

561 F 2005 Lecture 3

Elementary Excitations Condensed Matter 1: Electronic States - Introduction

References: Phillips, Ch. 1,4; Pines, Ch. 3; Ashcroft Chs. 2,3,17; Mahan, 1.6 and 5.1; Doniach, Ch. 6; Fulde, Ch. 2.

In the Adiabatic Approximation, the states of the electrons are derived with the nuclei in instantaneous fixed positions. The states of the electrons can be determined for the nuclei at their equilibrium positions. This is a complete set of states.

Hartree-Fock Theory

The starting point for understanding interacting particles, was first applied to atoms in 1930 by Fock. This is a theory to first order in the interaction, i.e. it assumes wavefunctions are zero-order (the same as for non-interacting particles in an effective potential) and evaluates the energy to first order. The general formulas are given in many references. We will give the first quantized form here and the second quantized form later (see Phillips Ch. 4).

In this approach one writes a properly antisymmetrized determinant wavefunction for a fixed number N of electrons, and finds the single determinant that minimizes the total energy for the full interacting hamiltonian. The determinant wavefunction Φ can be written

$$\Phi = \frac{1}{(N!)^{1/2}} \begin{vmatrix} \phi_1(\mathbf{r}_1, \sigma_1) & \phi_1(\mathbf{r}_2, \sigma_2) & \phi_1(\mathbf{r}_3, \sigma_3) & \dots \\ \phi_2(\mathbf{r}_1, \sigma_1) & \phi_2(\mathbf{r}_2, \sigma_2) & \phi_2(\mathbf{r}_3, \sigma_3) & \dots \\ \phi_3(\mathbf{r}_1, \sigma_1) & \phi_3(\mathbf{r}_2, \sigma_2) & \phi_3(\mathbf{r}_3, \sigma_3) & \dots \\ \vdots & \vdots & \vdots & \dots \\ \vdots & \vdots & \vdots & \dots \end{vmatrix}, \quad (1)$$

where the $\phi_i(\mathbf{r}_j, \sigma_j)$ are single particle “spin-orbitals” each of which is a product of a function of the position $\psi_i^\sigma(\mathbf{r}_j)$ and a function of the spin variable $\alpha_i(\sigma_j)$. If the spin-orbitals are orthonormal the equations simplify greatly and Φ is normalized to 1. If the hamiltonian is independent of spin the expectation value of the hamiltonian is given by

$$\begin{aligned} \langle \Phi | \hat{H} | \Phi \rangle &= \sum_{i,\sigma} \int d\mathbf{r} \psi_i^{\sigma*}(\mathbf{r}) \left[-\frac{1}{2} \nabla^2 + V_{\text{ext}}(\mathbf{r}) \right] \psi_i^\sigma(\mathbf{r}) + E_{II} \\ &+ \frac{1}{2} \sum_{i,j,\sigma_i,\sigma_j} \int d\mathbf{r} d\mathbf{r}' \psi_i^{\sigma_i*}(\mathbf{r}) \psi_j^{\sigma_j*}(\mathbf{r}') \frac{1}{|\mathbf{r} - \mathbf{r}'|} \psi_i^{\sigma_i}(\mathbf{r}) \psi_j^{\sigma_j}(\mathbf{r}') \\ &- \frac{1}{2} \sum_{i,j,\sigma} \int d\mathbf{r} d\mathbf{r}' \psi_i^{\sigma*}(\mathbf{r}) \psi_j^{\sigma*}(\mathbf{r}') \frac{1}{|\mathbf{r} - \mathbf{r}'|} \psi_j^\sigma(\mathbf{r}) \psi_i^\sigma(\mathbf{r}'). \end{aligned} \quad (2)$$

The first terms are single-body expectation values and the third and fourth terms are the direct and exchange interactions among electrons. The equations are simplified by including the $i = j$ “self-interaction,” which cancels in the sum of direct and exchange terms. When this term is included, the sum over all orbitals gives the density and the direct term is simply the Hartree Coulomb energy. The “exchange” term, which acts only between same spin electrons since the spin parts of the orbitals are orthogonal for opposite spins.

The Hartree-Fock approach is to minimize the total energy with respect to all degrees of freedom in the wavefunction with the restriction that it has the form (1). Enforcing

orthonormality can be done by Lagrange multipliers. If the spin functions are quantized along an axis, variation of $\psi_i^{\sigma*}(\mathbf{r})$ for each spin σ leads to the Hartree–Fock equations

$$\left[-\frac{1}{2}\nabla^2 + V_{\text{ext}}(\mathbf{r}) + \sum_{j,\sigma_j} \int d\mathbf{r}' \psi_j^{\sigma_j*}(\mathbf{r}') \psi_j^{\sigma_j}(\mathbf{r}') \frac{1}{|\mathbf{r} - \mathbf{r}'|} \right] \psi_i^\sigma(\mathbf{r}) - \sum_j \int d\mathbf{r}' \psi_j^{\sigma_j*}(\mathbf{r}') \psi_i^\sigma(\mathbf{r}') \frac{1}{|\mathbf{r} - \mathbf{r}'|} \psi_j^\sigma(\mathbf{r}) = \varepsilon_i^\sigma \psi_i^\sigma(\mathbf{r}). \quad (3)$$

Note the form of the final exchange term that involves the exchange with other single particle orbitals.

Koopmans' theorem for meaning of the eigenvalues: the energies to remove electrons *if other electrons are not allowed to not respond*. (Eigenvalues of empty orbitals are addition energies to add electrons assuming the occupied states do not change. There are large errors due to fact that empty states are affected by the full repulsion but are not part of the exchange.)

Jellium

Jellium is the simplest condensed matter system - where the nuclei are replaced by a uniform positive background. Together with the uniform electrons this forms a uniform neutral system with no average Coulomb potential. The hamiltonian for Jellium is:

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

where it is understood that the divergent Coulomb sum is cancelled by the nuclear background.

The density parameter r_s is defined by $\frac{4}{3}\pi r_s^3 = \frac{1}{n} = \text{volume per electron in atomic units}$ ($a_0 = \text{Bohr radii}$).

- High Density: $r_s \ll 1$, kinetic energy dominates
- Low Density: $r_s \gg 1$, potential energy dominates.
- Real materials at intermediate r_s : (Al, $r_s = 2$; Si, $r_s = 2$; Na, $r_s = 4$; Cs, $r_s = 6$.)

The Fermi momentum is given by $k_F r_s = 1.92$, and for the non-interacting case the kinetic energy per electron is $\frac{3}{5}E_F = \frac{2.21}{r_s^2} \text{ Ryd.}$ (Pines, p. 58.)

Hartree theory: Sommerfeld non-interacting electron model

Eigenstates are plane waves $\frac{1}{\Omega} \exp(i\mathbf{k}\cdot\mathbf{r})$ with energy $\varepsilon(k) = k^2/2$ in atomic units. This agrees semi-quantitatively with many properties of real metals: Specific heat; spin susceptibility; band width; etc.

Terrible failure for binding energy - repulsive at all densities

Hartree-Fock Theory for Jellium

Reasonable for binding energy

Terrible failure for all properties of the bands: specific heat; spin susceptibility; band width; etc.

Hartree-Fock treatment of interactions leads to correction of non-interacting electron energies. The integrals can be done analytically (See Phillips, Pines, Ashcroft and Mermin), leading to

$$\varepsilon_k = \frac{1}{2}k^2 + \frac{k_F}{\pi}f(x), \quad (5)$$

where $x = k/k_F$ and

$$f(x) = - \left(1 + \frac{1-x^2}{2x} \ln \left| \frac{1+x}{1-x} \right| \right). \quad (6)$$

The factor $f(x)$ is negative for all x ; at the bottom of the band ($x = 0$), $f(0) = -2$, and at large x it approaches zero. Near the Fermi surface ($x = 1$), $f(x)$ varies rapidly and has a divergent slope (a log singularity), as was first pointed by Bardeen. (See figures in Ashcroft and Mermin, Ch. 17; Mahan, Ch. 5.; Phillips Ch. 5) This is a disaster for any application of Hartree-Fock to metals and totally disagrees with experiments. Nevertheless the limiting value at $x = 1$ is well defined, $f(x \rightarrow 1) = -1$. Thus in the Hartree-Fock approximation, exchange increases the band width W by $\Delta W = k_F/\pi$.

The total exchange energy per electron (see below) gives a very reasonable approximation to the true energy, unlike the Hartree approximation.

Note: Many results are easier to derive using the second quantized Form of the hamiltonian. We will come back to this.

Exchange Hole and exchange energy

In general in any many-body system (boson or fermion) the pair distribution function can be defined by

$$g(r, r') = \frac{1}{\rho(r)} \frac{1}{\rho(r')} p(r, r') \quad (7)$$

where

$$p(r, r') = \langle \Psi | \sum_{i \neq j} \delta(r - r_i) \delta(r - r_j) | \Psi \rangle \quad (8)$$

is the joint probability of simultaneously finding an electron at points r and r' . The function $g(r, r')$ is defined so that it is unity in an uncorrelated system and $g(r, r') \rightarrow 1$ at large distance in any system. The difference from unity $g(r, r') - 1$ is defined to be the exchange-correlation hole. It is straightforward to show from the definition above that

$$\int dr' (g(r, r') - 1) \rho(r') = -1. \quad (9)$$

In the H-F approximation the exchange hole can be found directly from the orbitals. The result for Jellium is (see Mahan, Ch. 5)

$$g_{\uparrow\downarrow}(r, r') = \frac{1}{2} \quad (10)$$

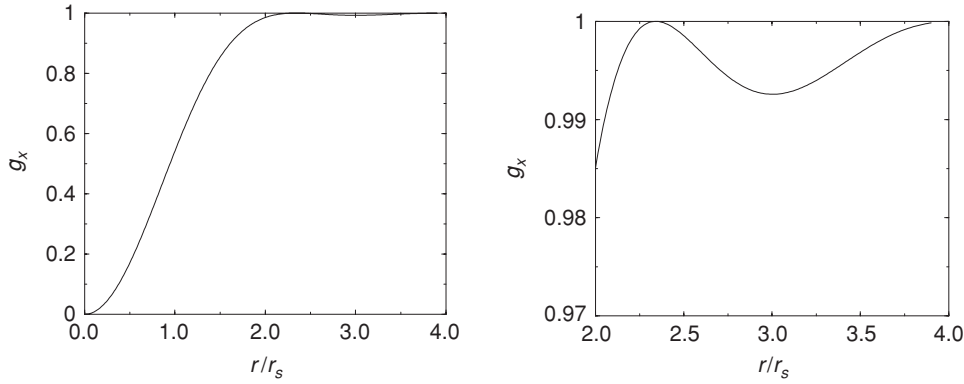


Figure 1: Exchange hole $g_x(r)$ in the homogeneous electron gas, plotted as a function of r/r_s , where r_s is the average distance between electrons in an unpolarized system. The magnitude decreases rapidly with oscillation, as shown in the greatly expanded right-hand figure. Note the similarity to the calculated pair correlation function for parallel spins in Fig. 2.

(i.e. uncorrelated) and

$$g_{\uparrow\uparrow}(r, r') = \frac{1}{2}[1 - \phi(|r - r'|)^2], \quad \phi(r) = \frac{2}{N} \sum_k \exp(ikr). \quad (11)$$

In 3 dimensions, the result is (Mahan, p. 402)

$$\phi(r) = \frac{3}{k_F r} [\sin(k_F r) - (k_F r) \cos(k_F r)]. \quad (12)$$

The function g_x is plotted in Fig. 1. Note that g_x is always less than 1. See the tail on the expanded scale at the right.

In k-space one can define the static structure factor which for a homogeneous system can be written (see Pines and Fulde)

$$S(k) = \int d^3r \rho(r) \exp(ikr) \quad (13)$$

$$= \frac{1}{N} \langle \Psi | \sum_{i,j} \exp(-ik(r_i - r_j)) | \Psi \rangle \quad (14)$$

$$= \frac{1}{N} \langle \Psi | \rho_{-k} \rho_k | \Psi \rangle \quad (15)$$

which includes the self-term. For a homogeneous system,

$$g(r) = \frac{1}{N} \sum_k (S(k) - 1) \exp(ikr) \quad (16)$$

For an uncorrelated system $S(k) = 1$, $k \neq 0$, and $S(0) = N$, (self term). (Some texts define S without the self term, so that $S(0) = 0$, e.g., Mahan, p. 74.)

In the H-F approximation, there is a simple expression for $S(k)$, given by Pines (p. 75). For $k \neq 0$, define $x = \frac{k}{2k_F}$, in which case

$$S(k) = \frac{3}{2}x - \frac{1}{2}x^3, x < 1 \quad (17)$$

$$S(k) = 1, x > 1 \quad (18)$$

A main point is that $S(k) = 1$ for $k > 2k_F$, so that the the particles are uncorrelated except for the Pauli exclusion between states with $k < k_F$.

The exchange energy can be interpreted as the interaction of each electron with its exchange hole. (In general, there is a similar interpretation for the correlation hole, but this can NOT be interpreted as the correlation energy, because the kinetic energy also changes due to correlations. More on this later.)

The exchange energy can be derived in many ways. One is by integrating over the removal energies for electrons and eliminating the double-counting terms. Another is to use the exchange hole directly, which is most convenient to do in k-space (Pines, p 68-69; Philips), and which is most convenient to do after introducing second quantization. The result is

For example, the exchange energy can be derived as (Pines, p 68-69)

$$E_x = -\frac{0.458}{r_s} \text{Hartree} = -\frac{0.916}{r_s} \text{Ryd}. \quad (19)$$

As Pines points out (p. 77) the exchange energy is directly related to the mean square density fluctuations, and the attractive exchange energy can be considered as due to the reduction in the mean square density fluctuations at small $k < 2k_F$.

Beyond Hartree-Fock: Correlations

Here we only give the main points that it is difficult to go beyond H-F. In finite systems, one finds the configuration-interaction expansion which grows exponentially with the number of particles. In condensed matter expansions formally diverge (Gellmann-Bruckner). What to do? Can we simply screen the Coulomb interactions? No. Fixes the disaster at the Fermi surface, but ruins the cohesive energy.

Correlation can be calculated by many-body techniques. I order to see the effects we show in Fig. 2 calculated by Monte Carlo methods. Ignore the comparison with models and only notice the general forms. Note that the effect of correlation on antiparallel spins is almost negligible (it does not change with r_s), whereas it is important for parallel spins. For large r_s the antiparallel spins are kept apart by the repulsive interactions almost as much as the parallel spins.

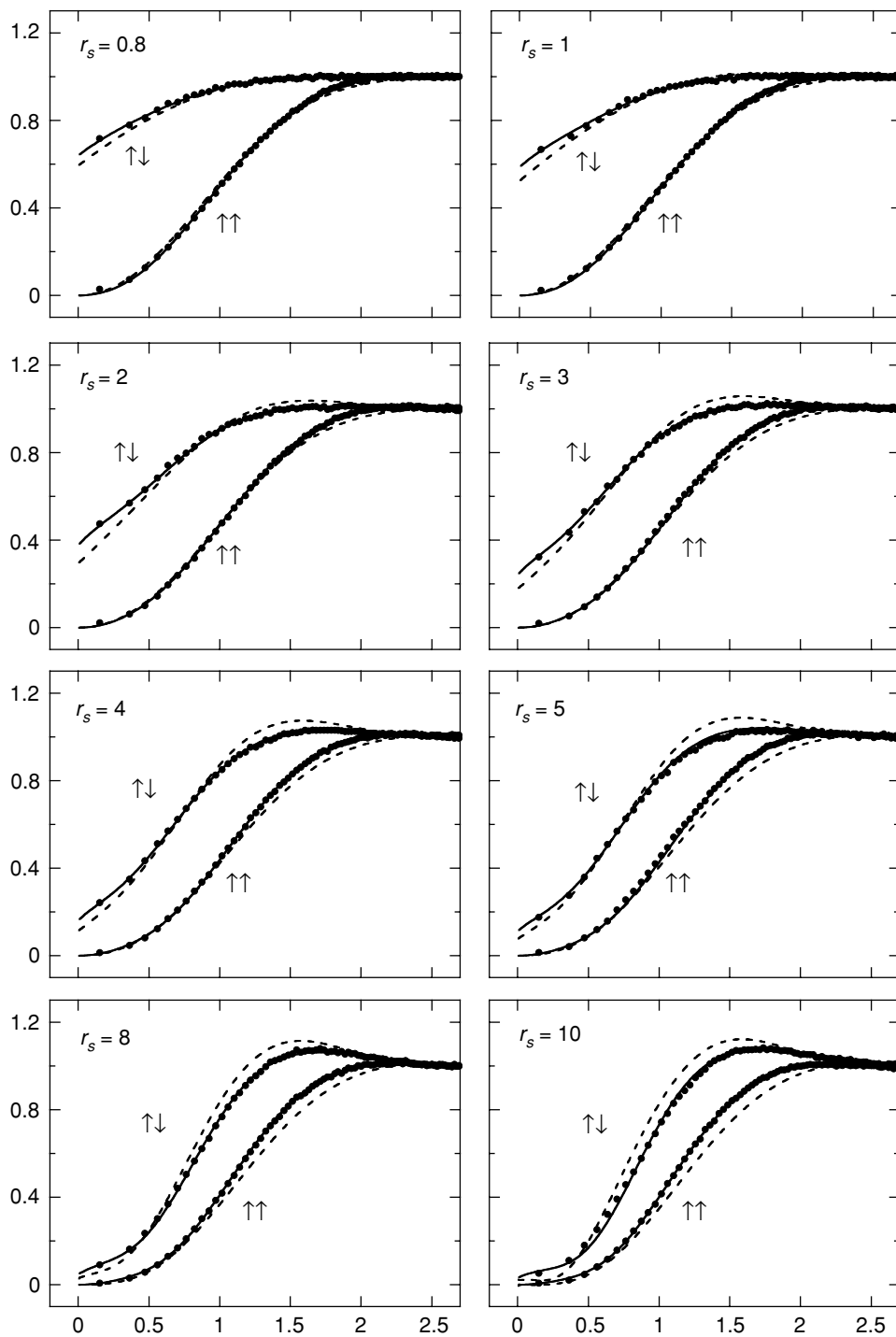


Figure 2: Spin-resolved normalized pair-correlation function $g_{xc}(r)$ for the unpolarized homogeneous electron gas as a function of scaled separation r/r_s , for r_s varying from $r_s = 0.8$ to $r_s = 10$. Dots, QMC data of Ortiz(1999); dashed line, Perdew–Wang model; solid line, coupling constant integrated form. From From Bachelet (2000). See Figure 5.5 of Martin for sources.

Conclusions

- Electrons at ordinary densities in materials have important effects of correlations
- Hartree reasonable in some ways. Why? Unreasonable in others. Why?
- Hartree-Fock reasonable in some ways. Why? Unreasonable in others. Why?
- Exchange-Correlation Hole: general definitions
- Exchange hole in H-F approximation
- How to go beyond H-F?

Introduction to experiments

- Scattering
- Photoemission