DENSITY FUNCTIONAL THEORY

AN INTRODUCTION

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FOREWORD BY THE AUTHOR

These notes are designed to provide a basic introduction to the computational technique of Density Functional Theory (DFT) for the solution of complex many-body problems in condensed matter physics to complete neophytes in the field. The notes are designed to be self-contained and, apart from familiarity with elementary Quantum Mechanics and the Sommerfeld Free electron model for metals, no previous knowledge on methods for electronic structure calculations in solids is assumed. A brief introductory overview of the concepts of exchange and correlation effects between electrons, the Hartree-Fock Theory of solids and other theoretical background topics which tie quite naturally with the discussion on DFT, is offered in the first section of the document. As a word of caution, I cannot guarantee that the material presented in these notes is either complete or entirely accurate, and indeed it is not intended to be used as a substitute for consulting the relevant literature on the subject listed at the end of the document. If you have any suggestions for corrections and/or improvements, please e-mail me at: g.mogni1@physics.ox.ac.uk

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1. RECAPITULATION ON THE THEORY OF INDISTINGUISHEABLE PARTICLES AND EXCHANGE FORCES

It is a well known theorem in Quantum Mechanics that for an ensemble of N identical (indistinguisheable) particles, the N-particle Hamiltonian $\widehat{H_N}$ remains unvaried under the exchange of any two particle labels i and j, and can be therefore expressed as an ''eigenfunction'' of the particle-exchange operator $\widehat{P_{ij}}$ with eigenvalue +1:

$$\widehat{P_{ij}}\,\widehat{H_N}(i,j) = \widehat{H_N}(j,i) = +1\,\widehat{H_N}(i,j) \tag{1.1}$$

$\widehat{H_N}$ is said to be exchange-symmetric. Consequently, for identical particles, the operation of particle exchange cannot affect the overall particle probability density:

$$\left|\Psi_N(i,j)\right|^2 = \left|\Psi_N(j,i)\right|^2 \rightarrow \widehat{P_{ij}}\Psi_N(i,j) = \Psi_N(j,i) = \pm\ \Psi_N(i,j) \tag{1.2}$$

The N-particle wavefunction $\Psi_N(i,j)$ is therefore also required to have exchange-symmetry and be an eigenfunction of $\widehat{P_{ij}}$ with an eigenvalue of either +1 (in which case $\Psi_N(i,j)$ is said to be exchange-symmetric) or -1 (exchange-antisymmetric). This leads to the well-known separation of the physical properties of identical particles into the two categories of Bosons ($\Psi_N(i,j)$ exchange-symmetric, integer spin quantum numbers) and Fermions ($\Psi_N(i,j)$ exchange-antisymmetric, half-integer spin quantum numbers). Here we shall deal exclusively with identical spin-1/2 fermions and investigate the consequences of their indistiguisheability in the context of the electronic properties of metals.

The most general linear combination of the N occupied orthonormal single-particle wavefunctions $\psi_i(\vec{r_j},\sigma_j) = \phi_i(\vec{r_j})\chi_i(\sigma_j)$ (where $\phi_i(\vec{r_j})$ and $\chi_i(\sigma_j)$ denote respectively the spatial and spin parts of the ith eigenstate for particle j) for a system of N identical fermions which is antisymmetric under the exchange of any two particle labels is given by the determinant (known as the Slater determinant) of the following NxN square matrix:

$$\Psi_N = \frac{1}{\sqrt{N!}}\begin{pmatrix} \psi_1(\vec{r_1},\sigma_1) & \psi_1(\vec{r_2},\sigma_2) & \cdots & \psi_1(\vec{r_N},\sigma_N) \\ \psi_2(\vec{r_1},\sigma_1) & & \ddots & \vdots \\ \vdots & & & \\ \psi_N(\vec{r_1},\sigma_1) & & \cdots & \psi_N(\vec{r_N},\sigma_N) \end{pmatrix} \tag{1.3}$$

where the $1/\sqrt{N!}$ factor in front ensures that the wavefunction is correctly normalized to unity. The Slater determinant can also be written more compactly as:

$$\Psi_N = A\left\{\psi_1(\vec{r_1},\sigma_1),\psi_2(\vec{r_2},\sigma_2).....\psi_N(\vec{r_N},\sigma_N)\right\} \quad \text{where } A = \frac{1}{\sqrt{N!}}\sum_{i=1}^{N!}(-1)^{p_i}\,P_i \tag{1.4}$$

where in the expression for A (known as the antisymmetrization operator), Pi represents the ith permutation of the electronic coordinates (N! permutations in total) and $(-1)^{p_i}$ is +1 if the permutation is even and -1 if the permutation is odd)

The exchange-antisymmetry of Ψ_N follows from the general property of determinants that if any two columns (corresponding to two different particle labels in this case) are interchanged, then the determinant changes sign. Furthermore, the other general property that if any two rows of a determinant are equivalent then the determinant is automatically zero leads to the Pauli Exclusion Principle: for Ψ_N to be non-zero, no two identical fermions can lie in the same single-particle state and consequently have the same set of Quantum Numbers.

For N=2, it turns out that the spatial componenent $\Phi_2^{\pm}$ and spin component $X_2^{\pm}$ of the total wavefunction Ψ_2 can each be written in exchange-symmetric (+) and antisymmetric (-) forms:

$$\Phi_2^{\pm}(\vec{r}_1,\vec{r}_2)=\frac{\phi_a(\vec{r}_1)\phi_b(\vec{r}_2)\pm\phi_a(\vec{r}_2)\phi_b(\vec{r}_1)}{\sqrt{2}} \quad \text{if } a\neq b \tag{1.5}$$

$$\begin{aligned} &m_S=+1\rightarrow|\chi_\uparrow\rangle_1|\chi_\uparrow\rangle_2\\ X_2^{+}(S=1)\rightarrow\ &m_S=0\rightarrow 1/\sqrt{2}\left(|\chi_\uparrow\rangle_1|\chi_\downarrow\rangle_2+|\chi_\downarrow\rangle_1|\chi_\uparrow\rangle_2\right)\\ &m_S=-1\rightarrow|\chi_\downarrow\rangle_1|\chi_\downarrow\rangle_2 \end{aligned} \tag{1.6}$$

$$X_2^{-}(S=0,m_S=0)=1/\sqrt{2}\left(|\chi_\uparrow\rangle_1|\chi_\downarrow\rangle_2-|\chi_\downarrow\rangle_1|\chi_\uparrow\rangle_2\right) \tag{1.7}$$

where the three distinct symmetric eignstates (1.6) for the total spin quantum number S=1 are commonly referred to as ''spin-triplet'', whereas the antisymmetric one (1.7) for S=0 as ''spin-singlet''. The spatial and spin wavefunctions can be combined together following the requirement that Ψ_2 must be overall exchange-antisymmetric. Therefore one can have either $\Psi_2=\Phi_2^{-}X_2^{+}$ or $\Psi_2=\Phi_2^{+}X_2^{-}$.

The simulatenous probability of finding the two identical fermions at the same point in space $\vec{r}_1=\vec{r}_2=\vec{r}$ is given by:

$$P^{(2)}(\vec{r})=\left|\Phi_2(\vec{r},\vec{r})\right|^2 \tag{1.8}$$

Therefore, depending on whether $\Psi_2=\Phi_2^{-}X_2^{+}$ or $\Psi_2=\Phi_2^{+}X_2^{-}$, we have the following two possibilities:

- Case 1: $\Psi_2=\Phi_2^{+}X_2^{-}\rightarrow\left|\Phi_2^{+}(\vec{r},\vec{r})\right|^2=2\left|\phi_a(\vec{r})\right|^2\left|\phi_b(\vec{r})\right|^2$: the probability of finding the two fermions at the same point in space is enhanced by a factor of two with respect to the case of distinguisheable particles (for which there is no exchange-symmetry requirement on the many-body wavefunction, which can therefore be written as a simple product of the single particle wavefunctions). The antisymmetry requirement for Ψ_2 has therefore indirectly introduced a new attractive force between the two fermions, termed exchange-force (or exchange-interaction), which is never observed for distinguisheable particles.

- Case 2: $\Psi_2 = \Phi_2^- \mathrm{X}_2^+ \rightarrow \left|\Phi_2^-(\vec{r},\vec{r})\right|^2 = 0$: the probability of finding the two fermions at the same point in space is null, which means that in this case the two fermions experience a repulsive exchange force.

As a result of the presence of this exchange force, the motion of the two identical fermions is said to be correlated. In the case of distinguishebeable particles on the other hand, their individual motions are still Quantum Mechanical but remain uncorrelated and the particles behave independently.

This type of correlation is observed even in the absence of direct particle-particle interactions (e.g. Coulomb electrostatic forces). If the two identical particles do not mutually interact, the exchange force has no impact on the total energy of the system E_2 (which will then still given by the sum of the two single-particle energies ε_1 and ε_2). If on the other hand the s=1/2 fermions are taken to be electrons and the repulsive Coulomb interaction between them is suddenly switched on (without modifying the single-particle wavefunctions), the exchange force has the effect of splitting the total energy into two values, depending on whether the two-electron system is found to lie in a spin singlet or triplet state. For the spin singlet state, the attractive exchange force has in fact the effect of destabilizing the system and raising the overall Coulomb potential energy, and vice versa for the spin triplet state. As a result, all other things being equal, the exchange interaction produces an energetic preference for the Spin Triplet states. This change in energy attributable to the exchange forces is known as the exchange energy. The Coulomb force by itself is always repulsive, and therefore increases E_2 by a constant amount called Hartree (or direct) energy.

The Exchange and Hartree energies are easy to calculate analytically for the case of two interacting electrons. We start from the expression for the total Hamiltonian for the two-electron system:

$$\widehat{H}_2 = \underbrace{\sum_{i=1}^{2}\left(-\frac{\hbar^2}{2m_e}\nabla_i^{\,2}\right)}_{\sum_i \widehat{h}_i} + \frac{e^2}{4\pi\varepsilon_o\left|\vec{r_1}-\vec{r_2}\right|} \tag{1.9}$$

where the first term is the non-interacting part of the Hamiltonian (in this case just the sum of the kinetic energies of the two electrons-no external potential is assumed to be acting on the system), and the second term is the repulsive Coulomb potential energy. Since both the Hartree and exchange energies arise from the Coulomb term of the Hamiltonian, their values can be calculated by taking its expectation value for the two types of spatial wavefunctions $\Phi_2^{\pm}$:

$$\left\langle \Phi_2^{\pm} \middle| \frac{e^2}{4\pi\varepsilon_o\left|\vec{r_1}-\vec{r_2}\right|} \Phi_2^{\pm} \right\rangle \quad \text{where} \quad \Phi_2^{\pm}(\vec{r}_1,\vec{r_2}) = \frac{\phi_a(\vec{r_1})\phi_b(\vec{r_2}) \pm \phi_a(\vec{r_2})\phi_b(\vec{r_1})}{\sqrt{2}} \tag{1.10}$$

The Hartree energy arises from the terms in the inner product that do not depend on the sign of Φ_2 :

$$\begin{aligned}\frac{1}{2}\phi_a^*(\vec{r_1})\phi_b^*(\vec{r_2})\phi_a(\vec{r_1})\phi_b(\vec{r_2}) &= \frac{1}{2}\left|\phi_a(\vec{r_1})\right|^2\left|\phi_b(\vec{r_2})\right|^2 \\ \frac{1}{2}\phi_b^*(\vec{r_1})\phi_a^*(\vec{r_2})\phi_b(\vec{r_1})\phi_a(\vec{r_2}) &= \frac{1}{2}\left|\phi_b(\vec{r_1})\right|^2\left|\phi_a(\vec{r_2})\right|^2\end{aligned} \tag{1.11}$$

Since the particles are identical, the two terms above are equal:

$$E_{Hartree} = \int d^3\vec{r_1}d^3\vec{r_2}\left|\phi_a(\vec{r_1})\right|^2\frac{e^2}{4\pi\varepsilon_o\left|\vec{r_1}-\vec{r_2}\right|}\left|\phi_b(\vec{r_2})\right|^2 \tag{1.12}$$

The exchange energy on the other hand emerges from the sign-dependent cross terms:

$$\begin{aligned}&\pm\frac{1}{2}\phi_a^*(\vec{r_1})\phi_b^*(\vec{r_2})\phi_b(\vec{r_1})\phi_a(\vec{r_2}) \\ &\pm\frac{1}{2}\phi_b^*(\vec{r_1})\phi_a^*(\vec{r_2})\phi_a(\vec{r_1})\phi_b(\vec{r_2})\end{aligned} \tag{1.13}$$

For the same reason as above, the two terms above are equivalent, and so:

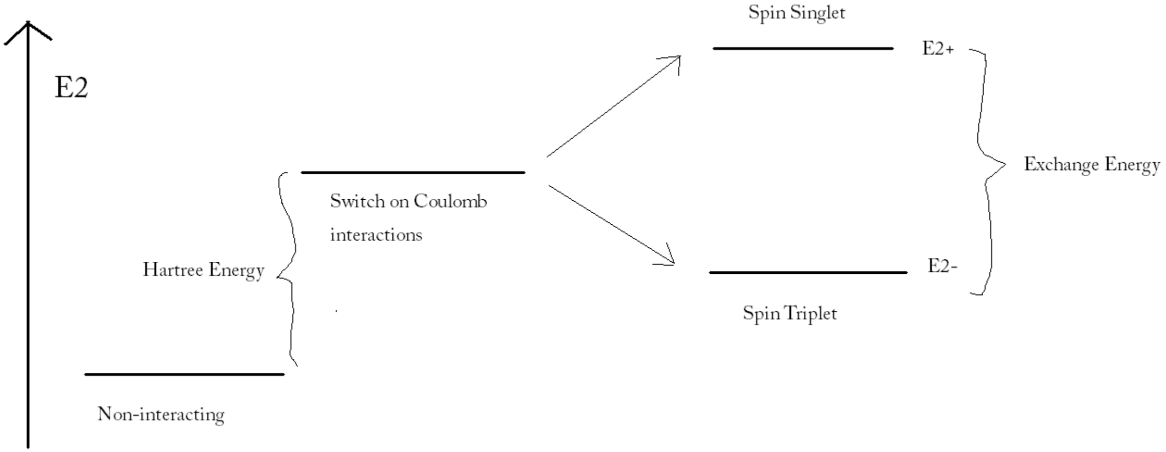
$$E_{Exchange} = \pm\int d^3\vec{r_1}d^3\vec{r_2}\phi_a^*(\vec{r_1})\phi_b^*(\vec{r_2})\frac{e^2}{4\pi\varepsilon_o\left|\vec{r_1}-\vec{r_2}\right|}\phi_b(\vec{r_1})\phi_a(\vec{r_2}) \tag{1.14}$$

Adding all the various contributions, we obtain the total energy E_2 :

$$E_2^{\pm} = \left\langle\Phi_2^{\pm}\middle|\widehat{H}_2\Phi_2^{\pm}\right\rangle = \sum_{i=1}^{2}\frac{p_i^{\,2}}{2m_e} + E_{Hartree} \pm E_{Exchange} \tag{1.15}$$

The exchange forces therefore introduce the spin-dependence on E_2 illustrated in the energy-level diagram of fig 1.1:

Fig 1.1: Energy level diagram showing the splitting of the total two-electron energy due to the exchange interaction



2. EXPANDING THE PROBLEM TO A REAL CRYSTALLINE SOLID

Our starting point is the hamiltonian for the system of N electrons and M positively-charged nuclei (or ions) in a crystalline solid, neglecting all relativistic and magnetic effects:

$$\widehat{H_N} = -\frac{\hbar^2}{2m_e}\sum_{i=1}^{N}\nabla_i^{\,2} - \sum_{i,I=1}^{N,M}\frac{Z_I e^2}{\left|\vec{r_i}-\vec{R_I}\right|} + \frac{1}{2}\sum_{i,j}^{i\neq j}\frac{e^2}{\left|\vec{r_i}-\vec{r_j}\right|} - \sum_{I=1}^{M}\frac{\hbar^2}{2M_I}\nabla_I^{\,2} + \frac{1}{2}\sum_{I,J}^{I\neq J}\frac{Z_I Z_J e^2}{\left|\vec{R_I}-\vec{R_J}\right|} \qquad (2.1)$$

where the electrons are denoted by lower case subscripts and the nuclei, with charge Z_I and mass M_I, are denoted by upper case subscripts. The terms of the Hamiltonian represent, from left to right, the kinetic energy of the electrons, the attractive potential acting on the electrons due to the nuclei, the repulsive electron-electron interaction, the kinetic energy of the nuclei and finally the repulsive internuclear electrostatic interaction (in this and the inter-electron interaction terms, the factor of ½ in front is introduced to avoid double-counting of particle pairs whereas the upper condition in the sums is to exclude unphysical self-interactions). This general form is still valid if the bare nuclear Coulomb interaction is replaced by a pseudopotential that takes into account effects of core electrons. From a fundamental point of view it is impossible to calculate the electronic properties of a metal analytically by such an elementary equation as (2.1) because of the enormously complicating effects of the interactions between electrons. The issue central to the theory of electronic structure is therefore the development of approximate methods using simplifying physical ideas to treat electronic interactions and correlations with sufficient accuracy that one can predict the diverse array of phenomena exhibited by matter, starting from (2.1).

There is only one type of term in the general hamiltonian that can be regarded as "small", the inverse mass of the nuclei $1/M_I$. If we first set the mass of the nuclei to infinity, then the kinetic energy of the nuclei can be ignored. This is the Bom-Oppenhcimer or adiabatic approximation, which is an excellent approximation for many purposes. The final term, the electrostatic nucleus-nucleus (or ion-ion) interaction, is essential in the total energy calculation, but is only a classical additive term if the nuclei are assumed fixed and can therefore be neglected. Thus we shall focus on the hamiltonian for the electron cloud of the crystal only, in which the positions of the nuclei are fixed at the points R of the underlying Bravais lattice of the crystal structure.

The fundamental N-electron Schroedinger equation for the theory of electronic structure in a metal can therefore be reduced to:

$$\left[\underbrace{\sum_{i=1}^{N}\left(-\frac{\hbar^2}{2m_e}\nabla_i^{\,2}+V_{ion}(r_i)\right)}_{\sum_i \hat{h}_i} + \frac{1}{2}\sum_{i,j}^{i\neq j}\frac{e^2}{\left|\vec{r_i}-\vec{r_j}\right|}\right]\Psi_N(\vec{r_1},\sigma_1;\vec{r_2},\sigma_2;\ldots\vec{r_N},\sigma_N) = E_N\Psi_N(\vec{r_1},\sigma_1;\vec{r_2},\sigma_2\ldots\vec{r_N},\sigma_N)$$

$$\text{where } V_{ion}(\vec{r_i}) = -\sum_{I=1}^{M}\frac{Z_I e^2}{\left|\vec{r_i}-\vec{R_I}\right|}$$

(2.2)

3. THE HARTREE EQUATIONS

The proper choice of the potential U(r) appearing in the Schroedinger equation for just one of the electrons considered above

$$-\frac{\hbar^2}{2m_e}\nabla^2\psi(\vec{r})+U(\vec{r})\psi(\vec{r})=\varepsilon\psi(\vec{r}) \tag{3.1}$$

is a subtle problem. Underlying this problem is the question of how best to represent the effects of electron-electron interactions. One simplifying idea is suggested by asking what choice of U(r) would make equation (3.1) least unreasonable. Evidently U(r) should include the potentials of the ions:

$$U_{ion}(\vec{r})=-Ze^2\sum_{I=1}^{M}\frac{1}{\left|\vec{r}-\vec{R}_I\right|} \tag{3.2}$$

The inter-electron interactions can of course be ignored altogether under the so-called ''independent electron approximation'', which leads to the well established Sommerfeld Free electron model[1]. It is most productive however to incorporate (at least approximately) the fact that the electron feels the electric fields of all the other electrons when seeking an expression for U(r). If we treated the remaining electrons as a smooth distribution of negative charge with charge density ρ, the potential energy of the given electron in their field would be:

$$U_{el}(\vec{r})=-e\int d\vec{r}\,'\rho(\vec{r}\,')\frac{1}{\left|\vec{r}-\vec{r}\,'\right|} \tag{3.3}$$

The contribution of an electron in the level ψ_i (we let i stand for both the spin and orbital quantum numbers of the one-electron level) to the charge density would be:

$$\rho_i(\vec{r})=-e\left|\psi_i(\vec{r})\right|^2 \tag{3.4}$$

The total electronic charge density would then be:

$$\rho(\vec{r})=-e\sum_i\left|\psi_i(\vec{r})\right|^2 \tag{3.5}$$

where the sum extends over all occupied one-electron states in the metal

Placing (3.5) in (3.3) and letting $U(\vec{r})=U_{el}(\vec{r})+U_{ion}(\vec{r})$ we arrive at the following one-electron Schroedinger equation:

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[1] The reader unfamiliar with the independent-electron approximation and the free electron gas model of metals should refer to chapters 2 and 3 of Ref. 1

$$-\frac{\hbar^2}{2m_e}\nabla^2\psi_i(\vec{r})+U_{ion}(\vec{r})\psi_i(\vec{r})+\left[e^2\sum_j\int d\vec{r}\,'\left|\psi_j(\vec{r}\,')\right|^2\frac{1}{\left|\vec{r}-\vec{r}\,'\right|}\right]\psi_i(\vec{r})=\varepsilon_i\psi_i(\vec{r}) \qquad (3.6)$$

The set of equations (3.6) (there is one for each occupied one-electron level $\psi_i(\vec{r})$) is known as the Hartree equations. These nonlinear equations for the one-electron wave functions and energies are solved, in practice, by iteration: a form is guessed for $U_{el}(\vec{r})$ (the term in brackets in (3.6)) on the basis of which the equations are solved. A new $U_{el}(\vec{r})$ is then computed from the resulting wave functions, $\psi_i(\vec{r})$, and the new Schroedinger equation is solved once again. Ideally, the procedure is continued until further iterations do not materially alter the potential (for this reason the Hartree approximation is also known as the "self-consistent field approximation").

The Hartree approximation fails to represent the way in which the particular (as opposed to the average) configuration of the other N - 1 electrons affects the electron under consideration, for Eq. (3.6) describes the electron as interacting only with the field obtained by averaging over the positions of the remaining electrons (with a weight determined by their wave functions). As crude an approximation as this is to the full Schroedinger equation (2.2), it still leads to a mathematical task of considerable numerical complexity.

The most significant shortcoming of the Hartree approximation however is of physical rather than computational nature. The inadequacy emerges if we return to the exact N-electron Schrodinger equation, eq. (2.2), and cast it into the equivalent variational form, which asserts that a solution to (2.2) is given by any state Ψ_N that makes stationary the quantity:

$$\left\langle \widehat{H_N} \right\rangle = E_N = \frac{\left\langle \Psi_N \middle| H_N \Psi_N \right\rangle}{\left\langle \Psi_N \middle| \Psi_N \right\rangle} \qquad (3.7)$$

where the denominator ensures that the wavefunctions have been properly normalized. In particular, the ground-state wave function is that Ψ_N that minimizes (3.7). It can be shown that the Hartree equations (3.6) follow from minimizing (3.7) over a Ψ_N of the form:

$$\Psi_N(\vec{r_1},\sigma_1;\vec{r_2},\sigma_2;.....;\vec{r_N},\sigma_N)=\psi_1(\vec{r_1},\sigma_1)\psi_2(\vec{r_1},\sigma_1)....\psi_N(\vec{r_N},\sigma_N) \qquad (3.8)$$

where the $\psi_i(\vec{r_i},\sigma_i)$ are a set of N orthonormal one-electron wave functions. Thus the Hartree equations give the best approximation to the full N-electron wave function that can be represented as a simple product of one-electron levels.

The wave function (3.8), however, is incompatible with the requirement of exchange-antisymmetry for the Ψ_N of an ensemble of identical fermions such as the sea of electrons in a crystal:

$$\Psi_N(\vec{r_1},\sigma_1;.....\vec{r_i},\sigma_i;....;\vec{r_s},\sigma_s;....;\vec{r_N},\sigma_N)=-\Psi_N(\vec{r_1},\sigma_1;.....\vec{r_s},\sigma_s;....;\vec{r_i},\sigma_i;....;\vec{r_N},\sigma_N)$$

(3.9)

4. THE HARTREE-FOCK APPROXIMATION

The simplest generalization of the Hartree approximation that incorporates the exchange-antisymmetry requirement (3.9) is to replace the trial wave function (3.8) by a Slater determinant (see Eq. (1.3)) of N orthonormal one-electron wave functions to be determined. This is the starting point for a new attempt at estimating the ground state energy of a N-electron system commonly referred to as thee Hartree-Fock (HF) approximation. The lowest energy N-particle state which can be written as a Slater determinant is therefore called the HF ground state wavefunction Ψ_N^{HF}. Like the simple Hartree theory, the HF method is only approximative as the true (exact) ground-state wavefunction for the system of electrons in a real crystal generally assumes forms much more complicated than a simple Slater Determinant. To determine the unknown single particle wavefunctions and consequently Ψ_N^{HF}, we first need to evaluate the total energy E_N via (3.7), which we will then later minimize to obtain the HF ground state energy E_N^{HF}. In essence, the derivation of the HF equations that follows can be viewed as a generalization of the computation of the exchange energy for 2 electrons given at the end of section 1 to the case of N electrons. From now on, we shall assume that all N electrons in the crystal have parallel spin, since as explained in section 1, this is the spin configuration that minimizes the total energy of the system in the presence of inter-electron Coulomb interactions.

The first step consists in evaluating the part of the inner product in the numerator of (3.7) involving the non-interacting part of the Hamiltonian of the N-electron system (2.2), which can be written simply as a sum of one-electron hamiltonians:

$$\sum_{i=1}^{N}\left\langle \Psi_N \middle| \hat{h}(\vec{r}_i)\Psi_N \right\rangle = \sum_{i=1}^{N}\left\langle A\left\{\psi_1(\vec{r}_1,\sigma_1),\psi_2(\vec{r}_2,\sigma_2)....\psi_N(\vec{r}_N,\sigma_N)\right\} \middle| \hat{h}(\vec{r}_i)A\left\{\psi_1(\vec{r}_1,\sigma_1),\psi_2(\vec{r}_2,\sigma_2)....\psi_N(\vec{r}_N,\sigma_N)\right\}\right\rangle$$

$$\text{where } \sum_{i=1}^{N}\hat{h}(\vec{r}_i) = \sum_{i=1}^{N}\left(-\frac{\hbar^2}{2m_e}\nabla_i^2 + V_{ion}(r_i)\right)$$

(4.1)

where the compact notation for the Slater determinant (Eq. (1.4)) has been used. It turns out that the N! terms in the determinant on the LHS all make the same contribution to the sum. This can be seen by considering for example the second term in the determinant on the LHS, which involves an odd permutation of electron coordinates 1 and 2 and is therefore preceded by a minus sign:

$$\sum_{i=1}^{N}\left\langle -\psi_1(\vec{r}_2,\sigma_2),\psi_2(\vec{r}_1,\sigma_1)....\psi_N(\vec{r}_N,\sigma_N) \middle| \hat{h}(\vec{r}_i)A\left\{\psi_1(\vec{r}_1,\sigma_1),\psi_2(\vec{r}_2,\sigma_2)....\psi_N(\vec{r}_N,\sigma_N)\right\}\right\rangle$$

$$= \left\langle -\psi_1(\vec{r}_2,\sigma_2),\psi_2(\vec{r}_1,\sigma_1)....\psi_N(\vec{r}_N,\sigma_N) \middle| \left(\hat{h}(\vec{r}_1)+\hat{h}(\vec{r}_2)+......\right)\frac{1}{\sqrt{N!}}\left(\psi_1(\vec{r}_1,\sigma_1),\psi_2(\vec{r}_2,\sigma_2)....\psi_N(\vec{r}_N,\sigma_N)-\psi_1(\vec{r}_2,\sigma_2),\psi_2(\vec{r}_1,\sigma_1)....\psi_N(\vec{r}_N,\sigma_N)+.....\right)\right\rangle$$

(4.2)

Now we perform a simple substitution / renaming of integration variables r1, σ1 → r2, σ2:

$$=\left\langle -\psi_1(\vec{r}_1,\sigma_1),\psi_2(\vec{r}_2,\sigma_2)....\psi_N(\vec{r}_N,\sigma_N)\middle|\left(\hat{h}(\vec{r}_2)+\hat{h}(\vec{r}_1)+......\right)\frac{1}{\sqrt{N!}}\left(\psi_1(\vec{r}_2,\sigma_2),\psi_2(\vec{r}_1,\sigma_1)....\psi_N(\vec{r}_N,\sigma_N)-\psi_1(\vec{r}_1,\sigma_1),\psi_2(\vec{r}_2,\sigma_2)....\psi_N(\vec{r}_N,\sigma_N)+.....\right)\right\rangle \quad (4.3)$$

Moving the minus sign across from the left to the right, we recover the first term in the determinant on the LHS:

$$\sum_{i=1}^{N}\left\langle \psi_1(\vec{r}_1,\sigma_1),\psi_2(\vec{r}_2,\sigma_2)....\psi_N(\vec{r}_N,\sigma_N)\middle|\hat{h}(\vec{r}_i)A\left\{\psi_1(\vec{r}_1,\sigma_1),\psi_2(\vec{r}_2,\sigma_2)....\psi_N(\vec{r}_N,\sigma_N)\right\}\right\rangle \quad (4.4)$$

We therefore conclude that the first and second terms make the same contribution to the sum in the determinant on the LHS. Hence we can replace the LHS determinant with the first term multiplied by N!:

$$\sum_{i=1}^{N}\left\langle \Psi_N\middle|\hat{h}(\vec{r}_i)\Psi_N\right\rangle=\underbrace{\frac{N!}{\sqrt{N!}}}_{\sqrt{N!}}\sum_{i=1}^{N}\left\langle \psi_1(\vec{r}_1,\sigma_1),\psi_2(\vec{r}_2,\sigma_2)....\psi_N(\vec{r}_N,\sigma_N)\middle|\hat{h}(\vec{r}_i)A\left\{\psi_1(\vec{r}_1,\sigma_1),\psi_2(\vec{r}_2,\sigma_2)....\psi_N(\vec{r}_N,\sigma_N)\right\}\right\rangle \quad (4.5)$$

The single-particle wavefunctions are orthonormal, and this means that only the identical permutation from the sum implied by the determinant on the RHS makes a non-zero contribution to the overall integral:

$$\begin{aligned}\sum_{i=1}^{N}\left\langle \Psi_N\middle|\hat{h}(\vec{r}_i)\Psi_N\right\rangle&=\sum_{i=1}^{N}\left\langle\left(\psi_1(\vec{r}_1,\sigma_1),\psi_2(\vec{r}_2,\sigma_2)....\psi_N(\vec{r}_N,\sigma_N)\right)\middle|\hat{h}(\vec{r}_i)\left(\psi_1(\vec{r}_1,\sigma_1),\psi_2(\vec{r}_2,\sigma_2)....\psi_N(\vec{r}_N,\sigma_N)\right)\right\rangle\\&=\sum_{i=1}^{N}\left\langle\psi_i(\vec{r}_i,\sigma_i)\middle|\hat{h}(\vec{r}_i)\psi_i(\vec{r}_i,\sigma_i)\right\rangle\end{aligned} \quad (4.6)$$

As far as the non-interacting part of the Hamiltonian is concerned, it does not therefore matter whether we use a fully antisymmetrized wavefunction Ψ_N or a simple product of the single-particle wavefunctions.

Now we evaluate the inner product involving the electron-electron interaction part of the Hamiltonian (2.2), that is the two-electron operator that takes into account the Coulomb energy between electrons:

$$\frac{1}{2}\sum_{i,j}^{i\neq j}\langle \Psi_N | \frac{e^2}{4\pi\varepsilon_0|\underline{r}_i-\underline{r}_j|} | \Psi_N\rangle =$$

$$\frac{1}{2}\sum_{i,j}^{i\neq j}\langle A\{\psi_1(\underline{r}_1,\sigma_1)\psi_2(\underline{r}_2,\sigma_2)\dots\psi_N(\underline{r}_N,\sigma_N)\} | \frac{e^2}{4\pi\varepsilon_0|\underline{r}_i-\underline{r}_j|} |$$

$$A\{\psi_1(\underline{r}_1,\sigma_1)\psi_2(\underline{r}_2,\sigma_2)\dots\psi_N(\underline{r}_N,\sigma_N)\}\rangle$$

$$=\frac{1}{2}\sqrt{N!}\sum_{i,j}^{i\neq j}\langle \psi_1(\underline{r}_1,\sigma_1)\psi_2(\underline{r}_2,\sigma_2)\dots\psi_N(\underline{r}_N,\sigma_N) | \frac{e^2}{4\pi\varepsilon_0|\underline{r}_i-\underline{r}_j|} |$$

$$A\{\psi_1(\underline{r}_1,\sigma_1)\psi_2(\underline{r}_2,\sigma_2)\dots\psi_N(\underline{r}_N,\sigma_N)\}\rangle$$

(4.7)

For given i,j, all terms which involve permutations of electrons other than the ith and jth electrons are zero, since the single-particle wavefunctions are orthonormal:

$$=\frac{1}{2}\sum_{i,j}^{i\neq j}\Big(\langle \psi_i(\underline{r}_i,\sigma_i)\psi_j(\underline{r}_j,\sigma_j) | \frac{e^2}{4\pi\varepsilon_0|\underline{r}_i-\underline{r}_j|} | \psi_i(\underline{r}_i,\sigma_i)\psi_j(\underline{r}_j,\sigma_j)\rangle$$

$$-\langle \psi_i(\underline{r}_i,\sigma_i)\psi_j(\underline{r}_j,\sigma_j) | \frac{e^2}{4\pi\varepsilon_0|\underline{r}_i-\underline{r}_j|} | \psi_j(\underline{r}_i,\sigma_i)\psi_i(\underline{r}_j,\sigma_j)\rangle\Big)$$

(4.8)

Putting together the two parts of the integral, Eqs (4.6) and (4.8):

$$E_N=\frac{\left\langle \Psi_N \middle| \widehat{H_N}\Psi_N\right\rangle}{\left\langle \Psi_N \middle| \Psi_N\right\rangle}=\sum_{i=1}^{N}\left\langle \psi_i \middle| \hat{h}(\vec{r_i})\psi_i\right\rangle+\frac{1}{2}\sum_{i,j}^{i\neq j}\left(\left\langle \psi_i\psi_j \middle| \frac{e^2}{4\pi\varepsilon_o r_{ij}}\psi_i\psi_j\right\rangle-\left\langle \psi_i\psi_j \middle| \frac{e^2}{4\pi\varepsilon_o r_{ij}}\psi_j\psi_i\right\rangle\right)$$

(4.9)

where:

HARTREE/COULOMB INTEGRAL

$$\left\langle \psi_i\psi_j \middle| \frac{e^2}{4\pi\varepsilon_o r_{ij}}\psi_i\psi_j\right\rangle=\oiint d^3(\vec{r},\sigma)d^3(\vec{r}\,',\sigma')\left|\psi_i(\vec{r},\sigma)\right|^2\left|\psi_j(\vec{r}\,',\sigma')\right|^2\frac{e^2}{4\pi\varepsilon_o\left|\vec{r}-\vec{r}\,'\right|} \qquad (4.10)$$

EXCHANGE INTEGRAL

$$\left\langle \psi_i \psi_j \left| \frac{e^2}{4\pi\varepsilon_o r_{ij}} \psi_j \psi_i \right. \right\rangle = \oiint d^3(\vec{r},\sigma) d^3(\vec{r}\,',\sigma') \psi_i^*(\vec{r},\sigma) \psi_j^*(\vec{r}\,',\sigma') \frac{e^2}{4\pi\varepsilon_o \left|\vec{r}-\vec{r}\,'\right|} \psi_j(\vec{r},\sigma) \psi_i(\vec{r}\,',\sigma') \delta_{\sigma_i,\sigma_j}$$

(4.11)

These two integral equations can be compared with (1.12) and (1.14) for the two-electron case. Note that we have followed the usual convention of excluding the unphysical self-interaction terms (i=j) from the sums in (4.9), but even including them would have not affected the final result since the two terms in the Hartree and Exchange integrals would have then cancelled each other. The delta Kronecker term $\delta_{\sigma_i,\sigma_j}$ at the end of the exchange integral serves as a reminder that HF theory makes provision only for exchange interactions between parallel-spin electrons, and that if the electron spins are antiparallel (σ ≠ σ′) the exchange integral vanishes altogether. Furthermore, it can be shown formally, by expressing the Coulomb potential in terms of its inverse FT, that the integrand of Eq. (4.11) is always positive for the case σ = σ′. The proof is given below:

$$\left\langle \psi_i \psi_j \left| \frac{e^2}{4\pi\varepsilon_0 r_{ij}} \right| \psi_j \psi_i \right\rangle =$$

$$\oiint d^3r\, d^3r'\, \psi_i^*(\underline{r})\, \psi_j^*(\underline{r}')\, \frac{e^2}{4\pi\varepsilon_0 |\underline{r}-\underline{r}'|}\, \psi_j(\underline{r})\, \psi_i(\underline{r}')$$

$$= \frac{e^2}{\varepsilon_0 (2\pi)^3} \int d^3K \frac{1}{K^2} \oiint d^3r\, d^3r'\, \psi_i^*(\underline{r})\, \psi_j^*(\underline{r}')\, e^{i\underline{K}\cdot(\underline{r}-\underline{r}')}\, \psi_j(\underline{r}) \psi_i(\underline{r}')$$

$$= \frac{e^2}{\varepsilon_0 (2\pi)^3} \int d^3K \frac{1}{K^2} \int d^3r\, \psi_i^*(\underline{r}) \psi_j(\underline{r}) e^{i\underline{K}\cdot\underline{r}} \int d^3r'\, \psi_j^*(\underline{r}') \psi_i(\underline{r}') e^{-i\underline{K}\cdot\underline{r}'}$$

$$= \frac{e^2}{\varepsilon_0 (2\pi)^3} \int d^3K \frac{1}{K^2} \left| \int d^3r\, \psi_i^*(\underline{r})\, \psi_j(\underline{r}) e^{i\underline{K}\cdot\underline{r}} \right|^2 > 0$$

QED

This allows us to confirm the result deduced qualitatively in section 1 that exchange interaction always introduces a spin dependence on the system (even though our starting point, the N-electron Hamiltonian, was itself spin-independent), and in particular that the repulsive exchange force between parallel spin electrons always leads to a net lowering of the total system energy E_N . The spin dependence of the total energy and the fact that, for electrons, ferromagnetic alignment is the most energetically favourable configuration (Hund's rule) represent the origins of magnetism in solids.

The next step in the derivation of the HF Ground state wavefunction Ψ_N^{HF} and ground state energy E_N^{HF} is to minimize (4.9) with respect to the set of single-particle wavefunctions {ψ$_i$}. This can be done by following the theory of constrained minimization and introducing a set of Lagrange parameters ε_i to satisfy the ortonormality constraint $<\psi_i|\psi_j>=\delta_{ij}$. The functional $G(\{\psi_i\})$ to be minimized with respect to $\{\psi_i\}$ can therefore be written as:

$$G\left(\{\psi_i\}\right)=\sum_{i=1}^{N}\left\langle\psi_i\left|\widehat{h}_i\psi_i\right.\right\rangle+\frac{1}{2}\sum_{i,j}^{i\neq j}\left(\left\langle\psi_i\psi_j\left|\frac{e^2}{4\pi\varepsilon_o r_{ij}}\psi_i\psi_j\right.\right\rangle-\left\langle\psi_i\psi_j\left|\frac{e^2}{4\pi\varepsilon_o r_{ij}}\psi_j\psi_i\right.\right\rangle\right)-\sum_{i=1}^{N}\varepsilon_i\left\langle\psi_i\left|\psi_i\right.\right\rangle \tag{4.12}$$

Now we calculate the variation δG upon varying the spatial part of the orbital from ψ_i to $\psi_i+\delta\psi_i$:

$$\begin{aligned}\delta G\left(\{\psi_i\}\right)=&\sum_{i=1}^{N}\left(\left\langle\delta\psi_i\left|\widehat{h}_i\psi_i\right.\right\rangle+\left\langle\psi_i\left|\widehat{h}_i\left(\delta\psi_i\right)\right.\right\rangle\right)\\&+\frac{1}{2}\sum_{i,j}^{i\neq j}\left(\left\langle\delta\psi_i\psi_j\left|\frac{e^2}{4\pi\varepsilon_o r_{ij}}\psi_i\psi_j\right.\right\rangle-\left\langle\delta\psi_i\psi_j\left|\frac{e^2}{4\pi\varepsilon_o r_{ij}}\psi_j\psi_i\right.\right\rangle\right)\\&+\frac{1}{2}\sum_{i,j}^{i\neq j}\left(\left\langle\psi_i\psi_j\left|\frac{e^2}{4\pi\varepsilon_o r_{ij}}\delta\psi_i\psi_j\right.\right\rangle-\left\langle\psi_i\psi_j\left|\frac{e^2}{4\pi\varepsilon_o r_{ij}}\psi_j\delta\psi_i\right.\right\rangle\right)\\&-\sum_{i=1}^{N}\left(\varepsilon_i\left\langle\delta\psi_i\left|\psi_i\right.\right\rangle+\varepsilon_i\left\langle\psi_i\left|\delta\psi_i\right.\right\rangle\right)\end{aligned} \tag{4.13}$$

This expression contains two sets of terms, one containing $\delta\psi_i^*$, the other containing $\delta\psi_i$. In the following we will postulate that, in order to minimize the energy δG=0 for arbitrary variations $\delta\psi_i$, the terms containing $\delta\psi_i^*$ and those containing $\delta\psi_i$ must both independently be zero. Considering terms containing $\delta\psi_i^*$ first:

$$\delta G\left(\{\psi_i\}\right)=\sum_{i=1}^{N}\left(\left\langle\delta\psi_i\left|\widehat{h}_i\psi_i\right.\right\rangle\right)+\frac{1}{2}\sum_{i,j}^{i\neq j}\left(\left\langle\delta\psi_i\psi_j\left|\frac{e^2}{4\pi\varepsilon_o r_{ij}}\psi_i\psi_j\right.\right\rangle-\left\langle\delta\psi_i\psi_j\left|\frac{e^2}{4\pi\varepsilon_o r_{ij}}\psi_j\psi_i\right.\right\rangle\right)-\sum_{i=1}^{N}\left(\varepsilon_i\left\langle\delta\psi_i\left|\psi_i\right.\right\rangle\right)=0 \tag{4.14}$$

Since the variations are arbitrary we must have that the term multiplying any chosen $\delta\psi_i^*$ must be zero:

$$\begin{aligned}
&\widehat{h}_i \left|\psi_i\right\rangle + \sum_j \left(\left\langle \psi_j \left| \frac{e^2}{4\pi\varepsilon_o r_{ij}} \psi_i \psi_j \right.\right\rangle - \left\langle \psi_j \left| \frac{e^2}{4\pi\varepsilon_o r_{ij}} \psi_j \psi_i \right.\right\rangle \right) - \varepsilon_i \left|\psi_i\right\rangle = 0 \rightarrow \\
&\left(-\frac{\hbar^2}{2m_e} \nabla^2 + V_{ion}(\vec{r}) \right) \psi_i(\vec{r}) + \\
&\underbrace{\sum_{j \neq i} \oint d^3 r' \left|\psi_j(\vec{r}')\right|^2 \frac{e^2}{4\pi\varepsilon_o \left|\vec{r} - \vec{r}'\right|} \psi_i(\vec{r})}_{\text{COULOMB POTENTIAL}} - \qquad (4.15) \\
&\underbrace{\sum_{j \neq i} \oint d^3 r' \psi_j^*(\vec{r}') \psi_i(\vec{r}') \frac{e^2}{4\pi\varepsilon_o \left|\vec{r} - \vec{r}'\right|} \psi_j(\vec{r}) \delta_{\sigma_j, \sigma_i}}_{\text{EXCHANGE POTENTIAL}} = \varepsilon_i \psi_i(\vec{r})
\end{aligned}$$

Eq (4.15) represents a generalization of the Hartree Equations known as the Hartree-Fock equations, which determine the set of orthonormal $\{\psi_i\}$ that minimize the energy functional, thus reducing the N-electron problem formally to a one-electron problem. The HF equations may at first appearance look like a set of Schroedinger equations for each single-particle wavefunction ψ_i, but one needs not forget that the ε term on their RHS represents the Lagrange multiplier and it is not possible to interpret it as the corresponding single-electron energy.

To determine the HF ground state we therefore need to find self-consistently N solutions $\{\psi_i\}$ to the HF equations, one for each electron, with lowest ε_i (i=1-N). Higher lying, unoccupied orbitals do not enter the HF equations. Once all the HF single-electron wavefunctions have been found, the HF ground state Ψ_N^{HF} can be found by building the corresponding Slater determinant. The HF estimate for the ground-state energy E_N^{HF} is then given by:

$$E_N^{HF} = \left\langle \Psi_N^{HF} \left| \widehat{H_N} \Psi_N^{HF} \right.\right\rangle \neq \sum_i \varepsilon_i > E_N^{TRUE} \qquad (4.16)$$

where E_N^{TRUE} represents the true ground state energy of the N-electron system. The HF estimate E_N^{HF} obtained through the simplifying assumption that Ψ_N^{HF} has the shape of a Slater determinant therefore always provides an upper bound to the true ground state energy. The difference between HF and true ground state energies is called the correlation energy. Note that the correlation energy is not a quantity with physical significance; it merely represents the error incurred in making a fairly crude first-order approximation and therefore refers to the part of the electron correlations which are not being captured by the HF approximation.

The physical meaning of the Lagrange eigenvalue ε_i on the RHS of (4.15) is provided by Koopman's theorem: The eigenvalue of a filled (empty) orbital ψ_i is equal to the change in the total energy if an electron is subtracted from (added to) the system, i.e. decreasing (increasing) the size of the determinant by omitting (adding) a row and column involving a particular orbital ψ_i keeping all the other orbitals the same. If the ith electron is taken out of the N-electron system we can therefore write the subtracted energy as:

$$\Delta E_N = \left\langle \Psi_N^{HF} \,|\, H_N \,|\, \Psi_N^{HF} \right\rangle - \left\langle \Psi_{N-1}^{HF} \,|\, H_N \,|\, \Psi_{N-1}^{HF} \right\rangle = \varepsilon_i \tag{4.17}$$

The HF equations differ from the Hartree equations (3.6) by the additional exchange term on the left side. The complexity introduced by the exchange term is considerable, as it is non-local, non-linear and spin dependent. As a result, the HF equations are in general quite intractable, and can be solved only in special cases such as the homogeneous electron gas described in the next section.

5. THE HARTREE-FOCK THEORY OF THE HOMOGENEOUS ELECTRON GAS

The simplest model system representing condensed matter is the homogeneous electron gas, in which the nuclei are replaced by a uniform positively charged background. Since all independent-particle terms can be calculated analytically, this is an ideal model system for understanding the effects of correlation. A homogeneous system is completely specified by its electron density, $n = N_e / V$ (where N_e is the total number of electrons and V is the volume of the system). The density can in turn be characterized by the parameter r_s, defined as the radius of a sphere containing one electron on average:

$$\frac{4\pi}{3} r_s^3 = V/N_e = \frac{1}{n} \rightarrow r_s = \left(\frac{3}{4\pi n} \right)^{1/3} \tag{5.1}$$

Thus r_s is a measure of the average distance between electrons in the gas.

The hamiltonian for the homogeneous system is derived by replacing the nuclei in (2.2) with a uniform positively charged background, which leads to:

$$\widehat{H_N} = -\frac{\hbar^2}{2m_e} \sum_i \nabla_i^2 + \frac{1}{2} \frac{4\pi}{\varepsilon_o} \left[\underbrace{\sum_{i,j}^{i \neq j} \frac{e^2}{\left| \vec{r_i} - \vec{r_j} \right|}}_{V_{el}} - \underbrace{\int d^3\vec{r} d^3\vec{r}\,' \frac{(ne)^2}{\left| \vec{r} - \vec{r}\,' \right|}}_{V_{ion}} \right] \tag{5.2}$$

The last term V_{ion} is the average potential energy due to the positive background.

The solution of the Hartree-Fock equations for this case can be found analytically. It turns out that the single-electron eigenstates which solve the HF equations are plane waves of the form:

$$\psi_i(\vec{r}) = \left(\frac{e^{i\vec{k_i} \cdot \vec{r}}}{\sqrt{V}} \right) \times (\sigma = \uparrow \text{ or } \sigma = \downarrow) \tag{5.3}$$

just as for non-interacting electrons (Sommerfeld free electron model). If plane waves are indeed solutions, then the electronic charge density that determines V_{el} will be uniform. However, in the homogeneous electron gas the ions are represented by a uniform distribution of positive charge with the same density as the electronic charge. Hence the potential of the ions is precisely canceled by the Hartree energy term: $V_{ion} + V_{el} = 0$. Only the exchange term survives, which is easily evaluated by writing the electron-electron Coulomb interaction in terms of its (inverse) Fourier transform:

$$\frac{e^2}{\left|\vec{r}-\vec{r}\,'\right|} = 4\pi e^2 \frac{1}{V}\sum_{\vec{k}} \frac{1}{k^2} e^{i\vec{k}\cdot(\vec{r}-\vec{r}\,')} \rightarrow 4\pi e^2 \int \frac{d\vec{k}}{(2\pi)^3} \frac{1}{k^2} e^{i\vec{k}\cdot(\vec{r}-\vec{r}\,')} \tag{5.4}$$

If (5.4) is substituted into the exchange term of the HF equations (4.15)) and the ψ_i are all taken to be plane waves of the form (5.3), then the exchange term in the HF equations becomes:

$$\begin{aligned} V_{exch}(\vec{r})\psi_i(\vec{r}) &= -\sum_{k'<k_F} \frac{1}{\sqrt[3]{V}} e^{i\vec{k}'\cdot\vec{r}} \oint d^3\vec{r}\,' e^{i\vec{k}\cdot\vec{r}\,'} e^{-i\vec{k}'\cdot\vec{r}\,'} \frac{e^2}{4\pi\varepsilon_o \left|\vec{r}-\vec{r}\,'\right|} \\ &= -\frac{e^{i\vec{k}\cdot\vec{r}}}{\sqrt[3]{V}} \sum_{k'<k_F} \oint d^3\vec{r}\,' e^{-i(\vec{k}-\vec{k}')\cdot(\vec{r}-\vec{r}\,')} \frac{e^2}{4\pi\varepsilon_o \left|\vec{r}-\vec{r}\,'\right|} \\ &= -\frac{e^{i\vec{k}\cdot\vec{r}}}{\varepsilon_o \sqrt[3]{V}} \sum_{k'<k_F} \frac{e^2}{\left|\vec{k}-\vec{k}'\right|^2} \end{aligned} \tag{5.5}$$

where the sum occurs over all wavevectors inside the Fermi Sphere of radius k_F (the Fermi wavevector) and a factor of 2 was included to account for spin degenceracy. The sum at then end of (5.5) can be calculated explicitly as follows:

$$S(k) = \frac{1}{V}\sum_{k'<k_F} \frac{1}{\left|\vec{k}-\vec{k}'\right|^2} = \frac{1}{(2\pi)^3} \int_{k'<k_F} d^3\vec{k}\,' \frac{1}{\left|\vec{k}-\vec{k}'\right|^2} \tag{5.6}$$

Take the fixed vector $\vec{k}$ to lie along the z-direction and work in spherical polars:

$$S(k) = \frac{1}{(2\pi)^3} \int_{k'<k_F} k'^2\, dk' \sin\theta d\theta d\phi \frac{1}{k'^2 - 2kk'\cos\theta + k^2} \tag{5.7}$$

Performing integration in ϕ yields factor 2π; performing integration in θ by substituting x=cosθ:

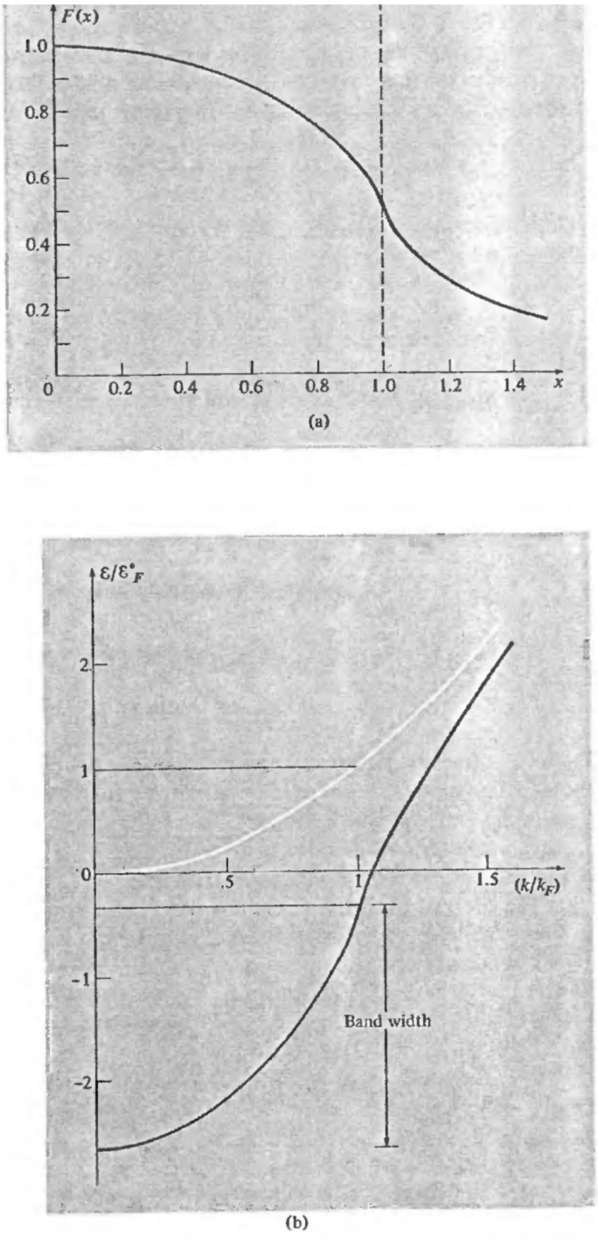
$$\begin{aligned} S(k) &= \frac{1}{4\pi^2}\frac{1}{k}\int_0^{k_F} k' \ln\left|\frac{k+k'}{k-k'}\right| dk' \\ &= \frac{1}{4\pi^2}\frac{1}{k}\left[kk' - \frac{1}{2}\left(k^2 - k'^2\right)\left|\frac{k+k'}{k-k'}\right|\right]_0^{k_F} \\ &= \frac{1}{(2\pi^2)} k_F F\left(\frac{k}{k_F}\right) \quad \text{where} \quad F(x) = \frac{1}{2} + \frac{1-x^2}{4x}\ln\left|\frac{1+x}{1-x}\right| \end{aligned} \tag{5.8}$$

The LHS of the HF equation therefore assumes the form:

$$\varepsilon(\vec{k}_i)\psi_i \quad \text{where} \quad \varepsilon(\vec{k}) = \frac{\hbar^2 k^2}{2m_e} - \frac{2e^2}{\pi} k_F F\left(\frac{k}{k_F}\right) \tag{5.9}$$

This shows that plane waves do indeed solve the HF equations, and that the energy of the one-electron level with wave vector k is given by (5.9). The exchange energy therefore provides a negative contribution to the total energy of the electron gas, which contributes to the binding energy of metals. The function F(x) is plotted in Figure 5.1a, and the energy ε(k) in Figure 5.1b:

Fig 5.1



(a) A plot of the function $F(x)$, defined by Eq. (17.20). Although the slope of this function diverges at $x = 1$, the divergence is logarithmic, and cannot be revealed by changing the scale of the plot. At large values of x the behavior is $F(x) \to 1/3x^2$. (b) The Hartree-Fock energy (17.19) may be written

$$\frac{\varepsilon_k}{\varepsilon_F^0} = \left[x^2 - 0.663\left(\frac{r_s}{a_0}\right)F(x)\right],$$

where $x = k/k_F$. This function is plotted here for $r_s/a_0 = 4$, and may be compared with the free electron energy (white line). Note that in addition to depressing the free electron energy substantially, the exchange term has led to a considerable increase in the bandwidth (in these units from 1 to 2.33), an effect not corroborated by experiments such as soft X-ray emission or photoelectron emission from metals, which purport to measure such bandwidths.

Although the Hartree-Fock one-electron levels continue to be plane waves, the energy of an electron in the level $e^{i\vec{k}\cdot\vec{r}}$ is now given by $\hbar^2k^2/2m$ plus a term describing the effects of the electron-electron exchange interaction. To compute the contribution of these interactions to the total energy of the N-electron system, we must sum this correction over all $k < k_F$, multiply by 2 (for the two spin levels that are occupied for each k), and divide by 2 (because, in summing the interaction energy of a given electron over all electrons, we are counting each electron pair twice). In this way we find that:

$$E = 2\sum_{k<k_F} \frac{\hbar^2k^2}{2m_e} - \frac{e^2k_F}{\pi}\sum_{k<k_F}\left[1+\frac{{k_F}^2-k^2}{2kk_F}\ln\left|\frac{k_F+k}{k_F-k}\right|\right] \tag{5.10}$$

if the two terms are converted into integrals using $\lim_{V\to\infty}\frac{1}{V}\sum_k F(k) = \int\frac{dk}{8\pi^3}F(k)$ and $N/V = k_F^3/3\pi^2$ we obtain:

$$\frac{E}{N} = \left[\frac{3}{5}\varepsilon_F - \frac{3}{4}\frac{e^2k_F}{\pi}\right] = \frac{e^2}{2a_o}\left[\frac{3}{5}(k_Fa_o)^2 - \frac{3}{2\pi}(k_Fa_o)\right] = \left[\underbrace{\frac{2.21}{(r_s/a_o)^2}}_{\text{KINETIC ENERGY}} - \underbrace{\frac{0.916}{(r_s/a_o)}}_{\text{EXCHANGE ENERGY}}\right]Ry$$

(5.11)

where the last expression is written in terms of the rydberg $\left(e^2/2a_o = 1Ry = 13.6eV\right)$ and the dimensionless parameter r_s/a_0, where a$_o$ is the Bohr radius. Since r_s/a_0 in metals is in the range from 2 to 6, the exchange term in (5.11) is quite comparable to the kinetic energy term in size, which indicates that electron-electron interactions cannot be overlooked when calculating electronic energy of a metal. Also by looking at equation (5.11) we can deduce that at high-densities (small rs) the Kinetic Energy dominates, and in spite of the electron-electron interaction the system behaves like an almost ideal Fermi Gas, whereas at low densities (high rs) exchange energy dominates. As the effect of Exchange interactions increases, the exchange energy leads to a full, ferromagnetic alignment of the electron spins. It is believed that this occurs in a range of 75 < rs < 100. At very low electron density (rs > 100), the electrons become localized in order to minimize their Coulomb repulsion due to the strong repulsive exchange forces. As a result the system undergoes a metal-insulator transition (Mott insulator). Wigner predicted that in this regime the free electron gas would crystallize on a regular BCC lattice (Wigner Crystallization).

With much labour the *exact* leading terms in a high-density (i.e. small r_s/a_0) expansion of the ground-state energy of the electron gas have been calculated:

$$\frac{E}{N} = \left[\frac{2.21}{(r_s/a_o)^2} - \frac{0.916}{(r_s/a_o)} + 0.0622\ln(r_s/a_o) - 0.096 + O(r_s/a_o)\right]Ry \tag{5.12}$$

Note that the first two terms are just the Hartree-Fock result (5.11). The next two terms in (5.12) and all other corrections to the Hartree-Fock result represent the correlation energy.

Equation (5.9) has one rather alarming feature: The derivative $\partial\varepsilon/\partial k$ becomes logarithmically infinite at $k = k_F$. Since $(1/\hbar)\partial\varepsilon/\partial k\,|_{k=k_F}$ is precisely the velocity of those electrons most important for metallic properties, this is an unsettling result. The singularity does not occur for a general non-coulombic potential, but can be traced back to the divergence of the Fourier transform $4\pi e^2/k^2$ of the interaction e^2/r at k=0. This in turn reflects the very long range of the inverse square force. If the Coulomb interaction were replaced, for example, by one of the form $e^2\left(e^{-k_o r}/r\right)$ then its Fourier transform would be $4\pi e^2/\left(k^2 + k_o{}^2\right)$, the k = 0 divergence would be eliminated, and the unphysical singularity of the Hartree-Fock energies removed. It can be argued that the potential appearing in the exchange term should be modified in just this way to take into account the fields of electrons other than the two at r and r', which rearrange themselves so as partially to cancel the fields the two electrons exert on one another. This effect, known as “screening," is of fundamental importance not only for its effects on the electron-electron interaction energy, but, more generally, in determining the behavior of any charge-carrying disturbance in a metal[2].

6. CORRELATION AND THE EXCHANGE-CORRELATION HOLE

As explained in preceding sections, the Hartree-Fock approximation (HFA) consists of neglecting all correlations *except* those required by the Pauli exclusion principle (i.e., exchange-interaction). We also explained that, within the framework of HF theory, only correlations between parallel spin electrons can be accounted for and that therefore the exchange term always has the effect of lowering the total energy. The effect of exchange may therefore be interpreted as the interaction of each electron with a positively-charged "exchange hole" surrounding it. The general features of correlation can be better understood by looking at the pair distribution function of the N-electron system (since the interactions always involve pairs of electrons).

In general, the joint probability $n(\vec{r},\sigma;\vec{r}\,',\sigma')$, known as the pair correlation function, of finding electrons of spin σ at point r and of spin σ′ at point r′ is given by :

$$\begin{aligned} n(\vec{r},\sigma;\overrightarrow{r'},\sigma') &= \left\langle \sum_{i\neq j}\delta(\vec{r}-\vec{r_i})\delta(\sigma-\sigma_i)\delta(\vec{r}\,'-\vec{r_j})\delta(\sigma'-\sigma_j)\right\rangle \\ &= N(N-1)\sum_{\sigma_3,\sigma_4\cdots}\int d\overrightarrow{r_3}\ldots d\overrightarrow{r_N}\left|\Psi_N(r,\sigma;r',\sigma';r_3,\sigma_3;\ldots,r_N,\sigma_N)\right|^2 \end{aligned} \qquad (6.1)$$

assuming Ψ_N is normalized to unity. For uncorrelated particles, the joint probability is just the product of probabilities, so that the measure of correlation is:

$$\Delta n(\vec{r},\sigma;\overrightarrow{r'},\sigma') = n(\vec{r},\sigma;\overrightarrow{r'},\sigma') - n(\vec{r},\sigma)n(\overrightarrow{r'},\sigma') \rightarrow n(\vec{r},\sigma;\overrightarrow{r'},\sigma') = n(\vec{r},\sigma)n(\overrightarrow{r'},\sigma') + \Delta n(\vec{r},\sigma;\overrightarrow{r'},\sigma') \qquad (6.2)$$

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[2] The discussion of screening is beyond the scope of these notes. The reader should consult any standard text on solid state physics

It is also useful to define the normalized pair distribution function:

$$g(\vec{r},\sigma;\vec{r}',\sigma')=\frac{n(\vec{r},\sigma;\vec{r}',\sigma')}{n(\vec{r},\sigma)n(\vec{r}',\sigma')}=1+\frac{\Delta n(\vec{r},\sigma;\vec{r}',\sigma')}{n(\vec{r},\sigma)n(\vec{r}',\sigma')} \tag{6.3}$$

which is unity for uncorrelated particles. The degree of correlation is therefore reflected in the quantity: $g(\vec{r},\sigma;\vec{r}',\sigma')-1$. Note that all long-range correlation is included in the average terms so that the remaining terms $\Delta n(\vec{r},\sigma;\vec{r}',\sigma')$ and $g(\vec{r},\sigma;\vec{r}',\sigma')-1$ are short range and vanish at large $\left|\vec{r}-\vec{r}'\right|$.

The exchange hole $\Delta n_x(\vec{r},\sigma;\vec{r}',\sigma')$ is given by $\Delta n(\vec{r},\sigma;\vec{r}',\sigma')$ in the HFA, where Ψ_N in (6.1) is approximated by the Slater determinant wavefunction. There are stringent conditions on the exchange hole: (l) it can never be positive, $\Delta n_x(\vec{r},\sigma;\vec{r}',\sigma')\leq 0$ (which means that $g_x(\vec{r},\sigma;\vec{r}',\sigma')\leq 1$), and (2) the integral of the exchange hole density $\Delta n_x(\vec{r},\sigma;\vec{r}',\sigma')$ over all r′ is exactly one missing electron per electron at any point r. This is a consequence of the fact that if one electron is at r, then that same electron cannot also be at r′.

The effects of correlation can be cast in terms of the remaining part of the pair correlation function beyond exchange, $\Delta n_C(\vec{r},\sigma;\vec{r}',\sigma')$:

$$\Delta n(\vec{r},\sigma;\vec{r}',\sigma')\equiv\Delta n_{xc}(\vec{r},\sigma;\vec{r}',\sigma')=\Delta n_x(\vec{r},\sigma;\vec{r}',\sigma')+\Delta n_c(\vec{r},\sigma;\vec{r}',\sigma') \tag{6.4}$$

Since the entire exchange-correlation hole obeys the sum rule that it integrates to 1, the correlation hole $\Delta n_C(\vec{r},\sigma;\vec{r}',\sigma')$ must integrate to zero, i.e. it merely redistributes the density of the hole.

In the case of the homogeneous electron gas, the form of the exchange hole can be calculated analytically within HF theory. To do this we have to take a closer look at the exchange term (5.5):

$$U_{exch}(r)\cdot\psi_k(\vec{r})=-\frac{e^{i\vec{k}\cdot\vec{r}}}{\sqrt[3]{V}}\sum_{k'<k_F}\oint d^3r'e^{-i(\vec{k}-\vec{k}')\cdot(\vec{r}-\vec{r}')}\frac{e^2}{4\pi\varepsilon_o\left|\vec{r}-\vec{r}'\right|} \tag{6.5}$$

From this we can define an exchange charge density:

$$\rho_k^{HF}(\vec{r}-\vec{r}')=-\frac{e}{V}\sum_{\substack{k'<k_F\\ \sigma'=\sigma}}e^{-i(\vec{k}-\vec{k}')\cdot(\vec{r}-\vec{r}')} \tag{6.6}$$

The exchange charge density is seen by a particular electron at location r as a result of its exchange interaction with the other electrons at location r′ in addition to the normal Coulomb charge density produced by the other electrons. The Coulomb charge density is uniform in the homogeneous electron gas, but the exchange charge density seen by a particular electron varies as a function of distance from the electron:

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

$$= -\frac{e}{V}e^{i\vec{k}\cdot\vec{r''}}\frac{1}{(2\pi)^3}\int_{k'<k_F} k'^2 \sin\theta dk' d\theta d\phi e^{-ik'\cdot r''\cos\theta} = -\frac{e}{V}e^{i\vec{k}\cdot\vec{r''}}\frac{1}{(2\pi)^2}\int_{k'<k_F} k'^2\, dk'\left[\frac{e^{-ik'\cdot r''\cos\theta}}{-ik'\cdot r''}\right]_0^{\pi}$$

$$= -\frac{e}{V}e^{i\vec{k}\cdot\vec{r''}}\frac{1}{(2\pi)^2}\int_{k'<k_F} k'^2\, dk\frac{\sin k'\cdot r''}{k'\cdot r''} = -\frac{3}{2}\frac{eN}{V}e^{i\vec{k}\cdot\vec{r''}}\frac{\sin k_F'\cdot r'' - k_F'\cdot r''\cos k_F'\cdot r''}{\left(k_F'\cdot r''\right)^3}$$

(6.7)

This still depends on the k-value of the particular electron under consideration. We can calculate an average exchange charge density (the exchange hole) by averaging over all electrons within the Fermi Sphere (same integration as above):

$$\begin{aligned}\overline{\rho}^{HF}(r) &= -\frac{3}{2}\frac{eN}{V}\frac{\sin k_F'\cdot r - k_F'\cdot r\cos k_F'\cdot r}{\left(k_F'\cdot r\right)^3}\frac{1}{\left(\frac{4}{3}\pi k_F^3\right)}\int_{k'<k_F} k^2\sin\theta dk d\theta d\phi e^{ik\cdot r\cos\theta} \\ &= -\frac{9}{2}\frac{eN}{V}\frac{(\sin k_F r - k_F r\cos k_F r)^2}{(k_F r)^6}\end{aligned} \qquad (6.8)$$

By adding to this the standard to this the standard Coulomb charge density eN/V we can calculate the total average charge density seen by a HF electron:

$$\rho_{tot}(r) = e\frac{N}{V}\left(1-\frac{9}{2}\frac{(k_F r\cos k_F r - \sin k_F r)^2}{\left(k_F r\right)^6}\right) \qquad (6.9)$$

Hence, as expected, exchange interactions have the effect of reducing the concentration of electrons with equal spin in the vicinity of each electron in the system. If the HF homogeneous electron gas is unpolarized ($N_{\uparrow} = N_{\downarrow} = N/2$), a plot of the electron charge concentration as a function of distance away from each electron is therefore expected to drop to ½ at the origin, where all the same-spin electrons are being repelled away.

For partially polarized cases, the exchange energy is just a sum of terms for the two spins, which can also be expressed in an alternative form in terms of the total density $n = n^{\uparrow} + n^{\downarrow}$ and the fractional polarization:

$$\zeta = \frac{n^{\uparrow} - n^{\downarrow}}{n}. \qquad (6.10)$$

It is straightforward to show that exchange in a polarized system has the form

$$\epsilon_x(n,\zeta) = \epsilon_x(n,0) + [\epsilon_x(n,1) - \epsilon_x(n,0)] f_x(\zeta),$$

where

$$f_x(\zeta) = \frac{1}{2}\frac{(1+\zeta)^{4/3} + (1-\zeta)^{4/3} - 2}{2^{1/3} - 1}, \tag{6.11}$$

Unlike the exchange energy, it is not possible to determine the correlation hole and energy analytically for a homogeneous electron gas. The discussion on methods to estimate the correlation energy is therefore delayed until section 11 on the Local Density Approximation within the theoretical framework of Density Functional Theory.

PART II: DENSITY FUNCTIONAL THEORY

7. INTRODUCTION

The HF equations were historically important as a milestone in treating the many-body problem in metals, as it was the first technique which allowed for a neat separation between exchange and correlation effects. In practice however treatise of HF equations is difficult, and requires careful further approximations. Furthermore, it has the other major disadvantage of not accounting for exchange effects between electrons with antiparallel spin. Hence the need for Density Functional Theory (DFT), a more powerful technique for calculating the ground state properties of many-body systems.

Density functional theory is a theory of correlated many-body systems that, similarly to HF theory, incorporates effects of interactions and correlations among the particles. As such, density functional theory has become the primary and most promising tool for calculation of electronic structure in condensed matter, and is increasingly important for quantitative studies of molecules and other finite systems. In particular, DFT owes much of its success to the development of approximate functionals such as the local density (LDA) and generalized-gradient approximation (GGA), both of which will be explained in detail in later sections of this document.

The modem formulation of density functional theory originated in a famous paper written by P. Hohenberg and W. Kohn in 1964[3]. These authors showed that a special role can be assigned to the density n(r) of particles in the ground state of a quantum many-body system: the density can be considered as a "basic variable," and all properties of the system, and in particular the ground state energy, can be considered to be unique *functionals*[4] of the ground state density. The ground state electron density can therefore be used as a replacement for the ground state many-body wavefunction Ψ_G which, as a result, can be disposed of altogether in the context of DFT:

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[3] P. Hohenberg and W. Kohn, "Inhomogeneous electron gas," *Phys. Rev.* 136:B864-871 , 1964.

[4] An introduction to the mathematical theory of functionals and functional derivatives is presented in Appendix A of this document.

$$\Psi_G = \Psi(\vec{r_1},\sigma_1;....;\vec{r_i},\sigma_i;....;\vec{r_j},\sigma_j;.....;\overrightarrow{r_N},\sigma_N) \xrightarrow{DFT} n(\vec{r}) = \left\langle \Psi_G \middle| \sum_{i=1}^{N} \delta(\vec{r}-\vec{r_i})\Psi_G \right\rangle \qquad (7.1)$$

where r_i is the position of the ith electron in the material. The attraction of density functional theory is evident by the fact that one equation for the density is remarkably simpler than the full many-body Schroeinger equation that involves *3N* degrees of freedom for *N* electrons. Also in 1965 appeared the other classic work of this field by W. Kohn and L. J. Sham[5] , whose formulation of density functional theory has become the basis of much of present-day methods for treating electrons in atoms, molecules, and condensed matter.

8. THOMAS-FERMI-DIRAC APPROXIMATION: EXAMPLE OF A FUNCTIONAL

The original density functional theory of quantum systems is the method of Thomas and Fermi proposed in 1927. Although their approximation is not accurate enough for present-day electronic structure calculations, the approach illustrates the way density functional theory works. In the original Thomas-Fermi method the material is idealized as a homogeneous gas of non-interacting electrons and the kinetic energy of the system electrons is approximated as an explicit functional of the density. Both Thomas and Fermi neglected exchange and correlation among the electrons; however, this was extended by Dirac in 1930, who formulated the local approximation for exchange still in use today. This leads to the energy functional for electrons in an external potential $V_{ext}(\vec{r})$:

$$E_{\mathrm{TF}}[n] = C_1 \int \mathrm{d}^3r\; n(\mathbf{r})^{(5/3)} + \int \mathrm{d}^3r\; V_{\mathrm{ext}}(\mathbf{r})n(\mathbf{r}) + C_2 \int \mathrm{d}^3r\; n(\mathbf{r})^{4/3} + \frac{1}{2}\int \mathrm{d}^3r\mathrm{d}^3r'\; \frac{n(\mathbf{r})n(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}, \qquad (8.1)$$

where the first term is the local approximation to the kinetic energy with: $C_1 = \frac{3}{10}\left(3\pi^2\right)^{(2/3)}$, the third term is the local exchange with $C_2 = -\frac{3}{4}\left(\frac{3}{\pi}\right)^{1/3}$ and the last term is the classical electrostatic Hartree energy.

The ground state density and energy can be found by minimizing the functional E[n] in (8.1) for all possible n(r) subject to the constraint on the total number of electrons:

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[5] W. Kohn and L. J. Sham, "Self-consistent equations including exchange and correlation effects," *Phys. Rev.* 140:A1133-1138, 1965.

$$\int d^3r \, n(\mathbf{r}) = N. \tag{8.2}$$

Using the method of Lagrange multipliers , the solution can be found by an unconstrained minimization of the functional:

$$\Omega_{\mathrm{TF}}[n] = E_{\mathrm{TF}}[n] - \mu \left\{ \int d^3r n(\mathbf{r}) - N \right\} \tag{8.3}$$

where the Lagrange multiplier μ is the Fermi energy. For small variations of the density $\delta n(\vec{r})$ the condition for a stationary point is:

$$\int d^3r \left\{ \Omega_{\mathrm{TF}}[n(\mathbf{r}) + \delta n(\mathbf{r})] - \Omega_{\mathrm{TF}}[n(\mathbf{r})] \right\} \rightarrow$$
$$\int d^3r \left\{ \frac{5}{3} C_1 n(\mathbf{r})^{2/3} + V(\mathbf{r}) - \mu \right\} \delta n(\mathbf{r}) = 0, \tag{8.4}$$

where $V(\vec{r}) = V_{ext}(\vec{r}) + V_{Hartree}(\vec{r}) + V_x(\vec{r})$ is the total potential. Since (8.4) must be satisfied for any function $\delta n(\vec{r})$, it follows that the functional is stationary if and only if the density and potential satisfy the relation:

$$\frac{1}{2}(3\pi^2)^{(2/3)} n(\mathbf{r})^{2/3} + V(\mathbf{r}) - \mu = 0. \tag{8.5}$$

The Thomas-Fermi approach has been applied, for example, to equations of state of the elements. However, the Thomas-Fermi type approach starts with approximations that are too crude, missing essential physics and chemistry, such as shell structures of atoms and binding of molecules. Thus it falls short of the goal of a useful description of electrons in matter. In order to make any progress and investigate more advanced techniques, we first need to gain a better understanding of the relation between the ground state density and the external potential $V_{ext}(\vec{r})$. This is the subject of the next section.

9. THE HOHENBERG-KOHN THEOREMS

The two Hohenbeg-Kohn (HK) theorems represent the fundamental theoretical framework over which all modern formulations of DFT are based. The formulation applies to any system of mutually interacting particles in an external (ionic) potential $V_{ext}(\vec{r})$, including any problem of N electrons and M fixed nuclei in a crystalline solid, where the hamiltonian can be written as a sum of the internal Hamiltonian of the electron cloud and the sum of the external potentials due to the nuclei acting on each electron :

$$H_N = H_{\text{int}} + V_{ext}(\vec{r}) = \underbrace{\sum_{i=1}^{N} -\frac{\hbar^2}{2m_e}\nabla_i^2 + \frac{1}{2}\sum_{i,j}^{i\neq j}\frac{e^2}{4\pi\varepsilon_o\left|\vec{r_i}-\vec{r_j}\right|}}_{H_{\text{int}}} + \underbrace{\sum_{i=1}^{N} v_{ext}(\vec{r_i})}_{V_{ext}}$$

$$\text{where } v_{ext}(\vec{r_i}) = -\sum_{k=1}^{M}\frac{Ze^2}{4\pi\varepsilon_o\left|\vec{r_i}-\vec{R_k}\right|}$$

(9.1)

The relations established by Hohenberg and Kohn are illustrated in Fig. 9.1 and can be started as follows:

- **Theorem I**: For any system of interacting particles in an external potential $V_{ext}(\vec{r})$ the potential $V_{ext}(\vec{r})$ is determined uniquely, except for a constant, by the ground state particle density $n_O(\vec{r})$

  Corollary I: Since the hamiltonian is thus fully determined, except for a constant shift of the energy, it follows that the many-body wavefunctions for all states (ground and excited) are determined. Therefore all properties of the system are completely determined given only the ground state density $n_O(\vec{r})$

- **Theorem II**: A universal functional for the energy E[n] in terms of the density n(r) can be defined, valid for any external potential $V_{ext}(\vec{r})$. For any particular $V_{ext}(\vec{r})$ the exact ground state energy of the system is the global minimum value of this functional, and the density n(r) that minimizes the functional is the exact ground state density $n_O(\vec{r})$

  Corollary II: The functional E[n] alone is sufficient to determine the exact ground state energy and density. In general, excited states of the electrons must be determined by other means

$$\begin{tikzcd} V_{\text{ext}}(\mathbf{r}) \arrow[d, Rightarrow] & n_0(\mathbf{r}) \arrow[l, Rightarrow, "\text{HK}"'] \\ \Psi_i(\{\mathbf{r}\}) \arrow[r, Rightarrow] & \Psi_0(\{\mathbf{r}\}) \arrow[u, Rightarrow] \end{tikzcd}$$

Fig 9.1: Schematic representation of the HK theorem. The smaller arrows denote the usual solution of the Schroedinger equation where the potential $V_{ext}(\vec{r})$ determines all states of the system $\Psi_i(\{\vec{r}\})$, including the ground state $\Psi_o(\{\vec{r}\})$ and ground state density $n_O(\vec{r})$. The long arrow labeled ''HK'' denotes the HK theorem, which completes the circle.

Proof of Theorem I: density as a basic variable

Consider first Theorem I, using the general expressions given in (7.1) and (3.7) for the density and energy in terms of the many-body wavefunction. Suppose that there were two different external potentials $V_{ext}^{(1)}(\vec{r})$ and $V_{ext}^{(2)}(\vec{r})$ which differ by more than a constant and which lead to the same ground state density $n_O(\vec{r})$. The two external potentials lead to two different Hamiltonians $\widehat{H}^{(1)}$ and $\widehat{H}^{(2)}$ (the internal Hamiltonian is assumed to stay the same) which have different ground state many-body wavefunctions, $\Psi^{(1)}$ and $\Psi^{(2)}$. These two wavefunctions are in turn hypothesized to have the same ground state density $n_O(\vec{r})$. Since $\Psi^{(2)}$ is not the ground state of $\widehat{H}^{(1)}$ it follows that

$$E^{(1)} = \langle \Psi^{(1)} | \hat{H}^{(1)} | \Psi^{(1)} \rangle < \langle \Psi^{(2)} | \hat{H}^{(1)} | \Psi^{(2)} \rangle. \tag{9.2}$$

The strict inequality follows if the ground state is non-degenerate, which we will assume here. The last term in (9.2) can be written

$$\begin{aligned} \langle \Psi^{(2)} | \hat{H}^{(1)} | \Psi^{(2)} \rangle &= \langle \Psi^{(2)} | \hat{H}^{(2)} | \Psi^{(2)} \rangle + \langle \Psi^{(2)} | \hat{H}^{(1)} - \hat{H}^{(2)} | \Psi^{(2)} \rangle \\ &= E^{(2)} + \int \mathrm{d}^3 r \left[V_{\text{ext}}^{(1)}(\mathbf{r}) - V_{\text{ext}}^{(2)}(\mathbf{r}) \right] n_0(\mathbf{r}), \end{aligned} \tag{9.3}$$

so that

$$E^{(1)} < E^{(2)} + \int \mathrm{d}^3 r \left[V_{\text{ext}}^{(1)}(\mathbf{r}) - V_{\text{ext}}^{(2)}(\mathbf{r}) \right] n_0(\mathbf{r}). \tag{9.4}$$

On the other hand if we consider $E^{(2)}$ in exactly the same way, we find the same equation with superscripts (1) and (2) interchanged:

$$E^{(2)} < E^{(1)} + \int \mathrm{d}^3 r \left[V_{\text{ext}}^{(2)}(\mathbf{r}) - V_{\text{ext}}^{(1)}(\mathbf{r}) \right] n_0(\mathbf{r}). \tag{9.5}$$

Now if we add together (9.5) and (9.4) , we arrive at the contradictory inequality $E^{(1)} + E^{(2)} < E^{(1)} + E^{(2)}$. This establishes the desired result: there cannot be two different external potentials differing by more than a constant which give rise to the same non-degenerate ground state charge density. The density therefore uniquely determines the extemal potential to within a constant. The corollary follows since the hamiltonian is uniquely determined (except for a constant) by the external potential and hence by the ground state density. Then, in principle, the wavefunction of any state is determined by solving the Schrodinger equation with this hamiltonian. Among all the solutions which are consistent with the given density, the unique ground state wavefunction is the one that has the lowest energy.

Despite the appeal of this result, it is clear from the reasoning that no prescription has been given to solve the problem. Since all that was proved is that $n_O(\vec{r})$ uniquely determines $V_{ext}(\vec{r})$, we are still left with the problem of solving the many-body problem in the presence of $V_{ext}(\vec{r})$. For example, for electrons in materials, the external potential is the Coulomb potential due to the nuclei in the periodic crystal structure of the material. The theorem only requires that the electron density uniquely determines the positions and types of nuclei, which can also easily be proven from elementary quantum mechanics. At this level we have gained nothing: we are still faced with the original problem of many interacting electrons moving in the potential due to the nuclei.

Proof of Theorem II: universal functional for the energy E[n] in terms of the density n(r)

The second theorem is just as easily proven once one has carefully defined the meaning of a functional of the density. Since all properties such as the kinetic energy, etc…., are uniquely determined if n(r) is specified, then each such property can be viewed as a functional of n(r), including the total HK energy functional:

$$\begin{aligned} E_{\mathrm{HK}}[n] &= T[n] + E_{\mathrm{int}}[n] + \int \mathrm{d}^3r \; V_{\mathrm{ext}}(\mathbf{r})n(\mathbf{r}) + E_{II} \\ &\equiv F_{\mathrm{HK}}[n] + \int \mathrm{d}^3r \; V_{\mathrm{ext}}(\mathbf{r})n(\mathbf{r}) + E_{II}, \end{aligned} \qquad (9.6)$$

where E_{II} is the interaction energy of the nuclei among themselves. The functional $F_{HK}[n]$ defined in (9.6)includes all internal energies, kinetic and potential, of the interacting electron system:

$$F_{\mathrm{HK}}[n] = T[n] + E_{\mathrm{int}}[n], \qquad (9.7)$$

which must be universal (the same for all electron systems, independent of the external potential $V_{ext}(\vec{r})$) since the kinetic energy and interaction energy of the particles are functionals only of the density.

Now consider a system with the ground state density $n^{(1)}(\vec{r})$ corresponding to external potential $V_{ext}^{(1)}(\vec{r})$. Following the discussion above, the Hohenberg-Kohn functional is equal to the expectation value of the hamiltonian in the unique ground state, which has wavefunction $\Psi^{(1)}$:

$$E^{(1)} = E_{\mathrm{HK}}[n^{(1)}] = \langle \Psi^{(1)} | \hat{H}^{(1)} | \Psi^{(1)} \rangle . \tag{9.8}$$

Now consider a different density, say $n^{(2)}(\vec{r})$, which necessarily corresponds to a different wavefunction $\Psi^{(2)}$. It follows immediately that the energy $E^{(2)}$ of this state is greater than $E^{(1)}$, since

$$E^{(1)} = \langle \Psi^{(1)} | \hat{H}^{(1)} | \Psi^{(1)} \rangle < \langle \Psi^{(2)} | \hat{H}^{(1)} | \Psi^{(2)} \rangle = E^{(2)} . \tag{9.9}$$

Thus the energy given by (9.6) in terms of the Hohenberg-Kohn functional evaluated for the correct ground state density $n_O(\vec{r})$ is indeed lower than the value of this expression for any other density n(r). It follows that if the functional $F_{HK}[n]$ was known, then by minimizing the total energy of the system, (9.6), with respect to variations in the density function n(r), one would find the exact ground state density and energy. This establishes Corollary II. Note that the functional only determines the ground state properties; it does not provide any guidance concerning excited states.

The challenge posed by the Hohenberg-Kohn theorems is how to make use of the reformulation of many-body theory in terms of functionals of the density. The form of the functionals in the theorems is still unknown, and it is easy to show that these must be non-local functionals, depending simultaneously upon n(r) at different positions r, which are difficult to cast in any simple form. It is important to emphasize that density functional theory does not provide a way to understand the properties of a material merely by looking at the form of the density. Although the density is in principle sufficient, the relation is very subtle and no one has found a way to extract directly from the density any general set of properties. e.g. whether the material is a metal or an insulator.

This leads us to the Kohn-Sham approach, the success of which is based upon the fact that it includes the kinetic energy of non-interacting electrons in terms of independent particle wavefunctions, in addition to interaction terms explicitly modelled as functionals of the density. There is in fact no known way to go directly from the density to the kinetic energy. Because the kinetic energy is treated in terms of orbitals - not as an explicit functional of the density - it builds in all the quantum properties that have no simple relation to the density

10. THE KOHM SHAM EQUATIONS

The Kohn-Sham approach is to replace the difficult interacting many-body system obeying the Hamiltonian (9.1) with a different auxiliary system that can be solved more easily. The ansatz of Kohn and Sham assumes that the ground state density of the original interacting system is equal to that of some chosen non-interacting system. This leads to independent-particle equations for the non-interacting system, the Kohn-Sham equations, that can be considered exactly soluble (in practice by numerical means) with all the difficult many-body terms incorporated into an exchange-correlation functional of the density. By solving the equations one can compute the ground state density and ground state energy of the original interacting system with the accuracy limited only by the approximations in the exchange-correlation functional.

Indeed, the Kohn-Sham approach has led to very useful approximations that are now the basis of most calculations that attempt to make "first-principles" or "ab initio" predictions for the properties of condensed matter and large molecular systems. The local density approximation (LDA) or various generalized-gradient approximations (GGAs) described below, are remarkably accurate, most notably for "wide-band" systems, such as the group IV and II-V semiconductors, sp-bonded metals like Na and AI, insulators like diamond, NaCl, and molecules with covalent and/or ionic bonding. However, these approximations fail for many strongly correlated cases including the copper oxide planar materials which are antiferromagnetic insulators for exactly half filled bands, whereas the LDA or present GGA functionals find them to be metals. This leads to the present situation in which there is great interest in utilizing and improving the density functional approach, to build upon the many successes of current approximations and to overcome the known deficiencies and failures in strongly correlated electron systems.

Here we will consider the Kohn-Sham ansatz for the ground state, which is by far the most widespread way in which the theory has been applied. However, in the big picture this is only the first step. The fundamental theorems of density functional theory show that in principle the ground state density determines everything. A great challenge in present theoretical work is to develop methods for calculating excited state properties, but this lies beyond the scope of this short introduction.

The Kohn-Sham ansatz rests upon two assumptions:

1. The exact ground state density can be represented by the ground state density of an auxiliary system of non-interacting particles (i.e. a system where the independent-electron approximation applies). This leads to the relation of the actual and auxiliary systems shown in Fig. 10.1:

$$\begin{tikzcd}
V_{\mathrm{ext}}(\mathbf{r}) \arrow[r, Leftarrow, "\mathrm{HK}"] \arrow[d, Rightarrow] & n_0(\mathbf{r}) \arrow[r, Leftrightarrow, "\mathrm{KS}"] & n_0(\mathbf{r}) \arrow[r, Rightarrow, "\mathrm{HK}_0"] & V_{\mathrm{KS}}(\mathbf{r}) \arrow[d, Rightarrow] \\
\Psi_i(\{\mathbf{r}\}) \arrow[r, Rightarrow] & \Psi_0(\{\mathbf{r}\}) \arrow[u, Rightarrow] & \psi_{i=1,N_e}(\mathbf{r}) \arrow[u, Rightarrow] & \psi_i(\mathbf{r}) \arrow[l, Rightarrow]
\end{tikzcd}$$

Fig 10.1: Schematic representation of the Kohm-Sham ansatz. The label HK_0 denotes the HK theorem applied to the non-interacting auxiliary system of electrons. The arrow labelled KS provides the connection in both directions between the many-body interacting and independent-particle systems. Therefore, in principle, solution of the independent-particle Kohm-Sham problem determines all properties of the original full interacting many-body system.

This assumption has never been proven in general. It is obviously true for the homogeneous gas, it can be demonstrated easily for any one- or two-electron problem, and it has been shown by Kohn and Sham for small deviations from the homogeneous gas. However, no general proofs have been developed yet. Nevertheless, results of calculations appear very "reasonable" and detailed tests have shown that it is possible to fit the best numerical densities in many cases. We will follow the standard practice and proceed under the assumption that the Kohn-Sham ansatz is either valid or is good enough to be useful in practical calculations.

2. The auxiliary hamiltonian is chosen to have the usual kinetic operator and an effective local potential $V_{eff}^{\sigma}(\vec{r})$ acting on an electron of spin σ at point r. The local form is not essential, but it is an extremely useful simplification that is often taken as the defining characteristic of the Kohn-Sham approach. We still assume that the external potential $\widehat{V_{ext}}$ is spin independent; nevertheless, except in cases that are spin symmetric, the auxiliary effective potential $V_{eff}^{\sigma}(\vec{r})$ must depend upon spin in order give the correct density for each spin.

The actual calculations are performed on the auxiliary independent-particle system defined by the auxiliary Hamiltonian:

$$H_{aux}^{\sigma} = -\frac{\hbar^2}{2m_e}\nabla^2 + V^{\sigma}(\vec{r}) \tag{10.1}$$

At this point the form of $V^{\sigma}(\vec{r})$ is not specified and the expressions must apply for all $V^{\sigma}(\vec{r})$ in some range, in order to define functionals for a range of densities. For a system of $N = N^{\uparrow} + N^{\downarrow}$ independent electrons each obeying this hamiltonian, the ground state has one electron in each of the N^{σ} orbitals $\psi_i^{\sigma}(\vec{r})$ with the lowest eigenvalues ε_i^{σ} of the Hamiltonian (10.1). The density or the auxiliary system is given by sums of squares of the orbitals for each spin:

$$n(\vec{r}) = \sum_{\sigma} n(\vec{r},\sigma) = \sum_{\sigma}\sum_{i=1}^{N^{\sigma}} \left|\psi_i^{\sigma}(\vec{r})\right|^2 \tag{10.2}$$

Furthermore, the total independent-particle kinetic energy Ts is given by:

$$T_S = -\frac{\hbar^2}{2m_e}\sum_{\sigma}\sum_{i=1}^{N^\sigma}\left\langle \psi_i^\sigma \left| \nabla^2 \psi_i^\sigma \right.\right\rangle = \frac{\hbar^2}{2m_e}\sum_{\sigma}\sum_{i=1}^{N^\sigma}\left|\nabla \psi_i^\sigma\right|^2 \tag{10.3}$$

and finally we define the classical Coulomb interaction energy of the electron density n(r) interacting with itself (the Hartree energy):

$$E_{Hartree}\left[n\right] = \frac{1}{2}\int d^3r d^3r' \frac{n(\vec{r})n(\vec{r}')}{\left|\vec{r}-\vec{r}'\right|} \tag{10.4}$$

At this stage, the Kohn-Sham approach to the full interacting many-body problem consists in rewriting the Hohenberg-Kohn expression for the ground state energy functional (9.6) in the form:

$$E_{KS} = T_S[n] + \int d\vec{r} V_{ext}(\vec{r})n(\vec{r}) + E_{Hartree}[n] + E_{II} + E_{xc}[n] \tag{10.5}$$

Here $V_{ext}(\vec{r})$ is the external potential due to the nuclei and any other external fields (assumed to be independent of spin) and E_{II} is the interaction between the nuclei. Thus the sum of the terms involving $V_{ext}, E_{Hartree}, \text{ and } E_{II}$ forms a neutral grouping that is well defined. As explained at the end of the previous section, a distinct feature of thee KS approach is the independent-particle kinetic energy T_S, which is given explicitly as a functional of the orbitals as opposed to the density; however, Ts for each spin σ must still be a unique functional of the density $n(\vec{r},\sigma)$ by application of the Hohenberg-Kohn arguments applied to the independent-particle hamiltonian (10.1).

All many-body effects of exchange and correlation are grouped together into the exchange correlation energy functional $E_{xc}[n]$. Comparing the Hohenberg-Kohn, (9.6), and Kohn Sham, (10.5) , expressions for the total energy shows that E_{xc} can be written in terms of the Hohenberg-Kohn functional (9.7) as:

$$\begin{aligned} E_{xc}[n] &= F_{HK}[n] - (T_S[n] + E_{Hartree}[n]) \rightarrow \\ E_{xc}[n] &= \left\langle \hat{T} \right\rangle - T_S[n] + \left\langle \hat{V}_{\text{int}} \right\rangle - E_{Hartree}[n] \end{aligned} \tag{10.6}$$

Here [n] denotes a functional of the density $n(\vec{r},\sigma)$ which depends upon both position in space r and spin σ. One can see that $E_{xc}[n]$ must be a functional since the right-hand sides of the equations are all functionals. The latter equation shows explicitly that E_{xc} is just the difference of the kinetic and the internal interaction energies of the true interacting many body system from those of the fictitious independent-particle system with electron-electron interactions replaced by the Hartree energy. If the universal functional $E_{xc}[n]$ defined in (10.6) were known, then the exact ground state energy and density of the many-body electron problem could be found by solving the Kohn-Sham equations for independent-particles. To the extent that an approximate form for $E_{xc}[n]$ describes the true exchange-correlation energy, the Kohn-Sham method provides a feasible approach for estimating these quantities.

Solution of the Kohn-Sham auxiliary system for the ground state can be viewed as the problem of minimization of the Kohm-Sham energy functional (10.5) with respect to either the density $n(\vec{r},\sigma)$ or the effective potential $V_{eff}^{\sigma}(\vec{r})$. Since Ts (10.3) is explicitly expressed as a functional of the orbitals but all other terms are considered to be functionals of the density, one can vary the wavefunctions and use the chain rule to derive the variational equation:

$$\frac{\delta E_{\mathrm{KS}}}{\delta\psi_i^{\sigma *}(\mathbf{r})} = \frac{\delta T_s}{\delta\psi_i^{\sigma *}(\mathbf{r})} + \left[\frac{\delta E_{\mathrm{ext}}}{\delta n(\mathbf{r},\sigma)} + \frac{\delta E_{\mathrm{Hartree}}}{\delta n(\mathbf{r},\sigma)} + \frac{\delta E_{\mathrm{xc}}}{\delta n(\mathbf{r},\sigma)}\right]\frac{\delta n(\mathbf{r},\sigma)}{\delta\psi_i^{\sigma *}(\mathbf{r})} = 0, \tag{10.7}$$

subject to the orthonormalization constraints

$$\langle\psi_i^{\sigma}|\psi_j^{\sigma'}\rangle = \delta_{i,j}\delta_{\sigma,\sigma'}. \tag{10.8}$$

Using expressions (10.2) and (10.3) for $n^{\sigma}(\vec{r})$ and T_S, which give:

$$\frac{\delta T_s}{\delta\psi_i^{\sigma *}(\mathbf{r})} = -\frac{1}{2}\nabla^2\psi_i^{\sigma}(\mathbf{r}); \frac{\delta n^{\sigma}(\mathbf{r})}{\delta\psi_i^{\sigma *}(\mathbf{r})} = \psi_i^{\sigma}(\mathbf{r}), \tag{10.9}$$

and the Lagrange multiplier method for handling the constraints (10.8), this leads to the Kohn-Sham Schrodinger-like equations:

$$(H_{\mathrm{KS}}^{\sigma} - \varepsilon_i^{\sigma})\psi_i^{\sigma}(\mathbf{r}) = 0, \tag{10.10}$$

where the ε_i are the eigenvalues, and H_{KS} is the effective Hamiltonian:

$$H_{KS}^{\sigma}(\vec{r}) = -\frac{\hbar^2}{2m_e}\nabla^2 + V_{KS}^{\sigma}(\vec{r}) \tag{10.11}$$

with

$$\begin{aligned} V_{KS}^{\sigma}(\vec{r}) &= V_{ext}(\vec{r}) + \frac{\delta E_{Hartree}}{\delta n(\vec{r},\sigma)} + \frac{\delta E_{xc}}{\delta n(\vec{r},\sigma)} \\ &= V_{ext}(\vec{r}) + V_{Hartree}(\vec{r}) + V_{xc}^{\sigma}(\vec{r}) \end{aligned} \tag{10.12}$$

Equations (10.10) - (10.12) are the well-known Kohn-Sham equations, with the resulting density $n(\vec{r},\sigma)$ and total ground-state energy E_{KS} given by (10.2) and (10.5) respectively. The equations have the form of independent-particle equations with a local effective potential that must be found self-consistently with the resulting density. Furthermore, it follows from the Hohenberg-Kohn theorems that the ground state density uniquely determines the potential at the minimum (except for a trivial constant), so that there is a unique Kohn-Sham potential $V_{eff}^{\sigma}(\vec{r})|_{\min} \equiv V_{KS}^{\sigma}(\vec{r})$ associated with any given interacting electron system.

The defining quality of the Kohn-Sham approach is that by explicitly separating out the independent particle kinetic energy and the long-range Hartree terms, the remaining exchange correlation functional $E_{xc}[n]$ can reasonably be approximated as a local or nearly local functional of the density. This means that the energy $E_{xc}[n]$ can be expressed in the form:

$$E_{\mathrm{xc}}[n] = \int \mathrm{d}\mathbf{r}\; n(\mathbf{r})\epsilon_{\mathrm{xc}}([n], \mathbf{r}), \qquad (10.13)$$

where $\varepsilon_{xc}\left(\left[n\right],\vec{r}\right)$ is an energy per electron at point r that depends only upon the density $n(\vec{r},\sigma)$ in some neighbourhood of point r. Although the energy density $\varepsilon_{xc}\left(\left[n\right],\vec{r}\right)$ is not uniquely defined by the integral (10.13), a physically motivated definition of $\varepsilon_{xc}\left(\left[n\right],\vec{r}\right)$ follows from the analysis of the exchange correlation hole. An informative relation of $\varepsilon_{xc}\left(\left[n\right],\vec{r}\right)$ to the exchange-correlation hole can be found using the so-called "coupling constant integration formula". In this case the electronic charge is varied from zero (the non - interacting case) to the actual value, with the added constraint that the density must be kept constant during this variation. Then all other terms remain constant and the change in energy is given by

$$E_{\mathrm{xc}}[n] = \int_0^{e^2} \mathrm{d}\lambda \langle\Psi_\lambda|\frac{\mathrm{d}V_{\mathrm{int}}}{\mathrm{d}\lambda}|\Psi_\lambda\rangle - E_{\mathrm{Hartree}}[n] = \frac{1}{2}\int \mathrm{d}^3r\, n(\mathbf{r}) \int \mathrm{d}^3r' \frac{\bar{n}_{\mathrm{xc}}(\mathbf{r},\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|},$$

(10.14)

where $\overline{n_{xc}}(\vec{r},\vec{r}\,')$ is the coupling-constant-averaged hole:

$$\bar{n}_{\mathrm{xc}}(\mathbf{r},\mathbf{r}') = \int_0^1 \mathrm{d}\lambda\, n_{\mathrm{xc}}^{\lambda}(\mathbf{r},\mathbf{r}'). \qquad (10.15)$$

Here $n_{xc}(\vec{r},\vec{r}\,')$ is the hole summed over parallel $(\sigma=\sigma')$ and antiparallel $(\sigma\neq\sigma')$ spins. Furthermore, the integral in (10.14) involves only the spherical average of the hole density.

Together with (10.13), Eq. (10.14) shows that the exchange-correlation density $\varepsilon_{xc}\left([n],\vec{r}\right)$ can be written as

$$\epsilon_{\mathrm{xc}}([n],\mathbf{r})=\frac{1}{2}\int \mathrm{d}^3r'\,\frac{\bar{n}_{\mathrm{xc}}(\mathbf{r},\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}. \tag{10.16}$$

This is an important result which shows that the exact exchange-correlation energy can be understood in terms of the potential energy due to the exchange-correlation hole averaged over the interaction from $e^2=0$ to $e^2=1$. For $e^2=0$ the wavefunction is just the independent-particle Kohn-Sham wavefunction so that $n^0_{xc}(\vec{r},\sigma,\vec{r}\,',\sigma')=n_x(\vec{r},\sigma,\vec{r}\,',\sigma')$. Thus $E_{xc}[n]$ can be considered as an interpolation between the exchange-only and the full correlated energies at the given density $n(\vec{r},\sigma)$. Analysis of the nature of the averaged hole $\overline{n_{xc}}(\vec{r},\vec{r}\,')$ is one of the primary approaches for developing improved approximations for $E_{xc}[n]$.

The exchange-correlation potential $V^{\sigma}_{xc}(\vec{r})$ is the functional derivative of E_{xc}, which can then be written as

$$V^{\sigma}_{\mathrm{xc}}(\mathbf{r})=\epsilon_{\mathrm{xc}}([n],\mathbf{r})+n(\mathbf{r})\frac{\delta\epsilon_{\mathrm{xc}}([n],\mathbf{r})}{\delta n(\mathbf{r},\sigma)}, \tag{10.17}$$

The Kohn-Sham potential V_{KS} is defined by the requirement that it yield the exact density. This is an exacting requirement that must be accomplished by the properties of V_{XC} , since all the other terms in $V^{\sigma}_{KS}(\vec{r})=V_{ext}(\vec{r})+V_{Hartree}(\vec{r})+V^{\sigma}_{xc}(\vec{r})$ are known or are simple explicit functionals of the density. Thus one way to determine $V^{\sigma}_{xc}(\vec{r})$ is the requirement that $V^{\sigma}_{KS}(\vec{r})$ lead to the exact density. Conversely, the application of the Hohenberg-Kohn theorem to the Kohn-Sham non-interacting system implies that the exact density can be fit by only one $V^{\sigma}_{xc}(\vec{r})$ which is unique except for an additive constant.

As for the case of HF theory, the Lagrange eigenvalues ε^{σ}_{i} in (10.10) have no obvious physical meaning. There is only one exception: the highest eigenvalue in a finite system, which is minus the ionization energy $-I$. This follows from the fact that the asymptotic long-range density of a bound system is governed by the occupied state with highest eigenvalue, and since the density is assumed to be exact, so must the eigenvalue be exact. However, no other eigenvalue is guaranteed to be correct by the Kohn-Sham construction. Nevertheless, the eigenvalues have a well-defined mathematical meaning within the theory and they can be used to construct physically meaningful quantities. In particular, it can be shown that the eigenvalue corresponds to the derivative of the total energy with respect to occupation of a state. This is often known as the Slater-Janak theorem:

$$\varepsilon_i = \frac{\mathrm{d}E_{\mathrm{total}}}{\mathrm{d}n_i} = \int \mathrm{d}\mathbf{r} \frac{\mathrm{d}E_{\mathrm{total}}}{\mathrm{d}n(\mathbf{r})} \frac{\mathrm{d}n(\mathbf{r})}{\mathrm{d}n_i}. \qquad (10.18)$$

The Kohn-Sham approach places even heavier emphasis on the ground state than the Hohenberg-Kohn theorems. Thus questions arise as to what properties of a material should be given correctly by Kohn-Sham theory, if the exchange correlation functional was known exactly.

- Is the spin density correct in Kohn-Sham theory?
  Yes. A spin-dependent effective potential is introduced specifically to give the correct density and spin density.

- Are static charge and spin susceptibilities given correctly by the ground state functional?
  Yes. All static susceptibilities are second derivatives of ground state energies with respect to external fields. Thus they must be given correctly by the variation of the ground state Kohn-Sham functional as functions of external fields

- Is the macroscopic polarization in a crystal given correctly by the Kohn-Sham theory in terms of the density $n(\vec{r})$ in the bulk of the crystal?
  No. It has long been known that the polarization could not be derived simply from the density. Recent developments derive the polarization from the phases of the wavefunctions, not given correctly by the Kohn-Sham orbitals

- Is the exact Fermi surface of a metal given by eigenvalues in the exact Kohn-Sham theory?
  No. Even though the density is reproduced, the Fermi surface may not be correct due to the requirement of a local potential

- Must a Mott insulator- an insulator due to correlations among the electrons - be predicted correctly by the eigenvalues in the exact Kohn-Sham theory?
  No. This follows from the above arguments on a metal that the Fermi surface is not correct in general.

- Are excitation energies given correctly by the eigenvalues of the Kohn-Sham equations?
  No. The eigenvalues are not the true energies for adding or subtracting electrons, nor for neutral excitations

- Is any excitation energy given correctly by an eigenvalue of the Kohn-Sham equations?

Yes. The highest eigenvalue in a finite system must be correct since that state dominates the long-range tail of the density, which is defined to be correct.

- Is it possible to determine excitation energies by any means using the Kohn-Sham theory? Yes. This question is in the spirit of the Hohenberg-Kohn existence proofs. Since the Kohn-Sham density is exact by construction, it follows from the Hohenberg-Kohn theorems that all properties are determined since the entire hamiltonian is determined. Thus there should be some way to use the Kohn-Sham potential and eigenfunctions to determine all excitations exactly, but this requires a theory beyond the naive use of Kohn-Sham eigenvalues. One approach is to use the eigenstates as the basis for a many-body calculation, which is literally done in configuration interaction, Monte Carlo, and many-body perturbation theory calculations. Other formulations incorporate excitations into the Kohn-Sham approach itself, most importantly, time-dependent Kohn-Sham theory.

It has already been stressed before that density functional theory has evolved into today's most widely used method for electronic structure calculations in solids because of the development and the success of practical, approximate and not overly computationally-demanding functionals. In particular, the quantity of crucial importance in the Kohn-Sham approach is the exchange-correlation energy which is expressed as a functional of the density $E_{xc}[n]$. For this reason, the next two sections are devoted to the description of two widespread approximations for this functional: the local density approximation (LDA) and examples of generalized-gradient approximations (GGAs).

11. THE LOCAL SPIN DENSITY APPROXIMATION (LSDA)

Already in their seminal paper, Kohn and Sham pointed out that solids can often be considered as close to the limit of the homogeneous electron gas which we already described in the context of HF theory. In that limit, it is known that the effects of exchange and correlation are local in character, and they proposed making the local density approximation (LDA) (or more generally the local spin density approximation (LSDA)) in which the exchange-correlation energy is simply an integral over all space, with the exchange-correlation energy density at each point assumed to be the same as in a homogeneous electron gas of interacting electrons with that same local density:

$$\begin{aligned} E_{\mathrm{xc}}^{\mathrm{LSDA}}[n^{\uparrow}, n^{\downarrow}] &= \int \mathrm{d}^3 r\, n(\mathbf{r})\, \epsilon_{\mathrm{xc}}^{\mathrm{hom}}(n^{\uparrow}(\mathbf{r}), n^{\downarrow}(\mathbf{r})) \\ &= \int \mathrm{d}^3 r\, n(\mathbf{r}) [\epsilon_{x}^{\mathrm{hom}}(n^{\uparrow}(\mathbf{r}), n^{\downarrow}(\mathbf{r})) + \epsilon_{c}^{\mathrm{hom}}(n^{\uparrow}(\mathbf{r}), n^{\downarrow}(\mathbf{r}))]. \end{aligned} \qquad (11.1)$$

The LSDA can be formulated in terms of either two spin densities $n^{\uparrow}(\vec{r})$ and $n^{\downarrow}(\vec{r})$, or the total density $n(\vec{r})$ and the fractional spin polarization $\xi(\vec{r})$:

$$\zeta(\mathbf{r}) = \frac{n^{\uparrow}(\mathbf{r}) - n^{\downarrow}(\mathbf{r})}{n(\mathbf{r})}. \qquad (11.2)$$

The LSDA is the most general local approximation. For unpolarized systems the LDA is found simply by setting $n^{\uparrow}(\vec{r}) = n^{\downarrow}(\vec{r}) = n(\vec{r})/2$.

Once one has made the local ansatz of the L(S)DA, then all the rest follows. Since the functional $E_{xc}[n^{\uparrow}, n^{\downarrow}]$ is universal, it follows that it is exactly the same as for the homogeneous gas. The only information needed is the exchange-correlation energy of the homogeneous gas as a function of density. Since the exchange energy of the homogeneous gas can be calculated analytically using HF theory (see eq. (5.11)) , the local density approximation simply bows down to fitting numerical correlation energies for the homogeneous gas. A variety of LDA expressions for the correlation energy have been proposed with time, and the most celebrated are summarized below for reference purposes. In all cases, the correlation potential is given by:

$$V_c(r_s) = \epsilon_c(r_s) - \frac{r_s}{3}\frac{d\epsilon_c(r_s)}{dr_s}. \qquad (11.3)$$

where rs is given by Eq. (5.1)

The first quantitative form for the correlation energy of a homogeneous gas was proposed in the 1930s by Wigner, as an interpolation between low- and high-density limits. At low density the electrons form a "Wigner crystal" and the correlation energy is just the electrostatic energy of point charges on the corresponding body- centered cubic lattice. At the time, it was thought that the exchange energy per electron approached a constant in the high-density limit, and Wigner proposed the simple interpolation:

$$\varepsilon_C = -\frac{0.44}{r_S + 7.8} \quad \text{(in atomic units = Hartree)} \qquad (11.4)$$

Correct treatment of correlation confounded many-body theory for decades until the work of Gellmann and Breuckner, who calculated the correlation energy exactly in the high-density limit $r_S \to 0$. For an unpolarized gas the result is:

$$\varepsilon_C(r_S) \to 0.311\ln(r_S) - 0.048 + r_S(A\ln(r_S) + C) + ... \qquad (11.5)$$

where the ln terms are the signature of non-analyticity that causes so much difficulty. At low density the system can be considered a Wigner crystal with zero point motion leading to:

$$\varepsilon_C(r_S) \rightarrow \frac{a_1}{r_S} + \frac{a_2}{{r_S}^{3/2}} + \frac{a_3}{{r_S}^2} + ... \tag{11.6}$$

There has been considerable work in the intervening years, including the well-known form by Hedin-Lundqvist (HL), derived from many-body perturbation theory using the random phase approximation (RPA):

$$\epsilon_c^{\mathrm{HL}}(r_s) = -\frac{Ce^2}{2}\left[(1+x^3)\log\left(1+\frac{1}{x}\right) + \frac{x}{2} - x^2 - \frac{1}{3}\right], \tag{11.7}$$

where A = 21, C = 0.045, and $x = r_S / A$. The correlation potential is:

$$V_c^{\mathrm{HL}}(r_s) = -\frac{Ce^2}{2}\log\left(1+\frac{1}{x}\right), \tag{11.8}$$

The most accurate results for ground state properties are actually found from quantum Monte Carlo (QMC) calculations for interacting many-body systems. These results have been fitted to analytic forms for $\varepsilon_C(r_S)$, leading to two widely used functionals due to Perdew and Zunger (PZ) and Vosko, Wilkes, and Nusiar (VWN), which are very similar quantitatively:

Perdew-Zunger (PZ):

$$\begin{aligned} \epsilon_c^{\mathrm{PZ}}(r_s) &= -0.0480 + 0.0311n(r_s) - m0.0116r_s + 0.0020r_sn(r_s), \qquad r_s < 1 \\ &= -0.1423/(1 + 1.9529\sqrt{r_s} + M0.3334r_s), \qquad r_s > 1. \end{aligned}$$

(11.9)

The expression for V_c^{PZ} is not given here since it is lengthy, but it is straightforward.

Vosko-Wilkes-Nusiar (VWN)

$$\epsilon_c^{\mathrm{VWN}}(r_s) = \frac{Ae^2}{2}\left[\log\left[\frac{y^2}{Y(y)}\right] + \frac{2b}{Q}\tan^{-1}\left(\frac{Q}{2y+b}\right) - \frac{by_0}{Y(y_0)}\left\{\log\left[\frac{(y-y_0)^2}{Y(y)}\right] + \frac{2(b+2y_0)}{Q}\tan^{-1}\left(\frac{Q}{2y+b}\right)\right\}\right]$$

(11.10)

Here
$y = r_s^{1/2}, Y(y) = y^2 + by + c, Q = (4c - b^2)^{1/2}, y_o = -0.104, b = 3.72744, c = 12.935 \text{ and } A = 0.062$.
The corresponding potential can be obtained from Eq. (11.3) with:

$$r_s \frac{d\epsilon_c^{\mathrm{VWN}}(r_s)}{dr_s} = A\frac{e^2}{2}\frac{c(y-y_0) - by_0 y}{(y-y_0)(y^2+by+c)}. \qquad (11.11)$$

The QMC results for the correlation energy $\varepsilon_C(r_S)$ per electron in an unpolarized gas are shown in Fig. 11.1 where they are compared with the Wigner interpolation formula, RPA, and improved many-body calculations of Lindgren and Rosen:

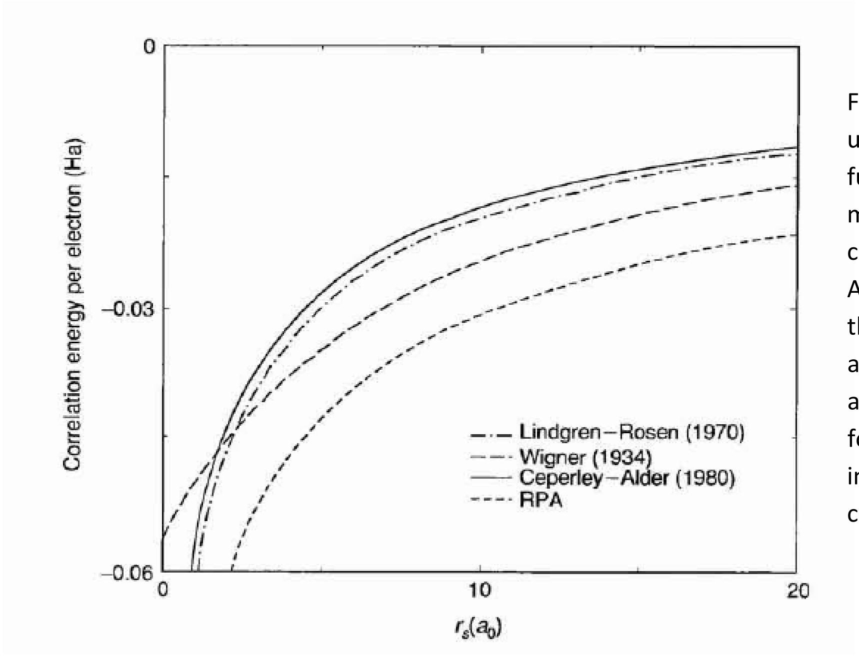

Fig. 11.1: Correlation energy of an unpolarized homogeneous electron gas as a function of the density parameter r_S. The most accurate results available are QMC calculations: the curve labelled ''Ceperley-Alder'' is the work of those authors fitted to the VWN interpolation formula ; the PZ fit is almost identical on this scale. In comparison are shown the Wigner interpolation formula, the HL RPA calculations, and an improved many-body perturbation calculation (Lindgren-Rosen)

One very important result is that for materials at typical solid densities ($r_S \approx 2-6$) the correlation energy is much smaller than the exchange energy; however, at very low densities (large rs) correlation becomes more important and dominates in the regime of the Wigner crystal ($r_S >\approx 80$)

The use of the QMC results in subsequent electronic structure calculations relies upon parameterized analytic forms for $E_c(r_s)$ fitted to the QMC energies calculated at many values of rs, mainly for unpolarized and fully polarized ($n^{\uparrow} = n$) cases, although some calculations have been done at intermediate polarization. The simplest form for the correlation energy as a function of spin polarization is the one made by PZ that correlation varies the same as exchange:

$$\epsilon_c(n,\zeta) = \epsilon_c(n,0) + [\epsilon_c(n,1) - \epsilon_c(n,0)]f_x(\zeta), \tag{11.12}$$

where $f_x(\xi)$ is given by (6.11). The key point is that the formulae fit the data well at typical densities and extrapolate correctly to the high- and low-density limits, (11.5) and (11.6).

As we already mentioned in the beginning of this section, the rationale behind the local approximation is that, for the densities typical of those found in solids, the range of the effects of exchange and correlation is rather short. However, this is not justified by a formal expansion in some small parameter, and one must test the extent to which it works by actual applications. We expect it will be best for solids close to a homogeneous electron gas (like a nearly-free-electron metal) and worst for very inhomogeneous cases, like for the case of atoms where the density must go continuously to zero outside the atom. Among the most obvious faults of the approximation is the spurious self-interaction term. In the Hartree-Fock approximation the unphysical self-term in the Hartree interaction was exactly cancelled by the non-local exchange interaction, as explained in section 4. However, in the local approximation to exchange, the cancellation is only approximate and there remain spurious self-interaction terms that are negligible in the homogeneous gas but large in confined systems such as atoms. Nevertheless, even in very inhomogeneous cases, the LSDA works remarkably well, the main reason being that it approximates the hole particularly well. The degree to which the LSDA is successful has made it useful in its own right, and has stimulated ideas for constructing improved functionals (such as the GGAs described in the next section).

12. GENERALIZED-GRADIENT APPROXIMATIONS (GGAs)

The success of the LSDA has led to the development of various Generalized-gradient approximations (GGAs) with marked improvement over LSDA for many cases. In this section we briefly describe some of the physical ideas that are the foundation for construction of GGAs. The first step beyond the local approximation is the introduction of a functional of the magnitude of the density gradient

$\left|\nabla n^{\sigma}\right|$ as well as the value n at each point. This is called a "gradient expansion approximation" (GEA). The low-order expansion of the exchange and correlation energies is known ; however, the GEA does not lead to consistent improvement over the LSDA, and indeed often yields worse results. The basic problem is that gradients in real materials are so large that the expansion breaks down.

The term generalized-gradient expansion (GGA) denotes a variety of ways proposed for functions that modify the behaviour at large gradients in such a way as to preserve desired properties. It is convenient to define the functional as a generalized form of (11.1):

$$E_{\mathrm{xc}}^{\mathrm{GGA}}[n^{\uparrow},n^{\downarrow}] = \int \mathrm{d}^3 r\, n(\mathbf{r})\epsilon_{\mathrm{xc}}(n^{\uparrow},n^{\downarrow},|\nabla n^{\uparrow}|,|\nabla n^{\downarrow}|,\ldots)$$
$$\equiv \int \mathrm{d}^3 r\, n(\mathbf{r})\epsilon_{x}^{\mathrm{hom}}(n)F_{\mathrm{xc}}(n^{\uparrow},n^{\downarrow},|\nabla n^{\uparrow}|,|\nabla n^{\downarrow}|,\ldots),$$
(12.1)

where F_{xc} is dimensionless and $\varepsilon_x^{\mathrm{hom}}(n)$ is the exchange energy of the unpolarized homogeneous electron gas given by (5.11).

For exchange, it is straightforward to show that there is a "spin-scaling relation":

$$E_x[n^{\uparrow},n^{\downarrow}] = \frac{1}{2}\left[E_x[2n^{\uparrow}] + E_x[2n^{\downarrow}]\right],$$
(12.2)

where $E_x[n]$ is the exchange energy for an unpolarized system of density $n(\vec{r})$. Thus for exchange we need to consider only the spin-unpolarized $F_x(n,|\nabla n|)$. It is natural to work in terms of dimensionless reduced density gradients of m-th order that can be defined by:

$$s_m = \frac{|\nabla^m n|}{(2k_F)^m n} = \frac{|\nabla^m n|}{2^m(3\pi^2)^{m/3}(n)^{(1+m/3)}}.$$ (12.3)

Since $k_F = 3(2\pi/3)^{1/3} r_S^{-1}$, s_m is proportional to the mth-order fractional variation in density normalized to the average distance between electrons r_s. The explicit expression for the first gradients can be written

$$s_1 \equiv s = \frac{|\nabla n|}{(2k_F)n} = \frac{|\nabla r_s|}{2(2\pi/3)^{1/3} r_s}.$$ (12.4)

The lowest order terms in the expansion of F_x have been calculated analytically:

$$F_x = 1 + \frac{10}{81} s_1^2 + \frac{146}{2025} s_2^2 + \cdots \quad (12.5)$$

Numerous forms for $F_x(n, s)$, where $s = s_1$, have been proposed. These can be illustrated by the three widely used forms of Becke (B88), Perdew and Wang (PW91), and Perdew, Burke, and Enzerhof (PBE). In Fig. 12.1, we compare the factors F_x for these three approximations.

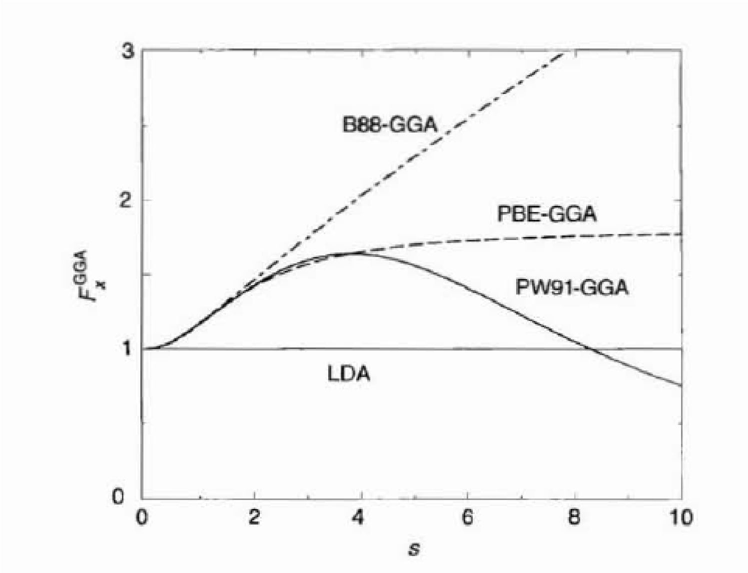

Fig 12.1: Exchange enhancement factor F_x as a function of the dimensionless density gradient *s* for various GGAs. Note that in the relevant range for most materials, $0 < s <\sim 3$, the magnitude of the exchange is increased by a factor ≈1.3-1.6

Most other approximations lead to an Fx that falls between B88 and PBE, so the qualitative results obtained by employing other functionals can be appreciated from the behavior of these functionals. As shown in Fig. 8.1, one can divide the GGA into two regions: (i) small s ($0 < s <\sim 3$) and (ii) large s ($s >\sim 3$) regions.

In region (i), which is relevant for most physical applications, different $F_x s$ have nearly identical shapes, which is the reason that different GGAs give similar improvement for many conventional systems with small density gradient contributions. Most importantly $F_x \geq 1$, so all the GGAs lead to an exchange energy lower than the LDA. Typically, there are more rapidly varying density regions in atoms than in condensed matter, which leads to greater lowering of the exchange energy in atoms than in molecules and solids. This results in the reduction of binding energy, correcting the LDA overbinding, and improving agreement with experiment, which is one of the most important characteristics of present GGAs.

In region (ii), the different limiting behaviors of $F_x s$ result from choosing different physical conditions for $s \to \infty$. In B88-GGA, $F_x^{B88-GGA}(s) \approx s/\ln(s)$ was chosen to give the correct exchange energy density ($\varepsilon_x \to -1/2r$). In PW91-GGA, choosing $F_x^{PW91-GGA}(s) \approx s^{-1/2}$ satisfies the Lieb-Oxford bound and the non-uniform scaling condition that must be satisfied if the functional is to have the proper limit for a thin layer or a line. In PBE-GGA, the non-uniform scaling condition was dropped in favour of a simplified parameterization with $F_x^{PBE-GGA}(s) \sim const$. The fact that different physical conditions lead to very different behaviors of $F_x s$ in region (ii) not only reflects the lack of knowledge of the large density gradient regions but also an inherent difficulty of the density gradient expansion in this region: even if one form of GGA somehow gives the correct result for a certain physical property while others fail, it is not guaranteed that the form is superior for other properties in which different physical conditions prevail.

Correlation is more difficult to cast in terms of a functional, but its contribution to the total energy is typically much smaller than the exchange. The lowest order gradient expansion at high density has been determined to be:

$$F_c = \frac{\epsilon_c^{\mathrm{LDA}}(n)}{\epsilon_x^{\mathrm{LDA}}(n)}(1 - 0.219,51 s_1^2 + \cdots). \qquad (12.6)$$

For large density gradients the magnitude of correlation energy decreases and vanishes as $s_1 \to \infty$. This decrease can be qualitatively understood since large gradients are associated with strong confining potentials that increase level spacings and reduce the effect of interactions compared to the independent-electron terms. As an example of a GGA for correlation, Fig. 12.2 shows the correlation enhancement factor $F_c^{PBE-GGA}$ for the PBE functional, which is almost identical to that for the PW91-GGA.

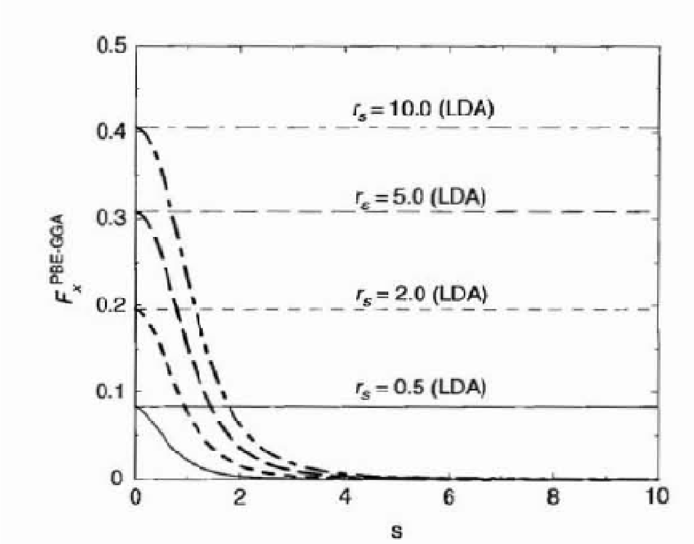

Fig 12.2: Correlation enhancement factor F_c at different electron densities r_s as a function of the dimensionless density gradient *s* for the PBE functional. Other functionals are qualitatively similar

The PBE form is probably the simplest GGA functional, and hence we give it as an explicit example. The PBE functional for exchange is given by a simple form for the enhancement factor $F_X(s)$. The form is chosen with $F_x(0) = 1$ (so that the local approximation is recovered) and F_x → constant at large s:

$$F_x(s) = 1 + \kappa - \kappa/(1 + \mu s^2/\kappa), \tag{12.7}$$

where $\kappa = 0.804$ is chosen to satisfy the Lieb-Oxford bound. The value of $\mu = 0.21951$ is chosen to recover the linear response form of the local approximation, i.e. it is chosen to cancel the term from the correlation. This may seem strange, but it is done to agree better with quantum Monte Carlo calculations. This choice violates the known expansion at low s given in Eq. (12.5), with the rationale of better fitting the entire functional.

The form for correlation is expressed as the local correlation plus an additive term both of which depend upon the gradients and the spin polarization. The form chosen to satisfy several conditions is:

$$E_c^{\text{GGA-PBE}}[n^\uparrow, n^\downarrow] = \int \mathrm{d}^3 r \, n \left[\epsilon_c^{\text{hom}}(r_s, \zeta) + H(r_s, \zeta, t)\right], \tag{12.8}$$

where $\zeta = \left(n^\uparrow - n^\downarrow\right)/n$ is the spin polarization, r_S is the local value of the density parameter, and t is a dimensionless gradient $t = |\nabla n|/(2\phi k_{TF} n)$. Here $\phi = \left((1+\zeta)^{2/3} + (1-\xi)^{2/3}\right)/2$ and t is scaled by the screening Thomas-Fermi wavevector k_{TF} rather than k_F . The final form is:

$$H = \frac{e^2}{a_0} \gamma \phi^3 \log\left(1 + \frac{\beta}{\gamma} t^2 \frac{1 + At^2}{1 + At^2 + A^2 t^4}\right) \tag{12.9}$$

The function A is given by

$$A = \frac{\beta}{\gamma}\left[\exp\left(\frac{-\epsilon_c^{\text{hom}}}{\gamma \phi^3 \frac{e^2}{a_0}}\right) - 1\right]^{-1} \tag{12.10}$$

13. LDA AND GGA EXPRESSIONS FOR THE EXCHANGE-CORRELATION POTENTIAL

The part of the Kohn-Sham potential due to exchange and correlation $V_{xc}^{\sigma}(\vec{r})$ is defined by the functional derivative in (10.17). The potential can be expressed more directly for LDA and GGA functionals, (11.1) and (12.1), since they are expressed in terms of functions (not functionals) of the local density of each spin $n(\vec{r},\sigma)$ and its gradients at point r.

In the LDA, the form is very simple,

$$\delta E_{\mathrm{xc}}[n] = \sum_{\sigma} \int d\mathbf{r} \left[\epsilon_{\mathrm{xc}}^{\mathrm{hom}} + n \frac{\partial \epsilon_{\mathrm{xc}}^{\mathrm{hom}}}{\partial n^{\sigma}} \right]_{\mathbf{r},\sigma} \delta n(\mathbf{r},\sigma), \qquad (13.1)$$

so that the potential,

$$V_{\mathrm{xc}}^{\sigma}(\mathbf{r}) = \left[\epsilon_{\mathrm{xc}}^{\mathrm{hom}} + n \frac{\partial \epsilon_{\mathrm{xc}}^{\mathrm{hom}}}{\partial n^{\sigma}} \right]_{\mathbf{r},\sigma}, \qquad (13.2)$$

involves only ordinary derivatives of $\varepsilon_{xc}^{\mathrm{hom}}(n^{\uparrow},n^{\downarrow})$. Here the subscript $\vec{r},\sigma$ means the quantities in square brackets are evaluated for $n^{\sigma} = n(\vec{r},\sigma)$. The LDA exchange terms are particularly simple: since $\varepsilon_{x}^{\mathrm{hom}}(n^{\sigma})$ scales as $\left(n^{\sigma}\right)^{-1/3}$ it follows that:

$$V_{x}^{\sigma}(\mathbf{r}) = \frac{4}{3} \epsilon_{x}^{\mathrm{hom}}(n(\mathbf{r},\sigma)). \qquad (13.3)$$

In the GGA one can identify the potential by finding the change $\delta E_{xc}[n]$ to linear order in δn and $\delta \nabla n = \nabla \delta n$:

$$\delta E_{\mathrm{xc}}[n] = \sum_{\sigma} \int d\mathbf{r} \left[\epsilon_{\mathrm{xc}} + n \frac{\partial \epsilon_{\mathrm{xc}}}{\partial n^{\sigma}} + n \frac{\partial \epsilon_{\mathrm{xc}}}{\partial \nabla n^{\sigma}} \nabla \right]_{\mathbf{r},\sigma} \delta n(\mathbf{r},\sigma). \qquad (13.4)$$

The term in square brackets could be interpreted as the potential; however, a close inspection reveals that it does not have the form of a local potential because of the last term, which is a differential operator. There are three main approaches to handling the last term. The first is to find a local $V_{xc}^{\sigma}(\vec{r})$ by partial integration (see App. A) of the last term in the square brackets to give;

$$V_{\mathrm{xc}}^{\sigma}(\mathbf{r}) = \left[\epsilon_{\mathrm{xc}} + n\frac{\partial\epsilon_{\mathrm{xc}}}{\partial n^{\sigma}} - \nabla\left(n\frac{\partial\epsilon_{\mathrm{xc}}}{\partial\nabla n^{\sigma}}\right)\right]_{\mathbf{r},\sigma} \qquad (13.5)$$

This is the form most commonly used; however, it has the disadvantage that it requires higher derivatives of the density that can lead to pathological potentials and numerical difficulties, for example, near the nucleus or in the outer regions of atoms, where the density is rapidly varying or is very small.

A second approach is to use the operator form of $V_{xc}^{\sigma}(\vec{r})$ in (13.4) directly by modifying the Kohn Sham equations. Using the fact that the density can be written in terms of the wavefunctions ψ_i , the matrix elements of the operator can be written (for simplicity we omit the variables $\vec{r}$ and σ)

$$\langle\psi_j|\hat{V}_{\mathrm{xc}}|\psi_i\rangle = \int\left[\tilde{V}_{\mathrm{xc}}\psi_j^*\psi_i + \psi_j^*\mathbf{V}_{\mathrm{xc}}\cdot\nabla\psi_i + (\mathbf{V}_{\mathrm{xc}}\cdot\nabla\psi_j^*)\psi_i\right], \qquad (13.6)$$

where $\widetilde{V}_{xc} = \varepsilon_{xc} + n\left(\partial\varepsilon_{xc}/\partial n\right)$ and $\mathbf{V}_{\mathrm{xc}} = n\left(\partial\varepsilon_{xc}/\partial\nabla n\right)$. This form is numerically more stable, but however it requires inclusion of the additional vector operator in the Kohn-Sham equation, which may significantly increase the computational cost.

Finally, a different approach is to treat E_{XC} strictly as a function of the density, with the gradient terms defined by an operational definition in terms of the density. Then (13.4) can be written using the chain rule as:

$$\begin{aligned}\delta E_{\mathrm{xc}}[n] = {} & \sum_{\sigma}\int d\mathbf{r}\left[\epsilon_{\mathrm{xc}} + n\frac{\partial\epsilon_{\mathrm{xc}}}{\partial n^{\sigma}}\right]_{\mathbf{r},\sigma}\delta n(\mathbf{r},\sigma) \\ & + \sum_{\sigma}\int\int d\mathbf{r}d\mathbf{r}' n(\mathbf{r})\left[\frac{\partial\epsilon_{\mathrm{xc}}}{\partial\nabla n^{\sigma}}\right]_{\mathbf{r},\sigma}\frac{\delta\nabla n(\mathbf{r}')}{\delta n(\mathbf{r})}\delta n(\mathbf{r},\sigma),\end{aligned} \qquad (13.7)$$

where $\left(\delta\nabla n(\vec{r}\,')/\delta n(\vec{r})\right)$ denotes a functional derivative (which is independent of spin). For example, on a grid, the density for either spin is given only at grid points $n(\vec{r}_m)$ and the gradient at grid point r_m, $\nabla n(\overrightarrow{r_m})$, is determined by the density by a formula of the form:

$$\nabla n(\mathbf{r}_m) = \sum_{m'} \mathbf{C}_{m-m'} n(\mathbf{r}_{m'}), \qquad (13.8)$$

so that

$$\frac{\delta \nabla n(\mathbf{r}_m)}{\delta n(\mathbf{r}_{m'})} \rightarrow \frac{\partial \nabla n(\mathbf{r}_m)}{\partial n(\mathbf{r}_{m'})} = \mathbf{C}_{m-m'}. \qquad (13.9)$$

(Note that each $C_{m''} = \left\{ C^x_{m''}, C^y_{m''}, C^z_{m''} \right\}$ is a vector in the space coordinates). In a finite difference method, the coefficients $C_{m''}$ are nonzero for some finite range; in a Fourier transform method, the $C_{m''}$ follow simply by noting that

$$\nabla n(\mathbf{r}_m) = \sum_{\mathbf{G}} i\mathbf{G} n(\mathbf{G}) \mathrm{e}^{\mathrm{i}\mathbf{G}\cdot\mathbf{r}_m} = \frac{1}{N} \sum_{\mathbf{G},m'} i\mathbf{G} \mathrm{e}^{\mathrm{i}\mathbf{G}\cdot(\mathbf{r_m}-\mathbf{r_{m'}})} n(\mathbf{r}_{m'}). \qquad (13.10)$$

Finally, varying $n(r_m, \sigma)$ in the expression for E_{xc} and using the chain rule leads to

$$V^{\sigma}_{\mathrm{xc}}(\mathbf{r}_m) = \left[\epsilon_{\mathrm{xc}} + n \frac{\partial \epsilon_{\mathrm{xc}}}{\partial n} \right]_{\mathbf{r}_m, \sigma} + \sum_{m'} \left[n \frac{\partial \epsilon_{\mathrm{xc}}}{\partial |\nabla n|} \frac{\nabla n}{|\nabla n|} \right]_{\mathbf{r}_{m'}, \sigma} \mathbf{C}_{m'-m}. \qquad (13.11)$$

This form reduces the numerical problems associated with (13.5) without a vector operator as in (13.6). Note that $V^{\sigma}_{xc}(\overrightarrow{r_m})$ is a non-local function of $n(r_m, \sigma)$, the form of which depends upon the way the derivative is calculated. This is an advantage in actual calculations because it ensures consistency between E_{xc} and V_{xc}.

14. SOLVING THE KOHN-SHAM EQUATIONS

The solution procedure for the Kohn-Sham equations derived in Sec. 10 are summarized in the flow chart in Fig. 14.1.

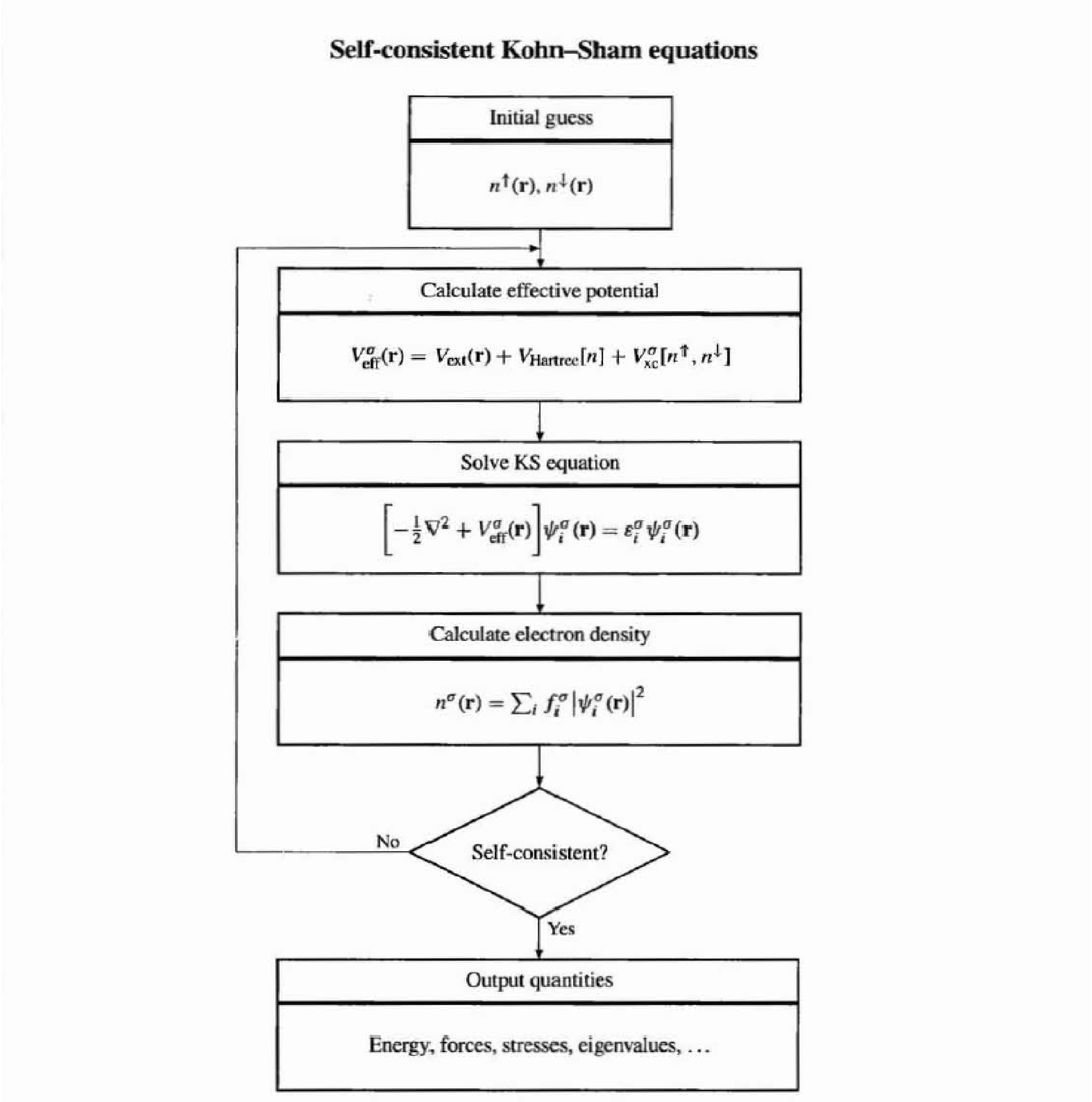

Fig 14.1: Schematic representation of the self-consistent loop for solution of the KS equations. In general, one must iterate two such loops simultaneously for the two spins, with the potential for each spin a functional of the density of both spins.

The Kohn-Sham equations are a set of Schroedinger-like independent-particle equations which must be solved subject to the condition that the effective potential $V_{eff}^{\sigma}(\vec{r})$ and the density $n(\vec{r},\sigma)$ are consistent. The explicit reference to spin will be dropped, except where needed, and notation V_{eff}

and n will be assumed to designate both space and spin dependence. An actual calculation utilizes a numerical procedure that successively changes V_{eff} and n to approach the self-consistent solution. The computationally intensive step in Fig. 13.1 is "solve KS equation" for a given potential V_{eff}. Here this step is considered a "black box" that uniquely solves the equations for a given input V^{in} to determine an output density n^{out}, i.e. $V^{in} \rightarrow n^{out}$. Conversely, for a given form of the xc functional, any density n determines a potential V_{eff}, as shown in the second box.

The problem is that, except at the exact solution, the input and output potentials and densities do not agree. To arrive at the solution one defines operationally a new potential $n^{out} \rightarrow V^{new}$, which can then start a new cycle with V^{new} as the new input potential V^{in}. Clearly, this procedure s can be made into the following iterative progression:

$$V_i \rightarrow n_i \rightarrow V_{i+1} \rightarrow n_{i+1} \rightarrow \ldots, \tag{14.1}$$

where i labels the step in the iteration. The progression converges with a judicious choice of the new potential in terms of the potential or density found at the previous step (or steps).

Methods for reaching self-consistency are described in section 16. However, it is first best to probe the nature of various possible total energy functionals. The expressions are needed for the final calculation of the energy and, in addition, the behavior of any of the functionals near the correct solution provides the basis for analysis of the convergence characteristics using that functional.

15. TOTAL ENERGY FUNCTIONALS

The subject of this section is the behaviour of various functionals, all of which have the same minimum energy solution of the Kohn-Sham equations, but behave differently away from the minimum. In terms of the Kohn-Sham equations, this means the behaviour as a functional of the difference of input and output quantities $\Delta V = V^{out} - V^{in}$ and $\Delta n = n^{out} - n^{in}$, where n^{out} is the resulting density from solving the KS equation with the potential V^{in}. It is essential to utilize correct variational expressions in order to have the desired variational properties.

We repeat here the original expression for the Kohn-Sham energy functional for convenience, with all the potential terms grouped together to define $E_{pot}[n]$:

$$\begin{aligned} E_{\mathrm{KS}} &= T_s[n] + E_{\mathrm{pot}}[n], \\ E_{\mathrm{pot}}[n] &= \int d\mathbf{r} V_{\mathrm{ext}}(\mathbf{r}) n(\mathbf{r}) + E_{\mathrm{Hartree}}[n] + E_{II} + E_{\mathrm{xc}}[n]. \end{aligned} \tag{15.1}$$

The first three terms on the right-hand side of the second equation together form a neutral grouping equal to the classical Coulomb interaction E^{CC} . Since the eigenvalues (the Lagrange parameter) of the Kohn-Sham equations are given by:

$$\varepsilon_i^\sigma = \langle \psi_i^\sigma | H_{KS}^\sigma | \psi_i^\sigma \rangle, \tag{15.2}$$

the kinetic energy can be expressed as

$$T_s = E_s - \sum_\sigma \int \mathrm{d}\mathbf{r}\; V^{\sigma,in}(\mathbf{r}) n^{\mathrm{out}}(\mathbf{r},\sigma), \tag{15.3}$$

where E_s is simply the sum of all the eigenvalues over all spins:

$$E_s = \sum_\sigma \sum_{i=1}^{N^\sigma} \varepsilon_i^\sigma . \tag{15.4}$$

The advantages of this formulation are that the eigenvalues are available in actual calculations and, furthermore, E_S in (15.4) is itself a functional.

Although the Kohn-Sham energy (15.1) is, in principle, a functional of the density, it is operationally a functional of the input potential $E_{KS}[V^{in}]$, as indicated in the flow chart (Fig. 14.1). (Note that we use V here to denote the potential for each spin, $V^\sigma(\vec{r})$). At any stage of a Kohn-Sham calculation when the energy is not at the minimum, V^{in} determines all the quantities in the energy. This is clearly shown if we write E_{KS} from (15.1) as:

$$E_{\mathrm{KS}}[V^{\mathrm{in}}] = E_s[V^{\mathrm{in}}] - \sum_\sigma \int \mathrm{d}\mathbf{r}\; V^{\sigma,in}(\mathbf{r}) n^{\mathrm{out}}(\mathbf{r},\sigma) + E_{\mathrm{pot}}[n^{\mathrm{out}}], \tag{15.5}$$

where the first two terms on the right-hand side are a convenient way of calculating the independent-particle kinetic energy as in (15.3), and E_{pot} is the sum of potential terms given in (15.1) evaluated for $n = n^{out}$. Since E_S is the sum of eigenvalues, (15.4), and $n^{out}(\vec{r},\sigma)$ is the output density, each determined directly by the potential V^{in} , clearly the energy E_{KS} is itself a functional of V^{in} .

The solution of the Kohn-Sham equations is for the potential V^{in} that minimizes the energy, (15.5). Then $V^{in} = V_{KS}$, the output density n^{out} is the ground state density n^o , and the potential and density are consistent with the relation in (10.12). The functional $E_{KS}[V^{in}]$ is variational and all other potentials lead to KS energies that are higher by an amount that is quadratic in the error $V^{in} - V_{KS}$. Near the minimum energy solution, the error in the energy must also be quadratic in the error in the density $\delta n = n^{out} - n^{o}$, so that:

$$E_{\mathrm{KS}}[V^{\mathrm{in}}] = E_{\mathrm{KS}}[V_{\mathrm{KS}}] + \frac{1}{2}\sum_{\sigma,\sigma'}\int \mathrm{d}\mathbf{r}\mathrm{d}\mathbf{r}' \left[\frac{\delta^2 E_{\mathrm{KS}}}{\delta n(\mathbf{r},\sigma)\delta n(\mathbf{r}',\sigma')}\right]_{n^0} \delta n(\mathbf{r},\sigma)\delta n(\mathbf{r}',\sigma'), \tag{15.6}$$

where the second term is always positive.

One can choose different expressions for the total energy functional that are given explicitly in terms of the density. The functional, known as the Harris-Weinert-Foulkes (HWF) functional, is cast in terms of the density n^{in} that, via (10.12), determines the input potential $V[n^{in}] \equiv V_{n^{in}}$. This in turn leads directly to the sum of eigenvalues, the first term on the right-hand side of (15.5). The energy is then defined by evaluating the functional $E_{pot}[n^{in}]$ in (15.1) in terms of the chosen input density $n^{in}(\vec{r},\sigma)$ (instead of the output density $n^{out}(\vec{r},\sigma)$ as in the Kohn-Sham functional):

$$E_{HWF}[n^{\mathrm{in}}] \equiv E_s[V_{n^{\mathrm{in}}}] - \sum_{\sigma}\int \mathrm{d}\mathbf{r}\; V^{\sigma}_{n^{\mathrm{in}}}(\mathbf{r}) n^{\mathrm{in}}(\mathbf{r},\sigma) + E_{\mathrm{pot}}[n^{\mathrm{in}}]. \tag{15.7}$$

The stationary properties of this functional can be understood straightforwardly. For a given input density n^{in} and potential $V_{n^{in}}$, the difference in the two expressions for the energy involves only the potential terms:

$$\begin{aligned} E_{\mathrm{KS}}[V^{\mathrm{in}}] - E_{HWF}[n^{\mathrm{in}}] = &\sum_{\sigma}\int \mathrm{d}\mathbf{r}\; V^{\sigma}_{n^{\mathrm{in}}}(\mathbf{r})\left[n^{\mathrm{out}}(\mathbf{r},\sigma) - n^{\mathrm{in}}(\mathbf{r},\sigma)\right] \\ &+ \left[E_{\mathrm{pot}}[n^{\mathrm{out}}] - E_{\mathrm{pot}}[n^{\mathrm{in}}]\right]. \end{aligned} \tag{15.8}$$

Near the correct solution where $\Delta n = n^{out} - n^{in}$ is small, one can expand the difference in (15.8) in powers of Δn . The linear terms cancel (which follows from the fact that $V^{\sigma}_{n^{in}}(\vec{r}) = \left[\delta E_{pot} \big/ \left(\delta n(\vec{r},\sigma)\right)\right]_{n^{in}}$) so that the lowest order terms are:

$$E_{\mathrm{KS}}[V^{\mathrm{in}}] - E_{HWF}[n^{\mathrm{in}}] \approx \frac{1}{2}\sum_{\sigma,\sigma'}\int \mathrm{d}\mathbf{r}\mathrm{d}\mathbf{r}' K(\mathbf{r},\sigma;\mathbf{r}',\sigma')_{n^{\mathrm{in}}} \Delta n(\mathbf{r},\sigma)\Delta n(\mathbf{r}',\sigma'), \tag{15.9}$$

where the kernel K is defined to be :

$$K(\mathbf{r},\sigma;\mathbf{r}',\sigma') \equiv \frac{\delta^2 E_{\mathrm{Hxc}}[n]}{\delta n(\mathbf{r},\sigma)\delta n(\mathbf{r}',\sigma')} = \frac{1}{|\mathbf{r}-\mathbf{r}'|}\delta_{\sigma,\sigma'} + \frac{\delta^2 E_{\mathrm{xc}}[n]}{\delta n(\mathbf{r},\sigma)\delta n(\mathbf{r}',\sigma')}, \tag{15.10}$$

evaluated for $n = n^{in}$ (Note that K has been defined in terms of $E_{Hxc}[n] \equiv E_{Hartree}[n] + E_{xc}[n]$; the other terms in $E_{pot}[n]$ do not contribute since they are constant or linear in n.) Since the differences in the energies are quadratic in the errors in the density, it follows that at the exact solution where $\Delta n(\vec{r},\sigma) = 0$, the HWF functional equals the usual Kohn-Sham energy and it is stationary. However, it is not variational, which can be seen from (15.9). Since the kernel K tends to be positive, then $E_{HWF}[n^{in}]$ is lower than $E_{KS}[V^{in}]$. Thus, even though $E_{KS}[V^{in}]$ is always above the Kohn-Sham ground-state energy (or equal at the exact solution), $E_{HWF}[n^{in}]$ may be lower by an amount that is second order in the error $\Delta n(\vec{r},\sigma)$.

The primary advantage of the explicit HWF functional of the density (15.7) is that, for densities near the correct solution, it can accurately approximate the true Kohn-Sham ground state energy. In particular, it is often an excellent approximation to stop the calculation after one calculation of eigenvalues with no self-consistency: in this case one does not even need to calculate the output density. This approach is remarkably successful if $n(\vec{r})$ is approximated by a sum of atomic densities. For this reason, In a full self-consistent calculation the HWF functional (15.7) is useful at each step of the iteration in Fig. 14.1. It is now standard to calculate both KS and HWF energies, (15.5) and (15.7), at each step in the iteration. It is also very useful to calculate both energies and treat the difference as a measure of the lack of self-consistency during a calculation.

It is also possible to define functionals of the density and potential varied independently, thus effectively combining the KS and HWF functionals together. We will denote n and V by n^{in} and V^{in} to emphasize that both are independent input functions. The expression is exactly the same as (15.7), except that V^{in} is regarded as an independent function so that the expression can be written:

$$E[V^{\mathrm{in}}, n^{\mathrm{in}}] = E_s[V^{\mathrm{in}}] - \sum_{\sigma} \int V^{\sigma,\mathrm{in}}(\mathbf{r}) n^{\mathrm{in}}(\mathbf{r},\sigma)\mathrm{d}\mathbf{r} + E_{\mathrm{pot}}[n^{\mathrm{in}}]. \tag{15.11}$$

The first term is solely a functional of V^{in}, the last term is a functional only of n^{in}, and the only coupling of V^{in} and n^{in} is through the simple bilinear second term. The properties of the functional can be seen clearly. Considering variations around any V^{in} and n^{in}, to linear order:

$$\delta E[V^{\mathrm{in}}, n^{\mathrm{in}}] = \sum_{\sigma} \int \left[V^{\sigma}_{n^{\mathrm{in}}}(\mathbf{r}) - V^{\sigma,\mathrm{in}}(\mathbf{r}) \right] \delta n(\mathbf{r}, \sigma) \mathrm{d}\mathbf{r} + \sum_{\sigma} \int \left[n^{\mathrm{out}}_{V^{\mathrm{in}}}(\mathbf{r}, \sigma) - n^{\mathrm{in}}(\mathbf{r}, \sigma) \right] \delta V^{\sigma}(\mathbf{r}) \mathrm{d}\mathbf{r}, \tag{15.12}$$

where $V^{\sigma}_{n^{in}}(\vec{r}) = \left[\delta E_{pot} \big/ \left(\delta n(\vec{r},\sigma) \right) \right]_{n^{in}}$ is the potential determined by the input density (as used in (15.7)) and $n^{out}_{V^{in}}(\vec{r},\sigma)$ is the output density determined by the potential V^{in} (as used in (15.5). Since the terms in brackets vanish at self-consistency, the functional is stationary and the value equals the Kohn-Sham energy $E_{KS}[V^{KS}]$.

16. ACHIEVING SELF-CONSISTENCY

A key problem is the choice of procedure for updating the potential V^{σ} or the density n^{σ} in each loop of the Kohn-Sham equations illustrated in Fig. 14.1. Obviously one can vary either V^{σ} or n^{σ}, but it is simpler to describe in terms of n^{σ}, which is unique, whereas V^{σ} is subject to shift by a constant. (The spin index σ is omitted below for simplicity)

The simplest approach is linear mixing, estimating an improved density input n^{in}_{i+1} at step $i+1$ as a fixed linear combination of n^{in}_{i} and n^{out}_{i} at step i:

$$n^{\mathrm{in}}_{i+1} = \alpha n^{\mathrm{out}}_{i} + (1-\alpha) n^{\mathrm{in}}_{i} = n^{\mathrm{in}}_{i} + \alpha (n^{\mathrm{out}}_{i} - n^{\mathrm{in}}_{i}). \tag{16.1}$$

This is the best choice in the absence of other information and is essentially moving in an approximate "steepest descent" direction for minimizing the energy.

Why cannot one simply take the output density at one step as the input to the next? What are the limits on α? How can one do better? The answers lie in linear analysis of the behavior near the minimum. As in (15.6), let us define the deviation from the correct density to be $\delta n \equiv n - n_{KS}$ at any step in the iteration. Then near the solution, the error in the output density to linear order in the error in the input is given by:

$$\delta n^{\mathrm{out}}[n^{\mathrm{in}}] = n^{\mathrm{out}} - n_{\mathrm{KS}} = (\tilde{\chi} + 1)(n^{\mathrm{in}} - n_{\mathrm{KS}}),$$

where

$$\tilde{\chi} + 1 = \frac{\delta n^{\mathrm{out}}}{\delta n^{\mathrm{in}}} = \frac{\delta n^{\mathrm{out}}}{\delta V^{\mathrm{in}}} \frac{\delta V^{\mathrm{in}}}{\delta n^{\mathrm{in}}}. \tag{16.2}$$

Here $\delta V^{in} / \delta n^{in}$ is K defined in (15.10). Thus the needed function $\tilde{\chi}$ can be calculated and is closely related to other uses of response functions. The best choice for the new density is of course one that would make the error zero. i.e. $n_{i+1}^{in} = n_{KS}$. Since n_i^{out} and n_i^{in} are known from step i, if $\tilde{\chi}$ is also known, then (16.2) can be solved for n_{KS} :

$$n_{\mathrm{KS}} = n_i^{\mathrm{in}} - \tilde{\chi}^{-1}\left(n_i^{\mathrm{out}} - n_i^{\mathrm{in}}\right). \tag{16.3}$$

If (9.23) were exact, this would be the answer and the iterations could stop; since it is not exact, this only gives the best input for the next iteration.

Although (16.3) is a more complex integral equation, it bears a strong resemblance to the linear-mixing equation (16.1). If we resolve the response function $\tilde{\chi}$ into eigenfunctions $\tilde{\chi}(\vec{r}, \vec{r}\,') = \sum_m \chi_m f_m(\vec{r}) f_m(\vec{r}\,')$, the eigenvalues χ_m give the optimal α for the change in density resolved into the density eigenvectors $f_m(\vec{r})$. Furthermore, the radius of convergence of the linear-mixing scheme is determined by the maximum eigenvalue $\tilde{\chi}_{\max}^{-1} = 1 / \tilde{\chi}_{\min}$ of the matrix $\tilde{\chi}^{-1}$. If a constant α is used, it is straightforward to show that the maximum error at iteration i varies as $\left(1 - \alpha \tilde{\chi}_{\max}^{-1}\right)^i$, so that the iterations converge only if $\alpha < 2 / \tilde{\chi}_{\max}^{-1} = 2 \tilde{\chi}_{\min}$.

Physically, the response of the system is a measure of the polarizability. Linear mixing with large α works well for strongly bound, rigid systems, such as regions near atom cores. However, convergence can be very difficult to achieve for "soft cases." for which metal surfaces are an especially difficult example.

A. MATHEMATICAL APPENDIX[6]

The difference between a function f(x) and a functional F[f] is that a function is defined to be a mapping of a variable x to a result (a number) f(x), whereas a functional is a mapping of an entire function f to a resulting number F[f] (in simple words, a function of a function). The functional F[f], denoted by square brackets, depends upon the function f over its range of definition f(x) in terms of its argument x. Here we describe some basic properties related to the functionals and their use in density functional theory

To illustrate functionals F[f] we first consider two simple examples:

- A definite integral of $w(x)\, f(x)$, where w(x) is some fixed weighting function.

$$I_w[f] = \int_{x_{\min}}^{x_{\max}} w(x) f(x) \mathrm{d}x. \qquad (17.1)$$

- The integral of $\left(f(x)\right)^{\alpha}$ where α is an arbitrary power:

$$I_\alpha[f] = \int_{x_{\min}}^{x_{\max}} (f(x))^\alpha \mathrm{d}x. \qquad (17.2)$$

A functional derivative is defined by a variation of the functional

$$\delta F[f] = F[f+\delta f] - F[f] = \int_{x_{\min}}^{x_{\max}} \frac{\delta F}{\delta f(x)} \delta f(x) \mathrm{d}x, \qquad (17.3)$$

where the quantity $\delta F / \delta f(x)$ is the functional derivative of F with respect to variation of f(x) at the point x. In Eq. (17.1), the fact that the functional is linear in f(x) leads to a simple result for the functional derivative:

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[6] These notes are intended to provide a very concise overview of the theory of functionals and of their use in the context of Density Functional Theory. For a complete explanation, see for example chapter 22 of ''Mathematical Methods for Physics and Engineering'' by KF Riley, MP Hobson, SJ Bence (2nd Edition, Cambridge University Press), or any other general textbook on Mathematical Methods.

$$\frac{\delta I_w}{\delta f(x)} = w(x). \quad (17.4)$$

The second example of a non-linear functional is of the form needed to minimize the Thomas-Fermi expression, Eq. (8.4):

$$\frac{\delta I_\alpha}{\delta f(x)} = \alpha (f(x))^{\alpha - 1}, \quad (17.5)$$

following the same rules as normal differentiation. In general, however, the functional derivative at point x depends also upon the function f(x) at all other points. Clearly, the definition can be extended to many variables and functions F[f1,f2, ...].

In Kohn-Sham density functional theory, the potential, Eq. (10.12), is a sum of functional derivatives. The external term has the linear form of Eq. (17.1); the Hartree term is also simple since it is bilinear; and $V_{xc}^{\sigma}(\vec{r})$ is found by varying the more complex functional having the form:

$$E_{\mathrm{xc}}[n] = \int n(\mathbf{r}) \epsilon_{\mathrm{xc}}(n(\mathbf{r}), |\nabla n(\mathbf{r})|) \mathrm{d}\mathbf{r}. \quad (17.6)$$

Variations of the gradient terms can be illustrated by the general form:

$$I[n] = \int g(f(\mathbf{r}), |\nabla f(\mathbf{r})|) \mathrm{d}\mathbf{r}, \quad (17.7)$$

so that varying the function f leads to:

$$\delta I[g, f] = \int \left[\frac{\delta g}{\delta f} \delta f(\mathbf{r}) + \frac{\delta g}{\delta |\nabla f|} \delta |\nabla f(\mathbf{r})| \right] \mathrm{d}\mathbf{r}. \quad (17.8)$$

Now using:

$$\delta|\nabla f(\mathbf{r})| = \delta\nabla f(\mathbf{r})\cdot\frac{\nabla f(\mathbf{r})}{|\nabla f(\mathbf{r})|} = \frac{\nabla f(\mathbf{r})}{|\nabla f(\mathbf{r})|}\cdot\nabla[\delta f(\mathbf{r})] \qquad (17.9)$$

and integrating by parts, one finds a standard form of variations of gradients:

$$\delta I[g, f] = \int \left\{ \frac{\delta g}{\delta f} - \nabla\cdot\left[\frac{\delta \mathbf{g}}{\delta|\nabla \mathbf{f}|}\frac{\nabla\mathbf{f}(\mathbf{r})}{|\nabla\mathbf{f}(\mathbf{r})|}\right]\right\}\delta f(\mathbf{r})d\mathbf{r}. \qquad (17.10)$$

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