may then obtain the total power absorbed by taking the difference between the absorption and stimulated emission rates, multiplying by photon energy and integrating over all pairs of initial and final states (remembering to account for spin degeneracy - a factor of 2);

$$\begin{aligned}P(\vec{q}, \omega) &= \hbar\omega W(\vec{q}, \omega), \\ &= 2\hbar\omega \sum_{i,f} (W_{i \rightarrow f} - W_{f \rightarrow i}), \\ &= 2\hbar\omega \frac{2\pi e^2 A_0^2}{\hbar m^2} \sum_{i,f} \left(|\langle \psi_f | e^{i\vec{q} \cdot \vec{r}} \vec{a} \cdot \vec{p} | \psi_i \rangle|^2 \delta(E_f - E_i - \hbar\omega) f(E_i) (1 - f(E_f)) \right. \\ &\quad \left. - |\langle \psi_i | e^{-i\vec{q} \cdot \vec{r}} \vec{a} \cdot \vec{p} | \psi_f \rangle|^2 \delta(E_i - E_f + \hbar\omega) f(E_f) (1 - f(E_i)) \right), \\ &= 2\hbar\omega \frac{2\pi e^2 A_0^2}{\hbar m^2} \sum_{i,f} |\langle \psi_f | e^{i\vec{q} \cdot \vec{r}} \vec{a} \cdot \vec{p} | \psi_i \rangle|^2 \delta(E_f - E_i - \hbar\omega) (f(E_i) - f(E_f)).\end{aligned}$$

where we have used the identity $|\langle \psi_f | e^{i\vec{q} \cdot \vec{r}} \vec{a} \cdot \vec{p} | \psi_i \rangle|^2 = |\langle \psi_i | e^{-i\vec{q} \cdot \vec{r}} \vec{a} \cdot \vec{p} | \psi_f \rangle|^2$

- Like for the longitudinal density response function , we can also use a classical argument to obtain a second expression for the power dissipated containing the dielectric function; (note σ is the complex transverse conductivity function).

$$\begin{aligned}\vec{E}(\vec{r}, t) &= -\frac{\partial \vec{A}(\vec{r}, t)}{\partial t} \\ &= i\omega A_0 \vec{a} e^{i(\vec{q} \cdot \vec{r} - \omega t)} + \text{c.c.} \\ &= E_0 \vec{a} e^{i(\vec{q} \cdot \vec{r} - \omega t)} + \text{c.c.} \quad (\vec{a} \perp \vec{q}) \\ \vec{J}(\vec{r}, t) &= \sigma(\vec{q}, \omega) E_0 \vec{a} e^{i(\vec{q} \cdot \vec{r} - \omega t)} + \text{c.c.}\end{aligned}$$

- The dissipated power due to the induced transverse current density, assuming it is parallel to E is then given by (only keeping terms at frequency ω),

$$\begin{aligned}P(\vec{q}, \omega) &= \int_V d^3 r \vec{J} \cdot \vec{E} \\ &= \int_V d^3 r \left(\sigma(\vec{q}, \omega) E_0 \vec{a} e^{i(\vec{q} \cdot \vec{r} - \omega t)} + \text{c.c.} \right) \times \left(E_0 \vec{a} e^{i(\vec{q} \cdot \vec{r} - \omega t)} + \text{c.c.} \right) \\ &= 2\sigma_1(\vec{q}, \omega) E_0^2 V \\ &= 2\sigma_1(\vec{q}, \omega) \omega^2 A_0^2 V\end{aligned}$$

- Hence,

$$\sigma_1(\vec{q}, \omega) = \frac{P(\vec{q}, \omega)}{2V\omega^2 A_0^2} = \frac{\hbar\omega W(\vec{q}, \omega)}{2V\omega^2 A_0^2}$$

- Again, as in lecture 5, using $\epsilon(\vec{q}, \omega) = 1 + \frac{i\sigma(\vec{q}, \omega)}{\epsilon_0\omega}$ gives

$$\begin{aligned}\epsilon_2(\vec{q}, \omega) &= \frac{\sigma_1}{\epsilon_0\omega}, \\ &= \frac{\hbar}{2V\epsilon_0} \frac{W(\vec{q}, \omega)}{\omega^2 A_0^2}, \\ &= \frac{2\pi e^2}{\epsilon_0 m^2 \omega^2} \frac{1}{V} \sum_{i,f} |\langle \psi_f | e^{i\vec{q} \cdot \vec{r}} \vec{a} \cdot \vec{p} | \psi_i \rangle|^2 \delta(E_f - E_i - \hbar\omega) (f(E_i) - f(E_f)).\end{aligned}$$

- Using the Kramers-Krönig relationships, ϵ_1 may also then be found, giving a general expression for the transverse dielectric function to describe the optical response of a system to independent electrons, without making assumptions about the nature of electronic states.

$$\begin{aligned}\epsilon_1(\vec{q}, \omega) &= 1 + \frac{1}{\pi} \mathcal{P} \int_{-\infty}^{\infty} \frac{\epsilon_2(\vec{q}, \omega')}{\omega' - \omega} d\omega' \\ &= 1 + \frac{2e^2 \hbar^2}{\epsilon_0 m^2 (E_f - E_i)^2} \frac{1}{V} \sum_{i,f} |\langle \psi_f | e^{i\vec{q} \cdot \vec{r}} \vec{a} \cdot \vec{p} | \psi_i \rangle|^2 \frac{f(E_i) - f(E_f)}{E_f - E_i - \hbar\omega}\end{aligned}$$

Optical Absorption

Transverse Dielectric Response in Semiconductors

- Assume the electronic states in a crystalline semiconductor are initial valence(v) and conduction (c) band Bloch states.
- We can then also assume that the Fermi-Dirac distribution function is 1 for valence states and 0 for conduction states. Therefore,

$$\begin{aligned}\langle \vec{r} | \psi_i \rangle &= \langle \vec{r} | \psi_{v,\vec{k}} \rangle = \frac{1}{\sqrt{V}} e^{i\vec{k} \cdot \vec{r}} U_{v,\vec{k}}(\vec{r}), \\ \langle \vec{r} | \psi_f \rangle &= \langle \vec{r} | \psi_{c,\vec{k}} \rangle = \frac{1}{\sqrt{V}} e^{i\vec{k} \cdot \vec{r}} U_{c,\vec{k}}(\vec{r}).\end{aligned}$$

- Using the orthogonality of Bloch functions on the second line, setting $\vec{r} = \vec{R}_n + \vec{r}'$, and defining N_c as the number of unit cells in the crystal, it is seen that the matrix element in Fermi's Golden rule for absorption is;

$$\begin{aligned}\langle \psi_f | e^{i\vec{q}\cdot\vec{r}} \vec{a} \cdot \vec{p} | \psi_i \rangle &= -\frac{i\hbar}{V} \int e^{-i\vec{k}'\cdot\vec{r}} U_{c,\vec{k}'}^*(\vec{r}) e^{i\vec{q}\cdot\vec{r}} \vec{a} \cdot \vec{\nabla}_{\vec{r}} \left(e^{i\vec{k}\cdot\vec{r}} U_{v,\vec{k}}(\vec{r}) \right) d^3 r \\ &= -\frac{i\hbar}{V} \int e^{i(\vec{k}+\vec{q}-\vec{k}')\cdot\vec{r}} U_{c,\vec{k}'}^*(\vec{r}) \left(\vec{a} \cdot \vec{\nabla}_{\vec{r}} U_{v,\vec{k}}(\vec{r}) + i\vec{a} \cdot \vec{k} U_{v,\vec{k}}(\vec{r}) \right) d^3 r \\ &= -\frac{i\hbar}{V} \left(\sum_{n=1}^{N_c} e^{i(\vec{k}+\vec{q}-\vec{k}')\cdot\vec{R}_n} \right) \int_{\text{unit cell}} e^{i(\vec{k}+\vec{q}-\vec{k}')\cdot\vec{r}'} U_{c,\vec{k}'}^*(\vec{r}') \vec{a} \cdot \vec{\nabla}_{\vec{r}'} U_{v,\vec{k}}(\vec{r}') d^3 r'\end{aligned}$$

- As the sum above will become non-zero only where the exponent is $2\pi i$ for all lattice points, we require

$$\sum_{n=1}^{N_c} e^{i(\vec{k}+\vec{q}-\vec{k}')\cdot\vec{R}_n} = N_c \delta_{\vec{k}+\vec{q},\vec{k}'}$$

- It is therefore possible to simplify the matrix element (using $\Delta = V/N_c$),

$$\langle \psi_f | e^{i\vec{q}\cdot\vec{r}} \vec{a} \cdot \vec{p} | \psi_i \rangle = -\frac{i\hbar}{\Delta} \int_{\text{unit cell}} U_{c,\vec{k}+\vec{q}}^*(\vec{r}) \vec{a} \cdot \vec{\nabla}_{\vec{r}} U_{v,\vec{k}}(\vec{r}) d^3 r$$

- Vertical transitions between two states where $k' \approx k$ can occur in two ways,

- Allowed direct transitions, where we may simply use the above in combination with the dipole approximation (for small \vec{q} , $\langle \psi_f | e^{i\vec{q}\cdot\vec{r}} A_0 \vec{a} \cdot \vec{p} | \psi_i \rangle \approx A_0 \vec{a} \cdot \langle \psi_f | \vec{p} | \psi_i \rangle$);

$$\begin{aligned}\langle \psi_f | e^{i\vec{q}\cdot\vec{r}} \vec{a} \cdot \vec{p} | \psi_i \rangle &= -\frac{i\hbar}{\Delta} \int_{\text{unit cell}} U_{c,\vec{k}+\vec{q}}^*(\vec{r}) \vec{a} \cdot \vec{\nabla}_{\vec{r}} U_{v,\vec{k}}(\vec{r}) d^3 r \\ &= \vec{a} \cdot \vec{p}_{cv}(\vec{k})\end{aligned}$$

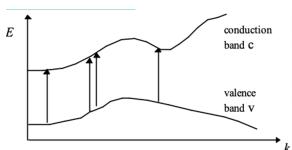
where transition dipole matrix element, $\vec{p}_{cv}(\vec{k}) = \frac{1}{\Delta} \int_{\text{cell}} U_{c,\vec{k}}^*(\vec{r}) \vec{p} U_{v,\vec{k}}(\vec{r}) d^3 r$

- Forbidden direct transitions, where for symmetry reasons the dipole transition matrix element for $q = 0$ is forbidden. Here, we develop a Taylor series around $q \approx 0$ and use the second order term;

$$\begin{aligned}U_{c,\vec{k}+\vec{q}}(\vec{r}) &\approx U_{c,\vec{k}}(\vec{r}) + \vec{q} \cdot \vec{\nabla}_{\vec{k}} U_{c,\vec{k}}(\vec{r}) + \dots \\ \implies \langle \psi_f | e^{i\vec{q}\cdot\vec{r}} \vec{a} \cdot \vec{p} | \psi_i \rangle &= \frac{1}{\Delta} \int_{\text{cell}} (\vec{q} \cdot \vec{\nabla}_{\vec{k}} U_{c,\vec{k}}(\vec{r})) \vec{a} \cdot \vec{p} U_{v,\vec{k}}(\vec{r}) d^3 r.\end{aligned}$$

- Assuming there are allowed direct transitions, we then find $\epsilon_2(\omega)$, where the sum over c, v runs over all bands which contribute to **vertical transitions** with energies $\hbar\omega$ as;

$$\begin{aligned}\epsilon_2(\omega) &= \epsilon_2(0, \omega) = \frac{2\pi e^2}{\varepsilon_0 m^2 \omega^2 V} \sum_{i,f} |\langle \psi_f | \vec{a} \cdot \vec{p} | \psi_i \rangle|^2 \delta(E_f - E_i - \hbar\omega) (f(E_i) - f(E_f)), \\ &= \frac{2\pi e^2}{\varepsilon_0 m^2 \omega^2} \sum_{c,v} \frac{1}{V} \int_{\vec{k}} |\vec{a} \cdot \vec{p}_{cv}(\vec{k})|^2 \delta(E_c(\vec{k}) - E_v(\vec{k}) - \hbar\omega), \\ &= \frac{2\pi e^2}{\varepsilon_0 m^2 \omega^2} \sum_{c,v} \int_{\text{BZ}} \frac{d^3 \vec{k}}{(2\pi)^3} |\vec{a} \cdot \vec{p}_{cv}(\vec{k})|^2 \delta(E_c(\vec{k}) - E_v(\vec{k}) - \hbar\omega).\end{aligned}$$

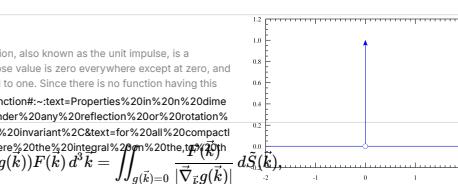


- This may be simplified using the definition of the dirac delta function in n-dimensions;

Dirac delta function

In mathematical analysis, the Dirac delta function, also known as the unit impulse, is a generalized function on the real numbers, whose value is zero everywhere except at zero, and whose integral over the entire real line is equal to one. Since there is no function having this

http://en.wikipedia.org/wiki/Dirac_delta_function#Properties
In mathematics, the Dirac delta function is a distribution that maps a function to its value at a point. It is often denoted by the symbol δ or δ(x). The Dirac delta function is not a function in the classical sense, but it is a useful mathematical object that appears in many contexts, such as quantum mechanics and signal processing.



- Where S is the surface in k -space where $g(\vec{k}) = E_c(\vec{k}) - E_v(\vec{k}) - \hbar\omega = 0$, we obtain

$$\epsilon_2(\omega) = \frac{e^2}{(2\pi)^2 \varepsilon_0 m^2 \omega^2} \sum_{c,v} \iint_S \frac{|\vec{a} \cdot \vec{p}_{cv}(\vec{k})|^2}{|\vec{\nabla}_{\vec{k}} (E_c(\vec{k}) - E_v(\vec{k}))|} d\tilde{S}(\vec{k})$$

Joint Density of States

- Assuming that $p_{cv}(k)$ varies slowly with k on the surface in k -space on which $g(\vec{k}) = E_c(\vec{k}) - E_v(\vec{k}) - \hbar\omega$, such that $|\vec{a} \cdot \vec{p}_{cv}(k)|^2$ can be replaced by its average value gives;

$$\epsilon_2(\omega) \approx \frac{e^2}{(2\pi)^2 \varepsilon_0 m^2 \omega^2} \sum_{c,v} \left\langle \left| \vec{a} \cdot \vec{p}_{cv}(\vec{k}) \right|^2 \right\rangle \iint_S \frac{d\tilde{S}(\vec{k})}{\left| \vec{\nabla}_{\vec{k}} (E_c(\vec{k}) - E_v(\vec{k})) \right|_{E_c(\vec{k}) - E_v(\vec{k}) = \hbar\omega}}$$

- Here, the integral over S contains the Joint density of states (JDOS) - a measure of the number of pairs in valence and conduction bands which meet the energy conservation condition for a vertical transition;

$$\begin{aligned}J_{cv}(\omega) &= 2 \int_{\text{B.Z.}} \frac{d^3 \vec{k}}{(2\pi)^3} \delta(E_c(\vec{k}) - E_v(\vec{k}) - \hbar\omega), \\ &= \frac{2}{(2\pi)^3} \iint_S \frac{d\tilde{S}(\vec{k})}{\left| \vec{\nabla}_{\vec{k}} (E_c(\vec{k}) - E_v(\vec{k})) \right|_{E_c(\vec{k}) - E_v(\vec{k}) = \hbar\omega}}.\end{aligned}$$

- Assuming that $E_c(\vec{k}) - E_v(\vec{k}) = E_g + \frac{\hbar^2 k_x^2}{2m_g} + \frac{\hbar^2 k_y^2}{2m_h}$ in a semiconductor, the JDOS between a parabolic valence band maximum and a parabolic conduction minimum is the 3D density of states (could also derive it the way done last year);

$$J_{cv}(\omega) = \frac{1}{2\pi^2} \left(\frac{2m^*}{\hbar^2} \right)^{3/2} \sqrt{\hbar\omega - E_g}$$

- It is apparent from the above that JDOS is dominated by points where the valence and conduction bands are parallel; $\vec{\nabla}_{\vec{k}} (E_c(\vec{k}) - E_v(\vec{k})) = 0$.

- These are critical points, which lead to Van-Hove singularities.

- At these points, band separation energy may be written in terms of three orthogonal k -space coordinates, forming quadric surfaces;

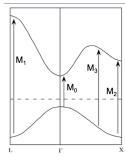
$$E_b(\vec{k}) = E_c(\vec{k}) - E_v(\vec{k}) = E_g + \alpha_1 k_1^2 + \alpha_2 k_2^2 + \alpha_3 k_3^2$$

- In 3D there are four types of critical points corresponding to the number of negative coefficients α_i .

- M_0 is a minimum in $E_b(\vec{k})$, where all three α_i are positive - ellipsoidal.

- M_1/M_2 are two types of saddle point in $E_b(\vec{k})$, where one or two α_i are negative - hyperboloids.

- M_3 is a maximum in $E_b(\vec{k})$ where all three α_i are negative - said in lecture.



- Each type of critical point has a characteristic frequency dependence of the JDOS near the critical point. The Van-Hove singularities are also sharper in one and two dimensions.

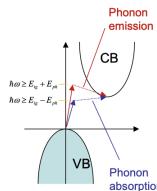
Indirect Bandgap Semiconductors

- In an indirect bandgap semiconductor, the minimum of the conduction band is at a different position in the Brillouin zone than the maximum of the valence band. Hence, a phonon is required for an optical transition in order to conserve momentum.
 - This can occur either via phonon emission or absorption. The absorption coefficient is then

$$\alpha(\omega) \propto \frac{(\hbar\omega - E_{ig} + E_{ph})^2}{e^{E_{ph}/k_B T} - 1} + \frac{(\hbar\omega - E_{ig} - E_{ph})^2}{1 - e^{-E_{ph}/k_B T}}$$

Phonon absorption Phonon emission
 $\hbar\omega \geq E_{ig} - E_{ph}$ $\hbar\omega \geq E_{ig} + E_{ph}$

- Here, E_{ph} is the energy of the phonon involved in the transition, E_{ig} is the energy of the indirect bandgap, $n_\eta = 1/(\exp(E_{ph}/k_B T) - 1)$ is the phonon occupation factor (proto probability of phonon absorption), and $n_\eta + 1 = 1/(1 - \exp(E_{ph}/k_B T))$ is the probability for photon emission from both stimulated and spontaneous emission processes.



- Plotting $\sqrt{\alpha(\omega)}$ shows an initial straight line where phonon absorption is observed ($\hbar\omega \geq E_{ig} - E_{ph}$), before a steeper gradient emerges when the phonon emission process is included at higher energy ($\hbar\omega \geq E_{ig} + E_{ph}$).
- Measuring the absorption spectrum allows for information about the photon spectrum of the crystal to be obtained.
- Indirect bandgap semiconductors are poor light emitters because indirect emission is slow and competes with non-radiative decay mechanisms. Hence, no silicon lasers.

L10/11 AQCMP - Strong Electron-Photon Interactions - Excitons

L9 AQCMP - Weak Electron-Photon Interactions

Bandstructure of III-V and group IV semiconductors

The effect of crystal momentum, k-p theory

Hybridisation of Atomic Orbitals
Spin-Orbit Interaction

Excitons

Mott-Wannier and Frenkel excitons

Wannier Excitons

Quantum Wells

Frenkel Excitons and Organic Semiconductors

Bose-Einstein Condensation in an Excitonic System

Excitons in Coupled Quantum Wells

Exciton Polaritons in Microcavities

L12 AQCMP - Electron-Phonon Interactions

Bandstructure of III-V and group IV semiconductors

- Common III-V semiconductors are GaAs and GaN. Common group IV semiconductors are Si and Ge.
 - The bandstructure for all of these around the Γ point contain a conduction electron (e) band minimum and three valence band maxima in close proximity; a heavy hole (hh) band with weaker dispersion, and light hole (lh) band with stronger dispersion and a split-off (so) band at an energy E_{so} below.
 - These features arise from the effect of crystal momentum, hybridisation of atomic orbitals in the crystal primitive basis and the spin-orbit interaction. Each of these contributions is now discussed in detail.

The effect of crystal momentum, k-p theory

- k-p theory allows band dispersion near the Γ point to be determined using energy gaps and optical matrix elements obtained from experiment.
- Considering the action of the Hamiltonian on Bloch state solutions gives

$$\begin{aligned} \hat{H} &= \frac{\vec{p}^2}{2m} + V(\vec{r}) \\ \implies \hat{H}\psi_{n,\vec{k}} &= E_{n,\vec{k}}\psi_{n,\vec{k}} \\ \implies \left(\frac{\vec{p}^2}{2m} + V(\vec{r})\right) e^{i\vec{k}\cdot\vec{r}} U_{n,\vec{k}}(\vec{r}) &= E_{n,\vec{k}} e^{i\vec{k}\cdot\vec{r}} U_{n,\vec{k}}(\vec{r}) \\ \implies \left(\frac{\vec{p}^2}{2m} + V(\vec{r})\right) U_{n,\vec{k}}(\vec{r}) + \underbrace{\left(\frac{(hk)^2}{2m} + \frac{\hbar}{2m} 2\vec{k} \cdot \vec{p}\right)}_{\hat{H}_1} U_{n,\vec{k}}(\vec{r}) &= E_{n,\vec{k}} U_{n,\vec{k}}(\vec{r}) \end{aligned}$$

- In the $\vec{k} \cdot \vec{p}$ method, \hat{H}_1 is considered as a perturbation to \hat{H} and dispersion relations at the Γ point are assumed to be minima, maxima or saddle-points.
- Using second-order perturbation theory,

$$E_{n,\vec{k}} = E_{n,0} + \langle U_{n,0} | \hat{H}_1 | U_{n,0} \rangle + \sum_{n' \neq n} \frac{|\langle U_{n',0} | \hat{H}_1 | U_{n,0} \rangle|^2}{E_{n,0} - E_{n',0}} + \dots$$

- The first order term gives

$$\begin{aligned}\langle U_{n,0} | \hat{H}_1 | U_{n,0} \rangle &= \frac{\hbar^2 k^2}{2m} \langle U_{n,0} | U_{n,0} \rangle + \frac{\hbar \vec{k}}{m} \cdot \langle U_{n,0} | \vec{p} | U_{n,0} \rangle \\ &= \frac{\hbar^2 k^2}{2m} + \frac{\hbar \vec{k}}{m} \cdot \langle U_{n,0} | \vec{p} | U_{n,0} \rangle\end{aligned}$$

- However, at a band minimum, maximum or saddlepoint,

$$\left\langle U_{n,0} \left| \frac{\vec{p}}{m} \right| U_{n,0} \right\rangle = \frac{1}{\hbar} \vec{\nabla}_{\vec{k}} E_n(\vec{k}) \Big|_{\vec{k}=0} = 0$$

- The second-order term gives matrix elements which may be determined from optical experiments;

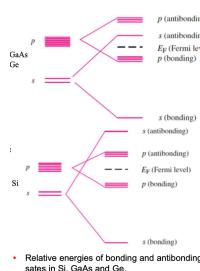
$$\begin{aligned}\langle U_{n',0} | \hat{H}_1 | U_{n,0} \rangle &= \left\langle U_{n',0} \left| \frac{\hbar^2 k^2}{2m} \right| U_{n,0} \right\rangle + \left\langle U_{n',0} \left| \frac{\hbar \vec{k} \cdot \vec{p}}{m} \right| U_{n,0} \right\rangle, \\ &= \frac{\hbar \vec{k}}{m} \cdot \langle U_{n',0} | \vec{p} | U_{n,0} \rangle, \quad \text{for } n' \neq n.\end{aligned}$$

- Combining the above gives the dispersion relation in each band n close to $k = 0$:

$$\begin{aligned}E_{n,\vec{k}} &\approx E_{n,0} + \frac{\hbar^2 k^2}{2m} + \frac{\hbar^2}{m^2} \sum_{n' \neq n} \frac{|\vec{k} \cdot \langle U_{n',0} | \vec{p} | U_{n,0} \rangle|^2}{E_{n,0} - E_{n',0}}, \\ &\approx E_{n,0} + \frac{\hbar^2 k^2}{2m_n^*}\end{aligned}$$

Hybridisation of Atomic Orbitals

- May write hopping matrix elements in terms of the two s and six p bands in the two-atom basis.



Spin-Orbit Interaction

- Using the spin-orbit hamiltonian;

$$\hat{H} = \hat{H}_p + \lambda \hat{\vec{L}} \cdot \hat{\vec{S}} = \hat{H}_p + \frac{\lambda}{2} (j^2 - \hat{L}^2 - \hat{S}^2)$$

- Defining the three degenerate bonding p states as

$$|p_{x,y,z}\rangle = \frac{1}{\sqrt{2}} (|p1_{x,y,z}\rangle + |p2_{x,y,z}\rangle)$$

- We may then create three degenerate eigenstates of L ;

$$\begin{aligned}|p^+\rangle &= -\frac{1}{\sqrt{2}} (|p_x\rangle + i|p_y\rangle), \\ |p^-\rangle &= \frac{1}{\sqrt{2}} (|p_x\rangle - i|p_y\rangle), \\ |p_z\rangle.\end{aligned}$$

- Including spin gives six basis states, which may then be used to find the matrix form of the hamiltonian. The eigenstates $|j, m_j\rangle$ and eigenenergies E_{j,m_j} are then;

$$\text{hh. } E_{3/2,+3/2} = E_p + \frac{\hbar^2}{2}; \quad |3/2, 3/2\rangle = |p^+\rangle |\uparrow\rangle,$$

$$E_{3/2,-3/2} = E_p + \frac{\hbar^2}{2}; \quad |3/2, -3/2\rangle = |p^-\rangle |\downarrow\rangle.$$

$$\text{lh. } E_{3/2,+1/2} = E_p + \frac{\lambda \hbar^2}{2}; \quad |3/2, 1/2\rangle = \sqrt{\frac{2}{3}} \left(\frac{1}{\sqrt{2}} |p^+\rangle |\downarrow\rangle + |p_z\rangle |\uparrow\rangle \right),$$

$$E_{3/2,-1/2} = E_p + \frac{\lambda \hbar^2}{2}; \quad |3/2, -1/2\rangle = \frac{1}{\sqrt{3}} \left(\sqrt{2} |p_z\rangle |\downarrow\rangle + |p^-\rangle |\uparrow\rangle \right).$$

$$\text{so. } E_{1/2,+1/2} = E_p - \lambda \hbar^2; \quad |1/2, 1/2\rangle = \sqrt{\frac{2}{3}} \left(-\frac{1}{\sqrt{2}} |p_z\rangle |\downarrow\rangle + |p^-\rangle |\uparrow\rangle \right),$$

$$E_{1/2,-1/2} = E_p - \lambda \hbar^2; \quad |1/2, -1/2\rangle = \frac{1}{\sqrt{3}} \left(-\sqrt{2} |p^+\rangle |\downarrow\rangle + |p_z\rangle |\uparrow\rangle \right).$$

- At $k = 0$ there is a four-fold degenerate $j = 3/2$ band and a doubly degenerate $j = 1/2$ band, which is split-off in energy by the spin-orbit interaction.

- $k \cdot p$ coupling lifts (gets rid of) the degeneracy of the $j = 3/2$ states away from $k = 0$, as the band dispersion depends on the wavefunctions, which are different.

- This results in a heavy hole $m_j = 3/2$ and a light hole $m_j = 1/2$ band.

- Band dispersion involves mixing with other bands; higher lying bands cause a negative curvature and lower lying bands cause a positive curvature.

Excitons

- At low temperatures, the formation of bound excitons causes distinct peaks just below the band edge in the GaAs absorption spectrum (note that the band gap varies with temperature)
- An exciton is a bound state of an electron and hole stabilised by their mutual Coulomb attraction. Hence, it has lower energy than the unbound electron and hole states.
 - In metals and doped semiconductors, the Coulomb interaction is strongly screened, so excitonic effects are not observed.
- Assuming the electron and hole are moving in a uniform background of dielectric constant $\epsilon \epsilon_0$ and the radius of exciton orbit is large compared to the lattice constant, then the energies of the bound states are given by a hydrogenic model - the Wannier equation;

$$\left(-\frac{\hbar^2}{2\mu} \nabla^2 - \frac{e^2}{4\pi\epsilon_0 r} \frac{1}{r} \right) F(\vec{r}) = \left(E_n - \frac{\hbar^2 K^2}{2M} - E_g \right) F(\vec{r})$$

where $\frac{1}{\mu} = \frac{1}{m_e^*} + \frac{1}{m_h^*}$, $M = m_e^* + m_h^*$, $\vec{K} = \vec{k}_e + \vec{k}_h$.

- Here, $F(\vec{r})$ is the exciton envelope function.

- This has eigenvalues

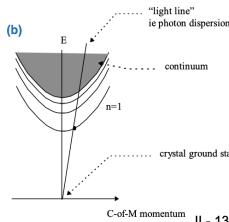
$$E_n = E_g + \frac{\hbar^2 K^2}{2M} - \frac{\mu}{m_e \epsilon^2} \frac{1}{n^2} \text{Ry}, \quad n = 1, 2, 3, \dots$$

Mott-Wannier and Frenkel excitons

- The hydrogenic model above gives an exciton radius of $r_n = \epsilon \frac{m_e}{\mu} a_B n^2$
- Mott-Wannier excitons are those where the exciton radius is large compared to the lattice constant.
 - They are well described by the hydrogenic model and are found in semiconductors with moderate screening and low effective mass (GaAs, Si)
- Frenkel excitons are those where the radius is comparable to the lattice constant.
 - They require a more molecular description and are found in low ϵ , high effective mass semiconductors, such as organic semiconductors or ionic crystals.

Wannier Excitons

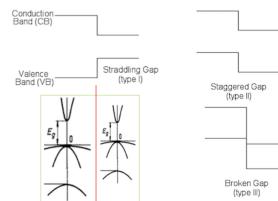
- Plotting the Wannier exciton energies against COM momentum (K) gives the figure below. Note the straight line is the dispersion relation of the incident photon.



- At points where the light-line intersects the exciton dispersion, excitons may be generated optically (conservation of energy and momentum are obeyed).
- In 3D, absorption above the band gap is strongly enhanced compared to this model, as the probability of finding an electron and hole in the same unit cell is enhanced by their Coulomb attraction.
- This enhances the absorption coefficient by the Sommerfeld enhancement factor.

Quantum Wells

- Different semiconductors have different electron affinities (conduction band energies) due to different band alignment. There are three primary semiconductor heterojunction arrangements depicted in the figure below.



- In a quantum well, the electronic states of electrons near the conduction band edge (and holes near the valence band edge) can be described by the particle-in-a-box model:

$$\left(-\frac{\hbar^2}{2m^*} \nabla^2 + V(z)\right) \psi(x, y, z) = E\psi(x, y, z)$$

- Using separation of variables $\psi(x, y, z) = X(x)Y(y)\phi(z)$ to solve this gives:

$$\begin{aligned} -\frac{dX}{dx^2} &= k_x^2 X \implies X = \exp(\pm ik_x x), \\ -\frac{dY}{dy^2} &= k_y^2 Y \implies Y = \exp(\pm ik_y y), \\ -\frac{\hbar^2}{2m^*} \frac{d\phi}{dz^2} + V(z)\phi &= E_z \phi, \text{ so for } E < V_0 \\ \phi(z) &= \phi_I = A \exp(\beta z) \text{ for } z \leq d/2, \\ &\implies \phi_{II} = C \exp(iqz) + D \exp(-iqz) \text{ for } |z| \leq d/2, \\ &= \phi_{III} = F \exp(-\beta z) \text{ for } z \geq -d/2, \end{aligned}$$

- Hence, we have plane waves parallel to the interface and bound states perpendicular to the interface.
- Note that if the effective mass is different in the well and barrier regions, then the current is constant across a boundary.
- Applying boundary conditions and normalisation produces a set of bound energy values E_n for the z-motion. Taking into account the x-y motion, the dispersion relation for electrons in each subband is

$$E_n(k_x, k_y) = E_n + \frac{\hbar^2}{2m^*} (k_x^2 + k_y^2) = E_n + \frac{\hbar^2}{2m^*} k_{\parallel}^2$$

- Each subband n has a parabolic dispersion relation in the plane of the film where the electrons are free to move in 2D
- The matrix element describing the strength of the optical absorption between occupied hole subbands and empty electron subbands is given by;

$$M_{i,f} = \vec{a} \cdot \langle \psi_f | \vec{p} | \psi_i \rangle = \int \psi_f^*(\vec{r}) (a_x p_x + a_y p_y + a_z p_z) \psi_i(\vec{r}) d^3 \vec{r}$$

where $\psi_i(\vec{r}) = \frac{1}{\sqrt{A}} e^{i\vec{k}_i \cdot \vec{r}} \phi_{n,h}(z)$ and $\psi_f(\vec{r}) = \frac{1}{\sqrt{A}} e^{i\vec{k}_f \cdot \vec{r}} \phi_{n',e}(z)$.

- Assuming incident light is normal to the plane of the quantum well, e.g. $\vec{a} = \hat{x}$, the overlap integrals give;

$$\begin{aligned} M_{n,n'} &= a_x \int \frac{1}{\sqrt{A}} e^{-i\vec{k}_f \cdot \vec{r}} \phi_{n',e}(z) \left(-i\hbar \frac{\partial}{\partial x} \right) \frac{1}{\sqrt{A}} e^{i\vec{k}_i \cdot \vec{r}} \phi_{n,h}(z) dx dy dz \\ &= a_x \hbar k_x \int \phi_{n',e}(z) \phi_{n,h}(z) dz. \end{aligned}$$

- As $\phi(z)$ has definite parity (even for odd n), this is only non-zero if both n and n' are either odd or even, with the strongest overlap where $n = n'$. In this case, the energy of transition is;

$$\begin{aligned} \hbar\omega &= E_{n,e}(\vec{k}) - E_{n,h}(\vec{k}) \\ &= E_g + E_n^h + E_n^e + \frac{\hbar^2 k_{\parallel}^2}{2m_h^*} + \frac{\hbar^2 k_{\parallel}^2}{2m_e^*} \\ &= E_g + E_n^h + E_n^e + \frac{\hbar^2 k_{\parallel}^2}{2\mu}. \end{aligned}$$

- Each intersubband transition from the n th hole to the n th electron subband contributes a 2D constant joint density of states such that

$$J_{n,n}(\omega) = \frac{2}{(2\pi)^2} \int d^3 \vec{k} \delta(E_{n,e}(\vec{k}) - E_{n,h}(\vec{k}) - \hbar\omega) = \frac{\mu}{\pi\hbar^2}$$

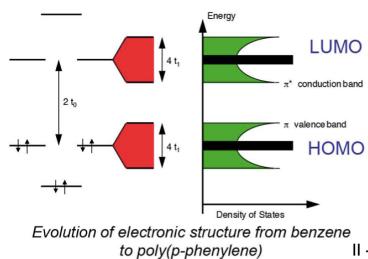
- Hence, the absorption spectrum of a quantum well exhibits a characteristic staircase shape. Here, two sets of transitions are observed - those from the n th heavy hole to the n th electron intersubband and similar transitions for the n th light hole.
- Below the step-like onset for a particular transitions, sharp excitonic absorption features are observed.
- In 2D, the Wannier exciton binding energies are

$$E_{n,n',\nu} = E_g + E_n^h + E_n^e - \frac{\mu}{m_e \varepsilon^2} \frac{1}{(\nu - \frac{1}{2})^2} Ry + \frac{\hbar^2 K_\parallel^2}{2M}$$

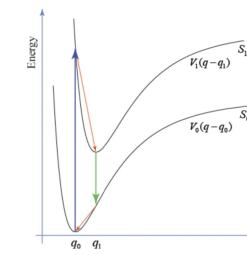
- Which are greater than the binding energies in 3D. However, the Sommerfeld enhancement factor accounting for Coulomb interaction increasing the probability to find an electron and hole in the same unit cell is less strong in 2D.
- In 2D, exciton radius sometimes approaches the Frenkel case.

Frenkel Excitons and Organic Semiconductors

- Organic semiconductors are conjugated (alternating single and double bond carbon backbone) organic molecules or polymers.
- This leaves their fourth electron in a singly-occupied p_z orbital perpendicular to the plane of the molecule defined by the σ bonds. These overlap, forming covalent π (bonding) and π^* (antibonding) states separated by an energy gap, making them transparent.
- Benzene molecules can form a linear chain of poly(*p*-phenylene), weakly bonded by van der Waals interactions, forming a band from each molecular orbital.
- The width of these bands depends on the strength of coupling between benzene molecules, and causes a narrowing in the HOMO LUMO bandgap into the visible range.



- Due to the weak van-der-Walls bonding and strong σ bonding, electron-hole pair excitations are normally localised on a single molecule. We therefore expect a high exciton binding energy (typically $\sim 0.5\text{eV}$, sufficient to invalidate the Wannier description).
 - Hence, excitons in organic semiconductors are good examples of Frenkel excitons.
- Electron-phonon coupling is strong in organic semiconductors.
 - Optical excitations cause organic conductors in ground state S_0 to change bond lengths and angles to form the first excited state S_1 . This is depicted in an energy vs configuration coordinate q diagram below ($V_1(q - q_0) \rightarrow V_1(q - q_1)$).

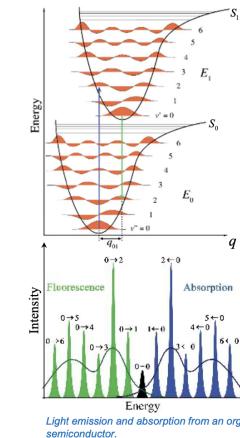


- Optical absorption / emission is fast compared to atomic motion, hence the vertical green and blue arrows. That the nuclei have the same position before and after transition is the Franck-Condon principle. Energy relaxation then occurs (red arrows).
- Absorption occurs between the lowest vibrational level $\psi_0^{(0)}(q)$ of the ground state S_0 to the vibrational states $\psi_n^{(1)}(q)$ of the excited state S_1 , giving rise to a sequence of vibrational replicas with intensities given by (blue intensity peaks below)

$$I_A(0 \rightarrow n) \propto \left| \int (\phi_n^{(1)}(q))^* \phi_0^{(0)}(q) dq \right|^2$$

- Emission occurs between the lowest vibrational level $\psi_0^{(1)}(q)$ of the excited state S_1 to the vibrational states $\psi_n^{(0)}(q)$ of the ground state S_0 , giving rise to an emission spectrum with intensities given by (green intensity peaks below)

$$I_E(0 \rightarrow n) \propto \left| \int (\phi_n^{(0)}(q))^* \phi_0^{(1)}(q) dq \right|^2$$



note how the blue and green arrows correspond to maxima in the intensity spectrum

- Strong excitonic effects in organic semiconductors can cause very high photoluminescence with efficiency around 100%.

- Note, photoluminescence is the process where a material absorbs photons at one energy and re-emits them at another energy.
- The emission colour can be tuned by selecting the chemical structure of the polymer, such as in OLEDs.

Bose-Einstein Condensation in an Excitonic System

- A Bose-Einstein condensate is a quantum state of matter in which a macroscopic number of particles occupy the system ground-state with $\epsilon = 0$ according to Bose-Einstein statistics.
- In 3D, the particle density of a Boson gas is

$$n = \frac{1}{V} \sum_{\vec{k}} \frac{1}{e^{(\epsilon_{\vec{k}} - \mu)/k_B T} - 1} = \int \frac{d^3 \vec{k}}{(2\pi)^3} \frac{1}{e^{(\epsilon_{\vec{k}} - \mu)/k_B T} - 1},$$

$$= \int_0^\infty \frac{1}{e^{(\epsilon - \mu)/k_B T} - 1} \rho(\epsilon) d\epsilon,$$

where $\rho(\epsilon) = \frac{m^{3/2}}{\sqrt{2\pi^2 \hbar^3}} \epsilon^{1/2}$.

■ This therefore determines the chemical potential of a system with given n and T .

- Using $z = \exp(\mu/k_B T)$ and $x = \epsilon/k_B T$ and $g_{3/2}(z) = \sum_{p=1}^{\infty} \frac{z^p}{p^{3/2}}$ by definition gives;

$$\begin{aligned} n &= \frac{m^{3/2}}{\sqrt{2}\pi^2 \hbar^3} (k_B T)^{3/2} \int_0^\infty \frac{ze^{-x}}{1 - ze^{-x}} x^{1/2} dx, \\ &= \frac{m^{3/2}}{\sqrt{2}\pi^2 \hbar^3} (k_B T)^{3/2} \left(\int_0^\infty \left(\sum_{p=1}^{\infty} z^p e^{-px} \right) x^{1/2} dx \right), \\ &= \frac{(mk_B T)^{3/2}}{\sqrt{2}\pi^2 \hbar^3} \sqrt{\pi} \sum_{p=1}^{\infty} \frac{z^p}{p^{3/2}}, \\ &= \frac{(mk_B T)^{3/2}}{2\pi^{3/2} \hbar^3} g_{3/2}(z), \\ &= \left(\frac{mk_B T}{2\pi \hbar^2} \right)^{3/2} g_{3/2}(z) = \left(\frac{mk_B T}{2\pi \hbar^2} \right)^{3/2} \left(z + \frac{z^2}{2^{3/2}} + \dots \right). \end{aligned}$$

■ Note that $g_{3/2}(z)$ is finite for $z \leq 1$, but diverges for $z > 1$.

- At high temperatures, $\mu < 0$ and $z \rightarrow 0$, so

$$\begin{aligned} g_{3/2}(z) &= n \left(\frac{2\pi \hbar^2}{mk_B T} \right)^{3/2} \approx z = e^{\mu/k_B T}, \\ \Rightarrow \mu &\approx -\frac{3}{2} k_B T \ln \left(\frac{mk_B T}{2\pi \hbar^2 n^{2/3}} \right) < 0. \end{aligned}$$

- At low temperatures, $\mu \rightarrow 0$ and $z \rightarrow 1$. Hence, the critical temperature for BEC is (as for $z > 1$, $g_{3/2}(z)$ diverges and $g_{3/2}(1) = 2.612$);

$$T_c = \frac{2\pi \hbar^2}{k_B m} \left(\frac{n}{2.612} \right)^{2/3} \propto n^{3/2}$$

- Below T_c , a finite fraction of particles condense to the $\epsilon = 0$ state, such that where n_0 is the number density of these particles,

$$\begin{aligned} n &= n_0 + \left(\frac{mk_B T}{2\pi \hbar^2} \right)^{3/2} g_{3/2}(1), \\ &= n_0 + \left(\frac{mk_B T}{2\pi \hbar^2} \right)^{3/2} \times 2.612, \\ \Rightarrow \frac{n_0}{n} &= 1 - \left(\frac{T}{T_c} \right)^{3/2}. \end{aligned}$$

■ As $\mu = 0$, a finite fraction of particles must be in the $\epsilon = 0$ state. Therefore, as this is all in the $V \rightarrow \infty$ limit, we must also have $N_0 \rightarrow \infty$.

- To realise a BEC in an excitonic system, the excitons must survive long enough to reach thermodynamic equilibrium. Hence, we wish to (check 19/11/24 14:25)

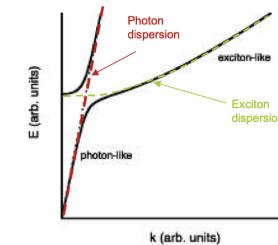
Excitons in Coupled Quantum Wells

- Applying an electric field to a coupled quantum well (two wells separated by a barrier) can separate the electrons and holes into adjacent wells.
- With a sufficiently thin barrier, their mutual Coulomb attraction is still active, but their wavefunctions no longer strongly overlap, decreasing recombination probability. This could be used to achieve thermalisation times.
- This is difficult to achieve in practice, as we must match electron / hole densities, have Coulomb effects dominate instead of kinetic effects, and achieve low disorder.

Exciton Polaritons in Microcavities

- A polariton is a coherent superposition of a photon and an exciton.
- Polaritons dispersion relations are photon-like for energies below the band gap and exciton-like for energies above the band gap.
- Where these dispersion relations cross, there is strong hybridisation between the photon and exciton states. This may be observed in microcavities where the optical path length is half-integer multiples of the emission wavelength, resulting in confined dispersion relations;

$$\omega = \frac{c}{N} |\vec{k}| = \frac{c}{N} \sqrt{k_{\parallel}^2 + k_{\perp}^2} = \frac{c}{N} \sqrt{k_{\parallel}^2 + \left(\frac{n\pi}{W} \right)^2}$$



- Polaritons are easier to study due to their lower effective mass, so they can be observed at higher T . However, they have very short lifetimes only sufficient to thermalise with other polaritons, not with the lattice itself.
- As incoming photon energy is increased, emission increasingly comes from states near $\vec{k}_{\parallel} = 0$.
- Measuring coherence of light from different positions of the condensate can provide the most convincing proof for the macroscopically coherent BEC polariton state.

L12 AQCMP - Electron-Phonon Interactions

L10/11 AQCMP - Strong Electron-Photon Interactions - Excitons

Manifestations of Electron-Phonon Interactions
 Hamiltonian for Electron-Phonon Coupling
 Boltzmann Theory
 Relaxation Time Approximation
 Scattering
 Phonon-Mediated Electron-Electron Interactions

Phonons in Crystals

- Denoting the positions of ions in a crystal around their equilibrium positions \vec{R}_n as $\vec{R}_n(t) = \vec{R}_n + \vec{s}_n$ and considering a Bravais lattice of N atoms of mass M each at a lattice site.
- The potential energy of this system is (noting the lack of first order term, as there is no forcing in equilibrium);

$$U_{\text{harm}} = \frac{1}{2} \sum_{n,m=1}^N \vec{s}_n \cdot \mathbf{D}(\vec{R}_n - \vec{R}_m) \cdot \vec{s}_m$$

- D is a matrix including the direct interactions between pairs of ions and the effect of changes in ion configuration from self-consistent changes in the ground-state electron density distribution.
- The crystal lattice Hamiltonian is then;

$$\hat{H} = \hat{T} + U_{\text{harm}} = \sum_{n=1}^N \frac{\vec{P}_n^2}{2M} + \frac{1}{2} \sum_{n,m=1}^N \vec{s}_n \cdot \mathbf{D}(\vec{R}_n - \vec{R}_m) \cdot \vec{s}_m \quad (1)$$

- Here, \vec{P}_n is the momentum conjugate to \vec{s}_n , and $D(\vec{R})$ are all real symmetric matrices obeying $D(\vec{R}) = D(-\vec{R})$ and $\sum_{\vec{R}} D(\vec{R}) = 0$.
- This Hamiltonian may be rewritten in terms of Bosonic annihilation and creation operators, so is a many-phonon Hamiltonian. Here, the operators take the form (from Ashcroft & Mermin C22), where each sum runs over all N Bravais lattice sites R_n ,

$$a_{\vec{q},\nu} = \frac{1}{\sqrt{N}} \sum_{n=1}^N e^{-i\vec{q} \cdot \vec{R}_n} \tilde{\epsilon}_{\nu}(\vec{q}) \cdot \left(\sqrt{\frac{M\omega_{\nu}(\vec{q})}{2\hbar}} \vec{s}_n + i\sqrt{\frac{1}{2\hbar M\omega_{\nu}(\vec{q})}} \vec{P}_n \right),$$

$$a_{\vec{q},\nu}^{\dagger} = \frac{1}{\sqrt{N}} \sum_{n=1}^N e^{i\vec{q} \cdot \vec{R}_n} \tilde{\epsilon}_{\nu}(\vec{q}) \cdot \left(\sqrt{\frac{M\omega_{\nu}(\vec{q})}{2\hbar}} \vec{s}_n - i\sqrt{\frac{1}{2\hbar M\omega_{\nu}(\vec{q})}} \vec{P}_n \right).$$

- Here, $\tilde{\epsilon}_{\nu}(\vec{q}) = (\epsilon_{\nu}^x(\vec{q}), \epsilon_{\nu}^y(\vec{q}), \epsilon_{\nu}^z(\vec{q}))$ for $\nu = 1, 2, 3$ are three orthogonal normal mode polarisation vectors corresponding to $\omega_{\nu}(\vec{q})$.
- Using the commutation rules for position and momentum $[s_n^i, P_m^j] = i\hbar\delta_{n,m}\delta_{i,j}$ and $[s_n^i, s_m^j] = [P_n^i, P_m^j] = 0$, the many-boson commutation rules may be derived; $[a_{\vec{q},\nu}, a_{\vec{q}',\nu'}^{\dagger}] = \delta_{\vec{q},\vec{q}'}\delta_{\nu,\nu'}$ and $[a_{\vec{q},\nu}, a_{\vec{q}',\nu'}] = [a_{\vec{q},\nu}^{\dagger}, a_{\vec{q}',\nu'}] = 0$.
- These operators increase or decrease the occupation number of a single-phonon state i .
- Using this to rewrite (1) gives;

$$\hat{H} = \sum_{\vec{q} \in BZ} \sum_{\nu=1}^3 \hbar\omega_{\nu}(\vec{q}) \left(a_{\vec{q},\nu}^{\dagger} a_{\vec{q},\nu} + \frac{1}{2} \right)$$

- This represents $3N$ independent harmonic oscillators, one for each wavevector \vec{q} in the Brillouin zone and one for each polarisation ν .
- The energy of the vibrational state of a crystal is therefore

$$E = \sum_{\vec{q},\nu} \hbar\omega_{\nu}(\vec{q}) \left(n_{\vec{q},\nu} + \frac{1}{2} \right)$$

- Substituting $\vec{s}_n(\vec{R}_n, t) = \tilde{\epsilon}(\vec{q}) e^{i(\vec{q} \cdot \vec{R}_n - \omega t)}$ into the lattice equations of motion $M \frac{d^2 \vec{s}_n}{dt^2} = -\vec{\nabla}_n U_{\text{harm}} = -\sum_m D(\vec{R}_n - \vec{R}_m) \cdot \vec{s}_m$ gives;

$$\tilde{D}(\vec{q}) \tilde{\epsilon}_{\nu}(\vec{q}) = M\omega_{\nu}^2(\vec{q}) \tilde{\epsilon}_{\nu}(\vec{q})$$

where $\tilde{D}(\vec{q}) = \sum_{n=1}^N D(\vec{R}_n) e^{-i\vec{q} \cdot \vec{R}_n}$ is the dynamical matrix

- $\tilde{D}(\vec{q})$ is 3×3 , real-symmetric and positive-definite, so has positive eigenvalues (phonon frequencies) and orthonormal polarisation vectors.

- For a Bravais lattice with a p -atom basis (number of atoms per lattice point), each \vec{q} has $3p$ phonon modes.
- Three branches are acoustic with $\lim_{q \rightarrow 0} \omega_{\nu}(\vec{q}) \rightarrow c_{\nu}(\vec{q})q$. These correspond to the three translational degrees of freedom. The atoms move in-phase at $\vec{q} \sim 0$.
- The other $3(p-1)$ branches are optical with $\lim_{q \rightarrow 0} \omega_{\nu}(\vec{q}) > 0$, corresponding to the number of vibrational degrees of freedom. The atoms move out-of-phase at $\vec{q} \sim 0$.
 - The phonon dispersion can be measured by neutron scattering, as neutrons interact strongly with the nucleus.
 - The specific heat capacity of a crystal also has a significant contribution from phonons;

$$C_V = \frac{\partial}{\partial T} \sum_{\nu} \int_{\text{1st BZ}} \frac{d^3 \vec{k}}{(2\pi)^3} \frac{\hbar\omega_{\nu}(\vec{k})}{e^{\hbar\omega_{\nu}(\vec{k})/k_B T} - 1} \propto T^3 \quad \text{as } T \rightarrow 0.$$

Manifestations of Electron-Phonon Interactions

- The dominant contribution to resistivity in common metals is electron-phonon interaction.
- Define the Debye temperature as $\hbar\Theta_D = k_B\Theta_D$ where ω_D is the highest frequency phonon mode. The temperature dependence of resistivity from electron-phonon scattering follows;

$$T \gg \Theta_D : \rho(T) \propto T,$$

$$T \ll \Theta_D : \rho(T) = \rho_0 (1 + AT^5 + \dots).$$

- Electron-phonon scattering is important in relaxation processes bringing a solid into thermal equilibrium. However, at lower temperatures, impurity scattering results in temperature-independent resistivity.
- By considering a second order process involving emission and subsequent absorption of a phonon, phonons may mediate an attractive interaction between pairs of electrons within the Debye energy of the Fermi surface of a metal.
- $H' = \sum_{\vec{k}, \vec{k}', \vec{q}} |M_{\vec{q}}|^2 \frac{\hbar\omega_{\vec{q}}}{(\epsilon_{\vec{k}} - \epsilon_{\vec{k}-\vec{q}})^2 - (\hbar\omega_{\vec{q}})^2} C_{\vec{k}+\vec{q}}^{\dagger} C_{\vec{k}-\vec{q}}^{\dagger} C_{\vec{k}'} C_{\vec{k}'-\vec{q}}$
 - This interaction causes Cooper pair formation, promoting conventional superconductivity.
 - Using hydrogen-based materials, conventional superconductivity can be seen at room temperature.
- In some materials, electron-phonon interactions are sufficiently strong to distort / polarise the surrounding lattice.
 - The electron plus its polarisation cloud is a polaron (a quasiparticle).
 - Below a critical velocity, a polaron travelling through a lattice remains intact. However, above this critical velocity, it emits longitudinal phonons.
 - There are also distinctions between large and small polarons, for which the spatial extent of the nuclear distortion is either large or similar compared to the lattice constant.

Hamiltonian for Electron-Phonon Coupling

- Considering a monatomic Bravais lattice, the electron-phonon interaction arises principally from the following term of the Hamiltonian;

$$\begin{aligned}\hat{H}_{\text{el-ion}} &= - \sum_{m=1}^N \sum_{n=1}^N \frac{Ze^2}{4\pi\varepsilon_0 |\vec{r}_m - \vec{R}_n|}, \\ &= \sum_{m=1}^N \sum_{n=1}^N V_{\text{ion}}(\vec{r}_m - \vec{R}_n(t)).\end{aligned}$$

Using $\vec{R}_n(t) = \vec{R}_n + \vec{s}_n(t)$ and assuming displacements are small, we get;

$$\begin{aligned}\hat{H}_{\text{el-ion}} &= \sum_{m=1}^N \sum_{n=1}^N V_{\text{ion}}(\vec{r}_m - \vec{R}_n - \vec{s}_n(t)) \\ &= \sum_{m=1}^N \sum_{n=1}^N (V_{\text{ion}}(\vec{r}_m - \vec{R}_n) - \vec{s}_n(t) \cdot \nabla_{\vec{R}_n} V_{\text{ion}}(\vec{r}_m - \vec{R}_n))\end{aligned}$$

This is the rigid-ion model and assumes that $V_{\text{ion}}(\vec{r})$ depends only on distance between the centre of the electron and the centre of the ion.

Inverting $a_{\vec{q},\nu}$ and $a_{\vec{q},\nu}^\dagger$, it may be shown that

$$\vec{s}_n = \frac{1}{\sqrt{N}} \sum_{\vec{q},\nu} \left(\frac{\hbar}{2M\omega_\nu(\vec{q})} \right)^{1/2} (a_{\vec{q},\nu} + a_{-\vec{q},\nu}^\dagger) e^{i\vec{q} \cdot \vec{R}_n} \tilde{\varepsilon}_\nu(\vec{q}),$$

It is then possible to rewrite $\hat{H}_{\text{el-ion}}$ as (neglecting the stationary part which determines ground-state properties);

$$\begin{aligned}\hat{H}_{\text{el-ph}} &= \sum_{m,n=1}^N \vec{s}_n(t) \cdot \nabla V_{\text{ion}}(\vec{r}_m - \vec{R}_n) \\ &= \sum_{m,n=1}^N \frac{1}{\sqrt{N}} \sum_{\vec{q},\nu} \sqrt{\frac{\hbar}{2M\omega_\nu(\vec{q})}} (a_{\vec{q},\nu} + a_{-\vec{q},\nu}^\dagger) e^{i\vec{q} \cdot \vec{R}_n} \tilde{\varepsilon}_\nu(\vec{q}) \cdot \nabla V_{\text{ion}}(\vec{r}_m - \vec{R}_n) \\ &= \sum_{m=1}^N h(\vec{r}_m).\end{aligned}$$

Here, $\hat{H} = \sum_{k=1}^N h(\vec{x}_k)$.

In second quantised form, $\hat{H} = \sum_{i,j} \langle \psi_i | h | \psi_j \rangle c_i^\dagger c_j$, so this becomes

$$\begin{aligned}\hat{H}_{\text{el-ph}} &= \sum_{\vec{k},\vec{k}',\lambda} \langle \vec{k}' | h(\vec{r}) | \vec{k} \rangle c_{\vec{k},\lambda}^\dagger c_{\vec{k},\lambda}, \\ &= \sum_{\vec{k},\vec{k}',\lambda} \sum_{n=1}^N \left(\frac{\hbar}{2MN\omega_\nu(\vec{q})} \right)^{1/2} (a_{\vec{q},\nu} + a_{-\vec{q},\nu}^\dagger) e^{i\vec{q} \cdot \vec{R}_n} \tilde{\varepsilon}_\nu(\vec{q}) \cdot \langle \vec{k}' | \nabla V_{\text{ion}}(\vec{r} - \vec{R}_n) | \vec{k} \rangle c_{\vec{k},\lambda}^\dagger c_{\vec{k},\lambda}, \\ &= \sum_{\vec{k},\vec{k}',\lambda} \left(\frac{\hbar}{2MN\omega_\nu(\vec{q})} \right)^{1/2} \tilde{\varepsilon}_\nu(\vec{q}) \cdot \sum_{n=1}^N e^{i\vec{q} \cdot \vec{R}_n} \langle \vec{k}' | \nabla V_{\text{ion}}(\vec{r} - \vec{R}_n) | \vec{k} \rangle (a_{\vec{q},\nu} + a_{-\vec{q},\nu}^\dagger) c_{\vec{k}',\lambda}^\dagger c_{\vec{k},\lambda}, \\ &= \sum_{\vec{k},\vec{k}',\lambda} M_{\vec{q},\nu}(\vec{k},\vec{k}') (a_{\vec{q},\nu} + a_{-\vec{q},\nu}^\dagger) c_{\vec{k}',\lambda}^\dagger c_{\vec{k},\lambda}.\end{aligned}$$

Note that here the spin of the electron is conserved, as $V_{\text{ion}}(\vec{r})$ is spin independent, and $c_{\vec{k},\lambda}^\dagger$ creates an electron in a Bloch state with wavevector \vec{k} and spin λ .

- The atomic form factor associated with a single ion potential $V_{\text{ion}}(\vec{r})$

$$V_a(\vec{q}) = \frac{N}{V} \int e^{-i\vec{q} \cdot \vec{r}} V_{\text{ion}}(\vec{r}) d^3 r$$

Inverting this relationship gives

$$\begin{aligned}V_{\text{ion}}(\vec{r}) &= \frac{1}{N} \sum_{\vec{q}} e^{i\vec{q} \cdot \vec{r}} V_a(\vec{q}) \\ \implies \langle \vec{k}' | \nabla V_{\text{ion}}(\vec{r} - \vec{R}_n) | \vec{k} \rangle &= \frac{1}{N} \sum_{\vec{q}} V_a(\vec{q}) i\vec{q} e^{-i\vec{q} \cdot \vec{R}_n} \langle \vec{k}' | e^{i\vec{q} \cdot \vec{r}} | \vec{k} \rangle.\end{aligned}$$

After some maths and assuming Bloch states (L12 p19), we find that;

$$\begin{aligned}M_{\vec{q},\nu}(\vec{k},\vec{k}') &= \left(\frac{\hbar}{2MN\omega_\nu(\vec{q})} \right)^{1/2} \tilde{\varepsilon}_\nu(\vec{q}) \cdot \sum_{n=1}^N e^{i\vec{q} \cdot \vec{R}_n} \langle \vec{k}' | \nabla V_{\text{ion}}(\vec{r} - \vec{R}_n) | \vec{k} \rangle, \\ &= i \sum_{\vec{G}} \left(\frac{\hbar}{2MN\omega_\nu(\vec{q})} \right)^{1/2} \tilde{\varepsilon}_\nu(\vec{q}) \cdot (\vec{q} + \vec{G}) V_a(\vec{q} + \vec{G}) \Delta_{\vec{k},\vec{k}'} \delta_{\vec{k},\vec{k}' + \vec{q} + \vec{G}}.\end{aligned}$$

Hence, $\hat{H}_{\text{el-ph}}$ is

$$\hat{H}_{\text{el-ph}} = \sum_{\vec{k},\lambda} \sum_{\vec{q},\nu} \left(\frac{\hbar}{2MN\omega_\nu(\vec{q})} \right)^{1/2} i \sum_{\vec{G}} \tilde{\varepsilon}_\nu(\vec{q}) \cdot (\vec{q} + \vec{G}) V_a(\vec{q} + \vec{G}) \Delta_{\vec{k} + \vec{q},\vec{k}} (a_{\vec{q},\nu}^\dagger + a_{-\vec{q},\nu}) c_{\vec{k} + \vec{q} + \vec{G},\lambda}^\dagger c_{\vec{k},\lambda}$$

This describes scattering processes where an electron scatters from state \vec{k} to $\vec{k} + \vec{q} + \vec{G}$, either through absorption of a phonon with wavevector \vec{q} or emission of a phonon with wavevector $-\vec{q}$.

For $\vec{G} = 0$, we have normal (N) processes, for $\vec{G} \neq 0$, we have Umklapp (U) processes, where \vec{G} brings $\vec{q} + \vec{k} + \vec{G}$ back into the first Brillouin zone.

Along high-symmetry directions, longitudinal ($\vec{q} \parallel \epsilon_l(\vec{q})$) can cause normal scattering, but transverse phonons cannot.

We therefore obtain the complete Hamiltonian for a coupled electron-phonon system (the Fröhlich Hamiltonian); (where do first two terms come from?)

$$\hat{H} = \sum_{\vec{k},\lambda} \epsilon_{\vec{k},\lambda}^\dagger c_{\vec{k},\lambda} + \sum_{\vec{q},\nu} \hbar\omega_{\vec{q},\nu} a_{\vec{q},\nu}^\dagger a_{\vec{q},\nu} + \sum_{\vec{k},\lambda} \sum_{\vec{q},\nu} M_{\vec{q},\nu}(\vec{k},\vec{k}') (a_{-\vec{q},\nu}^\dagger + a_{\vec{q},\nu}) c_{\vec{k} + \vec{q} + \vec{G},\lambda}^\dagger c_{\vec{k},\lambda}$$

Boltzmann Theory

Even for a perfectly crystalline material, resistivity is non-zero due to thermal distortions of the lattice, which act as scattering centres.

Boltzmann Transport Theory uses a distribution function $f(\vec{r}, \vec{k}, t)$ to describe an electron system. For a homogenous, isolated system, f would be the Fermi-Dirac distribution.

By framing the theory using Landau Fermi theory, it is possible to include quasiparticle-quasiparticle interactions using the local quasiparticle energy $\tilde{\epsilon}$. However, here we assume these interactions are weak and can be ignored. We also assume the phonon distribution is in equilibrium.

Each electron has an associated well-defined position, wavevector and band index, despite that in QM, \vec{k} and \vec{r} are conjugate variables, and this is incompatible with the extended nature of system Bloch states.

Nevertheless, a semiclassical electron state (wavepacket) may be constructed with a superposition of Bloch states around \vec{k} ;

$$\psi_n(\vec{r}, t) = \sum_{\vec{k}'} g(\vec{k}') \psi_{n,\vec{k}'}(\vec{r}) \exp \left(-i \frac{\epsilon_n(\vec{k}') t}{\hbar} \right)$$

where $g(\vec{k}') = 0$ if $|\vec{k}' - \vec{k}| > \Delta k$.

- For a group of electrons in a volume element d^3rd^3k in phase space, Liouville's theorem says that the equations of motion preserve the density of states in phase space, so $\frac{df}{dt} = 0$.
- Where electrons are either removed or injected into the volume element, such as by collisions, charged impurities, phonons or other scattering processes, f may change, giving the **Boltzmann equation**;

$$\frac{df}{dt} = \frac{\partial f}{\partial t} + \frac{d\vec{k}}{dt} \cdot \nabla_{\vec{k}}f + \frac{d\vec{r}}{dt} \cdot \nabla_{\vec{r}}f = \frac{\partial f}{\partial t} \Big|_{\text{collisions}}$$

- The time dependence on \vec{r} and \vec{k} can occur for example by a change of temperature from an external heat flow. The equations of motion (from Ehrenfest's theorem) then give

$$\begin{aligned}\frac{d\vec{r}}{dt} &= \vec{v}_{\vec{k}}(\vec{k}) = \frac{1}{\hbar} \nabla_{\vec{k}}\epsilon_n(\vec{k}), \\ \hbar \frac{d\vec{k}}{dt} &= -e \left(\vec{E}(\vec{r}, t) + \vec{v}_{\vec{k}} \times \vec{B}(\vec{r}, t) \right)\end{aligned}$$

Relaxation Time Approximation

- Assuming that a system subjected to a weak perturbation which is then allowed to relax returns to the ground state $f_0(\vec{k}, \vec{r})$ exponentially with a relaxation time $\tau(\epsilon_{\vec{k}}) = \tau_k$, with;

$$\frac{df}{dt} = \frac{\partial f}{\partial t} \Big|_{\text{coll}} = -\frac{f - f_0}{\tau(\epsilon_{\vec{k}})}$$

- This is the relaxation-time approximation and is a good approximation where $|f - f_0| \ll |f_0|$
- For a homogeneous system subject to $\vec{E}(t) = \vec{E}_0 e^{-i\omega t}$, the Boltzmann equation (in the relaxation-time approximation) takes the form;

$$\begin{aligned}\frac{\partial f}{\partial t} + \frac{1}{\hbar} \nabla_{\vec{k}}f \cdot (-e\vec{E}) &= -\frac{f - f_0}{\tau_k} \\ \text{keeping only linear } E \text{ terms and setting } f &= f_0 + f_1 \\ \implies \frac{1}{\hbar} \vec{v}_{\vec{k}}f_0 \cdot (-e\vec{E}) + \frac{\partial f_1}{\partial t} &= -\frac{f_1}{\tau_k}\end{aligned}$$

- Assuming $f_1(\vec{r}, \vec{k}, t) = \Phi(\vec{k})e^{-i\omega t}$ allows $\Phi(\vec{k})$ to be found as;

$$\begin{aligned}\Phi(\vec{k}) &= \frac{e\tau_k \vec{v}_{\vec{k}} \cdot \vec{E}_0}{1 - i\tau_k\omega} \frac{\partial f_0}{\partial \epsilon} \\ \implies f_1 &= \frac{\partial f_0}{\partial \epsilon} \frac{e\tau_k \vec{k} \cdot \vec{E}}{1 - i\tau_k\omega} = A(\omega, k)\vec{k} \cdot \vec{E}(2)\end{aligned}$$

- Using the above it is then possible to derive the ac conductivity of a metal in terms of its relaxation time;

$$\vec{J} = -\frac{2e}{(2\pi)^3} \int d^3\vec{k} \vec{v}_{\vec{k}} f_1 = \frac{2e^2}{(2\pi)^3} \int d^3\vec{k} \tau_k \left(-\frac{\partial f_0}{\partial \epsilon} \right) \vec{v}_{\vec{k}} \frac{\vec{v}_{\vec{k}} \cdot \vec{E}}{1 - i\tau_k\omega}$$

- As $\vec{v}_{\vec{k}} \vec{v}_{\vec{k}} \cdot \vec{E} = v_{\vec{k}} \otimes v_{\vec{k}} \vec{E}$, this obeys Ohm's law $\vec{J} = \sigma(\omega) \vec{E}$.
- In the DC limit ($\omega \rightarrow 0$) in an isotropic system at temperatures far below the Fermi temperature ($T \ll T_F$), this reduces to the Drude result with;

$$\sigma = \frac{ne^2\tau}{m}, \quad \rho = \frac{m}{ne^2\tau}.$$

Scattering

- For scattering from a static impurity potential, the collision integral is;

$$\begin{aligned}\frac{\partial f}{\partial t} \Big|_{\text{coll}} &= -\frac{1}{(2\pi)^3} \int d^3\vec{k}' \left(W(\vec{k}, \vec{k}')f(\vec{k}) (1 - f(\vec{k}')) - W(\vec{k}', \vec{k})f(\vec{k}') (1 - f(\vec{k})) \right) \\ &= -\frac{1}{(2\pi)^3} \int d^3\vec{k}' W(\vec{k}, \vec{k}') \left(f(\vec{k}) - f(\vec{k}') \right) \quad \text{where } W(\vec{k}, \vec{k}') = W(\vec{k}', \vec{k})\end{aligned}$$

- Using equation (2) in the elastic scattering case with $k = k'$ gives

$$\begin{aligned}f(\vec{k}) &= f_0(\vec{k}) + A(\vec{k})\vec{k} \cdot \vec{E} - f_0(\vec{k}) + A(\vec{k})\vec{k}' \cdot \vec{E} \\ \implies f(\vec{k}) - f(\vec{k}') &= A(\vec{k})(\vec{k} - \vec{k}') \cdot \vec{E}\end{aligned}$$

- After some maths (defining a coordinate system where $\vec{k} \parallel \hat{z}$), we then find

$$\frac{1}{\tau(\epsilon_{\vec{k}})} = \frac{1}{(2\pi)^3} \int d^3\vec{k}' W(\vec{k}, \vec{k}') (1 - \cos(\theta')) \quad (3)$$

- Note that forward scattering does not contribute to relaxation (?) and that relaxation time is temperature independent if the scattering rate $W(\vec{k}, \vec{k}')$ is temperature independent.

- Considering a metal with a density n_{imp} of point scatters with charge Ze . Within the Thomas-Fermi approximation, each gives a Yukawa potential;

$$\hat{V}(\vec{r}) = \frac{Ze^2}{4\pi\epsilon_0} \frac{e^{-q_{\text{TF}}r}}{r}, \quad \text{where } q_{\text{TF}}^2 = \frac{1}{\pi^2} \frac{me^2}{\hbar^2\epsilon_0} k_F$$

- Using plane waves $\langle \vec{r} | \vec{k} \rangle = \exp(i\vec{k} \cdot \vec{r}) / \sqrt{V}$ gives

$$\langle \vec{k} | \hat{V} | \vec{k} + \vec{q} \rangle = \frac{1}{V} \frac{e^2}{4\pi\epsilon_0} \int d^3r \frac{e^{-q_{\text{TF}}r}}{r} e^{i\vec{q} \cdot \vec{r}} = \frac{1}{V} \frac{e^2}{4\pi\epsilon_0} \frac{4\pi}{q^2 + q_{\text{TF}}^2}.$$

- Using Fermi's Golden rule gives

$$W(\vec{k}, \vec{k} + \vec{q}) = \frac{2\pi}{\hbar} V N_{\text{imp}} \left| \langle \vec{k} | \hat{V} | \vec{k} + \vec{q} \rangle \right|^2 \delta(\epsilon_{\vec{k}+\vec{q}} - \epsilon_{\vec{k}})$$

- Then using the relaxation rate (equation 3), assuming temperatures are well below the Fermi temperature such that all scattering occurs close to the Fermi surface ($|\vec{k} + \vec{q}| = |\vec{k}| = k_F$), and the identity;

$$\int_V \delta(g(\vec{k})) F(\vec{k}) d^3\vec{k} = \iint_{g(\vec{k})=0} \frac{F(\vec{k})}{|\vec{v}_{\vec{k}} g(\vec{k})|} d\tilde{S}(\vec{k}),$$

- Finally shows that $\tau(\epsilon_{\vec{k}}) = \tau$ is not dependent on \vec{k}

$$\frac{1}{\tau(\epsilon_{\vec{k}})} = \frac{2\pi}{\hbar} \left(\frac{Ze^2}{\epsilon_0} \right)^2 n_{\text{imp}} \frac{1}{(2\pi)^3} \frac{m}{\hbar^2 k_F} \times \int_0^{2\pi} d\phi' \int_0^{2k_F} dq q \left(\frac{1}{q^2 + q_{\text{TF}}^2} \right)^2 (1 - \cos(\theta')).$$

- With some more maths, it is shown that

$$\frac{1}{\tau} = \left(\frac{Ze^2}{\epsilon_0} \right)^2 n_{\text{imp}} \frac{1}{4\pi\hbar^3 k_F^3} \frac{m}{\hbar^2 k_F} \times \frac{1}{2} \left(-1 + \frac{1}{1 + (2k_F/q_{\text{TF}})^2} + \log(1 + (2k_F/q_{\text{TF}})^2) \right),$$

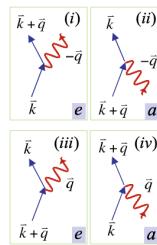
- Hence, for strong screening where $2k_F \ll q_{\text{TF}}$, $\frac{1}{\tau}$ is temperature independent. It does, however depend on the density of states $g_V(\epsilon_F)$)

$$\begin{aligned}\frac{1}{\tau} &\approx \left(\frac{Ze^2}{\epsilon_0} \right)^2 n_{\text{imp}} \frac{1}{4\pi\hbar^3 k_F^3} \frac{m}{\hbar^2 k_F} \cdot 4 \left(\frac{2k_F}{q_{\text{TF}}} \right)^4, \\ &= \frac{\pi}{\hbar} \left(\frac{Ze^2}{\epsilon_0 q_{\text{TF}}^2} \right)^2 n_{\text{imp}} g_V(\epsilon_F).\end{aligned}$$

- When considering electron-phonon interactions, we use , which in a simplified form is;

$$\hat{H}_{\text{el-ph}} = i \sum_{\mathbf{k}, \mathbf{q}, \lambda} g(\mathbf{q}) (a_{-\mathbf{q}}^\dagger + a_{\mathbf{q}}) c_{\mathbf{k}+\mathbf{q}, \lambda}^\dagger c_{\mathbf{k}, \lambda}, \quad \text{where} \quad g(\mathbf{q}) = q V_a(\mathbf{q}) \sqrt{\frac{\hbar}{2NM\omega_{\mathbf{q}}}}.$$

- There are four possible emission and absorption events, which may be represented in matrix form (below)



- Using Fermi's Golden rule and assuming spin degeneracy, the matrix elements imply that

$$\left. \frac{\partial f}{\partial t} \right|_{\text{coll}} = -\frac{2\pi}{\hbar} \sum_{\mathbf{q}} |g(\mathbf{q})|^2 \left[((N_{-\mathbf{q}} + 1)f(\mathbf{k})(1 - f(\mathbf{k} + \mathbf{q})) - N_{-\mathbf{q}}f(\mathbf{k} + \mathbf{q})(1 - f(\mathbf{k}))) \delta(\epsilon_{\mathbf{k}+\mathbf{q}} - \epsilon_{\mathbf{k}} + \hbar\omega_{-\mathbf{q}}) \right. \\ \left. - ((N_{\mathbf{q}} + 1)f(\mathbf{k} + \mathbf{q})(1 - f(\mathbf{k})) - N_{\mathbf{q}}f(\mathbf{k})(1 - f(\mathbf{k} + \mathbf{q}))) \delta(\epsilon_{\mathbf{k}+\mathbf{q}} - \epsilon_{\mathbf{k}} - \hbar\omega_{\mathbf{q}}) \right].$$

- Assuming low phonon energy, such that $\epsilon_{\vec{k}+\vec{q}} \approx \epsilon_{\vec{k}}$, assuming there is no spontaneous emission to remove the $+1$ in $N_{\pm\vec{q}} + 1$ and using $N_{\mathbf{q}} = N(\omega_{\mathbf{q}}) = \frac{1}{(e^{\hbar\omega_{\mathbf{q}}/k_B T} - 1)} = N_{-\mathbf{q}}$ finally gives;

$$\left. \frac{\partial f}{\partial t} \right|_{\text{coeff}} = -\frac{1}{(2\pi)^3} \int d^3 \vec{q} W(\vec{k}, \vec{k} + \vec{q}) (f(\vec{k}) - f(\vec{k} + \vec{q}))$$

where $W(\vec{k}, \vec{k} + \vec{q}) = \frac{4\pi}{\hbar} |g(\vec{q})|^2 N(\omega_{\vec{q}}) \delta(\epsilon_{\vec{k}+\vec{q}} - \epsilon_{\vec{k}})$

- It is conventional to parameterise $g(\vec{q})$ by $|g(\vec{q})|^2 = \gamma \hbar \omega_{\vec{q}} / 2g_V(\epsilon_F)$ where γ is the electron-phonon coupling constant. Usually $\gamma < 1$ in metals.

- Using equation (3) therefore gives

$$\frac{1}{\tau(\epsilon_{\vec{k}})} = \frac{2\pi}{\hbar} \frac{\gamma}{g_V(\epsilon_F)} \int \frac{d^3 \vec{q}}{(2\pi)^3} \hbar \omega_{\vec{q}} N(\omega_{\vec{q}}) (1 - \cos(\theta')) \delta(\epsilon_{\vec{k}+\vec{q}} - \epsilon_{\vec{k}})$$

- After lots of maths (slide 29), we find that

$$\frac{1}{\tau} = \begin{cases} 6\zeta(5)\gamma\pi^{\frac{k_B\Theta_D}{\hbar}}\left(\frac{T}{\Theta_D}\right)^5, & T \ll \Theta_D, \\ \gamma\pi^{\frac{k_B\Theta_D}{\hbar}}\left(\frac{T}{\Theta_D}\right), & T \gg \Theta_D. \end{cases}$$

where Riemann Zeta, $24\zeta(5) = \int_0^\infty \frac{y^4 dy}{e^y - 1}$

- Combining the results for Drude resistivity, point charge scattering and electron-phonon scattering results in the expected resistivity dependences;

$$T \gg \Theta_D : \rho(T) \propto T, \\ T \ll \Theta_D : \rho(T) = \rho_0 (1 + AT^5 + \dots).$$

- Boltzmann theory has many limitations;

- Relaxation time should really include contributions from all relevant scattering mechanisms.

- Wavelength of applied fields should be much larger than the lattice constant, or well-defined packets cannot be formed.
- Mean-free-path between two scattering events must be much greater than the Fermi wavelength, or scattering between wavepackets cannot be defined.
- Scattering potentials must be present with minimal strength, as we require an efficient relaxation mechanism.
 - This theory cannot apply to the free-electron model, as there is no way to limit the energy an electron can gain from a field.
- It may only be applied to phenomena in systems with dimensions larger than the de Broglie wavelength of the electrons, as quantum interference effects are excluded.
- Systems where the length scale over which the electron wavefunction preserves its phase is comparable to the sample dimension fall into the quantum transport regime.

Phonon-Mediated Electron-Electron Interactions

- A phonon-mediated electron-electron interaction is one where an electron emits a phonon, and this phonon is then absorbed by another electron.
- This is the origin of conventional superconductivity, as these phonon-mediated electron-electron interaction process can be attractive. We will demonstrate this using the Fröhlich Hamiltonian, but drop the spin and polarisation indices;

$$\hat{H} = \sum_{\vec{k}, \lambda} \epsilon_{\vec{k}} c_{\vec{k}, \lambda}^\dagger c_{\vec{k}, \lambda} + \sum_{\vec{q}, \nu} \hbar \omega_{\vec{q}, \nu} a_{\vec{q}, \nu}^\dagger a_{\vec{q}, \nu} + \sum_{\vec{k}, \lambda} \sum_{\vec{q}, \nu} M_{\vec{q}, \nu} (\vec{k}, \vec{k}') (a_{-\vec{q}, \nu}^\dagger + a_{\vec{q}, \nu}) c_{\vec{k} + \vec{q} + \vec{G}, \lambda}^\dagger c_{\vec{k}, \lambda}$$

- With a lot of maths (slides 32-34), we find the electron-phonon coupling results in an effective phonon-mediated interaction between electrons with

$$\hat{H}' = \hat{H}_0 + \sum_{\vec{k}, \vec{k}', \vec{q}} |M_{\vec{q}|^2 \left(\frac{\hbar \omega_{\vec{q}}}{(\epsilon_{\vec{k}-\vec{q}} - \epsilon_{\vec{k}})^2 - (\hbar \omega_{\vec{q}})^2} \right) \hat{c}_{\vec{k}+\vec{q}}^\dagger \hat{c}_{\vec{k}-\vec{q}}^\dagger \hat{c}_{\vec{k}} \hat{c}_{\vec{k}'} + \dots$$

- This interaction is attractive between electrons in the energy interval $|\epsilon_{\vec{k}} - \epsilon_{\vec{k}-\vec{q}}| < \hbar \omega_{\vec{q}} \leq \hbar \omega_D$ of each other / the Fermi energy. Note ω_D is the Debye phonon frequency (highest normal mode frequency in the crystal).

The end of the L12-13 handout includes a few useful derivations.

L13-14 AQCMP - Quantum Transport

[L12 AQCMP - Electron-Phonon Interactions](#)

Quantum vs Semiclassical Transport
Electronic Transport in a Semiconductor
Quasi-One-Dimensional Systems
Quantum Transport - The Landauer Formalism
Quantum Transport Through a Quantum Dot
DC Bias 'Spectroscopy' of a Quantum Dot
Quantum Transport in a 2D system

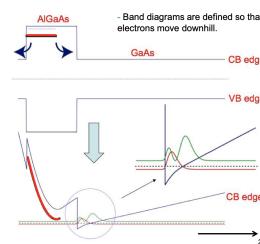
[L15-16 AQCMP - Superconductivity](#)

Quantum vs Semiclassical Transport

- Boltzmann theory works well in systems where phase coherence is unimportant.
 - In systems where phase coherence is important, quantum transport theory must be used. It is an exact linear-response approach.
 - Note that quantum effects appear greater in low-dimension systems and at low temperature.

Electronic Transport in a Semiconductor

- The lowest energy states in the conduction band of a crystalline semiconductor form an energy minimum of the form;
$$E_{\vec{k}} = \frac{\hbar^2}{2} \sum_{i,j=1}^3 \vec{k}_i (\hat{m}^*)^{-1}_{i,j} \vec{k}_j$$
- Here, $\vec{k} = (\vec{k}_1, \vec{k}_2, \vec{k}_3)$ is a Bloch wavevector and \hat{m}^* is the effective mass tensor.
- At the Γ point in GaAs, this takes the form $E_{\vec{k}} = \frac{\hbar^2}{2m^*} |\vec{k}|^2$ - the same as for electrons in free space.
 - Hence, electrons introduced to the conduction band of GaAs behave as though they are moving in free space.
- A two-dimensional electron system may be formed by molecular beam epitaxy (BME). First, producing a layer of GaAs, then adding a $Al_xGa_{1-x}As$ heterostructure above. Doping with Si during the growth of this stage produces a layer of n-type dopants.
 - This is modulation doping; the dopant layer does not conduct, as the doping level is set below the insulator-metal transition.
 - As the $Al_xGa_{1-x}As$ has a wider band gap than GaAs, electrons from the donor states fall to the GaAs to $Al_xGa_{1-x}As$ interface, reaching an equilibrium with the attraction from positive charge left in the doped layer.
 - This therefore forms a confined 2D electron gas. This is demonstrated below;



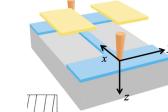
- This is a true many-fermion system and the Hilbert space grows exponentially with the number of particles. The governing Schrödinger equation is;

$$\left(\sum_{i=1}^N \left(\frac{(\hat{p}_{\vec{r}_i} + e\vec{A}(\vec{r}_i, t))^2}{2m^*} + V(\vec{r}_i, t) - \mu_i - \frac{\hbar}{4m^*c^2} (\vec{r}_i \times \vec{p}_i) \cdot \nabla V(\vec{r}_i, t) + \dots \right) + \sum_{i,j=1, i \neq j}^N \frac{e^2}{4\pi\epsilon_r\epsilon_0 |\vec{r}_i - \vec{r}_j|} \right) \Phi = i\hbar \frac{\partial \Phi}{\partial t}$$

- By applying a potential V_y to a surface Schottky gate, and therefore through the electron gas can be used to create an arbitrary two-dimensional potential landscape $V(x, y)$, such that the Schrödinger equation governing the quasiparticles of the system is;

$$\frac{1}{2m^*} \left(\vec{p} + e\vec{A} \right)^2 \Phi + V(x, y)\Phi = i\hbar \frac{\partial \Phi}{\partial t}.$$

Quasi-One-Dimensional Systems



- A quasi-one-dimensional system formed from a 2D system, aligned along the x-direction, like in the figure above, has the form

$$\left(\frac{\hat{p}_x^2}{2m^*} + V(y) \right) \Phi_{n,k}(x, y) = E_{n,k} \Phi_{n,k}(x, y).$$

- As the system has translational invariance in the x-direction, write $\Phi_{n,k}(x, y) = \exp(ikx)\phi_n(y)$. Substituting gives

$$\left(\frac{\hat{p}_x^2}{2m^*} + V(y) \right) \phi_n(y) = \left(E_{n,k} - \frac{\hbar^2 k^2}{2m^*} \right) \phi_n(y) = E_n \phi_n(y).$$

- Here, $\phi_n(y)$ is a subband wavefunction and E_n is a subband energy. It is also seen that

$$E_{n,k} = E_n + \frac{\hbar^2 k^2}{2m^*}$$

- Where $V(y) = \frac{1}{2}m^*\omega^2 y^2$, the solutions are those of the simple harmonic oscillator with

$$\phi_n(y) = \frac{1}{\sqrt{2^n n!}} \left(\frac{m\omega}{\hbar} \right)^{\frac{1}{2}} \exp \left(-\frac{m\omega y^2}{2\hbar} \right) H_n \left(\sqrt{\frac{m\omega}{\hbar}} y \right),$$

where Hermite polynomials $H_n(z) = (-1)^n e^{z^2} \frac{d^n}{dz^n} (e^{-z^2})$
and subband energies $E_n = \hbar\omega \left(n + \frac{1}{2} \right)$

- Considering a system of length L and cross-sectional area A lying along the x-direction.

- When a potential difference is applied, electrons at the negative x end have chemical potential $\mu - eV$ and temperature T . Electrons at the positive x end have chemical potential μ .
- Where $f_k(\mu) = [1 + \exp((E_k - \mu)/k_B T)]^{-1}$ is the Fermi-Dirac distribution and $v_k = \frac{1}{\hbar} \frac{dE_k}{dk}$ is the group velocity, the current density carried by a single k -state propagating in the positive x-direction is;

$$j_k = -\frac{e}{LA} v_k f_k(\mu - eV)$$

$$\Rightarrow I_k^+ = A j_k = -\frac{e}{L} v_k f_k(\mu - eV)$$

- Summing over k -states and converting to an integral gives

$$I^+ = -\frac{e}{L} \sum_{k=0}^{\infty} v_k f_k(\mu - eV)$$

$$= -\frac{e}{2\pi} \int_0^{\infty} dk v_k f_k(\mu - eV)$$

$$= -\frac{e}{2\pi} \int 0^{\infty} dk \frac{1}{\hbar} \frac{dE_k}{dk} f_k(\mu - eV) \quad (\text{subbing } v_g)$$

$$= -\frac{e}{\hbar} \int_0^{\infty} dE_k f_k(\mu - eV)$$

- For current flowing in the negative direction,

$$I^- = -\frac{e}{\hbar} \int_0^{\infty} dE_k f_k(\mu)$$

- Therefore, $I = I^+ - I^-$, implies

$$I = \frac{e}{h} \int_0^\infty dE_k (f_k(\mu) - f_k(\mu - eV))$$

- The conductance may then be found via $G = \lim_{V \rightarrow 0} \frac{I}{V}$, which results in

$$I = \frac{e}{h} \int_0^\infty dE_k \left(-\frac{\partial f_k}{\partial E_k} \right) eV$$

- As $T \rightarrow 0$, $-\frac{\partial f_k}{\partial E_k} = \delta(E_k - \mu)$, so

$$\begin{aligned} I &= \frac{e}{h} \int_0^\infty dE_k \delta(E_k - \mu) eV \\ &= \frac{e^2}{h} \\ \implies G &= \frac{e^2}{h} \end{aligned}$$

- The conductance of a 1D GaAs / AlGaAs heterostructure shows conductance steps at integer multiples of $2e^2/H$, where the factor of 2 is due to spin degeneracy and can be lifted by an applied magnetic field. To explain the finite width of risers between these steps requires the Landauer formalism.

Quantum Transport - The Landauer Formalism

- Here, we aim to derive an equation for the conductance of a general 2D quantum system with effective potential $V(x, y)$.
- Consider such a quantum system to be sandwiched between two infinite quasi-one-dimensional systems which act as conducting leads, each considered to have many occupied, propagating 1D subbands. The left lead is connected to a reservoir of chemical potential $\mu - eV$ and the right lead to one of chemical potential μ .
- Where $a_{k_n}^\pm$ and $b_{k_n}^\pm$ are current amplitudes are j_{k_n} is the current in the n^{th} 1D subband at wavevector k_n , then at each energy E , the wavefunctions of the leads are;

$$\begin{aligned} \Phi_L(x, y) &= \sum_{n=1}^{\infty} \frac{1}{j_{k_n}^{1/2}} a_{k_n}^+ \exp(i k_n x) \phi_{k_n}^+(y) + \sum_{n=1}^{\infty} \frac{1}{j_{k_n}^{1/2}} a_{k_n}^- \exp(-i k_n x) \phi_{k_n}^-(y), \\ \Phi_R(x, y) &= \sum_{n=1}^{\infty} \frac{1}{j_{k_n}^{1/2}} b_{k_n}^+ \exp(i k_n x) \phi_{k_n}^+(y) + \sum_{n=1}^{\infty} \frac{1}{j_{k_n}^{1/2}} b_{k_n}^- \exp(-i k_n x) \phi_{k_n}^-(y), \end{aligned}$$

- Therefore, as the leads are each at energy E , the wavevectors are solutions to

$$E = E_n + \frac{\hbar^2 k_n^2}{2m^*}$$

- For $E > E_n$, $\pm k_n$ are real, so represent propagating modes. For $E < E_n$, the wavevectors are pure imaginary and represent evanescent modes.
- The relationship between the current amplitudes $a_{k_n}^\pm$ and $b_{k_n}^\pm$ and the reflection amplitudes T_{k_n, k_m}^\pm and R_{k_n, k_m}^\pm (below) may be solved using the Schrödinger equation with boundary conditions.

$$\begin{aligned} \vec{b}_{k_n}^+ &= \sum_{m=1}^{\infty} T_{k_n, k_m}^+ \vec{a}_{k_m}^+ + \sum_{m=1}^{\infty} R_{k_n, k_m}^+ \vec{b}_{k_m}^-, \\ \vec{a}_{k_n}^- &= \sum_{m=1}^{\infty} R_{k_n, k_m}^- \vec{a}_{k_m}^- + \sum_{m=1}^{\infty} T_{k_n, k_m}^- \vec{b}_{k_m}^-. \end{aligned}$$

- Adding contributions to the time averaged current propagating to the right from all $k_n(m) = 2\pi m/L$, $m \in \mathbb{Z}^+$, and assuming the current in each subband is uncorrelated, such that $\langle a_{k_n, m}^\dagger a_{k_n, m}^\dagger \rangle_{\text{time}} = \langle |a_{k_n}^+|^2 \rangle_{\text{time}} \delta_{n,m}$ gives;

$$\begin{aligned} I^+ &= \sum_{k=0}^{\infty} \sum_{n=1}^{\infty} A \langle \vec{b}_{k,n}^\dagger \vec{b}_{k,n}^+ \rangle_{\text{time}} f_k(\mu - eV), \\ &= \sum_{k=0}^{\infty} \sum_{n,m=1}^{\infty} A \langle T_k^{+\dagger} T_k^+ \rangle_{n,m} \langle \vec{a}_{k,n}^\dagger \vec{a}_{k,n}^+ \rangle_{\text{time}} f_k(\mu - eV), \\ &= \sum_{k=0}^{\infty} \sum_{n=1}^{\infty} A \langle T_k^{+\dagger} T_k^+ \rangle_{n,n} \langle |a_{k,n}^+|^2 \rangle_{\text{time}} f_k(\mu - eV). \end{aligned}$$

- Note that subbands with imaginary k_n decay before reaching a reservoir, so do not contribute.

- In a propagating 1D subband, $\langle |\vec{a}_{k,n}^+|^2 \rangle_{\text{time}} = -e \cdot \frac{1}{LA} v_k$. Substituting this into the above, converting the k sum to an integral and substituting for v_k gives

$$\begin{aligned} I^+ &= -\frac{e}{h} \int_0^\infty dE \sum_{n,m=1}^N \langle (T_E^+)_{n,m} \rangle^2 f_E(\mu - eV), \\ I^- &= -\frac{e}{h} \int_0^\infty dE \sum_{n,m=1}^N \langle (T_E^-)_{n,m} \rangle^2 f_E(\mu) \\ \implies I &= \frac{e}{h} \int_0^\infty dE \sum_{n,m=1}^N \langle (T_E^+)_{n,m} \rangle^2 (f_E(\mu) - f_E(\mu - eV)) \end{aligned}$$

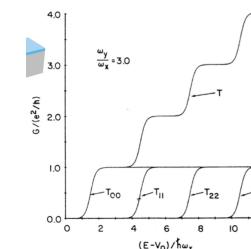
- The conductance is then given as

$$\begin{aligned} G &= \lim_{V \rightarrow 0} \frac{I}{V} = \frac{e^2}{h} \int_0^\infty dE \sum_{n,m=1}^N \langle (T_E^+)_{n,m} \rangle^2 \left[-\frac{\partial f}{\partial E} \right] \\ (\text{As } T \rightarrow 0) &= \frac{e^2}{h} \sum_{n,m=1}^N \langle (T_\mu^+)_{n,m} \rangle^2 = \frac{e^2}{h} \text{trace}(T_\mu^{+\dagger} T_\mu^+) \end{aligned}$$

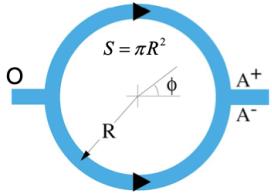
- For a saddle point potential of form, $V(x, y) = V_0 - \frac{1}{2} m^* \omega_x^2 x^2 + \frac{1}{2} m^* \omega_y^2 y^2$, the transmission coefficients are

$$\left| (T_E^+)_{n,m} \right|^2 = \delta_{n,m} \frac{1}{1 + \exp(-\pi \epsilon_n)} \quad \text{where } \epsilon_n = \frac{2}{E_x} \left[E - E_y \left(n + \frac{1}{2} \right) - V_0 \right]$$

- As the Landauer conductance is then $G(E) = \frac{e^2}{h} \sum_{n,m=1}^N \langle (T_E^+)_{n,m} \rangle^2$, it is thought this at least partially accounts for the finite sloping between conductivity plateaus.



- The conductance of an Aharonov-Bohm ring can be calculated using the Landauer equation for zero temperature, so only consider states at the Fermi surface.



- Assuming we can ignore paths over half a diameter, the conductance is

$$t_{OA} \approx t_{OA^+} + t_{OA^-} \approx \exp(i\phi_{A^+}) + \exp(i\phi_{A^-}) \\ \implies G = \frac{e^2}{h} |t_{OA}|^2 \approx \frac{e^2}{h} (2 \cos(\phi_{A^+} - \phi_{A^-}))$$

- Then using the gauge $\vec{A} = (-By/2, Bx/2)$ and noting that $\int_\pi^0 \vec{A} \cdot d\vec{l} = -\frac{BS}{2}$ with $S = \pi R^2$,

$$\varphi_{A^+} \approx \int_\pi^0 \vec{k} \cdot d\vec{l} \approx \int_\pi^0 \frac{\vec{p} + e\vec{A}}{\hbar} \cdot d\vec{l} \approx k_F \pi R - \frac{1}{2} \frac{e}{\hbar} BS, \\ \varphi_{A^-} \approx \int_{-\pi}^0 \vec{k} \cdot d\vec{l} \approx \int_{-\pi}^0 \frac{\vec{p} + e\vec{A}}{\hbar} \cdot d\vec{l} \approx k_F \pi R + \frac{1}{2} \frac{e}{\hbar} BS, \\ \implies \varphi_{A^+} - \varphi_{A^-} \approx -2\pi \frac{e}{\hbar} BS. \\ \implies G \approx \frac{e^2}{h} \left(2 + 2 \cos \left(2\pi \frac{e}{\hbar} BS \right) \right)$$

Quantum Transport Through a Quantum Dot

- Constructing a quasi-zero-dimensional system using a 2D quantum dot in a GaAs/AlGaAs heterostructure, assuming a spherically symmetric potential $V(r, \phi) = \frac{1}{2}m^* \omega_0^2 r^2$ and a symmetric gauge $\vec{A} = (-By/2, Bx/2, 0)$ gives the Schrödinger equation (after expanding a $(\hat{p} + e\vec{A})^2$ term);

$$\left(\frac{\hat{P}^2}{2m^*} + \frac{eB}{2m^*} \hat{L}_z + \frac{1}{2m^*} \left(\frac{eB}{2} \right)^2 r^2 + \frac{1}{2} m^* \omega_0^2 r^2 \right) \Phi(r, \phi) = E \Phi(r, \phi).$$

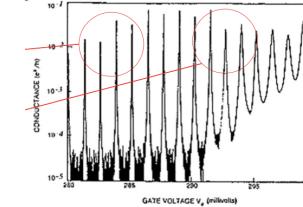
- This has Darwin-Fock eigenfunctions and eigenvalues;

$$\Phi_{n,l}(r, \phi) = R_n(r) e^{il\phi}, \quad E_{n,l} = \hbar \omega_C \left(b \left(n + \frac{1}{2} \right) + (b|l| - l) \frac{1}{2} \right), \\ \text{where } \omega_C = \frac{eB}{2m^*} \quad \text{and} \quad b = \sqrt{1 + 4 \frac{\omega_0^2}{\omega_C^2}}.$$

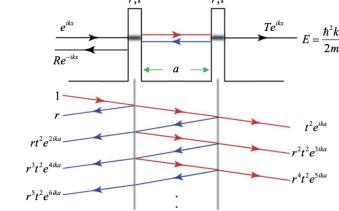
- Therefore, subject to different magnetic field strengths,

$$\lim_{B \rightarrow \infty} E_{n,l} = \hbar \omega_C (n + (|l| - l)/2 + 1/2), \\ \lim_{B \rightarrow 0} E_{n,l} = \hbar \omega_0 (2n + |l| + 1).$$

- The conductance for a quantum dot shows both; fine lines subject to temperature broadening with the shape and energy derivative of the Fermi-Dirac function (left in figure below), and broader Lorentzian peaks indicative of Breit-Wigner scattering from a resonant state (right in figure below).



- To continue mathematically, treat the quantum dot as a resonant cavity with barriers of the same reflection and transmission amplitude r, t .



- Summing the transmitted parts gives total transmission coefficient,

$$T = \frac{t^2 e^{ika}}{1 - e^{2ika} r^2} = |T| e^{i\theta} \\ \text{with } r^2 + t^2 = 1$$

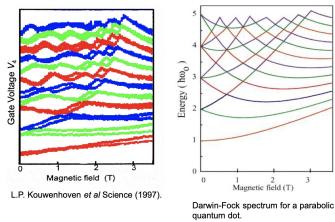
- Where $ka = k_n a = n\pi$, $T = 1$, displaying resonance. Around such a resonance, $t^2 \ll 1$, so expanding gives Breit-Wigner resonance;

$$T = (-1)^n \frac{t^2 e^{i(k-k_n)a}}{1 - r^2 e^{2i(k-k_n)a}} \\ \approx (-1)^n \frac{it^2/2}{(k - k_n)a + i\Gamma^2/2}, \\ \approx C_n \frac{i\Gamma/2}{(E - E_n) + i\Gamma/2},$$

- Here, E is incident electron energy, E_n is bound state energy, Γ is the width of the resonance and C_n is a constant. The phase can also be found as

$$\theta(t_{QD}) = \theta_n + \arctan \frac{2}{\Gamma} (E - E_n)$$

- This is good. However, the resonant peaks observed in the conductance of a quantum dot do not seem to be consistent with the Darwin-Fock spectrum. However, if we artificially remove offsets between traces in the experimental data, they become apparent.



- This is due to the dot and external gates behaving as a tiny capacitor. For a system with N electrons on the dot, such that the charge on the dot is $Q = -Ne$, the potential energy is;

$$\begin{aligned} U(Q) &= \int_0^Q \phi(Q)dQ \\ &= \int_0^Q \left(\frac{Q}{C} + \frac{Q_{\text{ext}}}{C} \right) dQ \\ &= \frac{Q^2}{2C} + Q \frac{Q_{\text{ext}}}{C} \\ \implies U(N) &= \frac{(Ne - Q_{\text{ext}})^2}{2C} - \frac{Q_{\text{ext}}^2}{2C} \end{aligned}$$

- Therefore, the energy to add an extra electron is

$$\begin{aligned} \Delta U &= U(N+1) - U(N) \\ &= \frac{1}{2C} (((N+1)e - Q_{\text{ext}})^2 - (Ne - Q_{\text{ext}})^2) \\ &= \frac{e}{C} \left(\left(N + \frac{1}{2} \right) e - Q_{\text{ext}} \right) \end{aligned}$$

- If $Q_{\text{ext}} = \left(N + \frac{1}{2} \right) e$, then $\Delta U = 0$, so current flows unimpeded, whereas if $Q_{\text{ext}} = Ne$, $\Delta U = \frac{e^2}{2C}$ and the current is suppressed. In this second case, the dot resistance will be large at low temperatures as $k_B T \ll \frac{e^2}{2C}$.
- Hence, there is an energy cost to putting an extra charge on the dot relative to the surroundings, whereas there is no energy cost to topping up the number of electrons on the dot to counteract the charge in the surrounding gates. This results in the Coulomb blockade - significantly reducing the conductance apart from where $Q_{\text{ext}} = \left(N + \frac{1}{2} \right) e$.
- This, however, has no dependence on the magnetic field, so cannot fully explain the observed offsets.

- To explain the difference fully, we must account for the energy of the quantum states ϵ_i , where the quantum term includes Hartee, exchange and correlation energies such that, where ΔU is the energy change on adding one electron,

$$\begin{aligned} U(N) &= \frac{(Ne - Q_{\text{ext}})^2}{2C} - \frac{Q_{\text{ext}}^2}{2C} + \sum_{i=1}^N \epsilon_i \\ \implies \Delta U &= \frac{(N+1/2)e^2 - eQ_{\text{ext}}}{C} + \epsilon_{N+1} \end{aligned}$$

- As $\Delta U = 0$ for $Q_{\text{ext}} = (N+1/2)e + \frac{C}{e}\epsilon_{N+1}$, the change in Q_{ext} between conductance peaks is

$$\Delta Q_{\text{ext}} = e + \frac{C}{e}(\epsilon_{N+1} - \epsilon_N)$$

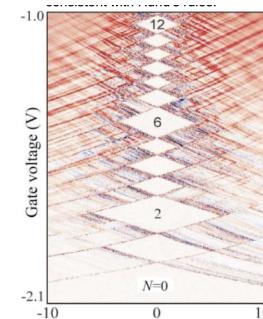
- This therefore requires a change in gate voltage

$$\Delta V_g = \frac{\Delta Q_{\text{ext}}}{C_g} = \frac{e}{C_g} + \frac{C}{C_g e}(\epsilon_{N+1} - \epsilon_N)$$

- This explains why resonances show both the Darwin-Fock spectrum and additional spacing between resonances resulting from the Coulomb blockade.

DC Bias 'Spectroscopy' of a Quantum Dot

- By measuring the differential conductance of a quantum dot ($\frac{dI}{dV_{\text{d.c.}}}$) with different d.c. biases, the band edge of the quantum dot may be moved.
- Whenever the chemical potential aligns with an energy level (controlled by adjusting V_g), a resonance occurs causing a peak in conductance.
- By finding the bias at which two resonant peaks merge, it is possible to determine the energy difference between two quantum dot states.
- Plotting differential conductance against $V_g - V_{\text{d.c.}}$ with $B = 0$ shows diamond shaped regions where $\frac{dI}{dV_{\text{d.c.}}} = 0$ due to Coulomb blockade.
- In these regions, N is fixed.
- This in fact reveals that quantum dots have a 2D shell structure consistent with Hund's rules, which enable the production of artificial 2D atoms.



Quantum Transport in a 2D system

- The Hall resistance of a 2DEG with carrier density n_c in a perpendicular magnetic field B shows a series of plateaux where an integer number of 2D Landau levels are filled;

$$R_{x,y} = \frac{h}{ne^2}, \quad n \in \mathbb{Z}^+, \quad n = n_c \frac{h}{eB}$$

- This is the Integer quantum Hall effect and is derived using the multi-probe Landauer-Büttiker formalism, which gives (slide 41-45, perhaps add more notes in lecture);

$$I_i = -\frac{e}{h}[N_i - R_{i,i}]\mu_i - \frac{e}{h} \sum_{j \neq i} T_{ij}\mu_j$$

- Here, the magnetic field produces confined 1D channels along the edges of the 2D system (edge states) which each carry a current in one direction, contributing $I = Ve^2/h$.

- For an ultra-high mobility two-dimensional electron gas, Hall plateau are seen with

$$R_{x,y} = \frac{h}{ne^2}, \quad n \in \mathbb{Q}^+, \quad n = n_c \frac{h}{eB}$$

- This is the fractional quantum Hall effect, which arises from the formation of composite fermions which carry magnetic flux.

- The simplest type carries two flux quanta that cancel the external magnetic field when $n = 1/2$, giving identical resistivity variations to those around $B = 0$.
 - This is due to the formation of composite quasiparticles forming - they may have 1,2,3 etc. components.
 - In diamagnetic materials, an applied magnetic field creates an opposing induced magnetic field; the FQHE is a form of diamagnetism.
- Should probably have more details on the quantum hall effect here - have a look through the updated slides

L15-16 AQCMP - Superconductivity

L13-14 AQCMP - Quantum Transport

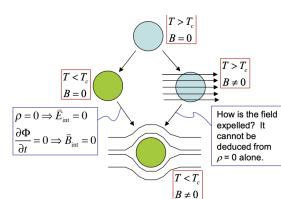
The BCS Theory of Superconductivity
 Phonon-Mediated Attractive Electron-Electron Interaction
 The BCS Ground-State Wavefunction
 BCS Theory at Zero Temperature
 BCS Theory at Finite Temperature
 Predictions of BCS Theory
 High- T_c Superconductivity

Superconductivity

- Considering a ring-shaped superconductor, the flux through the ring is $\Phi = \int \vec{B} \cdot d\vec{S}$. Noting that $E = 0$ inside the superconductor, it is seen that a current does not decay.

$$\int \nabla \times \vec{E} \cdot d\vec{S} = \oint \vec{E} \cdot d\vec{l} = -\frac{\partial}{\partial t} \int \vec{B} \cdot d\vec{S} = -\frac{\partial \Phi}{\partial t} = 0$$

- The current can be generated by applying an external magnetic field perpendicular to the face of the ring, such as to inside $\Phi = \int \vec{B}_{\text{ext}} \cdot d\vec{S}$. If the sample is now cooled below T_c and B_{ext} is switched off, then a current is generated within the ring such as to keep Φ constant.
- A superconductor expels a weak external magnetic field, such that the magnetic field inside the material is zero, $\vec{B} = \mu_0(\vec{H} + \vec{M}) = 0$. This is the Meissner-Ochsenfeld effect (is independent of zero resistivity).
- This results in the levitation of a magnet above a superconductor.



- Consider the inside of a superconducting rod wound in a solenoid. Here, we have that

$$\begin{aligned} \vec{B} = 0 &\implies \vec{M} = -\vec{H} \\ \implies \chi &= \left. \frac{dM}{dH} \right|_{H=0} = -1 \end{aligned}$$

- As $\chi = -1$, this is therefore a perfect diamagnet - the supercurrent induced by the external field H causes a magnetisation M which is directly opposite to H .
- There are two common forms of superconductivity, type I and type II;
 - In type I superconductivity, a perfect Meissner state as long as the magnetic field does not exceed a critical field strength $H_c(T)$. Above $H_c(T)$, the material returns to a normal state.
 - In type II superconductivity, there is a perfect Meissner state below $H_{c1}(T)$, whilst between $H_{c1}(T)$ and $H_{c2}(T)$, the magnetic flux partially penetrates into the sample.
 - In this partially penetrating stage, a regular triangular lattice of flux-bearing vortices forms, with a normal metal state forming inside each vortex. Outside the vortices, the sample is superconducting.

The BCS Theory of Superconductivity

- The Bardeen, Cooper and Schrieffer (BCS) theory makes several predictions in agreement with experiments, such as how the transition temperature for the onset of superconductivity depends on the mass of the crystal lattice ions with $\alpha = 1/2$;

$$T_c \propto M^{-\alpha}$$

- This suggests a phonon-mediated mechanism, as phonon energies also tend as $M^{-1/2}$.
- The theory also predicts an energy gap 2Δ in the density of states of the superconductor at the Fermi level (as measured) as well as the Meissner effect.
- BCS theory exploits the existence of an attractive interaction between two electrons mediated by phonons, resulting in the pairing of electrons outside a Fermi sea into a Cooper pair; and the construction of a coherent, many-particle wavefunction in which all electrons near the Fermi level are in Cooper pairs.

Phonon-Mediated Attractive Electron-Electron Interaction

- The electron-phonon interaction produces an effective interaction between electrons of the form;

$$\hat{H}' = \sum_{\vec{k}, \lambda} \epsilon_{\vec{k}} C_{\vec{k}, \lambda}^\dagger C_{\vec{k}, \lambda} + \sum_{\vec{k}, \vec{q}, \lambda, \lambda', \vec{q}'} |M_{\vec{q}}|^2 \frac{\hbar \omega_{\vec{q}}}{(\epsilon_{\vec{k}} - \epsilon_{\vec{k}-\vec{q}})^2 - (\hbar \omega_{\vec{q}})^2} C_{\vec{k}+\vec{q}, \lambda}^\dagger C_{\vec{k}-\vec{q}, \lambda'}^\dagger C_{\vec{k}, \lambda} C_{\vec{k}', \lambda'}$$

- Here, the interaction between electrons is attractive when $|\epsilon_{\vec{k}} - \epsilon_{\vec{k}-\vec{q}}| < \hbar \omega_{\vec{q}}$. Such attractive states exist in the shell of energies with width $\hbar \omega_D$ around the Fermi energy. Neglecting k -dependence in this shell (equivalent to assuming an attractive contact interaction $V(\vec{r}_1 - \vec{r}_2) = -\gamma^2 \delta(\vec{r}_1 - \vec{r}_2)$, we can approximate the Hamiltonian;

$$\hat{H}' = \sum_{\vec{k}, \lambda} \epsilon_{\vec{k}} C_{\vec{k}, \lambda}^\dagger C_{\vec{k}, \lambda} - \frac{1}{2} \gamma^2 \sum_{\vec{k}, \vec{q}, \lambda, \lambda'} C_{\vec{k}+\vec{q}, \lambda}^\dagger C_{\vec{k}-\vec{q}, \lambda'}^\dagger C_{\vec{k}, \lambda} C_{\vec{k}', \lambda'}$$

- Here, γ is a measure of the electron-phonon interaction strength.
- Considering the wavefunction of a pair of electrons under the influence of electron-phonon interaction to have the form

$$\Psi(\vec{r}_1, \sigma_1, \vec{r}_2, \sigma_2) = e^{i\vec{k}_{cm} \cdot \vec{R}_{cm}} \varphi(\vec{r}_1 - \vec{r}_2) \eta(\sigma_1, \sigma_2).$$

- Here, $\vec{R}_{cm} = (\vec{r}_1 - \vec{r}_2)/2$ is the COM and $\hbar \vec{k}_{cm}$ is the total momentum of the pair. Note that the state with k_{cm} will have the lowest energy.
- As most superconductors have spin-singlet pairs, also assume that η takes the form below. Also note that this implies φ must be symmetric.

$$\eta(\sigma_1, \sigma_2) = \frac{1}{\sqrt{2}} (\chi_\uparrow(\sigma_1) \chi_\downarrow(\sigma_2) - \chi_\downarrow(\sigma_1) \chi_\uparrow(\sigma_2))$$

- Assuming the electron gas is also homogenous, then we can expand φ in terms of plane wave states

$$\varphi(\vec{r}_1 - \vec{r}_2) = \frac{1}{V} \sum_{\vec{k}} \varphi_{\vec{k}} e^{i\vec{k} \cdot (\vec{r}_1 - \vec{r}_2)},$$

- We can therefore rewrite the wavefunction as

$$\begin{aligned} \Psi(\vec{r}_1, \sigma_1, \vec{r}_2, \sigma_2) &= \varphi(\vec{r}_1 - \vec{r}_2) \eta(\sigma_1, \sigma_2), \\ &= \sum_{\vec{k}} \varphi_{\vec{k}} \frac{1}{\sqrt{2}} \begin{vmatrix} e^{i\vec{k} \cdot \vec{r}_1} \chi_\uparrow(\sigma_1) & e^{i\vec{k} \cdot \vec{r}_2} \chi_\uparrow(\sigma_2) \\ e^{-i\vec{k} \cdot \vec{r}_1} \chi_\downarrow(\sigma_1) & e^{-i\vec{k} \cdot \vec{r}_2} \chi_\downarrow(\sigma_2) \end{vmatrix}. \end{aligned}$$

- Therefore, we take the Cooper pair trial wavefunction to be

$$|\Psi_\phi\rangle = \sum_{\langle\vec{k}\rangle} \varphi_{\vec{k}} c_{-\vec{k},\downarrow}^\dagger c_{\vec{k},\uparrow}^\dagger |0\rangle = \sum_{\langle\vec{k}\rangle} \varphi_{\vec{k}} |\psi_{\vec{k}}\rangle$$

with $|\psi_{\vec{k}}\rangle = c_{-\vec{k},\downarrow}^\dagger c_{\vec{k},\uparrow}^\dagger |0\rangle$

- Here, $\langle\vec{k}\rangle$ denotes that the sum is restricted to states where $E_F < \frac{\hbar^2 k^2}{2m} < E_F + \hbar\omega_D$, such as to not sum over the filled states, or those which are not attractive.

- Now calculating the energy of the Cooper pair from the Schrödinger equation using this trial wavefunction requires

$$\hat{H}' |\Psi\rangle = \left(\sum_{\vec{k},\lambda} \epsilon_{\vec{k}} C_{\vec{k},\lambda}^\dagger C_{\vec{k},\lambda} - \frac{1}{2} \gamma^2 \sum_{\vec{k},\vec{k}',\vec{q},\lambda,\lambda'} C_{\vec{k}+\vec{q},\lambda}^\dagger C_{\vec{k}-\vec{q},\lambda'}^\dagger C_{\vec{k},\lambda} C_{\vec{k}',\lambda'} \right) |\Psi\rangle = E |\Psi\rangle.$$

- After taking the scalar product such that $E \langle\psi_{\vec{k}}|\Psi_\phi\rangle = \langle\psi_{\vec{k}}|\hat{H}'|\Psi_\phi\rangle$, a lot of maths (slides 14-17) and collecting terms, we find that $E\phi = H\phi$ becomes;

$$E\varphi_{\vec{k}} = 2\epsilon_{\vec{k}}\varphi_{\vec{k}} - \gamma^2 \sum_{\langle\vec{k}\rangle} \varphi_{\vec{k}}$$

- For $E < 2E_F$, this has one eigenvalue and for $E > 2E_F$, there is a continuum of eigenvalues.

- Defining $C = \sum_{\langle\vec{k}\rangle} \varphi_{\vec{k}}$ as the Cooper pair energy gives

$$\varphi_{\vec{k}} = -\gamma^2 \frac{C}{E - 2\epsilon_{\vec{k}}}.$$

- Summing over \vec{k} , dividing by C , converting the sum to an integral and assuming the density of state is constant over the integration range gives

$$\begin{aligned} 1 &= -\gamma^2 \sum_{\langle\vec{k}\rangle} \frac{1}{E - 2\epsilon_{\vec{k}}}, \\ &= -\frac{\gamma^2 V}{(2\pi)^3} \int_{\langle\vec{k}\rangle} d^3\vec{k} \frac{1}{(E - 2E_F) - 2(\epsilon_{\vec{k}} - E_F)}, \\ &\approx -\gamma^2 V \rho(E_F) \int_0^{\hbar\omega_D} d\epsilon \frac{1}{\Delta E - 2\epsilon}. \end{aligned}$$

- Evaluating the integral where $\Delta E < 0$ gives

$$\begin{aligned} 1 &= \frac{1}{2} \gamma^2 V \rho(E_F) \ln \left(\frac{\Delta E - 2\hbar\omega_D}{\Delta E} \right) \\ &= \frac{1}{2} \zeta \ln \left(\frac{\Delta E - 2\hbar\omega_D}{\Delta E} \right) \end{aligned}$$

- Where $\zeta = \gamma^2 V \rho(E_F)$ is the electron-phonon coupling parameter. Therefore, the binding energy of the Cooper pair is

$$\begin{aligned} \Delta E &= -\frac{2\hbar\omega_D}{\exp(2/\zeta) - 1} < 0 \\ &\approx -2\hbar\omega_D \exp(-2/\zeta) \quad \text{with } \zeta \ll 1 \end{aligned}$$

- Therefore, the cooper pair is a bound state with binding energy $\Delta E < 0$. ΔE is exponentially small for small ζ , but always exists, even for arbitrarily weak attractive interaction.

- This also implies the Fermi sphere might be unstable against formation of Cooper pairs.

- The formation of Cooper pairs is responsible for superconductivity in many materials.

- Here we assumed s-wave symmetry, as the electron-electron interaction corresponds to an attractive point contact interaction and only s-waves have finite values at $r_1 = r_2$. However, if we had considered some other type of interaction, we could have considered wavefunction with p or d-wave symmetry;

$$\varphi(\vec{r}_1 - \vec{r}_2) = f(|\vec{r}_2 - \vec{r}_1|) Y_{l,m}(\theta, \phi)$$

- These are important in superfluid 3He and some high- T_c superconductors.

The BCS Ground-State Wavefunction

- As all electrons on the Fermi surface are unstable to the creation of Cooper pairs, and in analogy with a coherent state in quantum optics, we make the ansatz that the many-body ground-state wavefunction of these Cooper pairs is;

$$|\Psi_{BCS}\rangle = \text{const} \cdot \exp \left(\sum_{\vec{k}} \alpha_{\vec{k}} P_{\vec{k}}^\dagger \right) |0\rangle$$

- Note that the BCS vacuum state is different from that in the Cooper problem; $|0\rangle_{BCS} \neq |0\rangle_{\text{Cooper}}$. $|0\rangle$ is the state with no electrons in the band of Bloch states within $\pm\hbar\omega_D$ of the Fermi level, but states with energies below that are filled. Also note that here, the pair creation operator $P_{\vec{k}}^\dagger = c_{\vec{k},\uparrow}^\dagger c_{-\vec{k},\downarrow}^\dagger$.

- It can be shown that the commutation rules for a pair of creation operators gives

$$\begin{aligned} [P_{\vec{k}}^\dagger, P_{\vec{k}'}^\dagger] &= 0 \\ [P_{\vec{k}}, P_{\vec{k}'}] &= 0 \\ (P_{\vec{k}}^\dagger)^2 |0\rangle &= 0 \\ P_{\vec{k}} P_{\vec{k}}^\dagger |0\rangle &= 0 \\ [P_{\vec{k}}, P_{\vec{k}}^\dagger] &= 1 - n_{\vec{k},\uparrow} - n_{-\vec{k},\downarrow} \neq 1 \end{aligned}$$

- This final relationship implies the pair creation operators are not creating proper bosons. Combining the above, using that $\exp(A+B) = \exp(A)\exp(B)$ if $[A, B] = 0$, expanding out the exponential and noting that all squared or higher order terms vanish, we get

$$\begin{aligned} |\Psi_{BCS}\rangle &= \text{const} \cdot \prod_{\vec{k}} \exp(\alpha_{\vec{k}} P_{\vec{k}}^\dagger) |0\rangle \\ &= \text{const} \cdot \prod_{\vec{k}} (1 + \alpha_{\vec{k}} P_{\vec{k}}^\dagger) |0\rangle \end{aligned}$$

- Therefore, we can construct a normalised BCS ground-state wavefunction as

$$\begin{aligned} |\Psi_{BCS}\rangle &= \prod_{\vec{k}} (u_{\vec{k}}^* + v_{\vec{k}}^* P_{\vec{k}}^\dagger) |0\rangle \\ &= \prod_{\vec{k}} (u_{\vec{k}}^* + v_{\vec{k}}^* c_{\vec{k},\uparrow}^\dagger c_{-\vec{k},\downarrow}^\dagger) |0\rangle \\ \text{where } u_{\vec{k}}^* &= \frac{1}{\sqrt{1 + |\alpha_{\vec{k}}|^2}}, \quad v_{\vec{k}}^* = \frac{\alpha_{\vec{k}}}{\sqrt{1 + |\alpha_{\vec{k}}|^2}} \end{aligned}$$

- Note that this is normalised, as for each k , $|u_{\vec{k}}|^2 + |v_{\vec{k}}|^2 = 1$.
- Also note, the BCS wavefunction is a superposition of configurations with different number of Cooper pairs; it does not have a well-defined number of Cooper pairs.
- Also, writing $v_k = |v_k|e^{i\phi}$ gives a well-defined ϕ .
- Using only spin-singlet cooper pairs, we can write the BCS Hamiltonian as

$$\begin{aligned}\hat{H}_{BCS} &= \sum_{\vec{k}} \epsilon_{\vec{k}} (c_{\vec{k},\uparrow}^\dagger c_{\vec{k},\uparrow} + c_{\vec{k},\downarrow}^\dagger c_{\vec{k},\downarrow}) - \gamma^2 \sum_{\vec{k},\vec{k}'} c_{\vec{k},\uparrow}^\dagger c_{\vec{k},\downarrow}^\dagger c_{-\vec{k}',\downarrow} c_{\vec{k}',\uparrow}, \\ &= \sum_{\vec{k}} \epsilon_{\vec{k}} (n_{\vec{k},\uparrow} + n_{\vec{k},\downarrow}) - \gamma^2 \sum_{\vec{k},\vec{k}'} P_{\vec{k}}^\dagger P_{\vec{k}'}. \end{aligned}$$

- We may then determine $u_{\vec{k}}$ and $v_{\vec{k}}$ variationally by minimising the total energy $E = \langle \Psi_{BCS} | \hat{H}_{BCS} | \Psi_{BCS} \rangle$ subject to a constant number of particles, $\langle \hat{N} \rangle$ and wavefunction normalisation for each k (as above).

BCS Theory at Zero Temperature

- Using the anticommutation rules for the c^\dagger and c operators, and lots of maths, it can be shown that the average occupation of a particular Bloch state in the BCS wavefunction is;

$$\begin{aligned}\langle n_{\vec{k},\uparrow} \rangle &= \langle c_{\vec{k},\uparrow}^\dagger c_{\vec{k},\uparrow} \rangle = \langle \Psi_{BCS} | c_{\vec{k},\uparrow}^\dagger c_{\vec{k},\uparrow} | \Psi_{BCS} \rangle, \\ &= \left\langle 0 \left| \prod_{\vec{p}} (u_{\vec{p}} + v_{\vec{p}} c_{-\vec{p},\downarrow}^\dagger c_{\vec{p},\uparrow}) c_{\vec{k},\uparrow}^\dagger c_{\vec{k},\uparrow} \prod_{\vec{p}} (u_{\vec{p}}^* + v_{\vec{p}}^* c_{\vec{p},\uparrow}^\dagger c_{-\vec{p},\downarrow}) \right| 0 \right\rangle \\ &= |v_{\vec{k}}|^2 \end{aligned}$$

and

$$\langle n_{\vec{k},\downarrow} \rangle = |v_{\vec{k}}|^2$$

- We may also show that the two-particle term is;

$$\langle P_{\vec{k}}^\dagger P_{\vec{k}'} \rangle = v_{\vec{k}} v_{\vec{k}'}^* u_{\vec{k}} u_{\vec{k}'}^*$$

- And that the number of particles is

$$\begin{aligned}\langle \hat{N} \rangle &= \left\langle \sum_{\vec{k}} (n_{\vec{k},\uparrow} + n_{\vec{k},\downarrow}) \right\rangle, \\ &= \sum_{\vec{k}} (\langle n_{\vec{k},\uparrow} \rangle + \langle n_{\vec{k},\downarrow} \rangle), \\ &= 2 \sum_{\vec{k}} |v_{\vec{k}}|^2. \end{aligned}$$

- Combining the above, we find the ground-state energy as;

$$\begin{aligned}E_0 &= \langle \Psi_{BCS} | \hat{H}_{BCS} | \Psi_{BCS} \rangle, \\ &= \left\langle \Psi_{BCS} \left| \sum_{\vec{k}} \epsilon_{\vec{k}} (n_{\vec{k},\uparrow} + n_{\vec{k},\downarrow}) - \gamma^2 \sum_{\vec{k},\vec{k}'} P_{\vec{k}}^\dagger P_{\vec{k}'} \right| \Psi_{BCS} \right\rangle, \\ &= \sum_{\vec{k}} \epsilon_{\vec{k}} (\langle n_{\vec{k},\uparrow} \rangle + \langle n_{\vec{k},\downarrow} \rangle) - \gamma^2 \sum_{\vec{k},\vec{k}'} \langle P_{\vec{k}}^\dagger P_{\vec{k}'} \rangle, \\ &= 2 \sum_{\vec{k}} \epsilon_{\vec{k}} |v_{\vec{k}}|^2 - \gamma^2 \sum_{\vec{k},\vec{k}'} v_{\vec{k}} v_{\vec{k}'}^* u_{\vec{k}} u_{\vec{k}'}^*. \end{aligned}$$

- Using the normalisation condition $|u_{\vec{k}}|^2 + |v_{\vec{k}}|^2 = 1$, we rewrite this as

$$E_0 = \sum_{\vec{k}} \epsilon_{\vec{k}} (v_{\vec{k}} v_{\vec{k}}^* + 1 - u_{\vec{k}} u_{\vec{k}}^*) - \gamma^2 \sum_{\vec{k},\vec{k}'} v_{\vec{k}} v_{\vec{k}'}^* u_{\vec{k}} u_{\vec{k}'}^*.$$

- Now treating $v_{\vec{k}}$, $v_{\vec{k}}^*$, $u_{\vec{k}}$ and $u_{\vec{k}}^*$ as independent variables, and minimising E subject to the constraints that $\langle \hat{N} \rangle = N$ is a constant and $|u_{\vec{k}}|^2 + |v_{\vec{k}}|^2 = 1$ gives (where μ and $E_{\vec{k}}$ are Lagrange multipliers);

$$\begin{aligned}L &= E_0 - \mu \langle \hat{N} \rangle - \sum_{\vec{k}} E_{\vec{k}} (|u_{\vec{k}}|^2 + |v_{\vec{k}}|^2 - 1), \\ &= \sum_{\vec{k}} \epsilon_{\vec{k}} (v_{\vec{k}} v_{\vec{k}}^* + 1 - u_{\vec{k}} u_{\vec{k}}^*) - \gamma^2 \sum_{\vec{k},\vec{k}'} v_{\vec{k}} v_{\vec{k}'}^* u_{\vec{k}} u_{\vec{k}'}^* \\ &\quad - \mu \sum_{\vec{k}} (v_{\vec{k}} v_{\vec{k}}^* + 1 - u_{\vec{k}} u_{\vec{k}}^*) - \sum_{\vec{k}} E_{\vec{k}} (v_{\vec{k}} v_{\vec{k}}^* + u_{\vec{k}} u_{\vec{k}}^* - 1). \end{aligned}$$

- Taking derivatives with respect to $v_{\vec{k}}$ and $u_{\vec{k}}$ gives

$$\begin{aligned}\frac{\partial L}{\partial v_{\vec{k}}^*} &= \epsilon_{\vec{k}} v_{\vec{k}}^* - \gamma^2 \left(\sum_{\vec{k}'} u_{\vec{k}'} v_{\vec{k}'}^* \right) u_{\vec{k}}^* - \mu v_{\vec{k}}^* - E_{\vec{k}} v_{\vec{k}}^* = 0, \\ \frac{\partial L}{\partial u_{\vec{k}}^*} &= -\epsilon_{\vec{k}} u_{\vec{k}}^* - \gamma^2 \left(\sum_{\vec{k}'} v_{\vec{k}'} u_{\vec{k}'}^* \right) v_{\vec{k}}^* + \mu u_{\vec{k}}^* - E_{\vec{k}} u_{\vec{k}}^* = 0. \end{aligned}$$

- Now defining the BCS gap parameter as Δ below, and noticing that at zero temperature, $\langle c_{-\vec{k},\downarrow} c_{\vec{k},\uparrow} \rangle = u_{\vec{k}} v_{\vec{k}}^*$

$$\begin{aligned}\Delta &= \gamma^2 \sum_{\vec{k}} \langle P_{\vec{k}} \rangle = \gamma^2 \sum_{\vec{k}} \langle c_{-\vec{k},\downarrow} c_{\vec{k},\uparrow} \rangle, \\ &= \gamma^2 \sum_{\vec{k}} u_{\vec{k}} v_{\vec{k}}^* \quad (\text{at zero temperature}) \end{aligned}$$

- We may then rewrite the previous two equations in matrix form as

$$\begin{pmatrix} \epsilon_{\vec{k}} - \mu & -\Delta \\ -\Delta^* & -(\epsilon_{\vec{k}} - \mu) \end{pmatrix} \begin{pmatrix} v_{\vec{k}}^* \\ u_{\vec{k}}^* \end{pmatrix} = E_{\vec{k}} \begin{pmatrix} v_{\vec{k}}^* \\ u_{\vec{k}}^* \end{pmatrix}.$$

- This has solutions

$$\begin{aligned}E_{\vec{k}} &= \pm \sqrt{(\epsilon_{\vec{k}} - \mu)^2 + |\Delta|^2}, \\ U_{\vec{k}}^{(-)} &= \begin{pmatrix} v_{\vec{k}}^* \\ u_{\vec{k}}^* \end{pmatrix}, \quad U_{\vec{k}}^{(+)} = \begin{pmatrix} u_{\vec{k}} \\ -v_{\vec{k}} \end{pmatrix}, \\ \text{where } |v_{\vec{k}}|^2 &= \frac{1}{2} \left(1 - \frac{\epsilon_{\vec{k}} - \mu}{|E_{\vec{k}}|} \right), \quad |u_{\vec{k}}|^2 = \frac{1}{2} \left(1 + \frac{\epsilon_{\vec{k}} - \mu}{|E_{\vec{k}}|} \right). \end{aligned}$$

- Also note that Δ is a sum over all k , so is itself independent of k and has s-wave symmetry.

- We now use another relationship between $u_{\vec{k}}$, $v_{\vec{k}}^*$ and Δ to solve for Δ ; (where do these come from?)

$$\begin{aligned}(\epsilon_{\vec{k}} - \mu) v_{\vec{k}}^* - \Delta u_{\vec{k}}^* &= E_{\vec{k}} v_{\vec{k}}^*, \\ \Rightarrow (\epsilon_{\vec{k}} - \mu) u_{\vec{k}} v_{\vec{k}}^* - \Delta u_{\vec{k}} u_{\vec{k}}^* &= E_{\vec{k}} u_{\vec{k}} v_{\vec{k}}^*, \\ -(\epsilon_{\vec{k}} - \mu) u_{\vec{k}}^* - \Delta v_{\vec{k}}^* &= E_{\vec{k}} u_{\vec{k}}^*, \\ \Rightarrow -(\epsilon_{\vec{k}} - \mu) u_{\vec{k}} v_{\vec{k}}^* - \Delta v_{\vec{k}}^* &= E_{\vec{k}} u_{\vec{k}} v_{\vec{k}}^*. \end{aligned}$$

- Adding these equations and using the normalisation condition gives

$$u_{\vec{k}} v_{\vec{k}}^* = \frac{\Delta}{2|E_{\vec{k}}|}$$

- Summing this result over \vec{k} and multiplying by γ^2 gives;

$$\begin{aligned}\Delta &= \gamma^2 \sum_{\vec{k}} u_{\vec{k}} v_{\vec{k}}^* = \gamma^2 \sum_{\vec{k}} \frac{\Delta}{2|E_{\vec{k}}|} \\ \implies 1 &= \frac{\gamma^2}{2} \sum_{\vec{k}} \frac{1}{\sqrt{(\epsilon_{\vec{k}} - \mu)^2 + |\Delta|^2}}.\end{aligned}$$

- Converting this sum to an integral and noting that we now have a macroscopic number of Cooper pairs from the electrons within the energy shell $E_F = \pm \hbar\omega_D$ gives;

$$\begin{aligned}1 &= \frac{1}{2} \gamma^2 V \rho(E_F) \int_{-\hbar\omega_D}^{\hbar\omega_D} d\epsilon \frac{1}{\sqrt{\epsilon^2 + |\Delta|^2}}, \\ &= \xi \int_0^{\hbar\omega_D} d\epsilon \frac{1}{\sqrt{\epsilon^2 + |\Delta|^2}}, \\ &= \xi \operatorname{arcsinh} \left(\frac{\hbar\omega_D}{|\Delta|} \right)\end{aligned}$$

- Where $\xi = \gamma^2 V \rho(E_F)$ is the electron-phonon coupling parameter. Therefore, the zero temperature energy gap is

$$|\Delta(0)| = \frac{\hbar\omega_D}{\sinh(1/\xi)}$$

- For weak coupling, this becomes

$$|\Delta(0)| \approx 2\hbar\omega_d \exp(-1/\xi)$$

- This has a similar functional form to the binding energy in Cooper's problem for a single Cooper pair. This energy scale is also much smaller than that of other processes in solids, so is only expected at very low temperatures around 1K.
- This analysis is not valid where $\xi > 0.2 - 0.5$, as here the electron-phonon coupling effect must be accounted for (strong coupling).

BCS Theory at Finite Temperature

- Using the mean-field approximation and ignoring small or constant terms, the interaction part of the Hamiltonian may be written as

$$\begin{aligned}c_{\vec{k},\downarrow}^\dagger c_{\vec{-k},\downarrow}^\dagger c_{\vec{-k},\uparrow} c_{\vec{k},\uparrow} &= \left(\langle c_{\vec{k},\downarrow}^\dagger c_{\vec{-k},\downarrow}^\dagger \rangle + \langle c_{\vec{k},\downarrow}^\dagger c_{\vec{-k},\uparrow}^\dagger \rangle - \langle c_{\vec{k},\uparrow}^\dagger c_{\vec{-k},\downarrow}^\dagger \rangle \right) \times \\ &\quad \left(\langle c_{\vec{-k},\downarrow} c_{\vec{k},\uparrow}^\dagger \rangle + \langle c_{\vec{-k},\downarrow} c_{\vec{k},\uparrow} \rangle - \langle c_{\vec{-k},\uparrow} c_{\vec{k},\uparrow} \rangle \right), \\ &= \langle c_{\vec{k},\downarrow}^\dagger c_{\vec{-k},\downarrow}^\dagger \rangle \langle c_{\vec{-k},\downarrow} c_{\vec{k},\uparrow}^\dagger \rangle + \langle c_{\vec{k},\downarrow}^\dagger c_{\vec{-k},\downarrow}^\dagger \rangle \langle c_{\vec{-k},\downarrow} c_{\vec{k},\uparrow} \rangle - \langle c_{\vec{-k},\downarrow} c_{\vec{k},\uparrow}^\dagger \rangle \\ &\quad + \langle c_{\vec{k},\downarrow}^\dagger c_{\vec{-k},\downarrow}^\dagger - \langle c_{\vec{k},\uparrow}^\dagger c_{\vec{-k},\downarrow}^\dagger \rangle \rangle \langle c_{\vec{-k},\downarrow} c_{\vec{k},\uparrow} \rangle + \dots, \\ &\approx \langle c_{\vec{k},\downarrow}^\dagger c_{\vec{-k},\downarrow}^\dagger \rangle c_{\vec{-k},\downarrow} c_{\vec{k},\uparrow} + c_{\vec{k},\downarrow}^\dagger c_{\vec{-k},\downarrow}^\dagger \langle c_{\vec{-k},\downarrow} c_{\vec{k},\uparrow} \rangle + \dots\end{aligned}$$

- Now, noting that k sums are only over those in the energy range $\mu \pm \hbar\omega_D$ and using the definition $\hat{H}'_{BCS} = \hat{H}_{BCS} - \mu \langle N \rangle$ gives;

$$\begin{aligned}\hat{H}'_{BCS} &= \sum_{\vec{k}} \epsilon_{\vec{k}} (c_{\vec{k},\uparrow}^\dagger c_{\vec{k},\uparrow} + c_{\vec{-k},\downarrow}^\dagger c_{\vec{-k},\downarrow}) - \mu \langle \hat{N} \rangle - \gamma^2 \sum_{\vec{k},\vec{k}'} c_{\vec{k},\uparrow}^\dagger c_{\vec{-k},\downarrow}^\dagger c_{\vec{-k}',\uparrow} c_{\vec{k}',\downarrow}, \\ &\approx \sum_{\vec{k}} (\epsilon_{\vec{k}} - \mu) (c_{\vec{k},\uparrow}^\dagger c_{\vec{k},\uparrow} + c_{\vec{-k},\downarrow}^\dagger c_{\vec{-k},\downarrow}) - \gamma^2 \sum_{\vec{k},\vec{k}'} (\langle c_{\vec{k},\uparrow}^\dagger c_{\vec{-k},\downarrow}^\dagger \rangle c_{\vec{-k},\downarrow} c_{\vec{k}',\uparrow} + c_{\vec{k},\uparrow}^\dagger c_{\vec{-k},\downarrow}^\dagger \langle c_{\vec{-k},\downarrow} c_{\vec{k}',\uparrow} \rangle), \\ &\approx \sum_{\vec{k}} (\epsilon_{\vec{k}} - \mu) (c_{\vec{k},\uparrow}^\dagger c_{\vec{k},\uparrow} + c_{\vec{-k},\downarrow}^\dagger c_{\vec{-k},\downarrow}) - \sum_{\vec{k}} (\Delta^* c_{\vec{k},\uparrow}^\dagger c_{\vec{-k},\downarrow} + \Delta c_{\vec{k},\uparrow}^\dagger c_{\vec{-k},\downarrow}), \\ &\approx \sum_{\vec{k}} (\epsilon_{\vec{k}} - \mu) (n_{\vec{k},\uparrow} + n_{\vec{-k},\downarrow}) - \sum_{\vec{k}} (\Delta^* P_{\vec{k}} + \Delta P_{\vec{k}}^\dagger).\end{aligned}$$

- This is quadrating in creation and annihilation operators and can be diagonalised by the Bogoliubov-Valatin transformation by finding new field operators to diagonalise the Hamiltonian but still obey the correct commutation rules. Writing the Hamiltonian in quadratic form gives

$$\hat{H}'_{BCS} = \sum_{\vec{k}} \begin{pmatrix} c_{\vec{k},\uparrow}^\dagger & c_{\vec{-k},\downarrow} \end{pmatrix} \begin{pmatrix} \epsilon_{\vec{k}} - \mu & -\Delta \\ -\Delta^* & (\epsilon_{\vec{k}} - \mu) \end{pmatrix} \begin{pmatrix} c_{\vec{k},\uparrow} \\ c_{\vec{-k},\downarrow}^\dagger \end{pmatrix}.$$

- The 2x2 matrix has the same form as when calculating the BCS ground-state wavefunction, so also has solutions;

$$\begin{aligned}E_{\vec{k}} &= \pm \sqrt{(\epsilon_{\vec{k}} - \mu)^2 + |\Delta|^2}, \\ U_{\vec{k}}^{(-)} &= \begin{pmatrix} v_{\vec{k}}^* \\ u_{\vec{k}} \end{pmatrix}, \quad U_{\vec{k}}^{(+)} = \begin{pmatrix} u_{\vec{k}} \\ -v_{\vec{k}} \end{pmatrix}, \\ \text{where } |v_{\vec{k}}|^2 &= \frac{1}{2} \left(1 - \frac{\epsilon_{\vec{k}} - \mu}{|E_{\vec{k}}|} \right), \quad |u_{\vec{k}}|^2 = \frac{1}{2} \left(1 + \frac{\epsilon_{\vec{k}} - \mu}{|E_{\vec{k}}|} \right).\end{aligned}$$

- Now, defining a unitary transformation U with elements given by the components of the eigenvectors of the hamiltonian;

$$U = \begin{pmatrix} u_{\vec{k}} & v_{\vec{k}}^* \\ -v_{\vec{k}} & u_{\vec{k}}^* \end{pmatrix}$$

- Using this to diagonalise the Hamiltonian then gives

$$\begin{aligned}\begin{pmatrix} \epsilon_{\vec{k}} - \mu & -\Delta \\ -\Delta^* & (\epsilon_{\vec{k}} - \mu) \end{pmatrix} U &= U \begin{pmatrix} E_{\vec{k}} & 0 \\ 0 & -E_{\vec{k}} \end{pmatrix} \\ \implies \hat{H}'_{BCS} &= \sum_{\vec{k}} \begin{pmatrix} c_{\vec{k},\uparrow}^\dagger & c_{\vec{-k},\downarrow} \end{pmatrix} U \begin{pmatrix} E_{\vec{k}} & 0 \\ 0 & -E_{\vec{k}} \end{pmatrix} U^\dagger \begin{pmatrix} c_{\vec{k},\uparrow} \\ c_{\vec{-k},\downarrow}^\dagger \end{pmatrix}\end{aligned}$$

- The Bogoliubov-Valatin transformation then introduces

$$\begin{pmatrix} b_{\vec{k},\uparrow} \\ b_{\vec{-k},\downarrow}^\dagger \end{pmatrix} = U^\dagger \begin{pmatrix} c_{\vec{k},\uparrow} \\ c_{\vec{-k},\downarrow}^\dagger \end{pmatrix}.$$

- In terms of these operators, the Hamiltonian is diagonal;

$$\begin{aligned}\hat{H}'_{BCS} &= \sum_{\vec{k}} \begin{pmatrix} b_{\vec{k},\uparrow}^\dagger & b_{\vec{-k},\downarrow} \end{pmatrix} \begin{pmatrix} E_{\vec{k}} & 0 \\ 0 & -E_{\vec{k}} \end{pmatrix} \begin{pmatrix} b_{\vec{k},\uparrow} \\ b_{\vec{-k},\downarrow}^\dagger \end{pmatrix}, \\ &= \sum_{\vec{k}} (E_{\vec{k}} b_{\vec{k},\uparrow}^\dagger b_{\vec{k},\uparrow} - E_{\vec{k}} b_{\vec{-k},\downarrow}^\dagger b_{\vec{-k},\downarrow}).\end{aligned}$$

- These operators create quasiparticle excited states of the superconductor (Bogoliubov-Valatin quasiparticles).

- The BV quasiparticles never have energies less than $\pm\Delta$ near the chemical potential μ , so the excitation energies for adding or removing one of these quasiparticles are $E_{\vec{k}} \geq \Delta$ and $-E_{\vec{k}} \leq -\Delta$ respectively. Physical perturbations produce such quasiparticles with energy at least 2Δ .

- $b_{\vec{k},\lambda}$ satisfy the Fermionic anticommutation rules, are not present in the BCS ground state, and correspond to Fermionic quasiparticle excitations of energies $E_{\vec{k}} = \pm \sqrt{(\epsilon_{\vec{k}} - \mu)^2 - |\Delta|^2}$, so at finite temperature, the quasiparticle states are occupied according to the Fermi-Dirac distribution;

$$\langle b_{\vec{k},\uparrow}^\dagger b_{\vec{k},\uparrow} \rangle = f(E_{\vec{k}}) = \frac{1}{e^{E_{\vec{k}}/k_B T} + 1}, \quad \langle b_{\vec{-k},\downarrow}^\dagger b_{\vec{-k},\downarrow} \rangle = 1 - f(E_{\vec{k}}).$$

- By expressing the c operators in terms of the b operators and noting that the expectation values of the b -operators obey Fermi-Dirac statistics, we see that the gap parameter may be expressed as

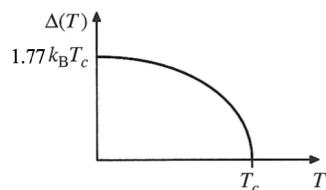
$$\begin{aligned}\Delta &= \gamma^2 \sum_{\vec{k}} \langle c_{-\vec{k},\downarrow} c_{\vec{k},\uparrow} \rangle \\ &= \gamma^2 \sum_{\vec{k}} u_k v_k^* (1 - 2f(E_{\vec{k}})) \\ &= \gamma^2 \sum_{\vec{k}} \frac{\Delta}{2|E_{\vec{k}}|} (1 - 2f(E_{\vec{k}})) \\ &= \gamma^2 \sum_{\vec{k}} \frac{\Delta}{2|E_{\vec{k}}|} \tanh\left(\frac{E_{\vec{k}}}{2k_B T}\right)\end{aligned}$$

- Therefore, dividing by Δ and converting the sum to an integral gives the gap equation, which for $T > 0$ can be solved to find the gap parameter;

$$1 \approx \xi \int_0^{\hbar\omega_D} d\epsilon \frac{1}{\sqrt{\epsilon^2 + |\Delta|^2}} \tanh\left(\frac{\sqrt{\epsilon^2 + |\Delta|^2}}{2k_B T}\right)$$

Predictions of BCS Theory

- Plotting the gap parameter Δ against temperature (below) is seen that $\Delta \rightarrow 0$ as $T \rightarrow T_c$, so it may be used as an order parameter for the phase transition.



- Where $\Delta \rightarrow 0$, is found that

$$k_B T_c = 1.13 \hbar \omega_D \exp\left(-\frac{1}{\xi}\right)$$

- This therefore predicts that $T_c \approx \omega_D \approx M^{-1/2}$ - **The Isotope effect**. Note, M is the mass of the crystal lattice ions, so may be changed by changing the isotope used, and this is in good agreement with experiment.

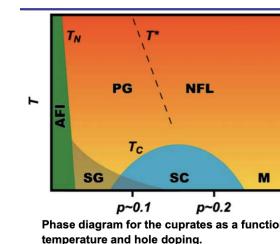
- Similarly, where $T \rightarrow 0$ it is found that

$$\frac{|\Delta(0)|}{k_B T_c} \approx \frac{2\hbar\omega_D \exp[-1/\xi]}{1.13\hbar\omega_D \exp[-1/\xi]} = 1.77.$$

- Persistent Current** - Now, we extend BCS theory to current-carrying Cooper pairs by pairing two electrons ($(\vec{k} + \vec{Q}, \uparrow)$ and $(-\vec{k} + \vec{Q}, \downarrow)$), such that each Cooper pair has total momentum $\vec{K} = 2\vec{Q}$.
 - If Q is sufficiently small, the COM kinetic energy is small compared to Δ .
 - In the current-carrying superconducting BCS state, all Cooper pairs have a common total momentum $2Q$.
 - Hence, degrading the current by changing the momentum of one electron pair costs at least 2Δ energy, and to degrade all electron pairs costs $2N\Delta$, which is prohibitive. Therefore, the current is un-degraded below T_c .
 - The only way to alter the current without such an energy penalty is to scatter all electron pairs simultaneously into a new coherent state with a different Q , such as by passing the supercurrent around a ring.

High - T_c Superconductivity

- All that is needed for high T_c superconductivity according to BCS theory are high-frequency phonons, strong electron-phonon coupling and a high density of states.
 - This is potentially achievable with metallic hydrogen and covalent compounds dominated by hydrogen. This is because hydrogen atoms can provide high frequency phonon modes and strong electron-phonon coupling.
 - In the case of H_2S , it is thought that at extremely high pressure, a metallic H_3S state is formed.
- High-temperature superconductivity can also be observed in a range of oxide compounds, mostly cuprates containing 2D sheets of CuO_2 .
 - The pairing mechanism for Cooper pairs here is unknown, but is thought to be superexchange related rather than arising from the electron-phonon interaction.
 - The critical temperatures in these materials are found to be much larger than expected from BCS theory.
 - It is also experimentally observed that for such materials, $\alpha = 0$, implying the attractive interaction causing the formation of Cooper pairs may not be phonon-mediated.
 - For example, in La_2CuO_4 , which takes a body-centred tetragonal structure, the CuO_2 planes are mainly responsible for condition and superconductivity.
 - Within undoped compounds, there is one spin 1/2 hole present in each Cu d- shell per site. However, the strong electron-electron interaction prevents hopping between copper sites and hence double occupation of the copper sites. Therefore, for charge to move, it must go via a non-magnetic oxygen ion by superexchange. Materials like this are antiferromagnetic Mott insulators.
 - Doping such a compound by introducing charges into the CuO_2 layers, such as by substitution of the La^{3+} by Sr^{2+} eventually allows electron hopping (not possible if all spins aligned).
 - It is also unusual that superconductivity and magnetism can exist closely, as the magnetism and Cooper pair formation mechanisms should compete.



Phase diagram for the cuprates as a function of temperature and hole doping.

- Introducing Zn impurities can suppress superconductivity near the impurity and form a quasiparticle scattering resonance.
 - An anisotropic spatial distribution of the suppression of the gap in the vicinity of the impurity, implies the gap parameter must have d-wave symmetry.