Advanced Solid State Theory

Magnetism, Superconductivity and Electron Correlation

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Source

This script has been prepared by Roser Valentí and Harald Jeschke on the basis of the following literature:

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In this course we will introduce density functional theory as a basic method to understand and investigate the electronic properties of solid state systems as well as a few many-body methods in order to describe correlation effects. We will provide a theoretical understanding of magnetism, superconductivity, quantum Hall effect, tolopogy in condensed matter systems and a few phenomena related to actual research.
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Inhaltsverzeichnis

Kapitel 1

Density functional theory

1.1 Introduction

The Hartree-Fock approximation is an approximate solution to the problem of interacting electrons. It constitutes an effective simple particle theory

$$H^{\alpha}_{eff}\varphi^{\sigma}_{k_\alpha}(\vec{r}) = -\frac{\hbar^2}{2m}\nabla^2 + V^{k_\alpha,\sigma}_{eff}(\vec{r})\varphi^{\sigma}_{k_\alpha}(\vec{r}) = \varepsilon^{\sigma}_{k_\alpha}\varphi^{\sigma}_{k_\alpha}(\vec{r}) \tag{1.1}$$

with an effective potential that depends on the state $\varphi^{\sigma}_{k_\alpha}(\vec{r})$, *i.e.* on the orbital indices k_α:

$$V^{k_\alpha,\sigma}_{eff}(\vec{r}) = V_{\text{ext}}(\vec{r}) + V_{Hartree}(\vec{r}) + V^{k_\alpha,\sigma}_{x}(\vec{r}) \tag{1.2}$$

Here, the “external” potential is that of the ionic cores

$$V_{\text{ext}}(\vec{r}) = \sum_n V(|\vec{r} - \vec{R}_n|) = \sum_n \frac{Z_n e^2}{|\vec{r} - \vec{R}_n|}\,, \tag{1.3}$$

the Hartree potential arises from the Coulomb interaction of an electron with the electrostatic potential generated by all the other electrons

$$V_{Hartree}(\vec{r}) = e^2 \int d^3r'\,\frac{n(\vec{r}')}{|\vec{r} - \vec{r}'|} \tag{1.4}$$

with

$$n(\vec{r}) = \left\langle \Phi \middle| \sum_{\alpha=1}^{N_e} \delta(\vec{r} - \vec{r}_\alpha) \middle| \Phi \right\rangle = \sum_{\alpha=1}^{N_e} \left|\varphi_{k_\alpha}(\vec{r})\right|^2 \tag{1.5}$$

The exchange operator $V^{k_\alpha,\sigma}_{x}(\vec{r})$ is given by

$$V^{k_\alpha,\sigma}_{x}(\vec{r}) = \, - e^2 \sum_\beta \int d^3\vec{r}'\, \varphi^{\sigma}_{k_\beta}{}^{*}(\vec{r}')\varphi^{\sigma}_{k_\alpha}(\vec{r}')\frac{1}{|\vec{r} - \vec{r}'|}\frac{\varphi^{\sigma}_{k_\beta}(\vec{r})}{\varphi^{\sigma}_{k_\alpha}(\vec{r})}\,; \tag{1.6}$$

it involves an integral over $\varphi^{\sigma}_{k_\alpha}(\vec{r})$ and all other $\varphi^{\sigma}_{k_\beta}(\vec{r})$ with the same spin. The complicated, nonlocal form of the exchange operator is the reason why the Hartree-Fock equations are difficult to solve for large systems; they are mostly used in quantum chemistry where molecules with a small number of atoms and thus of electrons are studied. Solution typically involves N_{basis}^4 integrals where N_{basis} is the size of the basis set. Hartree Fock also has a well-known unphysical feature which is a diverging velocity $v_F = \frac{d\varepsilon}{dk}\Big|_{k=k_F}$ at the Fermi surface in all metallic (*i.e.* ungapped) systems.

Exchange and correlation

The key problem of electronic structure is that the electrons form an interacting manybody system whith a wave function $\Psi(\vec{r}_i) = \Psi(\vec{r}_1, \vec{r}_2, \cdots, \vec{r}_N)$. Since the interactions involve always pairs of electrons, two-body correlation functions are sufficient to determine many properties like for example the total energy $E = \frac{\langle\Psi|H|\Psi\rangle}{\langle\Psi|\Psi\rangle} = \langle H\rangle$. Explicitly, the joint probability of finding electrons of spin σ at $\vec{r}$ and of spin σ' at $\vec{r}'$ is given by

$$\begin{aligned} n(\vec{r},\sigma,\vec{r}',\sigma') &= \Big\langle \sum_{\alpha,\beta} \delta(\vec{r}-\vec{r}_\alpha)\delta(\sigma-\sigma_\alpha)\delta(\vec{r}'-\vec{r}_\beta)\delta(\sigma'-\sigma_\beta)\Big\rangle \\ &= N(N-1)\sum_{\sigma_3,\sigma_4,\cdots}\int d^3r_3\cdots d^3r_N \left|\Psi(\vec{r},\sigma;\vec{r}',\sigma';\vec{r}_3,\sigma_3;\cdots;\vec{r}_N,\sigma_N)\right|^2 \end{aligned} \tag{1.7}$$

for normalized Ψ. For uncorrelated particles, the joint probability is just the product of probabilities, so that the measure of correlation is

$$\Delta n(\vec{r},\sigma;\vec{r}',\sigma') = n(\vec{r},\sigma;\vec{r}',\sigma') - n(\vec{r},\sigma)n(\vec{r}',\sigma') \tag{1.8}$$

and thus

$$n(\vec{r},\sigma,\vec{r}',\sigma') = n(\vec{r},\sigma)n(\vec{r}',\sigma') + \Delta n(\vec{r},\sigma;\vec{r}',\sigma') \tag{1.9}$$

It is also useful to define the normalized pair distribution

$$g(\vec{r},\sigma;\vec{r}',\sigma') = \frac{n(\vec{r},\sigma;\vec{r}',\sigma')}{n(\vec{r},\sigma)n(\vec{r}',\sigma')} = 1 + \frac{\Delta n(\vec{r},\sigma;\vec{r}',\sigma')}{n(\vec{r},\sigma)n(\vec{r}',\sigma')} \tag{1.10}$$

This is 1 for uncorrelated particles; correlation is measured by $g(\vec{r},\sigma;\vec{r}',\sigma') - 1$. 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 $|\vec{r}-\vec{r}'|$. The Hartree-Fock approximation (HFA) consists of neglecting all correlations except those required by the Pauli exclusion principle. The exchange term in the HFA contains the Pauli exclusion and the self interaction correction, *i.e.* it cancels a spurious self interaction contained in the Hartree term. Both effects lower the energy which can be interpreted as the interaction of each electron with a positive exchange hole surrounding it. 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, were Ψ is approximated by the single determinant wave function ϕ; one finds

$$\Delta n_{HFA}(\vec{r},\sigma;\vec{r}',\sigma') = \Delta n_x(\vec{r},\sigma;\vec{r}',\sigma') = -\,\delta_{\sigma\sigma'}\Big|\sum_{i,\alpha}\varphi_{k_\alpha}^{\sigma}{}^*(\vec{r})\varphi_{k_\alpha}^{\sigma}(\vec{r}')\Big|^2 \tag{1.11}$$

It is immediately clear that the exchange hole involves only electrons of the same spin and that the probability for finding two electrons of the same spin at the same point $\vec{r} = \vec{r}'$ vanishes (see eq. (1.9)). There are stringent conditions for the exchange hole: 1) it can never be positive, $\Delta n_x(\vec{r},\sigma;\vec{r}',\sigma') \leq 0$ (*i.e.* $\delta_x(\vec{r},\sigma;\vec{r}',\sigma') \leq 1$) and 2) the integral of the exchange hole density $\Delta n_x(\vec{r},\sigma;\vec{r}',\sigma')$ over all $\vec{r}'$ is exactly one missing electron per electron at point $\vec{r}$ (if one electron is at $\vec{r}$, then the same electron cannot be at $\vec{r}'$).

The exchange energy can be interpreted as the lowering of the energy due to each electron interacting with its positive exchange hole,

$$E_x = \left[\langle V_{\text{int}}\rangle - E_{\text{Hartree}}(n)\right]_{HFA} = \frac{1}{2}\sum_{\sigma}\int d^3r\, n(\vec{r})\int d^3r'\,\frac{\Delta n_x(\vec{r},\sigma;\vec{r}',\sigma')}{|\vec{r}-\vec{r}'|} \tag{1.12}$$

Correlation: The energy of a state of many electrons in the Hartree Fock approximation is the best possible wave function made from a single determinant. Improvement of the wave function to include correlation introduces extra degrees of freedom in the wave function and therefore always lowers the energy for any state, ground or excited; this lowering of the energy is called the **correlation energy** E_c. (This definition is not the only possible as a different reference state could be chosen, but it is the one leading to the smallest possible magnitude of E_c).

The effects of correlation can be cast in terms of the remaining part of the pair correlation beyond exchange:

$$\Delta n(\vec{r},\sigma;\vec{r}',\sigma') \equiv n_{x_c}(\vec{r},\sigma;\vec{r}',\sigma') = n_x(\vec{r},\sigma;\vec{r}',\sigma') + n_c(\vec{r},\sigma;\vec{r}',\sigma') \tag{1.13}$$

As the entire exchange-correlation hole obeys the sum rule that it integrates to 1, the correlation hole $n_c(\vec{r},\sigma;\vec{r}',\sigma')$ must integrate to zero, *i.e.* it merely redistributes the density of the hole. In general, correlation is most important for electrons of opposite spin as electrons of the same spin are automatically kept apart by the exclusion principle.

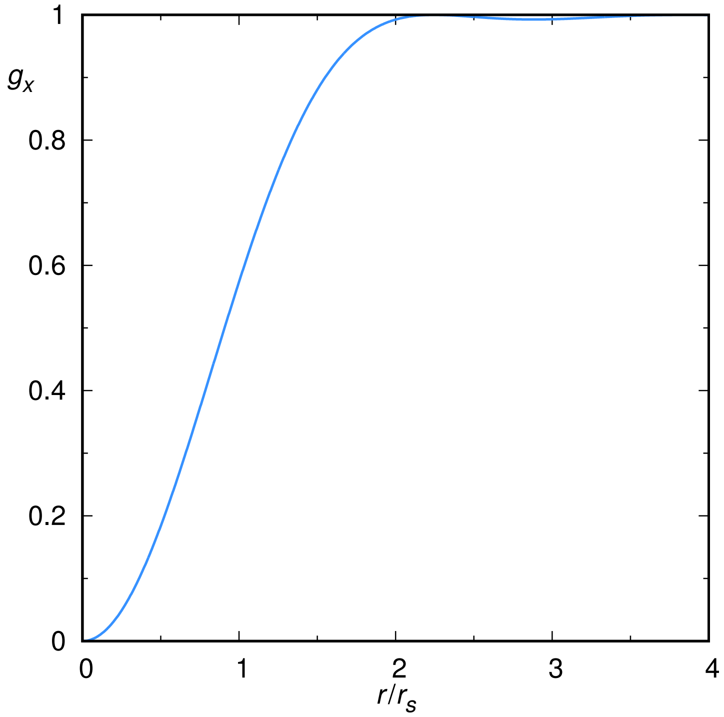

Abbildung 1.1: Exchange hole $g_x(\vec{r})$ in the homogeneous electron gas.

1.2 Foundations of density functional theory

Density functional theory has become the primary tool for calculation of electronic structure in condensed matter, and is increasingly importat for quantitative studies of molecules and other finite systems. In a famous 1964 paper[1], P. Hohenberg and W. Kohn showed that a special role can be assigned to the density of particles in the ground state of a quantum manybody system; the density can be considered as a basic variable, *i.e.* all properties of the system can be considered to be unique functionals of the ground state density. Hohenberg and Kohn formulated density funtional theory as an exact theory of manybody systems of interacting particles in an external potential $V_{\text{ext}}(\vec{r})$ including any problem of electrons and fixed nuclei, where the Hamiltonian can be written

$$\hat{H} = -\frac{\hbar^2}{2m}\sum_{\alpha}\nabla_{\alpha}^2 + \sum_{\alpha} V_{\text{ext}}(\vec{r}_{\alpha}) + \frac{1}{2}\sum_{i\neq j}\frac{e^2}{|\vec{r}_{\alpha}-\vec{r}_{\beta}|} \tag{1.14}$$

Density functional theory is based upon the following two theorems first proved by Hohenberg and Kohn:
Theorem 1: For any system of interacting particles in an external potential $V_{\text{ext}}(\vec{r})$, the potential $V_{\text{ext}}(\vec{r})$ is determined uniquely, except for a constant, by the ground state particle density $n_0(\vec{r})$.
Corollary 1: Since the Hamiltonian is thus fully determined except for a constant shift of the energy, it follows that the manybody wave functions for all stated (ground and excited) are determined. Therefore, all properties of the system are completely determined given only the ground state density $n_0(\vec{r})$.
Theorem 2: A universal functional for the energy $E[n]$ in terms of the density $n(\vec{r})$ can be defined, valid for any external potential $V_{\text{ext}}(\vec{r})$. For any particular $V_{\text{ext}}(\vec{r})$, the exact ground state energy of the system is the global minimum value for this functional, and the density $n(\vec{r})$ that minimizes the functional is the exact ground state state density $n_0(\vec{r})$.
Corollary 2: 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.
Schematic representation of the Hohenberg-Kohn theorem:

$$\begin{tikzcd}
V_{\text{ext}}(\vec{r}) \arrow[d, Rightarrow] & n_0(\vec{r}) \arrow[l, Rightarrow, "\text{HK}"'] \\
\Psi_i(\vec{r}) \arrow[r, Rightarrow] & \Psi_0(\vec{r}) \arrow[u, Rightarrow]
\end{tikzcd} \tag{1.15}$$

Small arrows indicate the usual solution of the Schödinger equation where the potential $V_{\text{ext}}(\vec{r})$ determines all states of the system $\Psi_i(\vec{r})$ including the ground state $\Psi_0(\vec{r})$ and ground state density $n_0(\vec{r})$. The large arrow indicates the Hohenberg-Kohn theorem which completes the circle.

Proof of theorem 1: density as a basic variable

We use the expressions:

$$n(\vec{r}) = \frac{\langle\Psi|n(\vec{r})|\Psi\rangle}{\langle\Psi|\Psi\rangle} = N\frac{\int d^3r_2\cdots d^3r_N \sum_{\sigma}|\Psi(\vec{r},\vec{r}_2,\vec{r}_3,\dots,\vec{r}_N)|^2}{\int d^3r_1 d^3r_2\cdots d^3r_N\,|\Psi(\vec{r}_1,\vec{r}_2,\vec{r}_3,\dots,\vec{r}_N)|^2} \tag{1.16}$$

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[1] P. Hohenberg and W. Kohn, *Inhomogeneous electron gas*, Phys. Rev. **136**, B 864 (1964).

for the density of particles, with the density operator

$$\vec{n}(\vec{r}) = \sum_{\alpha=1}^{N} \delta(\vec{r} - \vec{r}_\alpha) \tag{1.17}$$

and

$$E = \frac{\langle \Psi | \hat{H} | \Psi \rangle}{\langle \Psi | \Psi \rangle} = \langle \hat{H} \rangle = \langle \hat{T} \rangle + \langle \hat{V}_{\text{int}} \rangle + \int d^3r \, V_{\text{ext}}(\vec{r}) n(\vec{r}) + E_{II} \tag{1.18}$$

for the total energy, where expectation value of the external potential has been written explicitly as a simple integral over the density function. E_{II} is the electrostatic nucleus-nucleus interaction. Now we prove theorem 1 by *reductio ad absurdum.* Suppose that there were two different external potentials $V_{\text{ext}}^{(1)}(\vec{r})$ and $V_{\text{ext}}^{(2)}(\vec{r})$ which differ by more than a constant and which lead to the same ground state density $n(\vec{r})$. The two external potentials lead to two different Hamiltonians $\hat{H}^{(1)}$ and $\hat{H}^{(2)}$ which have different ground state wave functions $\Psi^{(1)}$ and $\Psi^{(2)}$ which are hypothesized to have the same ground state density $n_0(\vec{r})$. Since $\Psi^{(2)}$ is not the ground state of $\hat{H}^{(1)}$, it follows that

$$E^{(1)} = \langle \Psi^{(1)} | \hat{H}^{(1)} | \Psi^{(1)} \rangle < \langle \Psi^{(2)} | \hat{H}^{(1)} | \Psi^{(2)} \rangle \tag{1.19}$$

Here a nondegenerate ground state is assumed which simplifies the proof but is not essential. The last term can be written as

$$\begin{aligned} \langle \Psi^{(2)} | \hat{H}^{(1)} | \Psi^{(2)} \rangle &= \langle \Psi^{(2)} | \hat{H}^{(2)} | \Psi^{(2)} \rangle + \langle \Psi^{(2)} | \hat{H}^{(1)} - \hat{H}^{(2)} | \Psi^{(2)} \rangle \\ &= E^{(2)} + \int d^3r \left[V_{\text{ext}}^{(1)}(\vec{r}) - V_{\text{ext}}^{(2)}(\vec{r}) \right] n_0(\vec{r}) \,, \end{aligned} \tag{1.20}$$

so that

$$E^{(1)} < E^{(2)} + \int d^3r \left[V_{\text{ext}}^{(1)}(\vec{r}) - V_{\text{ext}}^{(2)}(\vec{r}) \right] n_0(\vec{r}) \,. \tag{1.21}$$

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:

$$E^{(2)} < E^{(1)} + \int d^3r \left[V_{\text{ext}}^{(2)}(\vec{r}) - V_{\text{ext}}^{(1)}(\vec{r}) \right] n_0(\vec{r}) \tag{1.22}$$

If we add Eqs. (1.21) and (1.22), we arrive at the contradictory inequality $E^{(1)} + E^{(2)} < E^{(1)} + E^{(2)}$. Thus, there cannot be two different external potentials differing by more than a constant which give rise to the same nondegenerate ground state density; the density uniquely determines the external potential to within a constant.

The corollary 1 follows since the Hamiltonian is uniquely determined (except for a constant) by the ground state density. Then, in principle, the wave function of any state is determined by solving the Schödinger equation with this Hamiltonian. Among all solutions consistent with the given density, the unique ground state wave function is the one that has the lowest energy. Of course, no prescription has yet been given to solve the problem. Still, the manybody problem in the presence of $V_{\text{ext}}(\vec{r})$ needs to be solved. For example, for electrons in materials where the external potential is the Coulomb potential due to the nuclei, the theorem only requires that the electron density uniquely determines the positions and types of nuclei.

Proof of theorem 2

The proof of theorem 2 requires proper definition of the meaning of a functional of the density and restricting the space of densities. We restrict to densities that are V-representable, *i.e.* densities $n(\vec{r})$ that are ground state densities of the electron Hamiltonian with some external potential V_{ext}. Within this space of densities, we construct functionals of the density. Since all properties such as the kinetic energy, etc. are uniquely determined if $n(\vec{r})$ is specified, each such property can be viewed as a functional of $n(\vec{r})$, including the total energy functional

$$\begin{aligned} E_{\text{HK}}[n] &= T[n] + E_{\text{int}}[n] + \int d^3r\, V_{\text{ext}}(\vec{r})n(\vec{r}) + E_{II} \\ &= F_{\text{HK}}[n] + \int d^3r\, V_{\text{ext}}(\vec{r})n(\vec{r}) + E_{II} \end{aligned} \tag{1.23}$$

where E_{II} is the interaction energy of the nuclei. The functional $F_{\text{HK}}[n]$ thus defined includes all internal energies, kinetic and potential of the interacting electron system

$$F_{\text{HK}}[n] = T[n] + E_{\text{int}}[n] \tag{1.24}$$

which must be universal by construction since the kinetic energy and interaction energy of the particles are functionals only of the density. Now consider a system with a ground state density $n^{(1)}(\vec{r})$ corresponding to the external potential $V^{(1)}_{\text{ext}}(\vec{r})$. the Hohenberg-Kohn functional is equal to the expectation value of the Hamiltonian in the unique ground state which has the wavefunction $\Psi^{(1)}$

$$E^{(1)} = E_{\text{HK}}[n^{(1)}] = \langle \Psi^{(1)} | \hat{H}^{(1)} | \Psi^{(1)} \rangle \tag{1.25}$$

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

$$E^{(1)} = \langle \Psi^{(1)} | \hat{H}^{(1)} | \Psi^{(1)} \rangle < \langle \Psi^{(2)} | \hat{H}^{(1)} | \Psi^{(2)} \rangle = E^{(2)} \tag{1.26}$$

Thus the energy given by (1.23) in terms of the Hohenberg-Kohn functional evaluated for the correct ground state density $n_0(\vec{r})$ is indeed lower than the value of this expression for any other density $n(\vec{r})$. This means that if the functional $F_{\text{HK}}[n]$ were known, then by minimizing the total energy of the system (1.23) with respect to variations in the density $n(\vec{r})$ one would find the exact ground state density and energy. This establishes corollary 2.

1.3 The Kohn-Sham ansatz

The Kohn-Sham approach is to replace the difficult interacting manybody system with a different auxiliary system that can be solved more easily - it is an *ansatz* because there is no unique prescription of how to choose the simpler auxiliary system. The *ansatz* 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 that can be considered exactly solvable with all the difficult manybody terms incorporated into an exchange-correlation functional of the density. By solving the equations one finds the ground state density and energy of the original interacting system with the accuracy limited only by the approximations in the exchange-correlation functional. These approximations, the most important of which are the local density approximation (LDA) and generalized gradient approximation (GGA) functionals will be discussed below. The Kohn-Sham *ansatz* for the ground state rests on two assumptions:
1) The exact ground state density can be represented by the ground state density of the auxiliary system of noninteracting particles. This is called **non-interacting-V-representability** (see scheme below)
2) The auxiliary Hamiltonian is chosen to have the usual kinetic energy operator and an effective local potential $V^{\sigma}_{eff}(\vec{r})$ acting on an electron of spin σ at point $\vec{r}$.
Schematic representation of the Kohn-Sham *ansatz*:

$$\begin{tikzcd}
V_{\text{ext}}(\vec{r}) \arrow[r, Leftarrow, "\text{HK}"] \arrow[d, Rightarrow] & n_0(\vec{r}) \arrow[r, Leftrightarrow, "\text{KS}"] & n_0(\vec{r}) \arrow[r, Rightarrow, "HK_0"] & V_{\text{KS}}(\vec{r}) \arrow[d, Rightarrow] \\
\Psi_i(\vec{r}) \arrow[r, Rightarrow] & \Psi_0(\vec{r}) \arrow[u, Rightarrow] & \psi_{i=1,\cdots,N_e}(\vec{r}) \arrow[u, Rightarrow] & \psi_i(\vec{r}) \arrow[l, Rightarrow]
\end{tikzcd} \tag{1.27}$$

HK_0 means Hohenberg-Kohn theorem applied to the noninteracting problem. The KS arrow indicates connection in both directions between the manybody and independent particle systems.
The actual calculations are performed on the auxiliary independent particle system defined by the auxiliary Hamiltonian

$$H^{\sigma}_{\text{aux}} = -\frac{1}{2}\nabla^2 + V^{\sigma}(\vec{r}) \tag{1.28}$$

$V^{\sigma}(\vec{r})$ will be specified later. For independent electrons, the ground state has one electron in each of the $N^{\sigma}(\sigma =\uparrow,\downarrow)$ orbitals $\psi^{\sigma}_i(\vec{r})$ with the lowest eigenvalues ε^{σ}_i of the Hamiltonian (1.28). The density of the auxiliary system is given by

$$n(\vec{r}) = \sum_{\sigma} n(\vec{r},\sigma) = \sum_{\sigma}\sum_{i=1}^{N^{\sigma}} \left|\psi^{\sigma}_i(\vec{r})\right|^2, \tag{1.29}$$

the independent particle kinetic energy T_s is given by

$$T_s = -\frac{1}{2}\sum_{\sigma}\sum_{i=1}^{N^{\sigma}}\langle\psi^{\sigma}_i|\nabla^2|\psi^{\sigma}_i\rangle = \frac{1}{2}\sum_{\sigma}\sum_{i=1}^{N^{\sigma}}\int d^3r\,\left|\nabla\psi^{\sigma}_i(\vec{r})\right|^2 \tag{1.30}$$

and we define the classical Coulomb interaction energy of the electron density $n(\vec{r})$ interacting with itself as

$$E_{\text{Hartree}}[n] = \frac{1}{2}\int d^3r\, d^3r'\,\frac{n(\vec{r})n(\vec{r}')}{|\vec{r}-\vec{r}'|} \tag{1.31}$$

The Kohn-Sham approach to the full interacting manybody problem is to rewrite the Hohenberg-Kohn expression for the ground state energy functional (1.23) as

$$E_{\text{KS}} = T_s[n] + \int d^3r\, V_{\text{ext}}(\vec{r})n(\vec{r}) + E_{\text{Hartree}}[n] + E_{II} + E_{\text{xc}}[n] \tag{1.32}$$

Here $V_{\text{ext}}(\vec{r})$ is the external potential due to the nuclei and any other external fields (assumed to be independent of spin). All manybody effects of exchange and correlation are grouped into the exchange-correlation energy E_{xc}. Comparing the Hohenberg-Kohn (1.23) and the Kohn-Sham (1.32) expressions for the total energy shows that E_{xc} can be written as

$$E_{\text{xc}}[n] = F_{\text{HK}}[n] - (T_s[n] + E_{\text{Hartree}}[n]) \tag{1.33}$$

or

$$E_{\text{xc}}[n] = \langle \hat{T} \rangle - T_s[n] + \langle \hat{V}_{\text{int}} \rangle - E_{\text{Hartree}}[n] \tag{1.34}$$

This shows that $E_{\text{xc}}[n]$ is just the difference of the kinetic and internal interaction energies of the interacting manybody system from those of the fictitious independent-particle system with electron-electron interactions replaced by the Hartree energy. As the universal functional $E_{\text{xc}}[n]$ of (1.32) is unknown, approximate forms for $E_{\text{xc}}[n]$ make the Kohn-Sham method a valuable approach for the ground state properties of the manybody electron system.

The Kohn-Sham variational equations

The solution of the Kohn-Sham auxiliary system for the ground state can be viewed as a problem of minimization with respect to either the density $n(\vec{r}, \sigma)$ or the effective potential $V^{\sigma}_{eff}(\vec{r})$. As T_s is expressed as a functional of the orbitals but all other terms are considered to be functionals of the density, one can vary the wave functions and use the chain rule to derive the variational equation

$$\frac{\delta E_{\text{KS}}}{\delta \psi_i^{\sigma *}(\vec{r})} = \frac{\delta T_s}{\delta \psi_i^{\sigma *}(\vec{r})} + \left[\frac{\delta E_{\text{ext}}}{\delta n(\vec{r}, \sigma)} + \frac{\delta E_{\text{Hartree}}}{\delta n(\vec{r}, \sigma)} + \frac{\delta E_{\text{xc}}}{\delta n(\vec{r}, \sigma)} \right] \frac{\delta n(\vec{r}, \sigma)}{\delta \psi_i^{\sigma *}(\vec{r})} = 0 \tag{1.35}$$

subject to normalization conditions

$$\langle \psi_i^{\sigma} | \psi_j^{\sigma'} \rangle = \delta_{ij} \delta_{\sigma\sigma'} \tag{1.36}$$

We use the expressions (1.29) and (1.30) for $n^{\sigma}(\vec{r})$ and T_s which give

$$\frac{\delta T_s}{\delta \psi_i^{\sigma *}(\vec{r})} = -\frac{1}{2} \nabla^2 \psi_i^{\sigma}(\vec{r}) \, ; \qquad \frac{\delta n^{\sigma}(\vec{r})}{\delta \psi_i^{\sigma *}(\vec{r})} = \psi_i^{\sigma}(\vec{r}) \tag{1.37}$$

and the method of Lagrange multipliers to handle the constraints:

$$\frac{\delta}{\delta \psi_i^{\sigma *}} \left\{ E_{\text{KS}} - \sum_{\sigma} \sum_{j=1}^{N^{\sigma}} \varepsilon_j^{\sigma} \left(\int d^3 r \, |\psi_i^{\sigma}(\vec{r})|^2 - 1 \right) \right\} = 0 \tag{1.38}$$

This variation leads to the Schrödinger-like **Kohn-Sham equations**

$$\left(H_{\text{KS}}^{\sigma} - \varepsilon_i^{\sigma} \right) \psi_i^{\sigma}(\vec{r}) = 0 \tag{1.39}$$

where ε_i^{σ} are eigenvalues and H_{KS} is the effective Hamiltonian (in Hartree atomics units)

$$H_{\text{KS}}^{\sigma}(\vec{r}) = -\frac{1}{2} \nabla^2 + V_{\text{KS}}^{\sigma}(\vec{r}) \tag{1.40}$$

with

$$\begin{aligned} V^{\sigma}_{\mathrm{KS}}(\vec{r}) &= V_{\mathrm{ext}}(\vec{r}) + \frac{\delta E_{\mathrm{Hartree}}}{\delta n(\vec{r},\sigma)} + \frac{\delta E_{\mathrm{xc}}}{\delta n(\vec{r},\sigma)} \\ &= V_{\mathrm{ext}}(\vec{r}) + V_{\mathrm{Hartree}}(\vec{r}) + V^{\sigma}_{\mathrm{xc}}(\vec{r}) \end{aligned} \tag{1.41}$$

These are the well-known Kohn-Sham equations[2]; they have the form of independent particle equations with a potential that must be found selfconsistently with the resulting density. The equations are independent of any approximation to the functional $E_{\mathrm{xc}}[n]$, and would lead to the exact ground state density and energy for the interacting system if the exact functional $E_{\mathrm{xc}}[n]$ were known. Furthermore, the Hohenberg-Kohn theorems guarantee that the ground state density uniquely determines the potential at the minimum, so that there is a unique Kohn-Sham potential $V^{\sigma}_{eff}(\vec{r})|_{\mathrm{min}} \equiv V^{\sigma}_{\mathrm{KS}}(\vec{r})$ associated with any given interacting electron system.

E_{xc}, V_{xc} and the exchange-correlation hole

The genius 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 $E_{\mathrm{xc}}[n]$ can reasonably be approximated as a local or nearly local functional of the density. This means that the energy E_{xc} can be expressed in the form

$$E_{\mathrm{xc}}[n] = \int d^3r\, n(\vec{r})\varepsilon_{\mathrm{xc}}([n],\vec{r}) \tag{1.42}$$

where $\varepsilon_{\mathrm{xc}}([n],\vec{r})$ is an energy per electron at point $\vec{r}$ that depends only on the density $n(\vec{r},\sigma)$ in some neighborhood of point $\vec{r}$. The exchange and correlation energy density can be related to the exchange correlation hole using the coupling constant integration. In general, the derivative of the energy with respect to any parameter λ in the Hamiltonian can be calculated using the variational property of the wave function:

$$\frac{\partial E}{\partial \lambda} = \langle \Psi_\lambda | \frac{\partial \hat{H}}{\partial \lambda} | \Psi_\lambda \rangle \tag{1.43}$$

and from this, an integral expression can be obtained for calculating energy differences between any two states connected by a continuous variation of the Hamiltonian:

$$\Delta E = \int_{\lambda_1}^{\lambda_2} d\lambda \frac{\partial E}{\partial \lambda} = \int_{\lambda_1}^{\lambda_2} d\lambda \langle \Psi_\lambda | \frac{\partial \hat{H}}{\partial \lambda} | \Psi_\lambda \rangle \tag{1.44}$$

Here, we are interested in varying the Hamiltonian continuously between the non-interacting and the fully interacting limits. For this we can use the parameter e^2 in the interaction energy, scale it by $e^2 \to e^2\lambda$ where λ is varied from 0 to 1. This we do only to the electron-electron interaction term (nuclear term is treated separately as external potential), and we find for the change in energy

$$\Delta E = \int_0^1 d\lambda \langle \Psi_\lambda | \frac{dV_{\mathrm{int}}}{d\lambda} | \Psi_\lambda \rangle \tag{1.45}$$

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[2] W. Kohn and L. J. Sham, *Self-consistent equations including exchange and correlation effects*, Phys. Rev. **140**, A 1133 (1965).

If we do this with the added constraints that the density must be kept constant during this variation, all other terms remain constant and the exchange correlation energy is given by

$$E_{\rm xc}[n] = \int_0^{e^2} d\lambda \langle \Psi_\lambda | \frac{dV_{\rm int}}{d\lambda} | \Psi_\lambda \rangle - E_{\rm Hartree}[n] = \frac{1}{2} \int d^3r\, n(\vec{r}) \int d^3r' \, \frac{\bar{n}_{\rm xc}(\vec{r}, \vec{r}')}{|\vec{r} - \vec{r}'|} \tag{1.46}$$

where $\bar{n}_{\rm xc}(\vec{r}, \vec{r}')$ is the coupling constant averaged hole

$$\bar{n}_{\rm xc}(\vec{r}, \vec{r}') = \int_0^1 d\lambda\, n^{\lambda}_{\rm xc}(\vec{r}, \vec{r}') \tag{1.47}$$

$n_{\rm xc}(\vec{r}, \vec{r}')$ is the exchange correlation hole summed over parallel ($\sigma = \sigma'$) and antiparallel ($\sigma \neq \sigma'$) spins. Thus, the exchange correlation density $\varepsilon_{\rm xc}([n], \vec{r})$ can be written as

$$\varepsilon_{\rm xc}([n], \vec{r}) = \frac{1}{2} \int d^3r' \, \frac{\bar{n}_{\rm xc}(\vec{r}, \vec{r}')}{|\vec{r} - \vec{r}'|} \tag{1.48}$$

This result 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 wave function is just the independent-particle Kohn-Sham wave function so that $n^0_{\rm xc}(\vec{r}, \sigma; \vec{r}', \sigma') = n_x(\vec{r}, \sigma; \vec{r}', \sigma')$ where the exchange hole is known from Eq. (1.11). Since the density everywhere is required to remain constant as λ is varied, $\varepsilon_{\rm xc}([n], \vec{r})$ is implicitly a functional of the density in all space. Thus $E_{\rm xc}[n]$ 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 averaged hole $\bar{n}_{\rm xc}(\vec{r}, \vec{r}')$ is one of the primary approaches for developing improved approximations for $E_{\rm xc}[n]$.

Exchange-correlation potential $V_{\rm xc}$

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

$$V^{\sigma}_{\rm xc}(\vec{r}) = \varepsilon_{\rm xc}([n], \vec{r}) + n(\vec{r}) \frac{\partial \varepsilon_{\rm xc}([n], \vec{r})}{\partial n(\vec{r}, \sigma)} \tag{1.49}$$

where $\varepsilon_{\rm xc}([n], \vec{r})$ is defined in (1.42) and is a functional of the density $n(\vec{r}', \sigma')$. $V_{\rm xc}$ is not a potential that can be identified with interactions between particles and it behaves in ways that seem paradoxical. The second term in (1.49), sometimes called response potential, is due to the change in the exchange correlation hole with density. In an insulator, this derivative is discontinuous at a band gap where the nature of the state changes discontinuously as a function of n. This leads to a derivative discontinuity where the Kohn-Sham potential for all the electrons in a crystal changes by a constant amount when a single electron is added. This can be understood by examining the kinetic energy. The great advance of the Kohn-Sham approach over the Thomas-Fermi approximation is the incorporation of orbitals to define the kinetic energy. In terms of orbitals, it is easy to see that the kinetic energy T_s for independent particles changes discontinuously in going from an occupied to an empty band since the $\psi^{\sigma}_i(\vec{r})$ are different for different bands. In terms of the density, this means that the formal density functional $T_s[n]$ has discontinuous derivaties at densities that correspond to filled bands. This is a direct consequence of quantum mechanics and is difficult to incorporate into an explicit density functional; also the true exchange-correlation potential must change discontinuously. These properties are not incorporated into any of the simple explicit functionals of the density, such as local density or generalized gradient approximations, but they occur naturally in orbital dependent formulations like the optimized effective potential (OEP).

Meaning of the Kohn-Sham eigenvalues

The Kohn-Sham eigenvalues, introduced as Lagrange multipliers, have no direct physical meaning, at least not that of the energies to add or substract electrons from the interacting manybody system (in analogy to Koopmas theorem for Hartree Fock). The exception is the highest eigenvalue in a finite system which is minus the ionization energy. Nevertheless, the eigenvalues have a well defined meaning within the theory and can be used to construct physically meaningful quantities. For example, they can be used to develop perturbation expressions for excitation energies, either in the form of a functional or in the form of explicit manybody calculations that use the Kohn-Sham eigenfunctions and eigenvalues as an input.

Within the Kohn-Sham formalism, the meaning of the eigenvalues, known as Janak theorem, is that the eigenvalue is the derivative of the total energy with respect to occupation of a state:

$$\varepsilon_i = \frac{dE_{\text{total}}}{dn_i} = \int d^3r\, \frac{dE_{\text{total}}}{dn(\vec{r})} \frac{dn(\vec{r})}{dn_i}\,. \tag{1.50}$$

1.4 Functionals for exchange and correlation

Even though the exact functional $E_{\text{xc}}[n]$ must be very complex, the great success of DFT is due to remarkably simple approximations.

The local spin density approximation (LSDA)

This approximation is based on the observation that solids can often be considered close to the limit of the homogeneous electron gas. In that limit, the effects of exchange and correlation are local in character. Thus, the local density approximation (LDA), which was already proposed by Kohn and Sham, takes the exchange-correlation energy as 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 with that density:

$$E_{\text{xc}}^{LSDA}[n^{\uparrow}, n^{\downarrow}] = \int d^3r\, n(\vec{r}) \varepsilon_{\text{xc}}^{hom}(n^{\uparrow}(\vec{r}), n^{\downarrow}(\vec{r})) \tag{1.51}$$

The axis of quantization of the spin is assumed to be the same at all points in space, but this can be generalized to a non-collinear spin case. The LSDA can be formulated either in the two spin densities $n^{\uparrow}(\vec{r})$ and $n^{\downarrow}(\vec{r})$, or in the total density $n(\vec{r})$ and the fractional spin polarization

$$\zeta(\vec{r}) = \frac{n^{\uparrow}(\vec{r}) - n^{\downarrow}(\vec{r})}{n(\vec{r})}\,. \tag{1.52}$$

Solving the Hartree-Fock equations for the homogeneous electron gas can be done analytically; one finds a dispersion (in atomic units)

$$\varepsilon_k = \frac{k^2}{2} + \frac{k_F}{\pi} f(x) \qquad \text{with} \qquad x = \frac{k}{k_F} \tag{1.53}$$

and

$$f(x) = -\left(1+\frac{1-x^2}{2x}\ln\left|\frac{1+x}{1-x}\right|\right) \tag{1.54}$$

where the second term is the matrix element for the exchange operator.
For a polarized system, exchange has the form

$$\varepsilon_x(n,\zeta) = \varepsilon_x(n,0) + \big[\varepsilon_x(n,1) - \varepsilon_x(n,0)\big] f_x(\zeta) \tag{1.55}$$

with

$$f_x(\zeta) = \frac{1}{2}\frac{(1+\zeta)^{4/3} + (1-\zeta)^{4/3} - 2}{2^{1/3}-1} \tag{1.56}$$

For unpolarized systems, the LDA is found by setting $n^{\uparrow}(\vec{r}) = n^{\downarrow}(\vec{r}) = {}^{n(\vec{r})}/_{2}$. The correlation energy of the inhomogeneous electron gas cannot be calculated analytically; it is calculated with manybody methods (RPA) or numerically with Quantum Monte Carlo. It has been parameterized using analytic forms, for example one that is the same as (1.55), as proposed by Perdew and Zunger.

Generalized gradient approximations (GGAs)

The first step beyond the local approximation is a functional of the gradient of the density $|\nabla n^{\sigma}|$ as well as its value n at each point. But a straightforward expansion can run into problems due to the violation of sum rules. The problem is that gradients in real materials are so large that the expansion breaks down. The term generalized gradient approximation denotes a variety of ways proposed for functions that modify the behavior at large gradients in such a way as to preserve the desired properties. The functional can be defined as a generalized form of (1.51)

$$\begin{aligned} E_{\mathrm{xc}}^{GGA}[n^{\uparrow}, n^{\downarrow}] &= \int d^3r\, n(\vec{r})\varepsilon_{\mathrm{xc}}(n^{\uparrow}, n^{\downarrow}, |\nabla n^{\uparrow}|, |\nabla n^{\downarrow}|, \cdots) \\ &\equiv \int d^3r\, n(\vec{r})\varepsilon_{\mathrm{xc}}^{hom}(n) F_{\mathrm{xc}}(n^{\uparrow}, n^{\downarrow}, |\nabla n^{\uparrow}|, |\nabla n^{\downarrow}|, \cdots) \end{aligned} \tag{1.57}$$

where F_{xc} is dimensionless and $\varepsilon_{xc}^{\mathrm{hom}}(n)$ is the exchange energy of the unpolarized gas. For exchange, there is a spin scaling relation

$$E_x\big[n^{\uparrow}, n^{\downarrow}\big] = \frac{1}{2}\Big[E_x\big[2n^{\uparrow}\big] + E_x\big[2n^{\downarrow}\big]\Big] \tag{1.58}$$

where $E_x[n]$ is the exchange energy for an unpolarized system. 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 mth order that can be defined by

$$s_m = \frac{|\nabla^m n|}{(2k_F)^m n} = \frac{\nabla^m n}{2^m(3\pi^2)^{m/3} n^{(1+m/3)}} \tag{1.59}$$

Since $k_F = 3(\frac{2\pi}{3})^{1/3}\frac{1}{r_s}$, s_m is proportional to the mth order fractional variation in density normalized to the average distance between electrons r_s, for example

$$s_1 \equiv s = \frac{|\nabla n|}{(2k_F)n} = \frac{|\nabla r_s|}{2(\frac{2\pi}{3})^{1/3} r_s} \tag{1.60}$$

The lowest order terms for F_x have been calculated analytically

$$F_x = 1 + \frac{10}{81}s_1^2 + \frac{146}{2025}s_2^2 + \cdots \tag{1.61}$$

Numerous forms $F_x(n, s)$ have been proposed; these can be illustrated (see Fig. 1.2) by the widely used forms of Becke (B88)[3], Perdew and Wang (PW99)[4] and Perdew, Burke and Ernzerhof (PBE)[5]. In the region that is most relevant for physical applications, $s < 3$, the three forms have similar shapes and lead to similar results. For the large s region, relatively little is known.

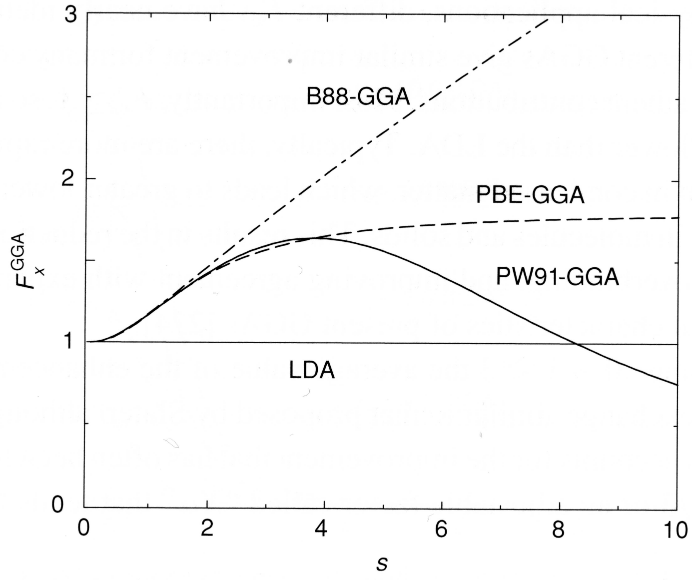

Abbildung 1.2: Exchange enhancement factor $F_x(n, s)$ as function of dimensionless density gradient s. From R. M. Martin, *Electronic Structure*, Cambridge University Press.

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[3] A. D. Becke, *Density-functional exchange-energy approximation with correct asymptotic behavior*, Phys. Rev. A **38**, 3098 (1988).

[4] J. P. Perdew and Y. Wang, *Accurate and simple analytic representation of the electron-gas correlation energy*, Phys. Rev. A **45**, 13244 (1992).

[5] J. P. Perdew, K. Burke and M. Ernzerhof, *Generalized gradient approximation made simple*, Phys. Rev. Lett. **77**, 3865 (1996).