

Lectures on Electrons in Solids

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Contents

1	Introduction	5
2	The Electron Gas	9
2.1	The Hamiltonian	9
2.2	Density Scaling	11
2.2.1	High-Density Limit	12
2.2.2	Low-Density Limit	12
3	Atomic Units and Dimensionless Equations	15
3.1	Hartree Units	16
3.2	Dimensionless Hamiltonian	17
4	Slater Determinants	19
4.1	Introduction	19
4.2	Non-Interacting Systems	19
4.3	Expectation Values	21
5	Exchange and Correlation	23
5.1	Introduction	23
5.2	Electron Density and Correlation Functions	24
5.2.1	Electron Density	24

5.2.2	Correlation Functions	25
5.3	Exchange in the Non-Interacting Electron Liquid	29
5.4	Exchange and Correlation in Real Systems	32
6	Density Functional Theory	35
6.1	History	35
6.2	Preliminaries	36
6.3	The Energy Functional	37
6.4	Contributions to the Energy Functional	38
6.5	The Kinetic Energy	39
6.6	The Exchange-Correlation Energy	40
6.7	Minimisation of the Energy Functional	42
6.8	Self-Consistency	43
6.9	How DFT Calculations Work	44
6.10	Quantum Molecular Dynamics	47
6.11	Strengths and Weaknesses	48
7	Elementary Excitations	49
7.1	Collective Modes	49
7.2	Quasiparticles	51

Chapter 1

Introduction

The first aim of these lectures is to convince you that some of the most familiar properties of ordinary matter can only be explained using quantum mechanics. By studying the interacting electron gas, you will gain a rough qualitative understanding of the most important of these quantum mechanical effects. The second aim is to help you understand the “standard model” of a solid as an assembly of non-interacting electrons moving in a fixed external potential. Although this model underlies almost all of undergraduate chemistry and solid-state physics, it appears implausible at first glance. The electron-ion interactions produce the band structures and chemical bonds studied in undergraduate solid-state physics courses, but why are the equally strong electron-electron interactions ignored? Plausible or not, the standard model explains the periodic table, most chemical reactions, and most of the transport properties of most solids. Density-functional theory and Landau’s quasiparticle concept are introduced to help account for this success.

To start things off, think about these two inherently quantum mechanical properties of solids:

Solids don’t collapse into unimaginably dense lumps: Without quantum mechanics, there would be nothing to stop your electrons from spiralling in to your nuclei, and your neutralised nuclei from clumping together under the influence of the strong force. Fortunately, QM says that localising a particle of mass m in a box of side L costs a kinetic energy of order $\hbar^2/(mL^2)$. It is this kinetic energy, rather than Coulomb repulsion, that saves the day. Fermi statistics also plays a role. If your electrons were to stop obeying the exclusion principle, they would all cluster together in the $1s$ state of every atom,

all your atoms would shrink, and you would end up very small indeed. The Pauli principle keeps the electrons apart and increases the KE cost of localisation.

The ions in solids are localised and “classical”, while the electrons are delocalised and “quantum mechanical”: The reason — the large mass difference between electrons and ions — is obvious, but the effect is quantum mechanical nevertheless. At typical solid-state densities, the confinement kinetic energy of the light electrons is comparable to the electronic potential energy, whereas the KE cost of confining the heavy ions near lattice sites is negligible. At very low densities, the KE/PE balance alters and electrons too can crystallise to form a *Wigner crystal* [1]. By contrast, in liquid ^4He , where the interatomic forces are comparatively weak (or perhaps I should say short-ranged) and the atoms light, the confinement KE (i.e., the zero-point motion) is sufficient to melt any crystal formed by the atoms [2]. Liquid ^4He therefore remains a quantum liquid (of atoms rather than electrons) down to absolute zero. To solidify it you have to apply pressure.

Although your electrons and nuclei take up only a tiny fraction of the space occupied by your body, you don’t often fall through the floor: Again you have confinement KE to thank. If you were to fall through the floor, your electron gas and the floor’s electron gas would have to occupy the same region of space. Because of the Pauli principle, the Fermi energy would rise and the KE would increase. Coulomb forces play a less important role.

The need to use quantum mechanics to understand the properties of solids should already be becoming apparent. The next two points emphasise the surprising “locality” of solids. Despite the long range of the Coulomb interaction and the sensitivity of the wavefunction to boundary conditions, most of the properties of solids are remarkably similar to those of small clusters of atoms. Few environmental influences appear to have a range greater than a few lattice parameters. This locality is related to the equally surprising success of the non-interacting electron model, discussed in the second point.

You can wave your arms independently: Given that Coulomb forces are so strong and long ranged, it is surprising that they cancel so perfectly. A few extra charges here and there, or even a few uncanceled dipoles, would produce enormous forces between macroscopic objects such as your arms. Suppose, for example, that you had two spheres a metre apart, each containing a mole (6×10^{23}) of electrons and the same number of protons. If you moved one in

every million electrons from one sphere to the other, the electrostatic attraction between the two spheres would be 83×10^6 N! Fortunately, screening (which is *not* innately quantum mechanical) helps to prevent strong electric fields from acting on macroscopic length scales.

Electron band theory works remarkably well: Almost all of chemistry and most of the electronic properties of solids can be understood quantitatively using the band or molecular-orbital theory of non-interacting electrons moving in a fixed external potential. Even our understanding of the periodic table rests on this assumption. Since the Coulomb forces between electrons are as strong as the Coulomb forces between electrons and nuclei, neglecting the electron-electron interaction appears ridiculous, and yet photo-emission and de Haas van Alphen experiments clearly see electron-like *quasiparticles* that are almost non-interacting. This is a profound surprise. The screened electron-electron interaction extends far enough (a lattice parameter or so) to reach plenty of other electrons, and so one might expect electron-electron scattering to be frequent. Landau's explanation of the weakness of the quasiparticle-quasiparticle interactions is discussed in the last of these lectures.

Chapter 2

The Electron Gas

The uniform electron gas (also known as jellium, the homogeneous electron/Fermi gas/liquid) is a very simple model solid in which the nuclei are smeared out into a fixed, uniform, positive charge density. The N electrons move through this inert positive background, which serves only to ensure overall charge neutrality. In many solids the effect of the ionic cores on the valence electrons can be modelled as a weak *pseudopotential*, so the jellium model is not nearly as bad as one might guess.

2.1 The Hamiltonian

Consider a cubical box of jellium of side L and volume $V = L^3$ subject to periodic boundary conditions. The electronic charge density $\rho = -en$, where $n = N/V$ is the electron number density. The electrons move through a uniform cancelling positive background $\rho_+ = en_+$, where $n_+ = n$. Both N and V are large. The Hamiltonian is

$$\begin{aligned} \hat{H} = & \sum_i \frac{\mathbf{p}_i^2}{2m} + \frac{1}{2} \sum_i \sum_{j(\neq i)} \frac{e^2}{4\pi\epsilon_0|\mathbf{r}_i - \mathbf{r}_j|} - \sum_i \int \frac{e^2 n_+ d^3 r}{4\pi\epsilon_0|\mathbf{r}_i - \mathbf{r}|} \\ & + \frac{1}{2} \int \int \frac{e^2 n_+ n_+ d^3 r d^3 r'}{4\pi\epsilon_0|\mathbf{r} - \mathbf{r}'|} . \end{aligned} \quad (2.1)$$

The Coulomb terms in this Hamiltonian cause problems because they are so long ranged and able to “wrap around” the periodic boundary conditions. How do we

make sure that they are well defined? Suppose that we replace $1/r$ by $e^{-\mu r}/r$, with

$$\begin{cases} \mu a_0, \mu r_s \ll 1 & \text{(don't change physics)} \\ \mu L \gg 1 & \text{(prevent wraparound)} \end{cases}$$

Here $a_0 \approx 0.529 \times 10^{-10}$ m is the Bohr radius (a length scale that emerges naturally in any system of interacting electrons — see below), and r_s , defined by the equation $4\pi r_s^3/3 = 1/n$, is a measure of the typical electron-electron separation. Expanding this modified Coulomb interaction as a Fourier series gives:

$$\frac{e^{-\mu r}}{r} = \sum_{\mathbf{k}} v_{\mathbf{k}} e^{i\mathbf{k}\cdot\mathbf{r}}, \quad \mathbf{k} = \frac{2\pi}{L}(n_x, n_y, n_z), \quad n_x, n_y, n_z \text{ integers} \quad (2.2)$$

Note that by representing the interaction as a Fourier series using \mathbf{k} vectors that fit into the box, we are forcing it to be periodic. This is sensible because the periodic boundary conditions tell us that (x, y, z) , $(x \pm L, y, z)$, $(x, y \pm L, z)$ and $(x, y, z \pm L)$ are all the same point.

The Fourier components $v_{\mathbf{k}}$ may be obtained in the normal way:

$$\begin{aligned} v_{\mathbf{k}} &= \frac{1}{V} \int_V \frac{e^{-\mu r}}{r} e^{-i\mathbf{k}\cdot\mathbf{r}} d^3r \\ &\approx \frac{1}{V} \int_{\text{all space}} \frac{e^{-\mu r}}{r} e^{-i\mathbf{k}\cdot\mathbf{r}} d^3r \\ &= \frac{4\pi}{V(k^2 + \mu^2)}. \end{aligned} \quad (2.3)$$

The $\mathbf{k}=\mathbf{0}$ electron-electron term in \hat{H} cancels with the electron-background and background-background terms (which involve only the $\mathbf{k} = \mathbf{0}$ component of the interaction because the background is uniform), leaving:

$$\hat{H} = \sum_i \frac{\mathbf{p}_i^2}{2m} + \frac{1}{2} \sum_i \sum_{j(\neq i)} \frac{e^2}{4\pi\epsilon_0} \sum_{\mathbf{k}(\neq \mathbf{0})} \frac{4\pi}{V(k^2 + \mu^2)} e^{i\mathbf{k}\cdot(\mathbf{r}_i - \mathbf{r}_j)}. \quad (2.4)$$

[Note: because the $j=i$ term is omitted from the sum over j , the cancellation of the $\mathbf{k}=\mathbf{0}$ terms is not perfect. However, the part that does not cancel is independent of system size and makes a negligible contribution to the (extensive) total energy in limit of large N and V .]

From now on, we simply write

$$\hat{H} = \sum_i \frac{\mathbf{p}_i^2}{2m} + \frac{1}{2} \sum_i \sum_{j(\neq i)} \frac{e^2}{4\pi\epsilon_0 |\mathbf{r}_i - \mathbf{r}_j|} \quad (2.5)$$

and assume that all this is understood.

2.2 Density Scaling

The electron gas has two length scales:

1. The “natural” length scale, the Bohr radius $a_0 = \frac{4\pi\epsilon_0\hbar^2}{me^2} \approx 0.529 \times 10^{-10}$ m, is determined by balancing KE and PE terms in the Hamiltonian:

$$\frac{e^2}{4\pi\epsilon_0 a_0} = \frac{\hbar^2}{ma_0^2}. \quad (2.6)$$

This length scale is common to all systems of interacting electrons.

2. The typical electron-electron distance. This is usually expressed in terms of an r_s value defined via:

$$\frac{4}{3}\pi r_s^3 = \frac{1}{n} = \text{average volume per electron}. \quad (2.7)$$

One therefore expects the properties of the electron gas to depend on the single dimensionless ratio r_s/a_0 . In most solids, this ratio is in the range 2–4. Since a_0 is the natural length scale of interacting electron systems, it is no surprise that r_s/a_0 is of order 1.

Consider an electron gas with a given r_s . Its Hamiltonian is:

$$\hat{H} = \sum_i \frac{\mathbf{p}_i^2}{2m} + \sum_i \sum_{j(\neq i)} \frac{e^2}{4\pi\epsilon_0 |\mathbf{r}_i - \mathbf{r}_j|}. \quad (2.8)$$

Introduce scaled distances $\mathbf{r}'_i = \mathbf{r}_i/r_s$ (and hence $r'_s = r_s/r_s = 1$) and the corresponding scaled momenta $\mathbf{p}'_i = -i\hbar\partial/\partial\mathbf{r}'_i = r_s\mathbf{p}_i$. Then

$$\hat{H} = \frac{1}{r_s^2} \sum_i \frac{\mathbf{p}'_i{}^2}{2m} + \frac{1}{r_s} \sum_i \sum_{j(\neq i)} \frac{e^2}{4\pi\epsilon_0 |\mathbf{r}'_i - \mathbf{r}'_j|}. \quad (2.9)$$

Hence, any electron gas is equivalent to a gas of “standard” density ($r'_s = 1$) with scaled KE and PE terms (i.e., different electron mass and charge).

- If $r_s \ll 1$ (the original gas was very dense), the rescaled Hamiltonian is dominated by the KE term (both KE and PE increase as r_s decreases, but the KE increases faster).
- If $r_s \gg 1$ (the original gas was very diffuse), the rescaled Hamiltonian is dominated by PE term (both KE and PE decrease as r_s increases, but KE decreases faster).

2.2.1 High-Density Limit

In this limit, the kinetic energy dominates and the interactions are irrelevant:

⇒ The non-interacting electron gas is a good approximation!

Equation (2.9) shows that the energy E of the fixed number N of electrons is proportional to $1/r_s^2$. Hence:

$$\begin{cases} E/N = \text{energy per electron} & \propto 1/r_s^2 \propto n^{2/3}, \\ E/V = \text{energy per unit volume} & \propto 1/r_s^5 \propto n^{5/3}. \end{cases} \quad (2.10)$$

To a first approximation, the wavefunction is that of a non-interacting electron gas:

$$\Psi \approx \frac{1}{\sqrt{N!}} \begin{vmatrix} \frac{e^{i\mathbf{k}_1 \cdot \mathbf{r}_1}}{\sqrt{V}} & \frac{e^{i\mathbf{k}_1 \cdot \mathbf{r}_2}}{\sqrt{V}} & \cdots & \frac{e^{i\mathbf{k}_1 \cdot \mathbf{r}_N}}{\sqrt{V}} \\ \frac{e^{i\mathbf{k}_2 \cdot \mathbf{r}_1}}{\sqrt{V}} & \frac{e^{i\mathbf{k}_2 \cdot \mathbf{r}_2}}{\sqrt{V}} & \cdots & \frac{e^{i\mathbf{k}_2 \cdot \mathbf{r}_N}}{\sqrt{V}} \\ \cdot & \cdot & \cdots & \cdot \\ \cdot & \cdot & \cdots & \cdot \\ \frac{e^{i\mathbf{k}_N \cdot \mathbf{r}_1}}{\sqrt{V}} & \frac{e^{i\mathbf{k}_N \cdot \mathbf{r}_2}}{\sqrt{V}} & \cdots & \frac{e^{i\mathbf{k}_N \cdot \mathbf{r}_N}}{\sqrt{V}} \end{vmatrix}. \quad (2.11)$$

2.2.2 Low-Density Limit

In this limit, the potential energy dominates and the kinetic energy is irrelevant:

⇒ A model of classical point-like charges is a good approximation!

Equation (2.9) shows that the energy E of the fixed number N of electrons is proportional to $1/r_s$. Hence:

$$\begin{cases} E/N = \text{energy per electron} & \propto 1/r_s \propto n^{1/3}, \\ E/V = \text{energy per unit volume} & \propto 1/r_s^4 \propto n^{4/3}. \end{cases} \quad (2.12)$$

Since we can ignore the kinetic energy, we can work out what happens by thinking classically. To minimise the Coulomb repulsion energy, the electrons move away

from each other and sit in localised point-like states. In most cases (I know no convincing general proof of this), the arrangement of point charges that minimises the Coulomb energy is crystalline and so the electrons freeze into a so-called *Wigner crystal* [1]. Nobody has yet seen a Wigner crystal in three dimensions (recent quantum Monte Carlo simulations [5] suggest that they should not form until r_s exceeds 60 or so), but they have been seen in thin layers of electrons adhering (by polarisation forces) to the surface of liquid Helium and in two-dimensional electron gases.

If the localised electron wavepackets were well separated from each other, the wavefunction of a Wigner crystal would look like this,

$$\Psi \approx \frac{1}{\sqrt{N!}} \begin{vmatrix} \phi(\mathbf{r}_1 - \mathbf{R}_1) & \phi(\mathbf{r}_2 - \mathbf{R}_1) & \dots & \phi(\mathbf{r}_N - \mathbf{R}_1) \\ \phi(\mathbf{r}_1 - \mathbf{R}_2) & \phi(\mathbf{r}_2 - \mathbf{R}_2) & \dots & \phi(\mathbf{r}_N - \mathbf{R}_2) \\ \cdot & \cdot & \dots & \cdot \\ \phi(\mathbf{r}_1 - \mathbf{R}_N) & \phi(\mathbf{r}_2 - \mathbf{R}_N) & \dots & \phi(\mathbf{r}_N - \mathbf{R}_N) \end{vmatrix}, \quad (2.13)$$

where $\phi(\mathbf{r} - \mathbf{R})$ is the wavepacket centred on lattice point \mathbf{R} . In a real Wigner crystal, however, the electron wavepackets minimise their kinetic energy by spreading out until they overlap to some extent and the Coulomb repulsion cost becomes too high to allow any further spreading. This introduces electron correlation effects that are not included in a simple determinantal wavefunction.

Since nobody has ever seen one, how do we know that Wigner crystals exist in three dimensions? The answer is simple: the crystals all around us are nothing other than “Wigner” crystals of ions, so there is really no room for doubt. In the case of liquid ^4He at 0K, which is crystalline under pressure but melts to form a quantum liquid when the pressure is released, we can even watch the zero-temperature phase transition between a Wigner crystal and a quantum fluid.

Real solids lie somewhere between the low density Wigner crystal limit and the high density non-interacting limit. Variational calculations based on a Hartree-Fock determinant of delocalised valence electron wavefunctions, which should be accurate at high enough density, give semi-quantitative results for most solids, but interaction and correlation effects have to be taken into account if accurate results are required.

Chapter 3

Atomic Units and Dimensionless Equations

Many research students do not understand how to select suitable systems of units or how to reduce physical equations to dimensionless form. These techniques are of such importance, both in computational and analytical work, that I have decided to discuss them here.

Why not SI units? When using computers, it is crucial to choose a system of units in which the important physical quantities have numerical values of order 1. If you leave factors of 6.6×10^{-34} and 1.6×10^{-19} floating around, you are likely to run into overflow or underflow errors, and you are certain to face serious rounding-error problems. In analytic calculations the choice of units is not so crucial, but the use of dimensionless equations is.

Why dimensionless equations? Consider, for example, the Schrödinger equation for a uniform electron gas. This is a complicated equation, the solutions of which depend on the values of m and e and on the average electron density n . How many parameters do you need to label all physically distinct solutions? Since some possible Schrödinger equations (and thus eigenfunctions) may be obtained from others by rescaling lengths, times, masses, and charges, the solution space may be smaller than you think. The easiest way to reach an unambiguous answer is to reduce the Schrödinger equation to dimensionless form. Any dimensionless parameters that remain are “real” parameters.

Another advantage of using dimensionless equations is that it saves writing.

With an appropriate choice of units, the numerical values of \hbar , e , m and $4\pi\epsilon_0$ can all be made equal to one. The dimensionless Schrödinger equation (which concerns only these numerical values) then looks particularly simple.

3.1 Hartree Units

The natural length and energy scales for atomic and solid-state physics are the Bohr radius,

$$a_0 = 1 \text{ Bohr radius} = \frac{4\pi\epsilon_0\hbar^2}{me^2} \approx 0.529 \times 10^{-10} \text{ m}, \quad (3.1)$$

and the Hartree,

$$1 \text{ Hartree} = \frac{\hbar^2}{ma_0^2} = \frac{e^2}{4\pi\epsilon_0 a_0} = \frac{me^4}{(4\pi\epsilon_0\hbar)^2} \approx 27.2 \text{ eV}. \quad (3.2)$$

(Some people prefer to use the Rydberg, where 1 Rydberg = 0.5 Hartree is the binding energy of a Hydrogen atom.)

In the Hartree atomic units used for the rest of these lectures, we choose:

$$\begin{aligned} \text{unit of charge : } & e && (\approx 1.6 \times 10^{-19} \text{ C}) \\ \text{unit of mass : } & m && (\approx 9.1 \times 10^{-31} \text{ kg}) \\ \text{unit of length : } & a_0 && (\approx 0.53 \text{ \AA}) \\ \text{unit of time : } & \frac{ma_0^2}{\hbar} = \frac{(4\pi\epsilon_0)^2\hbar^3}{me^4} && (\approx 2.4 \times 10^{-17} \text{ s}) \end{aligned} \quad (3.3)$$

Let $e_a (= 1)$ denote the numerical value of e in atomic units and $e_{\text{SI}} (= 1.6 \times 10^{-19})$ the numerical value of e in SI units. With no subscript, e means the physical charge of an electron, which is the same in any system of units: $e = e_{\text{SI}} \text{ Coulombs} = e_a \text{ atomic units of charge}$.

Then,

$$e_a = m_a = (a_0)_a = \left(\frac{ma_0^2}{\hbar} \right)_a = \left(\frac{(4\pi\epsilon_0)^2\hbar^3}{me^4} \right)_a = 1, \quad (3.4)$$

from which it follows that

$$\hbar_a = (4\pi\epsilon_0)_a = 1. \quad (3.5)$$

A quantity with dimensions of energy and numerical value 1 in atomic units is $\hbar^2/(ma_0^2)$. Hence, the atomic unit of energy is the Hartree.

3.2 Dimensionless Hamiltonian

The Hamiltonian of a crystal with electrons of charge $-e$ at positions \mathbf{r}_i and frozen classical nuclei of charge $Z_\alpha e$ at positions \mathbf{d}_α is

$$\sum_i \frac{\mathbf{p}_i^2}{2m} + \sum_{i>j} \frac{e^2}{4\pi\epsilon_0|\mathbf{r}_i - \mathbf{r}_j|} + \sum_{\alpha>\beta} \frac{Z_\alpha Z_\beta e^2}{4\pi\epsilon_0|\mathbf{d}_\alpha - \mathbf{d}_\beta|} - \sum_i \sum_\alpha \frac{Z_\alpha e^2}{4\pi\epsilon_0|\mathbf{r}_i - \mathbf{d}_\alpha|}. \quad (3.6)$$

Note that we have made the Born-Oppenheimer approximation: the nuclear kinetic energy and the influence of the nuclear motion on the electrons have both been ignored. The nuclei are so much heavier than the electrons that these assumptions are normally very accurate.

Introducing dimensionless position vectors $\mathbf{r}_{ia} = \mathbf{r}_i/a_0$ and $\mathbf{d}_{\alpha a} = \mathbf{d}_\alpha/a_0$, and dimensionless momenta $\mathbf{p}_{ia} = a_0\mathbf{p}_i/\hbar = -i\partial/\partial\mathbf{r}_{ia}$, the Hamiltonian becomes:

$$\frac{\hbar^2}{ma_0^2} \left[\frac{1}{2} \sum_i \mathbf{p}_{ia}^2 + \sum_{i>j} \frac{1}{|\mathbf{r}_{ia} - \mathbf{r}_{ja}|} + \sum_{\alpha>\beta} \frac{1}{|\mathbf{d}_{\alpha a} - \mathbf{d}_{\beta a}|} - \sum_i \sum_\alpha \frac{1}{|\mathbf{r}_{ia} - \mathbf{d}_{\alpha a}|} \right]. \quad (3.7)$$

[Remember that 1 Hartree = $\hbar^2/(ma_0^2) = e^2/(4\pi\epsilon_0 a_0)$.] The energy prefactor $\hbar^2/(ma_0^2)$ has numerical value 1 in atomic units, and so the dimensionless Hamiltonian is

$$\hat{H} = \frac{1}{2} \sum_i \mathbf{p}_{ia}^2 + \sum_{i>j} \frac{1}{|\mathbf{r}_{ia} - \mathbf{r}_{ja}|} + \sum_{\alpha>\beta} \frac{1}{|\mathbf{d}_{\alpha a} - \mathbf{d}_{\beta a}|} - \sum_i \sum_\alpha \frac{1}{|\mathbf{r}_{ia} - \mathbf{d}_{\alpha a}|}. \quad (3.8)$$

Solving this equation gives numerical values of distances in Bohr radii, energies in Hartrees, charges in units of e , and masses in units of m . The advantages of working with dimensionless equations have already been discussed. The main disadvantage is that you cannot use dimensional analysis to check your results — the only way to figure out the dimensions of the result of a calculation is from context.

From now on, although we work with dimensionless equations most of the time, we drop the awkward subscript “a” notation.

Chapter 4

Slater Determinants

4.1 Introduction

Although Slater determinants play a central role in many-fermion quantum mechanics, manipulations involving them appear very awkward and ugly at first. Fortunately, the language of creation and annihilation operators, which will be introduced later this year (probably by Derek Lee or Andrew Ho), renders much of the pain you are about to experience unnecessary. In effect, fermion creation and annihilation operators add and subtract rows and columns to and from Slater determinants. You have to go through the pain once in order to see how creation and annihilation operators work, but once you have understood them you need never suffer again.

4.2 Non-Interacting Systems

Consider first the non-interacting many-electron Schrödinger equation,

$$\sum_{i=1}^N \left(-\frac{1}{2} \nabla_i^2 + v(x_i) \right) \Psi(x_1, x_2, \dots, x_N) = E \Psi(x_1, x_2, \dots, x_N), \quad (4.1)$$

where $x_i \equiv (\mathbf{r}_i, s_i)$ is shorthand for the space and spin coordinates of electron i . Because the Hamiltonian is a sum of terms, each of which involves only one electron, this Schrödinger equation has separable solutions of the form,

$$\Psi(x_1, x_2, \dots, x_N) = \phi_1(x_1) \phi_2(x_2) \dots \phi_N(x_N), \quad (4.2)$$

where

$$\left(-\frac{1}{2}\nabla^2 + v(x)\right)\phi_i(x) = \epsilon_i\phi_i(x) \quad \text{and} \quad E = \sum_{i=1}^N \epsilon_i. \quad (4.3)$$

The many-particle ground state is obtained by setting every orbital $\phi_i(x)$ in the product equal to the one-particle ground state $\phi_0(x)$. Since the particles are supposed to be electrons, however, it makes more sense to insist that all the one-electron orbitals in the product be different. The many-electron wavefunction is then of the form used in the Hartree approximation.

Because the Hartree product is not totally antisymmetric, it cannot be a valid many-electron wavefunction. We can, however, write down a closely related antisymmetric wavefunction in the form of a *Slater determinant*,

$$\begin{aligned} \Psi &= \frac{1}{\sqrt{N!}} \begin{vmatrix} \phi_1(x_1) & \phi_1(x_2) & \dots & \phi_1(x_N) \\ \phi_2(x_1) & \phi_2(x_2) & \dots & \phi_2(x_N) \\ \vdots & \vdots & \dots & \vdots \\ \phi_N(x_1) & \phi_N(x_2) & \dots & \phi_N(x_N) \end{vmatrix} \\ &= \frac{1}{\sqrt{N!}} \sum_P (-1)^{\zeta_P} \phi_{P1}(x_1)\phi_{P2}(x_2)\dots\phi_{PN}(x_N), \end{aligned} \quad (4.4)$$

where the sum is over all permutations and ζ_P is the parity of permutation P . The Slater determinant is a linear combination of $N!$ different product states, distinguished only by permutations of their state labels. Since each product is an eigenfunction and all products have the same eigenvalue $E = \sum_{i \text{ occ}} \epsilon_i$, the determinant is also an eigenfunction with eigenvalue $E = \sum_{i \text{ occ}} \epsilon_i$.

The eigenfunctions of systems of non-interacting electrons are always Slater determinants (or perhaps linear combinations of degenerate determinants). Slater determinants are not exact eigenfunctions when the electrons are interacting, but the successes of Hartree-Fock theory show that they are reasonably good approximations in some cases. More generally, given any complete set of one-electron orbitals, the basis of Slater determinants constructed by choosing all possible selections of N orbitals spans the antisymmetric sector of the many-particle Hilbert space. Any many-electron wavefunction may therefore be written as a linear combination of Slater determinants.

4.3 Expectation Values

The results given in this section may have been proved in Dimitri's lectures last week; if not, try proving them yourselves.

A general one-electron operator takes the form,

$$\hat{O}(x_1, \dots, x_N) = \sum_{i=1}^N \hat{o}(x_i) \quad . \quad (4.5)$$

A well known example is the kinetic energy operator, for which $\hat{o}(x_i) = -\frac{1}{2}\nabla_i^2$. The expectation value of such an operator in a Hartree product wavefunction,

$$\Psi_{\text{prod}}(x_1, x_2 \dots, x_N) = \phi_1(x_1)\phi_2(x_2) \dots \phi_N(x_N) \quad , \quad (4.6)$$

where $\phi_1(\mathbf{r}), \phi_2(x), \dots, \phi_N(x)$ are members of an orthonormal set of one-electron orbitals, is

$$\langle \Psi_{\text{prod}} | \hat{O} | \Psi_{\text{prod}} \rangle = \sum_{i=1}^N \int \phi_i^*(x) \hat{o}(x) \phi_i(x) dx \quad . \quad (4.7)$$

If the product is antisymmetrised to form a Slater determinant,

$$D(x_1, x_2, \dots, x_N) = \frac{1}{\sqrt{N!}} \sum_P (-1)^{\zeta_P} \phi_{P1}(x_1) \phi_{P2}(x_2) \dots \phi_{PN}(x_N) \quad , \quad (4.8)$$

the expectation value is unchanged:

$$\langle D | \hat{O} | D \rangle = \sum_{i=1}^N \int \phi_i^*(x) \hat{o}(x) \phi_i(x) dx \quad . \quad (4.9)$$

In both cases, the expectation value of \hat{O} is a sum of contributions from every electron in the system. This was tacitly assumed in all your undergraduate atomic, molecular and solid-state physics courses.

A general two-electron operator takes the form,

$$\hat{O}(x_1, \dots, x_N) = \sum_{i>j}^N \hat{o}(x_i, x_j) \quad , \quad (4.10)$$

where the sum is over all distinct pairs of indices i and j (the restriction $i > j$ ensures that every pair is counted only once). A well known example is the electron-electron interaction, for which $\hat{o}(x_i, x_j)$ is $1/|\mathbf{r}_i - \mathbf{r}_j|$. The expectation value of

such an operator in a Hartree product wavefunction is

$$\langle \Psi_{\text{prod}} | \hat{O} | \Psi_{\text{prod}} \rangle = \sum_{i>j} \int \phi_i^*(x) \phi_j^*(x') \hat{o}(x, x') \phi_i(x) \phi_j(x') dx dx' . \quad (4.11)$$

The expectation value in a Slater determinant D is more complicated:

$$\begin{aligned} \langle D | \hat{O} | D \rangle &= \sum_{i>j} \int \phi_i^*(x) \phi_j^*(x') \hat{o}(x, x') \phi_i(x) \phi_j(x') dx dx' \\ &\quad - \sum_{i>j} \int \phi_j^*(x) \phi_i^*(x') \hat{o}(x, x') \phi_i(x) \phi_j(x') dx dx' . \end{aligned} \quad (4.12)$$

The first term is the expectation value for the Hartree product wavefunction; the second term, known as the exchange term, is something new.

Operators involving three or more electrons do not occur in solid-state physics.

Chapter 5

Exchange and Correlation

5.1 Introduction

Equation (4.12) is both more mysterious and more interesting than the corresponding equation for the expectation value of a one-electron operator. In the case when $\hat{o}(x, x') = 1/|\mathbf{r} - \mathbf{r}'|$, the first of the two terms becomes

$$\frac{1}{2} \int \frac{\sum_i |\phi_i(\mathbf{r})|^2 \sum_{j(\neq i)} |\phi_j(\mathbf{r}')|^2}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r} d\mathbf{r}' . \quad (5.1)$$

This is the sum of the Coulomb interaction energies of the charge densities associated with the occupied one-electron orbitals, and we could have guessed it would appear without going through all the mathematics. The second term, known as the *exchange* term, arises because pairs of electrons are kept apart by the Pauli principle (which is built into the determinantal wavefunction). As the electrons move around, the Pauli principle ensures that they do not get too close to each other, and this decreases the positive (i.e. repulsive) Coulomb energy of the electron liquid. The exchange term is therefore negative.

Real electrons are also kept apart because they are negatively charged and repel each other. This effect, called *correlation*, is not included in a simple Slater determinant wavefunction. Since Hartree-Fock calculations are (relatively) easy, the central (and still largely unsolved) problem of many-electron theory is to understand electron correlation.

To help us understand exchange and correlation in more detail, we now consider various quantities used to describe the correlated motion of pairs of objects. Much

of what follows is very general, applying just as well to classical systems such as cars on a road as to electrons in molecules and solids.

5.2 Electron Density and Correlation Functions

5.2.1 Electron Density

Define:

$$\begin{aligned} n(\mathbf{r}) &= \text{electron number density} \\ n(\mathbf{r})d\mathbf{r} &= \begin{cases} \text{expected number of electrons in } d\mathbf{r} \\ \text{probability of finding an electron in } d\mathbf{r} \end{cases} \end{aligned}$$

Consider a one-electron system in which the position of the electron is denoted by \mathbf{r}_1 . The electron density at some arbitrary point \mathbf{r} is

$$n(\mathbf{r}) = \sum_s |\phi(\mathbf{r}, s)|^2 = \int \phi^*(x_1)\delta(\mathbf{r} - \mathbf{r}_1)\phi(x_1)dx_1. \quad (5.2)$$

where, as usual, the integral dx_1 includes the spin summation. The operator $\hat{n}(\mathbf{r})$ for the electron density at \mathbf{r} is therefore $\delta(\mathbf{r} - \mathbf{r}_1)$.

In many-electron QM, the generalisation is

$$n(\mathbf{r}) = \int \Psi^*(x_1, \dots, x_N) \left[\sum_{i=1}^N \delta(\mathbf{r} - \mathbf{r}_i) \right] \Psi(x_1, \dots, x_N) dx_1 \dots dx_N, \quad (5.3)$$

and hence the operator for the electron density at \mathbf{r} is

$$\hat{n}(\mathbf{r}) = \sum_i^N \delta(\mathbf{r} - \mathbf{r}_i). \quad (5.4)$$

$$\left[\text{Check : } \int n(\mathbf{r}) d^3r = \langle \Psi | \int d^3r \sum_i^N \delta(\mathbf{r} - \mathbf{r}_i) | \Psi \rangle = \langle \Psi | N | \Psi \rangle = N. \right] \quad (5.5)$$

The electron density operator for the N -electron system is a one-electron operator of the standard form,

$$\hat{O} = \sum_{i=1}^N \hat{o}(x_i). \quad (5.6)$$

The expectation value of $\hat{n}(\mathbf{r})$ in a Slater determinant is therefore given by the standard result,

$$n(\mathbf{r}) = \langle D | \sum_{i=1}^N \delta(\mathbf{r} - \mathbf{r}_i) | D \rangle = \sum_{i \text{ occupied}} \left(\sum_s |\phi_i(\mathbf{r}, s)|^2 \right). \quad (5.7)$$

In a uniform system such as a non-interacting electron gas, the orbitals are plane waves of the form $\chi(s)e^{i\mathbf{k}\cdot\mathbf{r}}/\sqrt{V}$, where $\chi(s)$ is a normalised two-component spin vector. The electron density is then $n(\mathbf{r}) = N/V$ as expected.

5.2.2 Correlation Functions

Pair Density and Pair Correlation Function

In many-particle systems, we can also ask more interesting question such as:

What is the probability, $n(\mathbf{r}, \mathbf{r}')d\mathbf{r}d\mathbf{r}'$, of finding one electron in $d\mathbf{r}$ and another in $d\mathbf{r}'$?

If we could measure the positions of all N electrons in each of many identically prepared systems, the *pair density* $n(\mathbf{r}, \mathbf{r}')d\mathbf{r}d\mathbf{r}'$ would be the proportion of measurements in which electrons were found in *both* volume elements $d\mathbf{r}$ and $d\mathbf{r}'$.

Given $n(\mathbf{r}, \mathbf{r}')$, we could easily find, for example, the expected electron-electron interaction energy. The expectation value we require is the average of the interaction energies calculated for each of the large set of measurements of all the electronic positions. In a fraction $n(\mathbf{r}, \mathbf{r}')d\mathbf{r}d\mathbf{r}'$ of these measurements we find electrons in volume elements $d\mathbf{r}$ and $d\mathbf{r}'$, which contribute an amount $1/|\mathbf{r} - \mathbf{r}'|$ to the interaction energy. The overall average interaction energy is therefore given by

$$E_{ee} = \frac{1}{2} \int \int \frac{n(\mathbf{r}, \mathbf{r}')d\mathbf{r}d\mathbf{r}'}{|\mathbf{r} - \mathbf{r}'|}. \quad (5.8)$$

The Hartree approximation amounts to replacing $n(\mathbf{r}, \mathbf{r}')$ by $n(\mathbf{r})n(\mathbf{r}')$.

When \mathbf{r}' is far from \mathbf{r} , the probability of finding an electron in $d\mathbf{r}'$ should not depend on whether or not there is an electron in $d\mathbf{r}$. The electronic positions will be *uncorrelated* (in the sense of uncorrelated random variables) and $n(\mathbf{r}, \mathbf{r}')d\mathbf{r}d\mathbf{r}'$ will be the product of the probabilities of finding electrons in $d\mathbf{r}$ and $d\mathbf{r}'$:

$$n(\mathbf{r}, \mathbf{r}') \longrightarrow n(\mathbf{r})d\mathbf{r} \times n(\mathbf{r}')d\mathbf{r}' \quad \text{as} \quad |\mathbf{r} - \mathbf{r}'| \longrightarrow \infty. \quad (5.9)$$

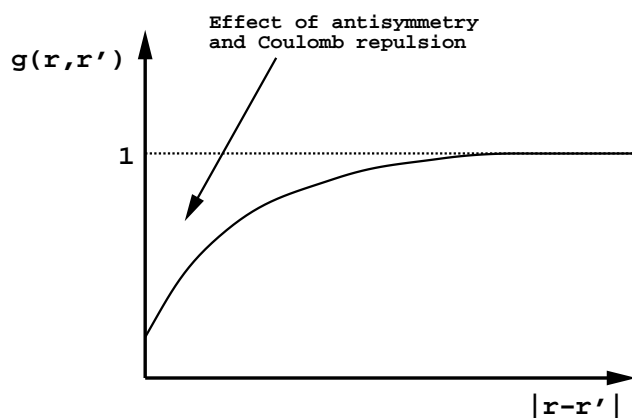


Figure 5.1: The pair-correlation function in an interacting electron gas.

When \mathbf{r}' is close to \mathbf{r} , one would expect $n(\mathbf{r}, \mathbf{r}') < n(\mathbf{r})n(\mathbf{r}')$ since electrons are kept apart by the Pauli principle (exchange) and by Coulomb repulsion (correlation).

The *pair correlation function* $g(\mathbf{r}, \mathbf{r}')$ is defined by

$$n(\mathbf{r}, \mathbf{r}') = n(\mathbf{r})g(\mathbf{r}, \mathbf{r}')n(\mathbf{r}') . \quad (5.10)$$

In an interacting jellium, $g(\mathbf{r}, \mathbf{r}')$ might look like the example shown in Fig. 5.1.

Pair Density Operator

The operator for the pair density is

$$\hat{n}(\mathbf{r}, \mathbf{r}') = \sum_{i=1}^N \sum_{\substack{j=1 \\ (j \neq i)}}^N \delta(\mathbf{r} - \mathbf{r}_i) \delta(\mathbf{r}' - \mathbf{r}_j) . \quad (5.11)$$

The easiest way to justify this definition is to consider an example. At the beginning of this section, we showed from the physical (probabilistic) definition of $n(\mathbf{r}, \mathbf{r}')$ that the expectation value of the electron-electron interaction energy was

$$E_{ee} = \frac{1}{2} \int \frac{n(\mathbf{r}, \mathbf{r}') d\mathbf{r} d\mathbf{r}'}{|\mathbf{r} - \mathbf{r}'|} . \quad (5.12)$$

Using the definition of the operator $\hat{n}(\mathbf{r}, \mathbf{r}')$, we can reproduce this result without difficulty:

$$\begin{aligned} \frac{1}{2} \int d\mathbf{r} d\mathbf{r}' \frac{n(\mathbf{r}, \mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} &= \langle \Psi | \frac{1}{2} \int d\mathbf{r} d\mathbf{r}' \left(\frac{\sum_i \sum_{j \neq i} \delta(\mathbf{r} - \mathbf{r}_i) \delta(\mathbf{r}' - \mathbf{r}_j)}{|\mathbf{r} - \mathbf{r}'|} \right) | \Psi \rangle \\ &= \langle \Psi | \frac{1}{2} \sum_i \sum_{j \neq i} \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|} | \Psi \rangle \\ &= E_{ee} . \end{aligned} \quad (5.13)$$

For this example, at least, it is clear the quantum mechanical operator $\hat{n}(\mathbf{r}, \mathbf{r}')$ is consistent with the probabilistic definition of $n(\mathbf{r}, \mathbf{r}')$ used above.

The Exchange-Correlation Hole

Remember the definition of $n(\mathbf{r}, \mathbf{r}')$:

$n(\mathbf{r}, \mathbf{r}') d\mathbf{r} d\mathbf{r}'$ is the probability of finding one electron in $d\mathbf{r}$ and another electron in $d\mathbf{r}'$.

An equivalent definition is:

$n(\mathbf{r}, \mathbf{r}') d\mathbf{r} d\mathbf{r}'$ is the probability of finding an electron in $d\mathbf{r}$ multiplied by the probability of finding an electron in $d\mathbf{r}'$ given that there is already one at \mathbf{r} .

Mathematically,

$$n(\mathbf{r}, \mathbf{r}') d\mathbf{r} d\mathbf{r}' = n(\mathbf{r}) d\mathbf{r} \times n(\mathbf{r}' | \mathbf{r}) d\mathbf{r}' , \quad (5.14)$$

where $n(\mathbf{r}' | \mathbf{r})$ is the density of electrons at \mathbf{r}' given that there is an electron at \mathbf{r} . Whenever there is an electron at \mathbf{r} there must be $N - 1$ in the rest of the system and hence

$$\int d\mathbf{r}' n(\mathbf{r}, \mathbf{r}') = n(\mathbf{r}) \times \int d\mathbf{r}' n(\mathbf{r}' | \mathbf{r}) = n(\mathbf{r}) \times (N - 1) . \quad (5.15)$$

The exchange-correlation (XC) hole, $n_{xc}(\mathbf{r}', \mathbf{r})$, is defined by

$$n(\mathbf{r}' | \mathbf{r}) = n(\mathbf{r}') + n_{xc}(\mathbf{r}, \mathbf{r}') . \quad (5.16)$$

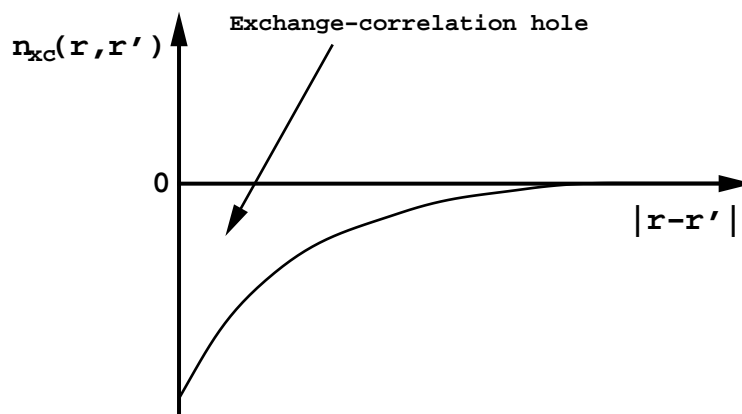


Figure 5.2: The exchange-correlation hole in an interacting electron gas.

In words, $n_{xc}(\mathbf{r}, \mathbf{r}')$ is the change in the electron density at \mathbf{r}' caused by the presence of an electron at \mathbf{r} . In an interacting electron gas, $n_{xc}(\mathbf{r}, \mathbf{r}')$ might look like the example shown in Fig. 5.2.

Since

$$\int d\mathbf{r}' n(\mathbf{r}'|\mathbf{r}) = N - 1, \quad (5.17)$$

it follows that

$$\int d\mathbf{r}' n_{xc}(\mathbf{r}, \mathbf{r}') = -1. \quad (5.18)$$

Every electron scoops out a hole of charge $+|e|$ in the surrounding electron liquid. If the hole is localised near the electron, the electron and hole make up a neutral “quasiparticle”.

This turns out to be a very important result, but so far it contains very little physics. The reason that the hole has charge $+|e|$ is simply electron counting — if there is an electron at \mathbf{r} then there are only $N - 1$ in the rest of the system. For the quasiparticle idea to make sense, we also need to show that the hole is localised near the electron.

In most solids it turns out that the hole is indeed centred on the electron and usually only a few Bohr radii across. In such cases, the XC hole screens the charge of the electron and the resulting quasiparticles are small and neutral and do not interact with each other unless they are close together. This is the reason why so many experiments on solids (think of photoemission, specific heat measurements, optical properties, ...) can be explained using simple mean-field or non-interacting electron

(actually weakly-interacting quasiparticle) models.

In the next section we calculate $n_{xc}(\mathbf{r}, \mathbf{r}')$ for a non-interacting electron liquid and show that it really is short ranged. Since we ignore the Coulomb interactions this is very surprising, but it is yet another consequence of the antisymmetry of the wavefunction. The hole you get when you ignore the interactions is called the exchange hole. It is not the same as the XC hole, but the electron counting argument is general and so both holes integrate to -1 .

5.3 Exchange in the Non-Interacting Electron Liquid

The ground state is

$$D(x_1, x_2, \dots, x_N) = \frac{1}{\sqrt{N!}} \begin{vmatrix} \phi_1(x_1) & \dots & \phi_1(x_N) \\ \vdots & & \vdots \\ \phi_N(x_1) & \dots & \phi_N(x_N) \end{vmatrix}, \quad (5.19)$$

where $\phi_i(x) = \psi_i(r)\chi_i(s)$, with $\psi_i(\mathbf{r}) = \frac{1}{\sqrt{V}}e^{i\mathbf{k}_i \cdot \mathbf{r}}$ and $\chi_i(s) = \delta_{s_i, s}$. The orbital spins s_i are either \uparrow or \downarrow . All spin-up and spin-down orbitals with $|\mathbf{k}_i| < k_F$ are occupied.

Since

$$\hat{n}(\mathbf{r}, \mathbf{r}') = \sum_i \sum_{j (\neq i)} \delta(\mathbf{r} - \mathbf{r}_i) \delta(\mathbf{r}' - \mathbf{r}_j) \quad (5.20)$$

is a two-particle operator of the standard form, its expectation value can be written as

$$\begin{aligned} n(\mathbf{r}, \mathbf{r}') &= \langle D | \sum_i \sum_{j (\neq i)} \delta(\mathbf{r} - \mathbf{r}_i) \delta(\mathbf{r}' - \mathbf{r}_j) | D \rangle \\ &= \sum_i \sum_{j (\neq i)} \left(\int \phi_i^*(x_1) \phi_j^*(x_2) \delta(\mathbf{r} - \mathbf{r}_1) \delta(\mathbf{r}' - \mathbf{r}_2) \phi_i(x_1) \phi_j(x_2) dx_1 dx_2 - \right. \\ &\quad \left. \int \phi_j^*(x_1) \phi_i^*(x_2) \delta(\mathbf{r} - \mathbf{r}_1) \delta(\mathbf{r}' - \mathbf{r}_2) \phi_i(x_1) \phi_j(x_2) dx_1 dx_2 \right) \\ &= \sum_i \sum_{j (\neq i)} \left(|\phi_i(\mathbf{r})|^2 |\phi_j(\mathbf{r}')|^2 - \delta_{s_i s_j} \phi_j^*(\mathbf{r}) \phi_i^*(\mathbf{r}') \phi_i(\mathbf{r}) \phi_j(\mathbf{r}') \right) \\ &= \sum_{\mathbf{k}_i s_i} \sum_{\substack{\mathbf{k}_j s_j \\ (\neq \mathbf{k}_i s_i)}} \left(\frac{1}{V^2} - \frac{\delta_{s_i s_j}}{V^2} e^{i(\mathbf{k}_i - \mathbf{k}_j) \cdot (\mathbf{r} - \mathbf{r}')} \right). \end{aligned} \quad (5.21)$$

It is informative to consider the possible $s_i s_j$ pairings individually; the full $n(\mathbf{r}, \mathbf{r}')$ is then obtained by summing the results for each distinct $s_i s_j$ pair.

Antiparallel spins

$$n_{\uparrow\downarrow}(\mathbf{r}, \mathbf{r}') (= n_{\downarrow\uparrow}(\mathbf{r}, \mathbf{r}')) = \sum_{\mathbf{k}_i} \sum_{\mathbf{k}_j} \frac{1}{V^2} = \frac{(N/2)(N/2)}{V^2} = n_{\uparrow} n_{\downarrow}. \quad (5.22)$$

Note that because $s_i \neq s_j$ the term with $\mathbf{k}_i = \mathbf{k}_j$ is included. The corresponding pair correlation function is

$$g_{\uparrow\downarrow}(\mathbf{r}, \mathbf{r}') = \frac{n_{\uparrow\downarrow}(\mathbf{r}, \mathbf{r}')}{n_{\uparrow} n_{\downarrow}} = 1. \quad (5.23)$$

Spin-parallel electrons are *uncorrelated* in the non-interacting system. This is not surprising since the only thing we have assumed is antisymmetry. In interacting systems the electrons avoid each other to minimise the Coulomb interaction energy and there are correlations even between spin-parallel electrons.

Parallel spins

$$n_{\uparrow\uparrow}(\mathbf{r}, \mathbf{r}') (= n_{\downarrow\downarrow}(\mathbf{r}, \mathbf{r}')) = \sum_{\mathbf{k}_i} \sum_{\mathbf{k}_j (\neq \mathbf{k}_i)} \left(\frac{1}{V^2} - \frac{1}{V^2} e^{i(\mathbf{k}_i - \mathbf{k}_j) \cdot (\mathbf{r} - \mathbf{r}')} \right). \quad (5.24)$$

In this case the two spins are the same and so the $\mathbf{k}_i = \mathbf{k}_j$ term is omitted. Fortunately, however, the summand vanishes when $\mathbf{k}_j = \mathbf{k}_i$ so we can forget this restriction. Assuming that the system is large, the sums can be turned into integrals in the usual way,

$$\sum_{\mathbf{k}} \longrightarrow \frac{V}{(2\pi)^3} \int d\mathbf{k}, \quad (5.25)$$

to get

$$n_{\uparrow\uparrow}(\mathbf{r}, \mathbf{r}') = n_{\uparrow} n_{\uparrow} - \int_{|\mathbf{k}| < k_F} \frac{d\mathbf{k}}{(2\pi)^2} \int_{|\mathbf{k}'| < k_F} \frac{d\mathbf{k}'}{(2\pi)^3} e^{i(\mathbf{k} - \mathbf{k}') \cdot (\mathbf{r} - \mathbf{r}')}. \quad (5.26)$$

The integrals may be evaluated and the result, which only depends on the inter-particle distance $\delta = |\mathbf{r} - \mathbf{r}'|$, is

$$g_{\uparrow\uparrow}(\delta) = \frac{n_{\uparrow\uparrow}(\delta)}{n_{\uparrow} n_{\uparrow}} = 1 - \left(\frac{3 \sin(k_F \delta) - 3(k_F \delta) \cos(k_F \delta)}{(k_F \delta)^3} \right)^2. \quad (5.27)$$

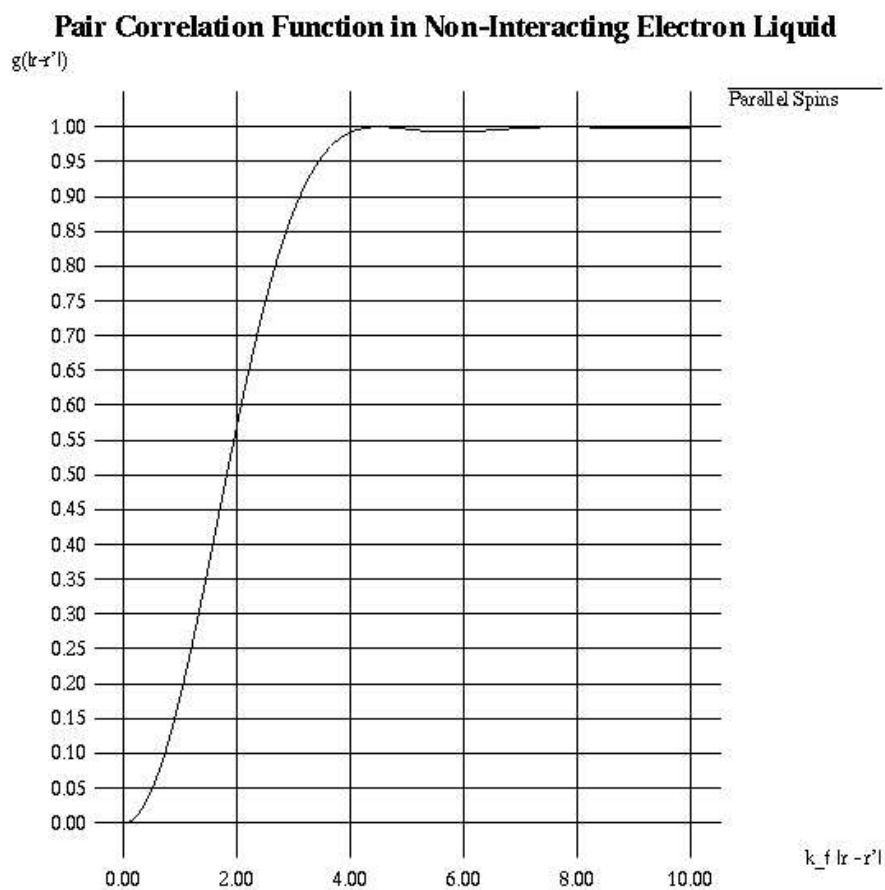


Figure 5.3: The spin-parallel pair correlation function in a non-interacting electron liquid.

Summary

Antisymmetry alone implies that spin-parallel electrons avoid each other (the “exchange hole”), but does not induce correlations between spin anti-parallel electrons.

In interacting systems (where Ψ is no longer a single Slater determinant) both parallel and anti-parallel electrons avoid each other. The “exclusion zone” formed about each electron is called its exchange-correlation hole.

In all cases, the hole (exchange or exchange-correlation) has charge $+|e|$, and so the electron + hole is a neutral object.

5.4 Exchange and Correlation in Real Systems

The full exchange-correlation hole cannot be calculated analytically in real systems, but it can be obtained using quantum Monte Carlo simulations. The following graphs show the results of some of the first calculations of this type, which were done here at Imperial College.

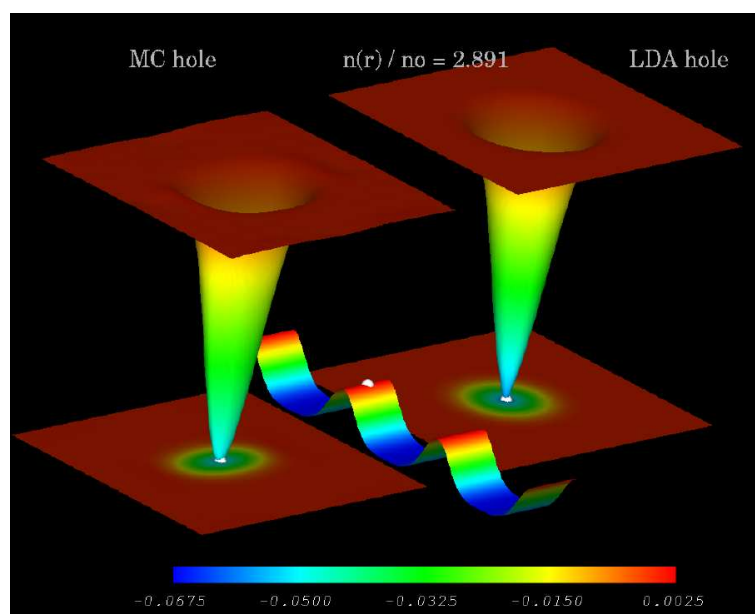


Figure 5.4: The exchange-correlation hole in a three-dimensional system of electrons. The electron density is indicated by the central ribbon and the white dot shows the position of the electron about which the hole is plotted. The left-hand panel shows the exchange-correlation hole calculated using the variational quantum Monte Carlo method; the right-hand panel shows the approximate hole used in the local density approximation to density functional theory.

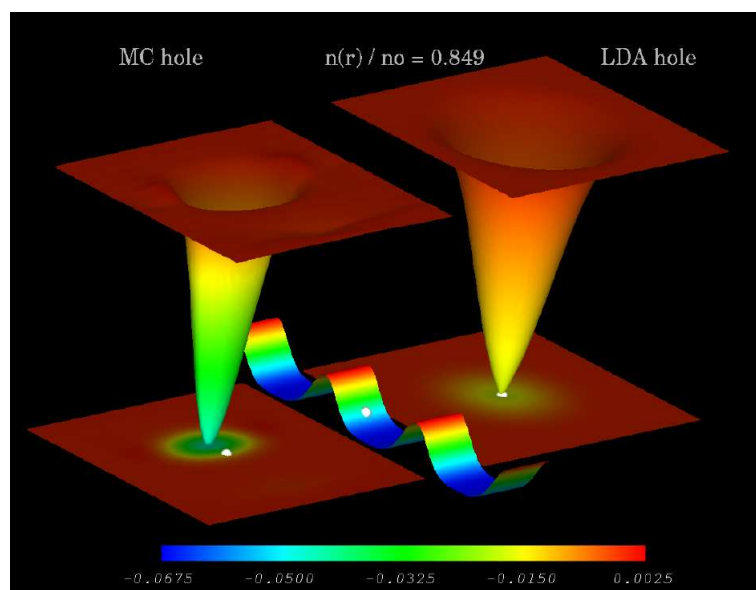


Figure 5.5: As Fig. 5.4, except that the electron about which the hole is plotted is in a region of intermediate electron density rather than at the density maximum.

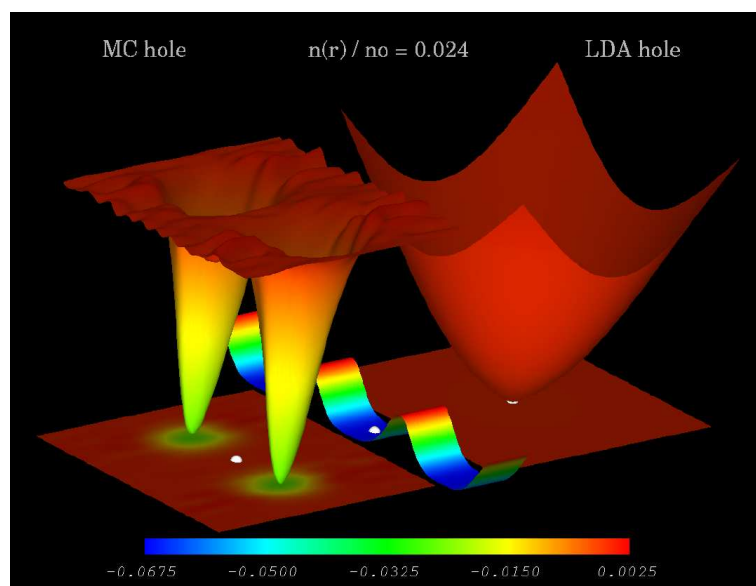


Figure 5.6: As Fig. 5.4, except that the electron about which the hole is plotted is in a region of very low electron density rather than at the density maximum.

Chapter 6

Density Functional Theory

6.1 History

The Hartree-Fock approach makes sense in the high-density limit but is obviously an approximation. Density functional theory (DFT) provides an *exact* mapping from a system of interacting electrons to a system of non-interacting electrons moving through an effective potential that depends on the electron density [7]. Solving this self-consistent non-interacting problem is easier than solving the Hartree-Fock equations and gives, in principle, the *exact* interacting ground-state energy E_0 and electron density for any given arrangement of the frozen (Born-Oppenheimer) nuclei. Since DFT allows us to calculate E_0 quickly and reliably, we can use it to study how the total energy depends on the positions of the nuclei. This tells us the forces on the nuclei and hence how they move around. (Newton's laws are useless for electrons, but better for the much more massive nuclei.) We can use these forces to find the equilibrium positions of the nuclei, watch the progress of a chemical reaction, or even follow the motion of a defect such as a dislocation. The success of DFT, which appears to be a theory of non-interacting electrons but in fact describes a system of interacting electrons, in part explains the success of the standard model of a solid as an assembly of non-interacting electrons moving in a fixed external potential.

DFT was invented in the mid-sixties but was largely ignored until the mid-eighties when computers became good enough to solve the DFT equations accurately. It is now used by thousands of physicists, chemists, geophysicists, materials scientists, and even biochemists. In recognition of its importance, Walter Kohn (a physicist)

and John Pople (a chemist who developed some of the mathematical and computational techniques used in DFT calculations) were awarded the 1998 Nobel prize in Chemistry.

6.2 Preliminaries

The many-electron eigenfunctions obey the many-electron Schrödinger equation:

$$\left(\frac{1}{2} \sum_i^N \mathbf{p}_i^2 + \sum_{i>j}^N \frac{e^2}{|\mathbf{r}_i - \mathbf{r}_j|} - \sum_i^N \sum_{\alpha}^M \frac{Z_{\alpha} e^2}{|\mathbf{r}_i - \mathbf{d}_{\alpha}|} + \sum_{\alpha>\beta}^M \frac{Z_{\alpha} Z_{\beta} e^2}{|\mathbf{d}_{\alpha} - \mathbf{d}_{\beta}|} \right) \Psi = E \Psi . \quad (6.1)$$

For simplicity, we shall often shorten this to

$$\left(\hat{T} + \hat{V}_{ee} + \hat{V}_{en} + E_{nn} \right) \Psi = E \Psi . \quad (6.2)$$

The positions \mathbf{d}_{α} of the nuclei affect the potential felt by the electrons and hence the electronic eigenfunctions Ψ , but the nuclei are *not* being treated as dynamical variables. Since we are working within the Born-Oppenheimer approximation, the nuclear positions are chosen first and the many-electron Schrödinger equation is solved for those fixed nuclear positions. The nuclear-nuclear interaction energy E_{nn} is therefore a constant.

The central quantity in DFT is the electron (number) density $n(\mathbf{r})$, the operator for which is

$$\hat{n}(\mathbf{r}) = \sum_i^N \delta(\mathbf{r} - \mathbf{r}_i) . \quad (6.3)$$

Since

$$\hat{V}_{en} = \sum_i^N V_{\text{nuc}}(\mathbf{r}_i) = \int V_{\text{nuc}}(\mathbf{r}) \sum_i^N \delta(\mathbf{r} - \mathbf{r}_i) d^3r , \quad (6.4)$$

the electron-nucleus interaction operator (or any other one-electron potential energy term) can be written in terms of the electron density operator:

$$\hat{V}_{en} = \int V_{\text{nuc}}(\mathbf{r}) \hat{n}(\mathbf{r}) d^3r . \quad (6.5)$$

Note that \mathbf{r} in this equation is a simple vector, not an operator; the electron position operators $\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N$ are buried in the definition of $\hat{n}(\mathbf{r})$. Taking an expectation value of Eq. (6.5) gives the obvious result:

$$\langle \Psi | \hat{V}_{en} | \Psi \rangle = \int V_{\text{nuc}}(\mathbf{r}) \langle \Psi | \hat{n}(\mathbf{r}) | \Psi \rangle d^3r = \int V_{\text{nuc}}(\mathbf{r}) n(\mathbf{r}) d^3r . \quad (6.6)$$

6.3 The Energy Functional

The explanation of DFT given here does not follow the original derivation of Hohenberg, Kohn and Sham [7], but takes the constrained search approach of Levy [8]. Although slightly longer than the original derivation, I find Levy's easier to understand and generally more illuminating.

The first step in any derivation of DFT is to show that there exists a functional, $E[n(\mathbf{r})]$, of the electron number density $n(\mathbf{r})$, which takes its minimum value, equal to the ground-state energy E_0 , when the density is the true ground state density $n_0(\mathbf{r})$. Levy manages this by giving an explicit construction of such a functional.

Given an operator \hat{O} , Levy defines an associated functional of the electron density, $O[n(\mathbf{r})]$, via:

$$O[n] = \text{Min}_{\Psi \rightarrow n(\mathbf{r})} \langle \Psi | \hat{O} | \Psi \rangle . \quad (6.7)$$

In words: given an electron density $n(\mathbf{r})$, the functional is evaluated by checking all possible normalized antisymmetric N -electron wavefunctions which give that density to find the one that minimizes $\langle \Psi | \hat{O} | \Psi \rangle$. This minimum value is the value assigned to the functional at the density $n(\mathbf{r})$. It can be shown that it is possible to find at least one N -electron wavefunction corresponding to any reasonable density $n(\mathbf{r})$, so the constrained search always produces a value.

The variational principle guarantees that the minimum value of the energy functional,

$$E[n] = \text{Min}_{\Psi \rightarrow n} \langle \Psi | \hat{H} | \Psi \rangle = \text{Min}_{\Psi \rightarrow n} \langle \Psi | \hat{T} + \hat{V}_{ee} + \hat{V}_{en} + E_{nn} | \Psi \rangle , \quad (6.8)$$

occurs when $n(\mathbf{r})$ is equal to the true ground-state density $n_0(\mathbf{r})$. The optimal wavefunction Ψ is then the true ground state Ψ_0 , and the value of the functional is the true ground-state energy:

$$E[n_0] = \text{Min}_{\Psi \rightarrow n_0} \langle \Psi | \hat{H} | \Psi \rangle = \langle \Psi_0 | \hat{H} | \Psi_0 \rangle = E_0 . \quad (6.9)$$

Since E_{nn} is a constant, and since the expectation value of \hat{V}_{en} gives the same result,

$$\langle \Psi | \hat{V}_{en} | \Psi \rangle = \int V_{en}(\mathbf{r}) n(\mathbf{r}) d\mathbf{r} , \quad (6.10)$$

for *all* wavefunctions Ψ yielding the density $n(\mathbf{r})$, the total energy functional may be written in the form

$$E[n] = \text{Min}_{\Psi \rightarrow n} \langle \Psi | \hat{T} + \hat{V}_{ee} | \Psi \rangle + \int V_{en}(\mathbf{r}) n(\mathbf{r}) d\mathbf{r} + E_{nn}$$

$$= F[n] + \int V_{\text{en}}(\mathbf{r})n(\mathbf{r})d\mathbf{r} + E_{\text{nn}} , \quad (6.11)$$

where the second equality defines the functional $F[n]$.

Because the definition of $F[n]$ makes no reference to the positions of the nuclei, the value of $F[n]$ depends on the electron density $n(\mathbf{r})$ only. It is thus a *universal* functional: given an input density $n(\mathbf{r})$, the value of $F[n]$ is fixed regardless of the nuclear charges or positions. (Remember that functionals such as $E[n]$ and $F[n]$ are defined for all reasonable input densities $n(\mathbf{r})$; the density that minimises $E[n]$ depends on the arrangement of ions, but that is a separate issue.) Since the functional $F[n]$ is the same in all solids, atoms and molecules, it could in principle be calculated once and for all.

6.4 Contributions to the Energy Functional

If, given a density $n(\mathbf{r})$, we could easily evaluate the functional $E[n(\mathbf{r})]$, the problem would now be almost solved: all that we would have to do to find the ground-state density and energy would be to vary $n(\mathbf{r})$ until the functional reached a minimum. Unfortunately, but not unexpectedly, evaluating the functional is equivalent to solving the full N -body problem and is out of the question. We therefore have to approximate. The reason DFT is useful is that excellent approximations are known.

To make approximating the energy functional easier, it helps to identify some of the contributions to $F[n]$. Since the definition of $F[n]$ involves an expectation value of the electron-electron interaction, one obvious contribution is the Hartree energy (the classical electrostatic energy of the electron charge cloud interacting with itself):

$$E_{\text{H}}[n] = \frac{1}{2} \int \int \frac{e^2 n(\mathbf{r})n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d^3r d^3r' . \quad (6.12)$$

Another large and easily recognisable contribution is the kinetic energy of the electrons. Although this is hard to write down, the kinetic energy functional, which is not the same, is quite straightforward:

$$T[n] = \text{Min}_{\Psi \rightarrow n} \langle \Psi | \hat{T} | \Psi \rangle . \quad (6.13)$$

Although there is no reason to assume that $T[n]$ is the same as the kinetic energy of the interacting electrons, it is at least of the same order of magnitude and turns out to be easier to calculate.

So far, then, we have identified two contributions that we believe should make up a large part of $F[n]$. The next step is to write:

$$E[n] = T[n] + E_H[n] + \int V_{\text{nuc}}(\mathbf{r})n(\mathbf{r}) d^3r + E_{\text{nn}} + E_{\text{xc}}[n]. \quad (6.14)$$

The terms we have identified have been written explicitly, and $E_{\text{xc}}[n]$, known as the exchange and correlation (XC) energy, is a “rubbish” term to take care of the rest of $F[n]$.

Like $F[n]$, the Hartree energy $E_H[n]$ and the kinetic energy $T[n]$ are universal functionals of the electron density and could, in principle, be calculated once and for all. Since

$$E_{\text{xc}}[n] = F[n] - T[n] - E_H[n], \quad (6.15)$$

it follows that the unknown exchange-correlation functional $E_{\text{xc}}[n]$ is also universal.

Given an electron density $n(\mathbf{r})$, the Hartree, electron-nuclear and nuclear-nuclear interaction energies are easily obtained. The only difficult terms are $T[n]$ and $E_{\text{xc}}[n]$, both of which are universal functionals of the electron density $n(\mathbf{r})$. It turns out that $T[n]$ can be evaluated exactly, but $E_{\text{xc}}[n]$ has to be approximated.

6.5 The Kinetic Energy

The definition of the kinetic energy functional,

$$T[n] = \text{Min}_{\Psi \rightarrow n} \langle \Psi | \hat{T} | \Psi \rangle, \quad (6.16)$$

may look rather mysterious at first but has a straightforward physical interpretation: $T[n]$ is the ground-state kinetic energy of a gas of *non-interacting* electrons with density $n(\mathbf{r})$.

Consider a system of N non-interacting electrons with the Hamiltonian

$$\begin{aligned} \hat{H}_{\text{non-int}} &= \sum_i^N \left(\frac{1}{2} \mathbf{p}_i^2 + V_{\text{eff}}(\mathbf{r}_i) \right) \\ &= \hat{T} + \int V_{\text{eff}}(\mathbf{r}) \hat{n}(\mathbf{r}) d\mathbf{r}. \end{aligned} \quad (6.17)$$

The corresponding non-interacting energy functional (defined for any reasonable density $\tilde{n}(\mathbf{r})$) is

$$\begin{aligned}
 E_{\text{non-int}}[\tilde{n}] &= \text{Min}_{\Psi \rightarrow \tilde{n}} \langle \Psi | \left(\hat{T} + \int V_{\text{eff}}(\mathbf{r}) \hat{n}(\mathbf{r}) d\mathbf{r} \right) | \Psi \rangle \\
 &= \text{Min}_{\Psi \rightarrow \tilde{n}} \langle \Psi | \hat{T} | \Psi \rangle + \int V_{\text{eff}}(\mathbf{r}) \tilde{n}(\mathbf{r}) d\mathbf{r} \\
 &= T[\tilde{n}] + \int V_{\text{eff}}(\mathbf{r}) \tilde{n}(\mathbf{r}) d\mathbf{r} .
 \end{aligned} \tag{6.18}$$

Consider the value of this functional when $\tilde{n}(\mathbf{r}) = n(\mathbf{r})$, where $n(\mathbf{r})$ is the ground-state density of the non-interacting Hamiltonian. The wavefunction $\Psi_{\text{non-int}}$ that minimises $\langle \Psi | \hat{T} + \int V_{\text{eff}}(\mathbf{r}) \hat{n}(\mathbf{r}) d\mathbf{r} | \Psi \rangle$ is then the non-interacting ground-state wavefunction, and the kinetic energy functional $T[n] = \langle \Psi_{\text{non-int}} | \hat{T} | \Psi_{\text{non-int}} \rangle$ is the non-interacting ground-state kinetic energy. This shows that $T[n]$ is the ground-state kinetic energy of a gas of *non-interacting* electrons with density $n(\mathbf{r})$. The potential $V_{\text{eff}}(\mathbf{r})$, which is often called the Kohn-Sham potential, has to be chosen such that the ground-state density of the non-interacting system is equal to $n(\mathbf{r})$ (assuming this can be done).

The following algorithm can be used to calculate $T[n]$:

- (i) Choose an external potential $V_{\text{eff}}(\mathbf{r})$.
- (ii) Solve the Schrödinger equation for a system of N non-interacting electrons moving through this potential.
- (iii) Adjust $V_{\text{eff}}(\mathbf{r})$ until the ground-state density of the system of non-interacting electrons is equal to the target density $n(\mathbf{r})$.
- (iv) $T[n]$ is equal to the kinetic energy of the non-interacting system.

6.6 The Exchange-Correlation Energy

All the complicated parts of the many-body problem have been hidden in the definition of the XC energy functional $E_{\text{xc}}[n]$. There is no hope of calculating this exactly, but it is possible to devise good approximations. The surprising accuracy of these approximations is the reason why DFT is so useful.

Remember that the XC energy functional was defined via the equation:

$$E[n] = T[n] + E_{\text{en}}[n] + E_{\text{H}}[n] + E_{\text{nn}} + E_{\text{xc}}[n] . \tag{6.19}$$

The main physical difference between the sum of the first four terms on the RHS of this equation and the full functional (i.e. all five terms) is that the full functional includes the effects of the XC hole. If one electron is at a point \mathbf{r}_0 , then both because of the electron-electron interactions and because of the Pauli principle, other electrons are kept away. Although the shape of the XC hole depends on \mathbf{r}_0 , the total amount of charge it contains is always exactly $+|e|$. The whole *quasiparticle* — the electron and its XC hole — is therefore neutral and expected to have only short-range interactions. This is the clue that leads to a sensible way of approximating the XC energy.

The short range of the quasiparticle interactions implies, presumably, that the shape of the XC hole around an electron at \mathbf{r}_0 only depends on nearby parts of the solid. The contribution that the region near \mathbf{r}_0 makes to the XC energy is therefore determined entirely by the local environment. Since the XC functional is a universal functional of $n(\mathbf{r})$, the local quantity upon which this contribution depends must be the electron density, $n(\mathbf{r})$, near $\mathbf{r} = \mathbf{r}_0$. If we assume that the hole is small compared with the length scale on which $n(\mathbf{r})$ varies (this is not true in most solids), it follows that the XC energy per electron near \mathbf{r}_0 must be almost the same as the XC energy per electron in a *uniform* electron gas of density $n(\mathbf{r}) = n(\mathbf{r}_0) = \text{constant}$. This idea of treating the region near \mathbf{r}_0 as if it were part of a uniform electron gas with density $n(\mathbf{r}_0)$ is similar to the idea underlying the Thomas-Fermi approximation.

Since the average number of electrons in the volume d^3r_0 is $n(\mathbf{r}_0)d^3r_0$, this suggests approximating the total XC energy using the formula:

$$E_{\text{xc}}[n] \approx \int_{\text{system}} \varepsilon_{\text{xc}}(n(\mathbf{r}_0))n(\mathbf{r}_0)d^3r_0, \quad (6.20)$$

where $\varepsilon_{\text{xc}}(n)$ is the XC energy per electron in a uniform electron gas of density n . This approximation, which is known as the local density approximation (LDA), has proved astonishingly successful (the reasons for this success are still not completely understood). Density-functional calculations based on the LDA can reproduce many of the physical properties (phonon frequencies, bond lengths, bond energies, . . .) of real solids and molecules to within a few percent.

Note that $\varepsilon_{\text{xc}}(n)$ is a simple function of its argument n (a number), *not* a functional of the full non-uniform electron density $n(\mathbf{r})$. To work out $\varepsilon_{\text{xc}}(n(\mathbf{r}_0))$, all you need to know is the value of the electron density $n(\mathbf{r}_0)$ at the single point \mathbf{r}_0 . The function $\varepsilon_{\text{xc}}(n)$ is known from the results of quantum Monte Carlo simulations of uniform electron gases, and several accurate and simple parameterisations are available.

6.7 Minimisation of the Energy Functional

We now know how to evaluate all the terms in the energy functional

$$E[n] = T[n] + E_{\text{en}}[n] + E_{\text{H}}[n] + E_{\text{nn}} + E_{\text{xc}}[n] . \quad (6.21)$$

To calculate the exact interacting ground-state density $n_0(\mathbf{r})$ (and hence the exact ground-state energy E_0), we have to find the density that minimises $E[n]$ subject to the normalisation constraint $\int n(\mathbf{r})d\mathbf{r} = N$. Mathematically, the ground-state density is determined by the stationarity condition,

$$\delta E = \int \frac{\delta E[n]}{\delta n(\mathbf{r})} \delta n(\mathbf{r})d\mathbf{r} = 0 , \quad (6.22)$$

which must hold for all density variations $\delta n(\mathbf{r})$ satisfying the normalisation conservation constraint

$$\int \delta n(\mathbf{r})d\mathbf{r} = 0 . \quad (6.23)$$

Let us start by working out the variations of E_{en} , E_{H} and E_{xc} (within the LDA), leaving the kinetic energy term for later. The electron-nuclear term is easy:

$$\begin{aligned} \delta E_{\text{en}} &= \delta \left(\int V_{\text{nuc}}(\mathbf{r})n(\mathbf{r})d^3r \right) \\ &= \int V_{\text{nuc}}(\mathbf{r})\delta n(\mathbf{r})d^3r . \end{aligned} \quad (6.24)$$

The Hartree term is also quite easy:

$$\begin{aligned} \delta E_{\text{H}} &= \delta \left(\frac{e^2}{2} \int \int \frac{n(\mathbf{r})n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d^3r d^3r' \right) \\ &= \frac{e^2}{2} \int \int \frac{n(\mathbf{r})\delta n(\mathbf{r}') + n(\mathbf{r}')\delta n(\mathbf{r})}{|\mathbf{r} - \mathbf{r}'|} d^3r d^3r' \\ &= \int \left(\int \frac{e^2 n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d^3r' \right) \delta n(\mathbf{r})d^3r \\ &= \int V_{\text{H}}([n], \mathbf{r})\delta n(\mathbf{r})d^3r , \end{aligned} \quad (6.25)$$

where $V_{\text{H}}([n], \mathbf{r})$ is the Hartree potential — the classical electrostatic potential arising from the electron density $n(\mathbf{r})$.

The functional derivative of the XC energy,

$$V_{\text{xc}}([n], \mathbf{r}) \equiv \frac{\delta E_{\text{xc}}[n]}{\delta n(\mathbf{r})}, \quad (6.26)$$

which is called the exchange-correlation potential, is unknown because $E_{\text{xc}}[n]$ is unknown, but is easy enough to work out within the LDA. Since

$$\begin{aligned} \delta E_{\text{xc}}^{\text{LDA}} &= \delta \left(\int \varepsilon_{\text{xc}}(n(\mathbf{r}_0)) n(\mathbf{r}_0) d^3 r_0 \right) \\ &= \int \left(\left. \frac{d\varepsilon_{\text{xc}}(n)}{dn} \right|_{n=n(\mathbf{r}_0)} + \varepsilon_{\text{xc}}(n(\mathbf{r}_0)) \right) \delta n(\mathbf{r}_0) d^3 r_0, \end{aligned} \quad (6.27)$$

we obtain

$$V_{\text{xc}}^{\text{LDA}}([n], \mathbf{r}) = \left. \frac{d\varepsilon_{\text{xc}}(n)}{dn} \right|_{n=n(\mathbf{r})} + \varepsilon_{\text{xc}}(n(\mathbf{r})). \quad (6.28)$$

The derivative of the kinetic energy functional will be considered in Sec. 6.8. For the time being, we simply write

$$\delta T[n] = \int \frac{\delta T[n]}{\delta n(\mathbf{r})} \delta n(\mathbf{r}) d\mathbf{r}. \quad (6.29)$$

The stationarity condition $\delta E = 0$ then becomes

$$\int \left(\frac{\delta T}{\delta n(\mathbf{r})} + V_{\text{nuc}}(\mathbf{r}) + V_{\text{H}}([n], \mathbf{r}) + V_{\text{xc}}([n], \mathbf{r}) \right) \delta n(\mathbf{r}) d^3 r = 0, \quad (6.30)$$

for all normalisation conserving variations $\delta n(\mathbf{r})$. We have not shown that the stationary point obtained by solving this equation is unique, but we know that the functional has at least one stationary point (the minimum we seek) and in practice this seems to be the only one.

6.8 Self-Consistency

Section 6.5 showed that $T[n]$ is the ground-state kinetic energy of a gas of non-interacting electrons moving in a potential $V_{\text{eff}}(\mathbf{r})$ chosen to ensure that the non-interacting ground-state density is $n(\mathbf{r})$. The non-interacting energy functional,

$$E_{\text{non-int}}[\tilde{n}] = T[\tilde{n}] + \int V_{\text{eff}}(\mathbf{r}) \tilde{n}(\mathbf{r}) d^3 r, \quad (6.31)$$

is therefore stationary when $\tilde{n}(\mathbf{r}) = n(\mathbf{r})$:

$$\delta E_{\text{non-int}} = \int \left(\frac{\delta T[n]}{\delta n(\mathbf{r})} + V_{\text{eff}}(\mathbf{r}) \right) \delta n(\mathbf{r}) d\mathbf{r} = 0, \quad (6.32)$$

for all normalisation conserving fluctuations $\delta n(\mathbf{r})$. This equation holds for any density $n(\mathbf{r})$, as long as $V_{\text{eff}}(\mathbf{r})$ is the potential that makes $n(\mathbf{r})$ the ground-state density of the non-interacting system.

Because of the constraint of normalisation conservation,

$$\int \delta n(\mathbf{r}) d\mathbf{r} = 0, \quad (6.33)$$

the $\mathbf{k}=\mathbf{0}$ Fourier component of $\delta T[n]/\delta n(\mathbf{r}) + V_{\text{eff}}(\mathbf{r})$ is not fixed by Eq. (6.32). All other Fourier components must be zero, however, and hence

$$\frac{\delta T[n]}{\delta n(\mathbf{r})} = -V_{\text{eff}}(\mathbf{r}) + \text{const.} \quad (6.34)$$

Substituting Eq. (6.34) into Eq. (6.30), and noting that the constant vanishes because of the normalisation constraint, we conclude that the interacting ground-state density is determined by the condition

$$\int \left(-V_{\text{eff}}(\mathbf{r}) + V_{\text{nuc}}(\mathbf{r}) + V_{\text{H}}([n], \mathbf{r}) + V_{\text{xc}}([n], \mathbf{r}) \right) \delta n(\mathbf{r}) d\mathbf{r} = 0. \quad (6.35)$$

The $\mathbf{k}=\mathbf{0}$ Fourier component is undetermined again, and so we obtain

$$V_{\text{eff}}(\mathbf{r}) = V_{\text{nuc}}(\mathbf{r}) + V_{\text{H}}([n], \mathbf{r}) + V_{\text{xc}}([n], \mathbf{r}) + \text{const.} \quad (6.36)$$

The value of the constant has no effect on the calculation of $T[n]$ (which is the only purpose of $V_{\text{eff}}(\mathbf{r})$) and so we can choose to set it to zero.

Let us think about what this means. The total energy functional is minimised when the potential $V_{\text{eff}}(\mathbf{r})$ appearing in the non-interacting Schrödinger equation with ground-state density $n(\mathbf{r})$ is exactly equal to $V_{\text{nuc}}(\mathbf{r}) + V_{\text{H}}([n], \mathbf{r}) + V_{\text{xc}}([n], \mathbf{r})$. Since V_{H} and V_{xc} depend on the electron density, this is a sort of *self-consistency condition*: the potential occurring in the non-interacting Schrödinger equation is determined by the ground-state electron density obtained by solving that equation.

6.9 How DFT Calculations Work

We now know that the exact ground-state density of the interacting system may be obtained by solving a non-interacting problem in which the potential $V_{\text{eff}}(\mathbf{r})$

depends self-consistently on the electron density $n(\mathbf{r})$. Assuming you have access to a reasonably powerful computer, here is how you actually do it:

1. Start with a reasonable guess, $n^{\text{in}}(\mathbf{r})$, for the ground-state electron density.
2. Work out the Hartree and XC potentials (within the LDA) for that input density, and hence obtain the effective potential:

$$V_{\text{eff}}([n^{\text{in}}], \mathbf{r}) = V_{\text{nuc}}(\mathbf{r}) + V_{\text{H}}([n^{\text{in}}], \mathbf{r}) + V_{\text{xc}}([n^{\text{in}}], \mathbf{r}) . \quad (6.37)$$

3. Solve the non-interacting Schrödinger equation,

$$\left(-\frac{1}{2}\nabla^2 + V_{\text{eff}}([n^{\text{in}}], \mathbf{r}) \right) \phi_i^{\text{out}}(\mathbf{r}) = \epsilon_i \phi_i^{\text{out}}(\mathbf{r}) , \quad (6.38)$$

to obtain the wavefunctions $\phi_i^{\text{out}}(\mathbf{r})$ and the output density

$$n^{\text{out}}(\mathbf{r}) = \sum_{i \text{ occ}} |\phi_i^{\text{out}}(\mathbf{r})|^2 . \quad (6.39)$$

The value of $T[n^{\text{out}}]$ is then given by

$$T[n^{\text{out}}] = \sum_{i \text{ occ}} \int (\phi_i^{\text{out}}(\mathbf{r}))^* \left(-\frac{1}{2}\nabla^2 \right) \phi_i^{\text{out}}(\mathbf{r}) d\mathbf{r} . \quad (6.40)$$

($T[n^{\text{in}}]$ is much harder to obtain.)

4. In general, you will find that $n^{\text{out}} \neq n^{\text{in}}$. Set $n^{\text{in}} = n^{\text{out}}$ and return to step 2.
5. Repeat steps 2–4 until the iteration converges and $n^{\text{out}}(\mathbf{r}) = n^{\text{in}}(\mathbf{r})$.
6. Once the iteration has converged, evaluate the energy functional $E[n]$. Gradients of the energy functional with respect to nuclear positions give the forces on the nuclei.

In practice, this simple iteration does not always converge and it is often necessary to use more sophisticated iterative schemes (analogous to the Newton-Raphson method). Once convergence (self-consistency) has been attained, however, the identical input and output densities are both equal to the ground-state density of the interacting system $n_0(\mathbf{r})$. The only approximation required is the LDA, and the ground-state density obtained would have been exact if the exact (unknown) XC functional had been used instead.

An alternative approach, more widely used these days, considers how the value of the total energy functional,

$$E[n^{\text{out}}] = T[n^{\text{out}}] + E_{\text{en}}[n^{\text{out}}] + E_H[n^{\text{out}}] + E_{\text{nn}} + E_{\text{xc}}[n^{\text{out}}], \quad (6.41)$$

changes as the one-electron orbitals $\phi_i^{\text{out}}(\mathbf{r})$ (and hence the density $n^{\text{out}}(\mathbf{r})$) are varied. Since $E[n^{\text{out}}]$ is minimised when $n^{\text{out}}(\mathbf{r})$ is the true ground-state density, we can seek the ground state directly by varying the members of a set of N orthonormal orbitals until the minimum is found. The minimisation is tackled using a standard downhill optimisation method such as the conjugate gradients algorithm. In effect, when using this approach, the orbitals $\phi_i^{\text{out}}(\mathbf{r})$ replace the density $n^{\text{out}}(\mathbf{r})$ as the fundamental quantities of the theory.

In either case, once the ground-state density n_0 and the corresponding effective potential $V_{\text{eff}}(\mathbf{r})$ and one-electron wavefunctions $\phi_i(\mathbf{r})$ have been found, the total ground-state energy is given by

$$E[n_0] = T[n_0] + E_{\text{en}}[n_0] + E_H[n_0] + E_{\text{nn}} + E_{\text{xc}}[n_0]. \quad (6.42)$$

Since

$$\begin{aligned} T[n_0] &= \sum_{i \text{ occ}} \int \phi_i^*(\mathbf{r}) \left[-\frac{1}{2} \nabla^2 \right] \phi_i(\mathbf{r}) d^3r \\ &= \sum_{i \text{ occ}} \int \phi_i^*(\mathbf{r}) \left[-\frac{1}{2} \nabla^2 + V_{\text{eff}}(\mathbf{r}) \right] \phi_i(\mathbf{r}) d^3r - \int V_{\text{eff}}(\mathbf{r}) n_0(\mathbf{r}) d^3r \\ &= \sum_{i \text{ occ}} \epsilon_i - \int V_{\text{eff}}(\mathbf{r}) n_0(\mathbf{r}) d^3r, \end{aligned} \quad (6.43)$$

the ground-state energy may also be written as

$$E = \sum_{i \text{ occ}} \epsilon_i - \int V_{\text{eff}}(\mathbf{r}) n_0(\mathbf{r}) d^3r + E_{\text{en}}[n_0] + E_H[n_0] + E_{\text{nn}} + E_{\text{xc}}[n_0]. \quad (6.44)$$

This form is interesting because of what it has to say about the standard model. The total ground-state energy is not just the sum of the one-electron eigenvalues, as might be expected, but includes additional density-dependent terms. Because these involve the density directly, rather than the individual one-electron orbitals, they turn out to be simpler than the sum of eigenvalues and can often be approximated using a pair potential. The non-pairwise chemical bonding contributions mainly arise from the sum of eigenvalues.

6.10 Quantum Molecular Dynamics

Density-functional calculations are comparatively easy to do. It is possible to study systems containing hundreds or even thousands of atoms and to calculate ground-state energies and interatomic forces very quickly. This makes it possible to carry out computer simulations in which the nuclei move according to Newton’s laws, but the forces on the nuclei are calculated using DFT. These “quantum molecular dynamics” simulations are much more accurate than classical molecular dynamics simulations based on crude models for the interatomic forces. They are so good that they can even be used to follow the progress of chemical reactions.

As the nuclei in a quantum molecular dynamics simulation move, the electronic Hamiltonian changes and the ground-state electron density and orbitals need to be recalculated. Fortunately, the nuclei move only a little in one molecular dynamics time step, and the orbitals from the previous time step provide a sensible starting point for the calculation of the new orbitals. This information can be used in many different ways, but one of the most interesting is the Car-Parrinello method [9], in which a *classical* molecular dynamics algorithm is used to evolve the nuclear positions and electronic orbitals together. The joint electronic and nuclear Lagrangian is

$$\mathcal{L} = \sum_i^N \frac{1}{2} \mu \int |\dot{\phi}_i(\mathbf{r})|^2 d\mathbf{r} + \sum_\alpha \frac{1}{2} M_\alpha \dot{\mathbf{d}}_\alpha^2 - E(\{\phi_i\}, \{\mathbf{d}_\alpha\}), \quad (6.45)$$

where $E(\{\phi_i\}, \{\mathbf{d}_\alpha\})$ is the Hohenberg-Kohn energy, regarded as a functional of the current set of one-electron orbitals $\{\phi_i\}$ and a function of the current set of nuclear positions $\{\mathbf{d}_\alpha\}$. The speed of the orbital dynamics is controlled by the “mass” parameter μ , which is typically a few hundred times the true electron mass. If μ is set equal to zero, the nuclei move over the potential surface $E(\{\phi_i\}, \{\mathbf{d}_\alpha\})$ according to Newton’s laws, exactly as described above.

It is important to understand that the electronic part of the Car-Parrinello Lagrangian is completely fictitious (the orbitals appear in a manner analogous to classical fields) and has nothing to do with the *real* (quantum mechanical) evolution of the electronic wavefunctions. As long as μ is much smaller than the nuclear mass, however, and especially if the electronic system has an energy gap, orbitals evolving according to the Car-Parrinello Lagrangian follow the nuclear motion almost adiabatically: if they start in the Born-Oppenheimer ground state for the original nuclear positions, they remain very close to the Born-Oppenheimer ground state throughout the simulation. This is all that is necessary to ensure the correct forces on the nuclei and hence the correct nuclear dynamics.

6.11 Strengths and Weaknesses

The results of DFT calculations are surprisingly accurate. Despite the crudeness of the LDA, most physical quantities come out right to within a percent or two. This is good enough for DFT to have all sorts of unexpected uses. Here are a few examples.

- What are the physical properties — viscosity, compressibility, etc. — of iron at the centre of the earth? Nobody knows, but DFT has been used to make predictions.
- How do enzymes function? DFT is being used to study how enzymes drive important biochemical reactions,
- Jupiter is about 90% hydrogen at high pressure and temperature, most of which exists in a fluid metallic state. Although these conditions cannot be reproduced experimentally, DFT may help us understand what is going on.
- What, exactly, happens when a solid starts to fracture? If DFT can give us a better idea of how the atoms around tiny cracks move, we might be able to improve our understanding of how to make strong materials.

The main drawbacks of DFT are:

- Although DFT calculations are fairly easy for small systems, they are too time consuming to be useful in examples such as the fracture problem above, which would require one to follow the motion of millions of atoms for millions of atomic vibration periods.
- DFT is a ground-state theory; it has little or nothing to say about excited states. (There is a generalisation called time-dependent DFT that can in principle tell you more.) In particular, the one-electron eigenvalues ϵ_i are not the excitation energies measured in experiments such as photoemission.
- Although DFT produces accurate ground-state densities and energies, these (and derived quantities such as interatomic forces) are the only things it can calculate. In particular, it does not tell you the many-electron ground-state wavefunction.
- In cases when the LDA is inadequate (e.g., in “strongly correlated” solids such as high-temperature superconductors), it is hard to know how to improve it. There is no systematic way to make the results more accurate.

Chapter 7

Elementary Excitations

We have seen that density functional theory allows the ground-state energies of solids and molecules to be calculated in a one-electron framework, partly explaining the success of the “standard model”, but there are many questions that ground-state theories such as DFT cannot answer. How do solids respond to experimental probes such as photons, beams of atoms or ions, the electrons emerging from an STM tip, or changes in temperature? What determines the electrical transport properties of solids? All of these questions are beyond the scope of a ground-state theory.

Many of these questions could be answered if we understood the low-energy ($< kT$ to a few eV) excitations of solids. The “elementary excitations” from which general low-energy excitations are made include quasiparticles, phonons (quantised lattice vibrations), plasmons (charge density waves), spin waves, polarons, excitons, and so on. The fascinating thing about most of these excitations is that, although the ground state from which they are created is overwhelmingly complicated, they themselves are usually (but not always) very simple. The quasiparticles in normal Fermi liquids, for example, behave much like non-interacting electrons or holes with renormalised masses.

7.1 Collective Modes

Consider, as an analogy, a suspension bridge. This too is very complicated, but for small departures from equilibrium the change ΔV in the potential energy V is

bound to be quadratic in the displacements:

$$\Delta V \approx \frac{1}{2} \sum_{i,j} \Delta x_i K_{ij} \Delta x_j , \quad (7.1)$$

where Δx_i is the displacement of the i^{th} piece of the bridge and K_{ij} is the real symmetric matrix of spring constants. By switching to the normal mode coordinates, Δu_i , we can diagonalise K_{ij} to get

$$\Delta V \approx \frac{1}{2} \sum_i \kappa_i (\Delta u_i)^2 . \quad (7.2)$$

All small excitations may be regarded as superpositions of these normal modes — the bridge itself is complicated, but its low-energy excitations are simple. For larger displacements, non-linear terms enter into the expression for ΔV and the normal modes begin to interact, but for small (low energy) excitations they are non-interacting.

The same ideas apply to phonons — the vibrational normal modes of solids. Now, however, quantum mechanics matters, and hence a mode of Bloch wavevector \mathbf{k} and frequency $\omega(\mathbf{k})$ has quantised values of crystal momentum and energy:

$$\mathbf{p}_n = n\hbar\mathbf{k} \quad (7.3)$$

$$\epsilon_n = \left(n + \frac{1}{2} \right) \hbar\omega(\mathbf{k}) . \quad (7.4)$$

In solid-state physics jargon, we say that this mode contains n phonons, each of energy $\hbar\omega$ and crystal momentum $\hbar\mathbf{k}$. If the number of phonons per unit volume is small, they will be non-interacting and “linear” simply because they hardly ever encounter one another. As the number of phonons per unit volume becomes larger, however, phonon-phonon scattering and creation/annihilation events will begin to become important. The general (but not universal) rule is:

SMALL EXCITATION ENERGIES \Rightarrow

SUPERPOSITIONS OF NON-INTERACTING EXCITATIONS

Solids have many other collective excitations of this type, the most important of which are plasmons and spin waves [4].

The need to understand this assortment of “-ons” explains why quantum field theory, which may be regarded as a general approach to the physics of low-energy excitations, plays an important role in solid-state physics. For the excitations of lowest energy and longestwavelength, in particular, the atomic “graininess” of solids

ceases to matter and simple continuum field theories suffice. The mathematical and physical analogy between the creation of excitations in a solid and the creation of particles in an accelerator is almost perfect: the elementary excitations correspond to the elementary particles, and the unimaginably complicated ground state of the solid corresponds to the equally complicated vacuum of particle physics.

7.2 Quasiparticles

The idea of linearity explains why one might hope to find simple collective excitations in solids, but does not account for the empirical observation that excited electrons and holes act almost like non-interacting particles, conserving their energies and crystal momenta for long times between infrequent scattering events. The solid may contain only a few excited electrons, and so it is reasonable to assume that these will rarely encounter each other, but what is stopping the excited electrons scattering from the enormous numbers of electrons in states well below E_F ? The Coulomb interactions are screened, but the screening length is of order a lattice parameter and there are plenty of other electrons within this range.

At first sight, therefore, it appears that excited electrons should not have well defined $\hbar\mathbf{k}$ and ϵ values; they ought to be undergoing almost continuous scattering events, and their initial energy and momentum should soon be redistributed over huge numbers of electrons and holes with smaller excitation energies.

It was Landau [3, 4] who first tried to explain why electron- and hole-like quasiparticles exist and why they are almost non-interacting. More rigorous and mathematical arguments have been devised since, but there can be no proof that quasiparticles always exist, since in some strongly-correlated systems they do not. In one-dimensional electron gases (usually known as a Luttinger liquids), for example, the charge and spin quantum numbers of the electrons (or holes) become associated with *different* elementary excitations: there are holons, which carry charge but no spin, and spinons, which carry spin but no charge [10]. One-dimensional electron gases exist in linear molecules, along rows of atoms on some surfaces, and in various artificial semiconductor structures, so these strange results have measurable consequences.

Consider a non-interacting electron gas with one extra electron in a state of momentum $\hbar\mathbf{k}$ and energy $E_F + \Delta$ just outside the Fermi sphere, as shown in Fig. 7.1.

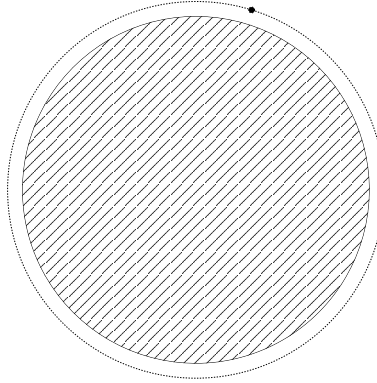


Figure 7.1: One additional electron in a state of wavevector \mathbf{k} and energy $E_F + \Delta = k^2/2$ just outside the Fermi sphere.

Now imagine “adiabatically” (i.e., infinitely slowly) switching on the interaction between the electrons. As the interaction increases in strength, the initial non-interacting state of total momentum,

$$\hbar\mathbf{k} + \sum_{k' < k_F} \hbar\mathbf{k}' = \hbar\mathbf{k} , \quad (7.5)$$

evolves continuously into an eigenstate of the interacting system. Since the scattering of one electron from another conserve total momentum (the interacting and non-interacting Hamiltonians both commute with the total momentum operator), the interacting state also has total momentum $\hbar\mathbf{k}$. A typical scattering event is shown in Fig. 7.2. If we ignore the possibility that the gradual switching on of the interaction might bring about a sudden phase transition (which, presumably, is what happens in systems such as the Luttinger liquid), this allows us to set up a one-to-one correspondence between states of the non-interacting and interacting systems.

The real question, though, is whether the interacting state of momentum $\hbar\mathbf{k}$ has any one-electron character left? As the interactions get stronger, the excited electron will undergo scattering events, changing momentum and losing energy by creating electron-hole pairs. These electron-hole pairs describe the polarisation of the medium around the electron.

By the time the interaction has reached full strength, one might expect that huge numbers of such collisions would have taken place, and hence that the interacting wavefunction would have become a complicated superposition of determinants with different sets of excited electron-hole pairs. If this were the case, the single-

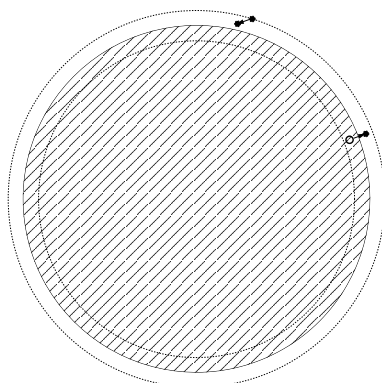


Figure 7.2: A scattering event in which the electron outside the Fermi sea loses momentum $\hbar\mathbf{q}$ and energy ϵ , creating an electron-hole pair of momentum $\hbar\mathbf{q}$ and energy ϵ .

particle character of the excited state would have been lost completely. Experimentally, of course, we know that is this not what happens.

Landau's insight was to realise that for low energy excited states (small Δ), the electron-electron scattering is strongly suppressed by the exclusion principle. If the extra electron has excitation energy Δ , it can only scatter from electrons within Δ of E_F . Electrons with $E' < E_F - \Delta$ cannot act as scatterers because their possible final states, which must all have energy less than $E' + \Delta$, are already occupied. For small Δ , the only possible scatterers are those within the Fermi sphere but outside the innermost sphere in Fig. 7.2. The total number of possible scatterers is thus proportional to Δ . Furthermore, for each such scatterer, initially in an occupied state \mathbf{k}' below E_F , the number of possible final states (i.e., the number of \mathbf{q} vectors one can find such that energy is conserved and the final state is empty) is also proportional to Δ . Hence, the overall scattering rate should be proportional to Δ^2 , and the scattering time and mean-free path should be proportional to $1/\Delta^2$.

This is why low-energy excitations behave so much like non-interacting electrons. As the interactions are switched on, the excited electron at \mathbf{k} with non-interacting energy $E(\mathbf{k})$ is “dressed” by clouds of virtual electron-hole pairs (+ magnetic fluctuations + phonons + ...). This changes its effective mass, $m \rightarrow m^*$, and dispersion relation, $E(\mathbf{k}) \rightarrow E^*(\mathbf{k})$, but the exclusion effect prevents it losing its one-electron character completely.

Many-electron systems in which the low-energy excitations are quasiparticle-like are called normal Fermi liquids, a class that includes most familiar metals, semiconductors and insulators. In “strongly-correlated” solids, however, the nature of

the ground state changes fundamentally as the interactions are switched on. In Luttinger liquids, it is known that no electron-like quasiparticles exist; in other cases, such as the CuO_2 -based high-temperature superconductors, there may still be remnants of the electron-like quasiparticles, but their properties are very different from those of non-interacting electrons.

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