

**Hartree-Fock theory and Exchange:** Hartree-Fock is a method to treat many-electron systems including electron-electron interactions. See the text chapter 17; this is an abbreviated coverage to accompany the lecture. The Hamiltonian is,

$$H = \sum_n \sum_{m \neq n} \frac{Z^2 e^2}{2|R_n - R_m|} - \sum_i \frac{\hbar^2 \nabla_i^2}{2m} - \sum_i \sum_n \frac{Ze^2}{|r_i - R_n|} + \sum_i \sum_{j \neq i} \frac{e^2}{2|r_i - r_j|}, \quad [1]$$

where  $Ze$  is the charge of the positive nuclei. A few notes on this: Here the crystal is assumed to have a basis of one atom, so that  $Z$  is a single number, however this would be easily generalized to include multiple types of atoms. The problem could also be simplified by treating the core electrons as inert, and calculating only the valence electron states – the effect of the core might then be replaced by a *pseudopotential*; see chapter 11 which has some discussion of such methods, still used today in modified form. Also the first term in eqn. [1] will be discarded here as a constant – recall that the when describing independent-electron behavior the effects of ion motions were also suppressed, since they can be treated adiabatically to an excellent level of approximation; this is the Born-Oppenheimer approximation. Thus we are assuming that the nuclei provide a fixed potential.

The all-electron eigenstates of [1] cannot be simple product wavefunctions given by  $\Psi = \psi_1(r_1 s_1) \psi_2(r_1 s_1) \dots \psi_N(r_1 s_1)$ , since such a state does not have the property of *sign reversal upon interchange of coordinates*, as required for Fermions. The Hartree-Fock theory assumes that the many-body electron wave-function has the form of a *Slater determinant*:

$$\Psi = \frac{1}{\sqrt{N!}} \begin{vmatrix} \psi_1(r_1 s_1) & \psi_1(r_2 s_2) & \dots & \dots & \psi_1(r_N s_N) \\ \psi_2(r_1 s_1) & \dots & \dots & \dots & \dots \\ \dots & \dots & \dots & \dots & \dots \\ \dots & \dots & \dots & \dots & \dots \\ \psi_N(r_1 s_1) & \dots & \dots & \dots & \psi_N(r_N s_N) \end{vmatrix}, \quad [2]$$

where the  $\psi_i$  are a set of  $N$  orthogonal single-particle wavefunctions, and  $r_i/s_i$  are translational/spin coordinates. (Note: I omitted vector symbols on the  $r$ 's.) The Slater determinant contains a sum of  $N!$  product functions, with the proper signs for coordinate exchange automatically incorporated through the form of the determinant. In this space of possible wavefunctions, we minimize the energy functional,  $\langle \Psi | H | \Psi \rangle$ , with respect to the  $N$  individual functions  $\psi_i$ . If  $\Psi$  were the exact form of the wavefunction, the minimized  $\langle \Psi | H | \Psi \rangle$ , would be the ground-state energy, however the result obtained here will be an approximation to the ground state within the restricted space of functions having the Slater determinant form.

Minimizing  $\langle \Psi | H | \Psi \rangle$  can be done through variational calculus. First, we will replace  $\psi_i(\vec{r}, s)$  by  $\varphi_i(\vec{r})|s_i\rangle$ , where the spin functions are shown as kets. Since the Hamiltonian [1] has no spin-dependence, the matrix elements  $\langle s_j | s_i \rangle$  simply yield 1 or 0. (Separating spin and translational

parts of  $\psi_i$  is not a particularly good approximation for systems such as heavy atoms where *spin-orbit* interactions are important, and the spin-separation is not an essential part of the Hartree-Fock theory. However it simplifies our treatment and makes clear the spin-dependence of the *exchange* interaction.) Proceeding this way,  $\langle \Psi | H | \Psi \rangle$  contains  $3N$ -fold spatial integrals covering the coordinates of the  $N$  electrons. The middle 2 terms of [1] contain only a single coordinate  $r_i$ , so that integrating the other  $(N-1)$  coordinates is trivial, yielding 0 or 1 since the functions are orthogonal and normalized. As a result, these two terms lead to the sum,

$$\frac{1}{N} \sum_{i,j} \int d^3 r_i \varphi_j^*(r_i) \left[ \frac{\hbar^2 \nabla_i^2}{2m} + \sum_n \frac{Ze^2}{|r_i - R_n|} \right] \varphi_j(r_i) \langle s_j | s_j \rangle, \text{ with a spin product which is simply 1. The}$$

integrals for the  $N$  different coordinates  $i$  are identical, so we can re-write this term including only the  $r_1$  coordinate, dispensing with the factor  $1/N$ .

The final term in [1] couples *pairs* of electrons. For this case  $\langle \Psi | H | \Psi \rangle$  consists of terms in which  $(N-2)$  integrals are trivially evaluated to 0 or 1, depending on whether there is the same orbital and spin state on both sides for a given coordinate. There are  $N(N-1)$  remaining integrals, and these are equivalent since the  $r_i$  are dummy indices for indistinguishable electrons. However there are two types of nonzero terms: those for which a given orbital corresponds to the same coordinate on both sites, and those for which the electron coordinate has been interchanged between orbitals on the two sides. We are left with,

$$\begin{aligned} \langle \Psi | H | \Psi \rangle &= \sum_j \int d^3 r_1 \varphi_j^*(r_1) \left[ \frac{\hbar^2 \nabla_1^2}{2m} + \sum_n \frac{Ze^2}{|r_1 - R_n|} \right] \varphi_j(r_1) \\ &+ \frac{1}{2} \sum_i \sum_{j \neq i} \int d^3 r_1 d^3 r_2 \varphi_j^*(r_1) \varphi_i^*(r_2) \frac{e^2}{|r_2 - r_1|} \varphi_j(r_1) \varphi_i(r_2) \quad . \quad [3] \\ &- \frac{1}{2} \sum_i \sum_{j \neq i} \int d^3 r_1 d^3 r_2 \varphi_j^*(r_1) \varphi_i^*(r_2) \frac{e^2}{|r_2 - r_1|} \varphi_j(r_2) \varphi_i(r_1) \delta_{s_1 s_2} \end{aligned}$$

The delta symbol comes about since the spin states of the exchanged electrons must be the same otherwise the spin product gives zero. Note that the “ $\neq$ ” specification on the summations can be omitted since the extra terms cancel.

The variational minimization of [3] with respect to the functions  $\varphi_i(\vec{r})$  must be constrained by the condition that  $\varphi_i(\vec{r})$  remain normalized,  $\int d^3 r \varphi_j^*(\vec{r}) \varphi_j(\vec{r}) = 1$ . This is done using standard variational calculus methods, introducing single-particle energies as a set of *Lagrange multipliers*,  $\varepsilon_i$ . The result is finally a set of  $N$  equations,

$$\begin{aligned} \varepsilon_i \varphi_i(r_1) &= \frac{\hbar^2 \nabla^2}{2m} \varphi_i(r_1) + U_{ion}(r_1) \varphi_i(r_1) \\ &+ \left[ \sum_{j \neq i} \int d^3 r_2 \varphi_j^*(r_2) \varphi_j(r_2) \frac{e^2}{|r_2 - r_1|} \right] \varphi_i(r_1) \quad , \quad [4] \\ &- \sum_{j \neq i} \int d^3 r_2 \varphi_j^*(r_2) \varphi_i(r_2) \frac{e^2}{|r_2 - r_1|} \varphi_j(r_1) \delta_{s_1 s_2} \end{aligned}$$

where the  $\epsilon_i$  assume the form of single-particle energies. In [4] the last line is the non-local exchange interaction (" $\epsilon_{ex}$ ") and the second line contains the direct interaction (" $\epsilon_{dir}$ ").  $\epsilon_{dir}$  is the interaction of an electron with the average potential of the other electrons, neglecting Pauli exclusion; the *Hartree approximation* includes this term but neglects the exchange term.

Going beyond Hartree-Fock, note that the exact energy due to electron-electron interactions is normally defined as:

$$\Delta\epsilon \equiv \epsilon_{dir} + \epsilon_{ex} + \epsilon_{corr} \quad [5]$$

which defines the correlation energy ( $\epsilon_{corr}$ ) as any part of the "true" interaction energy which is not included in Hartree-Fock theory. "Correlation" is in some ways a misnomer, since electron-electron correlations are already included in the Hartree-Fock theory, as seen for example in the exchange-correlation hole described below.

Note that the exchange interaction (and similar higher-order effects) are generally responsible for spontaneous magnetism. We will return to this later, but for example note the comparison of magnitudes on pp. 673-674 of the text: considering only the magnetic dipole interaction, the magnetic moments of two electrons located  $2\text{\AA}$  apart, less than or equal to a typical spacing in materials, have an interaction strength corresponding to a temperature of about 1 K. On the other hand, ferromagnetic iron orders at a temperature near 1000 K. Electrostatic interactions are responsible for this, and the spin-dependent exchange interaction demonstrates how this is possible.

**Free-electron solutions:** If the individual wavefunctions  $\phi_i(\vec{r})$  are identified as plane waves, and if the ion potential is replaced by a uniform positively-charged background ("jellium") then as discussed in class the Hartree-Fock exchange term adds a contribution to the total energy,

$$\Delta E = \frac{-3e^2 k_F}{4\pi} \text{ per electron, which is equivalent to,}$$

$$\Delta E = \frac{-3^{4/3} e^2}{4\pi^{1/3}} n^{1/3}. \quad [6]$$

The assumption that this is a local potential proportional to  $n^{1/3}$  is the starting point for the simplest form of local density approximation (LDA theory, below).

Note that even in the Hartree-Fock approximation there is correlation between electrons. An example is the *exchange-correlation hole* (for details see the book by Martin). If any two columns of the Slater determinant, [1], are the same, the determinant must vanish. This happens if  $s_1 = s_2$ , and  $r_1 = r_2$ . Therefore if two electrons with the same spin coincide at the same location the wavefunction vanishes at this point, and thus the *probability* that these electrons can coincide is zero. Indeed, it is the tendency for the electrons to avoid each other that leads to the reduction in energy (eqn. [6]) since the Coulomb repulsion is reduced. The vanishing probability can be expressed  $P(r_1, r_1) = 0$ , where  $P(r_1, r_2)$  is the pair-correlation function. For a Slater determinant  $P(r_1, r_2)$  can be obtained by integrating over all coordinates other than  $r_1$  and  $r_2$ :

$$P(r_1, r_2) \propto \iint d^3r_3 \dots d^3r_n \Psi^*(r_1 \dots r_N) \Psi(r_1 \dots r_N). \quad [7]$$

The "hole" in the probability occupies a region around  $r_1 = r_2$ : since  $\Psi$  contains  $k$ 's up to  $k_f$ , the electron gas can't change over a distance shorter than approximately  $1/k_f$ , which is the smallest

wavelength among occupied plane waves, so  $1/k_f$  should be on order of the hole size. Fig. 1 shows an exact free-electron calculation in the Hartree-Fock approximation, where  $r_s$  is the radius of a sphere that would contain one electron (equation 1.2 in the text). Since  $k_f$  is very close to  $2/r_s$  (text eqn. 2.23), we see that indeed the approximation works reasonably well.

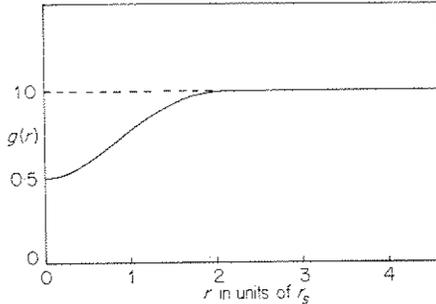


Fig. 1: Hartree-Fock exchange-correlation hole for free electrons. (Jones and March, *Theoretical Solid State Physics*)

**Correlations and interacting-electron effects:** The Hartree-Fock approximation works better for insulators or molecules than it does for metals; the reason is that a singularity appears in the Hartree-Fock solution at  $\varepsilon_F$  (equation 17.19 in the text), but the singularity is not so important for insulating systems with no states at  $\varepsilon_F$ . Also, Hartree-Fock theory works best at high-density; at low densities an electron gas can sacrifice kinetic energy to lessen its Coulomb interaction energy by becoming localized. For example, in the dilute limit the free-electron-gas ground state is a Wigner crystal, in which electrons localized to form a periodic electron crystal, as a means to avoid other electrons. The product wavefunctions from which the Slater determinant ([2]) is built are poor approximations to such localized states. This is an example of a *highly correlated* electron gas, with properties significantly different from the corresponding non-interacting gas. In very clean semiconductor systems, Wigner crystals have been observed (see for example *Physics Today*, Dec. 1990).

*Mott Insulators* are among the most recognized examples of highly correlated behavior. For example, CoO has odd valence, and would be a metal from conventional band theory. However, electron-electron interactions are strong, and the electrons instead localize, one per Co atom, resulting in an insulating antiferromagnet.  $\text{YBa}_2\text{Cu}_3\text{O}_7$  is also an insulating antiferromagnet, but a small change in the O concentration makes it a high- $T_c$  superconductor, one that cannot easily be treated from band theory. For another example see *Nature*, **415**, 39 (2002), for discussion of a Mott insulator in a Bose-Einstein condensate.

Thus, *correlation* is the term used to describe certain electron-interaction effects, especially those that go beyond the Hartree-Fock approximation, and observed in dilute or low-mass electron systems. A competing effect, *screening* is a concept referring to the tendency of electrons to screen out charge disturbances, including the interaction term in the Hamiltonian, and this helps to show why simple metals can behave so much like weakly-interacting electron systems.

**Density-Functional Theory (DFT):** Hohenberg and Kohn (1964) showed that the ground-state energy of an electron system can be obtained exactly by calculating the density,  $n = |\Psi|^2$ , not requiring the wavefunction itself. Since  $n$  is a function of  $r$ , the energy is a *functional* of  $n$ ,  $E[n(r)]$  (hence, a Density Functional). The density  $n(r)$  is a unique solution which minimizes the

energy. As a real function this is easier to handle than the complex wavefunction, and the density-functional theory has become the basis for practical computational methods for electronic structure, and also some important conceptual approaches. Note that to write the kinetic energy as a functional of  $n$  alone does not seem obvious, since the momentum is related to the phase change of the wavefunction. (For example, plane-wave states all have the same uniform density, even though their kinetic energy varies widely.) However recall that for instance for non-interacting free electrons the kinetic energy per electron is  $(3/5)\epsilon_F$ , proportional to  $n^{2/3}$ ; indeed depends only on the density.

A difficulty with density functional theory is that determining  $n(r)$  alone does not provide all the information one typically wants to know. For example just to understand whether the solid is a metal or insulator requires considerable further work. Much modern electronic theory is based on the further ansatz of Kohn and Sham (1965); starting with the density functional idea, they used a variational method to produce an effective one-electron equation. Much like the ordinary Schrödinger equation, the Kohn-Sham equation is the analog of [4], except that the non-local exchange term (the last line of [4]) has been replaced by an effective exchange-correlation potential ( $V^{XC}$ ). This is in principle exact, and the goal of realistic calculations is to write down the (possibly nonlocal) correct  $V^{XC}$  producing solutions which best approach reality. Note that  $V^{XC}$  is itself not an actual potential energy, it is an effective potential constructed to produce effective single particle wave-functions which can be assembled to produce the real  $n(r)$ . Consult a recent text for more detail on this theory, for instance Mahan has a brief description, and Marder provides a more detailed development of the theory.

Following this method, the general idea is that a wave-function must be found that solves the Kohn-Sham equation using the potential produced by its own density, in a self-consistent way. This is done iteratively, in a process such as the following:  $\psi_{eff} \rightarrow n(r) \rightarrow V^{XC} \rightarrow \psi_{eff}$ , which can be repeated until (hopefully) a stable self-consistent solution is found. In general this is called the Self-Consistent Field (SCF) method, a term which is also sometimes applied to solving the Hartree-Fock equations alone.

**Local-Density Approximation (LDA) and modern methods:** One of the simplest density-functional solutions is taken from eqn [6] above, by setting  $V^{XC}$  equal to  $E[n]$  from that equation. This is a completely local approximation to  $V^{XC}$ , an idea dating originally to Slater. This is an example of the Local Density Approximation, and this simple form for the potential alone yields surprisingly reasonable results in electronic structure calculations.

LDA calculations today use more complicated functionals than the  $n^{1/3}$  free-electron Hartree-Fock solution. Using quantum Monte-Carlo methods, exact solutions can be obtained computationally for cases such as the uniform electron gas; Ceperley and Alder (1980) used such calculations to yield accurate numerical results for  $E[n]$ , which were parameterized, originally by Perdew and Zunger (1981), yielding a numerical expression that provides a good approximation for  $V_{xc}$ , with considerable improvement in accuracy. Solving an LDA problem, one still needs to choose a basis set for the effective wavefunctions making up  $n(r)$ ; for example plane waves are often used for solids, and there are other popular choices such as localized Wannier orbits or muffin-tin-type orbitals. There are many standard computational packages which may be used

for this, including a number of popular free packages. If using one of these, the wavefunction choice depends on which package you chose.

What distinguishes LDA is the reliance on a potential calculated for a uniform  $n(r)$ . One can go beyond this by expanding in gradients of  $n$  (Gradient Corrections), for example the “GGA” or Generalized Gradient Approximations are widely used (see Kurth *et al.* (1999)). Another method of extending beyond LDA is the GW approximation; see Aryasetiawan and Gunnarsson, (1998). These and related methods are generally the basis for "ab initio" calculations reported today, used in condensed matter physics as well as in molecular physics and chemistry. The ab initio terminology refers to the reliance on nominally exact solutions solved based on the Schrödinger (or Dirac) equation for the uniform electron gas. However approximations must still be made, for example accounting for density gradients and the choice of basis set. Thus these models can do poorly if ill-chosen for a given system. Jones and Gunnarsson, (1989) and the books by Martin *et al.* (2004, 2016) and Singh & Nordstrom (2006) give good reviews of these methods, and extensions such as those that allow the electron spins to become imbalanced (LSDA and related methods).

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