

Lecture Notes on Condensed Matter Physics
(A Work in Progress)

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0.1 Preface

This is a proto-preface. A more complete preface will be written after these notes are completed.

These lecture notes are intended to supplement a graduate level course in condensed matter physics.

Chapter 0

Introductory Information

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A strong emphasis of this class will be on learning how to calculate. I plan to cover the following topics this quarter:

Transport: Boltzmann equation, transport coefficients, cyclotron resonance, magnetoresistance, thermal transport, electron-phonon scattering

Mesoscopic Physics: Landauer formula, conductance fluctuations, Aharonov-Bohm effect, disorder, weak localization, Anderson localization

Magnetism: Weak vs. strong, local vs. itinerant, Hubbard and Heisenberg models, spin wave theory, magnetic ordering, Kondo effect

Other: Linear response theory, Fermi liquid theory (time permitting)

There will be about four assignments and a take-home final examination. I will be following my own notes, which are available from the course web site.

0.1 References

- D. Feng and G. Jin, Introduction to Condensed Matter Physics (I)
(World Scientific, Singapore, 2005)
New and with a distinctly modern flavor and set of topics. Looks good.
- N. Ashcroft and N. D. Mermin, Solid State Physics
(Saunders College Press, Philadelphia, 1976)
Beautifully written, this classic text is still one of the best comprehensive guides.
- M. Marder, Condensed Matter Physics
(John Wiley & Sons, New York, 2000)
A thorough and advanced level treatment of transport theory in gases, metals, semiconductors, insulators, and superconductors.
- D. Pines, Elementary Excitations in Solids
(Perseus, New York, 1999)
An advanced level text on the quantum theory of solids, treating phonons, electrons, plasmons, and photons.
- P. L. Taylor and O. Heinonen, A Quantum Approach to Condensed Matter Physics
(Cambridge University Press, New York, 2002)
A modern, intermediate level treatment of the quantum theory of solids.
- J. M. Ziman, Principles of the Theory of Solids
(Cambridge University Press, New York, 1979).
A classic text on solid state physics. Very readable.

- C. Kittel, *Quantum Theory of Solids*
(John Wiley & Sons, New York, 1963)
A graduate level text with several detailed derivations.
- H. Smith and H. H. Jensen, *Transport Phenomena*
(Oxford University Press, New York, 1989).
A detailed and lucid account of transport theory in gases, liquids, and solids, both classical and quantum.
- J. Imry, *Introduction to Mesoscopic Physics*
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- M. Janssen, *Fluctuations and Localization*
(World Scientific, Singapore, 2001)
- A. Auerbach, *Interacting Electrons and Quantum Magnetism*
(Springer-Verlag, New York, 1994)
- N. Spaldin, *Magnetic Materials*
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(Springer-Verlag, New York, 2001)

Chapter 1

Boltzmann Transport

1.1 References

- H. Smith and H. H. Jensen, Transport Phenomena
- N. W. Ashcroft and N. D. Mermin, Solid State Physics, chapter 13.
- P. L. Taylor and O. Heinonen, Condensed Matter Physics, chapter 8.
- J. M. Ziman, Principles of the Theory of Solids, chapter 7.

1.2 Introduction

Transport is the phenomenon of currents flowing in response to applied fields. By ‘current’ we generally mean an electrical current \mathbf{j} , or thermal current \mathbf{j}_q . By ‘applied field’ we generally mean an electric field \mathcal{E} or a temperature gradient ∇T . The currents and fields are linearly related, and it will be our goal to calculate the coefficients (known as transport coefficients) of these linear relations. Implicit in our discussion is the assumption that we are always dealing with systems near equilibrium.

1.3 Boltzmann Equation in Solids

1.3.1 Semiclassical Dynamics and Distribution Functions

The semiclassical dynamics of a wavepacket in a solid are described by the equations

$$\frac{d\mathbf{r}}{dt} = \mathbf{v}_n(\mathbf{k}) = \frac{1}{\hbar} \frac{\partial \varepsilon_n(\mathbf{k})}{\partial \mathbf{k}} \quad (1.1)$$

$$\frac{d\mathbf{k}}{dt} = -\frac{e}{\hbar} \mathbf{E}(\mathbf{r}, t) - \frac{e}{\hbar c} \mathbf{v}_n(\mathbf{k}) \times \mathbf{B}(\mathbf{r}, t). \quad (1.2)$$

Here, n is the band index and $\varepsilon_n(\mathbf{k})$ is the dispersion relation for band n . The wavevector is \mathbf{k} ($\hbar\mathbf{k}$ is the ‘crystal momentum’), and $\varepsilon_n(\mathbf{k})$ is periodic under $\mathbf{k} \rightarrow \mathbf{k} + \mathbf{G}$, where \mathbf{G} is any reciprocal lattice vector. These formulae are valid only at sufficiently weak fields. They neglect, for example, Zener tunneling processes in which an electron may change its band index as it traverses the Brillouin zone. We also neglect the spin-orbit interaction in our discussion.

We are of course interested in more than just a single electron, hence to that end let us consider the distribution function $f_n(\mathbf{r}, \mathbf{k}, t)$, defined such that¹

$$f_{n\sigma}(\mathbf{r}, \mathbf{k}, t) \frac{d^3r d^3k}{(2\pi)^3} \equiv \begin{matrix} \# \text{ of electrons of spin } \sigma \text{ in band } n \text{ with positions within} \\ d^3r \text{ of } \mathbf{r} \text{ and wavevectors within } d^3k \text{ of } \mathbf{k} \text{ at time } t. \end{matrix} \quad (1.3)$$

Note that the distribution function is dimensionless. By performing integrals over the distribution function, we can obtain various physical quantities. For example, the current density at \mathbf{r} is given by

$$\mathbf{j}(\mathbf{r}, t) = -e \sum_{n,\sigma} \int_{\hat{\Omega}} \frac{d^3k}{(2\pi)^3} f_{n\sigma}(\mathbf{r}, \mathbf{k}, t) \mathbf{v}_n(\mathbf{k}). \quad (1.4)$$

The symbol $\hat{\Omega}$ in the above formula is to remind us that the wavevector integral is performed only over the first Brillouin zone.

We now ask how the distribution functions $f_{n\sigma}(\mathbf{r}, \mathbf{k}, t)$ evolve in time. To simplify matters, we will consider a single band and drop the indices $n\sigma$. It is clear that in the absence of collisions, the distribution function must satisfy the continuity equation,

$$\frac{\partial f}{\partial t} + \boldsymbol{\nabla} \cdot (\mathbf{u} f) = 0. \quad (1.5)$$

This is just the condition of number conservation for electrons. Take care to note that $\boldsymbol{\nabla}$ and \mathbf{u} are *six*-dimensional phase space vectors:

$$\mathbf{u} = (\dot{x}, \dot{y}, \dot{z}, \dot{k}_x, \dot{k}_y, \dot{k}_z) \quad (1.6)$$

$$\boldsymbol{\nabla} = \left(\frac{\partial}{\partial x}, \frac{\partial}{\partial y}, \frac{\partial}{\partial z}, \frac{\partial}{\partial k_x}, \frac{\partial}{\partial k_y}, \frac{\partial}{\partial k_z} \right). \quad (1.7)$$

¹We will assume three space dimensions. The discussion may be generalized to quasi-two dimensional and quasi-one dimensional systems as well.

Now note that as a consequence of the dynamics (1.1,1.2) that $\nabla \cdot \mathbf{u} = 0$, *i.e.* phase space flow is *incompressible*, provided that $\varepsilon(\mathbf{k})$ is a function of \mathbf{k} alone, and not of \mathbf{r} . Thus, in the absence of collisions, we have

$$\frac{\partial f}{\partial t} + \mathbf{u} \cdot \nabla f = 0 . \quad (1.8)$$

The differential operator $D_t \equiv \partial_t + \mathbf{u} \cdot \nabla$ is sometimes called the ‘convective derivative’.

EXERCISE: Show that $\nabla \cdot \mathbf{u} = 0$.

Next we must consider the effect of collisions, which are not accounted for by the semi-classical dynamics. In a collision process, an electron with wavevector \mathbf{k} and one with wavevector \mathbf{k}' can instantaneously convert into a pair with wavevectors $\mathbf{k} + \mathbf{q}$ and $\mathbf{k}' - \mathbf{q}$ (modulo a reciprocal lattice vector \mathbf{G}), where \mathbf{q} is the wavevector transfer. Note that the total wavevector is preserved ($\text{mod } \mathbf{G}$). This means that $D_t f \neq 0$. Rather, we should write

$$\frac{\partial f}{\partial t} + \dot{\mathbf{r}} \cdot \frac{\partial f}{\partial \mathbf{r}} + \dot{\mathbf{k}} \cdot \frac{\partial f}{\partial \mathbf{k}} = \left(\frac{\partial f}{\partial t} \right)_{\text{coll}} \equiv \mathcal{I}_{\mathbf{k}}\{f\} \quad (1.9)$$

where the right side is known as the *collision integral*. The collision integral is in general a *function* of \mathbf{r} , \mathbf{k} , and t and a *functional* of the distribution f . As the \mathbf{k} -dependence is the most important for our concerns, we will write $\mathcal{I}_{\mathbf{k}}$ in order to make this dependence explicit. Some examples should help clarify the situation.

First, let’s consider a very simple model of the collision integral,

$$\mathcal{I}_{\mathbf{k}}\{f\} = -\frac{f(\mathbf{r}, \mathbf{k}, t) - f^0(\mathbf{r}, \mathbf{k})}{\tau(\varepsilon(\mathbf{k}))} . \quad (1.10)$$

This model is known as the *relaxation time approximation*. Here, $f^0(\mathbf{r}, \mathbf{k})$ is a static distribution function which describes a *local equilibrium* at \mathbf{r} . The quantity $\tau(\varepsilon(\mathbf{k}))$ is the *relaxation time*, which we allow to be energy-dependent. Note that the collision integral indeed depends on the variables $(\mathbf{r}, \mathbf{k}, t)$, and has a particularly simple functional dependence on the distribution f .

A more sophisticated model might invoke Fermi’s golden rule, Consider elastic scattering from a static potential $\mathcal{U}(\mathbf{r})$ which induces transitions between different momentum states. We can then write

$$\mathcal{I}_{\mathbf{k}}\{f\} = \frac{2\pi}{\hbar} \sum_{\mathbf{k}' \in \hat{\Omega}} |\langle \mathbf{k}' | \mathcal{U} | \mathbf{k} \rangle|^2 (f_{\mathbf{k}'} - f_{\mathbf{k}}) \delta(\varepsilon_{\mathbf{k}} - \varepsilon_{\mathbf{k}'}) \quad (1.11)$$

$$= \frac{2\pi}{\hbar V} \int_{\hat{\Omega}} \frac{d^3 k'}{(2\pi)^3} |\hat{\mathcal{U}}(\mathbf{k} - \mathbf{k}')|^2 (f_{\mathbf{k}'} - f_{\mathbf{k}}) \delta(\varepsilon_{\mathbf{k}} - \varepsilon_{\mathbf{k}'}) \quad (1.12)$$

where we abbreviate $f_{\mathbf{k}} \equiv f(\mathbf{r}, \mathbf{k}, t)$. In deriving the last line we’ve used plane wave wave-

functions² $\psi_{\mathbf{k}}(\mathbf{r}) = \exp(i\mathbf{k} \cdot \mathbf{r})/\sqrt{V}$, as well as the result

$$\sum_{\mathbf{k} \in \hat{\Omega}} A(\mathbf{k}) = V \int_{\hat{\Omega}} \frac{d^3k}{(2\pi)^3} A(\mathbf{k}) \quad (1.13)$$

for smooth functions $A(\mathbf{k})$. Note the factor of V^{-1} in front of the integral in eqn. 1.12. What this tells us is that for a bounded localized potential $\mathcal{U}(\mathbf{r})$, the contribution to the collision integral is inversely proportional to the size of the system. This makes sense because the number of electrons scales as V but the potential is only appreciable over a region of volume $\propto V^0$. Later on, we shall consider a finite density of scatterers, writing $\mathcal{U}(\mathbf{r}) = \sum_{i=1}^{N_{\text{imp}}} U(\mathbf{r} - \mathbf{R}_i)$, where the impurity density $n_{\text{imp}} = N_{\text{imp}}/V$ is finite, scaling as V^0 . In this case $\hat{\mathcal{U}}(\mathbf{k} - \mathbf{k}')$ apparently scales as V , which would mean $\mathcal{I}_{\mathbf{k}}\{f\}$ scales as V , which is unphysical. As we shall see, the random positioning of the impurities means that the $\mathcal{O}(V^2)$ contribution to $|\hat{\mathcal{U}}(\mathbf{k} - \mathbf{k}')|^2$ is *incoherent* and averages out to zero. The coherent piece scales as V , canceling the V in the denominator of eqn. 1.12, resulting in a finite value for the collision integral in the thermodynamic limit (*i.e.* neither infinite nor infinitesimal).

Later on we will discuss electron-phonon scattering, which is *inelastic*. An electron with wavevector \mathbf{k}' can scatter into a state with wavevector $\mathbf{k} = \mathbf{k}' - \mathbf{q} \bmod \mathbf{G}$ by absorption of a phonon of wavevector \mathbf{q} or emission of a phonon of wavevector $-\mathbf{q}$. Similarly, an electron of wavevector \mathbf{k} can scatter into the state \mathbf{k}' by emission of a phonon of wavevector $-\mathbf{q}$ or absorption of a phonon of wavevector \mathbf{q} . The matrix element for these processes depends on \mathbf{k} , \mathbf{k}' , and the polarization index of the phonon. Overall, energy is conserved. These considerations lead us to the following collision integral:

$$\begin{aligned} \mathcal{I}_{\mathbf{k}}\{f, n\} = & \frac{2\pi}{\hbar V} \sum_{\mathbf{k}', \lambda} |g_{\lambda}(\mathbf{k}, \mathbf{k}')|^2 \left\{ (1 - f_{\mathbf{k}}) f_{\mathbf{k}'} (1 + n_{\mathbf{q}, \lambda}) \delta(\varepsilon_{\mathbf{k}} + \hbar\omega_{\mathbf{q}\lambda} - \varepsilon_{\mathbf{k}'}) \right. \\ & + (1 - f_{\mathbf{k}}) f_{\mathbf{k}'} n_{-\mathbf{q}\lambda} \delta(\varepsilon_{\mathbf{k}} - \hbar\omega_{-\mathbf{q}\lambda} - \varepsilon_{\mathbf{k}'}) \\ & - f_{\mathbf{k}} (1 - f_{\mathbf{k}'}) (1 + n_{-\mathbf{q}\lambda}) \delta(\varepsilon_{\mathbf{k}} - \hbar\omega_{-\mathbf{q}\lambda} - \varepsilon_{\mathbf{k}'}) \\ & \left. - f_{\mathbf{k}} (1 - f_{\mathbf{k}'}) n_{\mathbf{q}\lambda} \delta(\varepsilon_{\mathbf{k}} + \hbar\omega_{\mathbf{q}\lambda} - \varepsilon_{\mathbf{k}'}) \right\} \delta_{\mathbf{q}, \mathbf{k}' - \mathbf{k} \bmod \mathbf{G}}, \end{aligned} \quad (1.14)$$

which is a functional of both the electron distribution $f_{\mathbf{k}}$ as well as the phonon distribution $n_{\mathbf{q}\lambda}$. The four terms inside the curly brackets correspond, respectively, to cases (a) through (d) in fig. 1.1.

While collisions will violate crystal momentum conservation, they do not violate conservation of particle number. Hence we should have³

$$\int d^3r \int_{\hat{\Omega}} \frac{d^3k}{(2\pi)^3} \mathcal{I}_{\mathbf{k}}\{f\} = 0. \quad (1.15)$$

²Rather than plane waves, we should use Bloch waves $\psi_{n\mathbf{k}}(\mathbf{r}) = \exp(i\mathbf{k} \cdot \mathbf{r}) u_{n\mathbf{k}}(\mathbf{r})$, where cell function $u_{n\mathbf{k}}(\mathbf{r})$ satisfies $u_{n\mathbf{k}}(\mathbf{r} + \mathbf{R}) = u_{n\mathbf{k}}(\mathbf{r})$, where \mathbf{R} is any direct lattice vector. Plane waves do not contain the cell functions, although they do exhibit Bloch periodicity $\psi_{n\mathbf{k}}(\mathbf{r} + \mathbf{R}) = \exp(i\mathbf{k} \cdot \mathbf{R}) \psi_{n\mathbf{k}}(\mathbf{r})$.

³If collisions are purely local, then $\int_{\hat{\Omega}} \frac{d^3k}{(2\pi)^3} \mathcal{I}_{\mathbf{k}}\{f\} = 0$ at every point \mathbf{r} in space.

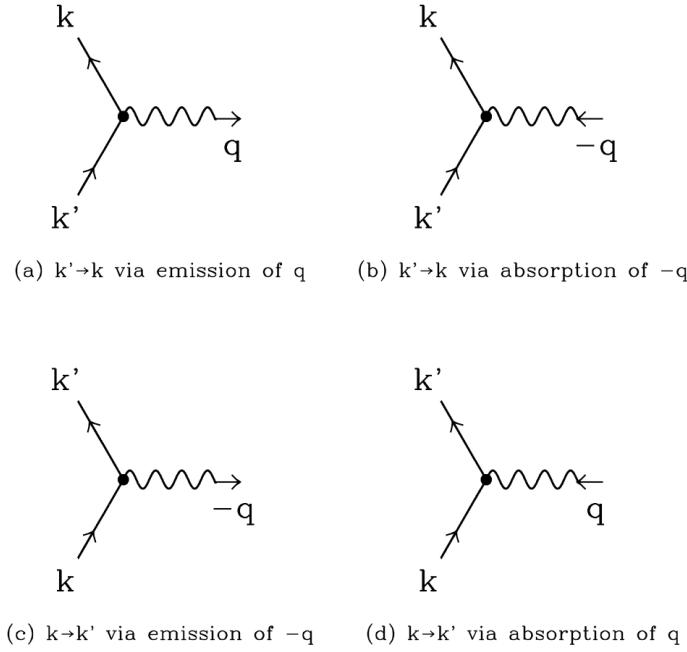


Figure 1.1: Electron-phonon vertices.

The total particle number,

$$N = \int d^3r \int_{\hat{\Omega}} \frac{d^3k}{(2\pi)^3} f(\mathbf{r}, \mathbf{k}, t) \quad (1.16)$$

is a *collisional invariant* - a quantity which is preserved in the collision process. Other collisional invariants include energy (when all sources are accounted for), spin (total spin), and crystal momentum (if there is no breaking of lattice translation symmetry)⁴. Consider a function $F(\mathbf{r}, \mathbf{k})$ of position and wavevector. Its average value is

$$\bar{F}(t) = \int d^3r \int_{\hat{\Omega}} \frac{d^3k}{(2\pi)^3} F(\mathbf{r}, \mathbf{k}) f(\mathbf{r}, \mathbf{k}, t) . \quad (1.17)$$

Taking the time derivative,

$$\begin{aligned} \frac{d\bar{F}}{dt} &= \frac{\partial \bar{F}}{\partial t} = \int d^3r \int_{\hat{\Omega}} \frac{d^3k}{(2\pi)^3} F(\mathbf{r}, \mathbf{k}) \left\{ -\frac{\partial}{\partial \mathbf{r}} \cdot (\dot{\mathbf{r}}f) - \frac{\partial}{\partial \mathbf{k}} \cdot (\dot{\mathbf{k}}f) + \mathcal{I}_{\mathbf{k}}\{f\} \right\} \\ &= \int d^3r \int_{\hat{\Omega}} \frac{d^3k}{(2\pi)^3} \left\{ \left[\frac{\partial F}{\partial \mathbf{r}} \cdot \frac{d\mathbf{r}}{dt} + \frac{\partial F}{\partial \mathbf{k}} \cdot \frac{d\mathbf{k}}{dt} \right] f + F \mathcal{I}_{\mathbf{k}}\{f\} \right\} . \end{aligned} \quad (1.18)$$

⁴Note that the relaxation time approximation violates all such conservation laws. Within the relaxation time approximation, there are no collisional invariants.

Hence, if F is preserved by the dynamics between collisions, then

$$\frac{d\bar{F}}{dt} = \int d^3r \int_{\hat{\Omega}} \frac{d^3k}{(2\pi)^3} F \mathcal{I}_k\{f\}, \quad (1.19)$$

which says that $\dot{\bar{F}}(t)$ changes only as a result of collisions. If F is a collisional invariant, then $\dot{\bar{F}} = 0$. This is the case when $F = 1$, in which case \bar{F} is the total number of particles, or when $F = \varepsilon(\mathbf{k})$, in which case \bar{F} is the total energy.

1.3.2 Local Equilibrium

The equilibrium Fermi distribution,

$$f^0(\mathbf{k}) = \left\{ \exp \left(\frac{\varepsilon(\mathbf{k}) - \mu}{k_B T} \right) + 1 \right\}^{-1} \quad (1.20)$$

is a space-independent and time-independent solution to the Boltzmann equation. Since collisions act *locally* in space, they act on short time scales to establish a *local equilibrium* described by a distribution function

$$f^0(\mathbf{r}, \mathbf{k}, t) = \left\{ \exp \left(\frac{\varepsilon(\mathbf{k}) - \mu(\mathbf{r}, t)}{k_B T(\mathbf{r}, t)} \right) + 1 \right\}^{-1} \quad (1.21)$$

This is, however, not a solution to the full Boltzmann equation due to the ‘streaming terms’ $\dot{\mathbf{r}} \cdot \partial_{\mathbf{r}} + \dot{\mathbf{k}} \cdot \partial_{\mathbf{k}}$ in the convective derivative. These, though, act on longer time scales than those responsible for the establishment of local equilibrium. To obtain a solution, we write

$$f(\mathbf{r}, \mathbf{k}, t) = f^0(\mathbf{r}, \mathbf{k}, t) + \delta f(\mathbf{r}, \mathbf{k}, t) \quad (1.22)$$

and solve for the deviation $\delta f(\mathbf{r}, \mathbf{k}, t)$. We will assume $\mu = \mu(\mathbf{r})$ and $T = T(\mathbf{r})$ are time-independent. We first compute the differential of f^0 ,

$$\begin{aligned} df^0 &= k_B T \frac{\partial f^0}{\partial \varepsilon} d\left(\frac{\varepsilon - \mu}{k_B T}\right) \\ &= k_B T \frac{\partial f^0}{\partial \varepsilon} \left\{ -\frac{d\mu}{k_B T} - \frac{(\varepsilon - \mu) dT}{k_B T^2} + \frac{d\varepsilon}{k_B T} \right\} \\ &= -\frac{\partial f^0}{\partial \varepsilon} \left\{ \frac{\partial \mu}{\partial \mathbf{r}} \cdot d\mathbf{r} + \frac{\varepsilon - \mu}{T} \frac{\partial T}{\partial \mathbf{r}} \cdot d\mathbf{r} - \frac{\partial \varepsilon}{\partial \mathbf{k}} \cdot d\mathbf{k} \right\}, \end{aligned} \quad (1.23)$$

from which we read off

$$\frac{\partial f^0}{\partial \mathbf{r}} = \left\{ \frac{\partial \mu}{\partial \mathbf{r}} + \frac{\varepsilon - \mu}{T} \frac{\partial T}{\partial \mathbf{r}} \right\} \left(-\frac{\partial f^0}{\partial \varepsilon} \right) \quad (1.24)$$

$$\frac{\partial f^0}{\partial \mathbf{k}} = \hbar \mathbf{v} \frac{\partial f^0}{\partial \varepsilon}. \quad (1.25)$$

We thereby obtain

$$\frac{\partial \delta f}{\partial t} + \mathbf{v} \cdot \nabla \delta f - \frac{e}{\hbar} \left[\mathbf{E} + \frac{1}{c} \mathbf{v} \times \mathbf{B} \right] \cdot \frac{\partial \delta f}{\partial \mathbf{k}} + \mathbf{v} \cdot \left[e \mathcal{E} + \frac{\varepsilon - \mu}{T} \nabla T \right] \left(-\frac{\partial f^0}{\partial \varepsilon} \right) = \mathcal{I}_{\mathbf{k}} \{ f^0 + \delta f \} \quad (1.26)$$

where $\mathcal{E} = -\nabla(\phi - \mu/e)$ is the gradient of the ‘electrochemical potential’; we’ll henceforth refer to \mathcal{E} as the electric field. Eqn (1.26) is a nonlinear integrodifferential equation in δf , with the nonlinearity coming from the collision integral. (In some cases, such as impurity scattering, the collision integral may be a linear functional.) We will solve a *linearized* version of this equation, assuming the system is always close to a state of local equilibrium.

Note that the inhomogeneous term in (1.26) involves the electric field and the temperature gradient ∇T . This means that δf is proportional to these quantities, and if they are small then δf is small. The gradient of δf is then of second order in smallness, since the external fields $\phi - \mu/e$ and T are assumed to be slowly varying in space. To lowest order in smallness, then, we obtain the following *linearized Boltzmann equation*:

$$\frac{\partial \delta f}{\partial t} - \frac{e}{\hbar c} \mathbf{v} \times \mathbf{B} \cdot \frac{\partial \delta f}{\partial \mathbf{k}} + \mathbf{v} \cdot \left[e \mathcal{E} + \frac{\varepsilon - \mu}{T} \nabla T \right] \left(-\frac{\partial f^0}{\partial \varepsilon} \right) = \mathcal{L} \delta f \quad (1.27)$$

where $\mathcal{L} \delta f$ is the *linearized collision integral*; \mathcal{L} is a linear operator acting on δf (we suppress denoting the \mathbf{k} dependence of \mathcal{L}). Note that we have not assumed that \mathbf{B} is small. Indeed later on we will derive expressions for high B transport coefficients.

1.4 Conductivity of Normal Metals

1.4.1 Relaxation Time Approximation

Consider a normal metal in the presence of an electric field \mathcal{E} . We’ll assume $\mathbf{B} = 0$, $\nabla T = 0$, and also that \mathcal{E} is spatially uniform as well. This in turn guarantees that δf itself is spatially uniform. The Boltzmann equation then reduces to

$$\frac{\partial \delta f}{\partial t} - \frac{\partial f^0}{\partial \varepsilon} e \mathbf{v} \cdot \mathcal{E} = \mathcal{I}_{\mathbf{k}} \{ f^0 + \delta f \} . \quad (1.28)$$

We’ll solve this by adopting the relaxation time approximation for $\mathcal{I}_{\mathbf{k}} \{ f \}$:

$$\mathcal{I}_{\mathbf{k}} \{ f \} = -\frac{f - f^0}{\tau} = -\frac{\delta f}{\tau} , \quad (1.29)$$

where τ , which may be \mathbf{k} -dependent, is the *relaxation time*. In the absence of any fields or temperature and electrochemical potential gradients, the Boltzmann equation becomes $\dot{\delta f} = -\delta f/\tau$, with the solution $\delta f(t) = \delta f(0) \exp(-t/\tau)$. The distribution thereby relaxes to the equilibrium one on the scale of τ .

Writing $\mathcal{E}(t) = \mathcal{E} e^{-i\omega t}$, we solve

$$\frac{\partial \delta f(\mathbf{k}, t)}{\partial t} - e \mathbf{v}(\mathbf{k}) \cdot \mathcal{E} e^{-i\omega t} \frac{\partial f^0}{\partial \varepsilon} = -\frac{\delta f(\mathbf{k}, t)}{\tau(\varepsilon(\mathbf{k}))} \quad (1.30)$$

and obtain

$$\delta f(\mathbf{k}, t) = \frac{e \mathcal{E} \cdot \mathbf{v}(\mathbf{k}) \tau(\varepsilon(\mathbf{k}))}{1 - i\omega \tau(\varepsilon(\mathbf{k}))} \frac{\partial f^0}{\partial \varepsilon} e^{-i\omega t}. \quad (1.31)$$

The equilibrium distribution $f^0(\mathbf{k})$ results in zero current, since $f^0(-\mathbf{k}) = f^0(\mathbf{k})$. Thus, the current density is given by the expression

$$\begin{aligned} j^\alpha(\mathbf{r}, t) &= -2e \int_{\hat{\Omega}} \frac{d^3k}{(2\pi)^3} \delta f v^\alpha \\ &= 2e^2 \mathcal{E}^\beta e^{-i\omega t} \int_{\hat{\Omega}} \frac{d^3k}{(2\pi)^3} \frac{\tau(\varepsilon(\mathbf{k})) v^\alpha(\mathbf{k}) v^\beta(\mathbf{k})}{1 - i\omega \tau(\varepsilon(\mathbf{k}))} \left(-\frac{\partial f^0}{\partial \varepsilon} \right). \end{aligned} \quad (1.32)$$

In the above calculation, the factor of two arises from summing over spin polarizations. The conductivity tensor is defined by the linear relation $j^\alpha(\omega) = \sigma_{\alpha\beta}(\omega) \mathcal{E}^\beta(\omega)$. We have thus derived an expression for the conductivity tensor,

$$\sigma_{\alpha\beta}(\omega) = 2e^2 \int_{\hat{\Omega}} \frac{d^3k}{(2\pi)^3} \frac{\tau(\varepsilon(\mathbf{k})) v^\alpha(\mathbf{k}) v^\beta(\mathbf{k})}{1 - i\omega \tau(\varepsilon(\mathbf{k}))} \left(-\frac{\partial f^0}{\partial \varepsilon} \right) \quad (1.33)$$

Note that the conductivity is a property of the *Fermi surface*. For $k_B T \ll \varepsilon_F$, we have $-\partial f^0 / \partial \varepsilon \approx \delta(\varepsilon_F - \varepsilon(\mathbf{k}))$ and the above integral is over the Fermi surface alone. Explicitly, we change variables to energy ε and coordinates along a constant energy surface, writing

$$d^3k = \frac{d\varepsilon dS_\varepsilon}{|\partial \varepsilon / \partial \mathbf{k}|} = \frac{d\varepsilon dS_\varepsilon}{\hbar |\mathbf{v}|}, \quad (1.34)$$

where dS_ε is the differential area on the constant energy surface $\varepsilon(\mathbf{k}) = \varepsilon$, and $\mathbf{v}(\mathbf{k}) = \hbar^{-1} \nabla_{\mathbf{k}} \varepsilon(\mathbf{k})$ is the velocity. For $T \ll T_F$, then,

$$\sigma_{\alpha\beta}(\omega) = \frac{e^2}{4\pi^3 \hbar} \frac{\tau(\varepsilon_F)}{1 - i\omega \tau(\varepsilon_F)} \int dS_F \frac{v^\alpha(\mathbf{k}) v^\beta(\mathbf{k})}{|\mathbf{v}(\mathbf{k})|}. \quad (1.35)$$

For free electrons in a parabolic band, we write $\varepsilon(\mathbf{k}) = \hbar^2 \mathbf{k}^2 / 2m^*$, so $v^\alpha(\mathbf{k}) = \hbar k^\alpha / m^*$. To further simplify matters, let us assume that τ is constant, or at least very slowly varying in the vicinity of the Fermi surface. We find

$$\sigma_{\alpha\beta}(\omega) = \delta_{\alpha\beta} \frac{2}{3m^*} \frac{e^2 \tau}{1 - i\omega \tau} \int d\varepsilon g(\varepsilon) \varepsilon \left(-\frac{\partial f^0}{\partial \varepsilon} \right), \quad (1.36)$$

where $g(\varepsilon)$ is the *density of states*,

$$g(\varepsilon) = 2 \int_{\hat{\Omega}} \frac{d^3k}{(2\pi)^3} \delta(\varepsilon - \varepsilon(\mathbf{k})). \quad (1.37)$$

The (three-dimensional) parabolic band density of states is found to be

$$g(\varepsilon) = \frac{(2m^*)^{3/2}}{2\pi^2\hbar^3} \sqrt{\varepsilon} \Theta(\varepsilon), \quad (1.38)$$

where $\Theta(x)$ is the step function. In fact, integrating (1.36) by parts, we only need to know about the $\sqrt{\varepsilon}$ dependence in $g(\varepsilon)$, and not the details of its prefactor:

$$\begin{aligned} \int d\varepsilon \varepsilon g(\varepsilon) \left(-\frac{\partial f^0}{\partial \varepsilon} \right) &= \int d\varepsilon f^0(\varepsilon) \frac{\partial}{\partial \varepsilon} (\varepsilon g(\varepsilon)) \\ &= \frac{3}{2} \int d\varepsilon g(\varepsilon) f^0(\varepsilon) = \frac{3}{2} n, \end{aligned} \quad (1.39)$$

where $n = N/V$ is the electron number density for the conduction band. The final result for the conductivity tensor is

$$\sigma_{\alpha\beta}(\omega) = \frac{ne^2\tau}{m^*} \frac{\delta_{\alpha\beta}}{1 - i\omega\tau} \quad (1.40)$$

This is called the *Drude model* of electrical conduction in metals. The dissipative part of the conductivity is $\text{Re } \sigma$. Writing $\sigma_{\alpha\beta} = \sigma\delta_{\alpha\beta}$ and separating into real and imaginary parts $\sigma = \sigma' + i\sigma''$, we have

$$\sigma'(\omega) = \frac{ne^2\tau}{m^*} \frac{1}{1 + \omega^2\tau^2}. \quad (1.41)$$

The peak at $\omega = 0$ is known as the *Drude peak*.

Here's an elementary derivation of this result. Let $\mathbf{p}(t)$ be the momentum of an electron, and solve the equation of motion

$$\frac{d\mathbf{p}}{dt} = -\frac{\mathbf{p}}{\tau} - e\mathcal{E}e^{-i\omega t} \quad (1.42)$$

to obtain

$$\mathbf{p}(t) = -\frac{e\tau\mathcal{E}}{1 - i\omega\tau} e^{-i\omega t} + \left[\mathbf{p}(0) + \frac{e\tau\mathcal{E}}{1 - i\omega\tau} \right] e^{-t/\tau}. \quad (1.43)$$

The second term above is a transient solution to the homogeneous equation $\dot{\mathbf{p}} + \mathbf{p}/\tau = 0$. At long times, then, the current $\mathbf{j} = -nep/m^*$ is

$$\mathbf{j}(t) = \frac{ne^2\tau}{m^*(1 - i\omega\tau)} \mathcal{E} e^{-i\omega t}. \quad (1.44)$$

In the Boltzmann equation approach, however, we understand that n is the conduction electron density, which does not include contributions from filled bands.

In solids the effective mass m^* typically varies over a small range: $m^* \approx (0.1 - 1) m_e$. The two factors which principally determine the conductivity are then the carrier density n and the scattering time τ . The *mobility* μ , defined as the ratio $\sigma(\omega = 0)/ne$, is thus (roughly) independent of carrier density⁵. Since $\mathbf{j} = -nev = \sigma\mathcal{E}$, where \mathbf{v} is an average carrier velocity, we have $\mathbf{v} = -\mu\mathcal{E}$, and the mobility $\mu = e\tau/m^*$ measures the ratio of the carrier velocity to the applied electric field.

⁵Inasmuch as both τ and m^* can depend on the Fermi energy, μ is not completely independent of carrier density.

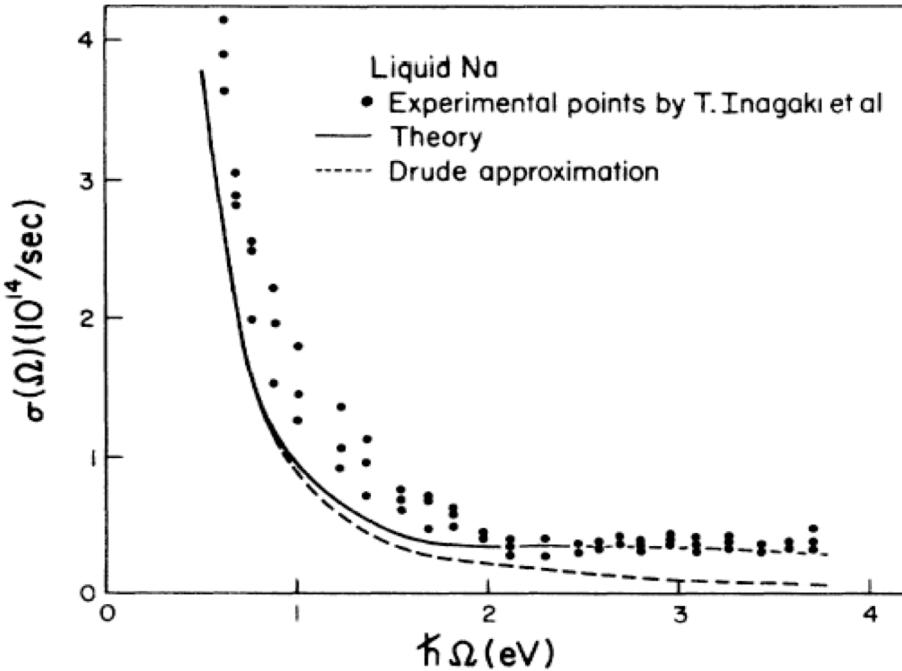


Figure 1.2: Frequency-dependent conductivity of liquid sodium by T. Inagaki *et al*, *Phys. Rev. B* **13**, 5610 (1976).

1.4.2 Optical Reflectivity of Metals and Semiconductors

What happens when an electromagnetic wave is incident on a metal? Inside the metal we have Maxwell's equations,

$$\nabla \times \mathbf{H} = \frac{4\pi}{c} \mathbf{j} + \frac{1}{c} \frac{\partial \mathbf{D}}{\partial t} \quad \Rightarrow \quad i\mathbf{k} \times \mathbf{B} = \left(\frac{4\pi\sigma}{c} - \frac{i\omega}{c} \right) \mathbf{E} \quad (1.45)$$

$$\nabla \times \mathbf{E} = -\frac{1}{c} \frac{\partial \mathbf{B}}{\partial t} \quad \Rightarrow \quad i\mathbf{k} \times \mathbf{E} = \frac{i\omega}{c} \mathbf{B} \quad (1.46)$$

$$\nabla \cdot \mathbf{E} = \nabla \cdot \mathbf{B} = 0 \quad \Rightarrow \quad i\mathbf{k} \cdot \mathbf{E} = i\mathbf{k} \cdot \mathbf{B} = 0 , \quad (1.47)$$

where we've assumed $\mu = \epsilon = 1$ inside the metal, ignoring polarization due to virtual interband transitions (*i.e.* from core electrons). Hence,

$$\mathbf{k}^2 = \frac{\omega^2}{c^2} + \frac{4\pi i\omega}{c^2} \sigma(\omega) \quad (1.48)$$

$$= \frac{\omega^2}{c^2} + \frac{\omega_p^2}{c^2} \frac{i\omega\tau}{1 - i\omega\tau} \equiv \epsilon(\omega) \frac{\omega^2}{c^2} , \quad (1.49)$$

where $\omega_p = \sqrt{4\pi n e^2 / m^*}$ is the *plasma frequency* for the conduction band. The dielectric function,

$$\epsilon(\omega) = 1 + \frac{4\pi i\sigma(\omega)}{\omega} = 1 + \frac{\omega_p^2}{\omega^2} \frac{i\omega\tau}{1 - i\omega\tau} \quad (1.50)$$

determines the complex refractive index, $N(\omega) = \sqrt{\epsilon(\omega)}$, leading to the electromagnetic dispersion relation $k = N(\omega) \omega/c$.

Consider a wave normally incident upon a metallic surface normal to \hat{z} . In the vacuum ($z < 0$), we write

$$\mathbf{E}(\mathbf{r}, t) = E_1 \hat{x} e^{i\omega z/c} e^{-i\omega t} + E_2 \hat{x} e^{-i\omega z/c} e^{-i\omega t} \quad (1.51)$$

$$\mathbf{B}(\mathbf{r}, t) = \frac{c}{i\omega} \nabla \times \mathbf{E} = E_1 \hat{y} e^{i\omega z/c} e^{-i\omega t} - E_2 \hat{y} e^{-i\omega z/c} e^{-i\omega t} \quad (1.52)$$

while in the metal ($z > 0$),

$$\mathbf{E}(\mathbf{r}, t) = E_3 \hat{x} e^{iN\omega z/c} e^{-i\omega t} \quad (1.53)$$

$$\mathbf{B}(\mathbf{r}, t) = \frac{c}{i\omega} \nabla \times \mathbf{E} = N E_3 \hat{y} e^{iN\omega z/c} e^{-i\omega t} \quad (1.54)$$

Continuity of $\mathbf{E} \times \hat{n}$ gives $E_1 + E_2 = E_3$. Continuity of $\mathbf{H} \times \hat{n}$ gives $E_1 - E_2 = N E_3$. Thus,

$$\frac{E_2}{E_1} = \frac{1 - N}{1 + N} \quad , \quad \frac{E_3}{E_1} = \frac{2}{1 + N} \quad (1.55)$$

and the reflection and transmission coefficients are

$$R(\omega) = \left| \frac{E_2}{E_1} \right|^2 = \left| \frac{1 - N(\omega)}{1 + N(\omega)} \right|^2 \quad (1.56)$$

$$T(\omega) = \left| \frac{E_3}{E_1} \right|^2 = \frac{4}{|1 + N(\omega)|^2} \quad (1.57)$$

We've now solved the electromagnetic boundary value problem.

Typical values – For a metal with $n = 10^{22} \text{ cm}^3$ and $m^* = m_e$, the plasma frequency is $\omega_p = 5.7 \times 10^{15} \text{ s}^{-1}$. The scattering time varies considerably as a function of temperature. In high purity copper at $T = 4 \text{ K}$, $\tau \approx 2 \times 10^{-9} \text{ s}$ and $\omega_p \tau \approx 10^7$. At $T = 300 \text{ K}$, $\tau \approx 2 \times 10^{-14} \text{ s}$ and $\omega_p \tau \approx 100$. In either case, $\omega_p \tau \gg 1$. There are then three regimes to consider.

- $\omega \tau \ll 1 \ll \omega_p \tau$:

We may approximate $1 - i\omega \tau \approx 1$, hence

$$\begin{aligned} N^2(\omega) &= 1 + \frac{i \omega_p^2 \tau}{\omega(1 - i\omega \tau)} \approx \frac{i \omega_p^2 \tau}{\omega} \\ N(\omega) &\approx \frac{1 + i}{\sqrt{2}} \left(\frac{\omega_p^2 \tau}{\omega} \right)^{1/2} \Rightarrow R \approx 1 - \frac{2\sqrt{2}\omega\tau}{\omega_p \tau} . \end{aligned} \quad (1.58)$$

Hence $R \approx 1$ and the metal reflects.

- $1 \ll \omega \tau \ll \omega_p \tau$:

In this regime,

$$N^2(\omega) \approx 1 - \frac{\omega_p^2}{\omega^2} + \frac{i \omega_p^2}{\omega^3 \tau} \quad (1.59)$$

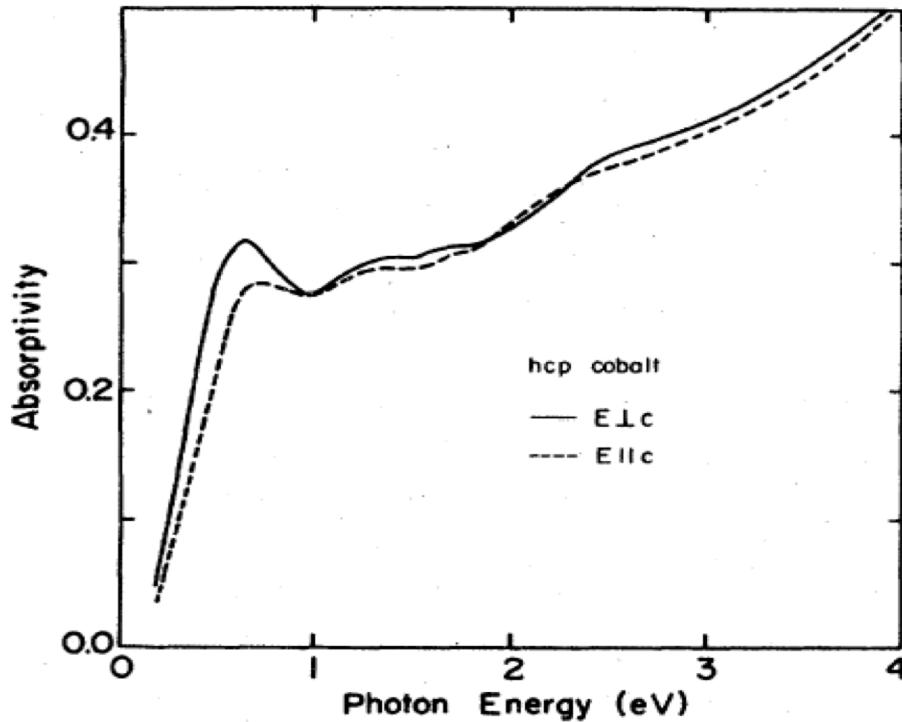


Figure 1.3: Frequency-dependent absorption of hcp cobalt by J. Weaver *et al.*, *Phys. Rev. B* **19**, 3850 (1979).

which is almost purely real and negative. Hence N is almost purely imaginary and $R \approx 1$. (To lowest nontrivial order, $R = 1 - 2/\omega_p\tau$.) Still high reflectivity.

- $1 \ll \omega_p\tau \ll \omega\tau$:

Here we have

$$N^2(\omega) \approx 1 - \frac{\omega_p^2}{\omega^2} \implies R = \frac{\omega_p}{2\omega} \quad (1.60)$$

and $R \ll 1$ – the metal is transparent at frequencies large compared to ω_p .

1.4.3 Optical Conductivity of Semiconductors

In our analysis of the electrodynamics of metals, we assumed that the dielectric constant due to all the filled bands was simply $\epsilon = 1$. This is not quite right. We should instead have written

$$\mathbf{k}^2 = \epsilon_\infty \frac{\omega^2}{c^2} + \frac{4\pi i\omega\sigma(\omega)}{c^2} \quad (1.61)$$

$$\epsilon(\omega) = \epsilon_\infty \left\{ 1 + \frac{\omega_p^2}{\omega^2} \frac{i\omega\tau}{1 - i\omega\tau} \right\}, \quad (1.62)$$

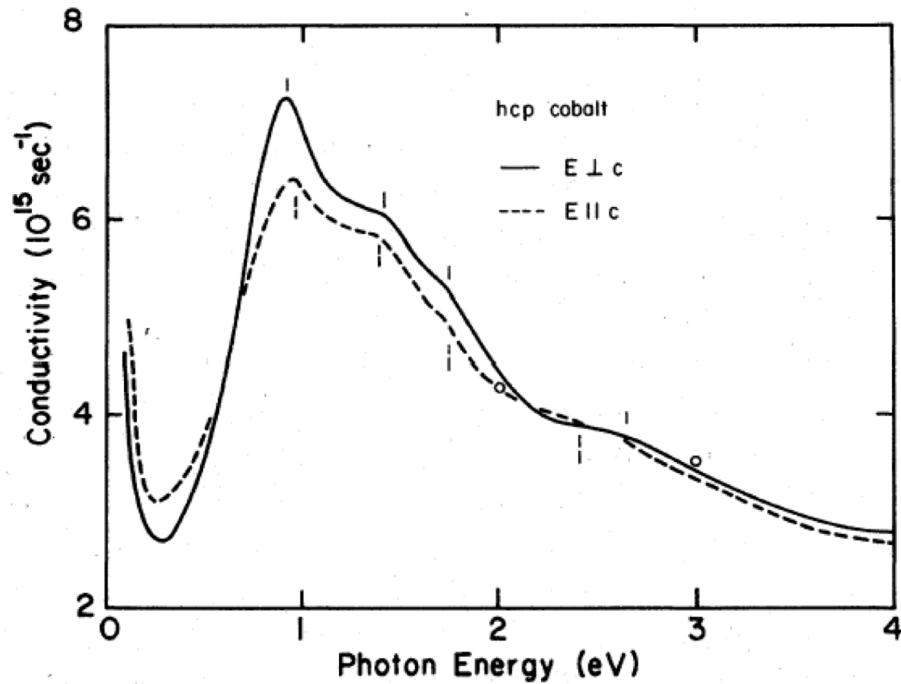


Figure 1.4: Frequency-dependent conductivity of hcp cobalt by J. Weaver *et al.*, *Phys. Rev. B* **19**, 3850 (1979). This curve is derived from the data of fig. 1.3 using a Kramers-Krönig transformation. A Drude peak is observed at low frequencies. At higher frequencies, interband effects dominate.

where ϵ_∞ is the dielectric constant due to virtual transitions to fully occupied (*i.e.* core) and fully unoccupied bands, at a frequency small compared to the interband frequency. The plasma frequency is now defined as

$$\omega_p = \left(\frac{4\pi n e^2}{m^* \epsilon_\infty} \right)^{1/2} \quad (1.63)$$

where n is the conduction electron density. Note that $\epsilon(\omega \rightarrow \infty) = \epsilon_\infty$, although again this is only true for ω smaller than the gap to neighboring bands. It turns out that for insulators one can write

$$\epsilon_\infty \simeq 1 + \frac{\omega_{pv}^2}{\omega_g^2} \quad (1.64)$$

where $\omega_{pv} = \sqrt{4\pi n_v e^2 / m_e}$, with n_v the number density of valence electrons, and ω_g is the energy gap between valence and conduction bands. In semiconductors such as Si and Ge, $\omega_g \sim 4$ eV, while $\omega_{pv} \sim 16$ eV, hence $\epsilon_\infty \sim 17$, which is in rough agreement with the experimental values of ~ 12 for Si and ~ 16 for Ge. In metals, the band gaps generally are considerably larger.

There are some important differences to consider in comparing semiconductors and metals:

- The carrier density n typically is much smaller in semiconductors than in metals, ranging from $n \sim 10^{16} \text{ cm}^{-3}$ in intrinsic (*i.e.* undoped, thermally excited at room temperature) materials to $n \sim 10^{19} \text{ cm}^{-3}$ in doped materials.
- $\epsilon_\infty \approx 10 - 20$ and $m^*/m_e \approx 0.1$. The product $\epsilon_\infty m^*$ thus differs only slightly from its free electron value.

Since $n_{\text{semi}} \lesssim 10^{-4} n_{\text{metal}}$, one has

$$\omega_p^{\text{semi}} \approx 10^{-2} \omega_p^{\text{metal}} \approx 10^{-14} \text{ s}. \quad (1.65)$$

In high purity semiconductors the mobility $\mu = e\tau/m^* \gtrsim 10^5 \text{ cm}^2/\text{Vs}$ the low temperature scattering time is typically $\tau \approx 10^{-11} \text{ s}$. Thus, for $\omega \gtrsim 3 \times 10^{15} \text{ s}^{-1}$ in the optical range, we have $\omega\tau \gg \omega_p\tau \gg 1$, in which case $N(\omega) \approx \sqrt{\epsilon_\infty}$ and the reflectivity is

$$R = \left| \frac{1 - \sqrt{\epsilon_\infty}}{1 + \sqrt{\epsilon_\infty}} \right|^2. \quad (1.66)$$

Taking $\epsilon_\infty = 10$, one obtains $R = 0.27$, which is high enough so that polished Si wafers appear shiny.

1.4.4 Optical Conductivity and the Fermi Surface

At high frequencies, when $\omega\tau \gg 1$, our expression for the conductivity, eqn. (1.33), yields

$$\sigma(\omega) = \frac{ie^2}{12\pi^3\hbar\omega} \int d\varepsilon \left(-\frac{\partial f^0}{\partial \varepsilon} \right) \int dS_\varepsilon |\mathbf{v}(\mathbf{k})|, \quad (1.67)$$

where we have presumed sufficient crystalline symmetry to guarantee that $\sigma_{\alpha\beta} = \sigma \delta_{\alpha\beta}$ is diagonal. In the isotropic case, and at temperatures low compared with T_F , the integral over the Fermi surface gives $4\pi k_F^2 v_F = 12\pi^3 \hbar n / m^*$, whence $\sigma = ine^2/m^*\omega$, which is the large frequency limit of our previous result. For a general Fermi surface, we can define

$$\sigma(\omega \gg \tau^{-1}) \equiv \frac{ine^2}{m_{\text{opt}}\omega} \quad (1.68)$$

where the *optical mass* m_{opt} is given by

$$\frac{1}{m_{\text{opt}}} = \frac{1}{12\pi^3\hbar n} \int d\varepsilon \left(-\frac{\partial f^0}{\partial \varepsilon} \right) \int dS_\varepsilon |\mathbf{v}(\mathbf{k})|. \quad (1.69)$$

Note that at high frequencies $\sigma(\omega)$ is purely imaginary. What does this mean? If

$$\mathcal{E}(t) = \mathcal{E} \cos(\omega t) = \frac{1}{2} \mathcal{E} (e^{-i\omega t} + e^{+i\omega t}) \quad (1.70)$$

then

$$\begin{aligned}\mathbf{j}(t) &= \frac{1}{2} \boldsymbol{\mathcal{E}} \left\{ \sigma(\omega) e^{-i\omega t} + \sigma(-\omega) e^{+i\omega t} \right\} \\ &= \frac{ne^2}{m_{\text{opt}}\omega} \boldsymbol{\mathcal{E}} \sin(\omega t),\end{aligned}\quad (1.71)$$

where we have invoked $\sigma(-\omega) = \sigma^*(\omega)$. The current is therefore 90° out of phase with the voltage, and the average over a cycle $\langle \mathbf{j}(t) \cdot \boldsymbol{\mathcal{E}}(t) \rangle = 0$. Recall that we found metals to be transparent for $\omega \gg \omega_p \gg \tau^{-1}$.

At zero temperature, the optical mass is given by

$$\frac{1}{m_{\text{opt}}} = \frac{1}{12\pi^3\hbar n} \int dS_F |\mathbf{v}(\mathbf{k})|. \quad (1.72)$$

The density of states, $g(\varepsilon_F)$, is

$$g(\varepsilon_F) = \frac{1}{4\pi^3\hbar} \int dS_F |\mathbf{v}(\mathbf{k})|^{-1}, \quad (1.73)$$

from which one can define the thermodynamic effective mass m_{th}^* , appealing to the low temperature form of the specific heat,

$$c_V = \frac{\pi^2}{3} k_B^2 T g(\varepsilon_F) \equiv \frac{m_{\text{th}}^*}{m_e} c_V^0, \quad (1.74)$$

where

$$c_V^0 \equiv \frac{m_e k_B^2 T}{3\hbar^2} (3\pi^2 n)^{1/3} \quad (1.75)$$

is the specific heat for a free electron gas of density n . Thus,

$$m_{\text{th}}^* = \frac{\hbar}{4\pi(3\pi^2 n)^{1/3}} \int dS_F |\mathbf{v}(\mathbf{k})|^{-1} \quad (1.76)$$

1.5 Calculation of the Scattering Time

1.5.1 Potential Scattering and Fermi's Golden Rule

Let us go beyond the relaxation time approximation and calculate the scattering time τ from first principles. We will concern ourselves with scattering of electrons from crystalline impurities. We begin with Fermi's Golden Rule⁶,

$$\mathcal{I}_{\mathbf{k}}\{f\} = \frac{2\pi}{\hbar} \sum_{\mathbf{k}'} |\langle \mathbf{k}' | \mathcal{U} | \mathbf{k} \rangle|^2 (f_{\mathbf{k}'} - f_{\mathbf{k}}) \delta(\varepsilon(\mathbf{k}) - \varepsilon(\mathbf{k}')), \quad (1.77)$$

⁶We'll treat the scattering of each spin species separately. We assume no spin-flip scattering takes place.

Metal	m_{opt}^*/m_e thy	m_{opt}^*/m_e expt	m_{th}^*/m_e thy	m_{th}^*/m_e expt
Li	1.45	1.57	1.64	2.23
Na	1.00	1.13	1.00	1.27
K	1.02	1.16	1.07	1.26
Rb	1.08	1.16	1.18	1.36
Cs	1.29	1.19	1.75	1.79
Cu	-	-	1.46	1.38
Ag	-	-	1.00	1.00
Au	-	-	1.09	1.08

Table 1.1: Optical and thermodynamic effective masses of monovalent metals. (Taken from Smith and Jensen).

where $\mathcal{U}(\mathbf{r})$ is a sum over individual impurity ion potentials,

$$\mathcal{U}(\mathbf{r}) = \sum_{j=1}^{N_{\text{imp}}} U(\mathbf{r} - \mathbf{R}_j) \quad (1.78)$$

$$|\langle \mathbf{k}' | \mathcal{U} | \mathbf{k} \rangle|^2 = V^{-2} |\hat{U}(\mathbf{k} - \mathbf{k}')|^2 \cdot \left| \sum_{j=1}^{N_{\text{imp}}} e^{i(\mathbf{k}-\mathbf{k}') \cdot \mathbf{R}_j} \right|^2, \quad (1.79)$$

where V is the volume of the solid and

$$\hat{U}(\mathbf{q}) = \int d^3 r U(\mathbf{r}) e^{-i\mathbf{q} \cdot \mathbf{r}} \quad (1.80)$$

is the Fourier transform of the impurity potential. Note that we are assuming a single species of impurities; the method can be generalized to account for different impurity species.

To make progress, we assume the impurity positions are random and uncorrelated, and we average over them. Using

$$\overline{\left| \sum_{j=1}^{N_{\text{imp}}} e^{i\mathbf{q} \cdot \mathbf{R}_j} \right|^2} = N_{\text{imp}} + N_{\text{imp}}(N_{\text{imp}} - 1) \delta_{\mathbf{q},0}, \quad (1.81)$$

we obtain

$$\overline{|\langle \mathbf{k}' | \mathcal{U} | \mathbf{k} \rangle|^2} = \frac{N_{\text{imp}}}{V^2} |\hat{U}(\mathbf{k} - \mathbf{k}')|^2 + \frac{N_{\text{imp}}(N_{\text{imp}} - 1)}{V^2} |\hat{U}(0)|^2 \delta_{\mathbf{k}\mathbf{k}'} . \quad (1.82)$$

EXERCISE: Verify eqn. (1.81).

We will neglect the second term in eqn. 1.82 arising from the spatial average ($\mathbf{q} = 0$ Fourier component) of the potential. As we will see, in the end it will cancel out. Writing

$f = f^0 + \delta f$, we have

$$\mathcal{I}_k\{f\} = \frac{2\pi n_{\text{imp}}}{\hbar} \int_{\hat{\Omega}} \frac{d^3 k'}{(2\pi)^3} |\hat{U}(\mathbf{k} - \mathbf{k}')|^2 \delta\left(\frac{\hbar^2 \mathbf{k}^2}{2m^*} - \frac{\hbar^2 \mathbf{k}'^2}{2m^*}\right) (\delta f_{\mathbf{k}'} - \delta f_{\mathbf{k}}) , \quad (1.83)$$

where $n_{\text{imp}} = N_{\text{imp}}/V$ is the number density of impurities. Note that we are assuming a parabolic band. We next make the *Ansatz*

$$\delta f_{\mathbf{k}} = \tau(\varepsilon(\mathbf{k})) e \boldsymbol{\mathcal{E}} \cdot \mathbf{v}(\mathbf{k}) \left. \frac{\partial f^0}{\partial \varepsilon} \right|_{\varepsilon(\mathbf{k})} \quad (1.84)$$

and solve for $\tau(\varepsilon(\mathbf{k}))$. The (time-independent) Boltzmann equation is

$$-e \boldsymbol{\mathcal{E}} \cdot \mathbf{v}(\mathbf{k}) \frac{\partial f^0}{\partial \varepsilon} = \frac{2\pi}{\hbar} n_{\text{imp}} e \boldsymbol{\mathcal{E}} \cdot \int_{\hat{\Omega}} \frac{d^3 k'}{(2\pi)^3} |\hat{U}(\mathbf{k} - \mathbf{k}')|^2 \delta\left(\frac{\hbar^2 \mathbf{k}^2}{2m^*} - \frac{\hbar^2 \mathbf{k}'^2}{2m^*}\right) \times \left(\tau(\varepsilon(\mathbf{k}')) \mathbf{v}(\mathbf{k}') \left. \frac{\partial f^0}{\partial \varepsilon} \right|_{\varepsilon(\mathbf{k}')} - \tau(\varepsilon(\mathbf{k})) \mathbf{v}(\mathbf{k}) \left. \frac{\partial f^0}{\partial \varepsilon} \right|_{\varepsilon(\mathbf{k})} \right) . \quad (1.85)$$

Due to the isotropy of the problem, we must have $\tau(\varepsilon(\mathbf{k}))$ is a function only of the magnitude of \mathbf{k} . We then obtain⁷

$$\frac{\hbar \mathbf{k}}{m^*} = \frac{n_{\text{imp}}}{4\pi^2 \hbar} \tau(\varepsilon(\mathbf{k})) \int_0^\infty dk' k'^2 \int d\hat{\mathbf{k}}' |\hat{U}(\mathbf{k} - \mathbf{k}')|^2 \frac{\delta(k - k')}{\hbar^2 k/m^*} \frac{\hbar}{m^*} (\mathbf{k} - \mathbf{k}') , \quad (1.86)$$

whence

$$\frac{1}{\tau(\varepsilon_F)} = \frac{m^* k_F n_{\text{imp}}}{4\pi^2 \hbar^3} \int d\hat{\mathbf{k}}' |U(k_F \hat{\mathbf{k}} - k_F \hat{\mathbf{k}}')|^2 (1 - \hat{\mathbf{k}} \cdot \hat{\mathbf{k}}') . \quad (1.87)$$

If the impurity potential $U(\mathbf{r})$ itself is isotropic, then its Fourier transform $\hat{U}(\mathbf{q})$ is a function of $q^2 = 4k_F^2 \sin^2 \frac{1}{2}\vartheta$ where $\cos \vartheta = \hat{\mathbf{k}} \cdot \hat{\mathbf{k}}'$ and $\mathbf{q} = \mathbf{k}' - \mathbf{k}$ is the transfer wavevector. Recalling the Born approximation for differential scattering cross section,

$$\sigma(\vartheta) = \left(\frac{m^*}{2\pi \hbar^2} \right)^2 |\hat{U}(\mathbf{k} - \mathbf{k}')|^2 , \quad (1.88)$$

we may finally write

$$\frac{1}{\tau(\varepsilon_F)} = 2\pi n_{\text{imp}} v_F \int_0^\pi d\vartheta \sigma_F(\vartheta) (1 - \cos \vartheta) \sin \vartheta \quad (1.89)$$

where $v_F = \hbar k_F/m^*$ is the Fermi velocity⁸. The *mean free path* is defined by $\ell = v_F \tau$.

⁷We assume that the Fermi surface is contained within the first Brillouin zone.

⁸The subscript on $\sigma_F(\vartheta)$ is to remind us that the cross section depends on k_F as well as ϑ .

Notice the factor $(1 - \cos \vartheta)$ in the integrand of (1.89). This tells us that forward scattering ($\vartheta = 0$) doesn't contribute to the scattering rate, which justifies our neglect of the second term in eqn. (1.82). Why should τ be utterly insensitive to forward scattering? Because $\tau(\varepsilon_F)$ is the *transport lifetime*, and forward scattering does not degrade the current. Therefore, $\sigma(\vartheta = 0)$ does not contribute to the ‘transport scattering rate’ $\tau^{-1}(\varepsilon_F)$. Oftentimes one sees reference in the literature to a ‘single particle lifetime’ as well, which is given by the same expression but without this factor:

$$\left\{ \begin{array}{l} \tau_{\text{sp}}^{-1} \\ \tau_{\text{tr}}^{-1} \end{array} \right\} = 2\pi n_{\text{imp}} v_F \int_0^\pi d\vartheta \sigma_F(\vartheta) \left\{ \begin{array}{l} 1 \\ (1 - \cos \vartheta) \end{array} \right\} \sin \vartheta \quad (1.90)$$

Note that $\tau_{\text{sp}} = (n_{\text{imp}} v_F \sigma_{F,\text{tot}})^{-1}$, where $\sigma_{F,\text{tot}}$ is the total scattering cross section at energy ε_F , a formula familiar from elementary kinetic theory.

To derive the single particle lifetime, one can examine the linearized time-*dependent* Boltzmann equation with $\mathcal{E} = 0$,

$$\frac{\partial \delta f_{\mathbf{k}}}{\partial t} = n_{\text{imp}} v_F \int d\hat{\mathbf{k}}' \sigma(\vartheta_{\mathbf{k}\mathbf{k}'}) (\delta f_{\mathbf{k}'} - \delta f_{\mathbf{k}}) , \quad (1.91)$$

where $v = \hbar k/m^*$ is the velocity, and where the kernel is $\vartheta_{\mathbf{k}\mathbf{k}'} = \cos^{-1}(\mathbf{k} \cdot \mathbf{k}')$. We now expand in spherical harmonics, writing

$$\sigma(\vartheta_{\mathbf{k}\mathbf{k}'}) \equiv \sigma_{\text{tot}} \sum_{L,M} \nu_L Y_{LM}(\hat{\mathbf{k}}) Y_{LM}^*(\hat{\mathbf{k}}') , \quad (1.92)$$

where as before

$$\sigma_{\text{tot}} = 2\pi \int_0^\pi d\vartheta \sin \vartheta \sigma(\vartheta) . \quad (1.93)$$

Expanding

$$\delta f_{\mathbf{k}}(t) = \sum_{L,M} A_{LM}(t) Y_{LM}(\hat{\mathbf{k}}) , \quad (1.94)$$

the linearized Boltzmann equation simplifies to

$$\frac{\partial A_{LM}}{\partial t} + (1 - \nu_L) n_{\text{imp}} v_F \sigma_{\text{tot}} A_{LM} = 0 , \quad (1.95)$$

whence one obtains a hierarchy of relaxation rates,

$$\tau_L^{-1} = (1 - \nu_L) n_{\text{imp}} v_F \sigma_{\text{tot}} , \quad (1.96)$$

which depend only on the total angular momentum quantum number L . These rates describe the relaxation of nonuniform distributions, when $\delta f_{\mathbf{k}}(t=0)$ is proportional to some spherical harmonic $Y_{LM}(\mathbf{k})$. Note that $\tau_{L=0}^{-1} = 0$, which reflects the fact that the total particle number is a collisional invariant. The single particle lifetime is identified as

$$\tau_{\text{sp}}^{-1} \equiv \tau_{L \rightarrow \infty}^{-1} = n_{\text{imp}} v_F \sigma_{\text{tot}} , \quad (1.97)$$

corresponding to a point distortion of the uniform distribution.

1.5.2 Screening and the Transport Lifetime

For a Coulomb impurity, with $U(\mathbf{r}) = -Ze^2/r$ we have $\hat{U}(\mathbf{q}) = -4\pi Ze^2/q^2$. Consequently,

$$\sigma_F(\vartheta) = \left(\frac{Ze^2}{4\varepsilon_F \sin^2 \frac{1}{2}\vartheta} \right)^2, \quad (1.98)$$

and there is a strong divergence as $\vartheta \rightarrow 0$, with $\sigma_F(\vartheta) \propto \vartheta^{-4}$. The transport lifetime diverges logarithmically! What went wrong?

What went wrong is that we have failed to account for *screening*. Free charges will rearrange themselves so as to screen an impurity potential. At long range, the effective (screened) potential decays exponentially, rather than as $1/r$. The screened potential is of the Yukawa form, and its increase at low q is cut off on the scale of the inverse screening length λ^{-1} . There are two types of screening to consider:

- Thomas-Fermi Screening : This is the typical screening mechanism in metals. A weak local electrostatic potential $\phi(\mathbf{r})$ will induce a change in the local electronic density according to $\delta n(\mathbf{r}) = e\phi(\mathbf{r})g(\varepsilon_F)$, where $g(\varepsilon_F)$ is the density of states at the Fermi level. This charge imbalance is again related to $\phi(\mathbf{r})$ through the Poisson equation. The result is a self-consistent equation for $\phi(\mathbf{r})$,

$$\begin{aligned} \nabla^2 \phi &= 4\pi e \delta n \\ &= 4\pi e^2 g(\varepsilon_F) \phi \equiv \lambda_{TF}^{-2} \phi. \end{aligned} \quad (1.99)$$

The Thomas-Fermi screening length is $\lambda_{TF} = (4\pi e^2 g(\varepsilon_F))^{-1/2}$.

- Debye-Hückel Screening : This mechanism is typical of ionic solutions, although it may also be of relevance in solids with ultra-low Fermi energies. From classical statistical mechanics, the local variation in electron number density induced by a potential $\phi(\mathbf{r})$ is

$$\delta n(\mathbf{r}) = n e^{e\phi(\mathbf{r})/k_B T} - n \approx \frac{n e\phi(\mathbf{r})}{k_B T}, \quad (1.100)$$

where we assume the potential is weak on the scale of $k_B T/e$. Poisson's equation now gives us

$$\begin{aligned} \nabla^2 \phi &= 4\pi e \delta n \\ &= \frac{4\pi n e^2}{k_B T} \phi \equiv \lambda_{DH}^{-2} \phi. \end{aligned} \quad (1.101)$$

A screened test charge Ze at the origin obeys

$$\nabla^2 \phi = \lambda^{-2} \phi - 4\pi Z e \delta(\mathbf{r}), \quad (1.102)$$

the solution of which is

$$U(\mathbf{r}) = -e\phi(\mathbf{r}) = -\frac{Ze^2}{r} e^{-r/\lambda} \implies \hat{U}(\mathbf{q}) = \frac{4\pi Z e^2}{q^2 + \lambda^{-2}}. \quad (1.103)$$

The differential scattering cross section is now

$$\sigma_F(\vartheta) = \left(\frac{Ze^2}{4\varepsilon_F} \cdot \frac{1}{\sin^2 \frac{1}{2}\vartheta + (2k_F\lambda)^{-2}} \right)^2 \quad (1.104)$$

and the divergence at small angle is cut off. The transport lifetime for screened Coulomb scattering is therefore given by

$$\begin{aligned} \frac{1}{\tau(\varepsilon_F)} &= 2\pi n_{\text{imp}} v_F \left(\frac{Ze^2}{4\varepsilon_F} \right)^2 \int_0^\pi d\vartheta \sin \vartheta (1 - \cos \vartheta) \left(\frac{1}{\sin^2 \frac{1}{2}\vartheta + (2k_F\lambda)^{-2}} \right)^2 \\ &= 2\pi n_{\text{imp}} v_F \left(\frac{Ze^2}{2\varepsilon_F} \right)^2 \left\{ \ln(1 + \pi\zeta) - \frac{\pi\zeta}{1 + \pi\zeta} \right\}, \end{aligned} \quad (1.105)$$

with

$$\zeta = \frac{4}{\pi} k_F^2 \lambda^2 = \frac{\hbar^2 k_F}{m^* e^2} = k_F a_B^*. \quad (1.106)$$

Here $a_B^* = \epsilon_\infty \hbar^2 / m^* e^2$ is the effective Bohr radius (restoring the ϵ_∞ factor). The resistivity is therefore given by

$$\rho = \frac{m^*}{ne^2\tau} = Z^2 \frac{h}{e^2} a_B^* \frac{n_{\text{imp}}}{n} F(k_F a_B^*), \quad (1.107)$$

where

$$F(\zeta) = \frac{1}{\zeta^3} \left\{ \ln(1 + \pi\zeta) - \frac{\pi\zeta}{1 + \pi\zeta} \right\}. \quad (1.108)$$

With $h/e^2 = 25,813 \Omega$ and $a_B^* \approx a_B = 0.529 \text{ \AA}$, we have

$$\rho = 1.37 \times 10^{-4} \Omega \cdot \text{cm} \times Z^2 \frac{n_{\text{imp}}}{n} F(k_F a_B^*). \quad (1.109)$$

Impurity Ion	$\Delta\rho$ per % ($\mu\Omega\text{-cm}$)	Impurity Ion	$\Delta\rho$ per % ($\mu\Omega\text{-cm}$)
Be	0.64	Si	3.2
Mg	0.60	Ge	3.7
B	1.4	Sn	2.8
Al	1.2	As	6.5
In	1.2	Sb	5.4

Table 1.2: Residual resistivity of copper per percent impurity.

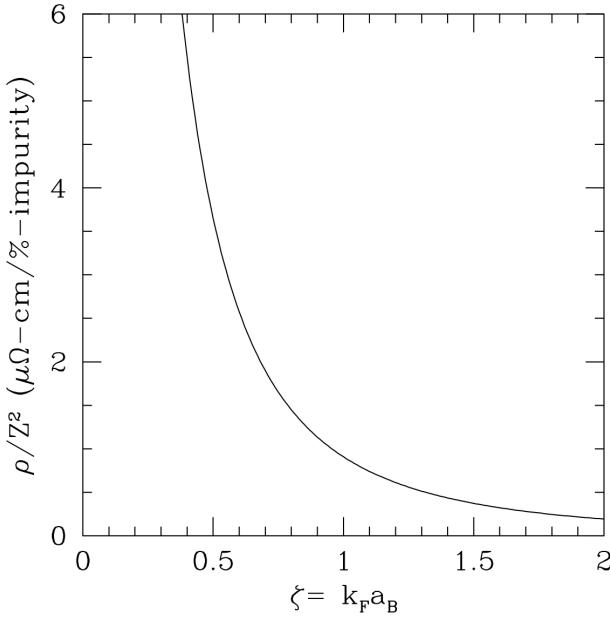


Figure 1.5: Residual resistivity per percent impurity.

1.6 Boltzmann Equation for Holes

1.6.1 Properties of Holes

Since filled bands carry no current, we have that the current density from band n is

$$\mathbf{j}_n(\mathbf{r}, t) = -2e \int_{\hat{\Omega}} \frac{d^3k}{(2\pi)^3} f_n(\mathbf{r}, \mathbf{k}, t) \mathbf{v}_n(\mathbf{k}) = +2e \int_{\hat{\Omega}} \frac{d^3k}{(2\pi)^3} \bar{f}_n(\mathbf{r}, \mathbf{k}, t) \mathbf{v}_n(\mathbf{k}) , \quad (1.110)$$

where $\bar{f} \equiv 1 - f$. Thus, we can regard the current to be carried by fictitious particles of charge $+e$ with a distribution $\bar{f}(\mathbf{r}, \mathbf{k}, t)$. These fictitious particles are called *holes*.

1. Under the influence of an applied electromagnetic field, the unoccupied levels of a band evolve as if they were occupied by real electrons of charge $-e$. That is, whether or not a state is occupied is irrelevant to the time evolution of that state, which is described by the semiclassical dynamics of eqs. (1.1, 1.2).
2. The current density due to a hole of wavevector \mathbf{k} is $+e \mathbf{v}_n(\mathbf{k})/V$.
3. The crystal momentum of a hole of wavevector \mathbf{k} is $\mathbf{P} = -\hbar\mathbf{k}$.
4. Any band can be described in terms of electrons or in terms of holes, but not both simultaneously. A “mixed” description is redundant at best, wrong at worst, and confusing always. However, it is often convenient to treat some bands within the electron picture and others within the hole picture.

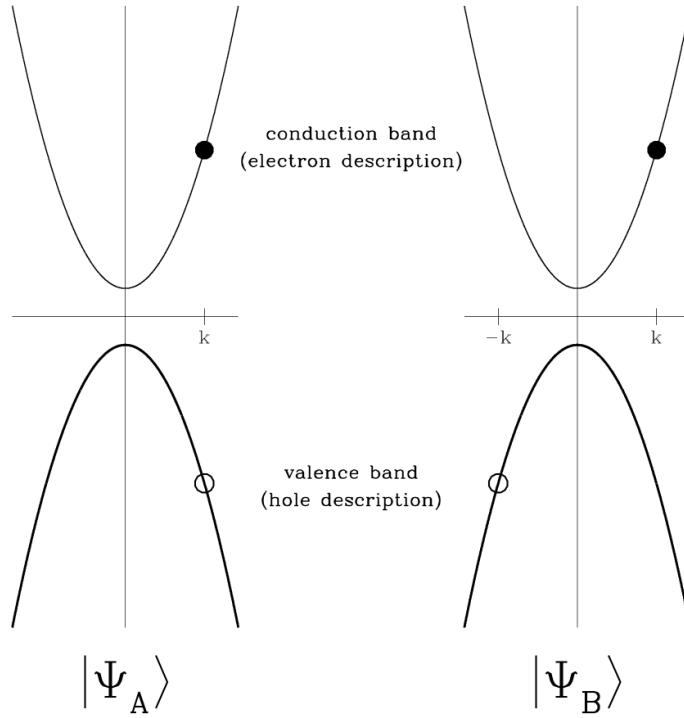


Figure 1.6: Two states: $|\Psi_A\rangle = e_k^\dagger h_k^\dagger |0\rangle$ and $|\Psi_B\rangle = e_k^\dagger h_{-k}^\dagger |0\rangle$. Which state carries more current? What is the crystal momentum of each state?

It is instructive to consider the exercise of fig. 1.6. The two states to be analyzed are

$$|\Psi_A\rangle = \psi_{c,k}^\dagger \psi_{v,k} |\Psi_0\rangle = e_k^\dagger h_k^\dagger |0\rangle \quad (1.111)$$

$$|\Psi_B\rangle = \psi_{c,k}^\dagger \psi_{v,-k} |\Psi_0\rangle = e_k^\dagger h_{-k}^\dagger |0\rangle , \quad (1.112)$$

where $e_k^\dagger \equiv \psi_{c,k}^\dagger$ is the creation operator for electrons in the conduction band, and $h_k^\dagger \equiv \psi_{v,k}$ is the creation operator for holes (and hence the destruction operator for electrons) in the valence band. The state $|\Psi_0\rangle$ has all states below the top of the valence band filled, and all states above the bottom of the conduction band empty. The state $|0\rangle$ is the same state, but represented now as a *vacuum* for conduction electrons and valence *holes*. The current density in each state is given by $j = e(v_h - v_e)/V$, where V is the volume (*i.e.* length) of the system. The dispersions resemble $\epsilon_{c,v} \approx \pm \frac{1}{2}E_g \pm \hbar^2 k^2 / 2m^*$, where E_g is the energy gap.

- State $|\Psi_A\rangle$:

The electron velocity is $v_e = \hbar k/m^*$; the hole velocity is $v_h = -\hbar k/m^*$. Hence, the total current density is $j \approx -2e\hbar k/m^*V$ and the total crystal momentum is $P = p_e + p_h = \hbar k - \hbar k = 0$.

- State $|\Psi_B\rangle$:

The electron velocity is $v_e = \hbar k/m^*$; the hole velocity is $v_h = -\hbar(-k)/m^*$. The

total current density is $j \approx 0$, and the total crystal momentum is $P = p_e + p_h = \hbar k - \hbar(-k) = 2\hbar k$.

Consider next the dynamics of electrons near the bottom of the conduction band and holes near the top of the valence band. (We'll assume a ‘direct gap’, *i.e.* the conduction band minimum is located directly above the valence band maximum, which we take to be at the Brillouin zone center $\mathbf{k} = 0$, otherwise known as the Γ point.) Expanding the dispersions about their extrema,

$$\varepsilon_v(\mathbf{k}) = \varepsilon_0^v - \frac{1}{2}\hbar^2 m_{\alpha\beta}^{v-1} k^\alpha k^\beta \quad (1.113)$$

$$\varepsilon_c(\mathbf{k}) = \varepsilon_0^c + \frac{1}{2}\hbar^2 m_{\alpha\beta}^{c-1} k^\alpha k^\beta. \quad (1.114)$$

The velocity is

$$v^\alpha(\mathbf{k}) = \frac{1}{\hbar} \frac{\partial \varepsilon}{\partial k^\alpha} = \pm \hbar m_{\alpha\beta}^{-1} k^\beta, \quad (1.115)$$

where the + sign is used in conjunction with m^c and the – sign with m^v . We compute the acceleration $\mathbf{a} = \ddot{\mathbf{r}}$ via the chain rule,

$$\begin{aligned} a^\alpha &= \frac{\partial v^\alpha}{\partial k^\beta} \cdot \frac{dk^\beta}{dt} \\ &= \mp e m_{\alpha\beta}^{-1} \left[E^\beta + \frac{1}{c} (\mathbf{v} \times \mathbf{B})^\beta \right] \end{aligned} \quad (1.116)$$

$$F^\alpha = m_{\alpha\beta} a^\beta = \mp e \left[E^\beta + \frac{1}{c} (\mathbf{v} \times \mathbf{B})^\beta \right]. \quad (1.117)$$

Thus, the hole wavepacket accelerates as if it has charge $+e$ but a *positive* effective mass.

Finally, what form does the Boltzmann equation take for holes? Starting with the Boltzmann equation for electrons,

$$\frac{\partial f}{\partial t} + \dot{\mathbf{r}} \cdot \frac{\partial f}{\partial \mathbf{r}} + \dot{\mathbf{k}} \cdot \frac{\partial f}{\partial \mathbf{k}} = \mathcal{I}_k\{f\}, \quad (1.118)$$

we recast this in terms of the hole distribution $\bar{f} = 1 - f$, and obtain

$$\frac{\partial \bar{f}}{\partial t} + \dot{\mathbf{r}} \cdot \frac{\partial \bar{f}}{\partial \mathbf{r}} + \dot{\mathbf{k}} \cdot \frac{\partial \bar{f}}{\partial \mathbf{k}} = -\mathcal{I}_k\{1 - \bar{f}\}$$

(1.119)

This then is the Boltzmann equation for the hole distribution \bar{f} . Recall that we can expand the collision integral functional as

$$\mathcal{I}_k\{f^0 + \delta f\} = \mathcal{L} \delta f + \dots \quad (1.120)$$

where \mathcal{L} is a linear operator, and the higher order terms are formally of order $(\delta f)^2$. Note that the zeroth order term $\mathcal{I}_k\{f^0\}$ vanishes due to the fact that f^0 represents a local equilibrium. Thus, writing $\bar{f} = \bar{f}^0 + \delta \bar{f}$

$$-\mathcal{I}_k\{1 - \bar{f}\} = -\mathcal{I}_k\{1 - \bar{f}^0 - \delta \bar{f}\} = \mathcal{L} \delta \bar{f} + \dots \quad (1.121)$$

and the linearized collisionless Boltzmann equation for holes is

$$\boxed{\frac{\partial \delta \bar{f}}{\partial t} - \frac{e}{\hbar c} \mathbf{v} \times \mathbf{B} \cdot \frac{\partial \delta \bar{f}}{\partial \mathbf{k}} - \mathbf{v} \cdot \left[e \mathcal{E} + \frac{\varepsilon - \mu}{T} \nabla T \right] \frac{\partial \bar{f}^0}{\partial \varepsilon} = \mathcal{L} \delta \bar{f}} \quad (1.122)$$

which is of precisely the same form as the electron case in eqn. (1.27). Note that the local equilibrium distribution for holes is given by

$$\boxed{\bar{f}^0(\mathbf{r}, \mathbf{k}, t) = \left\{ \exp \left(\frac{\mu(\mathbf{r}, t) - \varepsilon(\mathbf{k})}{k_B T(\mathbf{r}, t)} \right) + 1 \right\}^{-1}} \quad (1.123)$$

1.7 Magnetoresistance and Hall Effect

1.7.1 Boltzmann Theory for $\rho_{\alpha\beta}(\omega, \mathbf{B})$

In the presence of an external magnetic field \mathbf{B} , the linearized Boltzmann equation takes the form⁹

$$\frac{\partial \delta f}{\partial t} - e \mathbf{v} \cdot \mathcal{E} \frac{\partial f^0}{\partial \varepsilon} - \frac{e}{\hbar c} \mathbf{v} \times \mathbf{B} \cdot \frac{\partial \delta f}{\partial \mathbf{k}} = \mathcal{L} \delta f. \quad (1.124)$$

We will obtain an explicit solution within the relaxation time approximation $\mathcal{L} \delta f = -\delta f/\tau$ and the effective mass approximation,

$$\varepsilon(\mathbf{k}) = \pm \frac{1}{2} \hbar^2 m_{\alpha\beta}^{-1} k^\alpha k^\beta \implies v^\alpha = \pm \hbar m_{\alpha\beta}^{-1} k^\beta, \quad (1.125)$$

where the top sign applies for electrons and the bottom sign for holes. With $\mathcal{E}(t) = \mathcal{E} e^{-i\omega t}$, we try a solution of the form

$$\delta f(\mathbf{k}, t) = \mathbf{k} \cdot \mathbf{A}(\varepsilon) e^{-i\omega t} \equiv \delta f(\mathbf{k}) e^{-i\omega t} \quad (1.126)$$

where $\mathbf{A}(\varepsilon)$ is a vector function of ε to be determined. Each component A_α is a function of \mathbf{k} through its dependence on $\varepsilon = \varepsilon(\mathbf{k})$. We now have

$$(\tau^{-1} - i\omega) k^\mu A^\mu - \frac{e}{\hbar c} \epsilon_{\alpha\beta\gamma} v^\alpha B^\beta \frac{\partial}{\partial k^\gamma} (k^\mu A^\mu) = e \mathbf{v} \cdot \mathcal{E} \frac{\partial f^0}{\partial \varepsilon}, \quad (1.127)$$

where $\epsilon_{\alpha\beta\gamma}$ is the Levi-Civita tensor. Note that

$$\begin{aligned} \epsilon_{\alpha\beta\gamma} v^\alpha B^\beta \frac{\partial}{\partial k^\gamma} (k^\mu A^\mu) &= \epsilon_{\alpha\beta\gamma} v^\alpha B^\beta \left(A^\gamma + k^\mu \frac{\partial A^\mu}{\partial k^\gamma} \right) \\ &= \epsilon_{\alpha\beta\gamma} v^\alpha B^\beta \left(A^\gamma + \hbar k^\mu v^\gamma \frac{\partial A^\mu}{\partial \varepsilon} \right) \\ &= \epsilon_{\alpha\beta\gamma} v^\alpha B^\beta A^\gamma, \end{aligned} \quad (1.128)$$

⁹For holes, we replace $f^0 \rightarrow \bar{f}^0$ and $\delta f \rightarrow \delta \bar{f}$.

owing to the asymmetry of the Levi-Civita tensor: $\epsilon_{\alpha\beta\gamma} v^\alpha v^\gamma = 0$. Now invoke $\hbar k^\alpha = \pm m_{\alpha\beta} v^\beta$, and match the coefficients of v^α in each term of the Boltzmann equation. This yields,

$$\left[(\tau^{-1} - i\omega) m_{\alpha\beta} \pm \frac{e}{c} \epsilon_{\alpha\beta\gamma} B^\gamma \right] A^\beta = \pm \hbar e \frac{\partial f^0}{\partial \varepsilon} \mathcal{E}^\alpha . \quad (1.129)$$

Defining

$$\Gamma_{\alpha\beta} \equiv (\tau^{-1} - i\omega) m_{\alpha\beta} \pm \frac{e}{c} \epsilon_{\alpha\beta\gamma} B^\gamma , \quad (1.130)$$

we obtain the solution

$$\delta f = e v^\alpha m_{\alpha\beta} \Gamma_{\beta\gamma}^{-1} \mathcal{E}^\gamma \frac{\partial f^0}{\partial \varepsilon} . \quad (1.131)$$

From this, we can compute the current density and the conductivity tensor. The electrical current density is

$$\begin{aligned} j^\alpha &= -2e \int_{\hat{\Omega}} \frac{d^3k}{(2\pi)^3} v^\alpha \delta f \\ &= +2e^2 \mathcal{E}^\gamma \int_{\hat{\Omega}} \frac{d^3k}{(2\pi)^3} v^\alpha v^\nu m_{\nu\beta} \Gamma_{\beta\gamma}^{-1}(\varepsilon) \left(-\frac{\partial f^0}{\partial \varepsilon} \right) , \end{aligned} \quad (1.132)$$

where we allow for an energy-dependent relaxation time $\tau(\varepsilon)$. Note that $\Gamma_{\alpha\beta}(\varepsilon)$ is energy-dependent due to its dependence on τ . The conductivity is then

$$\sigma_{\alpha\beta}(\omega, \mathbf{B}) = 2\hbar^2 e^2 m_{\alpha\mu}^{-1} \left\{ \int_{\hat{\Omega}} \frac{d^3k}{(2\pi)^3} k^\mu k^\nu \left(-\frac{\partial f^0}{\partial \varepsilon} \right) \Gamma_{\nu\beta}^{-1}(\varepsilon) \right\} \quad (1.133)$$

$$= \pm \frac{2}{3} e^2 \int_{-\infty}^{\infty} d\varepsilon \varepsilon g(\varepsilon) \Gamma_{\alpha\beta}^{-1}(\varepsilon) \left(-\frac{\partial f^0}{\partial \varepsilon} \right) , \quad (1.134)$$

where the chemical potential is measured with respect to the band edge. Thus,

$$\sigma_{\alpha\beta}(\omega, \mathbf{B}) = n e^2 \langle \Gamma_{\alpha\beta}^{-1} \rangle , \quad (1.135)$$

where averages denoted by angular brackets are defined by

$$\langle \Gamma_{\alpha\beta}^{-1} \rangle \equiv \frac{\int_{-\infty}^{\infty} d\varepsilon \varepsilon g(\varepsilon) \left(-\frac{\partial f^0}{\partial \varepsilon} \right) \Gamma_{\alpha\beta}^{-1}(\varepsilon)}{\int_{-\infty}^{\infty} d\varepsilon \varepsilon g(\varepsilon) \left(-\frac{\partial f^0}{\partial \varepsilon} \right)} . \quad (1.136)$$

The quantity n is the carrier density,

$$n = \int_{-\infty}^{\infty} d\varepsilon g(\varepsilon) \times \begin{cases} f^0(\varepsilon) & \text{(electrons)} \\ \{1 - f^0(\varepsilon)\} & \text{(holes)} \end{cases} \quad (1.137)$$

EXERCISE: Verify eqn. (1.134).

For the sake of simplicity, let us assume an energy-independent scattering time, or that the temperature is sufficiently low that only $\tau(\varepsilon_F)$ matters, and we denote this scattering time simply by τ . Putting this all together, then, we obtain

$$\sigma_{\alpha\beta} = ne^2 \Gamma_{\alpha\beta}^{-1} \quad (1.138)$$

$$\rho_{\alpha\beta} = \frac{1}{ne^2} \Gamma_{\alpha\beta} = \frac{1}{ne^2} \left[(\tau^{-1} - i\omega) m_{\alpha\beta} \pm \frac{e}{c} \epsilon_{\alpha\beta\gamma} B^\gamma \right]. \quad (1.139)$$

We will assume that \mathbf{B} is directed along one of the principal axes of the effective mass tensor $m_{\alpha\beta}$, which we define to be $\hat{\mathbf{x}}$, $\hat{\mathbf{y}}$, and $\hat{\mathbf{z}}$, in which case

$$\rho_{\alpha\beta}(\omega, B) = \frac{1}{ne^2} \begin{pmatrix} (\tau^{-1} - i\omega) m_x^* & \pm eB/c & 0 \\ \mp eB/c & (\tau^{-1} - i\omega) m_y^* & 0 \\ 0 & 0 & (\tau^{-1} - i\omega) m_z^* \end{pmatrix} \quad (1.140)$$

where $m_{x,y,z}^*$ are the eigenvalues of $m_{\alpha\beta}$ and \mathbf{B} lies along the eigenvector $\hat{\mathbf{z}}$.

Note that

$$\rho_{xx}(\omega, B) = \frac{m_x^*}{ne^2\tau} (1 - i\omega\tau) \quad (1.141)$$

is *independent of B*. Hence, the *magnetoresistance*,

$$\Delta\rho_{xx}(B) = \rho_{xx}(B) - \rho_{xx}(0) \quad (1.142)$$

vanishes: $\Delta\rho_{xx}(B) = 0$. While this is true for a single parabolic band, deviations from parabolicity and contributions from other bands can lead to a nonzero magnetoresistance.

The conductivity tensor $\sigma_{\alpha\beta}$ is the matrix inverse of $\rho_{\alpha\beta}$. Using the familiar equality

$$\begin{pmatrix} a & b \\ c & d \end{pmatrix}^{-1} = \frac{1}{ad - bc} \begin{pmatrix} d & -b \\ -c & a \end{pmatrix}, \quad (1.143)$$

we obtain

$$\sigma_{\alpha\beta}(\omega, B) = ne^2 \tau \begin{pmatrix} \frac{(1-i\omega\tau)/m_x^*}{(1-i\omega\tau)^2 + (\omega_c\tau)^2} & \mp \frac{\omega_c\tau/\sqrt{m_x^* m_y^*}}{(1-i\omega\tau)^2 + (\omega_c\tau)^2} & 0 \\ \pm \frac{\omega_c\tau/\sqrt{m_x^* m_y^*}}{(1-i\omega\tau)^2 + (\omega_c\tau)^2} & \frac{(1-i\omega\tau)/m_y^*}{(1-i\omega\tau)^2 + (\omega_c\tau)^2} & 0 \\ 0 & 0 & \frac{1}{(1-i\omega\tau)m_z^*} \end{pmatrix} \quad (1.144)$$

where

$$\omega_c \equiv \frac{eB}{m_\perp^* c}, \quad (1.145)$$

with $m_{\perp}^* \equiv \sqrt{m_x^* m_y^*}$, is the *cyclotron frequency*. Thus,

$$\sigma_{xx}(\omega, B) = \frac{ne^2\tau}{m_x^*} \frac{1 - i\omega\tau}{1 + (\omega_c^2 - \omega^2)\tau^2 - 2i\omega\tau} \quad (1.146)$$

$$\sigma_{zz}(\omega, B) = \frac{ne^2\tau}{m_z^*} \frac{1}{1 - i\omega\tau}. \quad (1.147)$$

Note that $\sigma_{xx,yy}$ are field-dependent, unlike the corresponding components of the resistivity tensor.

1.7.2 Cyclotron Resonance in Semiconductors

A typical value for the effective mass in semiconductors is $m^* \sim 0.1 m_e$. From

$$\frac{e}{m_e c} = 1.75 \times 10^7 \text{ Hz/G}, \quad (1.148)$$

we find that $eB/m^*c = 1.75 \times 10^{11} \text{ Hz}$ in a field of $B = 1 \text{ kG}$. In metals, the disorder is such that even at low temperatures $\omega_c\tau$ typically is small. In semiconductors, however, the smallness of m^* and the relatively high purity (sometimes spectacularly so) mean that $\omega_c\tau$ can get as large as 10^3 at modest fields. This allows for a measurement of the effective mass tensor using the technique of *cyclotron resonance*.

The absorption of electromagnetic radiation is proportional to the dissipative (*i.e.* real) part of the diagonal elements of $\sigma_{\alpha\beta}(\omega)$, which is given by

$$\sigma'_{xx}(\omega, B) = \frac{ne^2\tau}{m_x^*} \frac{1 + (\lambda^2 + 1)s^2}{1 + 2(\lambda^2 + 1)s^2 + (\lambda^2 - 1)^2 s^4}, \quad (1.149)$$

where $\lambda = B/B_\omega$, with $B_\omega = m_{\perp}^* c \omega / e$, and $s = \omega\tau$. For fixed ω , the conductivity $\sigma'_{xx}(B)$ is then peaked at $B = B^*$. When $\omega\tau \gg 1$ and $\omega_c\tau \gg 1$, B^* approaches B_ω , where $\sigma'_{xx}(\omega, B_\omega) = ne^2\tau/2m_x^*$. By measuring B_ω one can extract the quantity $m_{\perp}^* = eB_\omega/\omega c$. Varying the direction of the magnetic field, the entire effective mass tensor may be determined.

For finite $\omega\tau$, we can differentiate the above expression to obtain the location of the cyclotron resonance peak. One finds $B = (1 + \alpha)^{1/2} B_\omega$, with

$$\begin{aligned} \alpha &= \frac{-(2s^2 + 1) + \sqrt{(2s^2 + 1)^2 - 1}}{s^2} \\ &= -\frac{1}{4s^4} + \frac{1}{8s^6} + \mathcal{O}(s^{-8}). \end{aligned} \quad (1.150)$$

As depicted in fig. 1.7, the resonance peak shifts to the left of B_ω for finite values of $\omega\tau$. The peak collapses to $B = 0$ when $\omega\tau \leq 1/\sqrt{3} = 0.577$.

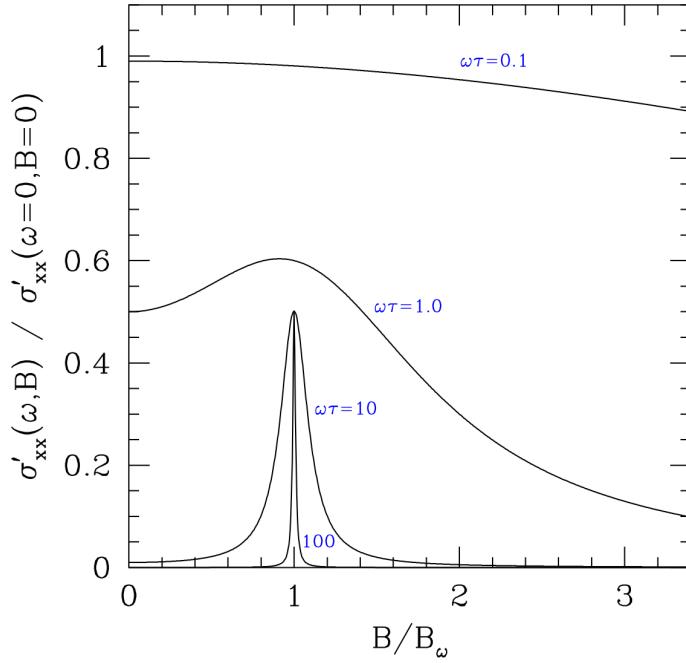


Figure 1.7: Theoretical cyclotron resonance peaks as a function of B/B_ω for different values of $\omega\tau$.

1.7.3 Magnetoresistance: Two-Band Model

For a semiconductor with both electrons and holes present – a situation not uncommon to metals either (*e.g.* Aluminum) – each band contributes to the conductivity. The individual band conductivities are *additive* because the electron and hole conduction processes occur *in parallel*, exactly as we would deduce from eqn. (1.4). Thus,

$$\sigma_{\alpha\beta}(\omega) = \sum_n \sigma_{\alpha\beta}^{(n)}(\omega) , \quad (1.151)$$

where $\sigma_{\alpha\beta}^{(n)}$ is the conductivity tensor for band n , which may be computed in either the electron or hole picture (whichever is more convenient). We assume here that the two distributions δf_c and δf_v evolve according to independent linearized Boltzmann equations, *i.e.* there is no interband scattering to account for.

The resistivity tensor of each band, $\rho_{\alpha\beta}^{(n)}$ exhibits no magnetoresistance, as we have found. However, if two bands are present, the total resistivity tensor ρ is obtained from $\rho^{-1} = \rho_c^{-1} + \rho_v^{-1}$, and

$$\rho = (\rho_c^{-1} + \rho_v^{-1})^{-1} \quad (1.152)$$

will in general exhibit the phenomenon of magnetoresistance.

Explicitly, then, let us consider a model with isotropic and nondegenerate conduction band

minimum and valence band maximum. Taking $\mathbf{B} = B\hat{\mathbf{z}}$, we have

$$\rho_c = \frac{(1 - i\omega\tau_c)m_c}{n_c e^2 \tau_c} \mathbb{I} + \frac{B}{n_c e c} \begin{pmatrix} 0 & 1 & 0 \\ -1 & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix} = \begin{pmatrix} \alpha_c & \beta_c & 0 \\ -\beta_c & \alpha_c & 0 \\ 0 & 0 & \alpha_c \end{pmatrix} \quad (1.153)$$

$$\rho_v = \frac{(1 - i\omega\tau_v)m_v}{n_v e^2 \tau_v} \mathbb{I} - \frac{B}{n_v e c} \begin{pmatrix} 0 & 1 & 0 \\ -1 & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix} = \begin{pmatrix} \alpha_v & -\beta_v & 0 \\ \beta_v & \alpha_v & 0 \\ 0 & 0 & \alpha_v \end{pmatrix}, \quad (1.154)$$

where

$$\alpha_c = \frac{(1 - i\omega\tau_c)m_c}{n_c e^2 \tau_c} \quad \beta_c = \frac{B}{n_c e c} \quad (1.155)$$

$$\alpha_v = \frac{(1 - i\omega\tau_v)m_v}{n_v e^2 \tau_v} \quad \beta_v = \frac{B}{n_v e c}, \quad (1.156)$$

we obtain for the upper left 2×2 block of ρ :

$$\begin{aligned} \rho_{\perp} &= \left[\left(\frac{\alpha_v}{\alpha_v^2 + \beta_v^2} + \frac{\alpha_c}{\alpha_c^2 + \beta_c^2} \right)^2 + \left(\frac{\beta_v}{\alpha_v^2 + \beta_v^2} + \frac{\beta_c}{\alpha_c^2 + \beta_c^2} \right)^2 \right]^{-1} \\ &\quad \times \begin{pmatrix} \frac{\alpha_v}{\alpha_v^2 + \beta_v^2} + \frac{\alpha_c}{\alpha_c^2 + \beta_c^2} & \frac{\beta_v}{\alpha_v^2 + \beta_v^2} + \frac{\beta_c}{\alpha_c^2 + \beta_c^2} \\ -\frac{\beta_v}{\alpha_v^2 + \beta_v^2} - \frac{\beta_c}{\alpha_c^2 + \beta_c^2} & \frac{\alpha_v}{\alpha_v^2 + \beta_v^2} + \frac{\alpha_c}{\alpha_c^2 + \beta_c^2} \end{pmatrix}, \end{aligned} \quad (1.157)$$

from which we compute the magnetoresistance

$$\frac{\rho_{xx}(B) - \rho_{xx}(0)}{\rho_{xx}(0)} = \frac{\sigma_c \sigma_v \left(\frac{\sigma_c}{n_c e c} - \frac{\sigma_v}{n_v e c} \right)^2 B^2}{(\sigma_c + \sigma_v)^2 + (\sigma_c \sigma_v)^2 \left(\frac{1}{n_c e c} + \frac{1}{n_v e c} \right)^2 B^2}$$

(1.158)

where

$$\sigma_c = \alpha_c^{-1} = \frac{n_c e^2 \tau_c}{m_c} \cdot \frac{1}{1 - i\omega\tau_c} \quad (1.159)$$

$$\sigma_v = \alpha_v^{-1} = \frac{n_v e^2 \tau_v}{m_v} \cdot \frac{1}{1 - i\omega\tau_v}. \quad (1.160)$$

Note that the magnetoresistance is *positive* within the two band model, and that it *saturates* in the high field limit:

$$\frac{\rho_{xx}(B \rightarrow \infty) - \rho_{xx}(0)}{\rho_{xx}(0)} = \frac{\sigma_c \sigma_v \left(\frac{\sigma_c}{n_c e c} - \frac{\sigma_v}{n_v e c} \right)^2}{(\sigma_c \sigma_v)^2 \left(\frac{1}{n_c e c} + \frac{1}{n_v e c} \right)^2}. \quad (1.161)$$

The longitudinal resistivity is found to be

$$\rho_{zz} = (\sigma_c + \sigma_v)^{-1} \quad (1.162)$$

and is independent of B .

In an intrinsic semiconductor, $n_c = n_v \propto \exp(-E_g/2k_B T)$, and $\Delta\rho_{xx}(B)/\rho_{xx}(0)$ is finite even as $T \rightarrow 0$. In the extrinsic (*i.e.* doped) case, one of the densities (say, n_c in a p-type material) vanishes much more rapidly than the other, and the magnetoresistance vanishes with the ratio n_c/n_v .

1.7.4 Hall Effect in High Fields

In the high field limit, one may neglect the collision integral entirely, and write (at $\omega = 0$)

$$-e \mathbf{v} \cdot \boldsymbol{\mathcal{E}} \frac{\partial f^0}{\partial \varepsilon} - \frac{e}{\hbar c} \mathbf{v} \times \mathbf{B} \cdot \frac{\partial \delta f}{\partial \mathbf{k}} = 0 . \quad (1.163)$$

We'll consider the case of electrons, and take $\boldsymbol{\mathcal{E}} = \mathcal{E} \hat{\mathbf{y}}$ and $\mathbf{B} = B \hat{\mathbf{z}}$, in which case the solution is

$$\delta f = \frac{\hbar c \mathcal{E}}{B} k_x \frac{\partial f^0}{\partial \varepsilon} . \quad (1.164)$$

Note that k_x is not a smooth single-valued function over the Brillouin-zone due to Bloch periodicity. This treatment, then, will make sense only if the derivative $\partial f^0 / \partial \varepsilon$ confines \mathbf{k} to a closed orbit within the first Brillouin zone. In this case, we have

$$j_x = 2ec \frac{\mathcal{E}}{B} \int_{\hat{\Omega}} \frac{d^3k}{(2\pi)^3} k_x \frac{\partial \varepsilon}{\partial k_x} \frac{\partial f^0}{\partial \varepsilon} \quad (1.165)$$

$$= 2ec \frac{\mathcal{E}}{B} \int_{\hat{\Omega}} \frac{d^3k}{(2\pi)^3} k_x \frac{\partial f^0}{\partial k_x} . \quad (1.166)$$

Now we may integrate by parts, if we assume that f^0 vanishes on the boundary of the Brillouin zone. We obtain

$$j_x = -\frac{2ec\mathcal{E}}{B} \int_{\hat{\Omega}} \frac{d^3k}{(2\pi)^3} f^0 = -\frac{nec}{B} \mathcal{E} . \quad (1.167)$$

We conclude that

$$\sigma_{xy} = -\sigma_{yx} = -\frac{nec}{B} , \quad (1.168)$$

independent of the details of the band structure. “Open orbits” – trajectories along Fermi surfaces which cross Brillouin zone boundaries and return in another zone – pose a subtler problem, and generally lead to a finite, *non-saturating* magnetoresistance.

For holes, we have $\bar{f}^0 = 1 - f^0$ and

$$j_x = -\frac{2ec\mathcal{E}}{B} \int_{\hat{\Omega}} \frac{d^3k}{(2\pi)^3} k_x \frac{\partial \bar{f}^0}{\partial k_x} = +\frac{nec}{B} \mathcal{E} \quad (1.169)$$

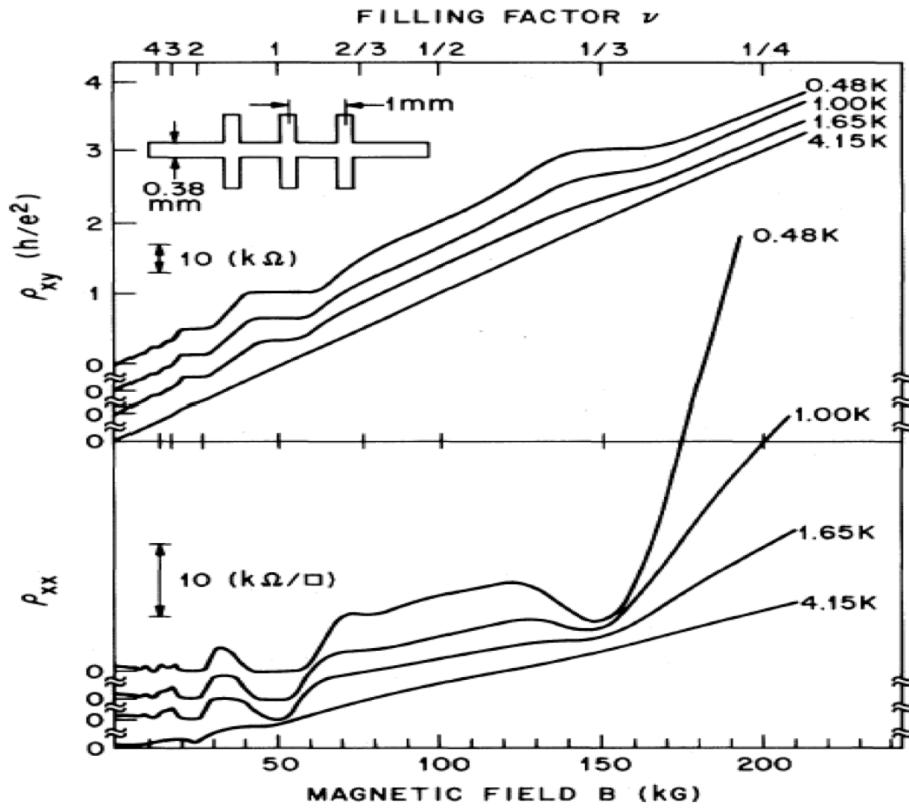


Figure 1.8: Nobel Prize winning magnetotransport data in a clean two-dimensional electron gas at a GaAs-AlGaAs inversion layer, from D. C. Tsui, H. L. Störmer, and A. C. Gossard, *Phys. Rev. Lett.* **48**, 1559 (1982). ρ_{xy} and ρ_{xx} are shown *versus* magnetic field for a set of four temperatures. The Landau level filling factor is $\nu = nhc/eB$. At $T = 4.2\text{ K}$, the Hall resistivity obeys $\rho_{xy} = B/nec$ ($n = 1.3 \times 10^{11} \text{ cm}^{-2}$). At lower temperatures, quantized plateaus appear in $\rho_{xy}(B)$ in units of h/e^2 .

and $\sigma_{xy} = +nec/B$, where n is the hole density.

We define the *Hall coefficient* $R_H = -\rho_{xy}/B$ and the *Hall number*

$$z_H \equiv -\frac{1}{n_{\text{ion}}ecR_H}, \quad (1.170)$$

where n_{ion} is the ion density. For high fields, the off-diagonal elements of both $\rho_{\alpha\beta}$ and $\sigma_{\alpha\beta}$ are negligible, and $\rho_{xy} = -\sigma_{xy}$. Hence $R_H = \mp 1/nec$, and $z_H = \pm n/n_{\text{ion}}$. The high field Hall coefficient is used to determine both the carrier density as well as the sign of the charge carriers; z_H is a measure of valency.

In Al, the high field Hall coefficient saturates at $z_H = -1$. Why is z_H negative? As it turns out, aluminum has both electron and hole bands. Its valence is 3; two electrons go into a filled band, leaving one valence electron to split between the electron and hole bands. Thus

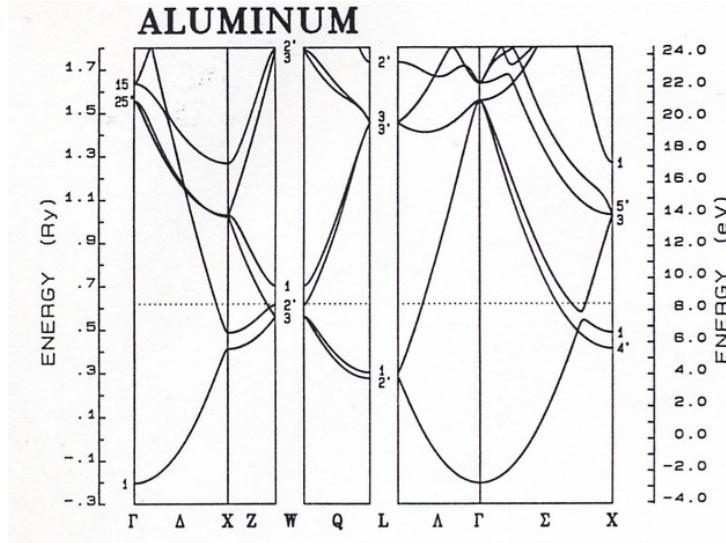


Figure 1.9: Energy bands in aluminum.

$n = 3n_{\text{ion}}$ The Hall conductivity is

$$\sigma_{xy} = (n_h - n_e) ec/B . \quad (1.171)$$

The difference $n_h - n_e$ is determined by the following argument. The *electron* density in the hole band is $n'_e = 2n_{\text{ion}} - n_h$, *i.e.* the total density of levels in the band (two states per unit cell) minus the number of empty levels in which there are holes. Thus,

$$n_h - n_e = 2n_{\text{ion}} - (n_e + n'_e) = n_{\text{ion}} , \quad (1.172)$$

where we've invoked $n_e + n'_e = n_{\text{ion}}$, since precisely one electron from each ion is shared between the two partially filled bands. Thus, $\sigma_{xy} = n_{\text{ion}}ec/B = nec/3B$ and $z_H = -1$. At lower fields, $z_H = +3$ is observed, which is what one would expect from the free electron model. Interband scattering, which is suppressed at high fields, leads to this result.

1.8 Thermal Transport

1.8.1 Boltzmann Theory

Consider a small region of solid with a fixed volume ΔV . The first law of thermodynamics applied to this region gives $T\Delta S = \Delta E - \mu\Delta N$. Dividing by ΔV gives

$$dq \equiv T ds = d\varepsilon - \mu dn , \quad (1.173)$$

where s is the entropy density, ε is energy density, and n the number density. This can be directly recast as the following relation among current densities:

$$\mathbf{j}_q = T\mathbf{j}_s = \mathbf{j}_\varepsilon - \mu\mathbf{j}_n , \quad (1.174)$$

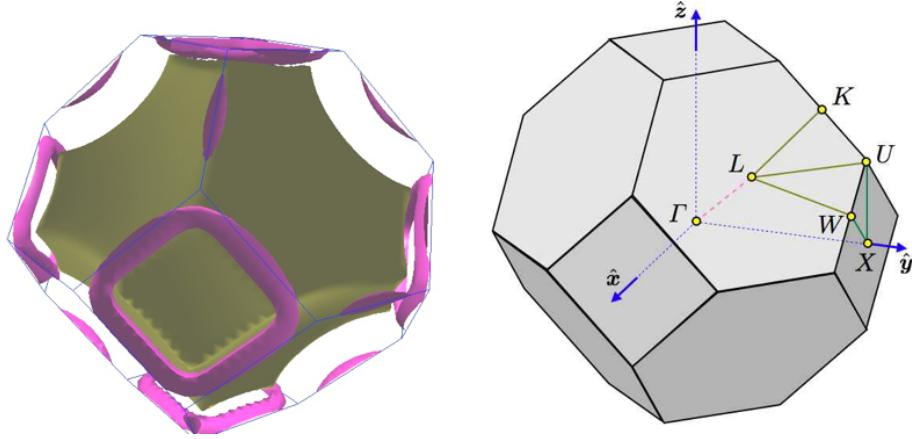


Figure 1.10: Fermi surfaces for electron (pink) and hole (gold) bands in Aluminum.

where $\mathbf{j}_n = \mathbf{j}/(-e)$ is the number current density, \mathbf{j}_ε is the energy current density,

$$\mathbf{j}_\varepsilon = 2 \int_{\hat{\Omega}} \frac{d^3k}{(2\pi)^3} \varepsilon \mathbf{v} \delta f , \quad (1.175)$$

and \mathbf{j}_s is the entropy current density. Accordingly, the thermal (heat) current density \mathbf{j}_q is defined as

$$\mathbf{j}_q \equiv T \mathbf{j}_s = \mathbf{j}_\varepsilon + \frac{\mu}{e} \mathbf{j} \quad (1.176)$$

$$= 2 \int_{\hat{\Omega}} \frac{d^3k}{(2\pi)^3} (\varepsilon - \mu) \mathbf{v} \delta f . \quad (1.177)$$

In the presence of a time-independent temperature gradient and electric field, linearized Boltzmann equation in the relaxation time approximation has the solution

$$\delta f = -\tau(\varepsilon) \mathbf{v} \cdot \left(e \mathcal{E} + \frac{\varepsilon - \mu}{T} \boldsymbol{\nabla} T \right) \left(-\frac{\partial f^0}{\partial \varepsilon} \right) . \quad (1.178)$$

We now consider both the electrical current \mathbf{j} as well as the thermal current density \mathbf{j}_q . One readily obtains

$$\mathbf{j} = -2e \int_{\hat{\Omega}} \frac{d^3k}{(2\pi)^3} \mathbf{v} \delta f \equiv L_{11} \mathcal{E} - L_{12} \boldsymbol{\nabla} T \quad (1.179)$$

$$\mathbf{j}_q = 2 \int_{\hat{\Omega}} \frac{d^3k}{(2\pi)^3} (\varepsilon - \mu) \mathbf{v} \delta f \equiv L_{21} \mathcal{E} - L_{22} \boldsymbol{\nabla} T \quad (1.180)$$

where the *transport coefficients* L^{11} etc. are matrices:

$$L_{11}^{\alpha\beta} = \frac{e^2}{4\pi^3\hbar} \int d\varepsilon \tau(\varepsilon) \left(-\frac{\partial f^0}{\partial \varepsilon} \right) \int dS_\varepsilon \frac{v^\alpha v^\beta}{|\mathbf{v}|} \quad (1.181)$$

$$L_{21}^{\alpha\beta} = TL_{12}^{\alpha\beta} = -\frac{e}{4\pi^3\hbar} \int d\varepsilon \tau(\varepsilon) (\varepsilon - \mu) \left(-\frac{\partial f^0}{\partial \varepsilon} \right) \int dS_\varepsilon \frac{v^\alpha v^\beta}{|\mathbf{v}|} \quad (1.182)$$

$$L_{22}^{\alpha\beta} = \frac{1}{4\pi^3\hbar T} \int d\varepsilon \tau(\varepsilon) (\varepsilon - \mu)^2 \left(-\frac{\partial f^0}{\partial \varepsilon} \right) \int dS_\varepsilon \frac{v^\alpha v^\beta}{|\mathbf{v}|}. \quad (1.183)$$

If we define the hierarchy of integral expressions

$$\mathcal{J}_n^{\alpha\beta} \equiv \frac{1}{4\pi^3\hbar} \int d\varepsilon \tau(\varepsilon) (\varepsilon - \mu)^n \left(-\frac{\partial f^0}{\partial \varepsilon} \right) \int dS_\varepsilon \frac{v^\alpha v^\beta}{|\mathbf{v}|} \quad (1.184)$$

then we may write

$$L_{11}^{\alpha\beta} = e^2 \mathcal{J}_0^{\alpha\beta} \quad L_{21}^{\alpha\beta} = TL_{12}^{\alpha\beta} = -e \mathcal{J}_1^{\alpha\beta} \quad L_{22}^{\alpha\beta} = \frac{1}{T} \mathcal{J}_2^{\alpha\beta}. \quad (1.185)$$

The linear relations in eqn. (1.180) may be recast in the following form:

$$\mathcal{E} = \rho \mathbf{j} + Q \nabla T \quad (1.186)$$

$$\mathbf{j}_q = \square \mathbf{j} - \kappa \nabla T, \quad (1.187)$$

where the matrices ρ , Q , \square , and κ are given by

$$\rho = L_{11}^{-1} \quad Q = L_{11}^{-1} L_{12} \quad (1.188)$$

$$\square = L_{21} L_{11}^{-1} \quad \kappa = L_{22} - L_{21} L_{11}^{-1} L_{12}, \quad (1.189)$$

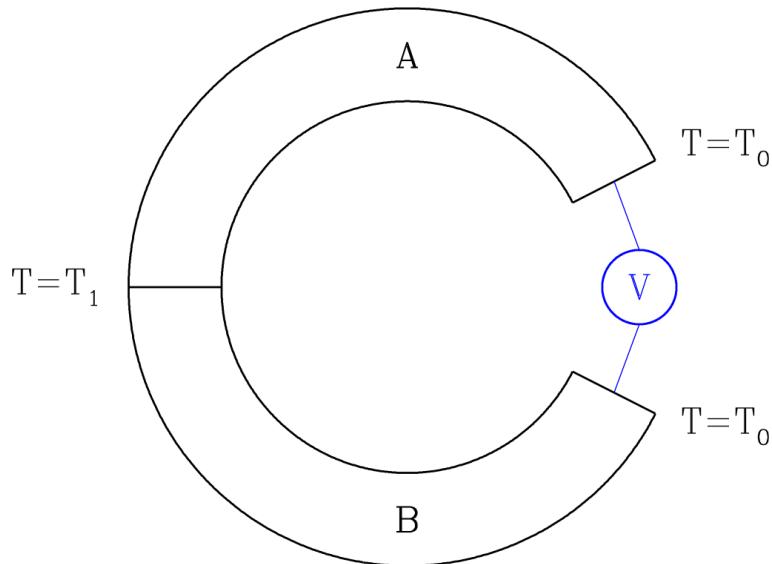
or, in terms of the \mathcal{J}_n ,

$$\rho = \frac{1}{e^2} \mathcal{J}_0^{-1} \quad Q = -\frac{1}{eT} \mathcal{J}_0^{-1} \mathcal{J}_1 \quad (1.190)$$

$$\square = -\frac{1}{e} \mathcal{J}_1 \mathcal{J}_0^{-1} \quad \kappa = \frac{1}{T} \left(\mathcal{J}_2 - \mathcal{J}_1 \mathcal{J}_0^{-1} \mathcal{J}_1 \right), \quad (1.191)$$

The names and physical interpretation of these four transport coefficients is as follows:

- ρ is the *resistivity*: $\mathcal{E} = \rho \mathbf{j}$ under the condition of zero thermal gradient (*i.e.* $\nabla T = 0$).
- Q is the *thermopower*: $\mathcal{E} = Q \nabla T$ under the condition of zero electrical current (*i.e.* $\mathbf{j} = 0$). Q is also called the *Seebeck coefficient*.
- \square is the *Peltier coefficient*: $\mathbf{j}_q = \square \mathbf{j}$ when $\nabla T = 0$.
- κ is the *thermal conductivity*: $\mathbf{j}_q = -\kappa \nabla T$ when $\mathbf{j} = 0$.



$$V = (Q_B - Q_A)(T_1 - T_0)$$

Figure 1.11: A thermocouple is a junction formed of two dissimilar metals. With no electrical current passing, an electric field is generated in the presence of a temperature gradient, resulting in a voltage $V = V_A - V_B$.

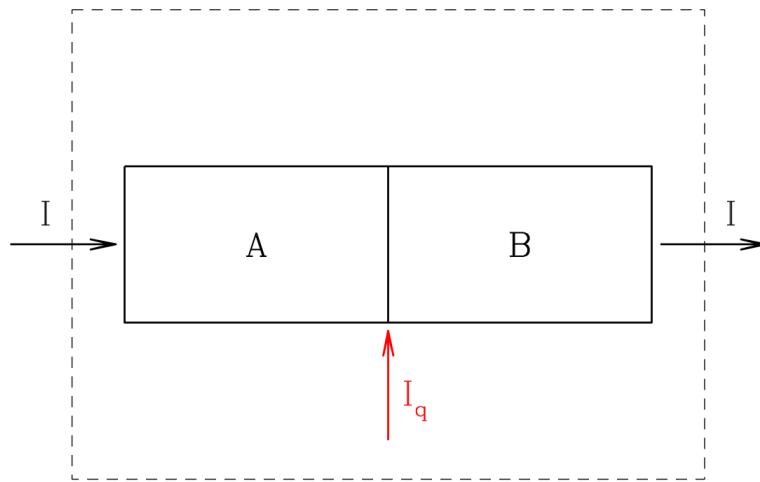
One practical way to measure the thermopower is to form a junction between two dissimilar metals, A and B. The junction is held at temperature T_1 and the other ends of the metals are held at temperature T_0 . One then measures a voltage difference between the free ends of the metals – this is known as the Seebeck effect. Integrating the electric field from the free end of A to the free end of B gives

$$V_A - V_B = - \int_A^B \mathcal{E} \cdot dl = (Q_B - Q_A)(T_1 - T_0) . \quad (1.192)$$

What one measures here is really the difference in thermopowers of the two metals. For an absolute measurement of Q_A , replace B by a superconductor ($Q = 0$ for a superconductor). A device which converts a temperature gradient into an emf is known as a *thermocouple*.

The Peltier effect has practical applications in refrigeration technology. Suppose an electrical current I is passed through a junction between two dissimilar metals, A and B. Due to the difference in Peltier coefficients, there will be a net heat current into the junction of $W = (\Pi_A - \Pi_B)I$. Note that this is proportional to I , rather than the familiar I^2 result from Joule heating. The sign of W depends on the direction of the current. If a second junction is added, to make an ABA configuration, then heat absorbed at the first junction will be liberated at the second.¹⁰

¹⁰To create a refrigerator, stick the cold junction inside a thermally insulated box and the hot junction outside the box.



$$I_q = (\Pi_B - \Pi_A) \cdot I$$

Figure 1.12: A sketch of a Peltier effect refrigerator. An electrical current I is passed through a junction between two dissimilar metals. If the dotted line represents the boundary of a thermally well-insulated body, then the body cools when $\Pi_B > \Pi_A$, in order to maintain a heat current balance at the junction.

1.8.2 The Heat Equation

We begin with the continuity equations for charge density ρ and energy density ε :

$$\frac{\partial \rho}{\partial t} + \nabla \cdot \mathbf{j} = 0 \quad (1.193)$$

$$\frac{\partial \varepsilon}{\partial t} + \nabla \cdot \mathbf{j}_\varepsilon = \mathbf{j} \cdot \mathbf{E} , \quad (1.194)$$

where \mathbf{E} is the electric field¹¹. Now we invoke local thermodynamic equilibrium and write

$$\begin{aligned} \frac{\partial \varepsilon}{\partial t} &= \frac{\partial \varepsilon}{\partial n} \frac{\partial n}{\partial t} + \frac{\partial \varepsilon}{\partial T} \frac{\partial T}{\partial t} \\ &= -\frac{\mu}{e} \frac{\partial \rho}{\partial t} + c_V \frac{\partial T}{\partial t} , \end{aligned} \quad (1.195)$$

where n is the electron *number density* ($n = -\rho/e$) and c_V is the specific heat. We may now write

$$\begin{aligned} c_V \frac{\partial T}{\partial t} &= \frac{\partial \varepsilon}{\partial t} + \frac{\mu}{e} \frac{\partial \rho}{\partial t} \\ &= \mathbf{j} \cdot \mathbf{E} - \nabla \cdot \mathbf{j}_\varepsilon - \frac{\mu}{e} \nabla \cdot \mathbf{j} \\ &= \mathbf{j} \cdot \mathbf{E} - \nabla \cdot \mathbf{j}_q . \end{aligned} \quad (1.196)$$

¹¹Note that it is $\mathbf{E} \cdot \mathbf{j}$ and *not* $\mathbf{E} \cdot \mathbf{j}$ which is the source term in the energy continuity equation.

Invoking $\mathbf{j}_q = \nabla j - \kappa \nabla T$, we see that if there is no electrical current ($\mathbf{j} = 0$), we obtain the *heat equation*

$$c_V \frac{\partial T}{\partial t} = \kappa_{\alpha\beta} \frac{\partial^2 T}{\partial x^\alpha \partial x^\beta}. \quad (1.197)$$

This results in a time scale τ_T for temperature diffusion $\tau_T = CL^2 c_V / \kappa$, where L is a typical length scale and C is a numerical constant. For a cube of size L subjected to a sudden external temperature change, L is the side length and $C = 1/3\pi^2$ (solve by separation of variables).

1.8.3 Calculation of Transport Coefficients

We will henceforth assume that sufficient crystalline symmetry exists (*e.g.* cubic symmetry) to render all the transport coefficients multiples of the identity matrix. Under such conditions, we may write $\mathcal{J}_n^{\alpha\beta} = \mathcal{J}_n \delta_{\alpha\beta}$ with

$$\mathcal{J}_n = \frac{1}{12\pi^3 \hbar} \int d\varepsilon \tau(\varepsilon) (\varepsilon - \mu)^n \left(-\frac{\partial f^0}{\partial \varepsilon} \right) \int dS_\varepsilon |\mathbf{v}|. \quad (1.198)$$

The low-temperature behavior is extracted using the Sommerfeld expansion,

$$\mathcal{I} \equiv \int_{-\infty}^{\infty} d\varepsilon H(\varepsilon) \left(-\frac{\partial f^0}{\partial \varepsilon} \right) = \pi \mathcal{D} \csc(\pi \mathcal{D}) H(\varepsilon) \Big|_{\varepsilon=\mu} \quad (1.199)$$

$$= H(\mu) + \frac{\pi^2}{6} (k_B T)^2 H''(\mu) + \dots \quad (1.200)$$

where $\mathcal{D} \equiv k_B T \frac{\partial}{\partial \varepsilon}$ is a dimensionless differential operator.¹²

To quickly derive the Sommerfeld expansion, note that

$$\left(-\frac{\partial f^0}{\partial \varepsilon} \right) = \frac{1}{k_B T} \frac{1}{[e^{(\varepsilon-\mu)/k_B T} + 1] [e^{(\mu-\varepsilon)/k_B T} + 1]}, \quad (1.201)$$

hence, changing variables to $x \equiv (\varepsilon - \mu)/k_B T$,

$$\begin{aligned} \mathcal{I} &= \int_{-\infty}^{\infty} dx \frac{H(\mu + x k_B T)}{(e^x + 1)(e^{-x} + 1)} = \int_{-\infty}^{\infty} dx \frac{e^{x\mathcal{D}}}{(e^x + 1)(e^{-x} + 1)} H(\varepsilon) \Big|_{\varepsilon=\mu} \\ &= 2\pi i \sum_{n=0}^{\infty} \text{Res} \left[\frac{e^{x\mathcal{D}}}{(e^x + 1)(e^{-x} + 1)} \right]_{x=(2n+1)i\pi} H(\varepsilon) \Big|_{\varepsilon=\mu}, \end{aligned} \quad (1.202)$$

¹²Remember that physically the fixed quantities are temperature and total carrier number density (or charge density, in the case of electron and hole bands), and *not* temperature and chemical potential. An equation of state relating n , μ , and T is then inverted to obtain $\mu(n, T)$, so that all results ultimately may be expressed in terms of n and T .

where we treat \mathcal{D} as if it were c -number even though it is a differential operator. We have also closed the integration contour along a half-circle of infinite radius, enclosing poles in the upper half plane at $x = (2n + 1)i\pi$ for all nonnegative integers n . To compute the residue, set $x = (2n + 1)i\pi + \epsilon$, and examine

$$\begin{aligned} \frac{e^{(2n+1)i\pi\mathcal{D}} e^{\epsilon\mathcal{D}}}{(1 - e^\epsilon)(1 - e^{-\epsilon})} &= -\frac{1 + \epsilon\mathcal{D} + \frac{1}{2}\epsilon^2\mathcal{D}^2 + \dots}{\epsilon^2 + \frac{1}{12}\epsilon^4 + \dots} \cdot e^{(2n+1)i\pi\mathcal{D}} \\ &= \left\{ -\frac{1}{\epsilon^2} - \frac{\mathcal{D}}{\epsilon} + \left(\frac{1}{12} - \frac{1}{2}\mathcal{D}^2\right) + \mathcal{O}(\epsilon) \right\} e^{(2n+1)i\pi\mathcal{D}}. \end{aligned} \quad (1.203)$$

We conclude that the residue is $-\mathcal{D} e^{(2n+1)i\pi\mathcal{D}}$. Therefore,

$$\begin{aligned} \mathcal{I} &= -2\pi i\mathcal{D} \sum_{n=0}^{\infty} e^{(2n+1)i\pi\mathcal{D}} H(\varepsilon) \Big|_{\varepsilon=\mu} \\ &= \pi\mathcal{D} \csc(\pi\mathcal{D}) H(\varepsilon) \Big|_{\varepsilon=\mu}, \end{aligned} \quad (1.204)$$

which is what we set out to show.

Let us now perform some explicit calculations in the case of a parabolic band with an energy-independent scattering time τ . In this case, one readily finds

$$\mathcal{J}_n = \frac{\sigma_0}{e^2} \mu^{-3/2} \pi\mathcal{D} \csc \pi\mathcal{D} \varepsilon^{3/2} (\varepsilon - \mu)^n \Big|_{\varepsilon=\mu}, \quad (1.205)$$

where $\sigma_0 = ne^2\tau/m^*$. Thus,

$$\mathcal{J}_0 = \frac{\sigma_0}{e^2} \left[1 + \frac{\pi^2}{8} \frac{(k_B T)^2}{\mu^2} + \dots \right] \quad (1.206)$$

$$\mathcal{J}_1 = \frac{\sigma_0}{e^2} \frac{\pi^2}{2} \frac{(k_B T)^2}{\mu} + \dots \quad (1.207)$$

$$\mathcal{J}_2 = \frac{\sigma_0}{e^2} \frac{\pi^2}{3} (k_B T)^2 + \dots, \quad (1.208)$$

from which we obtain the low- T results $\rho = \sigma_0^{-1}$,

$$Q = -\frac{\pi^2}{2} \frac{k_B^2 T}{e \varepsilon_F} \quad \kappa = \frac{\pi^2}{3} \frac{n\tau}{m^*} k_B^2 T, \quad (1.209)$$

and of course $\square = TQ$. The predicted universal ratio

$$\frac{\kappa}{\sigma T} = \frac{\pi^2}{3} (k_B/e)^2 = 2.45 \times 10^{-8} \text{ V}^2 \text{ K}^{-2}, \quad (1.210)$$

is known as the *Wiedemann-Franz law*. Note also that our result for the thermopower is unambiguously negative. In actuality, several nearly free electron metals have positive low-temperature thermopowers (Cs and Li, for example). What went wrong? We have neglected electron-phonon scattering!

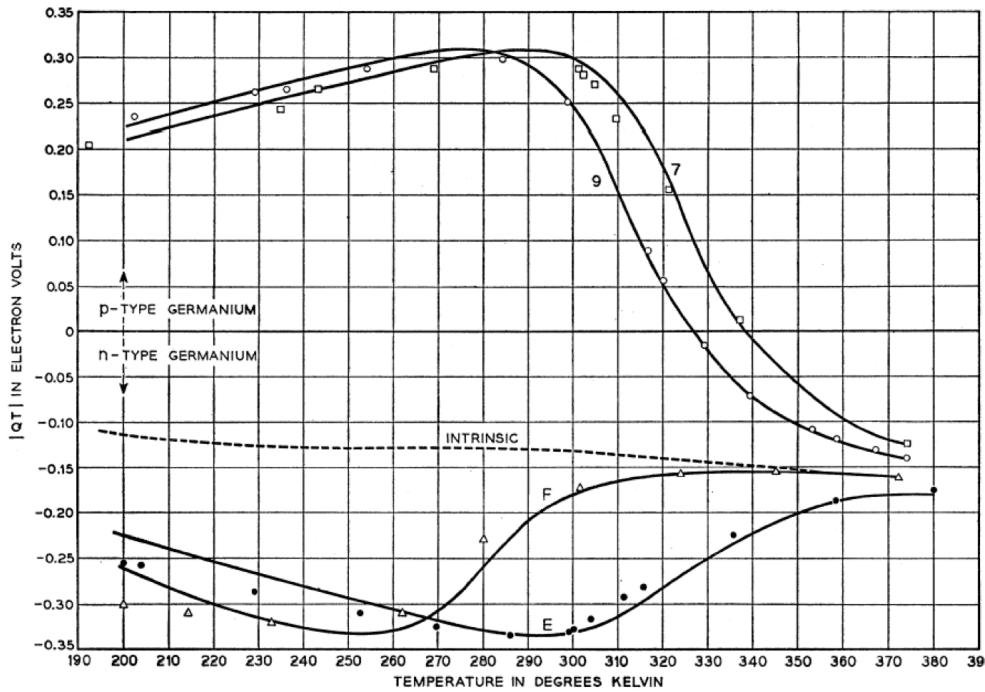


Figure 1.13: QT product for p -type and n -type Ge, from T. H. Geballe and J. W. Hull, *Phys. Rev.* **94**, 1134 (1954). Samples 7, 9, E, and F are distinguished by different doping properties, or by their resistivities at $T = 300\text{ K}$: $21.5\Omega\text{-cm}$ (7), $34.5\Omega\text{-cm}$ (9), $18.5\Omega\text{-cm}$ (E), and $46.0\Omega\text{-cm}$ (F).

1.8.4 Onsager Relations

Transport phenomena are described in general by a set of linear relations,

$$J_i = L_{ik} F_k , \quad (1.211)$$

where the $\{F_k\}$ are *generalized forces* and the $\{J_i\}$ are *generalized currents*. Moreover, to each force F_i corresponds a unique conjugate current J_i , such that the rate of internal entropy production is

$$\dot{S} = \sum_i F_i J_i \implies F_i = \frac{\partial \dot{S}}{\partial J_i} . \quad (1.212)$$

The Onsager relations (also known as *Onsager reciprocity*) states that

$$L_{ik}(\mathbf{B}) = \eta_i \eta_k L_{ki}(-\mathbf{B}) , \quad (1.213)$$

where η_i describes the parity of J_i under time reversal:

$$\mathcal{T} J_i = \eta_i J_i . \quad (1.214)$$

We shall not prove the Onsager relations.

The Onsager relations have some remarkable consequences. For example, they require, for $\mathbf{B} = 0$, that the thermal conductivity tensor κ_{ij} of any crystal must be symmetric, independent of the crystal structure. In general, this result does not follow from considerations of crystalline symmetry. It also requires that for every ‘off-diagonal’ transport phenomenon, *e.g.* the Seebeck effect, there exists a distinct corresponding phenomenon, *e.g.* the Peltier effect.

For the transport coefficients studied, Onsager reciprocity means that in the presence of an external magnetic field,

$$\rho_{\alpha\beta}(\mathbf{B}) = \rho_{\beta\alpha}(-\mathbf{B}) \quad (1.215)$$

$$\kappa_{\alpha\beta}(\mathbf{B}) = \kappa_{\beta\alpha}(-\mathbf{B}) \quad (1.216)$$

$$\square_{\alpha\beta}(\mathbf{B}) = T Q_{\beta\alpha}(-\mathbf{B}) . \quad (1.217)$$

Let’s consider an isotropic system in a weak magnetic field, and expand the transport coefficients to first order in \mathbf{B} :

$$\rho_{\alpha\beta}(\mathbf{B}) = \rho \delta_{\alpha\beta} + \nu \epsilon_{\alpha\beta\gamma} B^\gamma \quad (1.218)$$

$$\kappa_{\alpha\beta}(\mathbf{B}) = \kappa \delta_{\alpha\beta} + \varpi \epsilon_{\alpha\beta\gamma} B^\gamma \quad (1.219)$$

$$Q_{\alpha\beta}(\mathbf{B}) = Q \delta_{\alpha\beta} + \zeta \epsilon_{\alpha\beta\gamma} B^\gamma \quad (1.220)$$

$$\square_{\alpha\beta}(\mathbf{B}) = \square \delta_{\alpha\beta} + \theta \epsilon_{\alpha\beta\gamma} B^\gamma . \quad (1.221)$$

Onsager reciprocity requires $\square = T Q$ and $\theta = T \zeta$. We can now write

$$\mathcal{E} = \rho \mathbf{j} + \nu \mathbf{j} \times \mathbf{B} + Q \nabla T + \zeta \nabla T \times \mathbf{B} \quad (1.222)$$

$$\mathbf{j}_q = \square \mathbf{j} + \theta \mathbf{j} \times \mathbf{B} - \kappa \nabla T - \varpi \nabla T \times \mathbf{B} . \quad (1.223)$$

There are several new phenomena lurking!

- Hall Effect ($\frac{\partial T}{\partial x} = \frac{\partial T}{\partial y} = j_y = 0$)

An electrical current $\mathbf{j} = j_x \hat{\mathbf{x}}$ and a field $\mathbf{B} = B_z \hat{\mathbf{z}}$ yield an electric field \mathcal{E} . The Hall coefficient is $R_H = \mathcal{E}_y / j_x B_z = -\nu$.

- Ettingshausen Effect ($\frac{\partial T}{\partial x} = j_y = j_{q,y} = 0$)

An electrical current $\mathbf{j} = j_x \hat{\mathbf{x}}$ and a field $\mathbf{B} = B_z \hat{\mathbf{z}}$ yield a temperature gradient $\frac{\partial T}{\partial y}$. The Ettingshausen coefficient is $P = \frac{\partial T}{\partial y} / j_x B_z = -\theta / \kappa$.

- Nernst Effect ($j_x = j_y = \frac{\partial T}{\partial y} = 0$)

A temperature gradient $\nabla T = \frac{\partial T}{\partial x} \hat{\mathbf{x}}$ and a field $\mathbf{B} = B_z \hat{\mathbf{z}}$ yield an electric field \mathcal{E} . The Nernst coefficient is $\Lambda = \mathcal{E}_y / \frac{\partial T}{\partial x} B_z = -\zeta$.

- Righi-Leduc Effect ($j_x = j_y = \mathcal{E}_y = 0$)

A temperature gradient $\nabla T = \frac{\partial T}{\partial x} \hat{\mathbf{x}}$ and a field $\mathbf{B} = B_z \hat{\mathbf{z}}$ yield an orthogonal temperature gradient $\frac{\partial T}{\partial y}$. The Righi-Leduc coefficient is $\mathcal{L} = \frac{\partial T}{\partial y} / \frac{\partial T}{\partial x} B_z = \zeta / Q$.

1.9 Electron-Phonon Scattering

1.9.1 Introductory Remarks

We begin our discussion by recalling some elementary facts about phonons in solids:

- In a crystal with r atoms per unit cell, there are $3(r - 1)$ optical modes and 3 acoustic modes, the latter guaranteed by the breaking of the three generators of space translations. We write the phonon dispersion as $\omega = \omega_\lambda(\mathbf{q})$, where $\lambda \in \{1, \dots, 3r\}$ labels the phonon branch, and $\mathbf{q} \in \hat{\Omega}$. If j labels an acoustic mode, $\omega_j(\mathbf{q}) = c_j(\hat{\mathbf{q}}) q$ as $\mathbf{q} \rightarrow 0$.
- Phonons are bosonic particles with zero chemical potential. The equilibrium phonon distribution is

$$n_{\mathbf{q}\lambda}^0 = \frac{1}{\exp(\hbar\omega_\lambda(\mathbf{q})/k_B T) - 1}. \quad (1.224)$$

- The maximum phonon frequency is roughly given by the Debye frequency ω_D . The Debye temperature $\Theta_D = \hbar\omega_D \sim 100\text{ K} - 1000\text{ K}$ in most solids.

At high temperatures, equipartition gives $\langle (\delta\mathbf{R}_i)^2 \rangle \propto k_B T$, hence the effective scattering cross-section σ_{tot} increases as T , and $\tau \gtrsim 1/n_{\text{ion}} v_F \sigma_{\text{tot}} \propto T^{-1}$. From $\rho = m^*/ne^2\tau$, then, we deduce that the high temperature resistivity should be linear in temperature due to phonon scattering: $\rho(T) \propto T$. Of course, when the mean free path $\ell = v_F \tau$ becomes as small as the Fermi wavelength λ_F , the entire notion of coherent quasiparticle transport becomes problematic, and rather than continuing to grow we expect that the resistivity should saturate: $\rho(T \rightarrow \infty) \approx h/k_F e^2$, known as the *Ioffe-Regel limit*. For $k_F = 10^8 \text{ cm}^{-1}$, this takes the value $260 \mu\Omega \text{ cm}$.

1.9.2 Electron-Phonon Interaction

Let $\mathbf{R}_i = \mathbf{R}_i^0 + \delta\mathbf{R}_i$ denote the position of the i^{th} ion, and let $U(\mathbf{r}) = -Ze^2 \exp(-r/\lambda_{\text{TF}})/r$ be the electron-ion interaction. Expanding in terms of the ionic displacements $\delta\mathbf{R}_i$,

$$\mathcal{H}_{\text{el-ion}} = \sum_i U(\mathbf{r} - \mathbf{R}_i^0) - \sum_i \delta\mathbf{R}_i \cdot \nabla U(\mathbf{r} - \mathbf{R}_i^0), \quad (1.225)$$

where i runs from 1 to N_{ion} ¹³. The deviation $\delta\mathbf{R}_i$ may be expanded in terms of the vibrational normal modes of the lattice, *i.e.* the phonons, as

$$\delta R_i^\alpha = \frac{1}{\sqrt{N_{\text{ion}}}} \sum_{\mathbf{q}\lambda} \left(\frac{\hbar}{2\omega_\lambda(\mathbf{q})} \right)^{1/2} \hat{e}_\lambda^\alpha(\mathbf{q}) e^{i\mathbf{q} \cdot \mathbf{R}_i^0} (a_{\mathbf{q}\lambda} + a_{-\mathbf{q}\lambda}^\dagger). \quad (1.226)$$

¹³We assume a Bravais lattice, for simplicity.

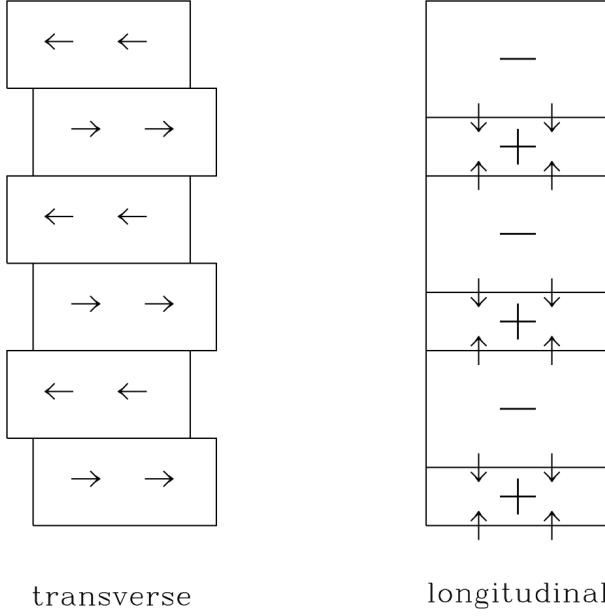


Figure 1.14: Transverse and longitudinal phonon polarizations. Transverse phonons do not result in charge accumulation. Longitudinal phonons create local charge buildup and therefore couple to electronic excitations via the Coulomb interaction.

The phonon polarization vectors satisfy $\hat{e}_\lambda(\mathbf{q}) = \hat{e}_\lambda^*(-\mathbf{q})$ as well as the generalized orthonormality relations

$$\sum_{\alpha} \hat{e}_{\lambda}^{\alpha}(\mathbf{q}) \hat{e}_{\lambda'}^{\alpha}(-\mathbf{q}) = M^{-1} \delta_{\lambda\lambda'} \quad (1.227)$$

$$\sum_{\lambda} \hat{e}_{\lambda}^{\alpha}(\mathbf{q}) \hat{e}_{\lambda}^{\beta}(-\mathbf{q}) = M^{-1} \delta_{\alpha\beta} , \quad (1.228)$$

where M is the ionic mass. The number of unit cells in the crystal is $N_{\text{ion}} = V/\Omega$, where Ω is the Wigner-Seitz cell volume. Again, we approximate Bloch states by plane waves $\psi_{\mathbf{k}}(\mathbf{r}) = \exp(i\mathbf{k} \cdot \mathbf{r})/\sqrt{V}$, in which case

$$\langle \mathbf{k}' | \nabla U(\mathbf{r} - \mathbf{R}_i^0) | \mathbf{k} \rangle = -\frac{i}{V} e^{i(\mathbf{k}-\mathbf{k}') \cdot \mathbf{R}_i^0} \frac{4\pi Z e^2 (\mathbf{k} - \mathbf{k}')}{(\mathbf{k} - \mathbf{k}')^2 + \lambda_{\text{TF}}^{-2}} . \quad (1.229)$$

The sum over lattice sites gives

$$\sum_{i=1}^{N_{\text{ion}}} e^{i(\mathbf{k}-\mathbf{k}'+\mathbf{q}) \cdot \mathbf{R}_i^0} = N_{\text{ion}} \delta_{\mathbf{k}', \mathbf{k}+\mathbf{q} \text{ mod } \mathbf{G}} , \quad (1.230)$$

so that

$$\mathcal{H}_{\text{el-ph}} = \frac{1}{\sqrt{V}} \sum_{\substack{\mathbf{k}\mathbf{k}'\sigma \\ q\lambda G}} g_\lambda(\mathbf{k}, \mathbf{k}') (a_{\mathbf{q}\lambda}^\dagger + a_{-\mathbf{q}\lambda}) \psi_{\mathbf{k}\sigma}^\dagger \psi_{\mathbf{k}'\sigma} \delta_{\mathbf{k}', \mathbf{k}+\mathbf{q}+\mathbf{G}} \quad (1.231)$$

with

$$g_\lambda(\mathbf{k}, \mathbf{k} + \mathbf{q} + \mathbf{G}) = -i \left(\frac{\hbar}{2\Omega\omega_\lambda(\mathbf{q})} \right)^{1/2} \frac{4\pi Ze^2}{(\mathbf{q} + \mathbf{G})^2 + \lambda_{\text{TF}}^{-2}} (\mathbf{q} + \mathbf{G}) \cdot \hat{\mathbf{e}}_\lambda^*(\mathbf{q}) . \quad (1.232)$$

In an isotropic solid¹⁴ ('jellium'), the phonon polarization at wavevector \mathbf{q} either is parallel to \mathbf{q} (longitudinal waves), or perpendicular to \mathbf{q} (transverse waves). We see that only longitudinal waves couple to the electrons. This is because transverse waves do not result in any local accumulation of charge density, and it is to the charge density that electrons couple, via the Coulomb interaction.

Restricting our attention to the longitudinal phonon, we have $\hat{\mathbf{e}}_L(\mathbf{q}) = \hat{\mathbf{q}}/\sqrt{M}$ and hence, for small $\mathbf{q} = \mathbf{k}' - \mathbf{k}$,

$$g_L(\mathbf{k}, \mathbf{k} + \mathbf{q}) = -i \left(\frac{\hbar}{2M\Omega} \right)^{1/2} \frac{4\pi Ze^2}{q^2 + \lambda_{\text{TF}}^{-2}} c_L^{-1/2} q^{1/2} , \quad (1.233)$$

where c_L is the longitudinal phonon velocity. Thus, for small \mathbf{q} we see that the electron-longitudinal phonon coupling $g_L(\mathbf{k}, \mathbf{k} + \mathbf{q}) \equiv g_q$ satisfies

$$|g_q|^2 = \lambda_{\text{el-ph}} \cdot \frac{\hbar c_L q}{g(\varepsilon_F)} , \quad (1.234)$$

where $g(\varepsilon_F)$ is the electronic density of states, and where the dimensionless *electron-phonon coupling constant* is

$$\lambda_{\text{el-ph}} = \frac{Z^2}{2Mc_L^2 \Omega g(\varepsilon_F)} = \frac{2Z}{3} \frac{m^*}{M} \left(\frac{\varepsilon_F}{k_B \Theta_s} \right)^2 , \quad (1.235)$$

with $\Theta_s \equiv \hbar c_L k_F / k_B$. Table 1.3 lists Θ_s , the Debye temperature Θ_D , and the electron-phonon coupling $\lambda_{\text{el-ph}}$ for various metals.

EXERCISE: Derive eqn. (1.235).

Metal	Θ_s	Θ_D	$\lambda_{\text{el-ph}}$	Metal	Θ_s	Θ_D	$\lambda_{\text{el-ph}}$
Na	220	150	0.47	Au	310	170	0.08
K	150	100	0.25	Be	1940	1000	0.59
Cu	490	315	0.16	Al	910	394	0.90
Ag	340	215	0.12	In	300	129	1.05

Table 1.3: Electron-phonon interaction parameters for some metals. Temperatures are in Kelvins.

¹⁴The jellium model ignores $\mathbf{G} \neq 0$ Umklapp processes.

1.9.3 Boltzmann Equation for Electron-Phonon Scattering

Earlier we had quoted the result for the electron-phonon collision integral,

$$\begin{aligned} \mathcal{I}_k\{f, n\} = & \frac{2\pi}{\hbar V} \sum_{k', \lambda} |g_\lambda(\mathbf{k}, \mathbf{k}')|^2 \left\{ (1 - f_k) f_{k'} (1 + n_{q\lambda}) \delta(\varepsilon_k + \hbar\omega_{q\lambda} - \varepsilon_{k'}) \right. \\ & + (1 - f_k) f_{k'} n_{-q\lambda} \delta(\varepsilon_k - \hbar\omega_{-q\lambda} - \varepsilon_{k'}) \\ & - f_k (1 - f_{k'}) (1 + n_{-q\lambda}) \delta(\varepsilon_k - \hbar\omega_{-q\lambda} - \varepsilon_{k'}) \\ & \left. - f_k (1 - f_{k'}) n_{q\lambda} \delta(\varepsilon_k + \hbar\omega_{q\lambda} - \varepsilon_{k'}) \right\} \delta_{q, k' - k \bmod G}. \end{aligned} \quad (1.236)$$

The four terms inside the curly brackets correspond, respectively, to cases (a) through (d) in fig. 1.1. The $(1 + n)$ factors in the phonon emission terms arise from both spontaneous as well as stimulated emission processes. There is no spontaneous absorption.

EXERCISE: Verify that in equilibrium $\mathcal{I}_k\{f^0, n^0\} = 0$.

In principle we should also write down a Boltzmann equation for the phonon distribution $n_{q\lambda}$ and solve the two coupled sets of equations. The electronic contribution to the phonon collision integral is written as $\mathcal{J}_{q\lambda}\{f, n\}$, with

$$\begin{aligned} \mathcal{J}_{q\lambda}\{f, n\} \equiv \left(\frac{\partial n_{q\lambda}}{\partial t} \right)_{\text{coll}} = & \frac{4\pi}{\hbar V} |g_{q\lambda}|^2 \sum_{k \in \hat{\Omega}} \left\{ (1 + n_{q\lambda}) f_{k+q} (1 - f_k) \right. \\ & \left. - n_{q\lambda} f_k (1 - f_{k+q}) \right\} \times \delta(\varepsilon_{k+q} - \varepsilon_k - \hbar\omega_{q\lambda}). \end{aligned} \quad (1.237)$$

Here, we will assume that the phonons are always in equilibrium, and take $n_{q\lambda} = n_{q\lambda}^0$. Phonon equilibrium can be achieved via anharmonic effects (*i.e.* phonon-phonon scattering), or by scattering of phonons from impurities or crystalline defects. At low temperatures,

$$\frac{1}{\tau(\omega)} = \begin{cases} A\omega^2 & \text{impurity scattering} \\ B\omega^2 T^3 & \text{anharmonic phonon scattering} \\ C/L & \text{boundary scattering } (L = \text{crystal size}) \end{cases} \quad (1.238)$$

where A , B , and C are constants.

We now linearize $\mathcal{I}_k\{f\}$, and obtain

$$\begin{aligned} \mathcal{L} \delta f = & \frac{2\pi}{\hbar V} \sum_{q\lambda} |g_{q\lambda}|^2 \left\{ \left[(1 - f_k^0 + n_{q\lambda}^0) \delta f_{k+q} - (f_{k+q}^0 + n_{q\lambda}^0) \delta f_k \right] \delta(\varepsilon_{k+q} - \varepsilon_k - \hbar\omega_{q\lambda}) \right. \\ & \left. - \left[(1 - f_{k+q}^0 + n_{-q\lambda}^0) \delta f_k - (f_k^0 + n_{-q\lambda}^0) \delta f_{k+q} \right] \delta(\varepsilon_{k+q} - \varepsilon_k + \hbar\omega_{-q\lambda}) \right\}. \end{aligned} \quad (1.239)$$

This integral operator must be inverted in order to solve for δf_k in

$$\mathcal{L} \delta f = e \mathbf{v} \cdot \boldsymbol{\mathcal{E}} \left(-\frac{\partial f^0}{\partial \varepsilon} \right). \quad (1.240)$$

Unfortunately, the inversion is analytically intractable – there is no simple solution of the form $\delta f_{\mathbf{k}} = e\tau_{\mathbf{k}} \mathbf{v}_{\mathbf{k}} \cdot \mathcal{E} (\partial f^0 / \partial \varepsilon)$ as there was in the case of isotropic impurity scattering. However, we can still identify the coefficient of $-\delta f_{\mathbf{k}}$ in $\mathcal{L} \delta f$ as the scattering rate $\tau_{\mathbf{k}}^{-1}$. As before, $\tau_{\mathbf{k}}$ in fact is a function of the energy $\varepsilon(\mathbf{k})$:

$$\frac{1}{\tau(\varepsilon)} = \frac{1}{4\pi^2 \hbar^2} \int d\varepsilon' \int dS_{\varepsilon'} \frac{|g_{\mathbf{k}'-\mathbf{k}}|^2}{|\mathbf{v}_{\mathbf{k}'}|} \left\{ [f^0(\varepsilon') + n_{\mathbf{k}'-\mathbf{k}}^0] \delta(\varepsilon' - \varepsilon - \hbar\omega_{\mathbf{k}'-\mathbf{k}}) + [1 + f^0(\varepsilon') + n_{\mathbf{k}'-\mathbf{k}}^0] \delta(\varepsilon' - \varepsilon + \hbar\omega_{\mathbf{k}'-\mathbf{k}}) \right\} \quad (1.241)$$

In an isotropic system, $\tau(\varepsilon(\mathbf{k}))$ is independent of $\hat{\mathbf{k}}$. This means we can take $\mathbf{k} = \sqrt{2m^*\varepsilon/\hbar^2} \hat{\mathbf{z}}$ in performing the above integral.

It is convenient to define the dimensionless function

$$\alpha^2 F(\omega) \equiv \frac{1}{8\pi^3 \hbar^2} \int dS_{\varepsilon'} \frac{|g_{\mathbf{k}'-\mathbf{k}}|^2}{|\mathbf{v}_{\mathbf{k}'}|} \delta(\omega - \omega_{\mathbf{k}'-\mathbf{k}}) . \quad (1.242)$$

For parabolic bands, one obtains

$$\begin{aligned} \alpha^2 F(\omega) &= \frac{1}{8\pi^3 \hbar^2} \frac{\lambda_{\text{el-ph}} \hbar\omega}{m^* k_F / \pi^2 \hbar^2} \frac{m^*}{\hbar k_F} k_F^2 \int d\hat{\mathbf{k}}' \delta(\omega - c_L k_F |\hat{\mathbf{k}}' - \hat{\mathbf{z}}|) \\ &= \lambda_{\text{el-ph}} \left(\frac{\hbar\omega}{k_B \Theta_s} \right)^2 \Theta(2k_B \Theta_s - \hbar\omega) . \end{aligned} \quad (1.243)$$

The scattering rate is given in terms of $\alpha^2 F(\omega)$ as

$$\frac{1}{\tau(\varepsilon)} = 2\pi \int_0^\infty d\omega \alpha^2 F(\omega) \left\{ f^0(\varepsilon + \hbar\omega) - f^0(\varepsilon - \hbar\omega) + 2n^0(\omega) + 1 \right\} . \quad (1.244)$$

At $T = 0$ we have $f^0(\varepsilon) = \Theta(\varepsilon_F - \varepsilon)$ and $n^0(\omega) = 0$, whence

$$\begin{aligned} \frac{1}{\tau(\varepsilon)} &= 2\pi \int_0^\infty d\omega \alpha^2 F(\omega) \left\{ \Theta(\varepsilon_F - \varepsilon - \hbar\omega) - \Theta(\varepsilon_F - \varepsilon + \hbar\omega) + 1 \right\} \\ &= \begin{cases} \frac{\lambda_{\text{el-ph}}}{12} \frac{2\pi}{\hbar} \cdot \frac{|\varepsilon - \varepsilon_F|^3}{(k_B \Theta_s)^2} & \text{if } |\varepsilon - \varepsilon_F| < 2k_B \Theta_s \\ \frac{2\lambda_{\text{el-ph}}}{3} \frac{2\pi}{\hbar} \cdot (k_B \Theta_s) & \text{if } |\varepsilon - \varepsilon_F| > 2k_B \Theta_s \end{cases} \end{aligned} \quad (1.245)$$

Note that $\tau(\varepsilon_F) = \infty$, unlike the case of impurity scattering. This is because at $T = 0$ there are no phonons! For $T \neq 0$, the divergence is cut off, and one obtains

$$\frac{1}{\tau(\mu)} = \frac{2\pi \lambda_{\text{el-ph}}}{\hbar} \frac{k_B T^3}{\Theta_s^2} G\left(\frac{2\Theta_s}{T}\right) \quad (1.246)$$

$$G(y) = \int_0^y dx \frac{x^2}{2 \sinh x} = \begin{cases} \frac{7}{4} \zeta(3) & \text{if } y = \infty \\ \frac{1}{4} y & \text{if } y \ll 1 , \end{cases} \quad (1.247)$$

and so

$$\frac{1}{\tau(\mu)} = \begin{cases} \frac{7\pi\zeta(3)}{2\hbar} \frac{k_B T^3}{\Theta_s^2} \lambda_{\text{el-ph}} & \text{if } T \ll \Theta_s \\ \frac{2\pi}{\hbar} k_B T \lambda_{\text{el-ph}} & \text{if } T \gg \Theta_s \end{cases} \quad (1.248)$$

This calculation predicts that $\tau \propto T^{-3}$ at low temperatures. This is correct if τ is the *thermal lifetime*. However, a more sophisticated calculation shows that the *transport lifetime* behaves as $\tau_{\text{tr}} \propto T^{-5}$ at low T . The origin of the discrepancy is our neglect of the $(1 - \cos \vartheta)$ factor present in the average of the momentum relaxation time. At low T , there is only small angle scattering from the phonons, and $\langle \vartheta^2 \rangle \propto \langle \mathbf{q}^2/k_F^2 \rangle \propto T^2$. The Wiedemann-Franz law, $\tau_\sigma = \tau_\kappa$, is valid for $k_B T \gtrsim \hbar c_L k_F$, as well as at low T in isotropic systems, where impurity scattering is the dominant mechanism. It fails at intermediate temperatures.

Chapter 2

Mesoscopia

2.1 References

- Y. Imry, Introduction to Mesoscopic Physics
- M. Janssen, Fluctuations and Localization
- D. Ferry and S. M. Goodnick, Transport in Nanostructures

2.2 Introduction

Current nanofabrication technology affords us the remarkable opportunity to study condensed matter systems on an unprecedented small scale. For example, small electron boxes known as *quantum dots* have been fabricated, with characteristic size ranging from 10 nm to 1 μm ; the smallest quantum dots can hold as few as one single electron, while larger dots can hold thousands. In systems such as these, one can probe discrete energy level spectra associated with quantization in a finite volume. Oftentimes systems are so small that Bloch's theorem and the theoretical apparatus of Boltzmann transport are of dubious utility.

2.3 The Landauer Formula

Consider a disordered one-dimensional wire connected on each end to reservoirs at fixed chemical potential μ_L and μ_R . For the moment, let us consider only a single spin species, or imagine that the spins are completely polarized. Suppose further that $\mu_L > \mu_R$, so that a current I flows from the left reservoir (L) to the right reservoir (R). Next, consider a cross-sectional surface Σ just to the right of the disordered region. We calculate the current

flowing past this surface as a sum over three terms:

$$I_\Sigma = -e \int d\varepsilon \mathcal{N}(\varepsilon) v(\varepsilon) \left\{ T(\varepsilon) f(\varepsilon - \mu_L) + R'(\varepsilon) f(\varepsilon - \mu_R) - f(\varepsilon - \mu_R) \right\}. \quad (2.1)$$

Here, $\mathcal{N}(\varepsilon)$ is the density of states in the leads per spin degree of freedom, and corresponding to motion in a given direction (right or left but not both); $v(\varepsilon)$ is the velocity, and $f(\varepsilon - \mu_{L,R})$ are the respective Fermi distributions. $T(\varepsilon)$ is the *transmission probability* that electrons of energy ε emerging from the left reservoir will end up in right reservoir; $R'(\varepsilon)$ is the *reflection probability* that electrons emerging from right reservoir will return to the right reservoir. The three terms on the right hand side of (2.1) correspond, respectively, to: (i) electrons emerging from L which make it through the wire and are deposited in R, (ii) electrons emerging from R which fail to ‘swim upstream’ to L and are instead reflected back into R, and (iii) all electrons emerging from reservoir R (note this contribution is of opposite sign). The transmission and reflection probabilities are obtained by solving for the quantum mechanical scattering due to the disordered region. If the incoming *flux amplitudes* from the left and right sides are i and i' , respectively, and the outgoing flux amplitudes on those sides o' and o , linearity of the Schrödinger equation requires that

$$\begin{pmatrix} o' \\ o \end{pmatrix} = \mathcal{S} \begin{pmatrix} i \\ i' \end{pmatrix} \quad ; \quad \mathcal{S} = \begin{pmatrix} r & t' \\ t & r' \end{pmatrix}. \quad (2.2)$$

The matrix \mathcal{S} is known as the *scattering matrix* (or S -matrix, for short). The S -matrix elements $r, t, etc.$ are reflection and transmission *amplitudes*. The reflection and transmission *probabilities* are given by

$$R = |r|^2 \quad T' = |t'|^2 \quad (2.3)$$

$$T = |t|^2 \quad R' = |r'|^2. \quad (2.4)$$

Going back to (2.1), let us assume that we are close to equilibrium, so the difference $\mu_R - \mu_L$ in chemical potentials is slight. We may then expand

$$f(\varepsilon - \mu_R) = f(\varepsilon - \mu_L) + f'(\varepsilon - \mu_L)(\mu_L - \mu_R) + \dots \quad (2.5)$$

and obtain the result

$$\begin{aligned} I &= e(\mu_R - \mu_L) \int d\varepsilon \mathcal{N}(\varepsilon) v(\varepsilon) \left(-\frac{\partial f^0}{\partial \varepsilon} \right) T(\varepsilon) \\ &= \frac{e}{h} (\mu_R - \mu_L) \int d\varepsilon \left(-\frac{\partial f^0}{\partial \varepsilon} \right) T(\varepsilon), \end{aligned} \quad (2.6)$$

valid to lowest order in $(\mu_R - \mu_L)$. We have invoked here a very simple, very important result for the one-dimensional density of states. Considering only states moving in a definite direction (left or right) and with a definite spin polarization (up or down), we have

$$\mathcal{N}(\varepsilon) d\varepsilon = \frac{dk}{2\pi} \implies \boxed{\mathcal{N}(\varepsilon) = \frac{1}{2\pi} \frac{dk}{d\varepsilon} = \frac{1}{hv(\varepsilon)}} \quad (2.7)$$

where $h = 2\pi\hbar$ is Planck's constant. Thus, there is a remarkable cancellation in the product $\mathcal{N}(\varepsilon) v(\varepsilon) = h^{-1}$. Working at $T = 0$, we therefore obtain

$$I = \frac{e}{h} (\mu_R - \mu_L) T(\varepsilon_F) , \quad (2.8)$$

where $T(\varepsilon_F)$ is the transmission probability at the Fermi energy. The chemical potential varies with voltage according to $\mu(V) = \mu(0) - eV$, hence the *conductance* $G = I/V$ is found to be

$$G = \frac{e^2}{h} T(\varepsilon_F) \quad (\text{per spin channel}) \quad (2.9)$$

$$= \frac{2e^2}{h} T(\varepsilon_F) \quad (\text{spin degeneracy included}) \quad (2.10)$$

The quantity h/e^2 is a conveniently measurable $25,813 \Omega$.

We conclude that *conductance is transmission* - G is e^2/h times the transmission probability $T(\varepsilon_F)$ with which an electron at the Fermi level passes through the wire. This has a certain intuitive appeal, since clearly if $T(\varepsilon_F) = 0$ we should expect $G = 0$. However, two obvious concerns should be addressed:

- The power dissipated should be $P = I^2 R = V^2 G$. Yet the scattering in the wire is assumed to be purely elastic. Hence no dissipation occurs within the wire at all, and the Poynting vector immediately outside the wire must vanish. What, then, is the source of the dissipation?
- For a perfect wire, $T(\varepsilon_F) = 1$, and $G = e^2/h$ (per spin) is finite. Shouldn't a perfect (*i.e.* not disordered) wire have *zero* resistance, and hence *infinite* conductance?

The answer to the first of these riddles is simple – all the dissipation takes place in the R reservoir. When an electron makes it through the wire from L to R, it deposits its excess energy $\mu_L - \mu_R$ in the R reservoir. The mechanism by which this is done is not our concern – we only need assume that there is *some* inelastic process (*e.g.* electron-phonon scattering, electron-electron scattering, *etc.*) which acts to equilibrate the R reservoir.

The second riddle is a bit more subtle. One solution is to associate the resistance h/e^2 of a perfect wire with the *contact resistance* due to the leads. The intrinsic conductance of the wire G_i is determined by assuming the wire resistance and contact resistances are in series:

$$G^{-1} = G_i^{-1} + \frac{h}{e^2} \implies G_i = \frac{e^2}{h} \frac{T(\varepsilon_F)}{1 - T(\varepsilon_F)} = \frac{e^2}{h} \frac{T(\varepsilon_F)}{R(\varepsilon_F)} , \quad (2.11)$$

where G_i is the intrinsic conductance of the wire, per spin channel. Now we see that when $T(\varepsilon_F) \rightarrow 1$ the intrinsic conductance diverges: $G_i \rightarrow \infty$. When $T \ll 1$, $G_i \approx G = (e^2/h)T$. This result (2.11) is known as the *Landauer Formula*.

To derive this result in a more systematic way, let us assume that the disordered segment is connected to the left and right reservoirs by perfect leads, and that the leads are not in

equilibrium at chemical potentials μ_L and μ_R but instead at $\tilde{\mu}_L$ and $\tilde{\mu}_R$. To determine $\tilde{\mu}_L$ and $\tilde{\mu}_R$, we compute the number density (per spin channel) in the leads,

$$n_L = \int d\varepsilon \mathcal{N}(\varepsilon) \left\{ [1 + R(\varepsilon)] f(\varepsilon - \mu_L) + T'(\varepsilon) f(\varepsilon - \mu_R) \right\} \quad (2.12)$$

$$n_R = \int d\varepsilon \mathcal{N}(\varepsilon) \left\{ T(\varepsilon) f(\varepsilon - \mu_L) + [1 + R'(\varepsilon)] f(\varepsilon - \mu_R) \right\} \quad (2.13)$$

and associate these densities with chemical potentials $\tilde{\mu}_L$ and $\tilde{\mu}_R$ according to

$$n_L = 2 \int d\varepsilon \mathcal{N}(\varepsilon) f(\varepsilon - \tilde{\mu}_L) \quad (2.14)$$

$$n_R = 2 \int d\varepsilon \mathcal{N}(\varepsilon) f(\varepsilon - \tilde{\mu}_R) , \quad (2.15)$$

where the factor of two accounts for both directions of motion. To lowest order, then, we obtain

$$2(\mu_L - \tilde{\mu}_L) = (\mu_L - \mu_R) T' \implies \tilde{\mu}_L = \mu_L + \frac{1}{2} T' (\mu_R - \mu_L) \quad (2.16)$$

$$2(\mu_R - \tilde{\mu}_R) = (\mu_R - \mu_L) T \implies \tilde{\mu}_R = \mu_R + \frac{1}{2} T (\mu_L - \mu_R) \quad (2.17)$$

and therefore

$$\begin{aligned} (\tilde{\mu}_L - \tilde{\mu}_R) &= \left(1 - \frac{1}{2}T - \frac{1}{2}T'\right) (\mu_L - \mu_R) \\ &= (1 - T) (\mu_L - \mu_R) , \end{aligned} \quad (2.18)$$

where the last equality follows from unitarity ($\mathcal{S}^\dagger \mathcal{S} = \mathcal{S} \mathcal{S}^\dagger = 1$). There are two experimental configurations to consider:

- *Two probe measurement* – Here the current leads are also used as voltage leads. The voltage difference is $\Delta V = (\mu_R - \mu_L)/e$ and the measured conductance is $G_{2\text{-probe}} = (e^2/h) T(\varepsilon_F)$.
- *Four probe measurement* – Separate leads are used for current and voltage probes. The observed voltage difference is $\Delta V = (\tilde{\mu}_R - \tilde{\mu}_L)/e$ and the measured conductance is $G_{4\text{-probe}} = (e^2/h) T(\varepsilon_F)/R(\varepsilon_F)$.

2.3.1 Example: Potential Step

Perhaps the simplest scattering problem is one-dimensional scattering from a potential step, $V(x) = V_0 \Theta(x)$. The potential is piecewise constant, hence the wavefunction is piecewise a plane wave:

$$x < 0 : \quad \psi(x) = I e^{ikx} + O' e^{-ikx} \quad (2.19)$$

$$x > 0 : \quad \psi(x) = O e^{ik'x} + I' e^{-ik'x} , \quad (2.20)$$

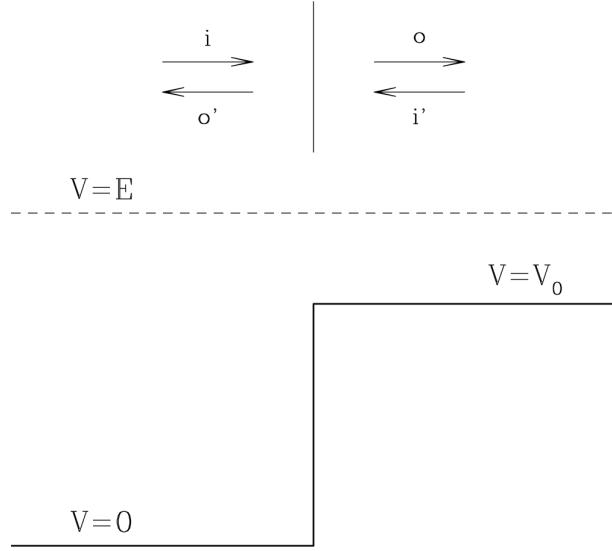


Figure 2.1: Scattering at a potential step.

with

$$E = \frac{\hbar^2 k^2}{2m} = \frac{\hbar^2 k'^2}{2m} + V_0 . \quad (2.21)$$

The requirement that $\psi(x)$ and its derivative $\psi'(x)$ be continuous at $x = 0$ gives us two equations which relate the four wavefunction amplitudes:

$$I + O' = O + I' \quad (2.22)$$

$$k(I - O') = k'(O - I') . \quad (2.23)$$

As emphasized earlier, the \mathcal{S} -matrix acts on flux amplitudes. We have

$$\begin{pmatrix} i \\ o' \end{pmatrix} = \sqrt{v} \begin{pmatrix} I \\ O' \end{pmatrix} , \quad \begin{pmatrix} o \\ i' \end{pmatrix} = \sqrt{v'} \begin{pmatrix} O \\ I' \end{pmatrix} , \quad (2.24)$$

with $v = \hbar k/m$ and $v' = \hbar k'/m$. One easily finds the \mathcal{S} -matrix, defined in eqn. 2.2, is given by

$$\mathcal{S} = \begin{pmatrix} t & r' \\ r & t' \end{pmatrix} = \begin{pmatrix} \frac{2\sqrt{\epsilon}}{1+\epsilon} & \frac{\epsilon-1}{1+\epsilon} \\ \frac{1-\epsilon}{1+\epsilon} & \frac{2\sqrt{\epsilon}}{1+\epsilon} \end{pmatrix} , \quad (2.25)$$

where $\epsilon \equiv v'/v = k'/k = \sqrt{1 - \frac{V_0}{E}}$, where $E = \epsilon_F$ is the Fermi energy. The two- and four-terminal conductances are then given by

$$G_{2\text{-probe}} = \frac{e^2}{h} |t|^2 = \frac{e^2}{h} \cdot \frac{4\epsilon}{(1+\epsilon)^2} \quad (2.26)$$

$$G_{4\text{-probe}} = \frac{e^2}{h} \frac{|t|^2}{|r|^2} = \frac{e^2}{h} \cdot \frac{4\epsilon}{(1-\epsilon)^2} . \quad (2.27)$$

Both are maximized when the transmission probability $T = |t|^2 = 1$ is largest, which occurs for $\epsilon = 1$, *i.e.* $k' = k$.

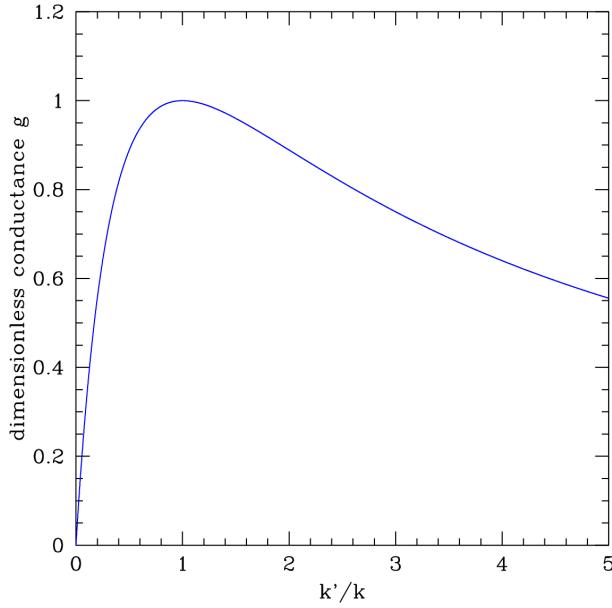


Figure 2.2: Dimensionless two-terminal conductance g versus k'/k for the potential step. The conductance is maximized when $k' = k$.

2.4 Multichannel Systems

The single channel scenario described above is obtained as a limit of a more general multichannel case, in which there are transverse degrees of freedom (due *e.g.* to finite cross-sectional area of the wire) as well. We will identify the transverse states by labels i . Within the perfect leads, the longitudinal and transverse energies are decoupled, and we may write

$$\varepsilon = \varepsilon_{\perp i} + \varepsilon_{\parallel}(k) , \quad (2.28)$$

where $\varepsilon_{\parallel}(k)$ is the one-dimensional dispersion due to motion along the wire (*e.g.* $\varepsilon_{\parallel}(k) = \hbar^2 k^2 / 2m^*$, $\varepsilon_{\parallel}(k) = -2t \cos ka$, *etc.*). k is the component of the wavevector along the axis of the wire. We assume that the transverse dimensions are finite, so fixing the Fermi energy ε_F in turn fixes the total number of transverse channels, N_c , which contribute to the transport:

$$N_c(\varepsilon) = \sum_i \Theta(\varepsilon - \varepsilon_{\perp i}) \quad (\text{continuum}) \quad (2.29)$$

$$= \sum_i \Theta(2t - |\varepsilon - \varepsilon_{\perp i}|) \quad (\text{tight binding}) . \quad (2.30)$$

Equivalently, an electron with energy ε in transverse state i has wavevector k_i which satisfies

$$\varepsilon_{\parallel}(k_i) = \varepsilon - \varepsilon_{\perp i} . \quad (2.31)$$

N_c is the number of real positive roots of (2.31). Typically $N_c \approx k_F^{d-1} A$, where A is the cross-sectional area and k_F is the Fermi wavevector. The velocity v_i is

$$v_i(\varepsilon) = \frac{1}{\hbar} \frac{\partial \varepsilon}{\partial k} \Big|_{k_i} = \frac{1}{\hbar} \frac{\partial \varepsilon_{||}(k)}{\partial k} \Big|_{k=k_i}. \quad (2.32)$$

The density of states $\mathcal{N}_i(\varepsilon)$ (per unit spin, per direction) for electrons in the i^{th} transverse channel is

$$\mathcal{N}_i(\varepsilon) = \int_{\hat{\Omega}} \frac{dk}{2\pi} \Theta(v(k)) \delta(\varepsilon - \varepsilon_{\perp i} - \varepsilon_{||}(k)) = \frac{1}{2\pi} \frac{dk}{d\varepsilon_{||}} \Big|_{k=k_i}, \quad (2.33)$$

so once again we have for the product $\hbar v_i(\varepsilon) \mathcal{N}_i(\varepsilon) = 1$.

Consider now a section of disordered material connected to perfect leads on the left and right. The solution to the Schrödinger equation on either side of the disordered region is

$$\psi_{\text{left}}(\mathbf{x}_{\perp}, z) = \sum_{j=1}^{N_c^L} \left\{ I_j e^{+ik_j z} + O'_j e^{-ik_j z} \right\} \varphi_j^L(\mathbf{x}_{\perp}) \quad (2.34)$$

$$\psi_{\text{right}}(\mathbf{x}_{\perp}, z) = \sum_{a=1}^{N_c^R} \left\{ O_a e^{+ik_a z} + I'_a e^{-ik_a z} \right\} \varphi_a^R(\mathbf{x}_{\perp}). \quad (2.35)$$

Here, we have assumed a general situation in which the number of transverse channels $N_c^{\text{L,R}}$ may differ between the left and right lead. The quantities $\{I_j, O'_j, O_a, I'_a\}$ are *wave function amplitudes*. The \mathcal{S} -matrix, on the other hand, acts on *flux amplitudes* $\{i_j, o'_j, o_a, i'_a\}$, which are related to the wavefunction amplitudes as follows:

$$i_j = v_i^{1/2} I_j \quad o_a = v_a^{1/2} O_a \quad (2.36)$$

$$o'_j = v_i^{1/2} O'_j \quad i'_a = v_a^{1/2} I'_a. \quad (2.37)$$

The \mathcal{S} -matrix is a $(N_c^R + N_c^L) \times (N_c^R + N_c^L)$ matrix,

$$\mathcal{S} = \begin{pmatrix} r_{N_c^L \times N_c^L} & t'_{N_c^L \times N_c^R} \\ t_{N_c^R \times N_c^L} & r'_{N_c^R \times N_c^R} \end{pmatrix} \quad (2.38)$$

which relates outgoing and incoming flux amplitudes:

$$\begin{pmatrix} o' \\ o \end{pmatrix} = \overbrace{\begin{pmatrix} r & t' \\ t & r' \end{pmatrix}}^{\mathcal{S}} \begin{pmatrix} i \\ i' \end{pmatrix}. \quad (2.39)$$

Unitarity of \mathcal{S} means that $\mathcal{S}^\dagger \mathcal{S} = \mathcal{S} \mathcal{S}^\dagger = \mathbb{I}$, where

$$\mathcal{S} = \begin{pmatrix} r & t' \\ t & r' \end{pmatrix} \quad \Rightarrow \quad \mathcal{S}^\dagger = \begin{pmatrix} r^\dagger & t^\dagger \\ t'^\dagger & r'^\dagger \end{pmatrix}, \quad (2.40)$$

and hence unitarity says

$$r_{ik} r_{jk}^* + t'_{ic} t'^*_j = \delta_{ij} \quad (2.41)$$

$$t_{ak} t_{bk}^* + r'_{ac} r'^*_b = \delta_{ab} \quad (2.42)$$

$$r_{ik} t_{ak}^* + t'_{ic} r'^*_a = 0 \quad (2.43)$$

or, in matrix notation,

$$r r^\dagger + t' t'^\dagger = r^\dagger r + t^\dagger t = \mathbb{I}_{N_c^L \times N_c^L} \quad (2.44)$$

$$t t^\dagger + r' r'^\dagger = t'^\dagger t' + r'^\dagger r' = \mathbb{I}_{N_c^R \times N_c^R} \quad (2.45)$$

$$r t^\dagger + t' r'^\dagger = r^\dagger t' + t^\dagger r' = \mathbb{O}_{N_c^L \times N_c^R} \quad (2.46)$$

$$t r^\dagger + r' t'^\dagger = t'^\dagger r + r'^\dagger t = \mathbb{O}_{N_c^R \times N_c^L} \quad (2.47)$$

We define the probabilities

$$R_i = \sum_{k=1}^{N_c^L} r_{ik} r_{ik}^* \quad T_a = \sum_{k=1}^{N_c^L} t_{ak} t_{ak}^* \quad (2.48)$$

$$T'_i = \sum_{c=1}^{N_c^R} t'_{ic} t'^*_i \quad R'_a = \sum_{c=1}^{N_c^R} r'^*_a r'_a , \quad (2.49)$$

for which it follows that

$$R_i + T'_i = 1 \quad , \quad R'_a + T_a = 1 \quad (2.50)$$

for all $i \in \{1, \dots, N_c^L\}$ and $a \in \{1, \dots, N_c^R\}$. Unitarity of the \mathcal{S} -matrix preserves particle flux:

$$|i|^2 - |i'|^2 = |o|^2 - |o'|^2 , \quad (2.51)$$

which is shorthand for

$$\sum_{j=1}^{N_c^L} |i_j|^2 + \sum_{a=1}^{N_c^R} |i'_a|^2 = \sum_{a=1}^{N_c^R} |o_a|^2 + \sum_{j=1}^{N_c^L} |o'_j|^2 . \quad (2.52)$$

Onsager reciprocity demands that $\mathcal{S}(-\mathbf{H}) = \mathcal{S}^t(\mathbf{H})$.

Let us now compute the current in the right lead flowing past the imaginary surface Σ

$$\begin{aligned}
 I_\Sigma &= -e \sum_{a=1}^{N_c^R} \int d\varepsilon \mathcal{N}_a(\varepsilon) v_a(\varepsilon) \left\{ \overbrace{\sum_{i=1}^{N_c^L} |t_{ai}(\varepsilon)|^2}^{T_a(\varepsilon)} f(\varepsilon - \mu_L) \right. \\
 &\quad \left. + \left[\overbrace{\sum_{b=1}^{N_c^R} |r'_{ab}(\varepsilon)|^2}^{R'_a(\varepsilon)} - 1 \right] f(\varepsilon - \mu_R) \right\} \\
 &= \frac{e}{h} (\mu_R - \mu_L) \int d\varepsilon \left(-\frac{\partial f^0}{\partial \varepsilon} \right) \sum_{a=1}^{N_c^R} T_a(\varepsilon). \tag{2.53}
 \end{aligned}$$

Thus, the result of a two-probe measurement would be

$$G_{2\text{-probe}} = \frac{eI}{\mu_R - \mu_L} = \frac{e^2}{h} \int d\varepsilon \left(-\frac{\partial f^0}{\partial \varepsilon} \right) \sum_{a=1}^{N_c^R} T_a(\varepsilon). \tag{2.54}$$

At zero temperature, then,

$$G_{2\text{-probe}} = \frac{e^2}{h} \text{Tr } tt^\dagger \tag{2.55}$$

where

$$\text{Tr } tt^\dagger = \text{Tr } t^\dagger t = \sum_{i=1}^{N_c^L} \sum_{a=1}^{N_c^R} |t_{ai}|^2. \tag{2.56}$$

To determine $G_{4\text{-probe}}$, we must compute the effective chemical potentials $\tilde{\mu}_L$ and $\tilde{\mu}_R$ in the leads. We again do this by equating expressions for the electron number density. In the left lead,

$$n_L = \sum_{i=1}^{N_c^L} \int d\varepsilon \mathcal{N}_i(\varepsilon) \left\{ [1 + R_i(\varepsilon)] f(\varepsilon - \mu_L) + T'_i(\varepsilon) f(\varepsilon - \mu_R) \right\} \tag{2.57}$$

$$= 2 \sum_i \int d\varepsilon \mathcal{N}_i(\varepsilon) f(\varepsilon - \tilde{\mu}_L) \tag{2.58}$$

$$\implies \tilde{\mu}_L = \mu_L - \frac{1}{2} \overline{T'} (\mu_L - \mu_R) \tag{2.59}$$

where $\overline{T'}$ is a weighted average,

$$\overline{T'} \equiv \frac{\sum_i v_i^{-1} T'_i}{\sum_i v_i^{-1}}. \tag{2.60}$$

Similarly, one obtains for the right lead,

$$n_R = \sum_{a=1}^{N_c^R} \int d\varepsilon \mathcal{N}_a(\varepsilon) \left\{ T_a(\varepsilon) f(\varepsilon - \mu_L) + [1 + R'_a(\varepsilon)] f(\varepsilon - \mu_R) \right\} \quad (2.61)$$

$$= 2 \sum_a \int d\varepsilon \mathcal{N}_a(\varepsilon) f(\varepsilon - \tilde{\mu}_R) \quad (2.62)$$

$$\implies \tilde{\mu}_R = \mu_R + \frac{1}{2} \bar{T} (\mu_L - \mu_R) \quad (2.63)$$

where

$$\bar{T} \equiv \frac{\sum_a v_a^{-1} T_a}{\sum_a v_a^{-1}}. \quad (2.64)$$

(We have assumed zero temperature throughout.) The difference in lead chemical potentials is thus

$$(\tilde{\mu}_L - \tilde{\mu}_R) = \left(1 - \frac{1}{2} \bar{T} - \frac{1}{2} \bar{T}'\right) \cdot (\mu_L - \mu_R). \quad (2.65)$$

Hence, we obtain the 4-probe conductance,

$$G_{\text{4-probe}} = \frac{e^2}{h} \frac{\sum_a T_a}{1 - \frac{1}{2} \left(\sum_i T'_i v_i^{-1} / \sum_i v_i^{-1} \right) - \frac{1}{2} \left(\sum_a T_a v_a^{-1} / \sum_a v_a^{-1} \right)} \quad (2.66)$$

2.4.1 Transfer Matrices: The Pichard Formula

The transfer matrix \mathcal{S} acts on incoming flux amplitudes to give outgoing flux amplitudes. This linear relation may be recast as one which instead relates flux amplitudes in the right lead to those in the left lead, *i.e.*

$$\begin{pmatrix} o' \\ o \end{pmatrix} = \overbrace{\begin{pmatrix} r & t' \\ t & r' \end{pmatrix}}^{\mathcal{S}} \begin{pmatrix} i \\ i' \end{pmatrix} \implies \begin{pmatrix} o \\ i' \end{pmatrix} = \overbrace{\begin{pmatrix} \mathcal{M}_{11} & \mathcal{M}_{12} \\ \mathcal{M}_{21} & \mathcal{M}_{22} \end{pmatrix}}^{\mathcal{M}} \begin{pmatrix} i \\ o' \end{pmatrix}. \quad (2.67)$$

\mathcal{M} is known as the *transfer matrix*. Note that each of the blocks of \mathcal{M} is of dimension $N_c^R \times N_c^L$, and \mathcal{M} itself is a rectangular $2N_c^R \times 2N_c^L$ matrix. The individual blocks of \mathcal{M} are readily determined:

$$o' = r i + t' i' \implies i' = -t'^{-1} r i + t'^{-1} o' \quad (2.68)$$

$$o = t i + r' i' \implies o = (t - r' t'^{-1} r) i + r' t'^{-1} o', \quad (2.69)$$

so we conclude

$$\mathcal{M}_{11} = t'^{-1} \quad \mathcal{M}_{12} = r' t'^{-1} \quad (2.70)$$

$$\mathcal{M}_{21} = -t'^{-1} r \quad \mathcal{M}_{22} = t'^{-1}. \quad (2.71)$$

WARNING: *None of this makes any sense if $N_c^L \neq N_c^R$!* The reason is that it is problematic to take the inverse of a rectangular matrix such as t or t' , as was blithely done

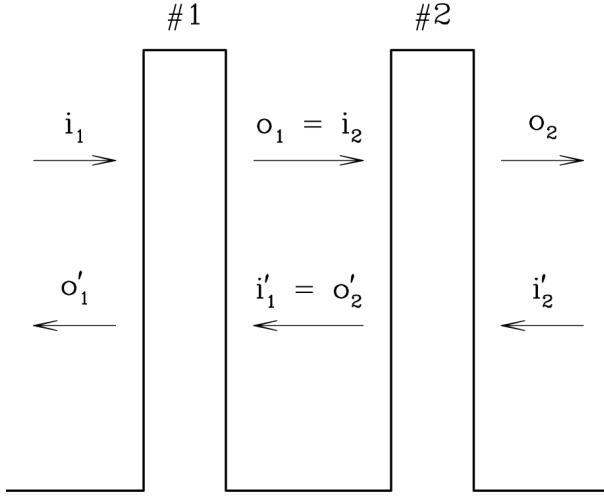


Figure 2.3: Two quantum scatterers in series. The right side data for scatterer #1 become the left side data for scatterer #2.

above in (2.68,2.69). We therefore must assume $N_c^R = N_c^L = N_c$, and that the scatterers are separated by identical perfect regions. Practically, this imposes no limitations at all, since the width of the perfect regions can be taken to be arbitrarily small.

EXERCISE: Show that $\mathcal{M}_{11} = t - r' t'^{-1} r = t^{\dagger-1}$.

The virtue of transfer matrices is that they are *multiplicative*. Consider, for example, two disordered regions connected by a region of perfect conductor. The outgoing flux o from the first region becomes the incoming flux i for the second, as depicted in fig. 2.3. Thus, if \mathcal{M}_1 is the transfer matrix for scatterer #1, and \mathcal{M}_2 is the transfer matrix for scatterer #2, the transfer matrix for the two scatterers in succession is $\mathcal{M} = \mathcal{M}_2 \mathcal{M}_1$:

$$\begin{pmatrix} o_2 \\ i'_2 \end{pmatrix} = \begin{pmatrix} \mathcal{M}_2^{11} & \mathcal{M}_2^{12} \\ \mathcal{M}_2^{21} & \mathcal{M}_2^{22} \end{pmatrix} \begin{pmatrix} i_2 \\ o'_2 \end{pmatrix} = \overbrace{\begin{pmatrix} \mathcal{M}_2^{11} & \mathcal{M}_2^{12} \\ \mathcal{M}_2^{21} & \mathcal{M}_2^{22} \end{pmatrix}}^{\mathcal{M} = \mathcal{M}_2 \mathcal{M}_1} \begin{pmatrix} \mathcal{M}_1^{11} & \mathcal{M}_1^{12} \\ \mathcal{M}_1^{21} & \mathcal{M}_1^{22} \end{pmatrix} \begin{pmatrix} i_1 \\ o'_1 \end{pmatrix}. \quad (2.72)$$

Clearly, then, if we have many scatterers in succession, this result generalizes to

$$\mathcal{M} = \mathcal{M}_N \mathcal{M}_{N-1} \cdots \mathcal{M}_1. \quad (2.73)$$

Unitarity of the \mathcal{S} -matrix means that the transfer matrix is *pseudo-unitary* in that it satisfies

$$\mathcal{M}^\dagger \Sigma \mathcal{M} = \Sigma \quad \text{where} \quad \Sigma = \begin{pmatrix} \mathbb{I}_{N_c \times N_c} & \mathbb{O}_{N_c \times N_c} \\ \mathbb{O}_{N_c \times N_c} & -\mathbb{I}_{N_c \times N_c} \end{pmatrix}. \quad (2.74)$$

This, in turn, implies conservation of the pseudo-norm,

$$|o|^2 - |i'|^2 = |i|^2 - |o'|^2, \quad (2.75)$$

which is simply a restatement of (2.51).

We now assert that

$$\left[\mathcal{M}^\dagger \mathcal{M} + (\mathcal{M}^\dagger \mathcal{M})^{-1} + 2 \cdot \mathbb{I} \right]^{-1} = \frac{1}{4} \begin{pmatrix} t^\dagger t & 0 \\ 0 & t' t'^\dagger \end{pmatrix}. \quad (2.76)$$

This result is in fact easily derived once one notes that

$$\mathcal{M}^{-1} = \Sigma \mathcal{M}^\dagger \Sigma = \begin{pmatrix} \mathcal{M}_{11}^\dagger & -\mathcal{M}_{21}^\dagger \\ -\mathcal{M}_{12}^\dagger & \mathcal{M}_{22}^\dagger \end{pmatrix}. \quad (2.77)$$

EXERCISE: Verify eqn. (2.76).

The 2-probe conductance (per spin channel) may now be written in terms of the transfer matrix as

$$G_{2\text{-probe}} = \frac{2e^2}{h} \text{Tr} \left[\mathcal{M}^\dagger \mathcal{M} + (\mathcal{M}^\dagger \mathcal{M})^{-1} + 2 \cdot \mathbb{I} \right]^{-1} \quad (2.78)$$

This is known as the *Pichard Formula*.

2.4.2 Discussion of the Pichard Formula

It is convenient to work in an eigenbasis of the Hermitian matrix $\mathcal{M}^\dagger \mathcal{M}$. The eigenvalues of $\mathcal{M}^\dagger \mathcal{M}$ are roots of the characteristic polynomial

$$p(\lambda) = \det(\lambda - \mathcal{M}^\dagger \mathcal{M}). \quad (2.79)$$

Owing to the pseudo-unitarity of \mathcal{M} , we have

$$\begin{aligned} p(\lambda) &= \det(\lambda - \mathcal{M}^\dagger \mathcal{M}) \\ &= \det(\lambda - \Sigma \mathcal{M}^{-1} \Sigma \cdot \Sigma \mathcal{M}^{\dagger-1} \Sigma) \\ &= \det(\lambda - \Sigma \mathcal{M}^{-1} \mathcal{M}^{\dagger-1} \Sigma) \\ &= \lambda^{2N_c} \det(\lambda^{-1} - \mathcal{M}^\dagger \mathcal{M}) / \det(\mathcal{M}^\dagger \mathcal{M}), \end{aligned} \quad (2.80)$$

from which we conclude that $p(\lambda) = 0$ implies $p(\lambda^{-1}) = 0$, and the eigenvalues of $\mathcal{M}^\dagger \mathcal{M}$ come in (λ, λ^{-1}) pairs. We can therefore write Pichard's formula as

$$G_{2\text{-probe}} = \frac{e^2}{h} \sum_{i=1}^{N_c} \frac{4}{\lambda_i + \lambda_i^{-1} + 2}, \quad (2.81)$$

where without loss of generality we assume $\lambda_i \geq 1$ for each $i \in \{1, \dots, N_c\}$. We define the i^{th} localization length ξ_i through

$$\lambda_i \equiv \exp\left(\frac{2L}{\xi_i}\right) \implies \xi_i = \frac{2L}{\ln \lambda_i}, \quad (2.82)$$

where L is the length of the disordered region. We now have

$$G_{\text{2-probe}} = \frac{e^2}{h} \sum_{i=1}^{N_c} \frac{2}{1 + \cosh(2L/\xi_i)} \quad (2.83)$$

If N_c is finite, then as $L \rightarrow \infty$ the $\{\xi_i\}$ converge to definite values, for a wide range of distributions $P(\mathcal{M}_n)$ for the individual scatterer transfer matrices. This follows from a version of the central limit theorem as applied to nonabelian multiplicative noise (*i.e.* products of random matrices), known as *Oseledec's theorem*. We may choose to order the eigenvalues such that $\lambda_1 < \lambda_2 < \dots < \lambda_{N_c}$, and hence $\xi_1 > \xi_2 > \dots > \xi_{N_c}$. In the $L \rightarrow \infty$ limit, then, the conductance is dominated by the largest localization length, and

$$G(L) \simeq \frac{4e^2}{h} e^{-2L/\xi_1} \quad (N_c \text{ finite}, L \rightarrow \infty). \quad (2.84)$$

(We have dropped the label ‘2-probe’ on G .) The quantity $\xi \equiv \xi_1$ is called the *localization length*, and it is dependent on the (Fermi) energy: $\xi = \xi(\varepsilon)$.

Suppose now that L is finite, and furthermore that $\xi_1 > 2L > \xi_{N_c}$. Channels for which $2L \ll \xi_j$ give $\cosh(2L/\xi_j) \approx 1$, and therefore contribute a quantum of conductance e^2/h to G . These channels are called *open*. Conversely, when $2L \gg \xi_j$, we have $\cosh(2L/\xi_j) \sim \frac{1}{2} \exp(2L/\xi_j) \gg 1$, and these *closed* channels each contribute $\Delta G_j = (2e^2/h)e^{-2L/\xi_j}$ to the conductance, a negligible amount. Thus,

$$G(L) \simeq \frac{e^2}{h} N_c^{\text{open}} \quad , \quad N_c^{\text{open}} \equiv \sum_{j=1}^{N_c} \Theta(\xi_j - 2L). \quad (2.85)$$

Of course, $N_c^{\text{closed}} = N_c - N_c^{\text{open}}$, although there is no precise definition for open *vs.* closed for channels with $\xi_j \sim 2L$. This discussion naturally leads us to the following classification scheme:

- When $L > \xi_1$, the system is in the *localized regime*. The conductance vanishes exponentially with L according to $G(L) \approx (4e^2/h) \exp(-2L/\xi)$, where $\xi(\varepsilon) = \xi_1(\varepsilon)$ is the *localization length*. In the localized regime, there are no open channels: $N_c^{\text{open}} = 0$.
- When $N_c^{\text{open}} = \ell N_c/L$, where ℓ is the *elastic scattering length*, one is in the *Ohmic regime*. In the Ohmic regime, for a d -dimensional system of length L and $((d-1)$ -dimensional) cross-sectional area A ,

$$G_{\text{Ohmic}} \approx \frac{e^2}{h} \frac{\ell}{L} k_F^{d-1} A = \frac{e^2}{h} k_F^{d-1} \ell \cdot \frac{A}{L}. \quad (2.86)$$

Note that G is proportional to the cross sectional area A and inversely proportional to the length L , which is the proper Ohmic behavior: $G = \sigma A/L$, where

$$\sigma \approx \frac{e^2}{h} k_F^{d-1} \ell \quad (2.87)$$

is the conductivity.

- When $L < \xi_{N_c}$, all the channels are open: $N_c^{\text{open}} = N_c$. The conductance is

$$G(L) = \frac{e^2}{h} N_c \approx \frac{e^2}{h} k_F^{d-1} A . \quad (2.88)$$

This is the *ballistic regime*.

If we keep $N_c \propto (k_F L)^{d-1}$, then for $L \rightarrow \infty$ Oseledec's theorem does not apply, because the transfer matrix is ∞ -dimensional. If $\xi_1(\varepsilon)$ nonetheless remains finite, then $G(L) \approx (4e^2/h) \exp(-L/\xi) \rightarrow 0$ and the system is in the localized regime. If, on the other hand, $\xi_1(\varepsilon)$ diverges as $L \rightarrow \infty$ such that $\exp(L/\xi_1)$ is finite, then $G > 0$ and the system is a conductor.

If we define $\nu_i \equiv \ln \lambda_i$, the dimensionless conductance $g = (h/e^2) G$ is given by

$$g = 2 \int_0^\infty d\nu \frac{\sigma(\nu)}{1 + \cosh \nu} , \quad (2.89)$$

where

$$\sigma(\nu) = \sum_{i=1}^{N_c} \delta(\nu - \nu_i) \quad (2.90)$$

is the density of ν values. This distribution is normalized so that $\int_0^\infty d\nu \sigma(\nu) = N_c$. Spectral properties of the $\{\nu_i\}$ thus determine the statistics of the conductance. For example, averaging over disorder realizations gives

$$\langle g \rangle = 2 \int_0^\infty d\nu \frac{\langle \sigma(\nu) \rangle}{1 + \cosh \nu} . \quad (2.91)$$

The average of g^2 , though, depends on the two-point correlation function, *viz.*

$$\langle g^2 \rangle = 4 \int_0^\infty d\nu \int_0^\infty d\nu' \frac{\langle \sigma(\nu) \sigma(\nu') \rangle}{(1 + \cosh \nu)(1 + \cosh \nu')} . \quad (2.92)$$

2.4.3 Two Quantum Resistors in Series

Let us consider the case of two scatterers in series. For simplicity, we will assume that $N_c = 1$, in which case the transfer matrix for a single scatterer may be written as

$$\mathcal{M} = \begin{pmatrix} 1/t^* & -r^*/t^* \\ -r/t' & 1/t' \end{pmatrix} . \quad (2.93)$$

A pristine segment of wire of length L has a diagonal transfer matrix

$$\mathcal{N} = \begin{pmatrix} e^{i\beta} & 0 \\ 0 & e^{-i\beta} \end{pmatrix} , \quad (2.94)$$

where $\beta = kL$. Thus, the composite transfer matrix for two scatterers joined by a length L of pristine wire is $\mathcal{M} = \mathcal{M}_2 \mathcal{N} \mathcal{M}_1$, *i.e.*

$$\mathcal{M} = \begin{pmatrix} 1/t_2^* & -r_2^*/t_2^* \\ -r_2/t_2' & 1/t_2' \end{pmatrix} \begin{pmatrix} e^{i\beta} & 0 \\ 0 & e^{-i\beta} \end{pmatrix} \begin{pmatrix} 1/t_1^* & -r_1^*/t_1^* \\ -r_1/t_1' & 1/t_1' \end{pmatrix}. \quad (2.95)$$

In fact, the inclusion of the transfer matrix \mathcal{N} is redundant; the phases $e^{\pm i\beta}$ can be completely absorbed via a redefinition of $\{t_1, t_1', r_1, r_1'\}$.

Extracting the upper left element of \mathcal{M} gives

$$\frac{1}{t^*} = \frac{e^{i\beta} - e^{-i\beta} r_1'^* r_2^*}{t_1^* t_2^*}, \quad (2.96)$$

hence the transmission coefficient T for the composite system is

$$T = \frac{T_1 T_2}{1 + R_1 R_2 - 2\sqrt{R_1 R_2} \cos \delta} \quad (2.97)$$

where $\delta = 2\beta + \arg(r_1' r_2)$. The dimensionless Landauer resistance is then

$$\begin{aligned} \mathcal{R} = \frac{R}{T} &= \frac{R_1 + R_2 - 2\sqrt{R_1 R_2} \cos \delta}{T_1 T_2} \\ &= \mathcal{R}_1 + \mathcal{R}_2 + 2\mathcal{R}_1 \mathcal{R}_2 - 2\sqrt{\mathcal{R}_1 \mathcal{R}_2 (1 + \mathcal{R}_1)(1 + \mathcal{R}_2)} \cos \delta. \end{aligned} \quad (2.98)$$

If we average over the random phase δ , we obtain

$$\langle \mathcal{R} \rangle = \mathcal{R}_1 + \mathcal{R}_2 + 2\mathcal{R}_1 \mathcal{R}_2. \quad (2.99)$$

The first two terms correspond to Ohm's law. The final term is unfamiliar and leads to a divergence of resistivity as a function of length. To see this, imagine that that $\mathcal{R}_2 = \varrho dL$ is small, and solve (2.99) iteratively. We then obtain a differential equation for the dimensionless resistance $\mathcal{R}(L)$:

$$d\mathcal{R} = (1 + 2\mathcal{R}) \varrho dL \implies \mathcal{R}(L) = \frac{1}{2} (e^{2\varrho L} - 1). \quad (2.100)$$

In fact, the distribution $P_L(\mathcal{R})$ is extremely broad, and it is more appropriate to average the quantity $\ln(1 + \mathcal{R})$. Using

$$\int_0^{2\pi} \frac{d\delta}{2\pi} \ln(a - b \cos \delta) = \ln \left(\frac{1}{2} a + \frac{1}{2} \sqrt{a^2 - b^2} \right) \quad (2.101)$$

with

$$a = 1 + \mathcal{R}_1 + \mathcal{R}_2 + 2\mathcal{R}_1 \mathcal{R}_2 \quad (2.102)$$

$$b = 2\sqrt{\mathcal{R}_1 \mathcal{R}_2 (1 + \mathcal{R}_1)(1 + \mathcal{R}_2)}, \quad (2.103)$$

we obtain the result

$$\langle \ln(1 + \mathcal{R}) \rangle = \ln(1 + \mathcal{R}_1) + \ln(1 + \mathcal{R}_2) . \quad (2.104)$$

We define the quantity

$$x(L) \equiv \ln \{1 + \mathcal{R}(L)\} , \quad (2.105)$$

and we observe

$$\langle x(L) \rangle = \varrho L \quad (2.106)$$

$$\langle e^{x(L)} \rangle = \frac{1}{2} (e^{2\varrho L} + 1) . \quad (2.107)$$

Note that $\langle e^x \rangle \neq e^{\langle x \rangle}$. The quantity $x(L)$ is an appropriately *self-averaging* quantity in that its root mean square fluctuations are small compared to its average, *i.e.* it obeys the central limit theorem. On the other hand, $\mathcal{R}(L)$ is *not* self-averaging, *i.e.* it is not normally distributed.

Abelian Multiplicative Random Processes

Let $p(x)$ be a distribution on the nonnegative real numbers, normalized according to

$$\int_0^\infty dx p(x) = 1 , \quad (2.108)$$

and define

$$X \equiv \prod_{i=1}^N x_i , \quad Y \equiv \ln X = \sum_{i=1}^N \ln x_i . \quad (2.109)$$

The distribution for Y is

$$\begin{aligned} P_N(Y) &= \int_0^\infty dx_1 \int_0^\infty dx_2 \cdots \int_0^\infty dx_N p(x_1) p(x_2) \cdots p(x_N) \delta \left(Y - \sum_{i=1}^N \ln x_i \right) \\ &= \int_{-\infty}^\infty \frac{d\omega}{2\pi} e^{i\omega Y} \left\{ \int_0^\infty dx p(x) e^{-i\omega \ln x} \right\}^N \\ &= \int_{-\infty}^\infty \frac{d\omega}{2\pi} e^{i\omega Y} \left[1 - i\omega \langle \ln x \rangle - \frac{1}{2} \omega^2 \langle \ln^2 x \rangle + \mathcal{O}(\omega^3) \right]^N \\ &= \int_{-\infty}^\infty \frac{d\omega}{2\pi} e^{i\omega(Y - N \langle \ln x \rangle)} e^{-\frac{1}{2} N \omega^2 (\langle \ln^2 x \rangle - \langle \ln x \rangle^2) + \mathcal{O}(\omega^3)} \\ &= \frac{1}{\sqrt{2\pi N \sigma^2}} e^{-(Y - N\mu)^2 / 2N\sigma^2} \cdot \left\{ 1 + \mathcal{O}(N^{-1}) \right\} , \end{aligned} \quad (2.110)$$

with

$$\mu = \langle \ln x \rangle , \quad \sigma^2 = \langle \ln^2 x \rangle - \langle \ln x \rangle^2 \quad (2.111)$$

and

$$\langle f(x) \rangle \equiv \int_0^\infty dx p(x) f(x) . \quad (2.112)$$

Thus, Y is normally distributed with mean $\langle Y \rangle = N\mu$ and standard deviation $\langle (Y - N\mu)^2 \rangle = N\sigma^2$. This is typical for extensive self-averaging quantities: the average is proportional to the size N of the system, and the root mean square fluctuations are proportional to \sqrt{N} . Since $\lim_{N \rightarrow \infty} Y_{\text{rms}}/\langle Y \rangle \sim \sigma/\sqrt{N}\mu \rightarrow 0$, we have that

$$P_{N \rightarrow \infty}(Y) \simeq \delta(Y - N\mu) . \quad (2.113)$$

This is the central limit theorem (CLT) at work. The quantity Y is a sum of independent random variables: $Y = \sum_i \ln x_i$, and is therefore normally distributed with a mean $\bar{Y} = N\mu$ and standard deviation $\sqrt{N}\sigma$, as guaranteed by the CLT. On the other hand, $X = \exp(Y)$ is *not* normally distributed. Indeed, one readily computes the moments of X to be

$$\langle X^k \rangle = e^{kN\mu} e^{Nk^2/2\sigma^2} , \quad (2.114)$$

hence

$$\frac{\langle X^k \rangle}{\langle X \rangle^k} = e^{Nk(k-1)/2\sigma^2} , \quad (2.115)$$

which increases exponentially with N . In particular, one finds

$$\frac{\sqrt{\langle X^2 \rangle - \langle X \rangle^2}}{\langle X \rangle} = \left(e^{N/\sigma^2} - 1 \right)^{1/2} . \quad (2.116)$$

The multiplication of random transfer matrices is a more difficult problem to analyze, owing to its essential nonabelian nature. However, as we have seen in our analysis of series quantum resistors, a similar situation pertains: it is the logarithm $\ln(1 + \mathcal{R})$, and not the dimensionless resistance \mathcal{R} itself, which is an appropriate self-averaging quantity.

2.4.4 Two Quantum Resistors in Parallel

The case of parallel quantum resistors is more difficult than that of series resistors. The reason for this is that the conduction path for parallel resistances is multiply connected, *i.e.* electrons can get from start to finish by traveling through either resistor #1 or resistor #2.

Consider electrons with wavevector $k > 0$ moving along a line. The wavefunction is

$$\psi(x) = I e^{ikx} + O' e^{-ikx} , \quad (2.117)$$

hence the transfer matrix \mathcal{M} for a length L of pristine wire is

$$\mathcal{M}(L) = \begin{pmatrix} e^{ikL} & 0 \\ 0 & e^{-ikL} \end{pmatrix} . \quad (2.118)$$

Now let's bend our wire of length L into a ring. We therefore identify the points $x = 0$ and $x = L = 2\pi R$, where R is the radius. In order for the wavefunction to be single-valued we must have

$$[\mathcal{M}(L) - \mathbb{I}] \begin{pmatrix} I \\ O' \end{pmatrix} = 0 , \quad (2.119)$$

and in order to have a nontrivial solution (*i.e.* I and O' not both zero), we must demand $\det(\mathcal{M} - \mathbb{I}) = 0$, which says $\cos kL = 1$, *i.e.* $k = 2\pi n/L$ with integer n . The energy is then quantized: $\varepsilon_n = \varepsilon_{\parallel}(k = 2\pi n/L)$.

Next, consider the influence of a vector potential on the transfer matrix. Let us assume the vector potential A along the direction of motion is nonzero over an interval from $x = 0$ to $x = d$. The Hamiltonian is given by the *Peierls substitution*,

$$\mathcal{H} = \varepsilon_{\parallel} \left(-i\partial_x + \frac{e}{\hbar c} A(x) \right) . \quad (2.120)$$

Note that we can write

$$\mathcal{H} = \Lambda^{\dagger}(x) \varepsilon_{\parallel} (-i\partial_x) \Lambda(x) \quad (2.121)$$

$$\Lambda(x) = \exp \left\{ \frac{ie}{\hbar c} \int_0^x dx' A(x') \right\} . \quad (2.122)$$

Hence the solutions $\psi(x)$ to $\mathcal{H}\psi = \varepsilon\psi$ are given by

$$\psi(x) = I \Lambda^{\dagger}(x) e^{ikx} + O' \Lambda^{\dagger}(x) e^{-ikx} . \quad (2.123)$$

The transfer matrix for a segment of length d is then

$$\mathcal{M}(d, A) = \begin{pmatrix} e^{ikd} e^{-i\gamma} & 0 \\ 0 & e^{-ikd} e^{-i\gamma} \end{pmatrix} \quad (2.124)$$

with

$$\gamma = \frac{e}{\hbar c} \int_0^d dx A(x) . \quad (2.125)$$

We are free to choose any gauge we like for $A(x)$. The only constraint is that the gauge-invariant content, which is encoded in the magnetic fluxes through every closed loop \mathcal{C} ,

$$\Phi_{\mathcal{C}} = \oint_{\mathcal{C}} \mathbf{A} \cdot d\mathbf{l} , \quad (2.126)$$

must be preserved. On a ring, there is one flux Φ to speak of, and we define the dimensionless flux $\phi = e\Phi/\hbar c = 2\pi\Phi/\phi_0$, where $\phi_0 = hc/e = 4.137 \times 10^{-7} \text{ G}\cdot\text{cm}^2$ is the Dirac flux quantum. In a field of $B = 1 \text{ kG}$, a single Dirac quantum is enclosed by a ring of radius $R = 0.11 \mu\text{m}$. It is convenient to choose a gauge in which A vanishes everywhere along our loop except for

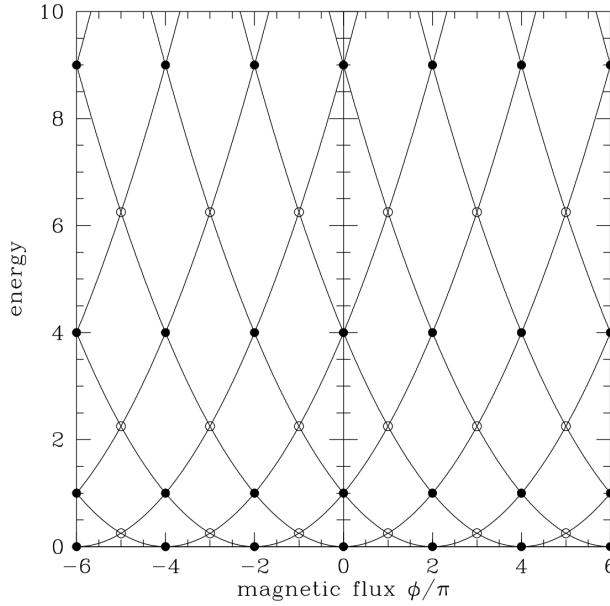


Figure 2.4: Energy *versus* dimensionless magnetic flux for free electrons on a ring. The degeneracies are lifted in the presence of a crystalline potential.

a vanishingly small region, in which all the accrued vector potential piles up in a δ -function of strength Φ . The transfer matrix for this infinitesimal region is then

$$\mathcal{M}(\phi) = \begin{pmatrix} e^{i\phi} & 0 \\ 0 & e^{i\phi} \end{pmatrix} = e^{i\phi} \cdot \mathbb{I}. \quad (2.127)$$

If $k > 0$ corresponds to clockwise motion around the ring, then the phase accrued is $-\gamma$, which explains the sign of ϕ in the above equation.

For a pristine ring, then, combining the two transfer matrices gives

$$\mathcal{M} = \begin{pmatrix} e^{ikL} & 0 \\ 0 & e^{-ikL} \end{pmatrix} \begin{pmatrix} e^{i\phi} & 0 \\ 0 & e^{i\phi} \end{pmatrix} = \begin{pmatrix} e^{ikL} e^{i\phi} & 0 \\ 0 & e^{-ikL} e^{i\phi} \end{pmatrix}, \quad (2.128)$$

and thus $\det(\mathcal{M} - \mathbb{I}) = 0$ gives the solutions,

$$\begin{aligned} kL &= 2\pi n - \phi && (\text{right-movers}) \\ kL &= 2\pi n + \phi && (\text{left-movers}) . \end{aligned}$$

Note that different n values are allowed for right- and left-moving branches since by assumption $k > 0$. We can simplify matters if we simply write $\psi(x) = A e^{ikx}$ with k unrestricted in sign, in which case $k = (2\pi n - \phi)/L$ with n chosen from the entire set of integers. The allowed energies for free electrons are then

$$\varepsilon_n(\phi) = \frac{2\pi^2 \hbar^2}{mL^2} \cdot \left(n - \frac{\phi}{2\pi}\right)^2, \quad (2.129)$$

which are plotted in fig. 2.4.

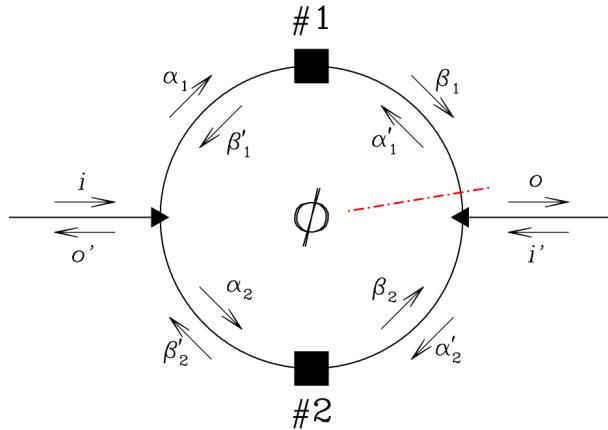


Figure 2.5: Scattering problem for a ring enclosing a flux Φ . The square and triangular blocks represent scattering regions and are described by 2×2 and 3×3 \mathcal{S} -matrices, respectively. The dot-dash line represents a cut across which the phase information due to the enclosed flux is accrued discontinuously.

Now let us add in some scatterers. This problem was first considered in a beautiful paper by Büttiker, Imry, and Azbel, *Phys. Rev. A* **30**, 1982 (1984). Consider the ring geometry depicted in fig. 2.5. We want to compute the \mathcal{S} -matrix for the ring. We now know how to describe the individual quantum resistors #1 and #2 in terms of \mathcal{S} -matrices (or, equivalently, \mathcal{M} -matrices). Assuming there is no magnetic field penetrating the wire (or that the wire itself is infinitesimally thin), we have $\mathcal{S} = \mathcal{S}^t$ for each scatterer. In this case, we have $t = t' = \sqrt{T} e^{i\alpha}$. We know $|r|^2 = |r'|^2 = 1 - |t|^2$, but in general r and r' may have different phases. The most general 2×2 transfer matrix, under conditions of time-reversal symmetry, depends on three parameters, which may be taken to be the overall transmission probability T and two phases:

$$\mathcal{M}(T, \alpha, \beta) = \frac{1}{\sqrt{T}} \begin{pmatrix} e^{i\alpha} & \sqrt{1-T} e^{i\beta} \\ \sqrt{1-T} e^{-i\beta} & e^{-i\alpha} \end{pmatrix}. \quad (2.130)$$

We can include the effect of free-particle propagation in the transfer matrix \mathcal{M} by multiplying \mathcal{M} on the left and the right by a free propagation transfer matrix of the form

$$\mathcal{N} = \begin{pmatrix} e^{i\theta/4} & 0 \\ 0 & e^{-i\theta/4} \end{pmatrix}, \quad (2.131)$$

where $\theta = kL = 2\pi kR$ is the phase accrued by a particle of wavevector k freely propagating once around the ring. \mathcal{N} is the transfer matrix corresponding to one quarter turn around the ring. One easily finds

$$\mathcal{M} \rightarrow \mathcal{N} \mathcal{M}(T, \alpha, \beta) \mathcal{N} = \mathcal{M}(T, \alpha + \frac{1}{2}\theta, \beta). \quad (2.132)$$

For pedagogical reasons, we will explicitly account for the phases due to free propagation, and write

$$\begin{pmatrix} \beta_1 \\ \alpha'_1 \end{pmatrix} = \mathcal{N} \mathcal{M}_1 \mathcal{N} \begin{pmatrix} \alpha_1 \\ \beta'_1 \end{pmatrix}, \quad \begin{pmatrix} \beta'_2 \\ \alpha_2 \end{pmatrix} = \mathcal{N} \widetilde{\mathcal{M}}_2 \mathcal{N} \begin{pmatrix} \alpha'_2 \\ \beta_2 \end{pmatrix}, \quad (2.133)$$

where $\widetilde{\mathcal{M}}_2$ is the transfer matrix for scatterer #2 going from right to left.

EXERCISE: Show that the right-to-left transfer matrix $\widetilde{\mathcal{M}}$ is related to the left-to-right transfer matrix \mathcal{M} according to

$$\widetilde{\mathcal{M}} = \Lambda \Sigma \mathcal{M}^\dagger \Sigma \Lambda , \quad (2.134)$$

where

$$\Sigma = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} \quad , \quad \Lambda = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} . \quad (2.135)$$

We now have to model the connections between the ring and the leads, which lie at the confluence of three segments. Accordingly, these regions are described by 3×3 \mathcal{S} -matrices. The constraints $\mathcal{S} = \mathcal{S}^\dagger$ (unitarity) and $\mathcal{S} = \mathcal{S}^t$ (time-reversal symmetry) reduce the number of independent real parameters in \mathcal{S} from 18 to 5. Further assuming that the scattering is symmetric with respect to the ring branches brings this number down to 3, and finally assuming \mathcal{S} is real reduces the dimension of the space of allowed \mathcal{S} -matrices to one. Under these conditions, the most general 3×3 \mathcal{S} -matrix may be written

$$\begin{pmatrix} -(a+b) & \sqrt{\epsilon} & \sqrt{\epsilon} \\ \sqrt{\epsilon} & a & b \\ \sqrt{\epsilon} & b & a \end{pmatrix} \quad (2.136)$$

where

$$(a+b)^2 + 2\epsilon = 1 \quad (2.137)$$

$$a^2 + b^2 + \epsilon = 1 . \quad (2.138)$$

The parameter ϵ , which may be taken as a measure of the coupling between the ring and the leads ($\epsilon = 0$ means ring and leads are decoupled) is restricted to the range $0 \leq \epsilon \leq \frac{1}{2}$. There are four solutions for each allowed value of ϵ :

$$a = \pm \frac{1}{2}(\sqrt{1-2\epsilon} - 1) \quad , \quad b = \pm \frac{1}{2}(\sqrt{1-2\epsilon} + 1) \quad (2.139)$$

and

$$a = \pm \frac{1}{2}(\sqrt{1-2\epsilon} + 1) \quad , \quad b = \pm \frac{1}{2}(\sqrt{1-2\epsilon} - 1) . \quad (2.140)$$

We choose the first pair, since it corresponds to the case $|b| = 1$ when $\epsilon = 0$, *i.e.* perfect transmission through the junction. We choose the top sign in (2.139).

We therefore have at the left contact,

$$\begin{pmatrix} o' \\ \alpha_2 \\ \alpha_1 \end{pmatrix} = \begin{pmatrix} -(a_L + b_L) & \sqrt{\epsilon}_L & \sqrt{\epsilon}_L \\ \sqrt{\epsilon}_L & a_L & b_L \\ \sqrt{\epsilon}_L & b_L & a_L \end{pmatrix} \begin{pmatrix} i \\ \beta'_2 \\ \beta'_1 \end{pmatrix} , \quad (2.141)$$

and at the right contact

$$\begin{pmatrix} o \\ \tilde{\alpha}'_1 \\ \alpha'_2 \end{pmatrix} = \begin{pmatrix} -(a_R + b_R) & \sqrt{\epsilon}_R & \sqrt{\epsilon}_R \\ \sqrt{\epsilon}_R & a_R & b_R \\ \sqrt{\epsilon}_R & b_R & a_R \end{pmatrix} \begin{pmatrix} i' \\ \tilde{\beta}_1 \\ \beta_2 \end{pmatrix} , \quad (2.142)$$

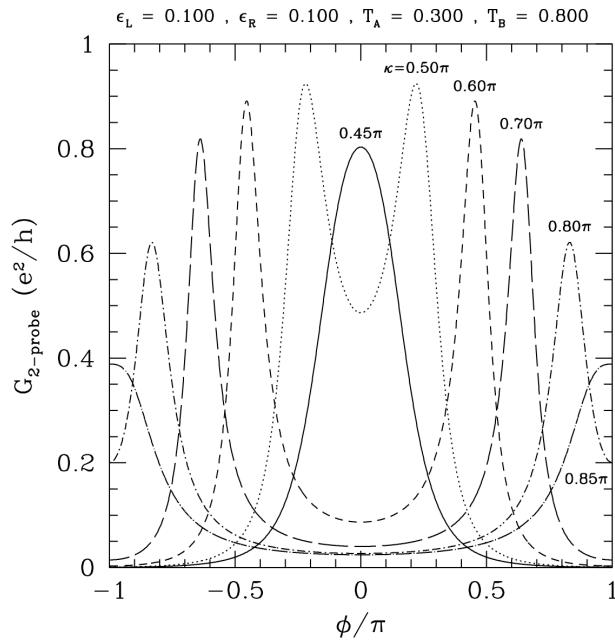


Figure 2.6: Two-probe conductance $G(\phi, \kappa)$ of a model ring with two scatterers. The enclosed magnetic flux is $\phi\hbar c/e$, and $\kappa = 2\pi kR$ (ring radius R). G vs. ϕ curves for various values of κ are shown.

where accounting for the vector potential gives us

$$\tilde{\beta}_1 = e^{i\phi} \beta_1 \quad , \quad \tilde{\alpha}'_1 = e^{i\phi} \alpha'_1 . \quad (2.143)$$

We set $i = 1$ and $i' = 0$, so that the transmission and reflection amplitudes are obtained from $t = o$ and $r = o'$.

From (2.141), we can derive the relation

$$\begin{pmatrix} \alpha_1 \\ \beta'_1 \end{pmatrix} = \overbrace{\frac{1}{b_L} \begin{pmatrix} b_L^2 - a_L^2 & a_L \\ -a_L & 1 \end{pmatrix}}^{\mathcal{Q}_L} \begin{pmatrix} \beta'_2 \\ \alpha_2 \end{pmatrix} + \frac{\sqrt{\epsilon_L}}{b_L} \begin{pmatrix} b_L - a_L \\ -1 \end{pmatrix} . \quad (2.144)$$

Similarly, from (2.142), we have

$$\begin{pmatrix} \alpha'_2 \\ \beta_2 \end{pmatrix} = \overbrace{\frac{1}{b_R} \begin{pmatrix} b_R^2 - a_R^2 & a_R \\ -a_R & 1 \end{pmatrix}}^{\mathcal{Q}_R} e^{i\phi} \begin{pmatrix} \beta_1 \\ \alpha'_1 \end{pmatrix} . \quad (2.145)$$

The matrices \mathcal{Q}_L and \mathcal{Q}_R resemble transfer matrices. However, they are not pseudo-unitary: $\mathcal{Q}^\dagger \Sigma \mathcal{Q} \neq \Sigma$. This is because some of the flux can leak out along the leads. Indeed, when

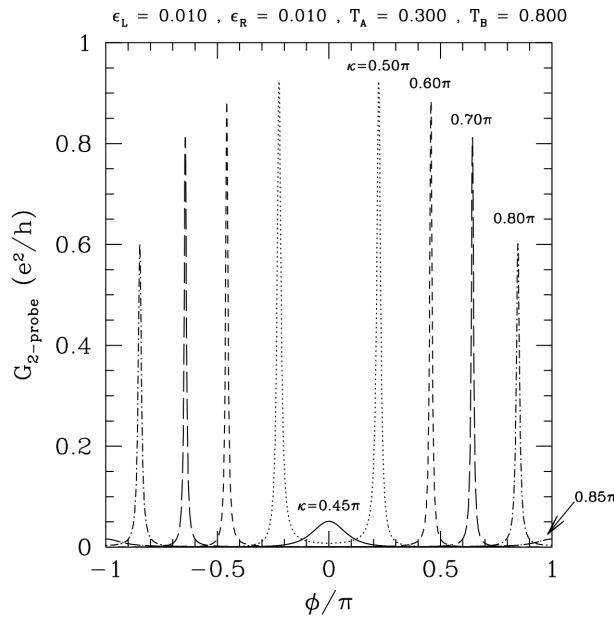


Figure 2.7: Two-probe conductance $G(\phi, \kappa)$ of a model ring with two scatterers. The enclosed magnetic flux is $\phi\hbar c/e$, and $\kappa = 2\pi kR$ (ring radius R). G vs. ϕ curves for various values of κ are shown. The coupling between leads and ring is one tenth as great as in fig. 2.6, and accordingly the resonances are much narrower. Note that the resonances at $\kappa = 0.45\pi$ and $\kappa = 0.85\pi$ are almost completely suppressed.

$\epsilon = 0$, we have $b = 1$ and $a = 0$, hence $\mathcal{Q} = 1$, which is pseudo-unitary (*i.e.* flux preserving). Combining these results with those in (2.133), we obtain the solution

$$\begin{pmatrix} \alpha_1 \\ \beta'_1 \end{pmatrix} = \left\{ \mathbb{I} - e^{i\phi} \mathcal{Q}_L \mathcal{N} \widetilde{\mathcal{M}}_2 \mathcal{N} \mathcal{Q}_R \mathcal{N} \mathcal{M}_1 \mathcal{N} \right\}^{-1} \frac{\sqrt{\epsilon_L}}{b_L} \begin{pmatrix} b_L - a_L \\ -1 \end{pmatrix}. \quad (2.146)$$

From this result, using (2.133), all the flux amplitudes can be obtained.

We can define the effective ring transfer matrix \mathcal{P} as

$$\mathcal{P} \equiv e^{i\phi} \mathcal{Q}_L \mathcal{N} \widetilde{\mathcal{M}}_2 \mathcal{N} \mathcal{Q}_R \mathcal{N} \mathcal{M}_1 \mathcal{N}, \quad (2.147)$$

which has the following simple interpretation. Reading from right to left, we first move $\frac{1}{4}$ -turn clockwise around the ring (\mathcal{N}). Then we encounter scatterer #1 (\mathcal{M}_1). After another quarter turn (\mathcal{N}), we encounter the right T-junction (\mathcal{Q}_R). Then it's yet another quarter turn (\mathcal{N}) until scatterer #2 (\mathcal{M}_2), and one last quarter turn (\mathcal{N}) brings us to the left T-junction (\mathcal{Q}_L), by which point we have completed one revolution. As the transfer matrix acts on both right-moving and left-moving flux amplitudes, it accounts for both clockwise as well as counterclockwise motion around the ring. The quantity

$$\{ \mathbb{I} - \mathcal{P} \}^{-1} = 1 + \mathcal{P} + \mathcal{P}^2 + \mathcal{P}^3 + \dots, \quad (2.148)$$

then sums up over all possible integer windings around the ring. In order to properly account for the effects of the ring, an infinite number of terms must be considered; these may be

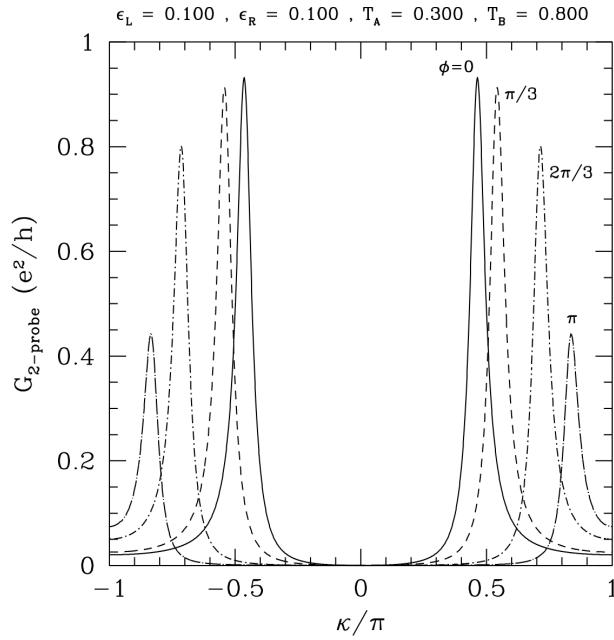


Figure 2.8: Two-probe conductance $G(\phi, \kappa)$ of a model ring with two scatterers. The enclosed magnetic flux is $\phi\hbar c/e$, and $\kappa = 2\pi kR$ (ring radius R). G vs. κ curves for various values of ϕ are shown.

resummed into the matrix inverse in (2.147). The situation is analogous to what happens when an electromagnetic wave reflects off a thin dielectric slab. At the top interface, the wave can reflect. However, it can also refract, entering the slab, where it may undergo an arbitrary number of internal reflections before exiting.

The transmission coefficient t is just the outgoing flux amplitude: $t = o$. We have from (2.142,2.133) that

$$\begin{aligned} t &= \sqrt{\epsilon_R} (\beta_1 e^{i\phi} + \beta_2) \\ &= \frac{\sqrt{\epsilon_R}}{b_R} (b_R - a_R - 1) \left(\frac{\beta_1}{\alpha'_1} \right) \\ &= \frac{\sqrt{\epsilon_L \epsilon_R}}{b_L b_R} (\mathcal{Y}_{12}^{-1} + \mathcal{Y}_{22}^{-1} - \mathcal{Y}_{11}^{-1} - \mathcal{Y}_{21}^{-1}) \end{aligned} \quad (2.149)$$

where

$$\mathcal{Y} = \mathcal{Q}_L \mathcal{N} \widetilde{\mathcal{M}}_2 \mathcal{N} \mathcal{Q}_R - e^{-i\phi} \mathcal{N}^{-1} \mathcal{M}_1^{-1} \mathcal{N}^{-1}. \quad (2.150)$$

It is straightforward to numerically implement the above calculation. Sample results are shown in figs. 2.6 and 2.8.

2.5 Universal Conductance Fluctuations in Dirty Metals

The conductance of a disordered metal is a function of the strength and location of the individual scatterers. We now ask, how does the conductance fluctuate when the position or strength of a scatterer or a group of scatterers is changed. From the experimental point of view, this seems a strange question to ask, since we generally do not have direct control over the position of individual scatterers within a bulk system. However, we can imagine changing some external parameter, such as the magnetic field B or the chemical potential μ (via the density n). Using computer modeling, we can even ‘live the dream’ of altering the position of a single scatterer to investigate its effect on the overall conductance. Naïvely, we would expect there to be very little difference in the conductance if we were to, say, vary the position of a single scatterer by a distance ℓ , or if we were to change the magnetic field by $\Delta B = \phi_0/A$, where A is the cross sectional area of the system. Remarkably, though, what is found both experimentally and numerically is that the conductance exhibits fluctuations with varying field B , chemical potential μ , or impurity configuration (in computer models). The root-mean-square magnitude of these fluctuations for a given sample is the same as that between different samples, and is on the order $\delta G \sim e^2/h$. These *universal conductance fluctuations* (UCF) are independent on the degree of disorder, the sample size, the spatial dimensions, so long as the inelastic mean free path (or *phase breaking length*) satisfies $L_\phi > L$, *i.e.* the system is mesoscopic.

Theoretically the phenomenon of UCF has a firm basis in diagrammatic perturbation theory. Here we shall content ourselves with understanding the phenomenon on a more qualitative level, following the beautiful discussion of P. A. Lee in *Physica* **140A**, 169 (1986). We begin with the multichannel Landauer formula,

$$G = \frac{e^2}{h} \text{Tr } tt^\dagger = \frac{e^2}{h} \sum_{a,j=1}^{N_c} |t_{aj}|^2. \quad (2.151)$$

The transmission amplitudes t_{aj} can be represented as a quantum mechanical sum over paths γ ,

$$t_{aj} = \sum_{\gamma} \mathcal{A}_{aj}(\gamma), \quad (2.152)$$

where $\mathcal{A}_{aj}(\gamma)$ is the probability amplitude for Feynman path γ to connect channels j and a . The sum is over all such Feynman paths, and ultimately we must project onto a subspace of definite energy – this is, in Lee’s own words, a ‘heuristic argument’. Now assume that the $\mathcal{A}_{aj}(\gamma)$ are independent complex random variables. The fluctuations in $|t_{aj}|^2$ are computed from

$$\begin{aligned} \langle |t_{aj}|^4 \rangle &= \sum_{\substack{\gamma_1, \gamma_2 \\ \gamma_3, \gamma_4}} \langle \mathcal{A}_{aj}(\gamma_1) \mathcal{A}_{aj}^*(\gamma_2) \mathcal{A}_{aj}(\gamma_3) \mathcal{A}_{aj}^*(\gamma_4) \rangle \\ &= 2 \left\langle \sum_{\gamma} |\mathcal{A}_{aj}(\gamma)|^2 \right\rangle^2 + \left\langle \sum_{\gamma} |\mathcal{A}_{aj}(\gamma)|^4 \right\rangle \\ &= 2 \langle |t_{aj}|^2 \rangle^2 \cdot \left\{ 1 + \mathcal{O}(M^{-1}) \right\}, \end{aligned} \quad (2.153)$$

where M is the (extremely large) number of paths in the sum over γ . As the $\mathcal{O}(M^{-1})$ term is utterly negligible, we conclude

$$\frac{\langle |t_{aj}|^4 \rangle - \langle |t_{aj}|^2 \rangle^2}{\langle |t_{aj}|^2 \rangle^2} = 1 . \quad (2.154)$$

Now since

$$\text{var}(G) = \langle G^2 \rangle - \langle G \rangle^2 \quad (2.155)$$

$$= \frac{e^4}{h^2} \sum_{\substack{a,a' \\ j,j'}} \left\{ \langle |t_{aj}|^2 |t_{a'j'}|^2 \rangle - \langle |t_{aj}|^2 \rangle \langle |t_{aj}|^2 \rangle \right\} , \quad (2.156)$$

we also need to know about the correlation between $|t_{aj}|^2$ and $|t_{a'j'}|^2$. The simplest assumption is to assume they are uncorrelated unless $a = a'$ and $j = j'$, *i.e.*

$$\langle |t_{aj}|^2 |t_{a'j'}|^2 \rangle - \langle |t_{aj}|^2 \rangle \langle |t_{aj}|^2 \rangle = \left(\langle |t_{aj}|^4 \rangle - \langle |t_{aj}|^2 \rangle^2 \right) \delta_{aa'} \delta_{jj'} , \quad (2.157)$$

in which case the conductance is given by a sum of N_c^2 independent real random variables, each of which has a standard deviation equal to its mean, *i.e.* equal to $\langle |t_{aj}|^2 \rangle$. According to the central limit theorem, then, the rms fluctuations of G are given by

$$\Delta G = \sqrt{\text{var}(G)} = \frac{e^2}{h} N_c \langle |t_{aj}|^2 \rangle . \quad (2.158)$$

Further assuming that we are in the Ohmic regime where $G = \sigma L^{d-2}$, with $\sigma \approx (e^2/h) k_F^{d-1} \ell$, and $N_c \approx (k_F L)^{d-1}$, we finally conclude

$$\langle |t_{aj}|^2 \rangle \approx \frac{1}{N_c} \cdot \frac{\ell}{L} \implies \Delta G \approx \frac{e^2}{h} \frac{\ell}{L} . \quad (2.159)$$

This result is much smaller than the correct value of $\Delta G \sim (e^2/h)$.

To reiterate the argument in terms of the dimensionless conductance g ,

$$g = \sum_{a,j} |t_{aj}|^2 \simeq N_c \cdot \frac{\ell}{L} \implies \langle |t_{aj}|^2 \rangle = \frac{g}{N_c^2} \quad (2.160)$$

$$\begin{aligned} \text{var}(g) &= \sum_{\substack{a,a' \\ j,j'}} \left\{ \langle |t_{aj}|^2 |t_{a'j'}|^2 \rangle - \langle |t_{aj}|^2 \rangle \langle |t_{aj}|^2 \rangle \right\} \\ &\approx \sum_{aj} \left\{ \langle |t_{aj}|^4 \rangle - \langle |t_{aj}|^2 \rangle^2 \right\} \\ &= \sum_{aj} \langle |t_{aj}|^2 \rangle^2 \approx N_c^2 \cdot \left(\frac{g}{N_c^2} \right)^2 = \frac{g^2}{N_c^2} \end{aligned} \quad (2.161)$$

$\implies \sqrt{\text{var}(g)} \approx \frac{g}{N_c} = \frac{\ell}{L} \quad (\text{WRONG!})$

(2.162)

What went wrong? The problem lies in the assumption that the contributions $\mathcal{A}_{aj}(\gamma)$ are independent for different paths γ . The reason is that in disordered systems there are certain preferred channels within the bulk along which the conduction paths run. Different paths γ will often coincide along these channels. A crude analogy: whether you're driving from La Jolla to Burbank, or from El Cajon to Malibu, eventually you're going to get on the 405 freeway – anyone driving from the San Diego area to the Los Angeles area must necessarily travel along one of a handful of high-volume paths. The same is not true of reflection, though! Those same two hypothetical drivers executing local out-and-back trips from home will in general travel along completely different, hence uncorrelated, routes. Accordingly, let us compute $\text{var}(N_c - g)$, which is identical to $\text{var}(g)$, but is given in terms of a sum over reflection coefficients. We will see that making the same assumptions as we did in the case of the transmission coefficients produces the desired result. We need only provide a sketch of the argument:

$$N_c - g = \sum_{i,j} |r_{ij}|^2 \simeq N_c \cdot \left(1 - \frac{\ell}{L}\right) \implies \langle |r_{ij}|^2 \rangle = \frac{N_c - g}{N_c^2}, \quad (2.163)$$

so

$$\begin{aligned} \text{var}(N_c - g) &= \sum_{\substack{i,i' \\ j,j'}} \left\{ \langle |r_{ij}|^2 |r_{i'j'}|^2 \rangle - \langle |r_{ij}|^2 \rangle \langle |r_{i'j'}|^2 \rangle \right\} \\ &\approx \sum_{ij} \left\{ \langle |r_{ij}|^4 \rangle - \langle |r_{ij}|^2 \rangle^2 \right\} \\ &= \sum_{ij} \langle |r_{ij}|^2 \rangle^2 \approx N_c^2 \cdot \left(\frac{N_c - g}{N_c^2} \right)^2 = \left(1 - \frac{\ell}{L}\right)^2 \end{aligned} \quad (2.164)$$

$$\implies \boxed{\sqrt{\text{var}(N_c - g)} = \sqrt{\text{var}(g)} = \left(1 - \frac{\ell}{L}\right)} \quad (2.165)$$

The assumption of uncorrelated *reflection* paths is not as problematic as that of uncorrelated *transmission* paths. Again, this is due to the existence of preferred internal channels within the bulk, along which transmission occurs. In reflection, though there is no need to move along identical segments.

There is another bonus to thinking about reflection *versus* transmission. Let's express the reflection probability as a sum over paths, *viz.*

$$|r_{ij}|^2 = \sum_{\gamma, \gamma'} \mathcal{A}_{ij}(\gamma) \mathcal{A}_{ij}^*(\gamma'). \quad (2.166)$$

Each path γ will have a time-reversed mate γ^T for which, in the absence of external magnetic fields,

$$\mathcal{A}_{ij}(\gamma) = \mathcal{A}_{ij}(\gamma^T). \quad (2.167)$$

This is because the action functional,

$$S[\mathbf{r}(t)] = \int_{t_1}^{t_2} dt \left\{ \frac{1}{2} m \dot{\mathbf{r}}^2 - V(\mathbf{r}) - \frac{e}{c} \mathbf{A}(\mathbf{r}) \cdot \dot{\mathbf{r}} \right\} \quad (2.168)$$

satisfies

$$S[\mathbf{r}(t)] = S[\mathbf{r}(-t)] \quad \text{if } \mathbf{B} = 0 . \quad (2.169)$$

There is, therefore, an extra *negative* contribution to the conductance G arising from *phase coherence of time-reversed paths*. In the presence of an external magnetic field, the path γ and its time-reversed mate γ^T have a relative phase $\eta = 4\pi\Phi_\gamma/\phi_0$, where Φ_γ is the magnetic flux enclosed by the path γ . A magnetic field, then, tends to destroy the phase coherence between time-reversed paths, and hence we expect a *positive magnetoconductance* (*i.e.* negative magnetoresistance) in mesoscopic disordered metals.

Conductance Fluctuations in Metallic Rings

The conductance of a ring must be periodic under $\Phi \rightarrow \Phi + n\phi_0$ for any integer n – rings with flux differing by an integer number of Dirac quanta are gauge-equivalent, provided no magnetic field penetrates the ring itself. The conductance as a function of the enclosed flux Φ must be of the form

$$G(\Phi) = G_{\text{cl}} + \sum_{m=1}^{\infty} G_m \cos\left(\frac{2\pi m\Phi}{\phi_0} + \alpha_m\right) \quad (2.170)$$

where G_{cl} is the classical (Boltzmann) conductance of the ring. The second harmonic $G_{m=2}$ is usually detectable and is in many cases much larger than the $m = 1$ term. The origin of the $m = 2$ term, which is periodic under $\Phi \rightarrow \Phi + \frac{1}{2}\phi_0$, lies in the interference between time-reversed paths of winding number ± 1 . The $m = 1$ fundamental is easily suppressed, *e.g.* by placing several rings in series.

2.5.1 Weak Localization

A more rigorous discussion of enhanced backscattering was first discussed by Altshuler, Aronov, and Spivak (AAS) in 1981. AAS showed that there are corrections to Boltzmann transport of the form $\sigma = \sigma_0 + \delta\sigma$, where $\sigma_0 = ne^2\tau/m^*$ is the Drude conductivity and (including a factor of 2 for spin),

$$\delta\sigma = -\frac{2e^2}{h} \ell^2 \cdot \frac{1}{V} \int d^d r \mathcal{C}(\mathbf{r}, \mathbf{r}) , \quad (2.171)$$

where ℓ is the elastic mean free path and $\mathcal{C}(\mathbf{r}, \mathbf{r}')$ is the *Cooperon propagator*, which satisfies

$$\left\{ -\ell^2 \left(\nabla + \frac{2ie}{\hbar c} \mathbf{A}(\mathbf{r}) \right)^2 + \frac{\tau}{\tau_\phi} \right\} \mathcal{C}(\mathbf{r}, \mathbf{r}') = \delta(\mathbf{r} - \mathbf{r}') , \quad (2.172)$$

where τ_ϕ is the inelastic collision time, $\tau_\phi = L_\phi^2/D$, where $D = v_F\ell = \ell^2/\tau$ is the diffusion constant. The linear differential operator

$$\mathcal{L} = -\ell^2 \left(\nabla + \frac{2ie}{\hbar c} \mathbf{A}(\mathbf{r}) \right)^2 \quad (2.173)$$

bears a strong resemblance to the Hamiltonian of a particle of charge $e^* = 2e$ in an external magnetic field $\mathbf{B} = \nabla \times \mathbf{A}$. Expanding in eigenfunctions of L , we obtain the solution

$$\left(\mathcal{L} + \frac{\tau}{\tau_\phi} \right) \mathcal{C}(\mathbf{r}, \mathbf{r}') = \delta(\mathbf{r} - \mathbf{r}') \quad (2.174)$$

$$\mathcal{L} \psi_\alpha(\mathbf{r}) = \lambda_\alpha \psi_\alpha(\mathbf{r}) \quad (2.175)$$

$$\mathcal{C}(\mathbf{r}, \mathbf{r}') = \sum_{\alpha} \frac{\psi_\alpha(\mathbf{r}) \psi_\alpha^*(\mathbf{r}')}{\lambda_\alpha + \frac{\tau}{\tau_\phi}} , \quad (2.176)$$

which resembles a Green's function from quantum mechanics, where the energy parameter is identified with $-\tau/\tau_\phi$. There is accordingly a path integral representation for $\mathcal{C}(\mathbf{r}, \mathbf{r}')$:

$$\mathcal{C}(\mathbf{r}_1, \mathbf{r}_2) = \int ds e^{-is\tau/\tau_\phi} \int_{\substack{\mathbf{r}(0)=\mathbf{r}_1 \\ \mathbf{r}(s)=\mathbf{r}_2}} \mathcal{D}\mathbf{r}[u] \exp \left\{ i \int_0^s du \left[\frac{1}{4\ell^2} \left(\frac{\partial \mathbf{r}}{\partial u} \right)^2 - \frac{2e}{\hbar c} \mathbf{A}(\mathbf{r}) \cdot \frac{\partial \mathbf{r}}{\partial u} \right] \right\} . \quad (2.177)$$

Notice that there is no potential term $V(\mathbf{r})$ in the action of (2.177). The effect of the static random potential here is to provide a ‘step length’ ℓ for the propagator. According to the AAS result (2.171), the corrections to the conductivity involve paths which begin and end at the same point \mathbf{r} in space. The charge $e^* = 2e$ which appears in the Cooperon action arises from adding up contributions due to time-reversed paths, as we saw earlier.

Let's try to compute $\delta\sigma$, which is called the *weak localization* correction to the conductivity. In the absence of an external field, the eigenvalues of \mathcal{L} are simply $\mathbf{k}^2\ell^2$, where $k_\mu = 2\pi n_\mu/L$. We then have

$$\mathcal{C}(\mathbf{r}, \mathbf{r}) = \int \frac{d^d k}{(2\pi)^d} \frac{1}{\mathbf{k}^2\ell^2 + \frac{\tau}{\tau_\phi}} . \quad (2.178)$$

A cutoff Λ is needed in dimensions $d \geq 2$ in order to render the integral convergent in the ultraviolet. This cutoff is the inverse step size for diffusion: $\Lambda \sim \ell^{-1}$. This gives, for $\tau \ll \tau_\phi$,

$$\delta\sigma_d \sim \frac{e^2}{h} \cdot \begin{cases} -\ell^{-1} & (d = 3) \\ -\ln(\tau_\phi/\tau) & (d = 2) \\ -\ell\sqrt{\tau_\phi/\tau} & (d = 1) \end{cases} \quad (2.179)$$

Let us now compute the magnetoconductance in $d = 2$. In the presence of a uniform magnetic field, \mathcal{L} has evenly spaced eigenvalues

$$\lambda_n = \left(n + \frac{1}{2} \right) \left(\frac{2\ell}{\ell_B} \right)^2 , \quad (2.180)$$

where $\ell_B = \sqrt{\hbar c/eB}$ is the magnetic length (for a charge $q = -e$ electron). Each of these

Landau levels has a macroscopic degeneracy of $2eBA/hc = A/\pi\ell_B^2$. Thus,

$$\begin{aligned}\delta\sigma(B) &= -\frac{2e^2}{h} \frac{\ell^2}{\pi\ell_B^2} \sum_{n=0}^{\ell_B^2/4\ell^2} \frac{1}{(n + \frac{1}{2})\frac{4\ell^2}{\ell_B^2} + \frac{\tau}{\tau_\phi}} \\ &= -\frac{e^2}{2\pi h} \sum_{n=0}^{\ell_B^2/4\ell^2} \frac{1}{n + \frac{1}{2} + \frac{\ell_B^2}{L_\phi^2}},\end{aligned}\quad (2.181)$$

where we have invoked $\tau/\tau_\phi = \ell^2/L_\phi^2$. The magnetoconductance is then

$$\delta\sigma(B) - \delta\sigma(0) = -\frac{1}{2\pi} \frac{e^2}{h} \left\{ \Psi\left(\frac{1}{2} + \frac{\ell_B^2}{4\ell^2}\right) - \Psi\left(\frac{1}{2} + \frac{\ell_B^2}{4L_\phi^2}\right) \right\}, \quad (2.182)$$

where

$$\Psi(z) = \frac{1}{\Gamma(z)} \frac{d\Gamma(z)}{dz} = \ln z + \frac{1}{2z} - \frac{1}{12z^2} + \dots \quad (2.183)$$

is the digamma function. If the field is weak, so that $\ell_B \gg \ell$, then

$$\delta\sigma(B) - \delta\sigma(0) = +\frac{1}{6\pi} \frac{e^2}{h} \left(\frac{L_\phi}{\ell_B} \right)^2, \quad (2.184)$$

which is positive, as previously discussed. The magnetic field suppresses phase coherence between time-reversed paths, and thereby promotes diffusion by suppressing the resonant backscattering contributions to $\delta\sigma$. At large values of the field, the behavior is logarithmic. Generally, we can write

$$\delta\sigma(B) - \delta\sigma(0) = \frac{1}{2\pi} \frac{e^2}{h} f\left(\frac{B}{B_\phi}\right), \quad (2.185)$$

where

$$\frac{2\pi B_\phi}{B} \equiv \frac{\ell_B^2}{4L_\phi^2} \implies B_\phi = \frac{\phi_0}{8\pi L_\phi^2} \quad (2.186)$$

and

$$f(x) = \ln x + \Psi\left(\frac{1}{2} + \frac{1}{x}\right) = \begin{cases} \frac{x^2}{24} & \text{as } x \rightarrow 0 \\ \ln x - 1.96351\dots & \text{as } x \rightarrow \infty \end{cases}. \quad (2.187)$$

2.6 Anderson Localization

In 1958, P. W. Anderson proposed that static disorder could lead to localization of electronic eigenstates in a solid. Until this time, it was generally believed that disorder gave rise to an elastic scattering length ℓ and a diffusion constant $D = v_F\ell$. The diffusion constant is related to the electrical conductivity through the Einstein relation: $\sigma = \frac{1}{2}e^2D(\varepsilon_F)\mathcal{N}(\varepsilon_F)$. If the states at the Fermi level are *localized*, then $D(\varepsilon_F) = 0$.

Anderson considered an electron propagating in a random potential:

$$\mathcal{H} = -\frac{\hbar^2}{2m} \nabla^2 + V(\mathbf{r}) , \quad (2.188)$$

where $V(\mathbf{r})$ is chosen from an ensemble of random functions. Physically, $V(\mathbf{r})$ is bounded and smooth, although often theorists often study uncorrelated ‘white noise’ potentials where the ensemble is described by the distribution functional

$$P[V(\mathbf{r})] = \exp \left\{ -\frac{1}{2\gamma} \int d^d r V^2(\mathbf{r}) \right\} , \quad (2.189)$$

for which

$$\langle V(\mathbf{r}) V(\mathbf{r}') \rangle = \gamma \delta(\mathbf{r} - \mathbf{r}') . \quad (2.190)$$

A tight binding version of this model would resemble

$$\mathcal{H} = -t \sum_{\langle ij \rangle} (c_i^\dagger c_j + c_j^\dagger c_i) + \sum_i \varepsilon_i c_i^\dagger c_i , \quad (2.191)$$

where the single site energies $\{\varepsilon_i\}$ are independently distributed according to some function $p(\varepsilon)$. The first term can be diagonalized by Fourier transform:

$$\mathcal{H}_0 = -t \sum_{\langle ij \rangle} (c_i^\dagger c_j + c_j^\dagger c_i) = -zt \sum_{\mathbf{k}} \gamma_{\mathbf{k}} c_{\mathbf{k}}^\dagger c_{\mathbf{k}} , \quad (2.192)$$

where $\gamma_{\mathbf{k}} = z^{-1} \sum_{\delta} e^{i\mathbf{k}\cdot\delta}$, where δ is a nearest neighbor direct lattice vector and z is the lattice coordination number; the bandwidth is $2zt$. What happens when we add the random potential term to (2.192)? Suppose the width of the distribution $p(\varepsilon)$ is W , e.g. $p(\varepsilon) = W^{-1} \Theta(\frac{1}{4}W^2 - \varepsilon^2)$, with $W \ll zt$. We expect that the band edges shift from $\pm zt$ to $\pm(zt + \frac{1}{2}W)$. The density of states must vanish for $|\varepsilon| > zt + \frac{1}{2}W$; the regions in the vicinity of $\pm(zt + \frac{1}{2}W)$ are known as *Lifshitz tails*.

Aside from the formation of Lifshitz tails, the density of states doesn’t change much. What does change is the character of the eigenfunctions. Suppose we can find a region of contiguous sites all of which have energies $\varepsilon_i \approx \frac{1}{2}W$. Then we could form an approximate eigenstate by concentrating the wavefunction in this region of sites, setting its phase to be constant throughout. This is an example of a *localized state*. We can think of such a state as a particle in a box – the electron binds itself to local fluctuations in the potential. Outside this region, the wavefunction decays, typically exponentially. Scattering states are then extended states, and are associated with ‘average’ configurations of the $\{\varepsilon_i\}$. The typical spatial extent of the localized states is given by the localization length $\xi(\varepsilon)$. The localization length diverges at the *mobility edges* as

$$\xi(\varepsilon) \sim |\varepsilon - \varepsilon_c|^{-\nu} . \quad (2.193)$$

There is no signature of the mobility edge in the density of states itself – $\mathcal{N}(\varepsilon)$ is completely smooth through the mobility edge ε_c .

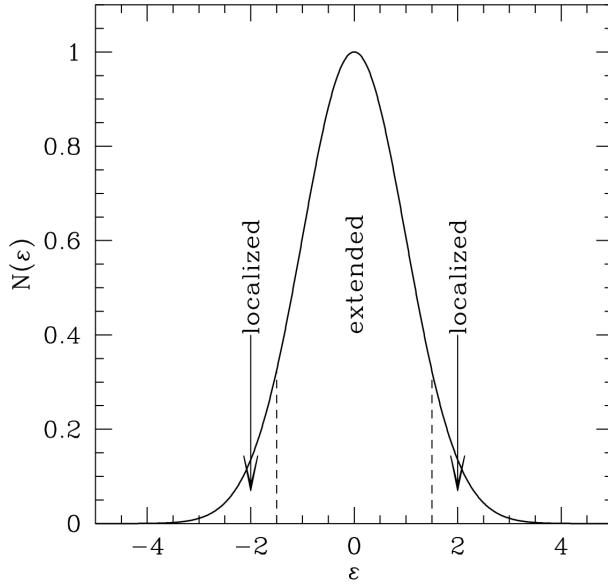


Figure 2.9: Schematic picture of density of states in a disordered system showing mobility edges (dashed lines) and localized states in band tails.

2.6.1 Characterization of Localized and Extended States

One way of characterizing the localization properties of quantum mechanical eigenstates (of \mathcal{H}) is to compute the *participation ratio* Q . The inverse participation ratio for the state α is given by

$$Q_\alpha^{-1} = \sum_i |\psi_\alpha(i)|^4 / \left(\sum_i |\psi_\alpha(i)|^2 \right)^2 \quad (\text{discrete}) \quad (2.194)$$

$$= \int d^d x |\psi_\alpha(x)|^4 / \left(\int d^d x |\psi_\alpha(x)|^2 \right)^2 \quad (\text{continuous}) \quad (2.195)$$

Consider the discrete case. If ψ_α is localized on a single site, then we have $\sum_i |\psi_\alpha(i)|^k = 1$ for all k , i.e. $Q_\alpha = 1$. But if ψ_α is spread evenly over N sites, then $Q_\alpha^{-1} = N/N^2 = N^{-1}$, and $Q_\alpha = N$. Hence, Q_α tells us approximately how many states $|i\rangle$ participate in the state $|\psi_\alpha\rangle$. The dependence of Q_α on the system size (linear dimension) L can be used as a diagnostic:

$$|\psi_\alpha\rangle \text{ localized} \implies Q_\alpha \propto L^0 \quad (2.196)$$

$$|\psi_\alpha\rangle \text{ extended} \implies Q_\alpha \propto L^\beta, \quad (2.197)$$

where $\beta > 0$.

Another way to distinguish extended from localized states is to examine their sensitivity to boundary conditions:

$$\psi(x_1, \dots, x_\mu + L, \dots, x_d) = e^{i\theta_\mu} \psi(x_1, \dots, x_\mu, \dots, x_d), \quad (2.198)$$

where $\mu \in \{1, \dots, d\}$. For periodic boundary conditions $\theta_\mu = 0$, while antiperiodic boundary conditions have $\theta_\mu = \pi$. For plane wave states, this changes the allowed wavevectors, so that $k_\mu \rightarrow k_\mu + \pi/L$. Thus, for an extended state,

$$\delta\varepsilon_{\text{ext}} = \varepsilon^{\text{pbc}} - \varepsilon^{\text{apbc}} \simeq \frac{\partial\varepsilon}{\partial k} \delta k \propto L^{-1}. \quad (2.199)$$

For a localized state,

$$\delta\varepsilon_{\text{loc}} \propto e^{-L/\xi(\varepsilon)}. \quad (2.200)$$

One defines the dimensionless *Thouless number*

$$\text{Th}(\varepsilon, L) = |\varepsilon^{\text{pbc}} - \varepsilon^{\text{apbc}}| \cdot \mathcal{N}(\varepsilon). \quad (2.201)$$

In the vicinity of a mobility edge, a scaling hypothesis suggests

$$\text{Th}(\varepsilon, L) = f(L/\xi(\varepsilon)), \quad (2.202)$$

where $f(x)$ is a *universal scaling function*.

As the Fermi level passes through the mobility edge into a region of localized states, the conductivity vanishes as

$$\sigma(\varepsilon_F) \sim |\varepsilon_F - \varepsilon_c|^s, \quad (2.203)$$

where $s > 0$. Since the density is a continuous function of ε_F , this can also be turned into a statement about the behavior of $\sigma(n)$:

$$\sigma(n) \sim (n - n_c)^s \Theta(n - n_c). \quad (2.204)$$

2.6.2 Numerical Studies of the Localization Transition

Pioneering work in numerical studies of the localization transition was performed by MacKinnon and Kramer in the early 1980's. They computed the localization length $\xi_M(W/t, E)$ for systems of dimension $M^{d-1} \times N$, from the formula

$$\xi_M^{-1}\left(\frac{W}{t}, E\right) = -\lim_{N \rightarrow \infty} \frac{1}{2N} \left\langle \ln \sum_{i,j=1}^{M^{d-1}} |G_{1i,Nj}(E)|^2 \right\rangle, \quad (2.205)$$

where $G(E) = (E + i\epsilon - \mathcal{H})^{-1}$ is the Green's function, and i, j label transverse sites. The average $\langle \dots \rangle$ is over disorder configurations. It is computationally very convenient to compute the localization length in this manner, rather than from exact diagonalization, because the Green's function can be computed recursively. For details, see A. MacKinnon and B. Kramer, *Phys. Rev. Lett.* **47**, 1546 (1981). Note also that it is $\langle |G|^2 \rangle$ which is computed, rather than $\langle G \rangle$. The reason for this is that the Green's function itself carries a complex phase which when averaged over disorder configurations results in a decay of $\langle G_{R,R'} \rangle$ on the scale of the elastic mean free path ℓ .

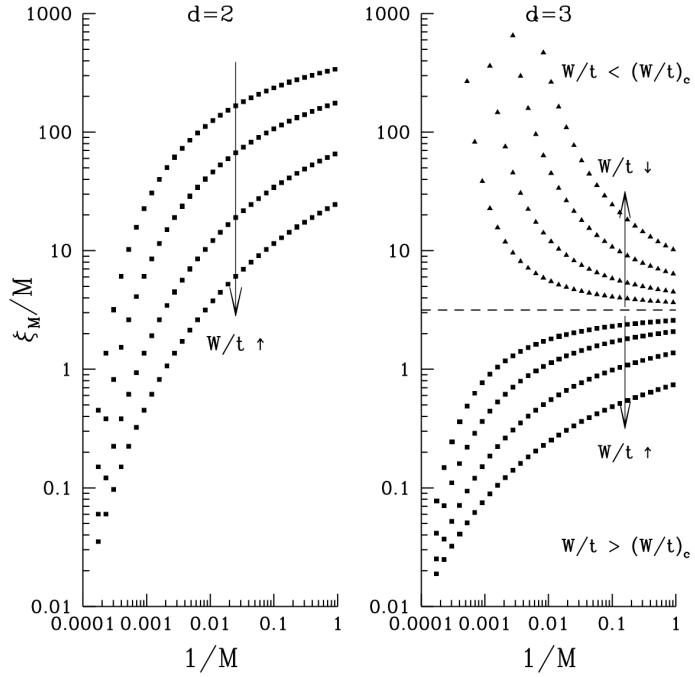


Figure 2.10: Mock-up of typical raw data from numerical study of localization length for $d = 2$ (left panel) and $d = 3$ (right panel) systems. For $d = 2$, $\xi_\infty(W/t)$ is finite and monotonically decreasing with increasing W/t . For $d = 3$, there is a critical value of W/t . For $W/t < (W/t)_c$, $\xi_M(W/t)$ diverges as $M \rightarrow \infty$; this is the extended phase. For $W/t > (W/t)_c$, $\xi_M(W/t)$ remains finite as $M \rightarrow \infty$; this is the localized phase.

MacKinnon and Kramer computed the localization length by employing the *Ansatz* of *finite size scaling*. They assumed that

$$\xi_M\left(\frac{W}{t}, E\right) = M f\left(\xi_\infty\left(\frac{W}{t}, E\right)/M\right), \quad (2.206)$$

where $f(x)$ is a universal scaling function which depends only on the dimension d . MK examined the band center, at $E = 0$; for $d > 2$ this is the last region to localize as W/t is increased from zero. A mock-up of typical raw data is shown in fig. 2.10.

In the $d = 2$ case, all states are localized. Accordingly, $\xi_M/M \rightarrow 0$ as $M \rightarrow \infty$, and $\xi_M(W/t)$ decreases with increasing W/t . In the $d = 3$ case, states at the band center are extended for weak disorder. As W/t increases, $\xi_M(W/t)$ decreases, but with $\xi_\infty(W/t)$ still divergent. At the critical point, $(W/t)_c$, this behavior changes. The band center states localize, and $\xi_\infty(W/t)$ is finite for $W/t > (W/t)_c$. If one rescales and plots ξ_M/M versus ξ_∞/M , the scaling function $f(x)$ is revealed. This is shown in fig. 2.11, which is from the paper by MacKinnon and Kramer. Note that there is only one branch to the scaling function for $d = 2$, but two branches for $d = 3$. MacKinnon and Kramer found $(W/t)_c \simeq 16.5$ for a disordered tight binding model on a simple cubic lattice.

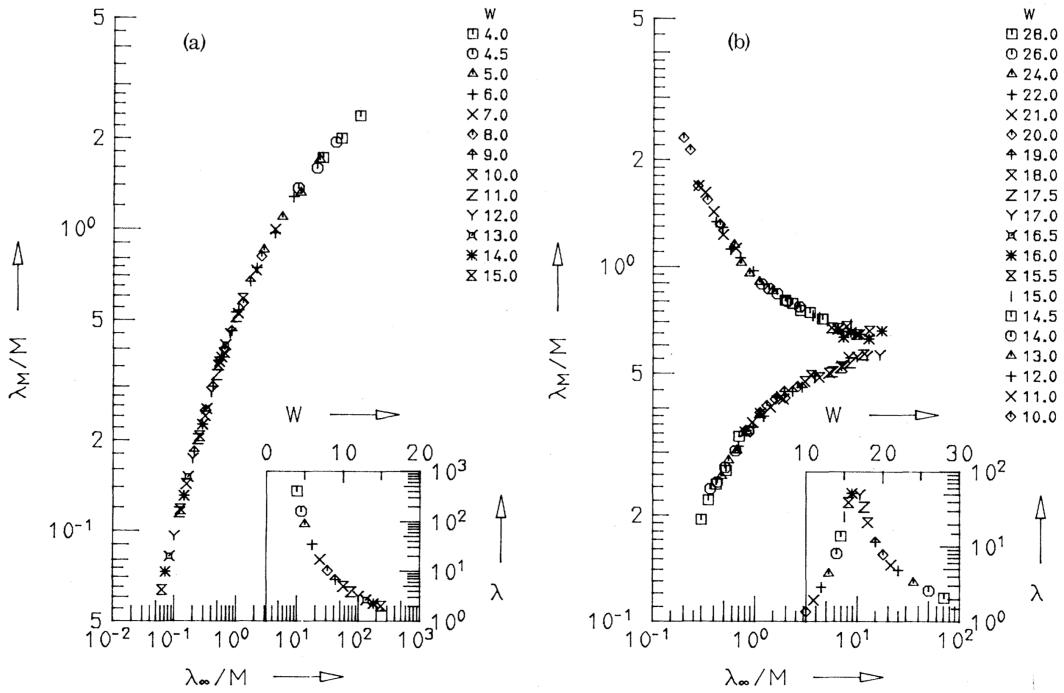


Figure 2.11: Scaling function λ_M/M versus λ_∞/M for the localization length λ_M of a system of thickness M for (a) $d = 2$, and (b) $d = 3$. Insets show the scaling parameter λ_∞ as a function of the disorder W . From A. MacKinnon and B. Kramer, *Phys. Rev. Lett.* **47**, 1546 (1981).

2.6.3 Scaling Theory of Localization

In the metallic limit, the dimensionless conductance of a L^d hypercube is given by the Ohmic result

$$g(L) = \frac{h\sigma}{e^2} L^{d-2}, \quad (2.207)$$

whereas in the localized limit we have, from Pichard's formula,

$$g(L) = 4 e^{-2L/\xi}. \quad (2.208)$$

It is instructive to consider the function,

$$\beta(g) \equiv \frac{d \ln g}{d \ln L}, \quad (2.209)$$

which describes the change of g when we vary the size of the system. We now know the limiting values of $\beta(g)$ for small and large g :

$$\text{metallic } (g \gg 1) \implies \beta(g) = d - 2 \quad (2.210)$$

$$\text{localized } (g \ll 1) \implies \beta(g) = -\frac{2L}{\xi} = \ln g + \text{const.} \quad (2.211)$$

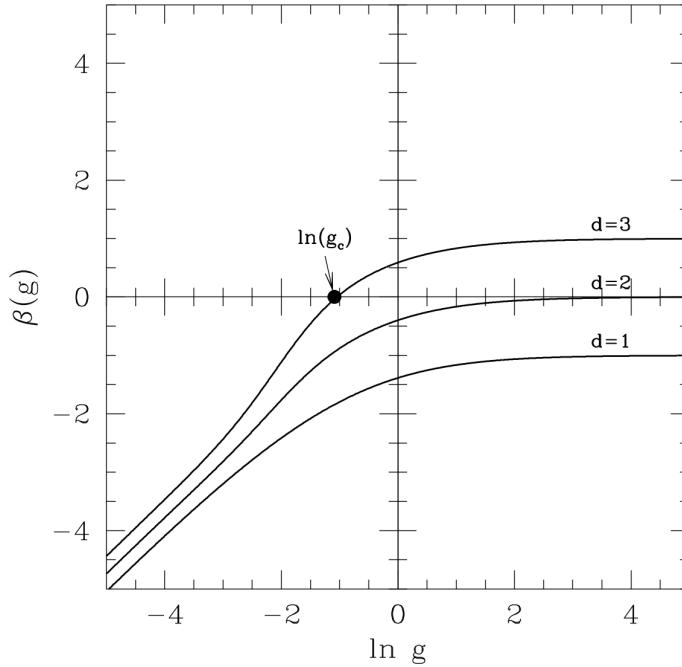


Figure 2.12: Sketch of the β -function for the localization problem for $d = 1, 2, 3$. A critical point exists at $g = g_c$ for the $d = 3$ case.

If we assume that $\beta(g)$ is a smooth monotonic function of g , we arrive at the picture in fig. 2.12. Note that in $d = 1$, we can compute $\beta(g)$ exactly, using the Landauer formula,

$$g = \frac{T}{1-T} , \quad (2.212)$$

where $T \propto \exp(-L/\xi)$. From this, we obtain

$$\beta_{d=1}(g) = -(1+g) \ln(1+g^{-1}) . \quad (2.213)$$

It should be stressed that the very existence of a β -function is hardly clear. If it does exist, it says that the conductance of a system of size L is uniquely determined by its conductance at some other length scale, typically chosen to be microscopic, e.g. $L_0 = \ell$. Integrating the β -function, we obtain an integral equation to be solved implicitly for $g(L)$:

$$\ln \left(\frac{L}{L_0} \right) = \int_{\ln g(L_0)}^{\ln g(L)} \frac{d \ln g}{\beta(g)} . \quad (2.214)$$

A priori it seems more likely, though, that as L is increased the changes to the conductance may depend on more than g alone. E.g. the differential change dg might depend on the entire distribution function $P(W)$ for the disorder.

Integrating the β -function: $d = 3$

We know $\beta(g \rightarrow 0) \simeq \ln g$ and $\beta(g \rightarrow \infty) = 1$, hence by the intermediate value theorem there is at least one point where $\beta(g)$ vanishes. Whenever g satisfies $\beta(g) = 0$, the conductance g is *scale invariant* – it does not change with increasing (or decreasing) system size L . We will assume the situation is reflected by the sketch of fig. 2.12, and that there is one such point, g_c .

We now apply (2.214). Not knowing the precise form of $\beta(g)$, we approximate it piecewise:

$$\beta(g) \simeq \begin{cases} 1 & \text{if } g \geq g_+ \\ \alpha \ln(g/g_c) & \text{if } g_- < g < g_+ \\ \ln g & \text{if } g < g_- , \end{cases} \quad (2.215)$$

where $\alpha = g_c \beta'(g_c)$. We determine g_+ and g_- by continuity:

$$\ln g_+ = \ln g_c + \frac{1}{\alpha} \quad (2.216)$$

$$\ln g_- = \frac{\alpha}{\alpha - 1} \ln g_c . \quad (2.217)$$

Now suppose we start with $g_0 = g_c + \delta g$, where $|\delta g| \ll 1$. We integrate out to $g = g_+$ and then from g_+ to $g \gg 1$:

$$\ln \left(\frac{L_+}{L_0} \right) = \int_{\ln g_0}^{\ln g_+} \frac{d \ln g}{\alpha \ln(g/g_c)} = \frac{1}{\alpha} \ln \left(\frac{\ln(g_+/g_c)}{\ln(g_0/g_c)} \right) \quad (2.218)$$

$$\ln \left(\frac{L}{L_+} \right) = \int_{\ln g_+}^{\ln g} d \ln g = \ln(g/g_+) , \quad (2.219)$$

which together imply

$$g(L) = A_+ g_c \cdot \frac{L}{L_0} \cdot (g_0 - g_c)^{1/\alpha} , \quad (2.220)$$

where $A_+ = (e\alpha/g_c)^{1/\alpha}$. The conductivity is

$$\sigma = \frac{e^2}{h} \cdot \frac{g}{L} = \frac{e^2}{h} \cdot \frac{A_+ g_c}{L_0} \cdot (g_0 - g_c)^{1/\alpha} . \quad (2.221)$$

If instead we start with $g_0 = g_c - \delta g$ and integrate out to large negative values of $\ln g$, then

$$\ln \left(\frac{L_-}{L_0} \right) = \int_{\ln g_0}^{\ln g_-} \frac{d \ln g}{\alpha \ln(g/g_c)} = \frac{1}{\alpha} \ln \left(\frac{\ln(g_c/g_-)}{\ln(g_c/g_0)} \right) \quad (2.222)$$

$$\ln \left(\frac{L}{L_-} \right) = \int_{\ln g_-}^{\ln g} \frac{d \ln g}{\ln g} = \ln \left(\frac{\ln g}{\ln g_-} \right) , \quad (2.223)$$

which says

$$g(L) = e^{-2L/\xi} \quad (2.224)$$

$$\xi = \frac{2L_0}{A_-} \cdot (g_c - g_0)^{-1/\alpha}, \quad (2.225)$$

with

$$A_- = \frac{\ln(1/g_-)}{g_c \cdot [\ln(g_c/g_-)]^{1/\alpha}}. \quad (2.226)$$

On the metallic side of the transition, when $g_0 > g_c$, we can identify a localization length through

$$g \equiv g_c/\xi, \quad (2.227)$$

which says

$$\xi = \frac{L_0}{A_+} (g_0 - g_c)^{-1/\alpha}. \quad (2.228)$$

Finally, since g_0 is determined by the value of the Fermi energy ε_F . we can define the *critical energy*, or *mobility edge* ε_c , through

$$g(L_0, \varepsilon_c) = g_c, \quad (2.229)$$

in which case

$$\delta g \equiv g(L_0, \varepsilon_F) - g_c = \left. \frac{\partial g(L_0, \varepsilon)}{\partial \varepsilon} \right|_{\varepsilon=\varepsilon_c} \cdot (\varepsilon_F - \varepsilon_c). \quad (2.230)$$

Thus, $\delta g \propto \delta \varepsilon \equiv (\varepsilon_F - \varepsilon_c)$.

Integrating the β -function: $d = 2$

In two dimensions, there is no fixed point. In the Ohmic limit $g \gg 1$, we have

$$\beta(g) = -\frac{c}{g} + \mathcal{O}(g^{-2}), \quad (2.231)$$

where c is a constant. Thus,

$$\ln\left(\frac{L}{L_0}\right) = \int_{\ln g_0}^{\ln g} \frac{d \ln g}{\beta(g)} = -\frac{g - g_0}{c} + \dots \quad (2.232)$$

and

$$g(L) = k_F \ell - c \ln(L/\ell), \quad (2.233)$$

where we have used the Drude result $g = k_F \ell$, valid for $L_0 = \ell$. We now see that the localization length ξ is the value of L for which the correction term is on the same order as g_0 : $\xi = \ell \exp(k_F \ell/c)$. A first principles treatment yields $c = \frac{2}{\pi}$. The metallic regime in $d = 2$ is often called the *weak localization* regime.

$2 + \epsilon$ dimensions

At or below $d = 2$ dimensions, there is no mobility edge and all eigenstates are localized. $d = 2$ is the lower critical dimension for the localization transition. Consider now the problem in $d = 2 + \epsilon$ dimensions. One has

$$\beta(g) = \epsilon - \frac{c}{g} + \mathcal{O}(g^{-2}) . \quad (2.234)$$

The critical conductance lies at $g_c = c/\epsilon$. For $\epsilon \rightarrow 0^+$, this is large enough that higher order terms in the expansion of the β -function can safely be ignored in the metallic limit. An analysis similar to that for $d = 3$ now yields

$$g > g_c \implies g(L) = \frac{h}{e^2} \sigma L^\epsilon \quad (2.235)$$

$$g < g_c \implies g(L) = e^{-2L/\xi} , \quad (2.236)$$

with

$$\sigma = \frac{e^2}{h} L_0^\epsilon \cdot (g_0 - g_c) \quad (2.237)$$

$$\xi = \frac{2L_0}{A_-} \cdot (g_c - g_0) . \quad (2.238)$$

Note that $\alpha = g_c \beta'(g_c) = +c/g_c = \epsilon$. We thus obtain

$$\xi(\varepsilon) \propto |\varepsilon - \varepsilon_c|^{-\nu} \quad (2.239)$$

with $\nu = 1 + \mathcal{O}(\epsilon)$. Close to the transition on the metallic side, the conductivity vanishes as

$$\sigma(\varepsilon) \propto |\varepsilon - \varepsilon_c|^s . \quad (2.240)$$

The relation $s = (d-2)\nu$, which follows from the above treatment, may be used to relate the localization length and conductivity critical exponents. (In $d = 3$, MacKinnon and Kramer obtained $\nu = s \simeq 1.2$.)

2.6.4 Finite Temperature

In the metallic regime, one obtains from the scaling theory,

$$\sigma_{d=3}(L) = \frac{e^2}{h} \cdot \left\{ \frac{2k_F^2 \ell}{3\pi} - \frac{2}{\pi^2} \left(\frac{1}{\ell} - \frac{1}{L} \right) \right\} \quad (2.241)$$

$$\sigma_{d=2}(L) = \frac{e^2}{h} \cdot \left\{ k_F \ell - \frac{2}{\pi} \ln \left(\frac{L}{\ell} \right) \right\} \quad (2.242)$$

$$\sigma_{d=1}(L) = \frac{e^2}{h} \cdot \left\{ 4\ell - 2(L - \ell) \right\} . \quad (2.243)$$

Clearly the $d = 1$ result must break down for even microscopic $L \gtrsim 3\ell$. The above results are computed using the β -function

$$\beta(g) = (d - 2) - \frac{c_d}{g} + \mathcal{O}(g^{-2}) , \quad (2.244)$$

where the coefficients c_d are computed from perturbation theory in the disorder.

At finite temperature, the cutoff becomes $\min(L, L_\phi)$, where $L_\phi = \sqrt{D\tau_\phi}$ is the inelastic scattering length and $D = v_F\ell$ is the diffusion constant. Suppose that $\tau_\phi(T) \propto T^{-p}$ as $T \rightarrow 0$, so that $L_\phi = a(T/T_0)^{-p/2}$, where T_0 is some characteristic temperature (*e.g.* the Debye temperature, if the inelastic mechanism is electron-phonon scattering). Then, for $L_\phi > L$,

$$\sigma_{d=3}(T) = \sigma_{d=3}^B - \frac{2}{\pi^2} \frac{e^2}{h} \left\{ \frac{1}{\ell} - \frac{1}{a} \left(\frac{T}{T_0} \right)^{p/2} \right\} \quad (2.245)$$

$$\sigma_{d=2}(T) = \sigma_{d=2}^B - \frac{2}{\pi} \frac{e^2}{h} \left\{ \ln \left(\frac{a}{\ell} \right) - \frac{p}{2} \ln \left(\frac{T}{T_0} \right) \right\} \quad (2.246)$$

$$\sigma_{d=1}(T) = \sigma_{d=1}^B - 2 \frac{e^2}{h} \left\{ a \left(\frac{T_0}{T} \right)^{p/2} - \ell \right\} , \quad (2.247)$$

where σ_d^B is the Boltzmann conductivity. Note that $\sigma(T)$ decreases with decreasing temperature, unlike the classic low T result for metals, where $\rho(T) = \rho_0 + AT^2$. *I.e.* usually $\rho(T)$ increases as T increases due to a concomitant decrease in transport scattering time τ . Weak localization physics, though, has the opposite effect, as the enhanced backscattering is suppressed as T increases and L_ϕ decreases. The result is that $\rho(T)$ starts to decrease as T is lowered from high temperatures, but turns around at low T and starts increasing again. This behavior was first observed in 1979 by Dolan and Osheroff, who studied thin metallic PdAu films, observing a logarithmic increase in $\rho_{d=2}(T)$ at the lowest temperatures.

Chapter 3

Linear Response Theory

3.1 Response and Resonance

Consider a damped harmonic oscillator subjected to a time-dependent forcing:

$$\ddot{x} + 2\gamma\dot{x} + \omega_0^2 x = f(t) , \quad (3.1)$$

where γ is the damping rate ($\gamma > 0$) and ω_0 is the natural frequency in the absence of damping¹. We adopt the following convention for the Fourier transform of a function $H(t)$:

$$H(t) = \int_{-\infty}^{\infty} \frac{d\omega}{2\pi} \hat{H}(\omega) e^{-i\omega t} \quad (3.2)$$

$$\hat{H}(\omega) = \int_{-\infty}^{\infty} dt H(t) e^{+i\omega t} . \quad (3.3)$$

Note that if $H(t)$ is a real function, then $\hat{H}(-\omega) = \hat{H}^*(\omega)$. In Fourier space, then, eqn. (3.1) becomes

$$(\omega_0^2 - 2i\gamma\omega - \omega^2) \hat{x}(\omega) = \hat{f}(\omega) , \quad (3.4)$$

with the solution

$$\hat{x}(\omega) = \frac{\hat{f}(\omega)}{\omega_0^2 - 2i\gamma\omega - \omega^2} \equiv \hat{\chi}(\omega) \hat{f}(\omega) \quad (3.5)$$

where $\hat{\chi}(\omega)$ is the *susceptibility function*:

$$\hat{\chi}(\omega) = \frac{1}{\omega_0^2 - 2i\gamma\omega - \omega^2} = \frac{-1}{(\omega - \omega_+)(\omega - \omega_-)} , \quad (3.6)$$

with

$$\omega_{\pm} = -i\gamma \pm \sqrt{\omega_0^2 - \gamma^2} . \quad (3.7)$$

¹Note that $f(t)$ has dimensions of acceleration.

The complete solution to (3.1) is then

$$x(t) = \int_{-\infty}^{\infty} \frac{d\omega}{2\pi} \frac{\hat{f}(\omega) e^{-i\omega t}}{\omega_0^2 - 2i\gamma\omega - \omega^2} + x_h(t) \quad (3.8)$$

where $x_h(t)$ is the homogeneous solution,

$$x_h(t) = A_+ e^{-i\omega_+ t} + A_- e^{-i\omega_- t}. \quad (3.9)$$

Since $\text{Im}(\omega_{\pm}) < 0$, $x_h(t)$ is a *transient* which decays in time. The coefficients A_{\pm} may be chosen to satisfy initial conditions on $x(0)$ and $\dot{x}(0)$, but the system ‘loses its memory’ of these initial conditions after a finite time, and in steady state all that is left is the inhomogeneous piece, which is completely determined by the forcing.

In the time domain, we can write

$$x(t) = \int_{-\infty}^{\infty} dt' \chi(t-t') f(t') \quad (3.10)$$

$$\chi(s) \equiv \int_{-\infty}^{\infty} \frac{d\omega}{2\pi} \hat{\chi}(\omega) e^{-i\omega s}, \quad (3.11)$$

which brings us to a very important and sensible result:

Claim: The response is *causal*, i.e. $\chi(t-t') = 0$ when $t < t'$, provided that $\hat{\chi}(\omega)$ is analytic in the upper half plane of the variable ω .

Proof: Consider eqn. (3.11). Of $\hat{\chi}(\omega)$ is analytic in the upper half plane, then closing in the UHP we obtain $\chi(s < 0) = 0$.

For our example (3.6), we close in the LHP for $s > 0$ and obtain

$$\begin{aligned} \chi(s > 0) &= (-2\pi i) \sum_{\omega \in \text{LHP}} \text{Res} \left\{ \frac{1}{2\pi} \hat{\chi}(\omega) e^{-i\omega s} \right\} \\ &= \frac{ie^{-i\omega_+ s}}{\omega_+ - \omega_-} + \frac{ie^{-i\omega_- s}}{\omega_- - \omega_+}, \end{aligned} \quad (3.12)$$

i.e.

$$\chi(s) = \begin{cases} \frac{e^{-\gamma s}}{\sqrt{\omega_0^2 - \gamma^2}} \sin \left(\sqrt{\omega_0^2 - \gamma^2} \right) \Theta(s) & \text{if } \omega_0^2 > \gamma^2 \\ \frac{e^{-\gamma s}}{\sqrt{\gamma^2 - \omega_0^2}} \sinh \left(\sqrt{\gamma^2 - \omega_0^2} \right) \Theta(s) & \text{if } \omega_0^2 < \gamma^2, \end{cases} \quad (3.13)$$

where $\Theta(s)$ is the step function: $\Theta(s \geq 0) = 1$, $\Theta(s < 0) = 0$. Causality simply means that events occurring after the time t cannot influence the state of the system at t . Note that, in general, $\chi(t)$ describes the time-dependent response to a δ -function impulse at $t = 0$.

3.1.1 Energy Dissipation

How much work is done by the force $f(t)$? Since the power applied is $P(t) = f(t) \dot{x}(t)$, we have

$$P(t) = \int_{-\infty}^{\infty} \frac{d\omega}{2\pi} (-i\omega) \hat{\chi}(\omega) \hat{f}(\omega) e^{-i\omega t} \int_{-\infty}^{\infty} \frac{d\nu}{2\pi} \hat{f}^*(\nu) e^{+i\nu t} \quad (3.14)$$

$$\Delta E = \int_{-\infty}^{\infty} dt P(t) = \int_{-\infty}^{\infty} \frac{d\omega}{2\pi} (-i\omega) \hat{\chi}(\omega) |\hat{f}(\omega)|^2. \quad (3.15)$$

Separating $\hat{\chi}(\omega)$ into real and imaginary parts,

$$\hat{\chi}(\omega) = \hat{\chi}'(\omega) + i\hat{\chi}''(\omega), \quad (3.16)$$

we find for our example

$$\hat{\chi}'(\omega) = \frac{\omega_0^2 - \omega^2}{(\omega_0^2 - \omega^2)^2 + 4\gamma^2\omega^2} = +\hat{\chi}'(-\omega) \quad (3.17)$$

$$\hat{\chi}''(\omega) = \frac{2\gamma\omega}{(\omega_0^2 - \omega^2)^2 + 4\gamma^2\omega^2} = -\hat{\chi}''(-\omega). \quad (3.18)$$

The energy dissipated may now be written

$$\Delta E = \int_{-\infty}^{\infty} \frac{d\omega}{2\pi} \omega \hat{\chi}''(\omega) |\hat{f}(\omega)|^2. \quad (3.19)$$

The even function $\hat{\chi}'(\omega)$ is called the *reactive* part of the susceptibility; the odd function $\hat{\chi}''(\omega)$ is the *dissipative* part. When experimentalists measure a *lineshape*, they usually are referring to features in $\omega \hat{\chi}''(\omega)$, which describes the absorption rate as a function of driving frequency.

3.2 Kramers-Kronig Relations

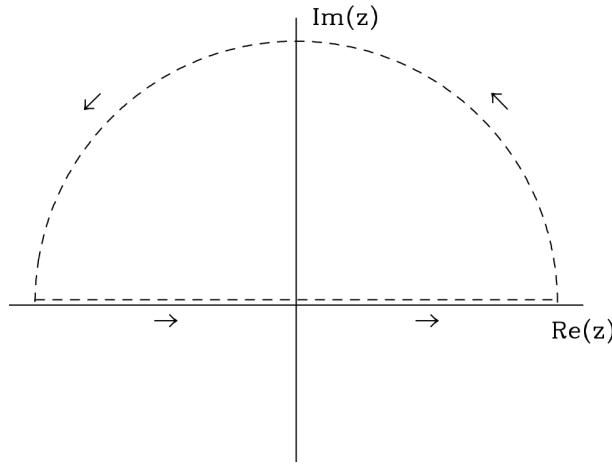
Let $\chi(z)$ be a complex function of the complex variable z which is analytic in the upper half plane. Then the following integral must vanish,

$$\oint_{\mathcal{C}} \frac{dz}{2\pi i} \frac{\chi(z)}{z - \zeta} = 0, \quad (3.20)$$

whenever $\text{Im}(\zeta) \leq 0$, where \mathcal{C} is the contour depicted in fig. 3.1.

Now let $\omega \in \mathbb{R}$ be real, and define the complex function $\chi(\omega)$ of the real variable ω by

$$\chi(\omega) \equiv \lim_{\epsilon \rightarrow 0^+} \chi(\omega + i\epsilon). \quad (3.21)$$

Figure 3.1: The complex integration contour \mathcal{C} .

Assuming $\chi(z)$ vanishes sufficiently rapidly that Jordan's lemma may be invoked (*i.e.* that the integral of $\chi(z)$ along the arc of \mathcal{C} vanishes), we have

$$\begin{aligned} 0 &= \int_{-\infty}^{\infty} \frac{d\nu}{2\pi i} \frac{\chi(\nu)}{\nu - \omega + i\epsilon} \\ &= \int_{-\infty}^{\infty} \frac{d\nu}{2\pi i} [\chi'(\nu) + i\chi''(\nu)] \left[\frac{\mathcal{P}}{\nu - \omega} - i\pi\delta(\nu - \omega) \right] \end{aligned} \quad (3.22)$$

where \mathcal{P} stands for ‘principal part’. Taking the real and imaginary parts of this equation reveals the *Kramers-Kronig relations*:

$$\chi'(\omega) = \mathcal{P} \int_{-\infty}^{\infty} \frac{d\nu}{\pi} \frac{\chi''(\nu)}{\nu - \omega} \quad (3.23)$$

$$\chi''(\omega) = -\mathcal{P} \int_{-\infty}^{\infty} \frac{d\nu}{\pi} \frac{\chi'(\nu)}{\nu - \omega} . \quad (3.24)$$

The Kramers-Kronig relations are valid for any function $\chi(z)$ which is analytic in the upper half plane.

If $\chi(z)$ is analytic everywhere off the $\text{Im}(z) = 0$ axis, we may write

$$\chi(z) = \int_{-\infty}^{\infty} \frac{d\nu}{\pi} \frac{\chi''(\nu)}{\nu - z} . \quad (3.25)$$

This immediately yields the result

$$\lim_{\epsilon \rightarrow 0^+} [\chi(\omega + i\epsilon) - \chi(\omega - i\epsilon)] = 2i \chi''(\omega) . \quad (3.26)$$

As an example, consider the function

$$\chi''(\omega) = \frac{\omega}{\omega^2 + \gamma^2} . \quad (3.27)$$

Then, choosing $\gamma > 0$,

$$\chi(z) = \int_{-\infty}^{\infty} \frac{d\omega}{\pi} \frac{1}{\omega - z} \cdot \frac{\omega}{\omega^2 + \gamma^2} = \begin{cases} i/(z + i\gamma) & \text{if } \text{Im}(z) > 0 \\ -i/(z - i\gamma) & \text{if } \text{Im}(z) < 0 . \end{cases} \quad (3.28)$$

Note that $\chi(z)$ is separately analytic in the UHP and the LHP, but that there is a branch cut along the $\text{Re}(z)$ axis, where $\chi(\omega \pm i\epsilon) = \pm i/(\omega \pm i\gamma)$.

EXERCISE: Show that eqn. (3.26) is satisfied for $\chi(\omega) = \omega/(\omega^2 + \gamma^2)$.

If we *analytically continue* $\chi(z)$ from the UHP into the LHP, we find a pole and no branch cut:

$$\tilde{\chi}(z) = \frac{i}{z + i\gamma} . \quad (3.29)$$

The pole lies in the LHP at $z = -i\gamma$.

3.3 Quantum Mechanical Response Functions

Now consider a general quantum mechanical system with a Hamiltonian \mathcal{H}_0 subjected to a time-dependent perturbation, $\mathcal{H}_1(t)$, where

$$\mathcal{H}_1(t) = - \sum_i Q_i \phi_i(t) . \quad (3.30)$$

Here, the $\{Q_i\}$ are a set of Hermitian operators, and the $\{\phi_i(t)\}$ are fields or potentials. Some examples:

$$\mathcal{H}_1(t) = \begin{cases} -\mathbf{M} \cdot \mathbf{B}(t) & \text{magnetic moment -- magnetic field} \\ \int d^3r \varrho(\mathbf{r}) \phi(\mathbf{r}, t) & \text{density -- scalar potential} \\ -\frac{1}{c} \int d^3r \mathbf{j}(\mathbf{r}) \cdot \mathbf{A}(\mathbf{r}, t) & \text{electromagnetic current -- vector potential} \end{cases}$$

We now ask, what is $\langle Q_i(t) \rangle$? We assume that the lowest order response is linear, *i.e.*

$$\langle Q_i(t) \rangle = \int_{-\infty}^{\infty} dt' \chi_{ij}(t - t') \phi_j(t') + \mathcal{O}(\phi_k \phi_l) . \quad (3.31)$$

Note that we assume that the $\mathcal{O}(\phi^0)$ term vanishes, which can be assured with a judicious choice of the $\{Q_i\}$ ². We also assume that the responses are all causal, *i.e.* $\chi_{ij}(t - t') = 0$ for

²If not, define $\delta Q_i \equiv Q_i - \langle Q_i \rangle_0$ and consider $\langle \delta Q_i(t) \rangle$.

$t < t'$. To compute $\chi_{ij}(t - t')$, we will use first order perturbation theory to obtain $\langle Q_i(t) \rangle$ and then functionally differentiate with respect to $\phi_j(t')$:

$$\chi_{ij}(t - t') = \frac{\delta \langle Q_i(t) \rangle}{\delta \phi_j(t')} . \quad (3.32)$$

The first step is to establish the result,

$$|\Psi(t)\rangle = \mathcal{T} \exp \left\{ -\frac{i}{\hbar} \int_{t_0}^t dt' [\mathcal{H}_0 + \mathcal{H}_1(t')] \right\} |\Psi(t_0)\rangle , \quad (3.33)$$

where \mathcal{T} is the *time ordering operator*, which places earlier times to the right. This is easily derived starting with the Schrödinger equation,

$$i\hbar \frac{d}{dt} |\Psi(t)\rangle = \mathcal{H}(t) |\Psi(t)\rangle , \quad (3.34)$$

where $\mathcal{H}(t) = \mathcal{H}_0 + \mathcal{H}_1(t)$. Integrating this equation from t to $t + dt$ gives

$$|\Psi(t + dt)\rangle = \left(1 - \frac{i}{\hbar} \mathcal{H}(t) dt \right) |\Psi(t)\rangle \quad (3.35)$$

$$|\Psi(t_0 + N dt)\rangle = \left(1 - \frac{i}{\hbar} \mathcal{H}(t_0 + (N - 1)dt) \right) \cdots \left(1 - \frac{i}{\hbar} \mathcal{H}(t_0) \right) |\Psi(t_0)\rangle , \quad (3.36)$$

hence

$$|\Psi(t_2)\rangle = U(t_2, t_1) |\Psi(t_1)\rangle \quad (3.37)$$

$$U(t_2, t_1) = \mathcal{T} \exp \left\{ -\frac{i}{\hbar} \int_{t_1}^{t_2} dt \mathcal{H}(t) \right\} . \quad (3.38)$$

$U(t_2, t_1)$ is a unitary operator (*i.e.* $U^\dagger = U^{-1}$), known as the *time evolution operator* between times t_1 and t_2 .

EXERCISE: Show that, for $t_1 < t_2 < t_3$ that $U(t_3, t_1) = U(t_3, t_2)U(t_2, t_1)$.

If $t_1 < t < t_2$, then differentiating $U(t_2, t_1)$ with respect to $\phi_i(t)$ yields

$$\frac{\delta U(t_2, t_1)}{\delta \phi_j(t)} = \frac{i}{\hbar} U(t_2, t) Q_j U(t, t_1) , \quad (3.39)$$

since $\partial \mathcal{H}(t)/\partial \phi_j(t) = -Q_j$. We may therefore write (assuming $t_0 < t, t'$)

$$\begin{aligned} \frac{\delta |\Psi(t)\rangle}{\delta \phi_j(t')} \Big|_{\{\phi_i=0\}} &= \frac{i}{\hbar} e^{-i\mathcal{H}_0(t-t')/\hbar} Q_j e^{-i\mathcal{H}_0(t'-t_0)/\hbar} |\Psi(t_0)\rangle \Theta(t - t') \\ &= \frac{i}{\hbar} e^{-i\mathcal{H}_0 t/\hbar} Q_j(t') e^{+i\mathcal{H}_0 t_0/\hbar} |\Psi(t_0)\rangle \Theta(t - t') , \end{aligned} \quad (3.40)$$

where

$$Q_j(t) \equiv e^{i\mathcal{H}_0 t/\hbar} Q_j e^{-i\mathcal{H}_0 t/\hbar} \quad (3.41)$$

is the operator Q_j in the time-dependent *interaction representation*. Finally, we have

$$\begin{aligned} \chi_{ij}(t - t') &= \frac{\delta}{\delta\phi_j(t')} \langle \Psi(t) | Q_i | \Psi(t) \rangle \\ &= \frac{\delta \langle \Psi(t) |}{\delta\phi_j(t')} Q_i | \Psi(t) \rangle + \langle \Psi(t) | Q_i \frac{\delta | \Psi(t) \rangle}{\delta\phi_j(t')} \\ &= \left\{ -\frac{i}{\hbar} \langle \Psi(t_0) | e^{-i\mathcal{H}_0 t_0/\hbar} Q_j(t') e^{+i\mathcal{H}_0 t/\hbar} Q_i | \Psi(t) \rangle \right. \\ &\quad \left. + \frac{i}{\hbar} \langle \Psi(t) | Q_i e^{-i\mathcal{H}_0 t/\hbar} Q_j(t') e^{+i\mathcal{H}_0 t_0/\hbar} | \Psi(t_0) \rangle \right\} \Theta(t - t') \\ &= \frac{i}{\hbar} \langle [Q_i(t), Q_j(t')] \rangle \Theta(t - t'), \end{aligned} \quad (3.42)$$

were averages are with respect to the wavefunction $|\Psi\rangle \equiv \exp(-i\mathcal{H}_0 t_0/\hbar)|\Psi(t_0)\rangle$, with $t_0 \rightarrow -\infty$, or, at finite temperature, with respect to a Boltzmann-weighted distribution of such states. To reiterate,

$$\boxed{\chi_{ij}(t - t') = \frac{i}{\hbar} \langle [Q_i(t), Q_j(t')] \rangle \Theta(t - t')}$$

(3.43)

This is sometimes known as the *retarded* response function.

3.3.1 Spectral Representation

We now derive an expression for the response functions in terms of the spectral properties of the Hamiltonian \mathcal{H}_0 . We stress that \mathcal{H}_0 may describe a fully interacting system. Write $\mathcal{H}_0|n\rangle = \hbar\omega_n|n\rangle$, in which case

$$\begin{aligned} \hat{\chi}_{ij}(\omega) &= \frac{i}{\hbar} \int_0^\infty dt e^{i\omega t} \langle [Q_i(t), Q_j(0)] \rangle \\ &= \frac{i}{\hbar} \int_0^\infty dt e^{i\omega t} \frac{1}{Z} \sum_{m,n} e^{-\beta\hbar\omega_m} \left\{ \langle m | Q_i | n \rangle \langle n | Q_j | m \rangle e^{+i(\omega_m - \omega_n)t} \right. \\ &\quad \left. - \langle m | Q_j | n \rangle \langle n | Q_i | m \rangle e^{+i(\omega_n - \omega_m)t} \right\}, \end{aligned} \quad (3.44)$$

where $\beta = 1/k_B T$ and Z is the partition function. Regularizing the integrals at $t \rightarrow \infty$ with $\exp(-\epsilon t)$ with $\epsilon = 0^+$, we use

$$\int_0^\infty dt e^{i(\omega - \Omega + i\epsilon)t} = \frac{i}{\omega - \Omega + i\epsilon} \quad (3.45)$$

to obtain the *spectral representation* of the (retarded) response function³,

$$\hat{\chi}_{ij}(\omega + i\epsilon) = \frac{1}{\hbar Z} \sum_{m,n} e^{-\beta\hbar\omega_m} \left\{ \frac{\langle m | Q_j | n \rangle \langle n | Q_i | m \rangle}{\omega - \omega_m + \omega_n + i\epsilon} - \frac{\langle m | Q_i | n \rangle \langle n | Q_j | m \rangle}{\omega + \omega_m - \omega_n + i\epsilon} \right\} \quad (3.46)$$

We will refer to this as $\hat{\chi}_{ij}(\omega)$; formally $\hat{\chi}_{ij}(\omega)$ has poles or a branch cut (for continuous spectra) along the $\text{Re}(\omega)$ axis. Diagrammatic perturbation theory does not give us $\hat{\chi}_{ij}(\omega)$, but rather the *time-ordered* response function,

$$\begin{aligned} \chi_{ij}^T(t - t') &\equiv \frac{i}{\hbar} \langle T Q_i(t) Q_j(t') \rangle \\ &= \frac{i}{\hbar} \langle Q_i(t) Q_j(t') \rangle \Theta(t - t') + \frac{i}{\hbar} \langle Q_j(t') Q_i(t) \rangle \Theta(t' - t) . \end{aligned} \quad (3.47)$$

The spectral representation of $\hat{\chi}_{ij}^T(\omega)$ is

$$\hat{\chi}_{ij}^T(\omega + i\epsilon) = \frac{1}{\hbar Z} \sum_{m,n} e^{-\beta\hbar\omega_m} \left\{ \frac{\langle m | Q_j | n \rangle \langle n | Q_i | m \rangle}{\omega - \omega_m + \omega_n - i\epsilon} - \frac{\langle m | Q_i | n \rangle \langle n | Q_j | m \rangle}{\omega + \omega_m - \omega_n + i\epsilon} \right\} \quad (3.48)$$

The difference between $\hat{\chi}_{ij}(\omega)$ and $\hat{\chi}_{ij}^T(\omega)$ is thus only in the sign of the infinitesimal $\pm i\epsilon$ term in one of the denominators.

Let us now define the real and imaginary parts of the product of expectations values encountered above:

$$\langle m | Q_i | n \rangle \langle n | Q_j | m \rangle \equiv A_{mn}(ij) + iB_{mn}(ij) . \quad (3.49)$$

That is⁴,

$$A_{mn}(ij) = \frac{1}{2} \langle m | Q_i | n \rangle \langle n | Q_j | m \rangle + \frac{1}{2} \langle m | Q_j | n \rangle \langle n | Q_i | m \rangle \quad (3.50)$$

$$B_{mn}(ij) = \frac{1}{2i} \langle m | Q_i | n \rangle \langle n | Q_j | m \rangle - \frac{1}{2i} \langle m | Q_j | n \rangle \langle n | Q_i | m \rangle . \quad (3.51)$$

Note that $A_{mn}(ij)$ is separately symmetric under interchange of either m and n , or of i and j , whereas $B_{mn}(ij)$ is separately antisymmetric under these operations:

$$A_{mn}(ij) = +A_{nm}(ij) = A_{nm}(ji) = +A_{mn}(ji) \quad (3.52)$$

$$B_{mn}(ij) = -B_{nm}(ij) = B_{nm}(ji) = -B_{mn}(ji) . \quad (3.53)$$

We define the *spectral densities*

$$\left\{ \begin{array}{l} \varrho_{ij}^A(\omega) \\ \varrho_{ij}^B(\omega) \end{array} \right\} \equiv \frac{1}{\hbar Z} \sum_{m,n} e^{-\beta\hbar\omega_m} \left\{ \begin{array}{l} A_{mn}(ij) \\ B_{mn}(ij) \end{array} \right\} \delta(\omega - \omega_n + \omega_m) , \quad (3.54)$$

³The spectral representation is sometimes known as the *Lehmann representation*.

⁴We assume all the Q_i are Hermitian, *i.e.* $Q_i = Q_i^\dagger$.

which satisfy

$$\varrho_{ij}^A(\omega) = +\varrho_{ji}^A(\omega) \quad , \quad \varrho_{ij}^A(-\omega) = +e^{-\beta\hbar\omega} \varrho_{ij}^A(\omega) \quad (3.55)$$

$$\varrho_{ij}^B(\omega) = -\varrho_{ji}^B(\omega) \quad , \quad \varrho_{ij}^B(-\omega) = -e^{-\beta\hbar\omega} \varrho_{ij}^B(\omega) . \quad (3.56)$$

In terms of these spectral densities,

$$\hat{\chi}'_{ij}(\omega) = \mathcal{P} \int_{-\infty}^{\infty} d\nu \frac{2\nu}{\nu^2 - \omega^2} \varrho_{ij}^A(\nu) - \pi(1 - e^{-\beta\hbar\omega}) \varrho_{ij}^B(\omega) = +\hat{\chi}'_{ij}(-\omega) \quad (3.57)$$

$$\hat{\chi}''_{ij}(\omega) = \mathcal{P} \int_{-\infty}^{\infty} d\nu \frac{2\omega}{\nu^2 - \omega^2} \varrho_{ij}^B(\nu) + \pi(1 - e^{-\beta\hbar\omega}) \varrho_{ij}^A(\omega) = -\hat{\chi}''_{ij}(-\omega). \quad (3.58)$$

For the time ordered response functions, we find

$$\hat{\chi}'_{ij}^{T}(\omega) = \mathcal{P} \int_{-\infty}^{\infty} d\nu \frac{2\nu}{\nu^2 - \omega^2} \varrho_{ij}^A(\nu) - \pi(1 + e^{-\beta\hbar\omega}) \varrho_{ij}^B(\omega) \quad (3.59)$$

$$\hat{\chi}''_{ij}^{T}(\omega) = \mathcal{P} \int_{-\infty}^{\infty} d\nu \frac{2\omega}{\nu^2 - \omega^2} \varrho_{ij}^B(\nu) + \pi(1 + e^{-\beta\hbar\omega}) \varrho_{ij}^A(\omega) . \quad (3.60)$$

Hence, knowledge of either the retarded or the time-ordered response functions is sufficient to determine the full behavior of the other:

$$[\hat{\chi}'_{ij}(\omega) + \hat{\chi}'_{ji}(\omega)] = [\hat{\chi}_{ij}^{T}(\omega) + \hat{\chi}_{ji}^{T}(\omega)] \quad (3.61)$$

$$[\hat{\chi}'_{ij}(\omega) - \hat{\chi}'_{ji}(\omega)] = [\hat{\chi}_{ij}^{T}(\omega) - \hat{\chi}_{ji}^{T}(\omega)] \times \tanh(\frac{1}{2}\beta\hbar\omega) \quad (3.62)$$

$$[\hat{\chi}''_{ij}(\omega) + \hat{\chi}''_{ji}(\omega)] = [\hat{\chi}_{ij}^{T}(\omega) + \hat{\chi}_{ji}^{T}(\omega)] \times \tanh(\frac{1}{2}\beta\hbar\omega) \quad (3.63)$$

$$[\hat{\chi}''_{ij}(\omega) - \hat{\chi}''_{ji}(\omega)] = [\hat{\chi}_{ij}^{T}(\omega) - \hat{\chi}_{ji}^{T}(\omega)] . \quad (3.64)$$

3.3.2 Energy Dissipation

The work done on the system must be positive! The rate at which work is done by the external fields is the power dissipated,

$$\begin{aligned} P &= \frac{d}{dt} \langle \Psi(t) | \mathcal{H}(t) | \Psi(t) \rangle \\ &= \left\langle \Psi(t) \left| \frac{\partial \mathcal{H}_1(t)}{\partial t} \right| \Psi(t) \right\rangle = - \sum_i \langle Q_i(t) \rangle \dot{\phi}_i(t) , \end{aligned} \quad (3.65)$$

where we have invoked the Feynman-Hellman theorem. The total energy dissipated is thus a functional of the external fields $\{\phi_i(t)\}$:

$$\begin{aligned} W &= \int_{-\infty}^{\infty} dt P(t) = - \int_{-\infty}^{\infty} dt \int_{-\infty}^{\infty} dt' \chi_{ij}(t-t') \dot{\phi}_i(t) \phi_j(t') \\ &= \int_{-\infty}^{\infty} \frac{d\omega}{2\pi} (-i\omega) \hat{\phi}_i^*(\omega) \hat{\chi}_{ij}(\omega) \hat{\phi}_j(\omega) . \end{aligned} \quad (3.66)$$

Since the $\{Q_i\}$ are Hermitian observables, the $\{\phi_i(t)\}$ must be real fields, in which case $\hat{\phi}_i^*(\omega) = \hat{\phi}_j(-\omega)$, whence

$$\begin{aligned} W &= \int_{-\infty}^{\infty} \frac{d\omega}{4\pi} (-i\omega) [\hat{\chi}_{ij}(\omega) - \hat{\chi}_{ji}(-\omega)] \hat{\phi}_i^*(\omega) \hat{\phi}_j(\omega) \\ &= \int_{-\infty}^{\infty} \frac{d\omega}{2\pi} \mathcal{M}_{ij}(\omega) \hat{\phi}_i^*(\omega) \hat{\phi}_j(\omega) \end{aligned} \quad (3.67)$$

where

$$\begin{aligned} \mathcal{M}_{ij}(\omega) &\equiv \frac{1}{2}(-i\omega) [\hat{\chi}_{ij}(\omega) - \hat{\chi}_{ji}(-\omega)] \\ &= \pi\omega (1 - e^{-\beta\hbar\omega}) (\varrho_{ij}^A(\omega) + i\varrho_{ij}^B(\omega)) . \end{aligned} \quad (3.68)$$

Note that as a matrix $M(\omega) = M^\dagger(\omega)$, so that $M(\omega)$ has real eigenvalues.

3.3.3 Correlation Functions

We define the *correlation function*

$$S_{ij}(t) \equiv \langle Q_i(t) Q_j(t') \rangle , \quad (3.69)$$

which has the spectral representation

$$\begin{aligned} \hat{S}_{ij}(\omega) &= 2\pi\hbar [\varrho_{ij}^A(\omega) + i\varrho_{ij}^B(\omega)] \\ &= \frac{2\pi}{Z} \sum_{m,n} e^{-\beta\hbar\omega_m} \langle m | Q_i | n \rangle \langle n | Q_j | m \rangle \delta(\omega - \omega_n + \omega_m) . \end{aligned} \quad (3.70)$$

Note that

$$\hat{S}_{ij}(-\omega) = e^{-\beta\hbar\omega} \hat{S}_{ij}^*(\omega) , \quad \hat{S}_{ji}(\omega) = \hat{S}_{ij}^*(\omega) . \quad (3.71)$$

and that

$$\hat{\chi}_{ij}(\omega) - \hat{\chi}_{ji}(-\omega) = \frac{i}{\hbar} (1 - e^{-\beta\hbar\omega}) \hat{S}_{ij}(\omega)$$

(3.72)

This result is known as the *fluctuation-dissipation theorem*, as it relates the equilibrium fluctuations $S_{ij}(\omega)$ to the dissipative quantity $\hat{\chi}_{ij}(\omega) - \hat{\chi}_{ji}(-\omega)$.

Time Reversal Symmetry

If the operators Q_i have a definite symmetry under time reversal, say

$$\mathcal{T} Q_i \mathcal{T}^{-1} = \eta_i Q_i , \quad (3.73)$$

then the correlation function satisfies

$$\hat{S}_{ij}(\omega) = \eta_i \eta_j \hat{S}_{ji}(\omega) . \quad (3.74)$$

3.3.4 Continuous Systems

The indices i and j could contain spatial information as well. Typically we will separate out spatial degrees of freedom, and write

$$S_{ij}(\mathbf{r} - \mathbf{r}', t - t') = \langle Q_i(\mathbf{r}, t) Q_j(\mathbf{r}', t') \rangle , \quad (3.75)$$

where we have assumed space and time translation invariance. The Fourier transform is defined as

$$\hat{S}(\mathbf{k}, \omega) = \int d^3 r \int_{-\infty}^{\infty} dt e^{-i\mathbf{k} \cdot \mathbf{r}} S(\mathbf{r}, t) \quad (3.76)$$

$$= \frac{1}{V} \int_{-\infty}^{\infty} dt e^{+i\omega t} \langle \hat{Q}(\mathbf{k}, t) \hat{Q}(-\mathbf{k}, 0) \rangle . \quad (3.77)$$

3.4 Example: $S = \frac{1}{2}$ Object in a Magnetic Field

Consider a $S = \frac{1}{2}$ object in an external field, described by the Hamiltonian

$$\mathcal{H}_0 = \gamma B_0 S^z \quad (3.78)$$

with $B_0 > 0$. (Without loss of generality, we can take the DC external field \mathbf{B}_0 to lie along \hat{z} .) The eigenstates are $|\pm\rangle$, with $\omega_{\pm} = \pm\frac{1}{2}\gamma B_0$. We apply a perturbation,

$$\mathcal{H}_1(t) = \gamma \mathbf{S} \cdot \mathbf{B}_1(t) . \quad (3.79)$$

At $T = 0$, the susceptibility tensor is

$$\begin{aligned} \chi_{\alpha\beta}(\omega) &= \frac{\gamma^2}{\hbar} \sum_n \left\{ \frac{\langle - | S^\beta | n \rangle \langle n | S^\alpha | - \rangle}{\omega - \omega_- + \omega_n + i\epsilon} - \frac{\langle - | S^\alpha | n \rangle \langle n | S^\beta | - \rangle}{\omega + \omega_- - \omega_n + i\epsilon} \right\} \\ &= \frac{\gamma^2}{\hbar} \left\{ \frac{\langle - | S^\beta | + \rangle \langle + | S^\alpha | - \rangle}{\omega + \gamma B_0 + i\epsilon} - \frac{\langle - | S^\alpha | + \rangle \langle + | S^\beta | - \rangle}{\omega - \gamma B_0 + i\epsilon} \right\} , \end{aligned} \quad (3.80)$$

where we have dropped the hat on $\hat{\chi}_{\alpha\beta}(\omega)$ for notational convenience. The only nonzero matrix elements are

$$\chi_{+-}(\omega) = \frac{\hbar\gamma^2}{\omega + \gamma B_0 + i\epsilon} \quad (3.81)$$

$$\chi_{-+}(\omega) = \frac{-\hbar\gamma^2}{\omega - \gamma B_0 + i\epsilon}, \quad (3.82)$$

or, equivalently,

$$\chi_{xx}(\omega) = \frac{1}{4}\hbar\gamma^2 \left\{ \frac{1}{\omega + \gamma B_0 + i\epsilon} - \frac{1}{\omega - \gamma B_0 + i\epsilon} \right\} = +\chi_{yy}(\omega) \quad (3.83)$$

$$\chi_{xy}(\omega) = \frac{i}{4}\hbar\gamma^2 \left\{ \frac{1}{\omega + \gamma B_0 + i\epsilon} + \frac{1}{\omega - \gamma B_0 + i\epsilon} \right\} = -\chi_{yx}(\omega). \quad (3.84)$$

3.4.1 Bloch Equations

The torque exerted on a magnetic moment $\boldsymbol{\mu}$ by a magnetic field \mathbf{H} is $\mathbf{N} = \boldsymbol{\mu} \times \mathbf{H}$, which is equal to the rate of change of the total angular momentum: $\dot{\mathbf{J}} = \mathbf{N}$. Since $\boldsymbol{\mu} = \gamma\mathbf{J}$, where γ is the gyromagnetic factor, we have $\dot{\boldsymbol{\mu}} = \gamma\boldsymbol{\mu} \times \mathbf{H}$. For noninteracting spins, the total magnetic moment, $\mathbf{M} = \sum_i \boldsymbol{\mu}_i$ then satisfies

$$\frac{d\mathbf{M}}{dt} = \gamma\mathbf{M} \times \mathbf{H}. \quad (3.85)$$

Now suppose that $\mathbf{H} = H_0 \hat{\mathbf{z}} + \mathbf{H}_\perp(t)$, where $\hat{\mathbf{z}} \cdot \mathbf{H}_\perp = 0$. In equilibrium, we have $\mathbf{M} = M_0 \hat{\mathbf{z}}$, with $M_0 = \chi_0 H_0$, where χ_0 is the static susceptibility. Phenomenologically, we assume that the relaxation to this equilibrium state is described by a longitudinal and transverse relaxation time, respectively known as T_1 and T_2 :

$$\dot{M}_x = \gamma M_y H_z - \gamma M_z H_y - \frac{M_x}{T_2} \quad (3.86)$$

$$\dot{M}_y = \gamma M_z H_x - \gamma M_x H_z - \frac{M_y}{T_2} \quad (3.87)$$

$$\dot{M}_z = \gamma M_x H_y - \gamma M_y H_x - \frac{M_z - M_0}{T_1}. \quad (3.88)$$

These are known as the *Bloch equations*. Mathematically, they are a set of coupled linear, first order, time-dependent, inhomogeneous equations. These may be recast in the form

$$\dot{M}^\alpha + R_{\alpha\beta} M^\beta = \psi^\alpha, \quad (3.89)$$

with $R_{\alpha\beta}(t) = T_{\alpha\beta}^{-1} - \gamma \epsilon_{\alpha\beta\delta} H^\delta(t)$, $\psi^\alpha = T_{\alpha\beta}^{-1} M_0^\beta$, and

$$T_{\alpha\beta} = \begin{pmatrix} T_2 & 0 & 0 \\ 0 & T_2 & 0 \\ 0 & 0 & T_1 \end{pmatrix}. \quad (3.90)$$

The formal solution is written

$$\mathbf{M}(t) = \int_0^t dt' U(t-t') \psi(t') + U(t) \psi(0) , \quad (3.91)$$

where the evolution matrix,

$$U(t) = \mathcal{T} \exp \left\{ - \int_0^t dt' R(t') \right\} , \quad (3.92)$$

is given in terms of the time-ordered exponential (earlier times to the right).

We can make analytical progress if we write $\mathbf{M} = M_0 \hat{\mathbf{z}} + \mathbf{m}$ and suppose $|\mathbf{H}_\perp| \ll H_0$ and $|\mathbf{m}| \ll M_0$, in which case we have

$$\dot{m}_x = \gamma H_0 m_y - \gamma H_y M_0 - \frac{m_x}{T_2} \quad (3.93)$$

$$\dot{m}_y = \gamma H_x M_0 - \gamma H_0 m_x - \frac{m_y}{T_2} \quad (3.94)$$

$$\dot{m}_z = -\frac{m_z}{T_1} , \quad (3.95)$$

which are equivalent to the following:

$$\ddot{m}_x + 2T_2^{-1}\dot{m}_x + (\gamma^2 H_0^2 + T_2^{-2})m_x = \gamma M_0(\gamma H_0 H_x - T_2^{-1}H_y - \dot{H}_y) \quad (3.96)$$

$$\ddot{m}_y + 2T_2^{-1}\dot{m}_y + (\gamma^2 H_0^2 + T_2^{-2})m_y = \gamma M_0(\gamma H_0 H_y + T_2^{-1}H_x + \dot{H}_x) \quad (3.97)$$

and $m_z(t) = m_z(0) \exp(-t/T_1)$. Solving the first two by Fourier transform,

$$(\gamma^2 H_0^2 + T_2^{-2} - \omega^2 - 2iT_2^{-2}\omega) \hat{m}_x(\omega) = \gamma M_0(\gamma H_0 H_x(\omega) + (i\omega - T_2^{-1})H_y(\omega)) \quad (3.98)$$

$$(\gamma^2 H_0^2 + T_2^{-2} - \omega^2 - 2iT_2^{-2}\omega) \hat{m}_y(\omega) = \gamma M_0(\gamma H_0 H_y(\omega) - (i\omega - T_2^{-1})H_x(\omega)) , \quad (3.99)$$

from which we read off

$$\chi_{xx}(\omega) = \frac{\gamma^2 H_0 M_0}{\gamma^2 H_0^2 + T_2^{-2} - \omega^2 - 2iT_2^{-1}\omega} = \chi_{yy}(\omega) \quad (3.100)$$

$$\chi_{xy}(\omega) = \frac{(i\omega - T_2^{-1}) \gamma M_0}{\gamma^2 H_0^2 + T_2^{-2} - \omega^2 - 2iT_2^{-1}\omega} = -\chi_{yx}(\omega) . \quad (3.101)$$

Note that Onsager reciprocity is satisfied:

$$\chi_{xy}(\omega, H_0) = \chi_{yx}^t(\omega, H_0) = \chi_{yx}(\omega, -H_0) = -\chi_{yx}(\omega, H_0) . \quad (3.102)$$

The lineshape is given by

$$\chi'_{xx}(\omega) = \frac{(\gamma^2 H_0^2 + T_2^{-2} - \omega^2) \gamma^2 H_0 M_0}{(\gamma^2 H_0^2 + T_2^{-2} - \omega^2)^2 + 4T_2^{-2}\omega^2} \quad (3.103)$$

$$\chi''_{xx}(\omega) = \frac{2\gamma H_0 M_0 T_2^{-1}\omega}{(\gamma^2 H_0^2 + T_2^{-2} - \omega^2)^2 + 4T_2^{-2}\omega^2} , \quad (3.104)$$

so a measure of the linewidth is a measure of T_2^{-1} .

3.5 Electromagnetic Response

Consider an interacting system consisting of electrons of charge $-e$ in the presence of a time-varying electromagnetic field. The electromagnetic field is given in terms of the 4-potential $A^\mu = (A^0, \mathbf{A})$:

$$\mathbf{E} = -\nabla A^0 - \frac{1}{c} \frac{\partial \mathbf{A}}{\partial t} \quad (3.105)$$

$$\mathbf{B} = \nabla \times \mathbf{A} . \quad (3.106)$$

The Hamiltonian for an N -particle system is

$$\begin{aligned} \mathcal{H}(A^\mu) &= \sum_{i=1}^N \left\{ \frac{1}{2m} \left(\mathbf{p}_i + \frac{e}{c} \mathbf{A}(\mathbf{x}_i, t) \right)^2 - e A^0(\mathbf{x}_i, t) + U(\mathbf{x}_i) \right\} + \sum_{i < j} v(\mathbf{x}_i - \mathbf{x}_j) \\ &= \mathcal{H}(0) - \frac{1}{c} \int d^3x j_\mu^p(\mathbf{x}) A^\mu(\mathbf{x}, t) + \frac{e^2}{2mc^2} \int d^3x n(\mathbf{x}) \mathbf{A}^2(\mathbf{x}, t) , \end{aligned} \quad (3.107)$$

where we have defined

$$n(\mathbf{x}) \equiv \sum_{i=1}^N \delta(\mathbf{x} - \mathbf{x}_i) \quad (3.108)$$

$$\mathbf{j}^p(\mathbf{x}) \equiv -\frac{e}{2m} \sum_{i=1}^N \left\{ \mathbf{p}_i \delta(\mathbf{x} - \mathbf{x}_i) + \delta(\mathbf{x} - \mathbf{x}_i) \mathbf{p}_i \right\} \quad (3.109)$$

$$j_0^p(\mathbf{x}) \equiv c e n(\mathbf{x}) . \quad (3.110)$$

Throughout this discussion we invoke covariant/contravariant notation, using the metric

$$g_{\mu\nu} = g^{\mu\nu} = \begin{pmatrix} -1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 1 \end{pmatrix} , \quad (3.111)$$

so that

$$j^\mu = (j^0, j^1, j^2, j^3) \equiv (j^0, \mathbf{j}) \quad (3.112)$$

$$j_\mu = g_{\mu\nu} j^\nu = (-j^0, j^1, j^2, j^3) \quad (3.113)$$

$$j_\mu A^\mu = j^\mu g_{\mu\nu} A^\nu = -j^0 A^0 + \mathbf{j} \cdot \mathbf{A} \equiv j \cdot \mathbf{A} \equiv j \cdot A \quad (3.114)$$

The quantity $j_\mu^p(\mathbf{x})$ is known as the *paramagnetic current density*. The physical current density $j_\mu(\mathbf{x})$ also contains a *diamagnetic* contribution:

$$j_\mu(\mathbf{x}) = -c \frac{\delta \mathcal{H}}{\delta A^\mu(\mathbf{x})} = j_\mu^p(\mathbf{x}) + j_\mu^d(\mathbf{x}) \quad (3.115)$$

$$j_\mu^d(\mathbf{x}) = -\frac{e^2}{mc} n(\mathbf{x}) \mathbf{A}(\mathbf{x}) = -\frac{e}{mc^2} j_0^p(\mathbf{x}) \mathbf{A}(\mathbf{x}) \quad (3.116)$$

$$j_0^d(\mathbf{x}) = 0 . \quad (3.117)$$

The electromagnetic response tensor $K_{\mu\nu}$ is defined via

$$\langle j_\mu(\mathbf{x}, t) \rangle = -\frac{c}{4\pi} \int d^3x' \int dt K_{\mu\nu}(\mathbf{x}t; \mathbf{x}'t') A^\nu(\mathbf{x}', t') , \quad (3.118)$$

valid to first order in the external 4-potential A^μ . From

$$\langle j_\mu^p(\mathbf{x}, t) \rangle = \frac{i}{\hbar c} \int d^3x' \int dt' \langle [j_\mu^p(\mathbf{x}, t), j_\nu^p(\mathbf{x}', t')] \rangle \Theta(t - t') A^\nu(\mathbf{x}', t') \quad (3.119)$$

$$\langle j_\mu^d(\mathbf{x}, t) \rangle = -\frac{e}{mc^2} \langle j_0^p(\mathbf{x}, t) \rangle A^\mu(\mathbf{x}, t) (1 - \delta_{\mu 0}) , \quad (3.120)$$

we conclude

$$\begin{aligned} K_{\mu\nu}(\mathbf{x}t; \mathbf{x}'t') &= \frac{4\pi}{i\hbar c^2} \langle [j_\mu^p(\mathbf{x}, t), j_\nu^p(\mathbf{x}', t')] \rangle \Theta(t - t') \\ &\quad + \frac{4\pi e}{mc^2} \langle j_0^p(\mathbf{x}, t) \rangle \delta(\mathbf{x} - \mathbf{x}') \delta(t - t') \delta_{\mu\nu} (1 - \delta_{\mu 0}) . \end{aligned} \quad (3.121)$$

The first term is sometimes known as the *paramagnetic response kernel*, $K_{\mu\nu}^p(x; x') = (4\pi i/\hbar c^2) \langle [j_\mu^p(x), j_\nu^p(x')] \rangle \Theta(t - t')$ is not directly calculable by perturbation theory. Rather, one obtains the time-ordered response function $K_{\mu\nu}^{p,T}(x; x') = (4\pi i/\hbar c^2) \langle T j_\mu^p(x) j_\nu^p(x') \rangle$, where $x^\mu \equiv (ct, \mathbf{x})$.

Second Quantized Notation

In the presence of an electromagnetic field described by the 4-potential $A^\mu = (c\phi, \mathbf{A})$, the Hamiltonian of an interacting electron system takes the form

$$\begin{aligned} \mathcal{H} &= \sum_\sigma \int d^3x \psi_\sigma^\dagger(\mathbf{x}) \left\{ \frac{1}{2m} \left(\frac{\hbar}{i} \nabla + \frac{e}{c} \mathbf{A} \right)^2 - eA^0(\mathbf{x}) + U(\mathbf{x}) \right\} \psi_\sigma(\mathbf{x}) \\ &\quad + \frac{1}{2} \sum_{\sigma, \sigma'} \int d^3x \int d^3x' \psi_\sigma^\dagger(\mathbf{x}) \psi_{\sigma'}^\dagger(\mathbf{x}') v(\mathbf{x} - \mathbf{x}') \psi_{\sigma'}(\mathbf{x}') \psi_\sigma(\mathbf{x}) , \end{aligned} \quad (3.122)$$

where $v(\mathbf{x} - \mathbf{x}')$ is a two-body interaction, *e.g.* $e^2/|\mathbf{x} - \mathbf{x}'|$, and $U(\mathbf{x})$ is the external scalar potential. Expanding in powers of A^μ ,

$$\mathcal{H}(A^\mu) = \mathcal{H}(0) - \frac{1}{c} \int d^3x j_\mu^p(\mathbf{x}) A^\mu(\mathbf{x}) + \frac{e^2}{2mc^2} \sum_\sigma \int d^3x \psi_\sigma^\dagger(\mathbf{x}) \psi_\sigma(\mathbf{x}) \mathbf{A}^2(\mathbf{x}) , \quad (3.123)$$

where the paramagnetic current density $j_\mu^p(\mathbf{x})$ is defined by

$$j_0^p(\mathbf{x}) = c e \sum_\sigma \psi_\sigma^\dagger(\mathbf{x}) \psi_\sigma(\mathbf{x}) \quad (3.124)$$

$$\mathbf{j}^p(\mathbf{x}) = \frac{ie\hbar}{2m} \sum_\sigma \left\{ \psi_\sigma^\dagger(\mathbf{x}) \nabla \psi_\sigma(\mathbf{x}) - (\nabla \psi_\sigma^\dagger(\mathbf{x})) \psi_\sigma(\mathbf{x}) \right\} . \quad (3.125)$$

3.5.1 Gauge Invariance and Charge Conservation

In Fourier space, with $q^\mu = (\omega/c, \mathbf{q})$, we have, for homogeneous systems,

$$\langle j_\mu(q) \rangle = -\frac{c}{4\pi} K_{\mu\nu}(q) A^\nu(q) . \quad (3.126)$$

Note our convention on Fourier transforms:

$$H(x) = \int \frac{d^4k}{(2\pi)^4} \hat{H}(k) e^{ik \cdot x} \quad (3.127)$$

$$\hat{H}(k) = \int d^4x H(x) e^{-ik \cdot x} , \quad (3.128)$$

where $k \cdot x \equiv k_\mu x^\mu = \mathbf{k} \cdot \mathbf{x} - \omega t$. Under a gauge transformation, $A^\mu \rightarrow A^\mu + \partial^\mu \Lambda$, i.e.

$$A^\mu(q) \rightarrow A^\mu(q) + i\Lambda(q) q^\mu , \quad (3.129)$$

where Λ is an arbitrary scalar function. Since the physical current must be unchanged by a gauge transformation, we conclude that $K_{\mu\nu}(q) q^\nu = 0$. We also have the continuity equation, $\partial^\mu j_\mu = 0$, the Fourier space version of which says $q^\mu j_\mu(q) = 0$, which in turn requires $q^\mu K_{\mu\nu}(q) = 0$. Therefore,

$$\boxed{\sum_\mu q^\mu K_{\mu\nu}(q) = \sum_\nu K_{\mu\nu}(q) q^\nu = 0} \quad (3.130)$$

In fact, the above conditions are identical owing to the reciprocity relations,

$$\text{Re } K_{\mu\nu}(q) = +\text{Re } K_{\nu\mu}(-q) \quad (3.131)$$

$$\text{Im } K_{\mu\nu}(q) = -\text{Im } K_{\nu\mu}(-q) , \quad (3.132)$$

which follow from the spectral representation of $K_{\mu\nu}(q)$. Thus,

$$\boxed{\text{gauge invariance} \iff \text{charge conservation}} \quad (3.133)$$

3.5.2 A Sum Rule

If we work in a gauge where $A^0 = 0$, then $\mathbf{E} = -c^{-1} \dot{\mathbf{A}}$, hence $\mathbf{E}(q) = iq^0 \mathbf{A}(q)$, and

$$\begin{aligned} \langle j_i(q) \rangle &= -\frac{c}{4\pi} K_{ij}(q) A^j(q) \\ &= -\frac{c}{4\pi} K_{ij}(q) \frac{c}{i\omega} E^j(q) \\ &\equiv \sigma_{ij}(q) E^j(q) . \end{aligned} \quad (3.134)$$

Thus, the conductivity tensor is given by

$$\sigma_{ij}(\mathbf{q}, \omega) = \frac{ic^2}{4\pi\omega} K_{ij}(\mathbf{q}, \omega) . \quad (3.135)$$

If, in the $\omega \rightarrow 0$ limit, the conductivity is to remain finite, then we must have

$$\int d^3x \int_0^\infty dt \left\langle [j_i^p(\mathbf{x}, t), j_j^p(0, 0)] \right\rangle e^{+i\omega t} = \frac{ie^2 n}{m} \delta_{ij} , \quad (3.136)$$

where n is the electron number density. This relation is spontaneously violated in a superconductor, where $\sigma(\omega) \propto \omega^{-1}$ as $\omega \rightarrow 0$.

3.5.3 Longitudinal and Transverse Response

In an isotropic system, the spatial components of $K_{\mu\nu}$ may be resolved into longitudinal and transverse components, since the only preferred spatial vector is \mathbf{q} itself. Thus, we may write

$$K_{ij}(\mathbf{q}, \omega) = K_{\parallel}(\mathbf{q}, \omega) \hat{q}_i \hat{q}_j + K_{\perp}(\mathbf{q}, \omega) (\delta_{ij} - \hat{q}_i \hat{q}_j) , \quad (3.137)$$

where $\hat{q}_i \equiv q_i/|\mathbf{q}|$. We now invoke current conservation, which says $q^\mu K_{\mu\nu}(q) = 0$. When $\nu = j$ is a spatial index,

$$q^0 K_{0j} + q^i K_{ij} = \frac{\omega}{c} K_{0j} + K_{\parallel} q_j , \quad (3.138)$$

which yields

$$K_{0j}(\mathbf{q}, \omega) = -\frac{c}{\omega} q^j K_{\parallel}(\mathbf{q}, \omega) = K_{j0}(\mathbf{q}, \omega) \quad (3.139)$$

In other words, the three components of $K_{0j}(q)$ are in fact completely determined by $K_{\parallel}(q)$ and q itself. When $\nu = 0$,

$$0 = q^0 K_{00} + q^i K_{i0} = \frac{\omega}{c} K_{00} - \frac{c}{\omega} \mathbf{q}^2 K_{\parallel} , \quad (3.140)$$

which says

$$K_{00}(\mathbf{q}, \omega) = \frac{c^2}{\omega^2} \mathbf{q}^2 K_{\parallel}(\mathbf{q}, \omega) \quad (3.141)$$

Thus, of the 10 freedoms of the symmetric 4×4 tensor $K_{\mu\nu}(q)$, there are only two independent ones – the functions $K_{\parallel}(q)$ and $K_{\perp}(q)$.

3.5.4 Neutral Systems

In neutral systems, we define the number density and number current density as

$$n(\mathbf{x}) = \sum_{i=1}^N \delta(\mathbf{x} - \mathbf{x}_i) \quad (3.142)$$

$$\mathbf{j}(\mathbf{x}) = \frac{1}{2m} \sum_{i=1}^N \left\{ \mathbf{p}_i \delta(\mathbf{x} - \mathbf{x}_i) + \delta(\mathbf{x} - \mathbf{x}_i) \mathbf{p}_i \right\} . \quad (3.143)$$

The charge and current susceptibilities are then given by

$$\chi(\mathbf{x}, t) = \frac{i}{\hbar} \langle [n(\mathbf{x}, t), n(0, 0)] \rangle \quad (3.144)$$

$$\chi_{ij}(\mathbf{x}, t) = \frac{i}{\hbar} \langle [j_i(\mathbf{x}, t), j_j(0, 0)] \rangle . \quad (3.145)$$

We define the longitudinal and transverse susceptibilities for homogeneous systems according to

$$\chi_{ij}(\mathbf{q}, \omega) = \chi_{\parallel}(\mathbf{q}, \omega) \hat{q}_i \hat{q}_j + \chi_{\perp}(\mathbf{q}, \omega) (\delta_{ij} - \hat{q}_i \hat{q}_j) . \quad (3.146)$$

From the continuity equation,

$$\nabla \cdot \mathbf{j} + \frac{\partial n}{\partial t} = 0 \quad (3.147)$$

follows the relation

$$\chi_{\parallel}(\mathbf{q}, \omega) = \frac{n}{m} + \frac{\omega^2}{\mathbf{q}^2} \chi(\mathbf{q}, \omega) . \quad (3.148)$$

EXERCISE: Derive eqn. (3.148).

The relation between $K_{\mu\nu}(q)$ and the neutral susceptibilities defined above is then

$$K_{00}(\mathbf{x}, t) = -4\pi e^2 \chi(\mathbf{x}, t) \quad (3.149)$$

$$K_{ij}(\mathbf{x}, t) = \frac{4\pi e^2}{c^2} \left\{ \frac{n}{m} \delta(\mathbf{x}) \delta(t) - \chi_{ij}(\mathbf{x}, t) \right\} , \quad (3.150)$$

and therefore

$$K_{\parallel}(\mathbf{q}, \omega) = \frac{4\pi e^2}{c^2} \left\{ \frac{n}{m} - \chi_{\parallel}(\mathbf{q}, \omega) \right\} \quad (3.151)$$

$$K_{\perp}(\mathbf{q}, \omega) = \frac{4\pi e^2}{c^2} \left\{ \frac{n}{m} - \chi_{\perp}(\mathbf{q}, \omega) \right\} . \quad (3.152)$$

3.5.5 The Meissner Effect and Superfluid Density

Suppose we apply an electromagnetic field \mathbf{E} . We adopt a gauge in which $A^0 = 0$, $\mathbf{E} = -c^{-1} \dot{\mathbf{A}}$, and $\mathbf{B} = \nabla \times \mathbf{A}$. To satisfy Maxwell's equations, we have $\mathbf{q} \cdot \mathbf{A}(\mathbf{q}, \omega) = 0$, i.e. $\mathbf{A}(\mathbf{q}, \omega)$ is purely transverse. But then

$$\langle \mathbf{j}(\mathbf{q}, \omega) \rangle = -\frac{c}{4\pi} K_{\perp}(\mathbf{q}, \omega) \mathbf{A}(\mathbf{q}, \omega) . \quad (3.153)$$

This leads directly to the Meissner effect whenever $\lim_{\mathbf{q} \rightarrow 0} K_{\perp}(\mathbf{q}, 0)$ is finite. To see this, we write

$$\begin{aligned} \nabla \times \mathbf{B} &= \nabla (\nabla \cdot \mathbf{A}) - \nabla^2 \mathbf{A} \\ &= \frac{4\pi}{c} \mathbf{j} + \frac{1}{c} \frac{\partial \mathbf{E}}{\partial t} \\ &= \frac{4\pi}{c} \left(-\frac{c}{4\pi} \right) K_{\perp}(-i\nabla, i\partial_t) \mathbf{A} - \frac{1}{c^2} \frac{\partial^2 \mathbf{A}}{\partial t^2} , \end{aligned} \quad (3.154)$$

which yields

$$\left(\nabla^2 - \frac{1}{c^2} \frac{\partial^2}{\partial t^2}\right) \mathbf{A} = K_{\perp}(-i\nabla, i\partial_t) \mathbf{A} . \quad (3.155)$$

In the static limit, $\nabla^2 \mathbf{A} = K_{\perp}(i\nabla, 0) \mathbf{A}$, and we define

$$\frac{1}{\lambda_L^2} \equiv \lim_{\mathbf{q} \rightarrow 0} K_{\perp}(\mathbf{q}, 0) . \quad (3.156)$$

λ_L is the *London penetration depth*, which is related to the *superfluid density* n_s by

$$n_s \equiv \frac{mc^2}{4\pi e^2 \lambda_L^2} \quad (3.157)$$

$$= n - m \lim_{\mathbf{q} \rightarrow 0} \chi_{\perp}(\mathbf{q}, 0) . \quad (3.158)$$

Ideal Bose Gas

We start from

$$\chi_{ij}(\mathbf{q}, t) = \frac{i}{\hbar V} \langle [j_i(\mathbf{q}, t), j_j(-\mathbf{q}, 0)] \rangle \quad (3.159)$$

$$j_i(\mathbf{q}) = \frac{\hbar}{2m} \sum_{\mathbf{k}} (2k_i + q_i) \psi_{\mathbf{k}}^\dagger \psi_{\mathbf{k}+\mathbf{q}} . \quad (3.160)$$

For the free Bose gas, with dispersion $\omega_{\mathbf{k}} = \hbar \mathbf{k}^2 / 2m$,

$$j_i(\mathbf{q}, t) = (2k_i + q_i) e^{i(\omega_{\mathbf{k}} - \omega_{\mathbf{k}+\mathbf{q}})t} \psi_{\mathbf{k}}^\dagger \psi_{\mathbf{k}+\mathbf{q}} \quad (3.161)$$

$$\begin{aligned} [j_i(\mathbf{q}, t), j_j(-\mathbf{q}, 0)] &= \frac{\hbar^2}{4m^2} \sum_{\mathbf{k}, \mathbf{k}'} (2k_i + q_i)(2k'_j - q_j) e^{i(\omega_{\mathbf{k}} - \omega_{\mathbf{k}+\mathbf{q}})t} \\ &\quad \times [\psi_{\mathbf{k}}^\dagger \psi_{\mathbf{k}+\mathbf{q}}, \psi_{\mathbf{k}'}^\dagger \psi_{\mathbf{k}'-\mathbf{q}}] \end{aligned} \quad (3.162)$$

Using

$$[AB, CD] = A[B, C]D + AC[B, D] + C[A, D]B + [A, C]DB , \quad (3.163)$$

we obtain

$$[j_i(\mathbf{q}, t), j_j(-\mathbf{q}, 0)] = \frac{\hbar^2}{4m^2} \sum_{\mathbf{k}} (2k_i + q_i)(2k_j + q_j) e^{i(\omega_{\mathbf{k}} - \omega_{\mathbf{k}+\mathbf{q}})t} \{n^0(\omega_{\mathbf{k}}) - n^0(\omega_{\mathbf{k}+\mathbf{q}})\} , \quad (3.164)$$

where $n^0(\omega)$ is the equilibrium Bose distribution⁵,

$$n^0(\omega) = \frac{1}{e^{\beta \hbar \omega} e^{-\beta \mu} - 1} . \quad (3.165)$$

⁵Recall that $\mu = 0$ in the condensed phase.

Thus,

$$\chi_{ij}(\mathbf{q}, \omega) = \frac{\hbar}{4m^2V} \sum_{\mathbf{k}} (2k_i + q_i)(2k_j + q_j) \frac{n^0(\omega_{\mathbf{k}+\mathbf{q}}) - n^0(\omega_{\mathbf{k}})}{\omega + \omega_{\mathbf{k}} - \omega_{\mathbf{k}+\mathbf{q}} + i\epsilon} \quad (3.166)$$

$$\begin{aligned} &= \frac{\hbar n_0}{4m^2} \left\{ \frac{1}{\omega + \omega_{\mathbf{q}} + i\epsilon} - \frac{1}{\omega - \omega_{\mathbf{q}} + i\epsilon} \right\} q_i q_j \\ &\quad + \frac{\hbar}{m^2} \int \frac{d^3k}{(2\pi)^3} \frac{n^0(\omega_{\mathbf{k}+\mathbf{q}/2}) - n^0(\omega_{\mathbf{k}-\mathbf{q}/2})}{\omega + \omega_{\mathbf{k}-\mathbf{q}/2} - \omega_{\mathbf{k}+\mathbf{q}/2} + i\epsilon} k_i k_j , \end{aligned} \quad (3.167)$$

where $n_0 = N_0/V$ is the condensate number density. Taking the $\omega = 0, \mathbf{q} \rightarrow 0$ limit yields

$$\chi_{ij}(\mathbf{q} \rightarrow 0, 0) = \frac{n_0}{m} \hat{q}_i \hat{q}_j + \frac{n'}{m} \delta_{ij} , \quad (3.168)$$

where n' is the density of uncondensed bosons. From this we read off

$$\chi_{\parallel}(\mathbf{q} \rightarrow 0, 0) = \frac{n}{m} , \quad \chi_{\perp}(\mathbf{q} \rightarrow 0, 0) = \frac{n'}{m} , \quad (3.169)$$

where $n = n_0 + n'$ is the total boson number density. The superfluid density, according to (3.158), is $n_s = n_0(T)$.

In fact, the ideal Bose gas is *not* a superfluid. Its excitation spectrum is too ‘soft’ - any superflow is unstable toward decay into single particle excitations.

3.6 Density-Density Correlations

In many systems, external probes couple to the number density $n(\mathbf{r}) = \sum_{i=1}^N \delta(\mathbf{r} - \mathbf{r}_i)$, and we may write the perturbing Hamiltonian as

$$\mathcal{H}_1(t) = - \int d^3r n(\mathbf{r}) U(\mathbf{r}, t) . \quad (3.170)$$

The response $\delta n \equiv n - \langle n \rangle_0$ is given by

$$\langle \delta n(\mathbf{r}, t) \rangle = \int d^3r' \int dt' \chi(\mathbf{r} - \mathbf{r}', t - t') U(\mathbf{r}', t') \quad (3.171)$$

$$\langle \delta \hat{n}(\mathbf{q}, \omega) \rangle = \chi(\mathbf{q}, \omega) \hat{U}(\mathbf{q}, \omega) , \quad (3.172)$$

where

$$\begin{aligned}\chi(\mathbf{q}, \omega) &= \frac{1}{\hbar V Z} \sum_{m,n} e^{-\beta \hbar \omega_m} \left\{ \frac{\left| \langle m | \hat{\mathbf{n}}_q | n \rangle \right|^2}{\omega - \omega_m + \omega_n + i\epsilon} - \frac{\left| \langle m | \hat{\mathbf{n}}_q | n \rangle \right|^2}{\omega + \omega_m - \omega_n + i\epsilon} \right\} \\ &= \frac{1}{\hbar} \int_{-\infty}^{\infty} d\nu S(\mathbf{q}, \nu) \left\{ \frac{1}{\omega + \nu + i\epsilon} - \frac{1}{\omega - \nu + i\epsilon} \right\} \end{aligned} \quad (3.173)$$

$$S(\mathbf{q}, \omega) = \frac{2\pi}{VZ} \sum_{m,n} e^{-\beta \hbar \omega_m} \left| \langle m | \hat{\mathbf{n}}_q | n \rangle \right|^2 \delta(\omega - \omega_n + \omega_m) . \quad (3.174)$$

Note that

$$\hat{\mathbf{n}}_q = \sum_{i=1}^N e^{-i\mathbf{q} \cdot \mathbf{r}_i} , \quad (3.175)$$

and that $\hat{\mathbf{n}}_q^\dagger = \hat{\mathbf{n}}_{-\mathbf{q}}$. $S(\mathbf{q}, \omega)$ is known as the *dynamic structure factor*. In a scattering experiment, where an incident probe (*e.g.* a neutron) interacts with the system via a potential $U(\mathbf{r} - \mathbf{R})$, where \mathbf{R} is the probe particle position, Fermi's Golden Rule says that the rate at which the incident particle deposits momentum $\hbar\mathbf{q}$ and energy $\hbar\omega$ into the system is given by

$$\begin{aligned}\mathcal{I}(\mathbf{q}, \omega) &= \frac{2\pi}{\hbar Z} \sum_{m,n} e^{-\beta \hbar \omega_m} \left| \langle m; \mathbf{p} | \mathcal{H}_1 | n; \mathbf{p} - \hbar\mathbf{q} \rangle \right|^2 \delta(\omega - \omega_n + \omega_m) \\ &= \frac{1}{\hbar} |\hat{U}(\mathbf{q})|^2 S(\mathbf{q}, \omega) . \end{aligned} \quad (3.176)$$

The quantity $|\hat{U}(\mathbf{q})|^2$ is called the *form factor*. In neutron scattering, the “on-shell” condition requires that the incident energy ε and momentum \mathbf{p} are related via the ballistic dispersion $\varepsilon = \mathbf{p}^2/2m_n$. Similarly, the final energy and momentum are related, hence

$$\varepsilon - \hbar\omega = \frac{\mathbf{p}^2}{2m_n} - \hbar\omega = \frac{(\mathbf{p} - \hbar\mathbf{q})^2}{2m_n} \implies \hbar\omega = \frac{\hbar\mathbf{q} \cdot \mathbf{p}}{m_n} - \frac{\hbar^2 \mathbf{q}^2}{2m_n} . \quad (3.177)$$

Hence, for fixed momentum transfer $\hbar\mathbf{q}$, ω can be varied by changing the incident momentum \mathbf{p} .

Another case of interest is the response of a system to a foreign object moving with trajectory $\mathbf{R}(t) = \mathbf{V}t$. In this case, $U(\mathbf{r}, t) = U(\mathbf{r} - \mathbf{R}(t))$, and

$$\begin{aligned}\hat{U}(\mathbf{q}, \omega) &= \int d^3r \int dt e^{-i\mathbf{q} \cdot \mathbf{r}} e^{i\omega t} U(\mathbf{r} - \mathbf{V}t) \\ &= 2\pi \delta(\omega - \mathbf{q} \cdot \mathbf{V}) \hat{U}(\mathbf{q})\end{aligned} \quad (3.178)$$

so that

$$\langle \delta n(\mathbf{q}, \omega) \rangle = 2\pi \delta(\omega - \mathbf{q} \cdot \mathbf{V}) \chi(\mathbf{q}, \omega) . \quad (3.179)$$

3.6.1 Sum Rules

From eqn. (3.174) we find

$$\begin{aligned} \int_{-\infty}^{\infty} \frac{d\omega}{2\pi} \omega S(\mathbf{q}, \omega) &= \frac{1}{VZ} \sum_{m,n} e^{-\beta \hbar \omega_m} \left| \langle m | \hat{n}_{\mathbf{q}} | n \rangle \right|^2 (\omega_n - \omega_m) \\ &= \frac{1}{\hbar V Z} \sum_{m,n} e^{-\beta \hbar \omega_m} \langle m | \hat{n}_{\mathbf{q}} | n \rangle \langle n | [\mathcal{H}, \hat{n}_{\mathbf{q}}^\dagger] | m \rangle \\ &= \frac{1}{\hbar V} \langle \hat{n}_{\mathbf{q}} [\mathcal{H}, \hat{n}_{\mathbf{q}}^\dagger] \rangle = \frac{1}{2\hbar V} \langle [\hat{n}_{\mathbf{q}}, [\mathcal{H}, \hat{n}_{\mathbf{q}}^\dagger]] \rangle , \end{aligned} \quad (3.180)$$

where the last equality is guaranteed by $\mathbf{q} \rightarrow -\mathbf{q}$ symmetry. Now if the potential is velocity independent, *i.e.* if

$$\mathcal{H} = -\frac{\hbar^2}{2m} \sum_{i=1}^N \nabla_i^2 + V(\mathbf{r}_1, \dots, \mathbf{r}_N) , \quad (3.181)$$

then with $\hat{n}_{\mathbf{q}}^\dagger = \sum_{i=1}^N e^{i\mathbf{q} \cdot \mathbf{r}_i}$ we obtain

$$\begin{aligned} [\mathcal{H}, \hat{n}_{\mathbf{q}}^\dagger] &= -\frac{\hbar^2}{2m} \sum_{i=1}^N [\nabla_i^2, e^{i\mathbf{q} \cdot \mathbf{r}_i}] \\ &= \frac{\hbar^2}{2im} \mathbf{q} \cdot \sum_{i=1}^N \left(\nabla_i e^{i\mathbf{q} \cdot \mathbf{r}_i} + e^{i\mathbf{q} \cdot \mathbf{r}_i} \nabla_i \right) \\ [\hat{n}_{\mathbf{q}}, [\mathcal{H}, \hat{n}_{\mathbf{q}}^\dagger]] &= \frac{\hbar^2}{2im} \mathbf{q} \cdot \sum_{i=1}^N \sum_{j=1}^N \left[e^{-i\mathbf{q} \cdot \mathbf{r}_j}, \nabla_i e^{i\mathbf{q} \cdot \mathbf{r}_i} + e^{i\mathbf{q} \cdot \mathbf{r}_i} \nabla_i \right] \\ &= N\hbar^2 \mathbf{q}^2 / m . \end{aligned} \quad (3.182)$$

We have derived the *f-sum rule*:

$$\int_{-\infty}^{\infty} \frac{d\omega}{2\pi} \omega S(\mathbf{q}, \omega) = \frac{N\hbar\mathbf{q}^2}{2mV} . \quad (3.184)$$

Note that this integral, which is the first moment of the structure factor, is *independent of the potential!*

$$\int_{-\infty}^{\infty} \frac{d\omega}{2\pi} \omega^n S(\mathbf{q}, \omega) = \frac{1}{\hbar V} \left\langle \hat{n}_{\mathbf{q}} \left[\overbrace{\mathcal{H}, [\mathcal{H}, \dots [\mathcal{H},}^{n \text{ times}}, \hat{n}_{\mathbf{q}}^\dagger] \dots] \right] \right\rangle . \quad (3.185)$$

Moments with $n > 1$ in general do depend on the potential. The $n = 0$ moment gives

$$\begin{aligned} S(\mathbf{q}) &\equiv \int_{-\infty}^{\infty} \frac{d\omega}{2\pi} \omega^n S(\mathbf{q}, \omega) = \frac{1}{\hbar V} \langle \hat{n}_{\mathbf{q}} \hat{n}_{\mathbf{q}}^\dagger \rangle \\ &= \frac{1}{\hbar} \int d^3r \langle n(\mathbf{r}) n(0) \rangle e^{-i\mathbf{q} \cdot \mathbf{r}} , \end{aligned} \quad (3.186)$$

which is the Fourier transform of the density-density correlation function.

Compressibility Sum Rule

The isothermal compressibility is given by

$$\kappa_T = -\frac{1}{V} \frac{\partial V}{\partial n} \Big|_T = \frac{1}{n^2} \frac{\partial n}{\partial \mu} \Big|_T . \quad (3.187)$$

Since a constant potential $U(\mathbf{r}, t)$ is equivalent to a chemical potential shift, we have

$$\langle \delta n \rangle = \chi(0, 0) \delta \mu \implies \kappa_T = \frac{1}{\hbar n^2} \lim_{\mathbf{q} \rightarrow 0} \int_{-\infty}^{\infty} \frac{d\omega}{\pi} \frac{S(\mathbf{q}, \omega)}{\omega} . \quad (3.188)$$

This is known as the *compressibility sum rule*.

3.7 Dynamic Structure Factor for the Electron Gas

The dynamic structure factor $S(\mathbf{q}, \omega)$ tells us about the spectrum of density fluctuations. The density operator $\hat{n}_{\mathbf{q}}^\dagger = \sum_i e^{i\mathbf{q} \cdot \mathbf{r}_i}$ increases the wavevector by \mathbf{q} . At $T = 0$, in order for $\langle n | \hat{n}_{\mathbf{q}}^\dagger | G \rangle$ to be nonzero (where $|G\rangle$ is the ground state, *i.e.* the filled Fermi sphere), the state n must correspond to a *particle-hole excitation*. For a given \mathbf{q} , the maximum excitation frequency is obtained by taking an electron just inside the Fermi sphere, with wavevector $\mathbf{k} = k_F \hat{\mathbf{q}}$ and transferring it to a state outside the Fermi sphere with wavevector $\mathbf{k} + \mathbf{q}$. For $|\mathbf{q}| < 2k_F$, the minimum excitation frequency is zero – one can always form particle-hole excitations with states adjacent to the Fermi sphere. For $|\mathbf{q}| > 2k_F$, the minimum excitation frequency is obtained by taking an electron just inside the Fermi sphere with wavevector $\mathbf{k} = -k_F \hat{\mathbf{q}}$ to an unfilled state outside the Fermi sphere with wavevector $\mathbf{k} + \mathbf{q}$. These cases are depicted graphically in fig. 3.2.

We therefore have

$$\omega_{\max}(q) = \frac{\hbar q^2}{2m} + \frac{\hbar k_F q}{m} \quad (3.189)$$

$$\omega_{\min}(q) = \begin{cases} 0 & \text{if } q \leq 2k_F \\ \frac{\hbar q^2}{2m} - \frac{\hbar k_F q}{m} & \text{if } q > 2k_F . \end{cases} \quad (3.190)$$

This is depicted in fig. 3.3. Outside of the region bounded by $\omega_{\min}(q)$ and $\omega_{\max}(q)$, there are no single pair excitations. It is of course easy to create *multiple pair* excitations with arbitrary energy and momentum, as depicted in fig. 3.4. However, these multipair states do not couple to the ground state $|G\rangle$ through a single application of the density operator $\hat{n}_{\mathbf{q}}^\dagger$, hence they have zero oscillator strength: $\langle n | \hat{n}_{\mathbf{q}}^\dagger | G \rangle = 0$ for any multipair state $|n\rangle$.

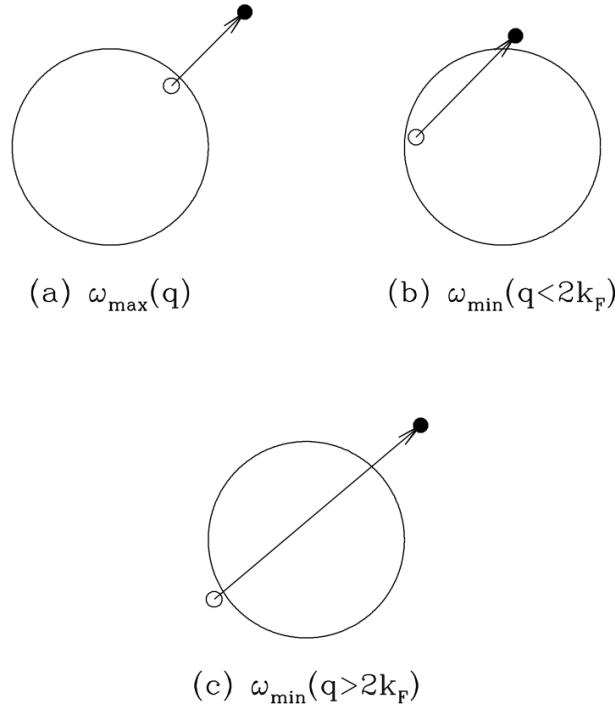


Figure 3.2: Minimum and maximum frequency particle-hole excitations in the free electron gas at $T = 0$. (a) To construct a maximum frequency excitation for a given \mathbf{q} , create a hole just inside the Fermi sphere at $\mathbf{k} = k_F \hat{\mathbf{q}}$ and an electron at $\mathbf{k}' = \mathbf{k} + \mathbf{q}$. (b) For $|\mathbf{q}| < 2k_F$ the minimum excitation frequency is zero. (c) For $|\mathbf{q}| > 2k_F$, the minimum excitation frequency is obtained by placing a hole at $\mathbf{k} = -k_F \hat{\mathbf{q}}$ and an electron at $\mathbf{k}' = \mathbf{k} + \mathbf{q}$.

3.7.1 Explicit $T = 0$ Calculation

We start with

$$S(\mathbf{r}, t) = \langle n(\mathbf{r}, t) n(0, 0) \rangle \quad (3.191)$$

$$= \int \frac{d^3 k}{(2\pi)^3} \int \frac{d^3 k'}{(2\pi)^3} e^{i\mathbf{k} \cdot \mathbf{r}} \sum_{i,j} \langle e^{-i\mathbf{k} \cdot \mathbf{r}_i(t)} e^{i\mathbf{k}' \cdot \mathbf{r}_j} \rangle. \quad (3.192)$$

The time evolution of the operator $\mathbf{r}_i(t)$ is given by $\mathbf{r}_i(t) = \mathbf{r}_i + \mathbf{p}_i t/m$, where $\mathbf{p}_i = -i\hbar\nabla_i$. Using the result

$$e^{A+B} = e^A e^B e^{-\frac{1}{2}[A,B]}, \quad (3.193)$$

which is valid when $[A, [A, B]] = [B, [A, B]] = 0$, we have

$$e^{-i\mathbf{k} \cdot \mathbf{r}_i(t)} = e^{i\hbar\mathbf{k}^2 t/2m} e^{-i\mathbf{k} \cdot \mathbf{r}} e^{-i\mathbf{k} \cdot \mathbf{p}_i t/m}, \quad (3.194)$$

hence

$$S(\mathbf{r}, t) = \int \frac{d^3 k}{(2\pi)^3} \int \frac{d^3 k'}{(2\pi)^3} e^{i\hbar\mathbf{k}^2 t/2m} e^{i\mathbf{k} \cdot \mathbf{r}} \sum_{i,j} \langle e^{-i\mathbf{k} \cdot \mathbf{r}_i} e^{i\mathbf{k} \cdot \mathbf{p}_i t/m} e^{i\mathbf{k}' \cdot \mathbf{r}_j} \rangle. \quad (3.195)$$

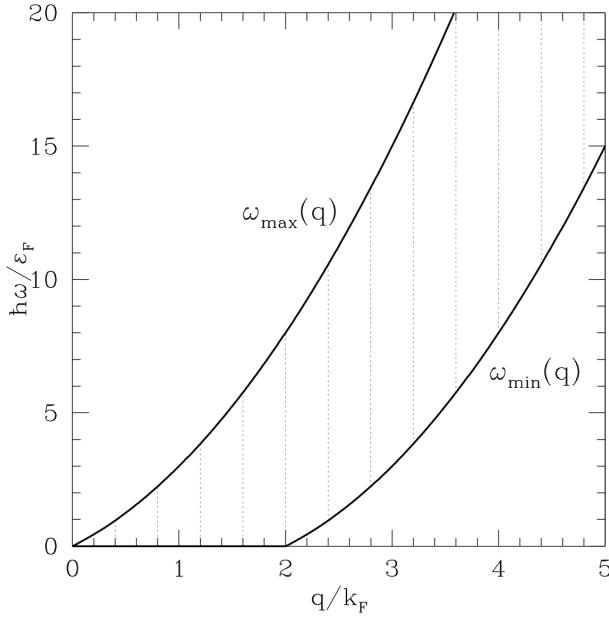


Figure 3.3: Minimum and maximum excitation frequency ω in units of ϵ_F/\hbar versus wavevector q in units of k_F . Outside the hatched areas, there are no *single pair* excitations.

We now break the sum up into diagonal ($i = j$) and off-diagonal ($i \neq j$) terms.

For the diagonal terms, with $i = j$, we have

$$\begin{aligned} \langle e^{-i\mathbf{k}\cdot\mathbf{r}_i} e^{i\mathbf{k}\cdot\mathbf{p}_i t/m} e^{i\mathbf{k}'\cdot\mathbf{r}_i} \rangle &= e^{-i\hbar\mathbf{k}\cdot\mathbf{k}'t/m} \langle e^{i(\mathbf{k}-\mathbf{k})\cdot\mathbf{r}_i} e^{i\mathbf{k}\cdot\mathbf{p}_i t/m} \rangle \\ &= e^{-i\hbar\mathbf{k}\cdot\mathbf{k}'t/m} \frac{(2\pi)^3}{NV} \delta(\mathbf{k} - \mathbf{k}') \sum_q \Theta(k_F - q) e^{-i\hbar\mathbf{k}\cdot\mathbf{q}t/m}, \end{aligned} \quad (3.196)$$

since the ground state $|G\rangle$ is a Slater determinant formed of single particle wavefunctions $\psi_{\mathbf{k}}(\mathbf{r}) = \exp(i\mathbf{q}\cdot\mathbf{r})/\sqrt{V}$ with $q < k_F$.

For $i \neq j$, we must include exchange effects. We then have

$$\begin{aligned} \langle e^{-i\mathbf{k}\cdot\mathbf{r}_i} e^{i\mathbf{k}\cdot\mathbf{p}_i t/m} e^{i\mathbf{k}'\cdot\mathbf{r}_j} \rangle &= \frac{1}{N(N-1)} \sum_{\mathbf{q}} \sum_{\mathbf{q}'} \Theta(k_F - q) \Theta(k_F - q') \\ &\quad \times \int \frac{d^3 r_i}{V} \int \frac{d^3 r_j}{V} e^{-i\hbar\mathbf{k}\cdot\mathbf{q}t/m} \left\{ e^{-i\mathbf{k}\cdot\mathbf{r}_i} e^{i\mathbf{k}'\cdot\mathbf{r}_j} \right. \\ &\quad \left. - e^{i(\mathbf{q}-\mathbf{q}'-\mathbf{k})\cdot\mathbf{r}_i} e^{i(\mathbf{q}'-\mathbf{q}+\mathbf{k}')\cdot\mathbf{r}_j} \right\} \\ &= \frac{(2\pi)^6}{N(N-1)V^2} \sum_{\mathbf{q}} \sum_{\mathbf{q}'} \Theta(k_F - q) \Theta(k_F - q') \\ &\quad \times e^{-i\hbar\mathbf{k}\cdot\mathbf{q}t/m} \left\{ \delta(\mathbf{k}) \delta(\mathbf{k}') - \delta(\mathbf{k} - \mathbf{k}') \delta(\mathbf{k} + \mathbf{q}' - \mathbf{q}) \right\}. \end{aligned} \quad (3.197)$$

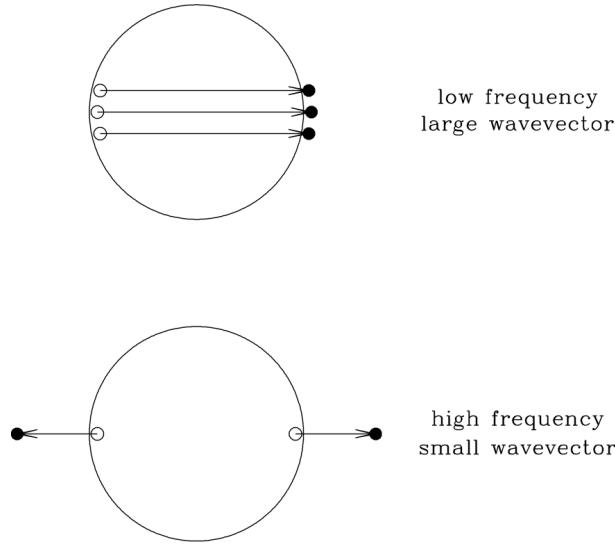


Figure 3.4: With multiple pair excitations, every part of (\mathbf{q}, ω) space is accessible. However, these states do not couple to the ground state $|G\rangle$ through a *single* application of the density operator $\hat{n}_{\mathbf{q}}^\dagger$.

Summing over the $i = j$ terms gives

$$S_{\text{diag}}(\mathbf{r}, t) = \int \frac{d^3k}{(2\pi)^3} e^{i\mathbf{k}\cdot\mathbf{r}} e^{-i\hbar k^2 t/2m} \int \frac{d^3q}{(2\pi)^3} \Theta(k_F - q) e^{-i\hbar \mathbf{k}\cdot\mathbf{q}t/m}, \quad (3.198)$$

while the off-diagonal terms yield

$$\begin{aligned} S_{\text{off-diag}} &= \int \frac{d^3k}{(2\pi)^3} e^{i\mathbf{k}\cdot\mathbf{r}} \int \frac{d^3q}{(2\pi)^3} \int \frac{d^3q'}{(2\pi)^3} \Theta(k_F - q) \Theta(k_F - q') \\ &\quad \times (2\pi)^3 \left\{ \delta(\mathbf{k}) - e^{+i\hbar k^2 t/2m} e^{-i\hbar \mathbf{k}\cdot\mathbf{q}t/m} \delta(\mathbf{q} - \mathbf{q}' - \mathbf{k}) \right\} \\ &= n^2 - \int \frac{d^3k}{(2\pi)^3} e^{i\mathbf{k}\cdot\mathbf{r}} e^{+i\hbar k^2 t/2m} \int \frac{d^3q}{(2\pi)^3} \Theta(k_F - q) \Theta(k_F - |\mathbf{k} - \mathbf{q}|) e^{-i\hbar \mathbf{k}\cdot\mathbf{q}t/m}, \end{aligned} \quad (3.199)$$

and hence

$$\begin{aligned} S(\mathbf{k}, \omega) &= n^2 (2\pi)^4 \delta(\mathbf{k}) \delta(\omega) + \int \frac{d^3q}{(2\pi)^3} \Theta(k_F - q) \left\{ 2\pi \delta\left(\omega - \frac{\hbar \mathbf{k}^2}{2m} - \frac{\hbar \mathbf{k} \cdot \mathbf{q}}{m}\right) \right. \\ &\quad \left. - \Theta(k_F - |\mathbf{k} - \mathbf{q}|) 2\pi \delta\left(\omega + \frac{\hbar \mathbf{k}^2}{2m} - \frac{\hbar \mathbf{k} \cdot \mathbf{q}}{m}\right) \right\} \\ &= (2\pi)^4 n^2 \delta(\mathbf{k}) \delta(\omega) + \int \frac{d^3q}{(2\pi)^3} \Theta(k_F - q) \Theta(|\mathbf{k} + \mathbf{q}| - k_F) \cdot 2\pi \delta\left(\omega - \frac{\hbar \mathbf{k}^2}{2m} - \frac{\hbar \mathbf{k} \cdot \mathbf{q}}{m}\right). \end{aligned} \quad (3.200)$$

For $\mathbf{k}, \omega \neq 0$, then,

$$\begin{aligned} S(\mathbf{k}, \omega) &= \frac{1}{2\pi} \int_0^{k_F} dq q^2 \int_{-1}^1 dx \Theta(\sqrt{k^2 + q^2 + 2kqx} - k_F) \delta\left(\omega - \frac{\hbar k^2}{2m} - \frac{\hbar k q}{m} x\right) \\ &= \frac{m}{2\pi\hbar k} \int_0^{k_F} dq q \Theta\left(\sqrt{q^2 + \frac{2m\omega}{\hbar}} - k_F\right) \int_{-1}^1 dx \delta\left(x + \frac{k}{2q} - \frac{m\omega}{\hbar k q}\right) \\ &= \frac{m}{4\pi\hbar k} \int_0^{k_F^2} du \Theta\left(u + \frac{2m\omega}{\hbar} - k_F^2\right) \Theta\left(u - \left|\frac{k}{2} - \frac{m\omega}{\hbar k}\right|^2\right). \end{aligned} \quad (3.201)$$

The constraints on u are

$$k_F^2 \geq u \geq \max\left(k_F^2 - \frac{2m\omega}{\hbar}, \left|\frac{k}{2} - \frac{m\omega}{\hbar k}\right|^2\right). \quad (3.202)$$

Clearly $\omega > 0$ is required. There are two cases to consider.

The first case is

$$k_F^2 - \frac{2m\omega}{\hbar} \geq \left|\frac{k}{2} - \frac{m\omega}{\hbar k}\right|^2 \implies 0 \leq \omega \leq \frac{\hbar k_F k}{m} - \frac{\hbar k^2}{2m}, \quad (3.203)$$

which in turn requires $k \leq 2k_F$. In this case, we have

$$\begin{aligned} S(\mathbf{k}, \omega) &= \frac{m}{4\pi\hbar k} \left\{ k_F^2 - \left(k_F^2 - \frac{2m\omega}{\hbar}\right) \right\} \\ &= \frac{m^2\omega}{2\pi\hbar^2 k}. \end{aligned} \quad (3.204)$$

The second case

$$k_F^2 - \frac{2m\omega}{\hbar} \leq \left|\frac{k}{2} - \frac{m\omega}{\hbar k}\right|^2 \implies \omega \geq \frac{\hbar k_F k}{m} - \frac{\hbar k^2}{2m}. \quad (3.205)$$

However, we also have that

$$\left|\frac{k}{2} - \frac{m\omega}{\hbar k}\right|^2 \leq k_F^2, \quad (3.206)$$

hence ω is restricted to the range

$$\frac{\hbar k}{2m} |k - 2k_F| \leq \omega \leq \frac{\hbar k}{2m} |k + 2k_F|. \quad (3.207)$$

The integral in (3.201) then gives

$$S(\mathbf{k}, \omega) = \frac{m}{4\pi\hbar k} \left\{ k_F^2 - \left|\frac{k}{2} - \frac{m\omega}{\hbar k}\right|^2 \right\}. \quad (3.208)$$

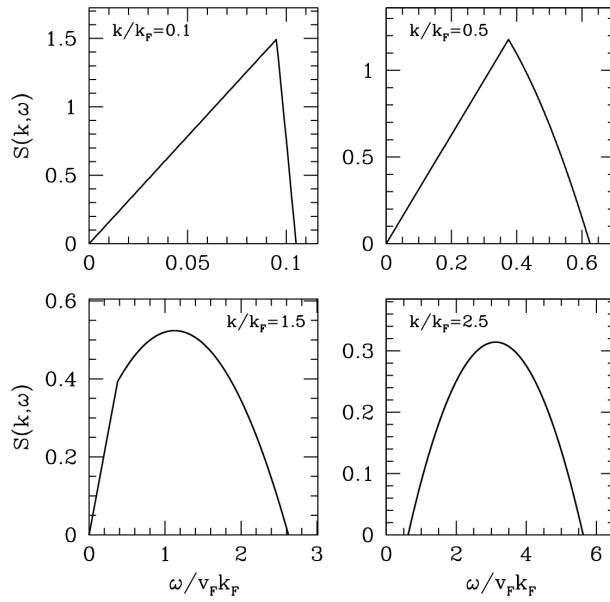


Figure 3.5: The dynamic structure factor $S(k, \omega)$ for the electron gas at various values of k/k_F .

Putting it all together,

$$S(\mathbf{k}, \omega) = \begin{cases} \frac{mk_F}{\pi^2 \hbar^2} \cdot \frac{\pi \omega}{2v_F k} & \text{if } 0 < \omega \leq v_F k - \frac{\hbar k^2}{2m} \\ \frac{mk_F}{\pi^2 \hbar^2} \cdot \frac{\pi k_F}{4k} \left[1 - \left(\frac{\omega}{v_F k} - \frac{k}{2k_F} \right)^2 \right] & \text{if } \left| v_F k - \frac{\hbar k^2}{2m} \right| \leq \omega \leq v_F k + \frac{\hbar k^2}{2m} \\ 0 & \text{if } \omega \geq v_F k + \frac{\hbar k^2}{2m} . \end{cases} \quad (3.209)$$

Integrating over all frequency gives the static structure factor,

$$S(\mathbf{k}) = \frac{1}{V} \langle n_{\mathbf{k}}^\dagger n_{\mathbf{k}} \rangle = \int_{-\infty}^{\infty} \frac{d\omega}{2\pi} S(\mathbf{k}, \omega) . \quad (3.210)$$

The result is

$$S(\mathbf{k}) = \begin{cases} \left(\frac{3k}{4k_F} - \frac{k^3}{16k_F^3} \right) n & \text{if } 0 < k \leq 2k_F \\ n & \text{if } k \geq 2k_F \\ Vn^2 & \text{if } k = 0 , \end{cases} \quad (3.211)$$

where $n = k_F^3 / 6\pi^2$ is the density (per spin polarization).

3.8 Charged Systems: Screening and Dielectric Response

3.8.1 Definition of the Charge Response Functions

Consider a many-electron system in the presence of a time-varying external charge density $\rho_{\text{ext}}(\mathbf{r}, t)$. The perturbing Hamiltonian is then

$$\begin{aligned}\mathcal{H}_1 &= -e \int d^3r \int d^3r' \frac{n(\mathbf{r}) \rho_{\text{ext}}(\mathbf{r}, t)}{|\mathbf{r} - \mathbf{r}'|} \\ &= -e \int \frac{d^3k}{(2\pi)^3} \frac{4\pi}{\mathbf{k}^2} \hat{\mathbf{n}}(\mathbf{k}) \hat{\rho}_{\text{ext}}(-\mathbf{k}, t) .\end{aligned}\quad (3.212)$$

The induced charge is $-e \delta n$, where δn is the induced number density:

$$\delta \hat{\mathbf{n}}(\mathbf{q}, \omega) = \frac{4\pi e}{\mathbf{q}^2} \chi(\mathbf{q}, \omega) \hat{\rho}_{\text{ext}}(\mathbf{q}, \omega) .\quad (3.213)$$

We can use this to determine the dielectric function $\epsilon(\mathbf{q}, \omega)$:

$$\nabla \cdot \mathbf{D} = 4\pi \rho_{\text{ext}} \quad (3.214)$$

$$\nabla \cdot \mathbf{E} = 4\pi (\rho_{\text{ext}} - e \langle \delta n \rangle) .\quad (3.215)$$

In Fourier space,

$$i\mathbf{q} \cdot \mathbf{D}(\mathbf{q}, \omega) = 4\pi \hat{\rho}_{\text{ext}}(\mathbf{q}, \omega) \quad (3.216)$$

$$i\mathbf{q} \cdot \mathbf{E}(\mathbf{q}, \omega) = 4\pi \hat{\rho}_{\text{ext}}(\mathbf{q}, \omega) - 4\pi e \langle \delta \hat{\mathbf{n}}(\mathbf{q}, \omega) \rangle ,\quad (3.217)$$

so that from $\mathbf{D}(\mathbf{q}, \omega) = \epsilon(\mathbf{q}, \omega) \mathbf{E}(\mathbf{q}, \omega)$ follows

$$\frac{1}{\epsilon(\mathbf{q}, \omega)} = \frac{i\mathbf{q} \cdot \mathbf{E}(\mathbf{q}, \omega)}{i\mathbf{q} \cdot \mathbf{D}(\mathbf{q}, \omega)} = 1 - \frac{\delta \hat{\mathbf{n}}(\mathbf{q}, \omega)}{Z \hat{\mathbf{n}}_{\text{ext}}(\mathbf{q}, \omega)} \quad (3.218)$$

$$= 1 - \frac{4\pi e^2}{\mathbf{q}^2} \chi(\mathbf{q}, \omega) .\quad (3.219)$$

A system is said to exhibit *perfect screening* if

$$\epsilon(\mathbf{q} \rightarrow 0, \omega = 0) = \infty \implies \lim_{\mathbf{q} \rightarrow 0} \frac{4\pi e^2}{\mathbf{q}^2} \chi(\mathbf{q}, 0) = 1 .\quad (3.220)$$

Here, $\chi(\mathbf{q}, \omega)$ is the usual density-density response function,

$$\chi(\mathbf{q}, \omega) = \frac{1}{\hbar V} \sum_n \frac{2\omega_{n\circ}}{\omega_{n\circ}^2 - (\omega + i\epsilon)^2} |\langle n | \hat{\mathbf{n}}_{\mathbf{q}} | 0 \rangle|^2 ,\quad (3.221)$$

where we content ourselves to work at $T = 0$, and where $\omega_{n\circ} \equiv \omega_n - \omega_{\circ}$ is the excitation frequency for the state $|n\rangle$.

From $\mathbf{j}_{\text{charge}} = \sigma \mathbf{E}$ and the continuity equation

$$i\mathbf{q} \cdot \langle \hat{\mathbf{j}}_{\text{charge}}(\mathbf{q}, \omega) \rangle = -ie\omega \langle \hat{\mathbf{n}}(\mathbf{q}, \omega) \rangle = i\sigma(\mathbf{q}, \omega) \mathbf{q} \cdot \mathbf{E}(\mathbf{q}, \omega) , \quad (3.222)$$

we find

$$\left(4\pi\hat{\rho}_{\text{ext}}(\mathbf{q}, \omega) - 4\pi e \langle \delta\hat{\mathbf{n}}(\mathbf{q}, \omega) \rangle \right) \sigma(\mathbf{q}, \omega) = -i\omega e \langle \delta\hat{\mathbf{n}}(\mathbf{q}, \omega) \rangle , \quad (3.223)$$

or

$$\frac{4\pi i}{\omega} \sigma(\mathbf{q}, \omega) = \frac{\langle \delta\hat{\mathbf{n}}(\mathbf{q}, \omega) \rangle}{e^{-1}\hat{\rho}_{\text{ext}}(\mathbf{q}, \omega) - \langle \delta\hat{\mathbf{n}}(\mathbf{q}, \omega) \rangle} = \frac{1 - \epsilon^{-1}(\mathbf{q}, \omega)}{\epsilon^{-1}(\mathbf{q}\omega)} = \epsilon(\mathbf{q}, \omega) - 1 . \quad (3.224)$$

Thus, we arrive at

$$\frac{1}{\epsilon(\mathbf{q}, \omega)} = 1 - \frac{4\pi e^2}{\mathbf{q}^2} \chi(\mathbf{q}, \omega) \quad , \quad \epsilon(\mathbf{q}, \omega) = 1 + \frac{4\pi i}{\omega} \sigma(\mathbf{q}, \omega)$$

(3.225)

Taken together, these two equations allow us to relate the conductivity and the charge response function,

$$\sigma(\mathbf{q}, \omega) = -\frac{i\omega}{\mathbf{q}^2} \frac{e^2 \chi(\mathbf{q}, \omega)}{1 - \frac{4\pi e^2}{\mathbf{q}^2} \chi(\mathbf{q}, \omega)} . \quad (3.226)$$

3.8.2 Static Screening: Thomas-Fermi Approximation

Imagine a time-independent, slowly varying electrical potential $\phi(\mathbf{r})$. We may define the ‘local chemical potential’ $\tilde{\mu}(\mathbf{r})$ as

$$\mu \equiv \tilde{\mu}(\mathbf{r}) - e\phi(\mathbf{r}) , \quad (3.227)$$

where μ is the bulk chemical potential. The local chemical potential is related to the local density by local thermodynamics. At $T = 0$,

$$\begin{aligned} \tilde{\mu}(\mathbf{r}) &\equiv \frac{\hbar^2}{2m} k_F^2(\mathbf{r}) = \frac{\hbar^2}{2m} \left(3\pi^2 n + 3\pi^2 \delta n(\mathbf{r}) \right)^{2/3} \\ &= \frac{\hbar^2}{2m} (3\pi^2 n)^{2/3} \left\{ 1 + \frac{2}{3} \frac{\delta n(\mathbf{r})}{n} + \dots \right\} , \end{aligned} \quad (3.228)$$

hence, to lowest order,

$$\delta n(\mathbf{r}) = \frac{3en}{2\mu} \phi(\mathbf{r}) . \quad (3.229)$$

This makes sense – a positive potential induces an increase in the local electron number density. In Fourier space,

$$\langle \delta\hat{\mathbf{n}}(\mathbf{q}, \omega = 0) \rangle = \frac{3en}{2\mu} \hat{\phi}(\mathbf{q}, \omega = 0) . \quad (3.230)$$

Poisson's equation is $-\nabla^2\phi = 4\pi\rho_{\text{tot}}$, *i.e.*

$$\begin{aligned} i\mathbf{q} \cdot \mathbf{E}(\mathbf{q}, 0) &= \mathbf{q}^2 \hat{\phi}(\mathbf{q}, 0) \\ &= 4\pi\hat{\rho}_{\text{ext}}(\mathbf{q}, 0) - 4\pi e \langle \delta\hat{\mathbf{n}}(\mathbf{q}, 0) \rangle \end{aligned} \quad (3.231)$$

$$= 4\pi\hat{\rho}_{\text{ext}}(\mathbf{q}, 0) - \frac{6\pi ne^2}{\mu} \hat{\phi}(\mathbf{q}, 0) , \quad (3.232)$$

and defining the Thomas-Fermi wavevector q_{TF} by

$$q_{\text{TF}}^2 \equiv \frac{6\pi ne^2}{\mu} , \quad (3.233)$$

we have

$$\hat{\phi}(\mathbf{q}, 0) = \frac{4\pi\hat{\rho}_{\text{ext}}(\mathbf{q}, 0)}{\mathbf{q}^2 + q_{\text{TF}}^2} , \quad (3.234)$$

hence

$$e \langle \delta\hat{\mathbf{n}}(\mathbf{q}, 0) \rangle = \frac{q_{\text{TF}}^2}{\mathbf{q}^2 + q_{\text{TF}}^2} \cdot \hat{\rho}_{\text{ext}}(\mathbf{q}, 0) \implies \boxed{\epsilon(\mathbf{q}, 0) = 1 + \frac{q_{\text{TF}}^2}{\mathbf{q}^2}} \quad (3.235)$$

Note that $\epsilon(\mathbf{q} \rightarrow 0, \omega = 0) = \infty$, so there is perfect screening.

The Thomas-Fermi wavelength is $\lambda_{\text{TF}} = q_{\text{TF}}^{-1}$, and may be written as

$$\lambda_{\text{TF}} = \left(\frac{\pi}{12} \right)^{1/6} \sqrt{r_s} a_B \simeq 0.800 \sqrt{r_s} a_B , \quad (3.236)$$

where r_s is the dimensionless free electron sphere radius, in units of the Bohr radius $a_B = \hbar^2/me^2 = 0.529\text{\AA}$, defined by $\frac{4}{3}\pi(r_s a_B)^3 n = 1$, hence $r_s \propto n^{-1/3}$. Small r_s corresponds to high density. Since Thomas-Fermi theory is a statistical theory, it can only be valid if there are many particles within a sphere of radius λ_{TF} , *i.e.* $\frac{4}{3}\pi\lambda_{\text{TF}}^3 n > 1$, or $r_s \lesssim (\pi/12)^{1/3} \simeq 0.640$. TF theory is applicable only in the high density limit.

In the presence of a δ -function external charge density $\rho_{\text{ext}}(\mathbf{r}) = Ze\delta(\mathbf{r})$, we have $\hat{\rho}_{\text{ext}}(\mathbf{q}, 0) = Ze$ and

$$\langle \delta\hat{\mathbf{n}}(\mathbf{q}, 0) \rangle = \frac{Zq_{\text{TF}}^2}{\mathbf{q}^2 + q_{\text{TF}}^2} \implies \boxed{\langle \delta n(\mathbf{r}) \rangle = \frac{Ze^{-r/\lambda_{\text{TF}}}}{4\pi r}} \quad (3.237)$$

Note the decay on the scale of λ_{TF} . Note also the perfect screening:

$$e \langle \delta\hat{\mathbf{n}}(\mathbf{q} \rightarrow 0, \omega = 0) \rangle = \hat{\rho}_{\text{ext}}(\mathbf{q} \rightarrow 0, \omega = 0) = Ze . \quad (3.238)$$

3.8.3 High Frequency Behavior of $\epsilon(\mathbf{q}, \omega)$

We have

$$\epsilon^{-1}(\mathbf{q}, \omega) = 1 - \frac{4\pi e^2}{\mathbf{q}^2} \chi(\mathbf{q}, \omega) \quad (3.239)$$

and, at $T = 0$,

$$\chi(\mathbf{q}, \omega) = \frac{1}{\hbar V} \sum_j |\langle j | \hat{n}_{\mathbf{q}}^\dagger | 0 \rangle|^2 \left\{ \frac{1}{\omega + \omega_{j0} + i\epsilon} - \frac{1}{\omega - \omega_{j0} + i\epsilon} \right\}, \quad (3.240)$$

where the number density operator is

$$\hat{n}_{\mathbf{q}}^\dagger = \begin{cases} \sum_i e^{i\mathbf{q} \cdot \mathbf{r}_i} & (1^{\text{st}} \text{ quantized}) \\ \sum_{\mathbf{k}} \psi_{\mathbf{k}+\mathbf{q}}^\dagger \psi_{\mathbf{k}} & (2^{\text{nd}} \text{ quantized: } \{\psi_{\mathbf{k}}, \psi_{\mathbf{k}'}^\dagger\} = \delta_{\mathbf{k}\mathbf{k}'} \} . \end{cases} \quad (3.241)$$

Taking the limit $\omega \rightarrow \infty$, we find

$$\chi(\mathbf{q}, \omega \rightarrow \infty) = -\frac{2}{\hbar V \omega^2} \sum_j |\langle j | \hat{n}_{\mathbf{q}}^\dagger | 0 \rangle|^2 \omega_{j0} = -\frac{2}{\hbar \omega^2} \int_{-\infty}^{\infty} \frac{d\omega'}{2\pi} \omega' S(\mathbf{q}, \omega') . \quad (3.242)$$

Invoking the f -sum rule, the above integral is $n\hbar\mathbf{q}^2/2m$, hence

$$\chi(\mathbf{q}, \omega \rightarrow \infty) = -\frac{n\mathbf{q}^2}{m\omega^2} , \quad (3.243)$$

and

$$\epsilon^{-1}(\mathbf{q}, \omega \rightarrow \infty) = 1 + \frac{\omega_p^2}{\omega^2} , \quad (3.244)$$

where

$$\omega_p \equiv \sqrt{\frac{4\pi n e^2}{m}} \quad (3.245)$$

is the *plasma frequency*.

3.8.4 Random Phase Approximation (RPA)

The electron charge appears nowhere in the free electron gas response function $\chi^0(\mathbf{q}, \omega)$. An interacting electron gas certainly does know about electron charge, since the Coulomb repulsion between electrons is part of the Hamiltonian. The idea behind the RPA is to obtain an approximation to the interacting $\chi(\mathbf{q}, \omega)$ from the noninteracting $\chi^0(\mathbf{q}, \omega)$ by self-consistently adjusting the charge so that the perturbing charge density is not $\rho_{\text{ext}}(\mathbf{r})$, but rather $\rho_{\text{ext}}(\mathbf{r}, t) - e \langle \delta n(\mathbf{r}, t) \rangle$. Thus, we write

$$e \langle \delta \hat{n}(\mathbf{q}, \omega) \rangle = \frac{4\pi e^2}{\mathbf{q}^2} \chi^{\text{RPA}}(\mathbf{q}, \omega) \hat{\rho}_{\text{ext}}(\mathbf{q}, \omega) \quad (3.246)$$

$$= \frac{4\pi e^2}{\mathbf{q}^2} \chi^0(\mathbf{q}, \omega) \left\{ \hat{\rho}_{\text{ext}}(\mathbf{q}, \omega) - e \langle \delta \hat{n}(\mathbf{q}, \omega) \rangle \right\} , \quad (3.247)$$

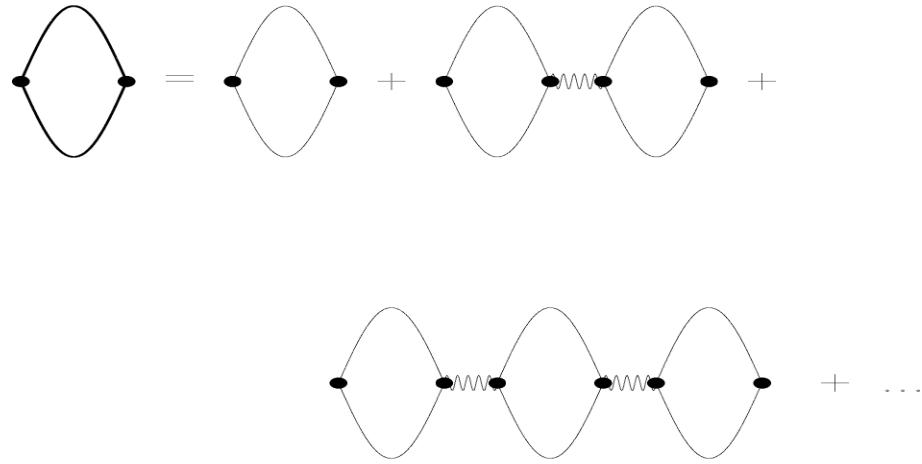


Figure 3.6: Perturbation expansion for RPA susceptibility bubble. Each bare bubble contributes a factor $\chi^0(\mathbf{q}, \omega)$ and each wavy interaction line $\hat{v}(\mathbf{q})$. The infinite series can be summed, yielding eqn. 3.249.

which gives

$$\boxed{\chi^{\text{RPA}}(\mathbf{q}, \omega) = \frac{\chi^0(\mathbf{q}, \omega)}{1 + \frac{4\pi e^2}{\mathbf{q}^2} \chi^0(\mathbf{q}, \omega)}} \quad (3.248)$$

Several comments are in order.

1. If the electron-electron interaction were instead given by a general $\hat{v}(\mathbf{q})$ rather than the specific Coulomb form $\hat{v}(\mathbf{q}) = 4\pi e^2/\mathbf{q}^2$, we would obtain

$$\chi^{\text{RPA}}(\mathbf{q}, \omega) = \frac{\chi^0(\mathbf{q}, \omega)}{1 + \hat{v}(\mathbf{q}) \chi^0(\mathbf{q}, \omega)} . \quad (3.249)$$

2. Within the RPA, there is perfect screening:

$$\lim_{\mathbf{q} \rightarrow 0} \frac{4\pi e^2}{\mathbf{q}^2} \chi^{\text{RPA}}(\mathbf{q}, \omega) = 1 . \quad (3.250)$$

3. The RPA expression may be expanded in an infinite series,

$$\chi^{\text{RPA}} = \chi^0 - \chi^0 \hat{v} \chi^0 + \chi^0 \hat{v} \chi^0 \hat{v} \chi^0 - \dots , \quad (3.251)$$

which has a diagrammatic interpretation, depicted in fig. 3.6. The perturbative expansion in the interaction \hat{v} may be resummed to yield the RPA result.

4. The RPA dielectric function takes the simple form

$$\epsilon^{\text{RPA}}(\mathbf{q}, \omega) = 1 + \frac{4\pi e^2}{\mathbf{q}^2} \chi^0(\mathbf{q}, \omega) . \quad (3.252)$$

5. Explicitly,

$$\text{Re } \epsilon^{\text{RPA}}(\mathbf{q}, \omega) = 1 + \frac{q_{\text{TF}}^2}{q^2} \left\{ \frac{1}{2} + \frac{k_{\text{F}}}{4q} \left[\left(1 - \frac{(\omega - \hbar q^2/2m)^2}{(v_{\text{F}}q)^2} \right) \ln \left| \frac{\omega - v_{\text{F}}q - \hbar q^2/2m}{\omega + v_{\text{F}}q - \hbar q^2/2m} \right| \right. \right. \\ \left. \left. + \left(1 - \frac{(\omega - \hbar q^2/2m)^2}{(v_{\text{F}}q)^2} \right) \ln \left| \frac{\omega - v_{\text{F}}q + \hbar q^2/2m}{\omega + v_{\text{F}}q + \hbar q^2/2m} \right| \right] \right\} \quad (3.253)$$

$$\text{Im } \epsilon^{\text{RPA}}(\mathbf{q}, \omega) = \begin{cases} \frac{\pi\omega}{2v_{\text{F}}q} \cdot \frac{q_{\text{TF}}^2}{q^2} & \text{if } 0 \leq \omega \leq v_{\text{F}}q - \hbar q^2/2m \\ \frac{\pi k_{\text{F}}}{4q} \left(1 - \frac{(\omega - \hbar q^2/2m)^2}{(v_{\text{F}}q)^2} \right) \frac{q_{\text{TF}}^2}{q^2} & \text{if } v_{\text{F}}q - \hbar q^2/2m \leq \omega \leq v_{\text{F}}q + \hbar q^2/2m \\ 0 & \text{if } \omega > v_{\text{F}}q + \hbar q^2/2m \end{cases} \quad (3.254)$$

6. Note that

$$\epsilon^{\text{RPA}}(\mathbf{q}, \omega \rightarrow \infty) = 1 - \frac{\omega_p^2}{\omega^2}, \quad (3.255)$$

in agreement with the f -sum rule, and

$$\epsilon^{\text{RPA}}(\mathbf{q} \rightarrow 0, \omega = 0) = 1 + \frac{q_{\text{TF}}^2}{q^2}, \quad (3.256)$$

in agreement with Thomas-Fermi theory.

7. At $\omega = 0$ we have

$$\epsilon^{\text{RPA}}(\mathbf{q}, 0) = 1 + \frac{q_{\text{TF}}^2}{q^2} \left\{ \frac{1}{2} + \frac{k_{\text{F}}}{2q} \left(1 - \frac{q^2}{4k_{\text{F}}^2} \right) \ln \left| \frac{q + 2k_{\text{F}}}{2 - 2k_{\text{F}}} \right| \right\}, \quad (3.257)$$

which is real and which has a singularity at $q = 2k_{\text{F}}$. This means that the long-distance behavior of $\langle \delta n(\mathbf{r}) \rangle$ must oscillate. For a local charge perturbation, $\rho_{\text{ext}}(\mathbf{r}) = Ze\delta(\mathbf{r})$, we have

$$\langle \delta n(\mathbf{r}) \rangle = \frac{Z}{2\pi^2 r} \int_0^\infty dq q \sin(qr) \left\{ 1 - \frac{1}{\epsilon(\mathbf{q}, 0)} \right\}, \quad (3.258)$$

and within the RPA one finds for long distances

$$\langle \delta n(\mathbf{r}) \rangle \sim \frac{Z \cos(2k_{\text{F}}r)}{r^3}, \quad (3.259)$$

rather than the Yukawa form familiar from Thomas-Fermi theory.

3.8.5 Plasmons

The RPA response function diverges when $\hat{v}(\mathbf{q}) \chi^0(\mathbf{q}, \omega) = -1$. For a given value of \mathbf{q} , this occurs for a specific value (or for a discrete set of values) of ω , *i.e.* it defines a dispersion relation $\omega = \Omega(\mathbf{q})$. The poles of χ^{RPA} and are identified with elementary excitations of the electron gas known as *plasmons*.

To find the plasmon dispersion, we first derive a result for $\chi^0(\mathbf{q}, \omega)$, starting with

$$\chi^0(\mathbf{q}, t) = \frac{i}{\hbar V} \langle [\hat{n}(\mathbf{q}, t), \hat{n}(-\mathbf{q}, 0)] \rangle \quad (3.260)$$

$$= \frac{i}{\hbar V} \left\langle \left[\sum_{\mathbf{k}\sigma} \psi_{\mathbf{k},\sigma}^\dagger \psi_{\mathbf{k}+\mathbf{q},\sigma}, \sum_{\mathbf{k}',\sigma'} \psi_{\mathbf{k}',\sigma'}^\dagger \psi_{\mathbf{k}'-\mathbf{q},\sigma'} \right] \right\rangle e^{i(\varepsilon(\mathbf{k}) - \varepsilon(\mathbf{k}+\mathbf{q}))t/\hbar} \Theta(t) , \quad (3.261)$$

where $\varepsilon(\mathbf{k})$ is the noninteracting electron dispersion. For a free electron gas, $\varepsilon(\mathbf{k}) = \hbar^2 \mathbf{k}^2 / 2m$. Next, using

$$[AB, CD] = A\{B, C\}D - \{A, C\}BD + CA\{B, D\} - C\{A, D\}B \quad (3.262)$$

we obtain

$$\chi^0(\mathbf{q}, t) = \frac{i}{\hbar V} \sum_{\mathbf{k}\sigma} (f_{\mathbf{k}} - f_{\mathbf{k}+\mathbf{q}}) e^{i(\varepsilon(\mathbf{k}) - \varepsilon(\mathbf{k}+\mathbf{q}))t/\hbar} \Theta(t) , \quad (3.263)$$

and therefore

$$\chi^0(\mathbf{q}, \omega) = 2 \int \frac{d^3k}{(2\pi)^3} \frac{f_{\mathbf{k}+\mathbf{q}} - f_{\mathbf{k}}}{\hbar\omega - \varepsilon(\mathbf{k} + \mathbf{q}) + \varepsilon(\mathbf{k}) + i\epsilon} . \quad (3.264)$$

Here,

$$f_{\mathbf{k}} = \frac{1}{e^{(\varepsilon(\mathbf{k}) - \mu)/k_B T} + 1} \quad (3.265)$$

is the Fermi distribution. At $T = 0$, $f_{\mathbf{k}} = \Theta(k_F - k)$, and for $\omega \gg v_F q$ we can expand $\chi^0(\mathbf{q}, \omega)$ in powers of ω^{-2} , yielding

$$\chi^0(\mathbf{q}, \omega) = -\frac{k_F^3}{3\pi^2} \cdot \frac{q^2}{m\omega^2} \left\{ 1 + \frac{3}{5} \left(\frac{\hbar k_F q}{m\omega} \right)^2 + \dots \right\} , \quad (3.266)$$

so the resonance condition becomes

$$\begin{aligned} 0 &= 1 + \frac{4\pi e^2}{q^2} \chi^0(\mathbf{q}, \omega) \\ &= 1 - \frac{\omega_p^2}{\omega^2} \cdot \left\{ 1 + \frac{3}{5} \left(\frac{v_F q}{\omega} \right)^2 + \dots \right\} . \end{aligned} \quad (3.267)$$

This gives the dispersion

$$\omega = \omega_p \left\{ 1 + \frac{3}{10} \left(\frac{v_F q}{\omega_p} \right)^2 + \dots \right\} . \quad (3.268)$$

Recall that the particle-hole continuum frequencies are bounded by $\omega_{\min}(q)$ and $\omega_{\max}(q)$, which are given in eqs. 3.190 and 3.189. Eventually the plasmon penetrates the particle-hole continuum, at which point it becomes heavily damped since it can decay into particle-hole excitations.

Chapter 4

Magnetism

4.1 References

- N. Ashcroft and N. D. Mermin, Solid State Physics
- R. M. White, Quantum Theory of Magnetism
- A. Auerbach, Interacting Electrons and Quantum Magnetism
- A. C. Hewson, The Kondo Problem to Heavy Fermions

4.2 Introduction

Magnetism arises from two sources. One is the classical magnetic moment due to a current density \mathbf{j} :

$$\mathbf{m} = \frac{1}{2c} \int d^3r \mathbf{r} \times \mathbf{j} . \quad (4.1)$$

The other is the intrinsic spin \mathbf{S} of a quantum-mechanical particle (typically the electron):

$$\mathbf{m} = g\mu_{\circ}\mathbf{S}/\hbar \quad ; \quad \mu_{\circ} = \frac{q\hbar}{2mc} = \text{magneton}, \quad (4.2)$$

where g is the g -factor (duh!). For the electron, $q = -e$ and $\mu_{\circ} = -\mu_{\text{B}}$, where $\mu_{\text{B}} = e\hbar/2mc$ is the Bohr magneton.

The Hamiltonian for a single electron is

$$\mathcal{H} = \frac{\boldsymbol{\pi}^2}{2m} + V(\mathbf{r}) + \frac{e\hbar}{2mc} \boldsymbol{\sigma} \cdot \mathbf{H} + \frac{\hbar}{4m^2c^2} \boldsymbol{\sigma} \cdot \nabla V \times \boldsymbol{\pi} + \frac{\hbar^2}{8mc^2} \nabla^2 V + \frac{(\boldsymbol{\pi}^2)^2}{8m^3c^2} + \dots , \quad (4.3)$$

where $\boldsymbol{\pi} = \mathbf{p} + \frac{e}{c}\mathbf{A}$. Where did this come from? From the Dirac equation,

$$i\hbar \frac{\partial \Psi}{\partial t} = \begin{pmatrix} mc^2 + V & c\boldsymbol{\sigma} \cdot \boldsymbol{\pi} \\ c\boldsymbol{\sigma} \cdot \boldsymbol{\pi} & -mc^2 + V \end{pmatrix} \Psi = E\Psi . \quad (4.4)$$

The wavefunction Ψ is a four-component Dirac spinor. Since mc^2 is the largest term for our applications, the upper two components of Ψ are essentially the positive energy components. However, the Dirac Hamiltonian mixes the upper two and lower two components of Ψ . One can ‘unmix’ them by making a canonical transformation,

$$\mathcal{H} \longrightarrow \mathcal{H}' \equiv e^{i\Lambda} \mathcal{H} e^{-i\Lambda}, \quad (4.5)$$

where Λ is Hermitian, to render \mathcal{H}' block diagonal. With $E = mc^2 + \varepsilon$, the effective Hamiltonian is given by (4.3). This is known as the Foldy-Wouthuysen transformation, the details of which may be found in many standard books on relativistic quantum mechanics and quantum field theory (*e.g.* Bjorken and Drell, Itzykson and Zuber, *etc.*). Note that the Dirac equation leads to $g = 2$. If we go beyond “tree level” and allow for radiative corrections within QED, we obtain a perturbative expansion,

$$g = 2 \left\{ 1 + \frac{\alpha}{2\pi} + \mathcal{O}(\alpha^2) \right\}, \quad (4.6)$$

where $\alpha = e^2/\hbar c \approx 1/137$ is the fine structure constant.¹

There are two terms in (4.3) which involve the electron’s spin:

$$\mathcal{H}_z = \frac{e\hbar}{2mc} \boldsymbol{\sigma} \cdot \mathbf{H} \quad (\text{Zeeman term}) \quad (4.7)$$

$$\mathcal{H}_{\text{so}} = \frac{\hbar}{4m^2c^2} \boldsymbol{\sigma} \cdot \nabla V \times (\mathbf{p} + \frac{e}{c}\mathbf{A}) \quad (\text{spin-orbit interaction}). \quad (4.8)$$

The numerical value for μ_B is

$$\mu_B = \frac{e\hbar}{2mc} = 5.788 \times 10^{-9} \text{ eV/G} \quad (4.9)$$

$$\mu_B/k_B = 6.717 \times 10^{-5} \text{ K/G}. \quad (4.10)$$

So on the scale of electron volts, laboratory scale fields ($H \lesssim 10^6$ G) are rather small. (And ~ 2000 times smaller for nucleons!).

The thermodynamic magnetization density is defined through

$$\mathbf{M} = -\frac{1}{V} \frac{\partial F}{\partial \mathbf{H}}, \quad (4.11)$$

where $F(T, V, \mathbf{H}, N)$ is the Helmholtz free energy. The susceptibility is then

$$\chi_{\alpha\beta}(\mathbf{r}, t | \mathbf{r}', t') = \frac{\delta \langle M^\alpha(\mathbf{r}, t) \rangle}{\delta H^\beta(\mathbf{r}', t')} = -\frac{\delta^2 F}{\delta H^\alpha(\mathbf{r}, t) \delta H^\beta(\mathbf{r}', t')}, \quad (4.12)$$

where F is replaced by a suitable generating function in the nonequilibrium case. Note that \mathbf{M} has the dimensions of \mathbf{H} .

¹Note that with $\mu_n = e\hbar/2m_p c$ for the nuclear magneton, $g_p = 2.793$ and $g_n = -1.913$. These results immediately suggest that there is composite structure to the nucleons, *i.e.* quarks.

4.2.1 Absence of Orbital Magnetism within Classical Physics

It is amusing to note that classical statistical mechanics cannot account for orbital magnetism. This is because the partition function is independent of the vector potential, which may be seen by simply shifting the origin of integration for the momentum \mathbf{p} :

$$Z(\mathbf{A}) = \text{Tr } e^{-\beta\mathcal{H}} = \int \frac{d^N\mathbf{r} d^N\mathbf{p}}{(2\pi\hbar)^{dN}} e^{-\beta\mathcal{H}(\{\mathbf{p}_i - \frac{q}{c}\mathbf{A}(\mathbf{r}_i), \mathbf{r}_i\})} \quad (4.13)$$

$$= \int \frac{d^N\mathbf{r} d^N\mathbf{p}}{(2\pi\hbar)^{dN}} e^{-\beta\mathcal{H}(\{\mathbf{p}_i, \mathbf{r}_i\})} = Z(\mathbf{A} = 0) . \quad (4.14)$$

Thus, the free energy must be independent of \mathbf{A} and hence independent of $\mathbf{H} = \nabla \times \mathbf{A}$, and $\mathbf{M} = -\partial F/\partial \mathbf{H} = 0$. This inescapable result is known as the Bohr-von Leeuwen theorem. Of course, classical statistical mechanics can describe magnetism due to intrinsic spin, *e.g.*

$$Z_{\text{Heisenberg}}(\mathbf{H}) = \prod_i \int \frac{d\hat{\Omega}_i}{4\pi} e^{\beta J \sum_{\langle ij \rangle} \hat{\Omega}_i \cdot \hat{\Omega}_j} e^{\beta g \mu_0 \mathbf{H} \cdot \sum_i \hat{\Omega}_i} \quad (4.15)$$

$$Z_{\text{Ising}}(H) = \sum_{\{\sigma_i\}} e^{\beta J \sum_{\langle ij \rangle} \sigma_i \sigma_j} e^{\beta g \mu_0 H \sum_i \sigma_i} . \quad (4.16)$$

Theories of magnetism generally fall into two broad classes: localized and itinerant. In the localized picture, we imagine a set of individual local moments \mathbf{m}_i localized at different points in space (typically, though not exclusively, on lattice sites). In the itinerant picture, we focus on delocalized Bloch states which also carry electron spin.

4.3 Basic Atomic Physics

4.3.1 Single electron Hamiltonian

We start with the single-electron Hamiltonian,

$$\mathcal{H} = \frac{1}{2m} \left(\mathbf{p} + \frac{e}{c} \mathbf{A} \right)^2 + V(\mathbf{r}) + g\mu_B \mathbf{H} \cdot \mathbf{s}/\hbar + \frac{1}{2m^2 c^2} \mathbf{s} \cdot \nabla V \times (\mathbf{p} + \frac{e}{c} \mathbf{A}) . \quad (4.17)$$

For a single atom or ion in a crystal, let us initially neglect effects due to its neighbors. In that case the potential $V(\mathbf{r})$ may be taken to be spherically symmetric, so with $\mathbf{l} = \mathbf{r} \times \mathbf{p}$, the first term in the spin-orbit part of the Hamiltonian becomes

$$\mathcal{H}_{\text{so}} = \frac{1}{2m^2 c^2} \mathbf{s} \cdot \nabla V \times \mathbf{p} = \frac{1}{2m^2 c^2} \frac{1}{r} \frac{\partial V}{\partial r} \mathbf{s} \cdot \mathbf{l} , \quad (4.18)$$

with $\nabla V = \hat{\mathbf{r}}(\partial V/\partial r)$. We adopt the gauge $\mathbf{A} = \frac{1}{2} \mathbf{H} \times \mathbf{r}$ so that

$$\frac{1}{2m} \left(\mathbf{p} + \frac{e}{c} \mathbf{A} \right)^2 = \frac{\mathbf{p}^2}{2m} + \frac{e}{2mc} \mathbf{H} \cdot \mathbf{l} + \frac{e^2}{8mc^2} (\mathbf{H} \times \mathbf{r})^2 . \quad (4.19)$$

Finally, restoring the full SO term, we have

$$\mathcal{H} = \frac{\mathbf{p}^2}{2m} + V(\mathbf{r}) + \frac{1}{\hbar} \mu_B (\mathbf{l} + 2\mathbf{s}) \cdot \mathbf{H} + \frac{1}{2m^2c^2} \frac{1}{r} \frac{\partial V}{\partial r} \mathbf{l} \cdot \mathbf{s} \quad (4.20)$$

$$+ \frac{e^2}{8mc^2} (\mathbf{H} \times \mathbf{r})^2 + \frac{\mu_B}{\hbar} \frac{rV'(r)}{4mc^2} 2\mathbf{s} \cdot [\mathbf{H} - \hat{\mathbf{r}}(\mathbf{H} \cdot \hat{\mathbf{r}})] . \quad (4.21)$$

The last term is usually negligible because $rV'(r)$ is on the scale of electron volts, while $mc^2 = 511 \text{ keV}$.² The $(\mathbf{H} \times \mathbf{r})^2$ breaks the rotational symmetry of an isolated ion, so in principle we cannot describe states by total angular momentum J . However, this effect is of order \mathbf{H}^2 , so if we only desire energies to order \mathbf{H}^2 , we needn't perturb the wavefunctions themselves with this term, *i.e.* we can simply treat it within first order perturbation theory, leading to an energy shift $\frac{e^2}{8mc^2} \langle \Psi | (\mathbf{H} \times \mathbf{r})^2 | \Psi \rangle$ in state $| n \rangle$.

4.3.2 The Darwin Term

If $V(\mathbf{r}) = -Ze^2/r$, then from $\nabla^2(1/r) = -4\pi\delta(\mathbf{r})$ we have

$$\frac{\hbar^2}{8m^2c^2} \nabla^2 V = \frac{Z\pi e^2 \hbar^2}{2m^2c^2} \delta(\mathbf{r}) , \quad (4.22)$$

which is centered at the nucleus. This leads to an energy shift for *s*-wave states,

$$\Delta E_{s\text{-wave}} = \frac{Z\pi e^2 \hbar^2}{2m^2c^2} |\psi(0)|^2 = \frac{\pi}{2} Z \alpha^2 a_B^3 |\psi(0)|^2 \cdot \frac{e^2}{a_B} , \quad (4.23)$$

where $\alpha = \frac{e^2}{\hbar c} \approx \frac{1}{137}$ is the fine structure constant and $a_B = \frac{\hbar^2}{me^2} \approx 0.529 \text{ \AA}$ is the Bohr radius. For large Z atoms and ions, the Darwin term contributes a significant contribution to the total energy.

4.3.3 Many electron Hamiltonian

The full N -electron atomic Hamiltonian, for nuclear charge Ze , is then

$$\begin{aligned} \mathcal{H} = & \sum_{i=1}^N \left[\frac{\mathbf{p}_i^2}{2m} - \frac{Ze^2}{r_i} \right] + \sum_{i < j}^N \frac{e^2}{|\mathbf{r}_i - \mathbf{r}_j|} + \sum_{i=1}^N \zeta(r_i) \mathbf{l}_i \cdot \mathbf{s}_i \\ & + \sum_{i=1}^N \left\{ \frac{\mu_B}{\hbar} (\mathbf{l}_i + 2\mathbf{s}_i) \cdot \mathbf{H} + \frac{e^2}{8mc^2} (\mathbf{H} \times \mathbf{r}_i)^2 \right\} , \end{aligned} \quad (4.24)$$

where $\mathbf{l}_i = \mathbf{r}_i \times \mathbf{p}_i$ and

$$\zeta(r) = \frac{Ze^2}{2m^2c^2} \frac{1}{r^3} = \frac{Z}{\hbar^2} \left(\frac{e^2}{\hbar c} \right)^2 \frac{e^2}{2a_B} \left(\frac{a_B}{r} \right)^3 . \quad (4.25)$$

²Exercise: what happens in the case of high Z atoms?

The total orbital and spin angular momentum are $\mathbf{L} = \sum_i \mathbf{l}_i$ and $\mathbf{S} = \sum_i \mathbf{s}_i$, respectively.

The full many-electron atom is too difficult a problem to solve exactly. Generally progress is made by using the Hartree-Fock method to reduce the many-body problem to an effective one-body problem. One starts with the interacting Hamiltonian

$$\mathcal{H} = \sum_{i=1}^N \left[\frac{\mathbf{p}_i^2}{2m} - \frac{Ze^2}{r_i} \right] + \sum_{i < j}^N \frac{e^2}{|\mathbf{r}_i - \mathbf{r}_j|}, \quad (4.26)$$

and treats \mathcal{H}_{so} as a perturbation, and writes the best possible single Slater determinant state:

$$\Psi_{\sigma_1 \dots \sigma_N}(\mathbf{r}_1, \dots, \mathbf{r}_N) = \mathcal{A} \left[\varphi_{1\sigma_1}(\mathbf{r}_1) \cdots \varphi_{N\sigma_N}(\mathbf{r}_N) \right], \quad (4.27)$$

where \mathcal{A} is the antisymmetrizer, and $\varphi_{i\sigma}(\mathbf{r})$ is a single particle wavefunction. In second-quantized notation, the Hamiltonian is

$$\mathcal{H} = \sum_{ij\sigma} T_{ij}^\sigma \psi_{i\sigma}^\dagger \psi_{j\sigma} + \sum_{ijkl} V_{ijkl}^{\sigma\sigma'} \psi_{i\sigma}^\dagger \psi_{j\sigma'}^\dagger \psi_{k\sigma'} \psi_{l\sigma}, \quad (4.28)$$

where

$$T_{ij}^\sigma = \int d^3r \varphi_{i\sigma}^*(\mathbf{r}) \left\{ -\frac{\hbar^2}{2m} \nabla^2 - \frac{Ze^2}{|\mathbf{r}|} \right\} \varphi_{j\sigma}(\mathbf{r}) \quad (4.29)$$

$$V_{ijkl}^{\sigma\sigma'} = \frac{1}{2} \int d^3r \int d^3r' \varphi_{i\sigma}^*(\mathbf{r}) \varphi_{j\sigma'}^*(\mathbf{r}') \frac{e^2}{|\mathbf{r} - \mathbf{r}'|} \varphi_{k\sigma'}(\mathbf{r}') \varphi_{l\sigma}(\mathbf{r}). \quad (4.30)$$

The Hartree-Fock energy is given by a sum over occupied orbitals:

$$E_{\text{HF}} = \sum_{i\sigma} T_{ii}^\sigma + \sum_{ij\sigma\sigma'} \left(V_{ijji}^{\sigma\sigma'} - V_{ijij}^{\sigma\sigma'} \delta_{\sigma\sigma'} \right). \quad (4.31)$$

The term $V_{ijji}^{\sigma\sigma'}$ is called the direct Coulomb, or ‘‘Hartree’’ term, and $V_{ijij}^{\sigma\sigma'} \delta_{\sigma\sigma'}$ is the exchange term. Introducing Lagrange multipliers $\varepsilon_{i\sigma}$ to enforce normalization of the $\{\varphi_{i\sigma}(\mathbf{r})\}$ and subsequently varying with respect to the wavefunctions yields the Hartree-Fock equations:

$$\left. \frac{\delta E_{\text{HF}}}{\delta \varphi_{i\sigma}(\mathbf{r})} \right|_{\langle \Psi | \Psi \rangle = 1} = 0 \quad \Rightarrow \quad (4.32)$$

$$\begin{aligned} \varepsilon_{i\sigma} \varphi_{i\sigma}(\mathbf{r}) &= \left\{ -\frac{\hbar^2}{2m} \nabla^2 - \frac{Ze^2}{r} \right\} \varphi_{i\sigma}(\mathbf{r}) + \sum_{j \neq i, \sigma'}^{\text{OCC}} \int d^3r' \frac{|\varphi_{j\sigma'}(\mathbf{r}')|^2}{|\mathbf{r} - \mathbf{r}'|} \varphi_{i\sigma}(\mathbf{r}) \\ &\quad - \sum_{j \neq i}^{\text{OCC}} \int d^3r' \frac{\varphi_{j\sigma}^*(\mathbf{r}') \varphi_{i\sigma}(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} \varphi_{j\sigma}(\mathbf{r}), \end{aligned} \quad (4.33)$$

which is a set of N coupled integro-differential equations. Multiplying by $\varphi_i^*(\mathbf{r})$ and integrating, we find

$$\varepsilon_{i\sigma} = T_{ii}^\sigma + 2 \sum_{j\sigma'}^{\text{OCC}} \left(V_{ijji}^{\sigma\sigma'} - V_{ijij}^{\sigma\sigma'} \delta_{\sigma\sigma'} \right). \quad (4.34)$$

It is a good approximation to assume that the Hartree-Fock wavefunctions $\varphi_i(\mathbf{r})$ are spherically symmetric, *i.e.*

$$\varphi_{i\sigma}(\mathbf{r}) = R_{nl}(r) Y_{lm}(\theta, \phi), \quad (4.35)$$

independent of σ . We can then classify the single particle states by the quantum numbers $n \in \{1, 2, \dots\}$, $l \in \{0, 1, \dots, n-1\}$, $m_l \in \{-l, \dots, +l\}$, and $m_s = \pm \frac{1}{2}$. The essential physics introduced by the Hartree-Fock method is that of *screening*. Close to the origin, a given electron senses a potential $-Ze^2/r$ due to the unscreened nucleus. Farther away, though, the nuclear charge is screened by the core electrons, and the potential decays faster than $1/r$. (Within the Thomas-Fermi approximation, the potential at long distances decays as $-Ce^2a_B^3/r^4$, where $C \simeq 100$ is a numerical factor, independent of Z .) Whereas states of different l and identical n are degenerate for the noninteracting hydrogenic atom, when the nuclear potential is screened, states of different l are no longer degenerate. Smaller l means smaller energy, since these states are localized closer to the nucleus, where the potential is large and negative and relatively unscreened. Hence, for a given n , the smaller l states fill up first. For a given l and n there are $(2s+1) \times (2l+1) = 4l+2$ states, labeled by the angular momentum and spin polarization quantum numbers m_l and m_s ; this group of orbitals is called a *shell*.

4.3.4 The Periodic Table

Based on the energetics derived from Hartree-Fock³, we can start to build up the Periodic Table. (Here I follow the pellucid discussion in G. Baym's *Lectures on Quantum Mechanics*, chapter 20.) Start with the lowest energy states, the 1s orbitals. Due to their lower angular momentum and concomitantly lower energy, the 2s states get filled before the 2p states. Filling the 1s, 2s, and 2p shells brings us to Ne, whose configuration is $(1s)^2 (2s)^2 (2p)^6$. Next comes the 3s and 3p shells, which hold eight more electrons, and bring us to Ar: $1s^2 2s^2 2p^6 3s^2 3p^6 = [\text{Ne}] 3s^2 3p^6$, where the symbol $[\text{Ne}]$ denotes the electronic configuration of neon. At this point, things start to get interesting. The 4s orbitals preempt the 3d orbitals, or at least most of the time. As we see from table 4.1, there are two anomalies

The 3d transition metal series ([Ar] core additions)				
Element (A^Z)	Sc^{21}	Ti^{22}	V^{23}	Cr^{24}
Configuration	$4s^2 3d^1$	$4s^2 3d^2$	$4s^2 3d^3$	$4s^1 3d^5$
Element (A^Z)	Fe^{26}	Co^{27}	Ni^{28}	Cu^{29}
Configuration	$4s^2 3d^6$	$4s^2 3d^7$	$4s^2 3d^8$	$4s^1 3d^{10}$
Element (A^Z)	Zn^{30}			
Configuration	$4s^2 3d^{10}$			

Table 4.1: Electronic configuration of 3d-series metals.

in the otherwise orderly filling of the 3d shell. Chromium's configuration is $[\text{Ar}] 4s^1 3d^5$ rather than the expected $[\text{Ar}] 4s^2 3d^4$, and copper's is $[\text{Ar}] 4s^1 3d^{10}$ and not $[\text{Ar}] 4s^2 3d^9$. In

³Hartree-Fock theory tends to overestimate ground state atomic energies by on the order of 1 eV per pair of electrons. The reason is that electron-electron correlations are not adequately represented in the Hartree-Fock many-body wavefunctions, which are single Slater determinants.

reality, the ground state is not a single Slater determinant and involves linear combinations of different configurations. But the largest weights are for Cr and Cu configurations with only one 4s electron. Zinc terminates the 3d series, after which we get orderly filling of the 4p orbitals.

Row five reiterates row four, with the filling of the 5s, 4d, and 5p shells. In row six, the lanthanide (4f) series interpolates between 6s and 5d (see also table 4.2), and the actinide (5f) series interpolates in row seven between 7s and 6d.

Shell:	1s	2s	2p	3s	3p	4s	3d	4p	5s
Termination:	He ²	Be ⁴	Ne ¹⁰	Mg ¹²	Ar ¹⁸	Ca ²⁰	Zn ³⁰	Kr ³⁶	Sr ³⁸
Shell:	4d	5p	6s	4f	5d	6p	7s	5f/6d	
Termination:	Cd ⁴⁶	Xe ⁵⁴	Ba ⁵⁶	Lu ⁷¹	Hg ⁸⁰	Rn ⁸⁶	Ra ⁸⁸	No ¹⁰²	

Table 4.2: Rough order in which shells of the Periodic Table are filled.

4.3.5 Splitting of Configurations: Hund's Rules

The electronic configuration does not uniquely specify a ground state. Consider, for example, carbon, whose configuration is $1s^2 2s^2 2p^2$. The filled 1s and 2s shells are inert. However, there are $\binom{6}{2} = 15$ possible ways to put two electrons in the 2p shell. It is convenient to label these states by total L , S , and J quantum numbers, where $\mathbf{J} = \mathbf{L} + \mathbf{S}$ is the total angular momentum. It is standard to abbreviate each such multiplet with the label $^{2S+1}L_J$, where $L = S, P, D, F, H$, etc.. For carbon, the largest L value we can get is $L = 2$, which requires $S = 0$ and hence $J = L = 2$. This 5-fold degenerate multiplet is then abbreviated 1D_2 . But we can also add together two $l = 1$ states to get total angular momentum $L = 1$ as well. The corresponding spatial wavefunction is antisymmetric, hence $S = 1$ in order to achieve an antisymmetric spin wavefunction. Since $|L - S| \leq J \leq |L + S|$ we have $J = 0$, $J = 1$, or $J = 2$ corresponding to multiplets 3P_0 , 3P_1 , and 3P_2 , with degeneracy 1, 3, and 5, respectively. The final state has $J = L = S = 0$: 1S_0 . The Hilbert space is then spanned by two $J = 0$ singlets, one $J = 1$ triplet, and two $J = 2$ quintuplets: $0 \oplus 0 \oplus 1 \oplus 2 \oplus 2$. That makes 15 states. Which of these is the ground state?

The ordering of the multiplets is determined by the famous *Hund's rules*:

1. The LS multiplet with the *largest* S has the lowest energy.
2. If the largest value of S is associated with several multiplets, the multiplet with the *largest* L has the lowest energy.
3. If an incomplete shell is not more than half-filled, then the lowest energy state has $J = |L - S|$. If the shell is more than half-filled, then $J = L + S$.

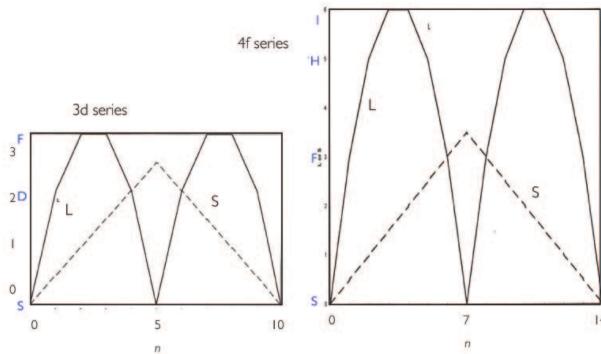


Figure 4.1: Variation of L , S , and J among the 3d and 4f series.

Hund's rules are largely empirical, but are supported by detailed atomic quantum many-body calculations. Basically, rule #1 prefers large S because this makes the spin part of the wavefunction maximally symmetric, which means that the spatial part is maximally antisymmetric. Electrons, which repel each other, prefer to exist in a spatially antisymmetric state. As for rule #2, large L expands the electron cloud somewhat, which also keeps the electrons away from each other.

Let's practice Hund's rules on a couple of ions:

- Mn^{4+} : The electronic configuration $[\text{Ar}] 4s^2 3d^3$ has an unfilled 3d shell with three electrons. First maximize S by polarizing all spins parallel (up, say), yielding $S = \frac{3}{2}$. Next maximize L consistent with Pauli exclusion, which says $L = 2 + 1 + 0 = 3$. Finally, since the shell is less than half-filled, $J = |L - S| = \frac{3}{2}$, and the ground state term is ${}^4\text{F}_{3/2}$.
- Fe^{2+} : The electronic configuration $[\text{Ar}] 4s^2 3d^6$ has an unfilled 3d shell with six electrons, or four holes. First maximize S by making the spins of the holes parallel, yielding $S = 2$. Next, maximize L consistent with Pauli exclusion, which says $L = 2 + 1 + 0 + (-1) = 2$ (adding L_z for the four holes). Finally, the shell is more than half-filled, which means $J = L + S = 4$. The ground state term is ${}^5\text{D}_4$.
- Nd^{3+} : The electronic configuration $[\text{Xe}] 6s^2 4f^3$ has an unfilled 4f shell with three electrons. First maximize S by making the electron spins parallel, yielding $S = \frac{3}{2}$. Next, maximize L consistent with Pauli exclusion: $L = 3 + 2 + 1 = 6$. Finally, since the shell is less than half-filled, we have $J = |L - S| = \frac{9}{2}$. The ground state term is ${}^4\text{I}_{9/2}$.

4.3.6 Spin-Orbit Interaction

Hund's third rule derives from an analysis of the spin-orbit Hamiltonian,

$$\mathcal{H}_{\text{so}} = \sum_{i=1}^N \zeta(r_i) \mathbf{l}_i \cdot \mathbf{s}_i . \quad (4.36)$$

This commutes with \mathbf{J}^2 , \mathbf{L}^2 , and \mathbf{S}^2 , so we can still classify eigenstates according to total J , L , and S . The Wigner-Eckart theorem then guarantees that within a given J multiplet, we can replace any tensor operator transforming as

$$\mathcal{R} T_{JM} \mathcal{R}^\dagger = \sum_{M'} \mathcal{D}_{MM'}^J(\alpha, \beta, \gamma) T_{JM'} , \quad (4.37)$$

where \mathcal{R} corresponds to a rotation through Euler angles α , β , and γ , by a product of a reduced matrix element and a Clebsch-Gordon coefficient:

$$\langle JM | T_{J''M''} | J'M' \rangle = C \begin{pmatrix} J & J' & J'' \\ M & M' & M'' \end{pmatrix} \langle J || T_{J''} || J' \rangle . \quad (4.38)$$

In other words, if two tensor operators have the same rank, their matrix elements are proportional. Both \mathcal{H}_{so} and $\mathbf{L} \cdot \mathbf{S}$ are products of rank $L = 1$, $S = 1$ tensor operators, hence we may replace

$$\mathcal{H}_{\text{so}} \longrightarrow \tilde{\mathcal{H}}_{\text{so}} = \Lambda \mathbf{L} \cdot \mathbf{S} , \quad (4.39)$$

where $\Lambda = \Lambda(N, L, S)$ must be computed from, say, the expectation value of \mathcal{H}_{so} in the state $|JLSJ\rangle$. This requires detailed knowledge of the atomic many-body wavefunctions. However, once Λ is known, the multiplet splittings are easily obtained:

$$\begin{aligned} \tilde{\mathcal{H}}_{\text{so}} &= \frac{1}{2} \Lambda (\mathbf{J}^2 - \mathbf{L}^2 - \mathbf{S}^2) \\ &= \frac{1}{2} \hbar^2 \Lambda (J(J+1) - L(L+1) - S(S+1)) . \end{aligned} \quad (4.40)$$

Thus,

$$E(N, L, S, J) - E(N, L, S, J-1) = \Lambda J \hbar^2 . \quad (4.41)$$

If we replace $\zeta(r_i)$ by its average, then we can find Λ by the following argument. If the last shell is not more than half filled, then by Hund's first rule, the spins are all parallel. Thus $S = \frac{1}{2}N$ and $\mathbf{s}_i = \mathbf{S}/N$, whence $\Lambda = \langle \zeta \rangle / 2S$. Finding $\langle \zeta \rangle$ is somewhat tricky. For $Z^{-1} \ll r/a_B \ll 1$, one can use the WKB method to obtain $\psi(r = a_B/Z) \sim \sqrt{Z}$, whence

$$\langle \zeta \rangle \sim \left(\frac{Ze^2}{\hbar c} \right)^2 \frac{me^4}{\hbar^4} \quad (4.42)$$

and

$$\Lambda \sim Z^2 \alpha^2 \hbar^{-2} \text{Ry} , \quad (4.43)$$

where $\alpha = e^2/\hbar c \simeq 1/137$. For heavy atoms, $Z\alpha \sim 1$ and the energy is on the order of that for the outer electrons in the atom.

For shells which are more than half filled, we treat the problem in terms of the *holes* relative to the filled shell case. Since filled shells are inert,

$$\mathcal{H}_{\text{so}} = - \sum_{j=1}^{N_h} \tilde{\mathbf{l}}_j \cdot \tilde{\mathbf{s}}_j , \quad (4.44)$$

where $N_h = 4l + 2 - N$. $\tilde{\mathbf{l}}_j$ and $\tilde{\mathbf{s}}_j$ are the orbital and spin angular momenta of the holes; $\mathbf{L} = -\sum_j \tilde{\mathbf{l}}_j$ and $\mathbf{S} = -\sum_j \tilde{\mathbf{s}}_j$. We then conclude $\Lambda = -\langle \zeta \rangle / 2S$. Thus, we arrive at Hund's third rule, which says

$$N \leq 2L + 1 \quad (\leq \text{half-filled}) \quad \Rightarrow \quad \Lambda > 0 \quad \Rightarrow \quad J = |L - S| \quad (4.45)$$

$$N > 2L + 1 \quad (> \text{half-filled}) \quad \Rightarrow \quad \Lambda < 0 \quad \Rightarrow \quad J = |L + S| . \quad (4.46)$$

4.3.7 Crystal Field Splittings

Consider an ion with a single d electron (*e.g.* Cr³⁺) or a single d hole (*e.g.* Cu²⁺) in a cubic or octahedral environment. The 5-fold degeneracy of the d levels is lifted by the crystal electric field. Suppose the atomic environment is octahedral, with anions at the vertices of the octahedron (typically O²⁻ ions). In order to minimize the Coulomb repulsion between the d electron and the neighboring anions, the $d_{x^2-y^2}$ and $d_{3z^2-r^2}$ orbitals are energetically disfavored, and this doublet lies at higher energy than the $\{d_{xy}, d_{xz}, d_{yz}\}$ triplet.

The crystal field potential is crudely estimated as

$$V_{\text{CF}} = \sum_{\mathbf{R}}^{(\text{nbrs})} V(\mathbf{r} - \mathbf{R}) , \quad (4.47)$$

where the sum is over neighboring ions, and V is the atomic potential.

The angular dependence of the cubic crystal field states may be written as follows:

$$\begin{aligned} d_{x^2-y^2}(\hat{\mathbf{r}}) &= \frac{1}{\sqrt{2}} Y_{2,2}(\hat{\mathbf{r}}) + \frac{1}{\sqrt{2}} Y_{2,-2}(\hat{\mathbf{r}}) \\ d_{3z^2-r^2}(\hat{\mathbf{r}}) &= Y_{2,0}(\hat{\mathbf{r}}) \\ d_{xy}(\hat{\mathbf{r}}) &= \frac{i}{\sqrt{2}} Y_{2,-2}(\hat{\mathbf{r}}) - \frac{i}{\sqrt{2}} Y_{2,2}(\hat{\mathbf{r}}) \\ d_{xz}(\hat{\mathbf{r}}) &= \frac{1}{\sqrt{2}} Y_{2,1}(\hat{\mathbf{r}}) + \frac{1}{\sqrt{2}} Y_{2,-1}(\hat{\mathbf{r}}) \\ d_{yz}(\hat{\mathbf{r}}) &= \frac{i}{\sqrt{2}} Y_{2,-1}(\hat{\mathbf{r}}) - \frac{i}{\sqrt{2}} Y_{2,1}(\hat{\mathbf{r}}) . \end{aligned} \quad (4.48)$$

Note that all of these wavefunctions are *real*. This means that the expectation value of L^z , and hence of general L^α , must vanish in any of these states. This is related to the phenomenon of *orbital quenching*, discussed below.

If the internal Hund's rule exchange energy J_H which enforces maximizing S is large compared with the ground state crystal field splitting Δ , then Hund's first rule is unaffected.

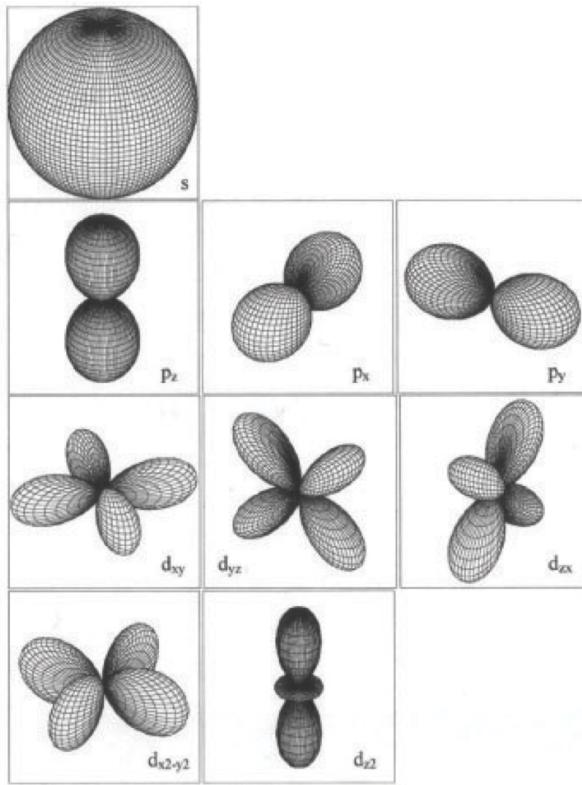


Figure 4.2: Effect on s , p , and d levels of a cubic crystal field.

However, there are examples of ions such as Co^{4+} for which $J_{\text{H}} < V_{\text{CF}}$. In such cases, the crystal field splitting wins and the ionic ground state is a *low spin state*. For Co^{4+} in an octahedral crystal field, the five 3d electrons all pile into the lower 3-fold degenerate t_{2g} manifold, and the spin is $S = \frac{1}{2}$. When the Hund's rule energy wins, the electrons all have parallel spin and $S = \frac{5}{2}$, which is the usual *high spin state*.

4.4 Magnetic Susceptibility of Atomic and Ionic Systems

To compute the susceptibility, we will need to know magnetic energies to order \mathbf{H}^2 . This can be computed via perturbation theory. Treating the $\mathbf{H} = 0$ Hamiltonian as \mathcal{H}_0 , we have

$$\begin{aligned} E_n(\mathbf{H}) = E_n(0) + \frac{1}{\hbar} \mu_{\text{B}} \mathbf{H} \cdot \langle n | \mathbf{L} + 2\mathbf{S} | n \rangle + \frac{e^2}{8mc^2} \langle n | \sum_{i=1}^{Z_{\text{ion}}} (\mathbf{H} \times \mathbf{r}_i)^2 | n \rangle \\ + \frac{1}{\hbar^2} \mu_{\text{B}}^2 H^\alpha H^\beta \sum_{n' \neq n} \frac{\langle n | L^\alpha + 2S^\alpha | n' \rangle \langle n' | L^\beta + 2S^\beta | n \rangle}{E_n - E_{n'}} + \mathcal{O}(H^3), \quad (4.49) \end{aligned}$$

where Z_{ion} is the number of electrons on the ion or atom in question. Since the $(\mathbf{H} \times \mathbf{r}_i)^2$ Larmor term is already second order in the field, its contribution can be evaluated in

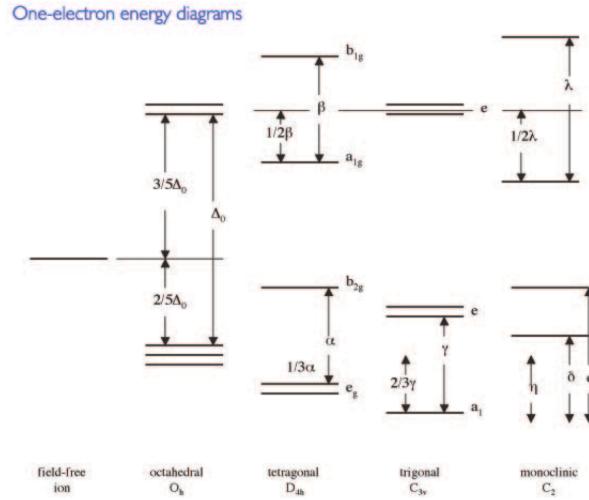


Figure 4.3: The splitting of one-electron states in different crystal field environments.

first order perturbation theory, *i.e.* by taking its expectation value in the state $|n\rangle$. The $(\mathbf{L}+2\mathbf{S}) \cdot \mathbf{H}$ term, which is linear in the field, is treated in second order perturbation theory.

4.4.1 Filled Shells: Larmor Diamagnetism

If the ground state $|G\rangle$ is a singlet with $\mathbf{J}|G\rangle = \mathbf{L}|G\rangle = \mathbf{S}|G\rangle = 0$, corresponding to a filled shell configuration, then the only contribution to the ground state energy shift is from the Larmor term,

$$\Delta E_0(\mathbf{H}) = \frac{e^2 \mathbf{H}^2}{12mc^2} \langle G | \sum_{i=1}^{Z_{\text{ion}}} \mathbf{r}_i^2 | G \rangle, \quad (4.50)$$

and the susceptibility is

$$\chi = -\frac{N}{V} \frac{\partial^2 \Delta E_0}{\partial H^2} = -\frac{ne^2}{6mc^2} \langle G | \sum_{i=1}^{Z_{\text{ion}}} \mathbf{r}_i^2 | G \rangle, \quad (4.51)$$

where $n = N/V$ is the density of ions or atoms in question. The sum is over all the electrons in the ion or atom. Defining the mean square ionic radius as

$$\langle \mathbf{r}^2 \rangle \equiv \frac{1}{Z_{\text{ion}}} \langle G | \sum_{i=1}^{Z_{\text{ion}}} \mathbf{r}_i^2 | G \rangle, \quad (4.52)$$

we obtain

$$\chi = -\frac{ne^2}{6mc^2} Z_{\text{ion}} \langle \mathbf{r}^2 \rangle = -\frac{1}{6} Z_{\text{ion}} n a_B^3 \left(\frac{e^2}{\hbar c} \right)^2 \frac{\langle r^2 \rangle}{a_B^2}. \quad (4.53)$$

Note that χ is dimensionless. One defines the *molar susceptibility* as

$$\begin{aligned}\chi^{\text{molar}} &\equiv N_A \chi / n = -\frac{1}{6} Z_{\text{ion}} N_A a_B^3 \left(\frac{e^2}{\hbar c} \right)^2 \langle (\mathbf{r}/a_B)^2 \rangle \\ &= -7.91 \times 10^{-7} Z_{\text{ion}} \langle (\mathbf{r}/a_B)^2 \rangle \text{ cm}^3/\text{mol}.\end{aligned}\quad (4.54)$$

Typically, $\langle (\mathbf{r}/a_B)^2 \rangle \sim 1$. Note that with $na_B^3 \simeq 0.1$, we have $|\chi| \lesssim 10^{-5}$ and $M = \chi H$ is much smaller than H itself.

Molar Susceptibilities of Noble Gas Atoms and Alkali and Halide Ions					
Atom or Ion	Molar Susceptibility	Atom or Atom or Ion	Molar Susceptibility	Atom or Atom or Ion	Molar Susceptibility
		He	-1.9	Li^+	-0.7
F^-	-9.4	Ne	-7.2	Na^+	-6.1
Cl^-	-24.2	Ar	-19.4	K^+	-14.6
Br^-	-34.5	Kr	-28	Rb^+	-22.0
I^-	-50.6	Xe	-43	Cs^+	-35.1

Table 4.3: Molar susceptibilities, in units of $10^{-6} \text{ cm}^3/\text{mol}$, of noble gas atoms and alkali and halide ions. (See R. Kubo and R. Nagamiya, eds., *Solid State Physics*, McGraw-Hill, 1969, p. 439.)

4.4.2 Partially Filled Shells: van Vleck Paramagnetism

There are two cases to consider here. The first is when $J = 0$, which occurs whenever the last shell is one electron short of being half-filled. Examples include Eu^{3+} ($4f^6$), Cr^{2+} ($3d^4$), Mn^{3+} ($3d^4$), etc. In this case, the first order term vanishes in ΔE_0 , and we have

$$\chi = -\frac{ne^2}{6mc^2} \langle \mathbf{G} | \sum_{i=1}^{Z_{\text{ion}}} \mathbf{r}_i^2 | \mathbf{G} \rangle + 2n\mu_B^2 \sum_{n \neq 0} \frac{|\langle n | L^z + 2S^z | \mathbf{G} \rangle|^2}{E_n - E_0}. \quad (4.55)$$

The second term is positive, favoring alignment of \mathbf{M} with \mathbf{H} . This is called *van Vleck paramagnetism*, and competes with the Larmor diamagnetism.

The second possibility is $J > 0$, which occurs in all cases except filled shells and shells which are one electron short of being half-filled. In this case, the first order term is usually dominant. We label the states by the eigenvalues of the commuting observables $\{\mathbf{J}^2, J^z, \mathbf{L}^2, \mathbf{S}^2\}$. From the Wigner-Eckart theorem, we know that

$$\langle JLSJ_z | \mathbf{L} + 2\mathbf{S} | JLSJ'_z \rangle = g_L(J, L, S) \langle JLSJ_z | \mathbf{J} | JLSJ'_z \rangle, \quad (4.56)$$

where

$$g_L(J, L, S) = \frac{3}{2} + \frac{S(S+1) - L(L+1)}{2J(J+1)} \quad (4.57)$$

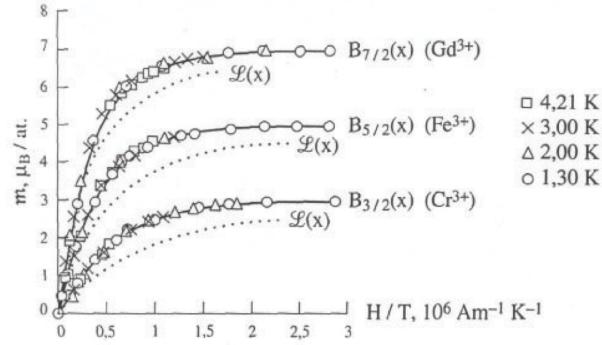


Figure 4.4: Reduced magnetization curves for three paramagnetic salts and comparison with Brillouin theory predictions. $\mathcal{L}(x) = B_{J \rightarrow \infty}(x) = \text{ctnh}(x) - x^{-1}$ is the Langevin function.

is known as the Landé g -factor. Thus, the effective Hamiltonian is

$$\mathcal{H}_{\text{eff}} = g_L \mu_B \mathbf{J} \cdot \mathbf{H}/\hbar. \quad (4.58)$$

The eigenvalues of \mathcal{H}_{eff} are $E_j = j \gamma H$, where $j \in \{-J, \dots, +J\}$ and $\gamma = g_L \mu_B$. The problem is reduced to an elementary one in statistical mechanics. The partition function is

$$Z = e^{-F/k_B T} = \sum_{j=-J}^J e^{-j\gamma H/k_B T} = \frac{\sinh((J + \frac{1}{2})\gamma H/k_B T)}{\sinh(\gamma H/2k_B T)}. \quad (4.59)$$

The magnetization density is

$$M = -\frac{N}{V} \frac{\partial F}{\partial H} = n\gamma J B_J(J\gamma H/k_B T), \quad (4.60)$$

where $B_J(x)$ is the *Brillouin function*,

$$B_J(x) = (1 + \frac{1}{2J}) \text{ctnh}\left[(1 + \frac{1}{2J})x\right] - \frac{1}{2J} \text{ctnh}(x/2J). \quad (4.61)$$

The magnetic susceptibility is thus

$$\begin{aligned} \chi(H, T) &= \frac{\partial M}{\partial H} = \frac{nJ^2\gamma^2}{k_B T} B'_J(J\gamma H/k_B T) \\ &= (Jg_L)^2 (na_B^3) (e^2/\hbar c)^2 \left(\frac{e^2/a_B}{k_B T} \right) B'_J(g\mu_B JH/k_B T) \end{aligned} \quad (4.62)$$

$$\chi(H = 0, T) = \frac{1}{3} (g_L \mu_B)^2 n \frac{J(J+1)}{k_B T}. \quad (4.63)$$

The inverse temperature dependence is known as *Curie's law*.

Does Curie's law work in solids? The $1/T$ dependence is very accurately reflected in insulating crystals containing transition metal and rare earth ions. We can fit the coefficient of the $1/T$ behavior by defining the 'magneton number' p according to

$$\chi(T) = n\mu_B^2 \frac{p^2}{3k_B T}. \quad (4.64)$$

The theory above predicts

$$p = g_L \sqrt{J(J+1)} . \quad (4.65)$$

One finds that the theory works well in the case of rare earth ions in solids. There, the 4f electrons of the rare earths are localized in the vicinity of the nucleus, and do not hybridize significantly with orbitals from neighboring ions. In transition metal compounds, however,

Calculated and Measured Magneton Numbers of Rare Earth Ions				
Ion	Electronic Configuration	Ground State Term $(2S+1)L_J$	magneton p_{theory}	magneton p_{expt}
La ³⁺	[Xe] 4f ⁰	¹ S ₀	0.00	< 0
Ce ³⁺	[Xe] 4f ¹	² F _{5/2}	2.54	2.4
Pr ³⁺	[Xe] 4f ²	³ H ₄	3.58	3.5
Nd ³⁺	[Xe] 4f ³	⁴ I _{9/2}	3.62	3.5
Pm ³⁺	[Xe] 4f ⁴	⁵ I ₄	2.68	—
Sm ³⁺	[Xe] 4f ⁵	⁶ H _{5/2}	0.84	1.5
Eu ³⁺	[Xe] 4f ⁶	⁷ F ₀	0.00	3.4
Gd ³⁺	[Xe] 4f ⁷	⁸ S _{7/2}	7.94	8.0
Tb ³⁺	[Xe] 4f ⁸	⁷ F ₆	9.72	9.5
Dy ³⁺	[Xe] 4f ⁹	⁶ H _{15/2}	10.63	10.6
Ho ³⁺	[Xe] 4f ¹⁰	⁵ I ₈	10.60	10.4
Er ³⁺	[Xe] 4f ¹¹	⁴ I _{15/2}	9.59	9.5
Tm ³⁺	[Xe] 4f ¹²	³ H ₆	7.57	7.3
Yb ³⁺	[Xe] 4f ¹³	² F _{7/2}	4.54	4.5
Lu ³⁺	[Xe] 4f ¹⁴	¹ S ₀	0.00	< 0

Table 4.4: Calculated and measured effective magneton numbers p for rare earth ions. (From N. W. Ashcroft and N. D. Mermin, *Solid State Physics*.) The discrepancy in the cases of Sm and Eu is due to the existence of low-lying multiplets above the ground state.

one finds poor agreement except in the case of S states ($L = 0$). This is because crystal field effects quench the orbital angular momentum, effectively rendering $L = 0$. Indeed, as shown in Table 4.5, the theory can be rescued if one ignores the ground state terms obtained by Hund's rules, and instead takes $L = 0$ and $J = S$, yielding $g_L = 2$.

4.5 Itinerant Magnetism of Noninteracting Systems

4.5.1 Pauli Paramagnetism

In a metal, the conduction electrons are delocalized and described by Bloch states. If we ignore the orbital effects of the magnetic field, we can easily compute the susceptibility at low fields and temperatures. At $T = 0$ and $H = 0$, \uparrow and \downarrow electrons fill respective Fermi

Calculated and Measured Magneton Numbers of Transition Metal Ions					
Ion	Electronic Configuration	Ground State Term $(2S+1)L_J$	magneton p_{theory}	magneton p_{theory}	magneton p_{expt}
Ti ³⁺	[Ar] 3d ¹	² D _{3/2}	1.55	1.73	—
V ⁴⁺	[Ar] 3d ¹	² D _{3/2}	1.55	1.73	1.8
V ³⁺	[Ar] 3d ²	³ F ₂	1.63	2.83	2.8
V ²⁺	[Ar] 3d ³	⁴ F _{3/2}	0.77	3.87	3.8
Cr ³⁺	[Ar] 3d ³	⁴ F _{3/2}	0.77	3.87	3.7
Mn ⁴⁺	[Ar] 3d ³	⁴ F _{3/2}	0.77	3.87	4.0
Cr ²⁺	[Ar] 3d ⁴	⁵ D ₀	0.00	4.90	4.8
Mn ³⁺	[Ar] 3d ⁴	⁵ D ₀	0.00	4.90	5.0
Mn ²⁺	[Ar] 3d ⁵	⁶ S _{5/2}	5.92	5.92	5.9
Fe ³⁺	[Ar] 3d ⁵	⁶ S _{5/2}	5.92	5.92	5.9
Fe ²⁺	[Ar] 3d ⁶	⁵ D ₄	6.70	4.90	5.4
Co ²⁺	[Ar] 3d ⁷	⁴ F _{9/2}	6.54	3.87	4.8
Ni ²⁺	[Ar] 3d ⁸	³ F ₄	5.59	2.83	3.2
Cu ²⁺	[Ar] 3d ⁹	² D _{5/2}	3.55	1.73	1.9

Table 4.5: Calculated and measured effective magneton numbers p for transition metal ions. (From N. W. Ashcroft and N. D. Mermin, *Solid State Physics*.) Due to the orbital quenching, the angular momentum is effectively $L = 0$.

sees out to wavevector k_F . In an external field \mathbf{H} , the Zeeman interaction splits the energies of the different polarization states:

$$\mathcal{H}_Z = \mu_B \boldsymbol{\sigma} \cdot \mathbf{H} . \quad (4.66)$$

Taking $\mathbf{H} = H \hat{z}$, and summing over all electrons, the Zeeman Hamiltonian becomes

$$\mathcal{H}_Z = \mu_B H (N_\uparrow - N_\downarrow) , \quad (4.67)$$

and the magnetization density is (still at $T = 0$)

$$M = -\frac{1}{V} \frac{\partial \mathcal{H}_Z}{\partial H} = \mu_B \frac{N_\downarrow - N_\uparrow}{V} . \quad (4.68)$$

Now since the energies of the \uparrow and \downarrow electrons are shifted by $\pm \mu_B H$, the change in their number is

$$\Delta N_\downarrow = -\Delta N_\uparrow = \mu_B H \cdot \frac{1}{2} g(\varepsilon_F) V , \quad (4.69)$$

where $g(\varepsilon_F)$ is the density of states per unit volume (including both spin species), at the Fermi energy. Putting this all together, we find

$$M = \mu_B^2 g(\varepsilon_F) H \equiv \chi_p H , \quad (4.70)$$

where $\chi_{\text{P}} = \mu_{\text{B}}^2 g(\varepsilon_{\text{F}})$ is the *Pauli susceptibility*. The Pauli susceptibility is positive, and hence is *paramagnetic*.

Using the formula for the density of states,

$$g(\varepsilon_{\text{F}}) = \frac{m^* k_{\text{F}}}{\pi^2 \hbar^2} , \quad (4.71)$$

we find

$$\chi_{\text{P}} = \frac{1}{4\pi^2} \frac{m^*}{m} \left(\frac{e^2}{\hbar c} \right)^2 (k_{\text{F}} a_{\text{B}}) . \quad (4.72)$$

Using $e^2/\hbar c \simeq 1/137.036$ and assuming $k_{\text{F}} a_{\text{B}} \approx 1$, we find $\chi_{\text{P}} \approx 10^{-6}$, which is comparable in magnitude (though opposite in sign) from the Larmor susceptibility of closed shells.

4.5.2 Landau Diamagnetism

Next, we investigate the orbital contribution. We assume a parabolic band, in which case

$$\mathcal{H} = \frac{1}{2m^*} (\mathbf{p} + \frac{e}{c} \mathbf{A})^2 + \mu_{\text{B}} \boldsymbol{\sigma} \cdot \mathbf{H} . \quad (4.73)$$

Appealing to the familiar results of a quantized charged particle in a uniform magnetic field, the energy levels are given by

$$\varepsilon(n, k_z, \sigma) = (n + \frac{1}{2}) \hbar \omega_c + \sigma \mu_{\text{B}} H + \frac{\hbar^2 k_z^2}{2m^*} , \quad (4.74)$$

where $\omega_c = eH/m^*c$ is the *cyclotron frequency*. Note that $\mu_{\text{B}} H = (\frac{m^*}{m}) \cdot \frac{1}{2} \hbar \omega_c$. The three-dimensional density of states is a convolution of the two-dimensional density of states,

$$g_{2\text{d}}(\varepsilon) = \frac{1}{2\pi\ell^2} \sum_{n=0}^{\infty} \delta(\varepsilon - (n + \frac{1}{2}) \hbar \omega_c) , \quad (4.75)$$

where $\ell = \sqrt{\hbar c/eH}$ is the magnetic length, and the one-dimensional density of states,

$$g_{1\text{d}}(\varepsilon) = \frac{1}{\pi} \frac{dk}{d\varepsilon} = \frac{\sqrt{m^*}}{\sqrt{2}\pi\hbar} \frac{1}{\sqrt{\varepsilon}} . \quad (4.76)$$

Thus,

$$g(\varepsilon) = \frac{\sqrt{m^*}}{\sqrt{2}\pi\hbar} \frac{1}{2\pi\ell^2} \sum_{n=0}^{\infty} \sum_{\sigma=\pm 1} \frac{\Theta(\varepsilon - \varepsilon_{n\sigma})}{\sqrt{\varepsilon - \varepsilon_{n\sigma}}} . \quad (4.77)$$

Thus, the grand potential,

$$\Omega(T, V, \mu, H) = -V k_{\text{B}} T \int_{-\infty}^{\infty} d\varepsilon g(\varepsilon) \ln \left\{ 1 + e^{(\mu - \varepsilon)/k_{\text{B}} T} \right\} \quad (4.78)$$

may be written as the sum,

$$\Omega(T, V, \mu, H) = -V k_B T \frac{\sqrt{m^*} e H}{\sqrt{8} \pi^2 \hbar^2 c} \sum_{n=0}^{\infty} \sum_{\sigma=\pm 1} F(\mu_{\sigma} - n \hbar \omega_c) , \quad (4.79)$$

with $\lambda = m^*/m$,

$$\mu_{\sigma} \equiv \mu - \frac{1}{2}(1 + \sigma \lambda) \hbar \omega_c , \quad (4.80)$$

and

$$F(\nu) = \int_0^{\infty} \frac{d\omega}{\sqrt{\omega}} \ln \left\{ 1 + e^{(\nu - \omega)/k_B T} \right\} . \quad (4.81)$$

We now invoke the Euler-MacLaurin formula,

$$\sum_{n=0}^{\infty} f(n) = \int_0^{\infty} dx f(x) + \frac{1}{2} f(0) - \frac{1}{12} f'(0) + \frac{1}{720} f'''(0) + \dots , \quad (4.82)$$

which gives

$$\Omega = -\frac{V k_B T m^{*3/2}}{2\sqrt{2} \pi^2 \hbar^3} \sum_{\sigma=\pm} \left\{ \int_{-\infty}^{\mu_{\sigma}} d\varepsilon F(\varepsilon) + \frac{1}{2} \hbar \omega_c F(\mu_{\sigma}) + \frac{1}{12} (\hbar \omega_c)^2 F'(\mu_{\sigma}) + \dots \right\} . \quad (4.83)$$

We now sum over σ and perform a Taylor expansion in $\hbar \omega_c \propto H$, yielding

$$\begin{aligned} \Omega(T, V, \mu, H) &= -\frac{V k_B T m^{*3/2}}{2\sqrt{2} \pi^2 \hbar^3} \sum_{\sigma=\pm} \left\{ \int_{-\infty}^{\mu} d\varepsilon F(\varepsilon) + \frac{1}{8} (\lambda^2 - \frac{1}{3})(\hbar \omega_c)^2 F'(\mu) + \mathcal{O}(H^4) \right\} \\ &= \left\{ 1 + \frac{1}{2} \left(1 - \frac{1}{3\lambda^2} \right) (\mu_B H)^2 \frac{\partial^2}{\partial \mu^2} + \mathcal{O}(H^4) \right\} \Omega(T, V, \mu, 0) . \end{aligned} \quad (4.84)$$

Thus,

$$M = -\frac{1}{V} \left(1 - \frac{1}{3\lambda^2} \right) \mu_B^2 H \frac{\partial^2 \Omega}{\partial \mu^2} \Big|_{H=0} , \quad (4.85)$$

and the zero field magnetic susceptibility is

$$\chi = \left(1 - \frac{1}{3\lambda^2} \right) \mu_B^2 \frac{\partial n}{\partial \mu} . \quad (4.86)$$

The quantity $\chi_P = \mu_B^2 (\partial n / \partial \mu)$ is simply the finite temperature Pauli susceptibility. The orbital contribution is negative, *i.e.* diamagnetic. Thus, $\chi = \chi_P + \chi_L$, where

$$\chi_L = -\frac{1}{3} (m/m^*)^2 \chi_P \quad (4.87)$$

is the *Landau diamagnetic susceptibility*. For free electrons, $\lambda = m/m^* = 1$ and $\chi_L = -\frac{1}{3} \chi_P$ resulting in a reduced – but still paramagnetic – total susceptibility. However, in

semiconductors it is common to find $m^* \approx 0.1 m$, in which case the Landau diamagnetic term overwhelms the Pauli paramagnetic term, and the overall susceptibility is negative.

In order to probe χ_p without the diamagnetic χ_L contribution, nuclear magnetic resonance (NMR) is used. NMR measures the effect of electron spins on the nuclear spins. The two are coupled via the hyperfine interaction,

$$\mathcal{H}_{\text{hf}} = \frac{2g_N\mu_B\mu_N}{\hbar^3 r^3} \left\{ \mathbf{L} \cdot \mathbf{I} - \mathbf{S} \cdot \mathbf{I} + (\hat{\mathbf{r}} \cdot \mathbf{S})(\hat{\mathbf{r}} \cdot \mathbf{I}) \right\} + \frac{16\pi g_N\mu_B\mu_N}{3\hbar} \mathbf{S} \cdot \mathbf{I} \delta(\mathbf{r}), \quad (4.88)$$

where g_N is the nuclear g -value, \mathbf{I} is the nuclear total angular momentum, and μ_N is the nuclear magneton.

4.6 Moment Formation in Interacting Itinerant Systems

4.6.1 The Hubbard Model

A noninteracting electron gas exhibits paramagnetism or diamagnetism, depending on the sign of χ , but never develops a spontaneous magnetic moment: $\mathbf{M}(\mathbf{H} = 0) = 0$. What gives rise to magnetism in solids? Overwhelmingly, the answer is that Coulomb repulsion between electrons is responsible for magnetism, in those instances in which magnetism arises. At first thought this might seem odd, since the Coulomb interaction is spin-independent. How then can it lead to a spontaneous magnetic moment?

To understand how Coulomb repulsion leads to magnetism, it is useful to consider a model interacting system, described by the Hamiltonian

$$\mathcal{H} = -\frac{1}{2} \sum_{i,j,\sigma} t_{ij} (c_{i\sigma}^\dagger c_{j\sigma} + c_{j\sigma}^\dagger c_{i\sigma}) + U \sum_i n_{i\uparrow} n_{i\downarrow} + \mu_B \mathbf{H} \cdot \sum_i c_{i\alpha}^\dagger \boldsymbol{\sigma}_{\alpha\beta} c_{i\beta}. \quad (4.89)$$

This is none other than the famous *Hubbard model*, which has served as a kind of Rosetta stone for interacting electron systems. The first term describes hopping of electrons along the links of some regular lattice ($\langle ij \rangle$ denotes a link between sites i and j). The second term describes the local (on-site) repulsion of electrons. This is a single orbital model, so the repulsion exists when one tries to put two electrons in the orbital, with opposite spin polarization. Typically the Hubbard U parameter is on the order of electron volts. The last term is the Zeeman interaction of the electron spins with an external magnetic field. Orbital effects can be modeled by associating a phase $\exp(iA_{ij})$ to the hopping matrix element t between sites i and j , where the directed sum of A_{ij} around a plaquette yields the total magnetic flux through the plaquette in units of $\phi_0 = hc/e$. We will ignore orbital effects here. Note that the interaction term is short-ranged, whereas the Coulomb interaction falls off as $1/|\mathbf{R}_i - \mathbf{R}_j|$. The Hubbard model is thus unrealistic, although screening effects in metals do effectively render the interaction to be short-ranged.

Within the Hubbard model, the interaction term is local and written as $Un_\uparrow n_\downarrow$ on any given site. This term favors a local moment. This is because the chemical potential will fix the

mean value of the total occupancy $n_\uparrow + n_\downarrow$, in which case it always pays to maximize the difference $|n_\uparrow - n_\downarrow|$.

4.6.2 Stoner Mean Field Theory

There are no general methods available to solve for even the ground state of an interacting many-body Hamiltonian. We'll solve this problem using a *mean field* theory due to Stoner. The idea is to write the occupancy $n_{i\sigma}$ as a sum of average and fluctuating terms:

$$n_{i\sigma} = \langle n_{i\sigma} \rangle + \delta n_{i\sigma}. \quad (4.90)$$

Here, $\langle n_{i\sigma} \rangle$ is the thermodynamic average; the above equation may then be taken as a definition of the fluctuating piece, $\delta n_{i\sigma}$. We assume that the average is site-independent. This is a significant assumption, for while we understand why each site should favor developing a moment, it is not clear that all these local moments should want to line up parallel to each other. Indeed, on a bipartite lattice, it is possible that the individual local moments on neighboring sites will be antiparallel, corresponding to an *antiferromagnetic* order of the pins. Our mean field theory will be one for *ferromagnetic* states.

We now write the interaction term as

$$\begin{aligned} n_{i\uparrow} n_{i\downarrow} &= \langle n_\uparrow \rangle \langle n_\downarrow \rangle + \langle n_\uparrow \rangle \delta n_{i\downarrow} + \langle n_\downarrow \rangle \delta n_{i\uparrow} + \overbrace{\delta n_{i\uparrow} \delta n_{i\downarrow}}^{(\text{fluct}^s)^2} \\ &= -\langle n_\uparrow \rangle \langle n_\downarrow \rangle + \langle n_\uparrow \rangle n_{i\downarrow} + \langle n_\downarrow \rangle n_{i\uparrow} + \mathcal{O}((\delta n)^2) \\ &= \frac{1}{4}(m^2 - n^2) + \frac{1}{2}n(n_{i\uparrow} + n_{i\downarrow}) + \frac{1}{2}m(n_{i\uparrow} - n_{i\downarrow}) + \mathcal{O}((\delta n)^2), \end{aligned} \quad (4.91)$$

where n and m are the average occupancy per spin and average spin polarization, each per unit cell:

$$n = \langle n_\downarrow \rangle + \langle n_\uparrow \rangle \quad (4.92)$$

$$m = \langle n_\downarrow \rangle - \langle n_\uparrow \rangle, \quad (4.93)$$

i.e. $\langle n_\sigma \rangle = \frac{1}{2}(n - \sigma m)$. The mean field grand canonical Hamiltonian $\mathcal{K} = \mathcal{H} - \mu\mathcal{N}$, may then be written as

$$\begin{aligned} \mathcal{K}^{\text{MF}} &= -\frac{1}{2} \sum_{i,j,\sigma} t_{ij} \left(c_{i\sigma}^\dagger c_{j\sigma} + c_{j\sigma}^\dagger c_{i\sigma} \right) - \left(\mu - \frac{1}{2}U n \right) \sum_{i\sigma} c_{i\sigma}^\dagger c_{i\sigma} \\ &\quad + (\mu_B H + \frac{1}{2}Um) \sum_{i\sigma} \sigma c_{i\sigma}^\dagger c_{i\sigma} + \frac{1}{4}N_{\text{sites}} U(m^2 - n^2), \end{aligned} \quad (4.94)$$

where we've quantized spins along the direction of \mathbf{H} , defined as \hat{z} . You should take note of two things here. First, the chemical potential is shifted *downward* (or the electron energies shifted *upward*) by an amount $\frac{1}{2}Un$, corresponding to the average energy of repulsion

with the background. Second, the effective magnetic field has been shifted by an amount $\frac{1}{2}Um/\mu_B$, so the effective field is

$$H_{\text{eff}} = H + \frac{Um}{2\mu_B}. \quad (4.95)$$

The *bare* single particle dispersions are given by $\varepsilon_\sigma(\mathbf{k}) = -\hat{t}(\mathbf{k}) + \sigma\mu_B H$, where

$$\hat{t}(\mathbf{k}) = \sum_{\mathbf{R}} t(\mathbf{R}) e^{-i\mathbf{k}\cdot\mathbf{R}}, \quad (4.96)$$

and $t_{ij} = t(\mathbf{R}_i - \mathbf{R}_j)$. Including the mean field effects, the *effective* single particle dispersions become

$$\tilde{\varepsilon}_\sigma(\mathbf{k}) = -\hat{t}(\mathbf{k}) - \frac{1}{2}Un + (\mu_B H + \frac{1}{2}Um)\sigma. \quad (4.97)$$

We now solve the mean field theory, by obtaining the free energy per site, $\varphi(n, T, H)$. First, note that $\varphi = \omega + 2\mu n$, where $\omega = \Omega/N_{\text{sites}}$ is the Landau, or grand canonical, free energy per site. This follows from the general relation $\Omega = F - \mu N$; note that the total electron number is $N = nN_{\text{sites}}$, since n is the electron number per unit cell (including both spin species). If $g(\varepsilon)$ is the density of states per unit cell (rather than per unit volume), then we have⁴

$$\varphi = \frac{1}{4}U(m^2 + n^2) + \bar{\mu}n - \frac{1}{2}k_B T \int_{-\infty}^{\infty} d\varepsilon g(\varepsilon) \left\{ \ln \left(1 + e^{(\bar{\mu} - \varepsilon - \Delta)/k_B T} \right) + \ln \left(1 + e^{(\bar{\mu} - \varepsilon + \Delta)/k_B T} \right) \right\} \quad (4.98)$$

where $\bar{\mu} \equiv \mu - Un$ and $\Delta \equiv \mu_B H + \frac{1}{2}Um$. From this free energy we derive two self-consistent equations for μ and m . The first comes from demanding that φ be a function of n and not of μ , *i.e.* $\partial\varphi/\partial\mu = 0$, which leads to

$$n = \frac{1}{2} \int_{-\infty}^{\infty} d\varepsilon g(\varepsilon) \left\{ f(\varepsilon - \Delta - \bar{\mu}) + f(\varepsilon + \Delta - \bar{\mu}) \right\}, \quad (4.99)$$

where $f(y) = [\exp(y/k_B T) + 1]^{-1}$ is the Fermi function. The second equation comes from minimizing f with respect to average moment m :

$$m = \frac{1}{2} \int_{-\infty}^{\infty} d\varepsilon g(\varepsilon) \left\{ f(\varepsilon - \Delta - \bar{\mu}) - f(\varepsilon + \Delta - \bar{\mu}) \right\}. \quad (4.100)$$

Here, we will solve the first equation, eq. 4.99, and use the results to generate a Landau expansion of the free energy φ in powers of m^2 . We assume that Δ is small, in which case we may write

$$n = \int_{-\infty}^{\infty} d\varepsilon g(\varepsilon) \left\{ f(\varepsilon - \bar{\mu}) + \frac{1}{2}\Delta^2 f''(\varepsilon - \bar{\mu}) + \frac{1}{24}\Delta^4 f'''(\varepsilon - \bar{\mu}) + \dots \right\}. \quad (4.101)$$

⁴Note that we have written $\mu n = \bar{\mu}n + \frac{1}{2}Un^2$, which explains the sign of the coefficient of n^2 .

We write $\bar{\mu}(\Delta) = \bar{\mu}_0 + \delta\bar{\mu}$ and expand in $\delta\bar{\mu}$. Since n is fixed in our (canonical) ensemble, we have

$$n = \int_{-\infty}^{\infty} d\varepsilon g(\varepsilon) f(\varepsilon - \bar{\mu}_0) , \quad (4.102)$$

which defines $\bar{\mu}_0(n, T)$.⁵ The remaining terms in the $\delta\bar{\mu}$ expansion of eqn. 4.101 must sum to zero. This yields

$$D(\bar{\mu}_0) \delta\bar{\mu} + \frac{1}{2}\Delta^2 D'(\bar{\mu}_0) + \frac{1}{2}(\delta\bar{\mu})^2 D'(\bar{\mu}_0) + \frac{1}{2}D''(\bar{\mu}_0) \Delta^2 \delta\bar{\mu} + \frac{1}{24}D'''(\bar{\mu}_0) \Delta^4 + \mathcal{O}(\Delta^6) = 0 , \quad (4.103)$$

where

$$D(\mu) = - \int_{-\infty}^{\infty} d\varepsilon g(\varepsilon) f'(\varepsilon - \mu) \quad (4.104)$$

is the thermally averaged *bare* density of states at energy μ . Note that the k^{th} derivative is

$$D^{(k)}(\mu) = - \int_{-\infty}^{\infty} d\varepsilon g^{(k)}(\varepsilon) f'(\varepsilon - \mu) . \quad (4.105)$$

Solving for $\delta\bar{\mu}$, we obtain

$$\delta\bar{\mu} = -\frac{1}{2}a_1\Delta^2 - \frac{1}{24}(3a_1^3 - 6a_1a_2 + a_3)\Delta^4 + \mathcal{O}(\Delta^6) , \quad (4.106)$$

where

$$a_k \equiv \frac{D^{(k)}(\bar{\mu}_0)}{D(\bar{\mu}_0)} . \quad (4.107)$$

After integrating by parts and inserting this result for $\delta\bar{\mu}$ into our expression for the free energy f , we obtain the expansion

$$\varphi(n, T, m) = \varphi_0(n, T) + \frac{1}{4}Um^2 - \frac{1}{2}D(\bar{\mu}_0)\Delta^2 + \frac{1}{8}\left(\frac{[D'(\bar{\mu}_0)]^2}{D(\bar{\mu}_0)} - \frac{1}{3}D''(\bar{\mu}_0)\right)\Delta^4 + \dots , \quad (4.108)$$

where prime denotes differentiation with respect to argument, at $m = 0$, and

$$\varphi_0(n, T) = \frac{1}{4}Un^2 + n\bar{\mu}_0 - \int_{-\infty}^{\infty} d\varepsilon \Gamma(\varepsilon) f(\varepsilon - \bar{\mu}_0) , \quad (4.109)$$

where $g(\varepsilon) = \Gamma'(\varepsilon)$, so $\Gamma(\varepsilon)$ is the integrated bare density of states per unit cell in the absence of any magnetic field (including both spin species).

⁵The Gibbs-Duhem relation guarantees that such an equation of state exists, relating any three intensive thermodynamic quantities.

We assume that H and m are small, in which case

$$\varphi = \varphi_0 + \frac{1}{2}am^2 + \frac{1}{4}bm^4 - \frac{1}{2}\chi_0 H^2 - \frac{U\chi_0}{2\mu_B} Hm + \dots , \quad (4.110)$$

where $\chi_0 = \mu_B^2 D(\bar{\mu}_0)$ is the Pauli susceptibility, and

$$a = \frac{1}{2}U\left(1 - \frac{1}{2}UD\right) , \quad b = \frac{1}{32}\left(\frac{(D')^2}{D} - \frac{1}{3}D''\right)U^4 , \quad (4.111)$$

where the argument of each $D^{(k)}$ above is $\bar{\mu}_0(n, T)$. The magnetization density (per unit cell, rather than per unit volume) is given by

$$M = -\frac{\partial\varphi}{\partial H} = \chi_0 H + \frac{U\chi_0}{2\mu_B} m . \quad (4.112)$$

Minimizing with respect to m yields

$$am + bm^3 - \frac{U\chi_0}{2\mu_B} H = 0 , \quad (4.113)$$

which gives, for small m ,

$$m = \frac{\chi_0}{\mu_B} \frac{H}{1 - \frac{1}{2}UD} . \quad (4.114)$$

We therefore obtain $M = \chi H$ with

$$\chi = \frac{\chi_0}{1 - \frac{U}{U_c}} , \quad (4.115)$$

where

$$U_c = \frac{2}{D(\bar{\mu}_0)} . \quad (4.116)$$

The denominator of χ increases the susceptibility above the bare Pauli value χ_0 , and is referred to as – I kid you not – the *Stoner enhancement*.

It is worth emphasizing that the magnetization per unit cell is given by

$$M = -\frac{1}{N_{\text{sites}}} \frac{\delta\mathcal{H}}{\delta H} = \mu_B m . \quad (4.117)$$

This is an operator identity and is valid for any value of m , and not only small m .

When $H = 0$ we can still get a magnetic moment, provided $U > U_c$. This is a consequence of the simple Landau theory we have derived. Solving for m when $H = 0$ gives $m = 0$ when $U < U_c$ and

$$m(U) = \pm \left(\frac{U}{2bU_c} \right)^{1/2} \sqrt{U - U_c} , \quad (4.118)$$

when $U > U_c$, and assuming $b > 0$. Thus we have the usual mean field order parameter exponent of $\beta = \frac{1}{2}$.

4.6.3 Antiferromagnetic Solution

In addition to ferromagnetism, there may be other ordered states which solve the mean field theory. One such example is antiferromagnetism. On a bipartite lattice, the antiferromagnetic mean field theory is obtained from

$$\langle n_{i\sigma} \rangle = \frac{1}{2}n + \frac{1}{2}\sigma e^{i\mathbf{Q}\cdot\mathbf{R}_i} m , \quad (4.119)$$

where $\mathbf{Q} = (\pi/a, \pi/a, \dots, \pi/a)$ is the antiferromagnetic ordering wavevector. The grand canonical Hamiltonian is then

$$\begin{aligned} \mathcal{K}^{\text{MF}} &= -\frac{1}{2} \sum_{i,j,\sigma} t_{ij} (c_{i\sigma}^\dagger c_{j\sigma} + c_{j\sigma}^\dagger c_{i\sigma}) - (\mu - \frac{1}{2}Un) \sum_{i\sigma} c_{i\sigma}^\dagger c_{i\sigma} \\ &\quad - \frac{1}{2}Um \sum_{i\sigma} e^{i\mathbf{Q}\cdot\mathbf{R}_i} \sigma c_{i\sigma}^\dagger c_{i\sigma} + \frac{1}{4}N_{\text{sites}} U(m^2 - n^2) \\ &= \frac{1}{2} \sum_{\mathbf{k}\sigma} \begin{pmatrix} c_{\mathbf{k},\sigma}^\dagger & c_{\mathbf{k}+\mathbf{Q},\sigma}^\dagger \end{pmatrix} \begin{pmatrix} \varepsilon(\mathbf{k}) - \mu + \frac{1}{2}Un & \frac{1}{2}\sigma Um \\ \frac{1}{2}\sigma Um & \varepsilon(\mathbf{k} + \mathbf{Q}) - \mu + \frac{1}{2}Un \end{pmatrix} \begin{pmatrix} c_{\mathbf{k},\sigma} \\ c_{\mathbf{k}+\mathbf{Q},\sigma} \end{pmatrix} \\ &\quad + \frac{1}{4}N_{\text{sites}} U(m^2 - n^2) , \end{aligned} \quad (4.120)$$

where $\varepsilon(\mathbf{k}) = -\hat{t}(\mathbf{k})$, as before. On a bipartite lattice, with nearest neighbor hopping only, we have $\varepsilon(\mathbf{k} + \mathbf{Q}) = -\varepsilon(\mathbf{k})$. The above matrix is diagonalized by a unitary transformation, yielding the eigenvalues

$$\lambda = \pm \Omega_{\varepsilon(\mathbf{k})} - \bar{\mu} \quad (4.121)$$

$$\Omega_\varepsilon = \sqrt{\varepsilon^2 + \Delta^2} , \quad (4.122)$$

with $\Delta = \frac{1}{2}Um$ and $\bar{\mu} = \mu - \frac{1}{2}Un$ as before. The free energy per unit cell is then

$$\varphi = \frac{1}{4}U(m^2 + n^2) + \bar{\mu}n - \frac{1}{2}k_B T \int_{-\infty}^{\infty} d\varepsilon g(\varepsilon) \left\{ \ln \left(1 + e^{(\bar{\mu} - \Omega_\varepsilon)/k_B T} \right) + \ln \left(1 + e^{(\bar{\mu} + \Omega_\varepsilon)/k_B T} \right) \right\} . \quad (4.123)$$

The mean field equations are then

$$n = \frac{1}{2} \int_{-\infty}^{\infty} d\varepsilon g(\varepsilon) \left\{ f(-\Omega_\varepsilon - \bar{\mu}) + f(\Omega_\varepsilon - \bar{\mu}) \right\} \quad (4.124)$$

$$\frac{1}{U} = \frac{1}{2} \int_{-\infty}^{\infty} d\varepsilon \frac{g(\varepsilon)}{2\Omega_\varepsilon} \left\{ f(-\Omega_\varepsilon - \bar{\mu}) - f(\Omega_\varepsilon - \bar{\mu}) \right\} . \quad (4.125)$$

As in the case of the ferromagnet, a paramagnetic solution with $m = 0$ always exists, in which case the second of the above equations is no longer valid.

4.6.4 Mean Field Phase Diagram of the Hubbard Model

Let us compare the mean field theories for the ferromagnetic and antiferromagnetic states at $T = 0$ and $H = 0$. Due to particle-hole symmetry, we may assume $0 \leq n \leq 1$ without loss of generality. (The solutions repeat themselves under $n \rightarrow 2 - n$.) For the paramagnet, we have

$$n = \int_{-\infty}^{\bar{\mu}} d\epsilon g(\epsilon) \quad (4.126)$$

$$\varphi = \frac{1}{4}Un^2 + \int_{-\infty}^{\bar{\mu}} d\epsilon g(\epsilon) \epsilon \quad , \quad (4.127)$$

with $\bar{\mu} = \mu - \frac{1}{2}Un$ is the ‘renormalized’ Fermi energy and $g(\epsilon)$ is the density of states per unit cell in the absence of any explicit (H) or implicit (m) symmetry breaking, including both spin polarizations.

For the ferromagnet,

$$n = \frac{1}{2} \int_{-\infty}^{\bar{\mu}-\Delta} d\epsilon g(\epsilon) + \frac{1}{2} \int_{-\infty}^{\bar{\mu}+\Delta} d\epsilon g(\epsilon) \quad (4.128)$$

$$\frac{4\Delta}{U} = \int_{\bar{\mu}-\Delta}^{\bar{\mu}+\Delta} d\epsilon g(\epsilon) \quad (4.129)$$

$$\varphi = \frac{1}{4}Un^2 - \frac{\Delta^2}{U} + \int_{-\infty}^{\bar{\mu}-\Delta} d\epsilon g(\epsilon) \epsilon + \int_{-\infty}^{\bar{\mu}+\Delta} d\epsilon g(\epsilon) \epsilon \quad . \quad (4.130)$$

Here, $\Delta = \frac{1}{2}Um$ is nonzero in the ordered phase.

Finally, the antiferromagnetic mean field equations are

$$n = \int_{\varepsilon_0}^{\infty} d\epsilon g(\epsilon) \quad (\bar{\mu} < 0) \quad (4.131)$$

$$= 2 - \int_{\varepsilon_0}^{\infty} d\epsilon g(\epsilon) \quad (\bar{\mu} > 0) \quad (4.132)$$

$$\frac{2}{U} = \int_{\varepsilon_0}^{\infty} d\epsilon \frac{g(\epsilon)}{\sqrt{\varepsilon^2 + \Delta^2}} \quad (4.133)$$

$$\varphi = \frac{1}{4}Un^2 + \frac{\Delta^2}{U} - \int_{\varepsilon_0}^{\infty} d\epsilon g(\epsilon) \sqrt{\varepsilon^2 + \Delta^2} \quad , \quad (4.134)$$

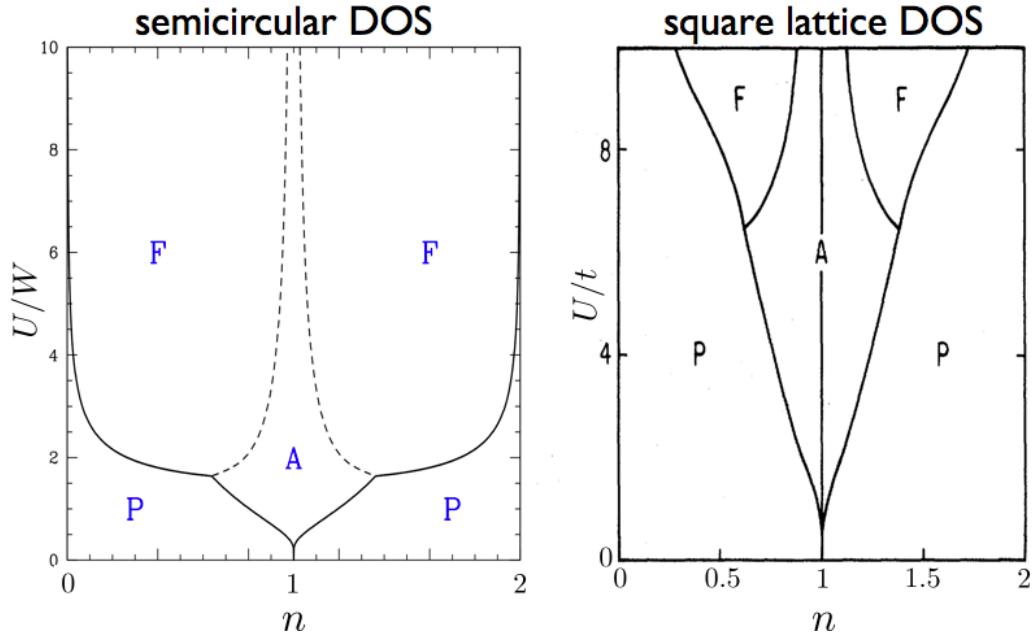


Figure 4.5: Mean field phase diagram of the Hubbard model, including paramagnetic (P), ferromagnetic (F), and antiferromagnetic (A) phases. Left panel: results using a semicircular density of states function of half-bandwidth W . Right panel: results using a two-dimensional square lattice density of states with nearest neighbor hopping t , from J. E. Hirsch, *Phys. Rev. B* **31**, 4403 (1985). The phase boundary between F and A phases is first order.

where $\varepsilon_0 = \sqrt{\bar{\mu}^2 - \Delta^2}$ and $\Delta = \frac{1}{2}Um$ as before. Note that $|\bar{\mu}| \geq \Delta$ for these solutions. Exactly at half-filling, we have $n = 1$ and $\bar{\mu} = 0$. We then set $\varepsilon_0 = 0$.

The paramagnet to ferromagnet transition may be first or second order, depending on the details of $g(\varepsilon)$. If second order, it occurs at $U_c^F = 1/g(\bar{\mu}_P)$, where $\bar{\mu}_P(n)$ is the paramagnetic solution for $\bar{\mu}$. The paramagnet to antiferromagnet transition is always second order in this mean field theory, since the RHS of eqn. (4.133) is a monotonic function of Δ . This transition occurs at $U_c^A = 2 \int_{\bar{\mu}_P}^{\infty} d\varepsilon g(\varepsilon) \varepsilon^{-1}$. Note that $U_c^A \rightarrow 0$ logarithmically for $n \rightarrow 1$, since $\bar{\mu}_P = 0$ at half-filling.

For large U , the ferromagnetic solution always has the lowest energy, and therefore if $U_c^A < U_c^F$, there will be a first-order antiferromagnet to ferromagnet transition at some value $U^* > U_c^F$. In fig. 4.5, I plot the phase diagram obtained by solving the mean field equations assuming a semicircular density of states $g(\varepsilon) = \frac{2}{\pi} W^{-2} \sqrt{W^2 - \varepsilon^2}$. Also shown is the phase diagram for the $d = 2$ square lattice Hubbard model obtained by J. Hirsch (1985).

How well does Stoner theory describe the physics of the Hubbard model? Quantum Monte Carlo calculations by J. Hirsch (1985) showed that the actual phase diagram of the $d = 2$ square lattice Hubbard Model exhibits no ferromagnetism for any n up to $U = 10$.

Furthermore, the antiferromagnetic phase is entirely confined to the vertical line $n = 1$. For $n \neq 1$ and $0 \leq U \leq 10$, the system is a paramagnet⁶. In order to achieve a ferromagnetic solution, it appears necessary to introduce geometric frustration, either by including a next-nearest-neighbor hopping amplitude t' or by defining the model on non-bipartite lattices. Numerical work by M. Ulmke (1997) showed the existence of a ferromagnetic phase at $T = 0$ on the FCC lattice Hubbard model for $U = 6$ and $n \in [0.15, 0.87]$ (approximately).

4.7 Interaction of Local Moments: the Heisenberg Model

While it is true that electrons have magnetic dipole moments, the corresponding dipole-dipole interactions in solids are usually negligible. This is easily seen by estimating the energy scale of the dipole-dipole interaction:

$$E_{\text{d-d}} = \frac{\mathbf{m}_1 \cdot \mathbf{m}_2 - 3(\mathbf{m}_1 \cdot \hat{\mathbf{n}})(\mathbf{m}_2 \cdot \hat{\mathbf{n}})}{|\mathbf{r}_1 - \mathbf{r}_2|^3}, \quad (4.135)$$

where $\hat{\mathbf{n}} = (\mathbf{r}_2 - \mathbf{r}_1)/|\mathbf{r}_2 - \mathbf{r}_1|$ is the direction vector pointing from \mathbf{r}_1 to \mathbf{r}_2 . Substituting $\mathbf{m} = -\mu_B \boldsymbol{\sigma}$, we estimate $E_{\text{d-d}}$ as

$$|E_{\text{d-d}}| \simeq \frac{\mu_B^2}{R^3} = \frac{e^2}{2a_B} \left(\frac{e^2}{\hbar c} \right)^2 \left(\frac{a_B}{R} \right)^3, \quad (4.136)$$

and with $R \simeq 2.5 \text{ \AA}$ we obtain $E_{\text{d-d}} \simeq 1 \mu\text{eV}$, which is tiny on the scale of electronic energies in solids. The dominant magnetic coupling comes from the Coulomb interaction.

4.7.1 Ferromagnetic Exchange of Orthogonal Orbitals

In the Wannier basis, we may write the Coulomb interaction as

$$\hat{V} = \frac{1}{2} \sum_{\substack{\mathbf{R}_1, \mathbf{R}_2 \\ \mathbf{R}_3, \mathbf{R}_4}} \sum_{\sigma, \sigma'} \langle \mathbf{R}_1 \mathbf{R}_2 | \frac{e^2}{|\mathbf{r} - \mathbf{r}'|} | \mathbf{R}_4 \mathbf{R}_3 \rangle c_{\mathbf{R}_1 \sigma}^\dagger c_{\mathbf{R}_2 \sigma'}^\dagger c_{\mathbf{R}_3 \sigma'} c_{\mathbf{R}_4 \sigma}, \quad (4.137)$$

where we have assumed a single energy band. The Coulomb matrix element is

$$\langle \mathbf{R}_1 \mathbf{R}_2 | \frac{e^2}{|\mathbf{r} - \mathbf{r}'|} | \mathbf{R}_4 \mathbf{R}_3 \rangle = \int d^3 r \int d^3 r' \varphi^*(\mathbf{r} - \mathbf{R}_1) \varphi^*(\mathbf{r}' - \mathbf{R}_2) \frac{e^2}{|\mathbf{r} - \mathbf{r}'|} \varphi(\mathbf{r}' - \mathbf{R}_3) \varphi(\mathbf{r} - \mathbf{R}_4). \quad (4.138)$$

Due to overlap factors, the matrix element will be small unless $\mathbf{R}_2 = \mathbf{R}_3$ and $\mathbf{R}_1 = \mathbf{R}_4$, in which case we obtain the *direct* Coulomb interaction,

$$\begin{aligned} V(\mathbf{R} - \mathbf{R}') &= \langle \mathbf{R} \mathbf{R}' | \frac{e^2}{|\mathbf{r} - \mathbf{r}'|} | \mathbf{R} \mathbf{R}' \rangle \\ &= \int d^3 r \int d^3 r' |\varphi(\mathbf{r} - \mathbf{R})|^2 \frac{e^2}{|\mathbf{r} - \mathbf{r}'|} |\varphi(\mathbf{r}' - \mathbf{R}')|^2. \end{aligned} \quad (4.139)$$

⁶A theorem due to Nagaoka establishes that the ground state is ferromagnetic for the case of a single hole in the $U = \infty$ system on bipartite lattices.

The direct interaction decays as $|\mathbf{R} - \mathbf{R}'|^{-1}$ at large separations. Were we to include only these matrix elements, the second quantized form of the Coulomb interaction would be

$$\begin{aligned}\hat{V}_{\text{direct}} &= \frac{1}{2} \sum_{\substack{\mathbf{R}\mathbf{R'} \\ \sigma\sigma'}} V(\mathbf{R} - \mathbf{R}') \left(n_{\mathbf{R}\sigma} n_{\mathbf{R}'\sigma'} - \delta_{\mathbf{R}\mathbf{R}'} \delta_{\sigma\sigma'} n_{\mathbf{R}\sigma} \right) \\ &= \sum_{\mathbf{R}} V(0) n_{\mathbf{R}\uparrow} n_{\mathbf{R}\downarrow} + \frac{1}{2} \sum_{\mathbf{R} \neq \mathbf{R}'} V(\mathbf{R} - \mathbf{R}') n_{\mathbf{R}} n_{\mathbf{R}'} ,\end{aligned}\quad (4.140)$$

where $n_{\mathbf{R}} \equiv n_{\mathbf{R}\uparrow} + n_{\mathbf{R}\downarrow}$. The first term is the on-site Hubbard repulsion; one abbreviates $U \equiv V(0)$.

A second class of matrix elements can be identified: those with $\mathbf{R}_1 = \mathbf{R}_3 \equiv \mathbf{R}$ and $\mathbf{R}_2 = \mathbf{R}_4 \equiv \mathbf{R}'$, with $\mathbf{R} \neq \mathbf{R}'$. These are the so-called *exchange* integrals:

$$\begin{aligned}J(\mathbf{R} - \mathbf{R}') &= \langle \mathbf{R} \mathbf{R}' | \frac{e^2}{|\mathbf{r} - \mathbf{r}'|} | \mathbf{R}' \mathbf{R} \rangle \\ &= \int d^3r \int d^3r' \varphi^*(\mathbf{r} - \mathbf{R}) \varphi^*(\mathbf{r}' - \mathbf{R}') \frac{e^2}{|\mathbf{r} - \mathbf{r}'|} \varphi(\mathbf{r}' - \mathbf{R}) \varphi(\mathbf{r} - \mathbf{R}') \\ &= \int d^3r \int d^3r' \varphi^*(\mathbf{r}) \varphi(\mathbf{r} + \mathbf{R} - \mathbf{R}') \frac{e^2}{|\mathbf{r} - \mathbf{r}'|} \varphi^*(\mathbf{r}' + \mathbf{R} - \mathbf{R}') \varphi(\mathbf{r}') .\end{aligned}\quad (4.141)$$

Note that $J(\mathbf{R} - \mathbf{R}')$ is real. The exchange part of \hat{V} is then

$$\hat{V}_{\text{exchange}} = -\frac{1}{2} \sum_{\substack{\mathbf{R} \neq \mathbf{R}' \\ \sigma\sigma'}} J(\mathbf{R} - \mathbf{R}') c_{\mathbf{R}\sigma}^\dagger c_{\mathbf{R}\sigma'} c_{\mathbf{R}'\sigma'}^\dagger c_{\mathbf{R}'\sigma} \quad (4.142)$$

$$= -\frac{1}{4} \sum_{\mathbf{R} \neq \mathbf{R}'} J(\mathbf{R} - \mathbf{R}') \left(n_{\mathbf{R}} n_{\mathbf{R}'} + \boldsymbol{\sigma}_{\mathbf{R}} \cdot \boldsymbol{\sigma}_{\mathbf{R}'} \right) . \quad (4.143)$$

The $n_{\mathbf{R}} n_{\mathbf{R}'}$ piece can be lumped with the direct density-density interaction. What is new is the Heisenberg interaction,

$$\hat{V}_{\text{Heis}} = - \sum_{\mathbf{R} \neq \mathbf{R}'} J(\mathbf{R} - \mathbf{R}') \mathbf{S}_{\mathbf{R}} \cdot \mathbf{S}_{\mathbf{R}'} . \quad (4.144)$$

$J(\mathbf{R} - \mathbf{R}')$ is usually positive, and this gives us an explanation of Hund's first rule, which says to maximize S . This raises an interesting point, because we know that the ground state spatial wavefunction for the general two-body Hamiltonian

$$\mathcal{H} = -\frac{\hbar^2}{2m} (\nabla_1^2 + \nabla_2^2) + V(|\mathbf{r}_1 - \mathbf{r}_2|) \quad (4.145)$$

is nodeless. Thus, for fermions, the ground state spin wavefunction is an antisymmetric singlet state, corresponding to $S = 0$. Yet the V^{3+} ion, with electronic configuration $[\text{Ar}] 3\text{d}^2$, has a triplet $S = 1$ ground state, according to Hund's first rule. Why don't the two 3d electrons have a singlet ground state, as the 'no nodes theorem' would seem to

imply? The answer must have to do with the presence of the core electrons. Two electrons in the 1s shell do have a singlet ground state – indeed that is the only possibility. But the two 3d electrons in V^{3+} are not independent, but must be orthogonalized to the core states. This in effect projects out certain parts of the wavefunction, rendering the no nodes theorem inapplicable.

4.7.2 Heitler-London Theory of the H_2 Molecule

The Hamiltonian for the H_2 molecule is

$$\begin{aligned} \mathcal{H} = & \frac{\mathbf{p}_1^2}{2m} - \frac{e^2}{|\mathbf{r}_1 - \mathbf{R}_a|} + \frac{\mathbf{p}_2^2}{2m} - \frac{e^2}{|\mathbf{r}_2 - \mathbf{R}_b|} \\ & + \frac{e^2}{|\mathbf{R}_a - \mathbf{R}_b|} - \frac{e^2}{|\mathbf{r}_1 - \mathbf{R}_b|} - \frac{e^2}{|\mathbf{r}_2 - \mathbf{R}_a|} + \frac{e^2}{|\mathbf{r}_1 - \mathbf{r}_2|}. \end{aligned} \quad (4.146)$$

The total wavefunction is antisymmetric: $\Psi(\mathbf{r}_1 \sigma_1, \mathbf{r}_2 \sigma_2) = -\Psi(\mathbf{r}_2 \sigma_2, \mathbf{r}_1 \sigma_1)$. The $N = 2$ electron case is special because the wavefunction factorizes into a product:

$$\Psi(\mathbf{r}_1 \sigma_1, \mathbf{r}_2 \sigma_2) = \Phi(\mathbf{r}_1, \mathbf{r}_2) \chi(\sigma_1, \sigma_2). \quad (4.147)$$

The spin wavefunction may either be symmetric (triplet, $S = 1$), or antisymmetric (singlet, $S = 0$):

$$|\chi\rangle = \begin{cases} |\uparrow\uparrow\rangle & S = 1 \\ \frac{1}{\sqrt{2}}(|\uparrow\downarrow\rangle + |\downarrow\uparrow\rangle) & S = 1 \\ |\downarrow\downarrow\rangle & S = 1 \\ \frac{1}{\sqrt{2}}(|\uparrow\downarrow\rangle - |\downarrow\uparrow\rangle) & S = 0. \end{cases} \quad (4.148)$$

A symmetric spin wavefunction requires an antisymmetric spatial one, and *vice versa*.

Despite the fact that \mathcal{H} does not explicitly depend on spin, the effective low-energy Hamiltonian for this system is

$$\mathcal{H}_{\text{eff}} = K + J\mathbf{S}_1 \cdot \mathbf{S}_2. \quad (4.149)$$

The singlet-triplet splitting is $\Delta E = E_{S=0} - E_{S=1} = -J$, so if $J > 0$ the ground state is the singlet, and if $J < 0$ the ground state is the three-fold degenerate triplet.

The one-electron 1s eigenfunction $\psi(\mathbf{r})$ satisfies the following eigenvalue equation:

$$\left\{ -\frac{\hbar^2}{2m} \nabla^2 - \frac{e^2}{r} \right\} \psi(\mathbf{r}) = \varepsilon_0(\mathbf{r}) \psi(\mathbf{r}). \quad (4.150)$$

In the Heitler-London approach, we write the two-electron wavefunction as a linear combination

$$\Phi(\mathbf{r}_1, \mathbf{r}_2) = \alpha \Phi_I(\mathbf{r}_1, \mathbf{r}_2) + \beta \Phi_{II}(\mathbf{r}_1, \mathbf{r}_2), \quad (4.151)$$

with

$$\Phi_I(\mathbf{r}_1, \mathbf{r}_2) = \psi(\mathbf{r}_1 - \mathbf{R}_a) \psi(\mathbf{r}_2 - \mathbf{R}_b) \equiv \psi_a(\mathbf{r}_1) \psi_b(\mathbf{r}_2) \quad (4.152)$$

$$\Phi_{II}(\mathbf{r}_1, \mathbf{r}_2) = \psi(\mathbf{r}_1 - \mathbf{R}_b) \psi(\mathbf{r}_2 - \mathbf{R}_a) \equiv \psi_b(\mathbf{r}_1) \psi_a(\mathbf{r}_2) . \quad (4.153)$$

Assuming the atomic orbital $\psi(\mathbf{r})$ to be normalized, we define the following integrals:

$$\Delta = \int d^3r \psi_a^*(\mathbf{r}) \psi_b(\mathbf{r}) \quad (4.154)$$

$$X = \int d^3r_1 \int d^3r_2 |\Phi_I(\mathbf{r}_1, \mathbf{r}_2)|^2 \left(\frac{e^2}{R_{ab}} + \frac{e^2}{r_{12}} - \frac{e^2}{r_{1b}} - \frac{e^2}{r_{2a}} \right) \quad (4.155)$$

$$= \int d^3r_1 \int d^3r_2 |\Phi_{II}(\mathbf{r}_1, \mathbf{r}_2)|^2 \left(\frac{e^2}{R_{ab}} + \frac{e^2}{r_{12}} - \frac{e^2}{r_{1a}} - \frac{e^2}{r_{2b}} \right)$$

$$Y = \int d^3r_1 \int d^3r_2 \Phi_I^*(\mathbf{r}_1, \mathbf{r}_2) \Phi_{II}(\mathbf{r}_1, \mathbf{r}_2) \left(\frac{e^2}{R_{ab}} + \frac{e^2}{r_{12}} - \frac{e^2}{r_{1b}} - \frac{e^2}{r_{2a}} \right) , \quad (4.156)$$

with $\mathbf{r}_{1a} = \mathbf{r}_1 - \mathbf{R}_a$, etc. The expectation value of \mathcal{H} in the state Φ is

$$\langle \Phi | \mathcal{H} | \Phi \rangle = (|\alpha|^2 + |\beta|^2)(2\varepsilon_0 + X) + (\alpha^*\beta + \beta^*\alpha)(2\varepsilon|\Delta|^2 + Y) , \quad (4.157)$$

and the self-overlap is

$$\langle \Phi | \Phi \rangle = |\alpha|^2 + |\beta|^2 + |\Delta|^2 (\alpha^*\beta + \beta^*\alpha) . \quad (4.158)$$

We now minimize $\langle \mathcal{H} \rangle$ subject to the condition that Φ be normalized, using a Lagrange multiplier E to impose the normalization. Extremizing with respect to α^* and β^* yields

$$\begin{pmatrix} 2\varepsilon_0 + X & 2\varepsilon_0|\Delta|^2 + Y \\ 2\varepsilon_0|\Delta|^2 + Y & 2\varepsilon_0 + X \end{pmatrix} \begin{pmatrix} \alpha \\ \beta \end{pmatrix} = E \begin{pmatrix} 1 & |\Delta|^2 \\ |\Delta|^2 & 1 \end{pmatrix} \begin{pmatrix} \alpha \\ \beta \end{pmatrix} , \quad (4.159)$$

and extremizing with respect to E yields the normalization condition

$$|\alpha|^2 + |\beta|^2 + |\Delta|^2 (\alpha^*\beta + \beta^*\alpha) = 1 . \quad (4.160)$$

The solutions are symmetric and antisymmetric states, with $\beta/\alpha = \pm 1$, corresponding to the energies

$$E_{\pm} = 2\varepsilon_0 + \frac{X \pm Y}{1 \pm |\Delta|^2} . \quad (4.161)$$

Note that E_+ is the energy of the spatially symmetric state, which means a spin singlet while E_- corresponds to the spatially antisymmetric spin triplet.

The singlet-triplet splitting is

$$J = E_- - E_+ = 2 \frac{Y - X|\Delta|^2}{1 - |\Delta|^4} . \quad (4.162)$$

If $J > 0$, the triplet lies higher than the singlet, which says the ground state is antiferromagnetic. If $J < 0$, the triplet lies lower, and the ground state is ferromagnetic. The energy difference is largely determined by the Y integral:

$$Y = \int d^3r_1 \int d^3r_2 \Upsilon^*(\mathbf{r}_1) \Upsilon(\mathbf{r}_2) \left(\frac{e^2}{R_{ab}} + \frac{e^2}{r_{12}} \right) - 2 \Delta^* \int d^3r \psi_a^*(\mathbf{r}) \frac{e^2}{|\mathbf{r} - \mathbf{R}_b|} \psi_b(\mathbf{r}), \quad (4.163)$$

with $\Upsilon(\mathbf{r}) = \psi_a^*(\mathbf{r}) \psi_b(\mathbf{r})$. The first term is positive definite for the Coulomb interaction. The second term competes with the first if the overlap is considerable. The moral of the story now emerges:

$$\begin{aligned} \text{weak overlap} &\implies \text{ferromagnetism } (J < 0) \\ \text{strong overlap} &\implies \text{antiferromagnetism } (J > 0). \end{aligned}$$

One finds that the H_2 molecule is indeed bound in the singlet state – the total energy has a minimum as a function of the separation $|\mathbf{R}_a - \mathbf{R}_b|$. In the triplet state, the molecule is unbound.

4.7.3 Failure of Heitler-London Theory

At large separations $R \equiv |\mathbf{R}_a - \mathbf{R}_b|$ the Heitler-London method describes two H atoms with tiny overlap of the electronic wavefunctions. But this tiny overlap is what determines whether the ground state is a total spin singlet or triplet (we ignore coupling to the nuclear spin). Sugiura obtained the following expression for the singlet-triplet splitting in the $R \rightarrow \infty$ limit:

$$J(R) \simeq \left[\frac{56}{45} - \frac{4}{15}\gamma - \frac{4}{15} \ln \left(\frac{R}{a_H} \right) \right] \left(\frac{R}{a_H} \right)^3 \left(\frac{e^2}{a_H} \right) e^{-2R/a_H}, \quad (4.164)$$

where $\gamma = 0.577\dots$ is the Euler constant and where $\psi(r) = (\pi a_H^3)^{-1/2} \exp(-r/a_H)$ is the hydrogenic wavefunction. This is negative for sufficiently large separations ($R > 50 a_H$). But this is a problem, since the eigenvalue problem is a Sturm-Liouville problem, hence the lowest energy eigenfunction must be spatially symmetric – *the singlet state must always lie at lower energy than the triplet*. The problem here is that Heitler-London theory does a good job on the wavefunction where it is large, *i.e.* in the vicinity of the protons, but a lousy job in the overlap region.

4.7.4 Herring's approach

Conyers Herring was the first to elucidate the failure of Heitler-London theory at large separations. He also showed how to properly derive a Heisenberg model for a lattice of

hydrogenic orbitals. Herring started with the symmetric spatial wavefunction

$$\Psi(\mathbf{r}_1, \dots, \mathbf{r}_N) = \prod_{i=1}^N \psi(\mathbf{r}_i - \mathbf{R}_i) . \quad (4.165)$$

This wavefunction would be appropriate were the electrons distinguishable. If we permute the electron coordinates using a spatial permutation $P_{\text{space}} \in \mathcal{S}_N$, we obtain another wavefunction of the same energy, E_0 . However, there will be an overlap between these states:

$$J_P \equiv \langle \Psi | \mathcal{H} - E_0 | P_r \Psi \rangle . \quad (4.166)$$

The effective Hamiltonian is then

$$\mathcal{H}_{\text{eff}} = E_0 + \sum_{P \in \mathcal{S}_N} J_P P_r . \quad (4.167)$$

A complete permutation P is a product of spatial and spin permutations: $P = P_r P_\sigma$, and the product when acting on an electronic wavefunction is $(-1)^P$, which is $+1$ for an even permutation and (-1) for an odd one⁷. Thus,

$$\mathcal{H}_{\text{eff}} = E_0 + \sum_{P \in \mathcal{S}_N} (-1)^P J_P P_\sigma . \quad (4.168)$$

The spin permutation operators P_σ may be written in terms of the Pauli spin matrices, once we note that the two-cycle (ij) may be written

$$P_{(ij)} = \frac{1}{2} + \frac{1}{2} \boldsymbol{\sigma}_i \cdot \boldsymbol{\sigma}_j . \quad (4.169)$$

Thus, accounting for only two-cycles, we have

$$\mathcal{H}_{\text{eff}} = E_0 - \frac{1}{4} \sum_{i \neq j} J_{ij} (1 + \boldsymbol{\sigma}_i \cdot \boldsymbol{\sigma}_j) . \quad (4.170)$$

For three-cycles, we have

$$\begin{aligned} P_{(ijk)} &= P_{(ik)} P_{(jk)} \\ &= \frac{1}{4} (1 + \boldsymbol{\sigma}_i \cdot \boldsymbol{\sigma}_k) (1 + \boldsymbol{\sigma}_j \cdot \boldsymbol{\sigma}_k) \\ &= \frac{1}{4} [1 + \boldsymbol{\sigma}_i \cdot \boldsymbol{\sigma}_j + \boldsymbol{\sigma}_j \cdot \boldsymbol{\sigma}_k + \boldsymbol{\sigma}_i \cdot \boldsymbol{\sigma}_k + i \boldsymbol{\sigma}_i \times \boldsymbol{\sigma}_j \cdot \boldsymbol{\sigma}_k] . \end{aligned} \quad (4.171)$$

4.8 Mean Field Theory

We begin with the Heisenberg Hamiltonian

$$\mathcal{H} = -\frac{1}{2} \sum_{i,j} J_{ij} \mathbf{S}_i \cdot \mathbf{S}_j - \gamma \sum_i \mathbf{H}_i \cdot \mathbf{S}_i , \quad (4.172)$$

⁷Here, ‘even’ and ‘odd’ refer to the number of 2-cycles into which a given permutation is decomposed.

and write

$$\mathbf{S}_i = \mathbf{m}_i + \delta\mathbf{S}_i , \quad (4.173)$$

where $\mathbf{m}_i = \langle \mathbf{S}_i \rangle$ is the thermodynamic average of \mathbf{S}_i . We therefore have

$$\begin{aligned} \mathbf{S}_i \cdot \mathbf{S}_j &= \mathbf{m}_i \cdot \mathbf{m}_j + \mathbf{m}_i \cdot \delta\mathbf{S}_j + \mathbf{m}_j \cdot \delta\mathbf{S}_i + \delta\mathbf{S}_i \cdot \delta\mathbf{S}_j \\ &= -\mathbf{m}_i \cdot \mathbf{m}_j + \mathbf{m}_i \cdot \mathbf{S}_j + \mathbf{m}_j \cdot \mathbf{S}_i + \delta\mathbf{S}_i \cdot \delta\mathbf{S}_j . \end{aligned} \quad (4.174)$$

The last term is quadratic in the fluctuations, and as an approximation we ignore it. This results in the following *mean field Hamiltonian*,

$$\begin{aligned} \mathcal{H}^{\text{MF}} &= +\frac{1}{2} \sum_{i,j} J_{ij} \mathbf{m}_i \cdot \mathbf{m}_j - \sum_i \left(\gamma \mathbf{H}_i + \sum_j J_{ij} \mathbf{m}_j \right) \cdot \mathbf{S}_i \\ &= E_0 - \gamma \sum_i \mathbf{H}_i^{\text{eff}} \cdot \mathbf{S}_i , \end{aligned} \quad (4.175)$$

where

$$E_0 = \frac{1}{2} \sum_{i,j} J_{ij} \mathbf{m}_i \cdot \mathbf{m}_j \quad (4.176)$$

$$\mathbf{H}_i^{\text{eff}} = \mathbf{H}_i + \gamma^{-1} \sum_j J_{ij} \mathbf{m}_j . \quad (4.177)$$

Note how the *effective field* $\mathbf{H}_i^{\text{eff}}$ is a sum of the external field \mathbf{H}_i and the *internal field* $\mathbf{H}_i^{\text{int}} = \gamma^{-1} \sum_j J_{ij} \mathbf{m}_j$. Self-consistency now requires that

$$\mathbf{m}_i = \frac{\text{Tr } \mathbf{S}_i \exp(\gamma \mathbf{H}_i^{\text{eff}} \cdot \mathbf{S}_i / k_B T)}{\text{Tr} \exp(\gamma \mathbf{H}_i^{\text{eff}} \cdot \mathbf{S}_i / k_B T)} , \quad (4.178)$$

where Tr means to sum or integrate over all local degrees of freedom (for site i). The free energy is then

$$F(\{\mathbf{m}_i\}) = \frac{1}{2} \sum_{i,j} J_{ij} \mathbf{m}_i \cdot \mathbf{m}_j - k_B T \sum_i \ln \text{Tr} \exp(\gamma \mathbf{H}_i^{\text{eff}} \cdot \mathbf{S}_i / k_B T) . \quad (4.179)$$

For classical systems, there are several common models:

- Ising Model with $S = \pm 1$:

$$\begin{aligned} m_i &= \tanh(\gamma H_i^{\text{eff}} / k_B T) \\ &= \tanh\left(\beta \gamma H_i + \beta \sum_j J_{ij} m_j\right) . \end{aligned} \quad (4.180)$$

The free energy is

$$F = \frac{1}{2} \sum_{i,j} J_{ij} m_i m_j - k_B T \sum_i \ln 2 \cosh\left(\beta \gamma H_i + \beta \sum_j J_{ij} m_j\right) . \quad (4.181)$$

- Ising Model with $S = -1, 0, +1$:

$$m_i = \frac{2 \sinh(\beta\gamma H_i + \beta \sum_j J_{ij} m_j)}{1 + 2 \cosh(\beta\gamma H_i + \beta \sum_j J_{ij} m_j)} \quad (4.182)$$

and

$$F = \frac{1}{2} \sum_{i,j} J_{ij} m_i m_j - k_B T \sum_i \ln \left\{ 1 + 2 \cosh \left(\beta\gamma H_i + \beta \sum_j J_{ij} m_j \right) \right\}. \quad (4.183)$$

- XY model with $\mathbf{S}_i = (\cos \theta_i, \sin \theta_i)$, $\mathbf{H} = H \hat{\mathbf{x}}$

$$m_i = \langle \cos \theta_i \rangle = \frac{\int_0^{2\pi} d\theta_i \cos \theta_i \exp(\gamma H_i^{\text{eff}} \cos \theta_i / k_B T)}{\int_0^{2\pi} d\theta_i \exp(\gamma H_i^{\text{eff}} \cos \theta_i / k_B T)} \quad (4.184)$$

$$= \frac{I_1(\beta\gamma H_i + \beta \sum_j J_{ij} m_j)}{I_0(\beta\gamma H_i + \beta \sum_j J_{ij} m_j)}, \quad (4.185)$$

where $I_n(z)$ is a modified Bessel function. The free energy is

$$F = \frac{1}{2} \sum_{i,j} J_{ij} m_i m_j - k_B T \sum_i \ln 2\pi I_0 \left(\beta\gamma H_i + \beta \sum_j J_{ij} m_j \right). \quad (4.186)$$

- O(3) model with $\mathbf{S}_i = (\sin \theta_i \cos \phi_i, \sin \theta_i \sin \phi_i, \cos \theta_i)$. Suppose that \mathbf{m}_i points in the direction of $\mathbf{H}_i^{\text{eff}}$. Then

$$m_i = \langle \cos \theta_i \rangle = \frac{2\pi \int_0^{2\pi} d\theta_i \sin \theta_i \cos \theta_i \exp(\gamma H_i^{\text{eff}} \cos \theta_i / k_B T)}{2\pi \int_0^{2\pi} d\theta_i \sin \theta_i \exp(\gamma H_i^{\text{eff}} \cos \theta_i / k_B T)} \quad (4.187)$$

$$= \operatorname{ctnh}(\gamma H_i^{\text{eff}} / k_B T) - \frac{k_B T}{\gamma H_i^{\text{eff}}} \quad (4.188)$$

$$= \operatorname{ctnh} \left(\beta\gamma H_i + \beta \sum_j J_{ij} m_j \right) - \frac{k_B T}{\gamma H_i + \sum_j J_{ij} m_j}. \quad (4.189)$$

The free energy is

$$F = \frac{1}{2} \sum_{i,j} J_{ij} m_i m_j - k_B T \sum_i \ln \left\{ \frac{4\pi \sinh \left(\beta\gamma H_i + \beta \sum_j J_{ij} m_j \right)}{\beta\gamma H_i + \beta \sum_j J_{ij} m_j} \right\}. \quad (4.190)$$

EXERCISE: Show that the self-consistency is equivalent to $\partial F / \partial m_i = 0$.

4.8.1 Ferromagnets

Ising Model – Let us assume that the system orders ferromagnetically, with $m_i = m$ on all sites. Then, defining

$$\hat{J}(\mathbf{q}) = \sum_{\mathbf{R}} J(\mathbf{R}) e^{-i\mathbf{q}\cdot\mathbf{R}}, \quad (4.191)$$

we have that the free energy per site, $f = F/N$, is

$$f(m) = \frac{1}{2} \hat{J}(0) \mathbf{m}^2 - k_B T \ln \text{Tr} \exp \left\{ (\gamma \mathbf{H} + \hat{J}(0) \mathbf{m}) \cdot \mathbf{S} / k_B T \right\}. \quad (4.192)$$

For the \mathbb{Z}_2 (Ising) model, we have

$$m = \tanh (\beta \gamma H + \beta \hat{J}(0)m), \quad (4.193)$$

a transcendental equation for m . For $H = 0$, we find $m = \tanh(\hat{J}(0)m/k_B T)$, which yields the Curie temperature $T_C = \hat{J}(0)/k_B$.

O(3) Model – We have $\mathbf{m} = m \hat{\mathbf{H}}$ lies along \mathbf{H} . In the $\mathbf{H} \rightarrow 0$ limit, there is no preferred direction. The amplitude, however, satisfies

$$\frac{\partial f}{\partial m} = 0 \Rightarrow m = \text{ctnh} (\hat{J}(0) m / k_B T) - \frac{k_B T}{\hat{J}(0) m}. \quad (4.194)$$

With $x \equiv \hat{J}(0) m / k_B T$, then,

$$\frac{k_B T}{\hat{J}(0)} x = \text{ctnh } x - \frac{1}{x} = \frac{x}{3} - \frac{x^3}{45} + \dots, \quad (4.195)$$

hence $T_c = \hat{J}(0)/3k_B$.

4.8.2 Antiferromagnets

If the lattice is bipartite, then we have *two* order parameters: \mathbf{m}_A and \mathbf{m}_B . Suppose $J_{ij} = -J < 0$ if i and j are nearest neighbors, and zero otherwise. The effective fields on the A and B sublattices are given by

$$\mathbf{H}_{A,B}^{\text{eff}} \equiv \mathbf{H} - \gamma^{-1} z J \mathbf{m}_{B,A}, \quad (4.196)$$

Note that the internal field on the A sublattice is $-\gamma^{-1} z J \mathbf{m}_B$, while the internal field on the B sublattice is $-\gamma^{-1} z J \mathbf{m}_A$. For the spin- S quantum Heisenberg model, where $S^z \in \{-S, \dots, +S\}$, we have

$$\text{Tr} \exp(\boldsymbol{\xi} \cdot \mathbf{S}) = \frac{\sinh(S + \frac{1}{2})\xi}{\sinh \frac{1}{2}\xi}, \quad (4.197)$$

hence, with $\boldsymbol{\xi} = \gamma \mathbf{H}_{A,B}^{\text{eff}} / k_B T$, we have

$$\langle \mathbf{S} \rangle = \hat{\boldsymbol{\xi}} S B_S(S\xi) \quad (4.198)$$

where $B_S(x)$ is the Brillouin function,

$$B_S(x) = \left(1 + \frac{1}{2S}\right) \operatorname{ctnh} \left(\left(1 + \frac{1}{2S}\right)x\right) - \frac{1}{2S} \operatorname{ctnh} \left(\frac{x}{2S}\right). \quad (4.199)$$

In order to best take advantage of the antiferromagnetic interaction and the external magnetic field, the ordered state is characterized by a *spin flop* in which \mathbf{m}_A and \mathbf{m}_B are, for weak fields, oriented in opposite directions in a plane perpendicular to \mathbf{H} , but each with a small component along \mathbf{H} .

When $H = 0$, the mean field equations take the form

$$m_A = SB_S(zJS m_B/k_B T) \quad (4.200)$$

$$m_B = SB_S(zJS m_A/k_B T), \quad (4.201)$$

where we have assumed \mathbf{m}_A and \mathbf{m}_B are antiparallel, with $\mathbf{m}_A = m_A \hat{\mathbf{n}}$ and $\mathbf{m}_B = -m_B \hat{\mathbf{n}}$, where $\hat{\mathbf{n}}$ is a unit vector. From the expansion of the Brillouin function, we obtain the Néel temperature $T_N = zJ/k_B$.

4.8.3 Susceptibility

For $T > T_c$ the system is paramagnetic, and there is a linear response to an external field,

$$\chi_{ij}^{\mu\nu} = \frac{\partial M_i^\mu}{\partial H_j^\nu} = \gamma \frac{\partial m_i^\mu}{\partial H_j^\nu} = -\frac{\partial^2 F}{\partial H_i^\mu \partial H_j^\nu} \quad (4.202)$$

$$= \frac{\gamma^2}{k_B T} \left\{ \langle S_i^\mu S_j^\nu \rangle - \langle S_i^\mu \rangle \langle S_j^\nu \rangle \right\} \quad (4.203)$$

where $\{i, j\}$ are site indices and $\{\mu, \nu\}$ are internal spin indices. The mean field Hamiltonian is, up to a constant,

$$\mathcal{H}^{\text{MF}} = -\gamma \sum_i \mathbf{H}_i^{\text{eff}} \cdot \mathbf{S}_i, \quad (4.204)$$

which is a sum of single site terms. Hence, the response within \mathcal{H}^{MF} must be purely local as well as isotropic. That is, for weak effective fields, using $\mathbf{M}_i = \gamma \mathbf{m}_i$,

$$\mathbf{M}_i = \chi_0 \mathbf{H}_i^{\text{eff}} = \chi_0 \mathbf{H}_i + \gamma^{-2} \chi_0 J_{ij} \mathbf{M}_j, \quad (4.205)$$

which is equivalent to

$$(\delta_{ij} - \gamma^{-2} \chi_0 J_{ij}) \mathbf{M}_j = \chi_0 \mathbf{H}_i, \quad (4.206)$$

and the mean field susceptibility is

$$\chi_{ij}^{\mu\nu} = [\chi_0^{-1} - \gamma^{-2} J]_{ij}^{-1} \delta^{\mu\nu}. \quad (4.207)$$

It is convenient to work in Fourier space, in which case the matrix structure is avoided and one has

$$\hat{\chi}(\mathbf{q}) = \frac{\chi_0}{1 - \gamma^{-2} \chi_0 \hat{J}(\mathbf{q})}. \quad (4.208)$$

The local susceptibility χ_0 is readily determined:

$$\begin{aligned} M^\mu &= \gamma \langle S^\mu \rangle = \gamma \frac{\text{Tr } \mathbf{S} \exp(\gamma \mathbf{H} \cdot \mathbf{S}/k_B T)}{\text{Tr } \exp(\gamma \mathbf{H} \cdot \mathbf{S}/k_B T)} \\ &= \gamma S B_S(S\gamma H/k_B T) \hat{H}^\mu, \end{aligned} \quad (4.209)$$

where $B_S(x)$ is the Brillouin function from eqn. 4.199. As $\mathbf{H} \rightarrow 0$ we have $\mathbf{M} = \chi_0 \mathbf{H}$, with

$$\chi_0^{\mu\nu} = \frac{\gamma^2}{k_B T} \cdot \frac{\text{Tr } (S^\mu S^\nu)}{\text{Tr } 1} \equiv \chi_0 \delta^{\mu\nu}, \quad (4.210)$$

where $\chi_0 = \frac{1}{N} \text{Tr } (\mathbf{S}^2)/\text{Tr } 1$, where N is the number of components of S^μ . Thus, for the Ising model ($N = 1$) we have $\chi_0^{\text{Ising}} = \gamma^2/k_B T$, while for the spin- S quantum Heisenberg model we have $\chi_0^{\text{Heis}} = S(S+1)\gamma^2/3k_B T$. Note that $\chi_0 \propto T^{-1}$; the splitting of the degenerate energy levels by the magnetic field is of little consequence at high temperatures.

In many cases one deals with ‘single ion anisotropy’ terms. For example, one can add to the Heisenberg Hamiltonian a term such as

$$\mathcal{H}_a = D \sum_i (S_i^z)^2, \quad (4.211)$$

which for $D < 0$ results in an *easy axis* anisotropy (*i.e.* the spins prefer to align along the \hat{z} -axis), and for $D > 0$ results in an *easy plane* anisotropy (*i.e.* the spins prefer to lie in the (x, y) plane). Since this term is already the sum of single site Hamiltonians, there is no need to subject it to a mean field treatment. One then obtains the mean field Hamiltonian

$$\mathcal{H}^{\text{MF}} = D \sum_i (S_i^z)^2 - \gamma \sum_i \mathbf{H}_i^{\text{eff}} \cdot \mathbf{S}_i. \quad (4.212)$$

In this case, χ_0 is now *anisotropic* in spin space. The general formula for χ_0 is

$$\chi_0^{\mu\nu} = \frac{\gamma^2}{k_B T} \langle S^\mu S^\nu \rangle \quad (4.213)$$

where the thermodynamic average is taken with respect to the single site Hamiltonian.⁸ One then has

$$\hat{\chi}_0^{\mu\nu}(\mathbf{q}) = \chi_0^{\mu\lambda} [\mathbb{I} - \gamma^{-2} \hat{J}(\mathbf{q}) \overset{\leftrightarrow}{\chi}_0]_{\lambda\nu}^{-1}, \quad (4.214)$$

where the matrix inverse is now in internal spin space.

4.8.4 Variational Probability Distribution

Here’s another way to derive mean field theory. Let Ω represent a configuration and let P_Ω be a probability distribution, normalized such that $\sum_\Omega P_\Omega = 1$. We define the entropy of the distribution as

$$S[P] = -k_B \sum_\Omega P_\Omega \ln P_\Omega. \quad (4.215)$$

⁸Note that in (4.210) the single site Hamiltonian is simply $\mathcal{H}_0 = 0$.

We now ask what distribution P_Ω minimizes the free energy $F = \langle \mathcal{H} \rangle - TS$. Working in an eigenbasis of \mathcal{H} , we have

$$F = \sum_{\Omega} P_{\Omega} E_{\Omega} + k_B T \sum_{\Omega} P_{\Omega} \ln P_{\Omega} . \quad (4.216)$$

We extremize F subject to the normalization constraint, which is implemented with a Lagrange multiplier λ . This means we form the extended function

$$F^*(\{P_{\Omega}\}, \lambda) = \sum_{\Omega} P_{\Omega} E_{\Omega} + k_B T \sum_{\Omega} P_{\Omega} \ln P_{\Omega} - \lambda \left(\sum_{\Omega} P_{\Omega} - 1 \right) , \quad (4.217)$$

and demand $dF^*/dP_{\Omega} = 0$ for all Ω as well as $dF^*/d\lambda = 0$. This results in the Boltzmann distribution,

$$P_{\Omega}^{\text{eq}} = \frac{1}{Z} e^{-E_{\Omega}/k_B T} , \quad Z = \sum_l e^{-E_l/k_B T} . \quad (4.218)$$

Thus, *any distribution other than P_{Ω}^{eq} results in a larger free energy.*

Mean field theory may be formulated in terms of a variational probability distribution. Thus, rather than working with the Boltzmann distribution P_{Ω}^{eq} , which is usually intractable, we invoke a trial distribution $P_{\Omega}(x_1, x_2, \dots)$, parameterized by $\{x_1, x_2, \dots\}$, and minimize the resultant $F = \langle \mathcal{H} \rangle - TS$ with respect to those parameters.

As an example, consider the Ising model with spins $\sigma_i = \pm 1$. Each configuration is given by the set of spin polarizations: $\Omega = \{\sigma_1, \dots, \sigma_N\}$. The full equilibrium probability distribution,

$$P_{\Omega}^{\text{eq}} = Z^{-1} \exp \left(\beta J \sum_{\langle ij \rangle} \sigma_i \sigma_j \right) , \quad (4.219)$$

with $\beta = 1/k_B T$, is too cumbersome to work with. We replace this with a variational single-site distribution,

$$P_{\Omega} = \prod_{j=1}^N P_i(\sigma_i) \quad (4.220)$$

$$P_i(\sigma_i) = \frac{1}{2}(1 + m_i) \delta_{\sigma_i, +1} + \frac{1}{2}(1 - m_i) \delta_{\sigma_i, -1} . \quad (4.221)$$

The variational parameters are $\{m_1, \dots, m_N\}$. Note that P_{Ω} is properly normalized, by construction.

The entropy of our trial distribution is decomposed into a sum over single site terms:

$$S[P] = \sum_i s(m_i) \quad (4.222)$$

$$s(m) = -k_B \left\{ \frac{1+m}{2} \ln \left(\frac{1+m}{2} \right) + \frac{1-m}{2} \ln \left(\frac{1-m}{2} \right) \right\} \quad (4.223)$$

The thermodynamic average $\langle \sigma_i \rangle$ is simply

$$\langle \sigma_i \rangle = \text{Tr } P_i(\sigma_i) \sigma_i = m_i , \quad (4.224)$$

hence from

$$\mathcal{H} = -\frac{1}{2} \sum_{i,j} J_{ij} \sigma_i \sigma_j - \gamma \sum_i H_i \sigma_i , \quad (4.225)$$

we derive the free energy

$$\begin{aligned} F(\{m_i\}) &= -\frac{1}{2} \sum_{i,j} J_{ij} m_i m_j - \gamma \sum_i H_i m_i \\ &\quad + k_B T \sum_i \left\{ \frac{1+m_i}{2} \ln \left(\frac{1+m_i}{2} \right) + \frac{1-m_i}{2} \ln \left(\frac{1-m_i}{2} \right) \right\} \end{aligned} \quad (4.226)$$

Varying with respect to each m_i , we obtain the coupled nonlinear mean field equations,

$$m_i = \tanh \left[\left(\sum_j J_{ij} m_j + \gamma H_i \right) / k_B T \right] . \quad (4.227)$$

For uniform magnetization ($m_i = m \forall i$), the free energy per site is

$$\begin{aligned} \frac{F}{N} &= -\frac{1}{2} \hat{J}(0) m^2 - \gamma H m + k_B T \left\{ \frac{1+m}{2} \ln \left(\frac{1+m}{2} \right) + \frac{1-m}{2} \ln \left(\frac{1-m}{2} \right) \right\} \\ &= \frac{1}{2} (k_B T - \hat{J}(0)) m^2 - \gamma H m + \frac{1}{12} k_B T m^4 + \frac{1}{30} k_B T m^6 + \dots \end{aligned} \quad (4.228)$$

To compute the correlations, we may use the expression

$$\chi_{ij}(T) = \frac{\gamma^2}{k_B T} \left\{ \langle \sigma_i \sigma_j \rangle - \langle \sigma_i \rangle \langle \sigma_j \rangle \right\} \quad (4.229)$$

$$= \frac{\partial M_i}{\partial H_j} = \gamma \frac{\partial m_i}{\partial H_j} = -\frac{\partial^2 F}{\partial H_i \partial H_j} . \quad (4.230)$$

Thus, there are two ways to compute the susceptibility. One is to evaluate the spin-spin *correlation function*, as in (4.229). The other is to differentiate the magnetization to obtain the *response function*, as in (4.230). The equality between the two – called the “fluctuation-dissipation theorem” – is in fact only valid for the equilibrium Boltzmann distribution P_Ω^{eq} . Which side of the equation should we use in our variational mean field theory? It is more accurate to use the response function. To roughly see this, let us write $P = P^{\text{eq}} + \delta P$, with δP small in some sense. The free energy is given by

$$F[P] = F[P^{\text{eq}}] + \delta P \cdot \frac{\delta F}{\delta P} \Big|_{P=P^{\text{eq}}} + \mathcal{O}((\delta P)^2) . \quad (4.231)$$

Our variational treatment guarantees that the second term vanishes, since we extremize F with respect to P . Thus, in some sense, the error in F is only of order $(\delta P)^2$. If we compute the correlation function using $\langle A \rangle = \text{Tr}(P A)$, where A is any operator, then the error will be linear in δP . So it is better to use the response function than the correlation function.

EXERCISE: Articulate the correspondence between this variational version of mean field theory and the ‘neglect of fluctuations’ approach we derived earlier.

4.9 Magnetic Ordering

The \mathbf{q} -dependent susceptibility in (4.208) diverges when $\gamma^{-2}\chi_0\hat{J}(\mathbf{q}) = 1$. As we know, such a divergence heralds the onset of a *phase transition* where there is a *spontaneous magnetization* in the ordered (*i.e.* low temperature) phase. Typically this happens at a particular wavevector \mathbf{Q} , or a set of symmetry related wavevectors $\{\mathbf{Q}_1, \mathbf{Q}_2, \dots\}$. The ordering wavevector is that value of \mathbf{q} which results in a *maximum* of $\hat{J}(\mathbf{q})$: $\max_{\mathbf{q}}\{\hat{J}(\mathbf{q})\} = \hat{J}(\mathbf{Q})$. The susceptibility, for isotropic systems, can be written

$$\hat{\chi}(\mathbf{q}) = \frac{\chi_0}{[1 - \gamma^{-2}\chi_0\hat{J}(\mathbf{Q})] + \gamma^{-2}\chi_0[\hat{J}(\mathbf{Q}) - \hat{J}(\mathbf{q})]} . \quad (4.232)$$

The critical temperature T_c is determined by the relation

$$\gamma^{-2}\chi_0(T_c)\hat{J}(\mathbf{Q}) = 1. \quad (4.233)$$

Expanding about $T = T_c$, and about $\mathbf{q} = \mathbf{Q}$, where

$$\hat{J}(\mathbf{q}) = \hat{J}(\mathbf{Q})\left\{1 - (\mathbf{q} - \mathbf{Q})^2R_*^2 + \dots\right\}, \quad (4.234)$$

we have

$$\hat{\chi}(\mathbf{q}) \approx \frac{\chi_0/R_*^2}{\xi^{-2}(T) + (\mathbf{q} - \mathbf{Q})^2}, \quad (4.235)$$

where

$$\xi^{-2}(T) = -\frac{\chi'_0(T_c)}{\chi_0(T_c)} \cdot R_*^{-2} \cdot (T - T_c). \quad (4.236)$$

Thus, $\xi(T) \propto (T - T_c)^{-1/2}$. The real space susceptibility $\chi(\mathbf{R}_i - \mathbf{R}_j)$ oscillates with wavevector \mathbf{Q} and decays on the scale of the correlation length $\xi(T)$.

- *Ferromagnet*: $J_{ij} = +J > 0$ if i and j are nearest neighbors; otherwise $J_{ij} = 0$. On a hypercubic lattice (d dimensions, $2d$ nearest neighbors), we then have

$$\hat{J}(\mathbf{q}) = J \sum_{\delta} e^{-i\mathbf{q}\cdot\delta} = 2J\{\cos(q_1a) + \cos(q_2a) + \dots + \cos(q_da)\}. \quad (4.237)$$

The ordering wavevector is $\mathbf{Q} = 0$, and $\hat{J}(\mathbf{Q}) = 2dJ$. For the spin- S Heisenberg model, then, $T_C = \frac{2}{3}dS(S+1)J/k_B$, and the susceptibility is

$$\hat{\chi}(\mathbf{q}) = \frac{\frac{1}{3}\gamma^2S(S+1)/k_B}{(T - T_C) + T_C d^{-1} \sum_{\nu=1}^d [1 - \cos(q_{\nu}a)]}. \quad (4.238)$$

The uniform susceptibility $\chi = \hat{\chi}(\mathbf{q} = 0)$ is then

$$\chi(T) = \frac{\gamma^2S(S+1)}{3k_B(T - T_C)}. \quad (4.239)$$

Ferromagnetic insulators: ferrites, EuO, TDAE-C₆₀.

- *Antiferromagnet:* $J_{ij} = -J < 0$ if i and j are nearest neighbors; otherwise $J_{ij} = 0$. On a hypercubic lattice (d dimensions, $2d$ nearest neighbors), we then have

$$\hat{J}(\mathbf{q}) = -J \sum_{\delta} e^{-i\mathbf{q}\cdot\delta} = -2J \{ \cos(q_1 a) + \cos(q_2 a) + \dots + \cos(q_d a) \}. \quad (4.240)$$

The ordering wavevector is $\mathbf{Q} = (\pi/a, \dots, \pi/a)$, at the zone corner, where $\hat{J}(\mathbf{Q}) = 2dJ$. For the spin- S Heisenberg model, then, $T_N = \frac{2}{3}dS(S+1)J/k_B$, and the susceptibility is

$$\hat{\chi}(\mathbf{q}) = \frac{\gamma^2 S(S+1)/3k_B}{(T - T_N) + T_N d^{-1} \sum_{\nu=1}^d [1 + \cos(q_{\nu} a)]}. \quad (4.241)$$

The uniform susceptibility $\chi = \hat{\chi}(\mathbf{q} = 0)$ is then

$$\chi(T) = \frac{\gamma^2 S(S+1)}{3k_B(T + T_N)}, \quad (4.242)$$

which *does not diverge*. Indeed, plotting $\chi^{-1}(T)$ versus T , one obtains an intercept along the T -axis at $T = -T_N$. This is one crude way of estimating the Néel temperature. What *does* diverge is the *staggered susceptibility* $\chi_{\text{stag}} \equiv \hat{\chi}(\mathbf{Q}, T)$, *i.e.* the susceptibility at the ordering wavevector:

$$\chi_{\text{stag}}(T) = \frac{\gamma^2 S(S+1)}{3k_B(T - T_N)}. \quad (4.243)$$

- *Frustrated Antiferromagnet:* On the triangular lattice, the antiferromagnetic state is frustrated. What does mean field theory predict? We begin by writing primitive direct lattice vectors $\{\mathbf{a}_1, \mathbf{a}_2\}$ and primitive reciprocal lattice vectors $\{\mathbf{b}_1, \mathbf{b}_2\}$:

$$\mathbf{a}_1 = a(1, 0) \quad \mathbf{b}_1 = \frac{4\pi}{a\sqrt{3}} \left(\frac{\sqrt{3}}{2}, -\frac{1}{2} \right) \quad (4.244)$$

$$\mathbf{a}_2 = a\left(\frac{1}{2}, \frac{\sqrt{3}}{2}\right) \quad \mathbf{b}_2 = \frac{4\pi}{a\sqrt{3}} (0, 1), \quad (4.245)$$

where a is the lattice constant. The six nearest neighbor vectors are then

$$\delta \in \left\{ \mathbf{a}_1, \mathbf{a}_2, \mathbf{a}_2 - \mathbf{a}_1, -\mathbf{a}_1, -\mathbf{a}_2, \mathbf{a}_1 - \mathbf{a}_2 \right\}, \quad (4.246)$$

and writing $\mathbf{q} \equiv x_1 \mathbf{b}_1 + x_2 \mathbf{b}_2$, we find

$$\hat{J}(\mathbf{q}) = -2J \{ \cos(2\pi x_1) + \cos(2\pi x_2) + \cos(2\pi x_1 - 2\pi x_2) \}. \quad (4.247)$$

We suspect that this should be maximized somewhere along the perimeter of the Brillouin zone. The face center lies at $(x_1, x_2) = (\frac{1}{2}, \frac{1}{2})$, where $\hat{J}(\mathbf{q}) = +2J$. However, an even greater value is obtained either of the two inequivalent zone corners, $(x_1, x_2) = (\frac{2}{3}, \frac{1}{3})$ and $(x_1, x_2) = (\frac{1}{3}, \frac{2}{3})$, where $\hat{J}(\mathbf{q}) = +3J$. Each of these corresponds to a *tripartite* division of the triangular lattice into three $\sqrt{3} \times \sqrt{3}$ triangular sublattices.

Antiferromagnetic insulators: MnO, CoO, FeO, NiO, La₂CuO₄.

- *Helimagnet*: Consider a cubic lattice system with mixed ferromagnetic and antiferromagnetic interactions:

$$J_{ij} = \begin{cases} +J_1 > 0 & 6 \text{ nearest neighbors} \\ -J_2 < 0 & 12 \text{ next-nearest neighbors} \\ 0 & \text{otherwise} . \end{cases} \quad (4.248)$$

Then

$$\begin{aligned} \hat{J}(\mathbf{q}) = 2J_1 & [\cos(q_x a) + \cos(q_y a) + \cos(q_z a)] \\ & - 4J_2 [\cos(q_x a) \cos(q_y a) + \cos(q_x a) \cos(q_z a) + \cos(q_y a) \cos(q_z a)] . \end{aligned} \quad (4.249)$$

The ordering wavevector is then

$$\mathbf{Q} = \begin{cases} a^{-1} \cos^{-1} \left(\frac{J_1}{4J_2} \right) (\hat{\mathbf{x}} + \hat{\mathbf{y}} + \hat{\mathbf{z}}) & \text{if } J_1 < 4J_2 \\ 0 & \text{if } J_1 \geq 4J_2 . \end{cases} \quad (4.250)$$

Thus, for $J_1 < 4J_2$ the order is *incommensurate* with the lattice. The maximum value of $\hat{J}(\mathbf{q})$ is

$$\hat{J}(\mathbf{Q}) = \begin{cases} \frac{3J_1^2}{4J_2} & \text{if } J_1 < 4J_2 \\ 6(J_1 - 2J_2) & \text{if } J_1 \geq 4J_2 , \end{cases} \quad (4.251)$$

hence incommensurate order sets in at $T_I = S(S+1)J_1^2/4k_B J_2$. The uniform susceptibility is

$$\hat{\chi}(0) = \frac{\gamma^2 S(S+1)/3k_B}{T - 8T_I \frac{J_2}{J_1} \left(1 - \frac{2J_2}{J_1} \right)} . \quad (4.252)$$

Thus,

$$\chi(T) \simeq \begin{cases} \frac{C}{T+T^*} & 0 < J_1 < 2J_2 \text{ (like AFM)} \\ \frac{C}{T-T^*} & 2J_2 < J_1 < 4J_2 \text{ (like FM)} . \end{cases} \quad (4.253)$$

4.9.1 Mean Field Theory of Anisotropic Magnetic Systems

Consider the anisotropic Heisenberg model,

$$\mathcal{H} = - \overbrace{\sum_{i < j} J_{ij}^{\parallel} \mathbf{S}_i \cdot \mathbf{S}_j}^{intra} - \overbrace{\sum_{i < j} J_{ij}^{\perp} \mathbf{S}_i \cdot \mathbf{S}_j}^{inter} - \gamma \sum_i \mathbf{H}_i \cdot \mathbf{S}_i . \quad (4.254)$$

Here, J_{ij}^{\parallel} only connects sites within the same plane (quasi-2d) or chain (quasi-1d), while J_{ij}^{\perp} only connects sites in different planes/chains. We assume that we have an adequate theory for isolated plains/chains, and we effect a mean field decomposition on the inter-plane/interchain term:

$$\mathbf{S}_i \cdot \mathbf{S}_j = -\langle \mathbf{S}_i \rangle \cdot \langle \mathbf{S}_j \rangle + \langle \mathbf{S}_i \rangle \cdot \mathbf{S}_j + \langle \mathbf{S}_j \rangle \cdot \mathbf{S}_i + \overbrace{\delta \mathbf{S}_i \cdot \delta \mathbf{S}_j}^{(\text{fluct})^2} , \quad (4.255)$$

resulting in the effective field

$$\mathbf{H}^{\text{eff}}(\mathbf{q}, \omega) = \mathbf{H}(\mathbf{q}, \omega) + \gamma^{-2} \hat{J}^{\perp}(\mathbf{q}_{\perp}) \mathbf{M}(\mathbf{q}, \omega) , \quad (4.256)$$

where $\mathbf{M}(\mathbf{q}, \omega) = \gamma \langle \mathbf{S}(\mathbf{q}, \omega) \rangle$. Thus,

$$\hat{\chi}(\mathbf{q}, \omega) = \frac{\hat{\chi}^{\parallel}(\mathbf{q}_{\parallel}, \omega)}{1 - \gamma^{-2} \hat{J}^{\perp}(\mathbf{q}_{\perp}) \hat{\chi}^{\parallel}(\mathbf{q}_{\parallel}, \omega)} , \quad (4.257)$$

where $\hat{\chi}^{\parallel}(\mathbf{q}_{\parallel}, \omega)$ is assumed known.

4.9.2 Quasi-1D Chains

Consider a ferromagnet on a cubic lattice where the exchange interaction along the \hat{z} -direction (\parallel) is much larger than that in the (x, y) plane (\perp). Treating the in-plane interactions via mean field theory, we have

$$\hat{\chi}(\mathbf{q}_{\perp}, q_z) = \frac{\hat{\chi}_{1D}(q_z)}{1 - \gamma^{-2} \hat{J}^{\perp}(\mathbf{q}_{\perp}) \hat{\chi}_{1D}(q_z)} , \quad (4.258)$$

with

$$\hat{J}^{\perp}(\mathbf{q}_{\perp}) = 2J_{\perp} \left\{ \cos(q_x a) + \cos(q_y a) \right\} . \quad (4.259)$$

For the Ising model we can compute $\hat{\chi}_{1D}(q_z)$ exactly using the high temperature expansion:

$$\langle \sigma_n \sigma_{n'} \rangle = \frac{\text{Tr} \left\{ \sigma_n \sigma_{n'} \prod_j (1 + \tanh(J_{\parallel}/k_B T) \sigma_j \sigma_{j+1}) \right\}}{\text{Tr} \prod_j (1 + \tanh(J_{\parallel}/k_B T) \sigma_j \sigma_{j+1})} \quad (4.260)$$

$$= \tanh^{|n-n'|}(J_{\parallel}/k_B T) . \quad (4.261)$$

Thus,

$$\hat{\chi}_{1D}(q_z) = \frac{\gamma^2}{k_B T} \sum_{n=-\infty}^{\infty} \tanh^{|n|}(J_{\parallel}/k_B T) e^{inq_z c} \quad (4.262)$$

$$= \frac{\gamma^2}{k_B T} \frac{1}{\cosh(2J_{\parallel}/k_B T) - \sinh(2J_{\parallel}/k_B T) \cos(q_z c)} \quad (4.263)$$

$$\approx \frac{2\pi\gamma^2}{ck_B T} \cdot \frac{1}{\pi} \frac{\xi^{-1}}{\xi^{-2} + q_z^2} ,$$

where c is the lattice spacing along the chains, and where the last approximation is valid for $q \rightarrow 0$ and $\xi \rightarrow \infty$. The correlation length in this limit is given by

$$\xi(T) \simeq \frac{c}{2} \exp(2J_{\parallel}/k_B T) . \quad (4.264)$$

Note that $\xi(T)$ diverges only at $T = 0$. This is consistent with the well-known fact that the *lower critical dimension* for systems with *discrete global symmetries* and *short-ranged interactions* is $d = 1$. That is to say that there is no spontaneous breaking of any discrete symmetry in one-dimension (with the proviso of sufficiently short-ranged interactions). For *continuous symmetries* the lower critical dimension is $d = 2$, which is the content of the Hohenberg-Mermin-Wagner (HMW) theorem.

Accounting for the residual interchain interactions via mean field theory, we obtain the anisotropic (in space) susceptibility

$$\hat{\chi}(\mathbf{q}_\perp, q_z) = \frac{\hat{\chi}_{1D}(q_z)}{1 - \gamma^{-2} \cdot 2J_\perp \{ \cos(q_x a) + \cos(q_y a) \} \cdot \hat{\chi}_{1D}(q_z)} . \quad (4.265)$$

Three-dimensional ordering at $\mathbf{Q} = 0$ sets in at $T = T_c$, which occurs when $\hat{\chi}(\mathbf{Q})$ has a pole. The equation for this pole is

$$4\gamma^{-2} J_\perp \chi_{1D} = 1 \quad \Rightarrow \quad \frac{4J_\perp}{k_B T_c} = \exp(-2J_\parallel/k_B T_c) . \quad (4.266)$$

This transcendental equation is equivalent to

$$x e^x = \frac{1}{\epsilon} \quad (4.267)$$

where $x = 2J_\parallel/k_B T_c$ and $\epsilon = 2J_\perp/J_\parallel$. The solution, for small ϵ , is

$$k_B T_c = \frac{2J_\parallel}{\ln(J_\parallel/2J_\perp)} + \dots . \quad (4.268)$$

Thus, $T_c > 0$ for all finite J_\perp , with T_c going to zero rather slowly as $J_\perp \rightarrow 0$.

Similar physics is present in the antiferromagnetic insulator phase of the cuprate superconductors. The antiferromagnetic (staggered) susceptibility of the two-dimensional Heisenberg model diverges as $T \rightarrow 0$ as $\chi_{2D}^{\text{stag}} \sim J^{-1} \exp(\rho J k_B T)$, where ρ is a dimensionless measure of quantum fluctuations. As in the $d = 1$ Ising case, there is no phase transition at any finite temperature, in this case owing to the HMW theorem. However, when the quasi-2D layers are weakly coupled with antiferromagnetic coupling J' (the base structure is a cubic perovskite), three-dimensional Néel ordering sets in at the antiferromagnetic wavevector $\mathbf{Q} = (\pi/a, \pi/a, \pi/c)$ at a critical temperature $T_N \approx J/k_B \ln(J/J')$.

4.10 Spin Wave Theory

Recall the SU(2) algebra of quantum spin: $[S^\alpha, S^\beta] = i\epsilon_{\alpha\beta\gamma} S^\gamma$ (set $\hbar = 1$ for convenience). Defining $S^\pm = S^x \pm iS^y$, we have, equivalently,

$$[S^z, S^\pm] = \pm S^\pm , \quad [S^+, S^-] = 2S^z . \quad (4.269)$$

The Holstein-Primakoff transformation (1940) maps the spin algebra onto that of a single bosonic oscillator:

$$S^+ = a^\dagger (2S - a^\dagger a)^{1/2} \quad (4.270)$$

$$S^- = (2S - a^\dagger a)^{1/2} a \quad (4.271)$$

$$S^z = a^\dagger a - S . \quad (4.272)$$

The state $|S^z = -S\rangle$ is the vacuum $|0\rangle$ in the boson picture. The highest weight state, $|S^z = +S\rangle$ corresponds to the state $|2S\rangle$ in the boson picture, *i.e.* an occupancy of $n = 2S$ bosons.

EXERCISE: Verify that the bosonic representation of the spin operators in (4.272) satisfies the SU(2) commutation relations of quantum spin.

What does it mean to take the square root of an operator like $2S - a^\dagger a$? Simple! Just evaluate it in a basis diagonal in $a^\dagger a$, *i.e.* the number basis:

$$a^\dagger a |n\rangle = n |n\rangle \Rightarrow (2S - a^\dagger a)^{1/2} |n\rangle = (2S - n)^{1/2} |n\rangle . \quad (4.273)$$

Note that physical boson states are restricted to $n \in \{0, 1, \dots, 2S\}$. What about states with $n > 2S$? The nice thing here is that we needn't worry about them at all, because S^+ , S^- , and S^z do not connect states with $0 \leq n \leq 2S$ to states with $n > 2S$. For example, when applying the spin raising operator S^+ to the highest weight state $|S^z = +S\rangle$, in boson language we have

$$S^+ |S^z = +S\rangle = a^\dagger (2S - a^\dagger a)^{1/2} |n = 2S\rangle = 0 , \quad (4.274)$$

as required.

While the HP transformation is exact, it really doesn't buy us anything unless we start making some approximations and derive a systematic expansion in ‘spin wave’ interactions.

4.10.1 Ferromagnetic Spin Waves

Consider the classical ground state $|F\rangle = |\downarrow\downarrow\dots\downarrow\rangle$ in which all spins are pointing ‘down’, with $S^z = -S$. In the boson language, the occupancy at each site is zero. This is in fact an eigenstate of the Heisenberg Hamiltonian

$$\mathcal{H} = - \sum_{i < j} J_{ij} \mathbf{S}_i \cdot \mathbf{S}_j \quad (4.275)$$

with eigenvalue $E_0 = -S^2 \sum_{i < j} J_{ij}$. If all the interactions are ferromagnetic, *i.e.* $J_{ij} > 0 \forall (i, j)$, then this state clearly is the ground state. We now express the Heisenberg interaction $\mathbf{S}_i \cdot \mathbf{S}_j$ in terms of the boson creation and annihilation operators. To this end, we perform a Taylor expansion of the radical,

$$(2S - a^\dagger a)^{1/2} = \sqrt{2S} \left\{ 1 - \frac{1}{2} \left(\frac{a^\dagger a}{2S} \right) - \frac{1}{8} \left(\frac{a^\dagger a}{2S} \right)^2 + \dots \right\} , \quad (4.276)$$

so that

$$\mathbf{S}_i \cdot \mathbf{S}_j = \frac{1}{2} S_i^+ S_j^- + \frac{1}{2} S_i^- S_j^+ + S_i^z S_j^z \quad (4.277)$$

$$= S a_i^\dagger \left(1 - \frac{a_i^\dagger a_i}{4S} + \dots \right) \left(1 - \frac{a_j^\dagger a_j}{4S} + \dots \right) a_j \quad (4.278)$$

$$\begin{aligned} &+ S \left(1 - \frac{a_i^\dagger a_i}{4S} + \dots \right) a_i a_j^\dagger \left(1 - \frac{a_j^\dagger a_j}{4S} + \dots \right) + (a_i^\dagger a_i - S)(a_j^\dagger a_j - S) \\ &= S^2 + S \left(a_i^\dagger a_j + a_j^\dagger a_i - a_i^\dagger a_i - a_j^\dagger a_j \right) + \left\{ a_i^\dagger a_i a_j^\dagger a_j - \frac{1}{4} a_i^\dagger a_i a_i^\dagger a_j - \frac{1}{4} a_i^\dagger a_j a_j^\dagger a_i - \frac{1}{4} a_j^\dagger a_j a_i^\dagger a_i \right\} + \mathcal{O}(1/S). \end{aligned} \quad (4.279)$$

Note that a systematic expansion in powers of $1/S$ can be performed. The Heisenberg Hamiltonian now becomes

$$\mathcal{H} = \underbrace{-S^2 \sum_{i < j} J_{ij}}_{\text{classical ground state energy } \mathcal{O}(S^2)} + \underbrace{S \sum_{i < j} J_{ij} (a_i^\dagger a_i + a_j^\dagger a_j - a_i^\dagger a_j - a_j^\dagger a_i)}_{\text{spin-wave Hamiltonian } \mathcal{H}_{\text{sw}}} + \underbrace{\mathcal{O}(S^0)}_{\text{spin-wave interactions}}. \quad (4.280)$$

We assume our sites are elements of a Bravais lattice, and we Fourier transform:

$$a_i = \frac{1}{\sqrt{N}} \sum_{\mathbf{q}} e^{i\mathbf{q} \cdot \mathbf{R}_i} a_{\mathbf{q}} \quad a_i^\dagger = \frac{1}{\sqrt{N}} \sum_{\mathbf{q}} e^{-i\mathbf{q} \cdot \mathbf{R}_i} a_{\mathbf{q}}^\dagger \quad (4.281)$$

$$a_{\mathbf{q}} = \frac{1}{\sqrt{N}} \sum_i e^{-i\mathbf{q} \cdot \mathbf{R}_i} a_i \quad a_{\mathbf{q}}^\dagger = \frac{1}{\sqrt{N}} \sum_i e^{i\mathbf{q} \cdot \mathbf{R}_i} a_i^\dagger. \quad (4.282)$$

Note that the canonical commutation relations are preserved by this transformation:

$$[a_i, a_j^\dagger] = \delta_{ij} \iff [a_{\mathbf{q}}, a_{\mathbf{q}'}^\dagger] = \delta_{\mathbf{q}\mathbf{q}'} . \quad (4.283)$$

Using the result

$$\frac{1}{N} \sum_i e^{i(\mathbf{q}-\mathbf{q}') \cdot \mathbf{R}_i} = \delta_{\mathbf{q}\mathbf{q}'}, \quad (4.284)$$

we obtain the spin-wave Hamiltonian

$$\mathcal{H}_{\text{sw}} = S \sum_{\mathbf{q}} [\hat{J}(0) - \hat{J}(\mathbf{q})] a_{\mathbf{q}}^\dagger a_{\mathbf{q}}, \quad (4.285)$$

from which we read off the spin-wave dispersion

$$\hbar\omega_{\mathbf{q}} = S [\hat{J}(0) - \hat{J}(\mathbf{q})] \quad (4.286)$$

$$= \frac{1}{6} S \left[\sum_{\mathbf{R}} J(\mathbf{R}) \mathbf{R}^2 \right] \mathbf{q}^2 + \mathcal{O}(q^4). \quad (4.287)$$

The above sum on \mathbf{R} converges if $J(R \rightarrow \infty) \sim R^{-(d+2+\epsilon)}$ with $\epsilon > 0$.

4.10.2 Static Correlations in the Ferromagnet

The transverse spin-spin correlation function is

$$\langle S_i^+ S_j^- \rangle = \langle a_i^\dagger (2S - a_i^\dagger a_i)^{1/2} (2S - a_j^\dagger a_j)^{1/2} a_j \rangle \quad (4.288)$$

$$= 2S \langle a_i^\dagger a_j \rangle + \mathcal{O}(S^0) \quad (4.289)$$

$$= 2S\Omega \int_{\hat{\Omega}} \frac{d^d k}{(2\pi)^d} \frac{e^{i\mathbf{k}\cdot(\mathbf{R}_j - \mathbf{R}_i)}}{e^{\hbar\omega_{\mathbf{k}}/k_B T} - 1} . \quad (4.290)$$

The longitudinal spin-spin correlation function is

$$\langle S_i^z S_j^z \rangle - \langle S_i^z \rangle \langle S_j^z \rangle = \langle a_i^\dagger a_i a_j^\dagger a_j \rangle - \langle a_i^\dagger a_i \rangle \langle a_j^\dagger a_j \rangle = \mathcal{O}(S^0) . \quad (4.291)$$

Note that the average spin polarization per site is

$$\langle S_i^z \rangle = -S + \langle a_i^\dagger a_i \rangle \quad (4.292)$$

$$= -S + \Omega \int_{\hat{\Omega}} \frac{d^d k}{(2\pi)^d} \frac{1}{e^{\hbar\omega_{\mathbf{k}}/k_B T} - 1} . \quad (4.293)$$

Now as $k \rightarrow 0$ the denominator above vanishes as k^2 , hence the average spin polarization per site *diverges* when $d \leq 2$. This establishes a “poor man’s version” of the HMW theorem: as infinite spin polarization is clearly absurd, there must have been something wrong with our implicit assumption that long-ranged order persists to finite T . In $d = 3$ dimensions, one finds $\langle S_i^z \rangle = -S + \mathcal{O}(T^{3/2})$.

4.10.3 Antiferromagnetic Spin Waves

The case of the ferromagnet is special because the classical ground state $|F\rangle$ is in fact a quantum eigenstate – indeed the ground state – of the ferromagnetic Heisenberg Hamiltonian.⁹ In the case of the Heisenberg antiferromagnet, this is no longer the case. The ground state itself is a linear combination of classical states. What is the classical ground state? For an antiferromagnet on a bipartite lattice,¹⁰ the classical ground state has each sublattice maximally polarized, with the magnetization on the two sublattices oppositely oriented. Choosing the axis of polarization as \hat{z} , this means $S_i^z = -S$ if $i \in A$ and $S_i^z = +S$ if $i \in B$. We’ll call this state $|N\rangle$, since it is a classical Néel state.

Let us assume that the lattice is a Bravais lattice with a two-element basis described by basis vectors 0 and δ . Thus, if \mathbf{R} is any direct lattice vector, an A sublattice site lies at \mathbf{R}

⁹Of course, $|F\rangle$ is also an eigenstate – the highest lying excited state – of the antiferromagnetic Heisenberg Hamiltonian.

¹⁰A bipartite lattice is one which may be decomposed into two sublattices A and B, such that all the neighbors of any site in A lie in B, and all the neighbors of any site in B lie in A. Examples of bipartite lattices: square, honeycomb, simple cubic, body-centered cubic, hexagonal. Examples of lattices which are not bipartite: triangular, Kagomé, face-centered cubic.

and a B site at $\mathbf{R} + \boldsymbol{\delta}$. The Heisenberg Hamiltonian is written

$$\mathcal{H} = - \sum_{\mathbf{R}, \mathbf{R}'} \left\{ \frac{1}{2} J_{\text{AA}}(\mathbf{R} - \mathbf{R}') \mathbf{S}_{\text{A}}(\mathbf{R}) \cdot \mathbf{S}_{\text{A}}(\mathbf{R}') + \frac{1}{2} J_{\text{BB}}(\mathbf{R} - \mathbf{R}') \mathbf{S}_{\text{B}}(\mathbf{R}) \cdot \mathbf{S}_{\text{B}}(\mathbf{R}') + J_{\text{AB}}(\mathbf{R} - \mathbf{R}' - \boldsymbol{\delta}) \mathbf{S}_{\text{A}}(\mathbf{R}) \cdot \mathbf{S}_{\text{B}}(\mathbf{R}') \right\}. \quad (4.294)$$

Here $\mathbf{S}_{\text{A}}(\mathbf{R})$ represents the spin on the A sublattice located at position \mathbf{R} , while $\mathbf{S}_{\text{B}}(\mathbf{R})$ represents the B sublattice spin located at $\mathbf{R} + \boldsymbol{\delta}$. The factor of $\frac{1}{2}$ multiplying the J_{AA} and J_{BB} terms avoids double-counting the AA and BB interactions. The Néel state will be the classical ground state if $J_{\text{AA}} > 0$ and $J_{\text{BB}} > 0$ and $J_{\text{AB}} < 0$. It may remain the ground state even if some of the interactions are frustrating, *i.e.* $J_{\text{AA}} < 0$, $J_{\text{BB}} < 0$, and/or $J_{\text{AB}} > 0$ between certain sites.

We'd like the Néel state $|\text{N}\rangle = |\uparrow\downarrow\uparrow\downarrow\dots\rangle$ to be the vacuum for the Holstein-Primakoff bosons. To accomplish this, we rotate the spin operators on the B sublattice by π about the $\hat{\mathbf{y}}$ -axis in the internal SU(2) space, sending $S^x \rightarrow -S^x$, $S^y \rightarrow S^y$, and $S^z \rightarrow -S^z$. In the language of HP bosons, we have the following:

$$\begin{array}{ll} \text{A Sublattice} & \text{B Sublattice} \\ S^+ = a^\dagger(2S - a^\dagger a)^{1/2} & S^+ = -(2S - b^\dagger b)^{1/2}b \\ S^- = (2S - a^\dagger a)^{1/2}a & S^- = -b^\dagger(2S - b^\dagger b)^{1/2} \\ S^z = a^\dagger a - S & S^z = S - b^\dagger b \end{array} \quad (4.295)$$

$$S^- = -b^\dagger(2S - b^\dagger b)^{1/2} \quad (4.296)$$

$$S^z = S - b^\dagger b \quad (4.297)$$

We may now write the Heisenberg interaction as an expansion in powers of $1/S$:

$$\mathbf{S}_{\text{A}}(\mathbf{R}) \cdot \mathbf{S}_{\text{A}}(\mathbf{R}') = S^2 + S \left(a_{\mathbf{R}}^\dagger a_{\mathbf{R}'} + a_{\mathbf{R}'}^\dagger a_{\mathbf{R}} - a_{\mathbf{R}}^\dagger a_{\mathbf{R}} - a_{\mathbf{R}'}^\dagger a_{\mathbf{R}'} \right) + \mathcal{O}(S^0) \quad (4.298)$$

$$\mathbf{S}_{\text{B}}(\mathbf{R}) \cdot \mathbf{S}_{\text{B}}(\mathbf{R}') = S^2 + S \left(b_{\mathbf{R}}^\dagger b_{\mathbf{R}'} + b_{\mathbf{R}'}^\dagger b_{\mathbf{R}} - b_{\mathbf{R}}^\dagger b_{\mathbf{R}} - b_{\mathbf{R}'}^\dagger b_{\mathbf{R}'} \right) + \mathcal{O}(S^0) \quad (4.299)$$

$$\mathbf{S}_{\text{A}}(\mathbf{R}) \cdot \mathbf{S}_{\text{B}}(\mathbf{R}') = -S^2 + S \left(a_{\mathbf{R}}^\dagger a_{\mathbf{R}'} + b_{\mathbf{R}}^\dagger b_{\mathbf{R}} - a_{\mathbf{R}}^\dagger b_{\mathbf{R}'}^\dagger - a_{\mathbf{R}} b_{\mathbf{R}'} \right) + \mathcal{O}(S^0). \quad (4.300)$$

Thus, the classical ground state energy is the $\mathcal{O}(S^2)$ term,

$$E_{\text{cl}} = S^2 \sum_{\mathbf{R}, \mathbf{R}'} \left\{ -\frac{1}{2} J_{\text{AA}}(\mathbf{R} - \mathbf{R}') - \frac{1}{2} J_{\text{BB}}(\mathbf{R} - \mathbf{R}') + J_{\text{AB}}(\mathbf{R} - \mathbf{R}' - \boldsymbol{\delta}) \right\}. \quad (4.301)$$

The spin-wave Hamiltonian is the $\mathcal{O}(S^1)$ piece,

$$\begin{aligned} \mathcal{H}_{\text{sw}} = -S \sum_{\mathbf{R}, \mathbf{R}'} \left\{ J_{\text{AA}}(\mathbf{R} - \mathbf{R}') \left(a_{\mathbf{R}}^\dagger a_{\mathbf{R}'} - a_{\mathbf{R}}^\dagger a_{\mathbf{R}} \right) + J_{\text{BB}}(\mathbf{R} - \mathbf{R}') \left(b_{\mathbf{R}}^\dagger b_{\mathbf{R}'} - b_{\mathbf{R}}^\dagger b_{\mathbf{R}} \right) \right. \\ \left. + J_{\text{AB}}(\mathbf{R} - \mathbf{R}' - \boldsymbol{\delta}) \left(a_{\mathbf{R}}^\dagger a_{\mathbf{R}} + b_{\mathbf{R}}^\dagger b_{\mathbf{R}} - a_{\mathbf{R}}^\dagger b_{\mathbf{R}'}^\dagger - a_{\mathbf{R}} b_{\mathbf{R}'} \right) \right\}. \end{aligned}$$

We now Fourier transform:

$$a_{\mathbf{R}} = \frac{1}{\sqrt{N}} \sum_{\mathbf{k}} e^{i\mathbf{k}\cdot\mathbf{R}} a_{\mathbf{k}} \quad a_{\mathbf{R}}^\dagger = \frac{1}{\sqrt{N}} \sum_{\mathbf{k}} e^{-i\mathbf{k}\cdot\mathbf{R}} a_{\mathbf{k}}^\dagger \quad (4.302)$$

$$b_{\mathbf{R}} = \frac{1}{\sqrt{N}} \sum_{\mathbf{k}} e^{i\mathbf{k}\cdot(\mathbf{R}+\delta)} b_{\mathbf{k}} \quad b_{\mathbf{R}}^\dagger = \frac{1}{\sqrt{N}} \sum_{\mathbf{k}} e^{-i\mathbf{k}\cdot(\mathbf{R}+\delta)} b_{\mathbf{k}}^\dagger, \quad (4.303)$$

which leads to

$$\begin{aligned} \sum_{\mathbf{R}, \mathbf{R}'} J_{AA}(\mathbf{R} - \mathbf{R}') a_{\mathbf{R}}^\dagger a_{\mathbf{R}'} &= \frac{1}{N} \sum_{\mathbf{k}, \mathbf{k}'} \sum_{\mathbf{R}, \mathbf{R}'} J_{AA}(\mathbf{R} - \mathbf{R}') e^{i(k' \cdot \mathbf{R}' - \mathbf{k} \cdot \mathbf{R})} a_{\mathbf{k}}^\dagger a_{\mathbf{k}'} \\ &= \sum_{\mathbf{k}} \hat{J}_{AA}(\mathbf{k}) a_{\mathbf{k}}^\dagger a_{\mathbf{k}} \end{aligned} \quad (4.304)$$

$$\begin{aligned} \sum_{\mathbf{R}, \mathbf{R}'} J_{AB}(\mathbf{R} - \mathbf{R}' - \delta) a_{\mathbf{R}}^\dagger b_{\mathbf{R}'}^\dagger &= \frac{1}{N} \sum_{\mathbf{k}, \mathbf{k}'} \sum_{\mathbf{R}, \mathbf{R}'} J_{AB}(\mathbf{R} - \mathbf{R}' - \delta) e^{i(k' \cdot (\mathbf{R}' + \delta) - \mathbf{k} \cdot \mathbf{R})} a_{\mathbf{k}}^\dagger b_{-\mathbf{k}'}^\dagger \\ &= \sum_{\mathbf{k}} \hat{J}_{AB}(\mathbf{k}) a_{\mathbf{k}}^\dagger b_{-\mathbf{k}}^\dagger, \end{aligned} \quad (4.305)$$

where, assuming J_{AA} , J_{BB} and J_{AB} are functions only of the magnitude of their arguments,

$$\hat{J}_{AA}(\mathbf{k}) \equiv \sum_{\mathbf{R}} J_{AA}(|\mathbf{R}|) e^{i\mathbf{k}\cdot\mathbf{R}} \quad (4.306)$$

$$\hat{J}_{BB}(\mathbf{k}) \equiv \sum_{\mathbf{R}} J_{BB}(|\mathbf{R}|) e^{i\mathbf{k}\cdot\mathbf{R}} \quad (4.307)$$

$$\hat{J}_{AB}(\mathbf{k}) \equiv \sum_{\mathbf{R}} J_{AB}(|\mathbf{R} + \delta|) e^{i\mathbf{k}\cdot(\mathbf{R} + \delta)}. \quad (4.308)$$

Note that $\hat{J}_{AA}(\mathbf{k}) = \hat{J}_{AA}(-\mathbf{k}) = [\hat{J}_{AA}(\mathbf{k})]^*$ (similarly for J_{BB}), and $\hat{J}_{AB}(\mathbf{k}) = [\hat{J}_{AB}(-\mathbf{k})]^*$.

The spin-wave Hamiltonian may now be written as

$$\begin{aligned} \mathcal{H}_{SW} = S \sum_{\mathbf{k}} \left\{ & \left(\hat{J}_{AA}(0) - \hat{J}_{AA}(\mathbf{k}) - \hat{J}_{AB}(0) \right) a_{\mathbf{k}}^\dagger a_{\mathbf{k}} + \left(\hat{J}_{BB}(0) - \hat{J}_{BB}(\mathbf{k}) - \hat{J}_{AB}(0) \right) b_{\mathbf{k}}^\dagger b_{\mathbf{k}} \right. \\ & \left. + \hat{J}_{AB}(\mathbf{k}) a_{\mathbf{k}}^\dagger b_{-\mathbf{k}}^\dagger + J_{AB}^*(\mathbf{k}) a_{\mathbf{k}} b_{-\mathbf{k}} \right\}. \end{aligned} \quad (4.309)$$

In other words,

$$\mathcal{H}_{SW} = \sum_{\mathbf{k}} \left\{ \Omega_{\mathbf{k}}^{AA} a_{\mathbf{k}}^\dagger a_{\mathbf{k}} + \Omega_{\mathbf{k}}^{BB} b_{\mathbf{k}}^\dagger b_{\mathbf{k}} + \Delta_{\mathbf{k}} a_{\mathbf{k}}^\dagger b_{-\mathbf{k}}^\dagger + \Delta_{\mathbf{k}}^* a_{\mathbf{k}} b_{-\mathbf{k}} \right\} \quad (4.310)$$

with

$$\Omega_{\mathbf{k}}^{AA} = S \left(\hat{J}_{AA}(0) - \hat{J}_{AA}(\mathbf{k}) - \hat{J}_{AB}(0) \right) \quad (4.311)$$

$$\Omega_{\mathbf{k}}^{BB} = S \left(\hat{J}_{BB}(0) - \hat{J}_{BB}(\mathbf{k}) - \hat{J}_{AB}(0) \right) \quad (4.312)$$

and

$$\Delta_{\mathbf{k}} = S \hat{J}_{AB}(\mathbf{k}) . \quad (4.313)$$

Henceforth we shall assume $J_{AA}(\mathbf{R}) = J_{BB}(\mathbf{R})$, so $\Omega_{\mathbf{k}}^{AA} = \Omega_{\mathbf{k}}^{BB} \equiv \Omega_{\mathbf{k}}$.

Note that the vacuum $|0\rangle$ for the a and b bosons is not an eigenstate of \mathcal{H}_{sw} , owing to the spin-wave pair creation term $\Delta_{\mathbf{k}}^* a_{\mathbf{k}} b_{-\mathbf{k}}$. This can be traced back to the effect on the Néel state of the Heisenberg interaction,

$$\mathbf{S}_i \cdot \mathbf{S}_j = \frac{1}{2} S_i^+ S_j^- + \frac{1}{2} S_i^- S_j^+ + S_i^z S_j^z . \quad (4.314)$$

If $i \in A$ and $j \in B$, then the term $S_i^+ S_j^-$ acts on the configuration $| -S, +S \rangle$ and converts it to $2S | -S+1, S-1 \rangle$. Nevertheless, we can diagonalize \mathcal{H}_{sw} by means of a canonical (but not unitary!) transformation, known as the *Bogoliubov transformation*. Note that for each $\mathbf{k} \in \hat{\Omega}$, the spin-wave Hamiltonian couples only four operators: $a_{\mathbf{k}}^\dagger$, $a_{\mathbf{k}}$, $b_{-\mathbf{k}}^\dagger$, and $b_{-\mathbf{k}}$. We write the Bogoliubov transformation as

$$a_{\mathbf{k}} = u_{\mathbf{k}} \alpha_{\mathbf{k}} - v_{\mathbf{k}}^* \beta_{-\mathbf{k}}^\dagger \quad (4.315)$$

$$a_{\mathbf{k}}^\dagger = u_{\mathbf{k}}^* \alpha_{\mathbf{k}}^\dagger - v_{\mathbf{k}} \beta_{-\mathbf{k}} \quad (4.316)$$

One can readily verify that this transformation preserves the canonical bosonic commutation relations,

$$[a_{\mathbf{k}}, a_{\mathbf{k}'}^\dagger] = [b_{\mathbf{k}}, b_{\mathbf{k}'}^\dagger] = [\alpha_{\mathbf{k}}, \alpha_{\mathbf{k}'}^\dagger] = [\beta_{\mathbf{k}}, \beta_{\mathbf{k}'}^\dagger] = \delta_{\mathbf{kk}'} \quad (4.317)$$

provided that

$$u_{\mathbf{k}}^* u_{\mathbf{k}} - v_{\mathbf{k}}^* v_{\mathbf{k}} = 1 . \quad (4.318)$$

The inverse transformation is

$$\alpha_{\mathbf{k}} = u_{\mathbf{k}}^* a_{\mathbf{k}} + v_{\mathbf{k}}^* b_{-\mathbf{k}}^\dagger \quad (4.319)$$

$$\alpha_{\mathbf{k}}^\dagger = u_{\mathbf{k}} a_{\mathbf{k}}^\dagger + v_{\mathbf{k}} b_{-\mathbf{k}} \quad (4.320)$$

We'll write

$$u_{\mathbf{k}} = \exp(i\eta_{\mathbf{k}}) \cosh(\theta_{\mathbf{k}}) \quad , \quad v_{\mathbf{k}} = \exp(-i\eta_{\mathbf{k}}) \sinh(\theta_{\mathbf{k}}) . \quad (4.321)$$

We may then write

$$a_{\mathbf{k}} = \exp(i\eta_{\mathbf{k}}) \cosh(\theta_{\mathbf{k}}) \alpha_{\mathbf{k}} - \exp(i\eta_{\mathbf{k}}) \sinh(\theta_{\mathbf{k}}) \beta_{-\mathbf{k}}^\dagger \quad (4.322)$$

$$b_{-\mathbf{k}} = \exp(i\eta_{\mathbf{k}}) \cosh(\theta_{\mathbf{k}}) \beta_{-\mathbf{k}} - \exp(i\eta_{\mathbf{k}}) \sinh(\theta_{\mathbf{k}}) \alpha_{\mathbf{k}}^\dagger \quad (4.323)$$

as well as the inverse

$$\alpha_{\mathbf{k}} = \exp(-i\eta_{\mathbf{k}}) \cosh(\theta_{\mathbf{k}}) a_{\mathbf{k}} + \exp(i\eta_{\mathbf{k}}) \sinh(\theta_{\mathbf{k}}) \beta_{-\mathbf{k}}^\dagger \quad (4.324)$$

$$\beta_{-\mathbf{k}} = \exp(-i\eta_{\mathbf{k}}) \cosh(\theta_{\mathbf{k}}) \beta_{-\mathbf{k}} + \exp(i\eta_{\mathbf{k}}) \sinh(\theta_{\mathbf{k}}) a_{\mathbf{k}}^\dagger . \quad (4.325)$$

Substituting into the expressions from \mathcal{H}_{sw} , we find

$$\begin{aligned}\Omega_{\mathbf{k}} (a_{\mathbf{k}}^\dagger a_{\mathbf{k}} + b_{\mathbf{k}}^\dagger b_{\mathbf{k}}) &= \Omega_{\mathbf{k}} \cosh(2\theta_{\mathbf{k}}) (\alpha_{\mathbf{k}}^\dagger \alpha_{\mathbf{k}} + \beta_{-\mathbf{k}}^\dagger \beta_{-\mathbf{k}} + 1) - \Omega_{\mathbf{k}} \\ &\quad - \Omega_{\mathbf{k}} \sinh(2\theta_{\mathbf{k}}) (\alpha_{\mathbf{k}}^\dagger \beta_{-\mathbf{k}}^\dagger + \alpha_{\mathbf{k}} \beta_{-\mathbf{k}})\end{aligned}\quad (4.326)$$

$$\begin{aligned}\Delta_{\mathbf{k}} a_{\mathbf{k}}^\dagger a_{-\mathbf{k}}^\dagger + \Delta_{\mathbf{k}}^* a_{\mathbf{k}} b_{-\mathbf{k}} &= -|\Delta_{\mathbf{k}}| \sinh(2\theta_{\mathbf{k}}) (\alpha_{\mathbf{k}}^\dagger \alpha_{\mathbf{k}} + \beta_{-\mathbf{k}}^\dagger \beta_{-\mathbf{k}} + 1) \\ &\quad + |\Delta_{\mathbf{k}}| \cosh(2\theta_{\mathbf{k}}) (\alpha_{\mathbf{k}}^\dagger \beta_{-\mathbf{k}}^\dagger + \alpha_{\mathbf{k}} \beta_{-\mathbf{k}}),\end{aligned}\quad (4.327)$$

where we have taken $\eta_{\mathbf{k}} = \frac{1}{2} \arg(\Delta_{\mathbf{k}})$. Up until now, $\theta_{\mathbf{k}}$ has been arbitrary. We now use this freedom to specify $\theta_{\mathbf{k}}$ such that the $(\alpha_{\mathbf{k}}^\dagger \beta_{-\mathbf{k}}^\dagger + \alpha_{\mathbf{k}} \beta_{-\mathbf{k}})$ terms vanish from \mathcal{H}_{sw} . This requires

$$|\Delta_{\mathbf{k}}| \cosh(2\theta_{\mathbf{k}}) - \Omega_{\mathbf{k}} \sinh(2\theta_{\mathbf{k}}) = 0 \implies \tanh(2\theta_{\mathbf{k}}) = \frac{|\Delta_{\mathbf{k}}|}{\Omega_{\mathbf{k}}}, \quad (4.328)$$

which means

$$\cosh(2\theta_{\mathbf{k}}) = \frac{\Omega_{\mathbf{k}}}{E_{\mathbf{k}}} , \quad \sinh(2\theta_{\mathbf{k}}) = \frac{|\Delta_{\mathbf{k}}|}{E_{\mathbf{k}}} \quad (4.329)$$

along with the dispersion relation

$$E_{\mathbf{k}} = \sqrt{\Omega_{\mathbf{k}}^2 - |\Delta_{\mathbf{k}}|^2}. \quad (4.330)$$

Finally, we may write the diagonalized spin-wave Hamiltonian as

$$\mathcal{H}_{\text{sw}} = \sum_{\mathbf{k}} E_{\mathbf{k}} (\alpha_{\mathbf{k}}^\dagger \alpha_{\mathbf{k}} + \beta_{\mathbf{k}}^\dagger \beta_{\mathbf{k}}) + \sum_{\mathbf{k}} (E_{\mathbf{k}} - \Omega_{\mathbf{k}}). \quad (4.331)$$

Note that $E_{\mathbf{k}} = E_{-\mathbf{k}}$ since $\hat{J}_{\text{AB}}(\mathbf{k}) = \hat{J}_{\text{AB}}^*(-\mathbf{k})$. The two terms above represent, respectively, the spin-wave excitation Hamiltonian, and the $\mathcal{O}(S^1)$ quantum correction to the ground state energy. Since $E_{\mathbf{k}} < \Omega_{\mathbf{k}}$, this correction is always negative.

As $\mathbf{k} \rightarrow 0$, we have, assuming cubic or higher symmetry,

$$\begin{aligned}\Omega_{\mathbf{k}} &= -S \sum_{\mathbf{R}} J_{\text{AB}}(|\mathbf{R} + \boldsymbol{\delta}|) + \frac{1}{6} S \mathbf{k}^2 \sum_{\mathbf{R}} J_{\text{AA}}(|\mathbf{R}|) \mathbf{R}^2 + \dots \\ &\equiv SW + SX\mathbf{k}^2 + \dots\end{aligned}\quad (4.332)$$

$$\begin{aligned}\Delta_{\mathbf{k}} &= +S \sum_{\mathbf{R}} J_{\text{AB}}(|\mathbf{R} + \boldsymbol{\delta}|) - \frac{1}{6} S \mathbf{k}^2 \sum_{\mathbf{R}} J_{\text{AB}}(|\mathbf{R} + \boldsymbol{\delta}|) |\mathbf{R} + \boldsymbol{\delta}|^2 + \dots \\ &\equiv -SW + SY\mathbf{k}^2 + \dots.\end{aligned}\quad (4.333)$$

The energy dispersion is linear: $E_{\mathbf{k}} = \hbar c |\mathbf{k}|$, where $c = S \sqrt{2W(X + Y)}$. Antiferromagnetic spin waves are Goldstone bosons corresponding to the broken continuous symmetry of global spin rotation. The dispersion vanishes linearly as $\mathbf{k} \rightarrow 0$, in contrast to the case of ferromagnetic spin waves, where $E_{\mathbf{k}}$ vanishes quadratically.

Reduction in Sublattice Magnetization

Let's compute the average of S^z for a spin on the A sublattice:

$$\begin{aligned}
 \langle S^z(\mathbf{R}) \rangle &= -S + \langle a_{\mathbf{R}}^\dagger a_{\mathbf{R}} \rangle \\
 &= -S + \frac{1}{N} \sum_{\mathbf{k}} \langle a_{\mathbf{k}}^\dagger a_{\mathbf{k}} \rangle \\
 &= -S + \frac{1}{N} \sum_{\mathbf{k}} \langle (u_{\mathbf{k}}^* \alpha_{\mathbf{k}}^\dagger - v_{\mathbf{k}} \beta_{-\mathbf{k}}) (u_{\mathbf{k}} \alpha_{\mathbf{k}} - v_{\mathbf{k}}^* \beta_{-\mathbf{k}}^\dagger) \rangle \\
 &= -S + v_0 \int_{\text{BZ}} \frac{d^d k}{(2\pi)^d} \left\{ \frac{\Omega_{\mathbf{k}}}{E_{\mathbf{k}}} \frac{1}{\exp(E_{\mathbf{k}}/k_B T) - 1} + \frac{1}{2} \left(\frac{\Omega_{\mathbf{k}}}{E_{\mathbf{k}}} - 1 \right) \right\}, \tag{4.334}
 \end{aligned}$$

where v_0 is the Wigner-Seitz cell volume, and the integral is over the first Brillouin zone. The deviation $\delta S^z = \langle a^\dagger a \rangle$ from the classical value $\langle S^z \rangle = -S$ is due to thermal and quantum fluctuations. Note that even at $T = 0$, when the thermal fluctuations vanish, there is still a reduction in sublattice magnetization due to quantum fluctuations. The Néel state satisfies the $S_i^z S_j^z$ part of the Heisenberg interaction, but the full interaction prefers neighboring spins to be arranged in *singlets*, which involves fluctuations about local Néel order.

We've seen that $\Omega_{\mathbf{k}} \simeq SW$ and $E_{\mathbf{k}} \simeq \hbar c |\mathbf{k}|$ as $\mathbf{k} \rightarrow 0$. Thus, the integrand behaves as T/\mathbf{k}^2 for the first term and as $1/|\mathbf{k}|$ for the second term. The integral therefore diverges in $d \leq 2$ at finite T and in $d = 1$ even at $T = 0$. Thermal and quantum fluctuations melt the classical ordered state.

4.10.4 Specific Heat due to Spin Waves

The long wavelength dispersion $\omega_{\mathbf{q}} = Aq^2$ has thermodynamic consequences. Consider a general case of a bosonic dispersion $\omega_{\mathbf{q}} = A|\mathbf{q}|^\sigma$. The internal energy for a system in d space dimensions is then

$$\begin{aligned}
 E(T) &= V \int \frac{d^d k}{(2\pi)^d} \frac{Ak^\sigma}{e^{\beta Aq^\sigma} - 1} \\
 &= \frac{AV\Omega_d}{(2\pi)^d} \left(\frac{k_B T}{A} \right)^{1+\frac{d}{\sigma}} \int_0^\infty du \frac{u^{d/\sigma}}{e^u - 1} \tag{4.335}
 \end{aligned}$$

where $\Omega_d = 2\pi^{d/2}/\Gamma(d/2)$ is the area of the unit sphere in d dimensions. Thus, $E(T) \propto T^{1+\frac{d}{\sigma}}$, leading to a low-temperature heat capacity of

$$C_V = \Gamma(2 + \frac{1}{2}d) \zeta(1 + \frac{1}{2}d) \frac{k_B V \Omega_d}{(2\pi)^d} \left(\frac{k_B T}{A} \right)^{d/\sigma}. \tag{4.336}$$

At high T , one must impose a cutoff at the edge of the Brillouin zone, where $k \sim \pi/a$, in order not to overcount the modes. One finds

$$E(T) = k_B T V \int_{\Omega} \frac{d^d k}{(2\pi)^d} = N k_B T , \quad (4.337)$$

where N is the number of unit cells. This simply is the Dulong-Petit result of $k_B T$ per mode.

For ferromagnetic spin waves, we found $\sigma = 2$, hence $C_V \propto T^{d/2}$ at low temperatures. As we shall see, for antiferromagnetic spin waves, one has $\sigma = 1$, as in the case of acoustic phonons, hence $C_V \propto T^d$.

Suppose we write the long-wavelength ferromagnetic spin-wave dispersion as $\hbar\omega_{\mathbf{q}} = CJ(\mathbf{q}a)^2$, where a is the lattice spacing, J is the nearest neighbor exchange, and C is a dimensionless constant. The ferromagnetic low-temperature specific heat is then

$$C_V^F = \Gamma(2 + \frac{1}{2}d) \zeta(1 + \frac{1}{2}d) \frac{k_B V \Omega_d}{(2\pi a)^d} \left(\frac{k_B T}{CJ} \right)^{d/2} , \quad (4.338)$$

hence $C_V^F \propto (T/\Theta_J)^{d/2}$, with $\Theta_J \equiv CJ/k_B$. Acoustic phonons with a $\omega_{\mathbf{k}} = \hbar c |\mathbf{k}|$ dispersion lead to a Debye heat capacity

$$C_V^D = \Gamma(2 + d) \zeta(1 + d) \frac{k_B V \Omega_d}{(2\pi a)^d} \left(\frac{k_B T}{\hbar c / a} \right)^d , \quad (4.339)$$

hence $C^D \propto (T/\Theta_D)^d$, with $\Theta_D \equiv \hbar c / a k_B$. Thus, at the lowest temperatures, the specific heat due to spin waves dominates, but at intermediate temperatures it is the phonon specific heat which dominates. The temperature scale T^* at which the two contributions are roughly equal is given by

$$(T^*/\Theta_J)^{d/2} \simeq (T^*/\Theta_D)^d \implies T^* \simeq \Theta_D^2 / \Theta_J . \quad (4.340)$$