VI. The Hohenberg-Kohn density functional theory

In view of the poor predictions of chemical bonds and molecular properties afforded by HF approximation and the high numerical price of wave function approaches, it is beneficial to seek out methods that circumvent the need to represent the many-body electronic wavefunction. We studied in detail two theories. One was based on the density, but had no real rigorous basis. The other was a method that assumed the electronic wave function is of the form applicable only for non-interacting electrons. We now want to describe a rigorous method that combines ideas of this type in a new way which is both rigorous and leads to very accurate approximations.

A. The first HK theorem

In electronic structure theory the Hamiltonian is given as:

\[ \hat{H} = \hat{T} + \hat{U} + \int v(r)\hat{n}(r) d^3r \]  

(6.1.1)

Where all symbols have been defined in XXX. The identity of the molecular system is captured in the external potential \( v(r) \). The other terms are “universal” i.e. the same for all molecules. In DFT they have a special symbol:

\[ \hat{F} = \hat{T} + \hat{U} \]  

(6.1.2)

Different Hamiltonians differ only by their external potential-density term:

\[ \hat{H} - \hat{H}' = \int (v(r) - v'(r))\hat{n}(r) d^3r \]  

(6.1.3)

This observation has a fundamental implication. Suppose we have two electronic wave functions \( \Psi_1 \) and \( \Psi_2 \) of \( N_e \) electrons which have the same density, i.e. for all \( r \):
\[
\langle \Psi_1 | \hat{n}(\mathbf{r}) | \Psi_1 \rangle = \langle \Psi_2 | \hat{n}(\mathbf{r}) | \Psi_2 \rangle \equiv n(\mathbf{r}). \quad (6.1.4)
\]

Now, if
\[
\langle \Psi_1 | \hat{F} | \Psi_1 \rangle < \langle \Psi_2 | \hat{F} | \Psi_2 \rangle \quad (6.1.5)
\]

Then:
\[
\langle \Psi_1 | \hat{F}' | \Psi_1 \rangle < \langle \Psi_2 | \hat{F}' | \Psi_2 \rangle \quad (6.1.6)
\]

Thus the inequality is independent of the position of the nuclei: only the wave functions affect it through the universal operator \( \hat{F} \). The external potential term drops out because both wave functions have the same density.

An interesting natural conclusions is that if Eq. (6.1.5) holds for one Hamiltonian the it holds for all Hamiltonians:
\[
\langle \Psi_1 | \hat{F}' | \Psi_1 \rangle < \langle \Psi_2 | \hat{F}' | \Psi_2 \rangle \quad (6.1.7)
\]

This fact will now be used to prove the first theorem of DFT, due to Hohenberg and Kohn:

**Theorem (Hohenberg-Kohn):** When two Hamiltonians differing only by a single particle potential term \( \hat{H} - \hat{H}' \equiv \int [v(\mathbf{r}) - v'(\mathbf{r})] \hat{n}(\mathbf{r}) d^3r \) have non degenerate ground states which integrate to the same density then these Hamiltonians are identical up to a constant (i.e. \( v(\mathbf{r}) = v'(\mathbf{r}) + \text{const} \)).

**Proof of the HK theorem:** Assume otherwise: \( \Psi \) is the GS of \( \hat{H} \) and \( \Psi' \) that of \( \hat{H}' \), both wave functions assumed real and have the same expectation values for the density at all points in space. The variational principle for \( \Psi \) dictates \( \langle \Psi | \hat{F} | \Psi \rangle < \langle \Psi' | \hat{F} | \Psi' \rangle \) which, as discussed in Eq. (6.1.7) means that \( \langle \Psi | \hat{F}' | \Psi \rangle < \langle \Psi' | \hat{F}' | \Psi' \rangle \) holds as well. But this latter inequality contradicts the variational principle for \( \Psi' \) as the ground state of \( \hat{H}' \), unless it differs from \( \hat{H} \) by at most a constant. ♦
This theorem allows one to think of the potential as a functional dependent on the density. Thus, in addition to the “usual”

\[ \nu \rightarrow \hat{H} \rightarrow \psi \rightarrow n \quad (6.1.8) \]

We now have:

\[ n \rightarrow \nu \rightarrow \hat{H} \rightarrow \psi \quad (6.1.9) \]

Thus "everything" about the molecule (all its properties) is in the above sense a functional of the ground-state density.

A generalization of the theorem, giving an inequality is:

**Theorem:** If \( n_i(r) \) is the density of the non-degenerate N-particle groundstate of \( \hat{H}_i = \hat{p} + \int v_i(r)n_i(r) d^3r \), where \( i = 1,2 \). Then, denoting \( \Delta X = X_1 - X_2 \), we have:

\[ \Delta n \neq 0 \quad \Rightarrow \quad \int \Delta n(r)\Delta \nu(r) d^3r < 0 \quad (6.1.10) \]

**Proof:** Suppose \( \Delta n \neq 0 \). Then \( \Psi_1 \neq \Psi_2 \) and because of non-degeneracy the following inequality is strict:

\[ \langle \Psi_1 | \hat{H}_1 | \Psi_1 \rangle < \langle \Psi_2 | \hat{H}_1 | \Psi_2 \rangle = \langle \Psi_2 | \hat{H}_2 | \Psi_2 \rangle + \int [v_1(r) - v_2(r)]n_2(r) d^3r \quad (6.1.11) \]

Denoting \( E_i = \langle \Psi_i | \hat{H}_i | \Psi_i \rangle \), we find:

\[ E_1 < E_2 + \int \Delta \nu(r)n_2(r) d^3r \quad (6.1.12) \]

And exchanging the indices \( 1 \mapsto 2 \):

\[ E_2 < E_1 - \int \Delta \nu(r)n_1(r) d^3r \quad (6.1.13) \]

Adding the two inequalities and cleaning up gives Eq. (6.1.10), QED \( \bullet \)
**B. The HK functional**

Since "everything" is a functional of the density, we can assert that the ground-state kinetic energy is a functional $T[n]$ of the density and so is the electron repulsion energy $U[n]$. We can thus define the Hohenberg-Kohn functional of v-rep densities as follows:

$$F_{HK}[n] = T[n] + U[n] = \langle \psi_{gs}[n]|\hat{T} + \hat{U}|\psi_{gs}[n]\rangle$$  \hspace{1cm} (6.2.1)

Where $\psi_{gs}[n]$ is a ground-state wave function with density $n$. $F_{HK}[n]$ is a universal functional, it is not limited to any particular molecular system. It is valid for all systems. We have of course no practical way to calculate $F_{HK}[n]$ in general.

Even the domain of definition of $F_{HK}$ is difficult to characterize. In fact, and perhaps unexpectedly, this domain is not even convex, as discovered by Levy and Perdew.

![Convex Sets](image)

Figure VI-1: A convex set is a set of points such that if $A$ and $B$ are in the set then any point $C$ on the straight line joining $A$ and $B$ is in the set as well. The left set is convex while the right set is not.

This means, that if $n_0$ and $n_{\pi/2}$ are two densities which are in the domain, it is not guaranteed that the convex sum $n_\theta \equiv (\cos^2 \theta)n_0 + (\sin^2 \theta)n_{\pi/2}$ (where $\theta$ is some parameter in the range $[0, \frac{\pi}{2}]$) is in it. Levy and Perdew showed an example where convexity fails by considering the case where both are densities are densities of two degenerate eigenstates of the same system (we...
discuss this in more detail below). Technically, we say that the domain of definition is not convex. However, suppose we do have three densities $n_0$, $n_{\pi/2}$ and $n_{\theta}$, where the latter is the convex sum of the two former densities. Suppose further that all three belong to the domain of definition of $F_{HK}$. Then $F_{HK}[n_{\theta}] \leq (\cos^2 \theta) F_{HK}[n_0] + (\sin^2 \theta) F_{HK}[n_{\pi/2}]$, i.e. $F_{HK}$ is a convex functional of the density (we discussed this concept in Chapter XXX). This is seen as a result of the variational theorem. Suppose $\Psi_{\theta}$ is the ground-state wave function, $v_{\theta}$ the potential and $\hat{H}_{\theta} = \hat{T} + \hat{U} + \hat{V}_{\theta}$ the Hamiltonian corresponding to $n_{\theta}$ then:

$$\langle \Psi_{\theta} | \hat{H}_{\theta} | \Psi_{\theta} \rangle \leq \langle \Psi_{0} | \hat{H}_{0} | \Psi_{0} \rangle$$

$$\langle \Psi_{\theta} | \hat{H}_{\theta} | \Psi_{\theta} \rangle \leq \langle \Psi_{\pi/2} | \hat{H}_{\theta} | \Psi_{\pi/2} \rangle$$

From this we have:

$$F_{HK}[n_{\theta}] = \langle \Psi_{\theta} | \hat{H}_{\theta} | \Psi_{\theta} \rangle - \int n_{\theta}(r)v_{\theta}(r)d^3r$$

$$\leq (\cos^2 \theta) \left[ \langle \Psi_{0} | \hat{H}_{\theta} | \Psi_{0} \rangle - \int n_{0}(r)v_{\theta}(r)d^3r \right]$$

$$+ (\sin^2 \theta) \left[ \langle \Psi_{\pi/2} | \hat{H}_{\theta} | \Psi_{\pi/2} \rangle - \int n_{\pi/2}(r)v_{\theta}(r)d^3r \right]$$

$$= (\cos^2 \theta) F_{HK}[n_0] + (\sin^2 \theta) F_{HK}[n_{\pi/2}]$$

We will see that the convexity property of $F_{HK}[n]$ has an important implication for the variational property of density functional theory, that we discuss in the next section.

**C. Minimum principle for density functional theory**

The second HK theorem establishes a minimum principle involving the density, and it can be used to "find" the density without direct reference to the concept of a "wave function".
Given a potential \( v(\mathbf{r}) \), consider the following functional for \( N \) electrons:

\[
E_v[n] = F_{HK}[n] + \int v(\mathbf{r}) n(\mathbf{r}) d^3 r \tag{6.3.1}
\]

The HK theorem II states that the density \( n_v \) which is the ground-state of \( v(\mathbf{r}) \) minimizes this functional. For \( n_v \) we know of course that:

\[
E_v[n_v] = \langle \psi_{gs}[n_v]| \hat{H} | \psi_{gs}[n_v] \rangle = E_{gs} \tag{6.3.2}
\]

Where \( \hat{H} = \hat{T} + \hat{V} + \hat{U} \). HK theorem II states that for any other \( v \)-rep density \( n' \) of \( N \) electrons:

\[
E_v[n_v] < E_v[n'] \tag{6.3.3}
\]

The proof is an immediate consequence of the quantum mechanical variational principle:

\[
E_v[n'] = \langle \psi_{gs}[n']| \hat{H} | \psi_{gs}[n'] \rangle > \langle \psi_{gs}[n_v]| \hat{H} | \psi_{gs}[n_v] \rangle = E_{gs} \tag{6.3.4}
\]

This theorem allows one to speak of a "minimum-principle" concerning the density. If we have an approximate \( E_v[n] \) we can find an approximation to the ground-state density \( n_v \), simply by finding the minimum.

The fact that \( F_{HK}[n] \) is convex (in the limited sense, since there is still the issue of domain of definition discussed below), as proved in the previous section, implies that \( E_v[n] \) is convex as well, since by adding a linear term to a function one cannot change its convex/non-convex character. The convexity is desirable since it assures that the minimum is not only global, but that there are no local minima as well, since a convex function (and functional) have no truly local minima. There is still the problem of the convexity of the domain and this spoils this useful conclusion. Below we show how to construct a functional with a convex domain. But then, we lose the convex property of the functional.
We now derive the basic equation of DFT (ignoring for the time being the problem of convexity of the domain). We need to minimize $E_v[n]$ under the constraint that $\int n(r) d^3r = N_e$. Thus we need to minimize the Lagrangian:

$$L_{v,N_e}[n] = E_v[n] - \mu \left[ \int n(r) d^3r - N_e \right]$$

(6.3.5)

Where the value of $\mu$ is varied until the constraint is respected. The final minimizing density obeys:

$$0 = \frac{\delta L_{v,N_e}[n]}{\delta n(r)} = \frac{\delta E_v[n]}{\delta n(r)} - \mu = \frac{\delta F_{HK}[n]}{\delta n(r)} + v(r) - \mu$$

(6.3.6)

This is the basic equation of DFT. It has no direct mention of the wavefunction. Once we find an approximation for $E_v[n]$ we can get an approximation for $n_e(r)$ from this equation.

The two theorems of HK put some rigor into the Thomas-Fermi approximation. In this KH theory $E_{TF}[n]$ is an approximation to $E_v[n]$ and the TF equations are an application of (6.3.5). Still, we know that TF theory is very poor for chemistry. This means that despite the added rigor, the TF approximation is too cumbersome for quantum chemistry.

**D. An interesting observation on the variational principle of non-interacting electrons**

Consider a system of $N$ non-interacting particles in a potential $v(r)$. Usually we may assume that the ground state of this system is a Slater wave function $\Phi = \det[\phi_1 ... \phi_N]$. The variational theorem states that their ground state energy is given by minimizing:

$$E[v] = \sum_{n=1}^{N} \langle \phi_n | \hat{\mathbf{H}} + \vec{v} | \phi_n \rangle - \sum_{n=1}^{N} \epsilon_n((\phi_n | \phi_n) - 1)$$

(6.4.1)
Where $\hat{T}_1 = -\frac{1}{2} \nabla^2$, $\varepsilon_n$ are Lagrange multipliers imposing the unit norm of each orbital. Minimizing leads to the equations:

\[
(\hat{T}_1 + \varepsilon)\phi_n = \varepsilon_n \phi_n \tag{6.4.2}
\]

After solving for the $N$ lowest energy eigenstates the energy is $E[v] = \sum_{n=1}^{N} \varepsilon_n$, the kinetic energy is $T[v] = \sum_{n=1}^{N} \langle \phi_n | \hat{T}_1 | \phi_n \rangle$ the density is $n(r) = \sum_{n=1}^{N} |\phi_n(r)|^2$.

Now consider a different problem. Suppose the density is given and one is required to find the system with this density that has the minimum kinetic energy $T$. This leads to the Lagrangian:

\[
T[n] = \sum_{n=1}^{N} \langle \phi_n | \hat{T}_1 | \phi_n \rangle + \int v(r) \left( \sum_{n=1}^{N} |\phi_n(r)|^2 - n(r) \right) - \sum_{n=1}^{N} \varepsilon_n (\langle \phi_n | \phi_n \rangle - 1) \tag{6.4.3}
\]

Now $v(r)$ are Lagrange multipliers and must be searched for in order that the constraint $n(r) = \sum_{n=1}^{N} |\phi_n(r)|^2$ be fulfilled. After minimizing we obtain the equations:

\[
(\hat{T}_1 + \varepsilon)\phi_n = \varepsilon_n \phi_n \tag{6.4.4}
\]

This equation rises from the attempt to compute $T[n]$ and is the same as Eq. (6.4.2) which rose as when $v$ was given and $E[v]$ was calculated. This shows that minimizing the kinetic energy under a given density invokes “the same” equations as minimizing the energy when the potential is given. This fact will be used in the Kohn-Sham method.
**E. The set of V-representable densities**

i. **V-rep densities correspond to ground states wave function of some potential well**

The HK theorem shows that the ground state density of a system uniquely determines the one body potential. This is a uniqueness statement: there is at most one potential associated with a density. An interesting twist is the reverse question: what are the conditions that a given density is the ground state density (GSD) of some system? Of course there are some preliminary conditions on the density: it must be non-negative and it must integrate to a positive integer:

\[
\begin{align*}
n(r) & \geq 0 \\
\int n(r)\,d^3r &= N_e
\end{align*}
\]  

But in general, we have no good criterion for deciding whether a given density \( n(r) \) is a GSD of some potential \( v(r) \). Densities which are GSDs of a potential are called "v-representable". In short v-rep.

When we say that everything is a functional of the density, we mean everything is a functional of a v-rep density.

ii. **Some non-v-representability issues**

We have seen in XXX that ground state wave functions of single particles is nodeless. A corollary from the above analysis is that a density of one particle with a node is not v-representable.

However, the density does not need to actually develop a zero for the density to be non-vrep. Consider the example by Englisch and Englisch:
If \( \psi(x) \) is a wavefunction then the potential is given by \( v(x) = \frac{1}{2} \frac{\psi''(x)}{\psi(x)} \). Using the above form for \( \alpha = \frac{1}{3} \), we find that the potential is infinite at the origin:

\[
n(x) \propto (1 + (x^2)\alpha^2)e^{-\sqrt{x^2}} \quad \frac{1}{4} \leq \alpha < \frac{1}{2}.
\]

Figure VI-2: Examples, following Englisch and Englisch, of a non-vrep density (in purple) and the corresponding potential which is singular. The left panel is a 1D example which the right panel is the radial 3D example.

In 3 dimensions simply replace \( x \) by \( r \) and \( \psi''(x) \) by \( \nabla^2 \psi(r) = \frac{1}{r^2} \left( r^2 \psi(r) \right)'' \) thus: \( v(r) = \frac{1}{2} \frac{(r^2 \psi(r))''}{r^2 \psi(r)} - \frac{1}{r^2} \). The first term of the potential is seen to dominated by a term going as \( \frac{1}{r^2} \) when \( r \to 0 \). This is a centrifugal barrier with \( \ell = 1 \). Subtracting this barrier exposes the bare potential, shown in Figure VI-2.

### iii. The set of v-rep densities of a given electron number is not convex

Degenerate Hamiltonians can generate non-vrep densities quiet easily. Thus, non-vrep densities are much more abundant than one may suspect. Let us see why there is a problem, in the following analysis due to Levy and Lieb (developed seperately at the same time more or less).

Suppose \( \hat{H} = \hat{T} + \int v(r)\hat{n}(r)d^3r + \hat{U} \) is a Hamiltonian with degenerate ground states, of energy \( E \) and full degeneracy \( Q \). Thus, \( \Psi_i, i = 1, \ldots, Q \) are Q ground
state wave functions with $< \Psi_i | \Psi_j > = \delta_{ij}$. There are infinitely many ways to define the $\Psi_i$. We select one arbitrarily. Denote: $n_i(r) = < \Psi_i | \hat{n}(r) | \Psi_i >$. Then, consider the density built as a convex sum of these degenerate-state densities:

$$n(r) = \sum_{i=1}^{Q} c_i n_i(r) \quad c_i > 0 \quad \sum_{i=1}^{Q} c_i = 1 \quad (6.5.2)$$

We now show that this density it is usually non-v-representable. Of course, it may happen (in rare cases) that a linear combination of the degenerate wave functions $\Psi = \sum_{i=1}^{Q} b_i \Psi_i$ yields $n(r) = < \Psi | \hat{n}(r) | \Psi >$. This case however is not ordinary and we consider the cases where this does not happen. We thus proceed to show that $n(r)$ cannot be the groundstate density of any other Hamiltonian as well. We do this by contradiction and assume existence of a wavefunction $\Psi'$ which is the GS of some $\hat{H}'$ and such that $< \Psi' | \hat{n}(r) | \Psi' > = n(r)$. The variational principle states $< \Psi_i | \hat{H}' | \Psi_i > > < \Psi' | \hat{H}' | \Psi' >$ for each $i$. Multiply by the positive $c_i$ (so the inequality is not spoiled) and sum over $i$, using $\sum_{i=1}^{Q} c_i = 1$, and obtain $\sum_{i=1}^{Q} c_i < \Psi_i | \hat{H}' | \Psi_i > > < \Psi' | \hat{H}' | \Psi' >$. Now use the same reasoning that led to Eq. (6.1.7) and replace $\hat{H}'$ by $\hat{H}$, obtaining:

$$\sum_{i=1}^{Q} c_i < \Psi_i | \hat{H} | \Psi_i > > < \Psi' | \hat{H} | \Psi' >$$. However, $< \Psi_i | \hat{H} | \Psi_i > = E$ and so this leads to $< \Psi' | \hat{H} | \Psi' > < E$ which contradicts of the variational principle for $\Psi_i$. Hence, $\Psi'$ cannot be the ground-state of any Hamiltonian.

Example: The above theorem is general and holds for any system of particles. We consider non-interacting electrons. Consider the density of non-interacting electrons in the potential well created by a a Lithium nucleus. The ground state is 4-fold degenerate $\Psi_1 = |1s^22s\rangle$, $\Psi_2 = |1s^22p_x\rangle$, $\Psi_3 = |1s^22p_y\rangle$, $\Psi_4 = |1s^22p_z\rangle$

with $\psi_{1s} = \frac{e^{-r}}{\sqrt{\pi}}$, $\psi_{2s} = \frac{e^{-2(r-2)}}{\sqrt{32\pi}}$, $\psi_{2p_x} = \frac{e^{r}x}{\sqrt{32\pi}}$, $\psi_{2p_y} = \frac{e^{r}y}{\sqrt{32\pi}}$, $\psi_{2p_z} = \frac{e^{r}z}{\sqrt{32\pi}}$.
The 4 densities are: 

\[
\begin{align*}
    n_1 &= 2n_{1s} + n_{2s}, \\
    n_2 &= 2n_{1s} + n_{2p_x}, \\
    n_3 &= 2n_{1s} + n_{2p_y}, \\
    n_4 &= 2n_{1s} + n_{2p_z}.
\end{align*}
\]

The average is given by:

\[
n(r) = \frac{1}{4} \sum_{i=1}^{4} n_i(r) = 2 \frac{e^{-2r}}{\pi} + \frac{e^{-r}}{128\pi} ((r - 2)^2 + r^2)
\]

This density is spherically symmetric and is plotted below, together with the density \(n_1(r)\) for comparison:

Figure VI-3: Left panel: The average density of \(n(r)\) plotted together with the almost identical density \(n_1(r)\) orbital. Both densities seem almost identical yet the latter is \(v\)-rep while the former not. Right panel: The difference between the two densities

This density is very naïve and there is no visible indications suggesting this is not (non-interacting) \(v\)-representable. We ave found that such convex sum densities are not \(v\)-representable in the sense that there is no Hamiltonian for which a ground-state yields the density. However, clearly these densities are associated with the potential \(v(r)\) which created the degenerate states. One can extend the Hohenberg-Kohn functional definition to deal with these convex sum densities in the following way. Given a density which is not \(v\)-representable in the usual way, we now call it non-pure-state \(v\)-representable. Then we will say that such a density is ensemble-\(v\)-representable and assume it is associated with the potential \(v(r)\) from which the degenerate ground-states \(\Psi_i\) were formed. Then for such a density the HK functional is written as:
Here, we implicitly made the identification $n \to v \to c_i$. The HK uniqueness theorem guaranteeing that only one potential $v$ can form a given $n$ can be extended also to this case (i.e. that $n \to v$ is meaningful) still holds. Furthermore, the minimum principle, i.e. that $E_v[n]$ with the more general $F_{HK}$ obtains its minimum at the density corresponding to $v(r)$ remains true.

### F. Levy-Lieb generalization of the HK functional

The minimum principle of HK is of crucial importance for density functional theory. Yet, the basic equation (Eq. (6.3.6)) which is the basis for development of DFT into a practical approach is somewhat problematic from the mathematical point of view. In order to define the functional derivative, one must ensure that there is an “open” neighborhood of the ground state density $n_v(r)$ for which $F_{HK}[n]$ can be defined for any density. As we saw, there is a fundamental problem is that of v-representability. The ensemble v-representability solved one kind of problems but it is not clear if there may be additional classes of non-v-representability. It is not possible to assume that any density that is positive and integrates to an integer is a density of a ground state wave function of a Hamiltonian. Furthermore, we cannot even assume that around a v-representable density there is an “open neighborhood” of v-representable densities.

In general one cannot waive the possibility that there may be densities which are not the ground state densities of any system and still are arbitrarily close to any $n_v(r)$ of interest. In such a case the functional derivative of $F_{HK}$ is formally undefined.
A way around these problems, developed separately by Levy and by Lieb is to formulate a functional $F_{LL}[n]$ defined for any density on the one hand and equal to $F_{HK}[n]$ for v-representable densities on the other which still allows for the same type of minimum principle as does the HK functional. We first note an important property of $F_{HK}[n]$. We say that the wave function $\Psi$ realizes the density $n(r)$ (and symbolize this as $\Psi \rightarrow n$) if:

$$\langle \Psi | \hat{n}(r) | \Psi \rangle = n(r) \quad \Leftrightarrow \quad \Psi \rightarrow n$$ \hspace{1cm} (6.5.4)

We will now show that for any wavefunction $\Psi$ which realizes $n(r)$

$$\Psi \rightarrow n \quad \Rightarrow \quad F_{HK}[n] \leq \langle \Psi | \hat{\mathcal{T}} + \hat{U} | \Psi \rangle$$ \hspace{1cm} (6.5.5)

This is a direct result of the variational principle: $F_{HK}[n] = E_{gs}[n] - \int v(r)n(r)d^3r \leq \langle \Psi | \hat{H} | \Psi \rangle - \int v(r)n(r)d^3r = \langle \Psi | \hat{\mathcal{T}} - \hat{\mathcal{V}} | \Psi \rangle = \langle \Psi | \hat{\mathcal{T}} + \hat{U} | \Psi \rangle$.

From this development we see also that the wave-function which realizes this minimum is the ground-state wave function and is denoted $\Psi_{gs}[n]$. One has therefore:

$$F_{HK}[n] = \min_{\Psi \rightarrow n} \langle \Psi | \hat{\mathcal{T}} + \hat{U} | \Psi \rangle$$ \hspace{1cm} (6.5.6)

Levy and Lieb decided to use this relation, valid only for v-rep densities as the definition of their functional, valid for any density:

$$F_{LL}[n] \equiv \min_{\Psi \rightarrow n} \langle \Psi | \hat{\mathcal{T}} + \hat{U} | \Psi \rangle$$ \hspace{1cm} (6.5.7)

Exercise: Show that for any density there is at least one wave function which realizes it

Solution: For a one-electron case this is trivial, since the density is non-negative we can take the wave function as $\Psi(r) = \sqrt{n(r)}$. For $N$ electrons, just “slice” $n(r)$ to $N$ non-overlapping parts each: positive, integrating to 1: (1) $n(r) = \sum_{k=1}^{N} n_k(r)$, (2) $n_k(r) \geq 0$, (3) $\phi_i(r)\phi_j(r) = \delta_{ij}n_j(r)$ where $\phi_k(r) = \sqrt{n_k(r)}$, and (4)
\[ \int n_k(r) = 1. \] This can be done in countless ways (with a good sharp knife). Then the determinant \( \Psi = [\phi_1 \phi_2 \ldots \phi_{N_e}] \), is a wavefunction which creates \( n(r) \).

The above exercise shows, that the definition in Eq. (6.5.7) makes sense for practically all densities. One can now use \( F_{LL}[n] \) instead of \( F_{HK}[n] \) in Eq. (6.3.1) and convert the Hohenberg-Kohn minimum principle to a variational-minimum principle. The search for the constrained minimum can be done using a Lagrange multiplier approach. We formulate the Lagrangian:

\[
\tilde{F}_{LL}[\Psi, n, v] \equiv \langle \Psi | \hat{T} + \hat{U} | \Psi \rangle + \int v(r) [\langle \hat{n}(r) \Psi | \Psi \rangle - n(r)] d^3r
\] (6.5.8)

Given \( n(r) \), one now find suitable Lagrange multipliers \( v(r) \) such that when minimizing \( F_{LL} \) with respect to an antisymmetric wave function \( \Psi \) leads to the constraint \( \langle \Psi | \hat{n}(r) | \Psi \rangle = n(r) \) at any \( r \). The search for a minimizing wave function will cease when the gradient is zero, so a necessary condition is:

\[
\frac{\delta}{\delta \Psi} F_{LL}[\Psi, n, v]_{\Psi = \Psi_{LL}, v = v_{LL}} = 0 = \left( \hat{T} + \hat{U} + \int v_{LL}(r)\hat{n}(r) d^3r \right) \Psi_{LL}
\] (6.5.9)

Thus, when \( n(r) \) is given, the Lagrange multiplier function \( v_{LL}(r) \) that imposes the condition defines a Hamiltonian \( \tilde{H}_{LL} = \hat{T} + \int v_{LL}(r)\hat{n}(r) d^3r + \hat{U} \).

Note that \( v_{LL}(r) \) is determined by the procedure up to a constant. If \( n(r) \) is v-rep then necessarily, by Kohn’s theorem, \( F_{LL}[n] = F_{HK}[n] \) and \( \Psi_{LL} \) is the groundstate wave function. However, we are not in general assured that \( \Psi_{LL} \) is always the ground state, since \( n(r) \) is not necessarily v-rep. Indeed, from (6.5.9), all we can say is that \( \Psi_{LL} \) must be some eigenstate of \( \tilde{H}_{LL} \).

Once the minimum is attained, one can take the functional derivative of \( F_{LL} \) by \( n(r) \). As with any constrained minimization, when the derivative of the
optimized solution is taken with respect to the constraints, one obtains the
Lagrange multiplied (see Error! Reference source not found.):
\[
\frac{\delta}{\delta n(r)} \tilde{F}_{\text{LL}}[\Psi, n, v] = -v_{\text{LL}}(r) \tag{6.5.10}
\]

Now, once the constrained minimum $F$ has been found, one can plug $F$ into
the HK scheme and consider the Lagrangian corresponding to $E_v = \tilde{F}_{\text{LL}} +
\int v(r)n(r)d^3r$:
\[
L_v[n] = \tilde{F}_{\text{LL}} + \int v(r)n(r)d^3r - \mu \left[ \int n(r)d^3r - N \right] \tag{6.5.11}
\]

If now one searches for the density that minimizes this functional one
immediately obtains:
\[
0 = \frac{\delta L_v}{\delta n(r)} = -v_{\text{LL}}(r) + v(r) - \mu \tag{6.5.12}
\]

Showing that the minimum of $E_v[n]$ is obtained when the density found
admits, as Lagrange multiplier $v_{\text{LL}}(r)$, the same potential as was give to start
with $v(r)$, up to a constant.

Even with the LL functional one problem is still not solved: convexity. While
the domain of definition is now finally convex, the functional has lost
convexity. A counterexample for convexity can be given, using the degenerate
system used above to prove that the domain of definition of the HK functional
is non-convex. Indeed, for that system, which had a potential $v(r)$ and
degenerate eigensstates $\Psi_i$ ($i = 1, ..., Q$) all of energy $E$:
Showing that for these densities the functional is concave (while for the case where $n_i$ and $\sum_i c_in_i$ are all v-rep the functional is convex). Therefore overall the functional is not convex.

Once again, it is possible to circumvent this problem by extending the definition to ensemble densities.

Exercise: Discuss the Levy approach for a given density $n(r)$ of a system of non-interacting electrons.

In this case the Hamiltonian is $\hat{H} = \hat{T} + \int v(r)\hat{n}(r)d^3r$ i.e. a 1-body Hamiltonian. Suppose $\psi_m$, $m = 1, 2, \ldots$ are the 1-particle states which are eigenstates of $\hat{H}_1 = \hat{T}_1 + \int v(r)\hat{n}(r)d^3r$:

$$-\frac{\hbar^2}{2m_e}\nabla^2\phi_m(r) + v(r)\phi_m(r) = \epsilon_m\phi_m(r)$$

Let us suppose orbital energy ordering, so that $\epsilon_1 \leq \epsilon_2 \leq \epsilon_3 \ldots$ If the density is “non-interacting v-rep” then it must be due to the Slater wave function $D_{gs} = |\phi_1 \cdots \phi_{N_e}|$ of the lowest energy $N_e$ orbitals. In this case, the kinetic energy is given by:

$$T_{LL}[n] = \sum_{m=1}^{N_e} \langle \phi_m | \hat{T} | \phi_m \rangle$$

And the functional derivative is:
If we are given a non-interacting non-v-rep density then we might find not a ground state but an excited determinant, for example: $D_{ex} = |\phi_1 \cdots \phi_{N_e-1} \phi_{N_e+1}|$. This leads to “holes” in the non-interacting system.

### G. The dilation inequality for the HK functional

We have already seen the the HF functional is convex. More exact properties are desirable, so that when one derives approximations to this functional, they can perhaps be forced to obey the known exact relations. One approach is to use dilation considerations. This will lead to an interesting inequality.

We will use the following symbol convention:

\[
\Psi_{\gamma}(r_1, r_2, \ldots, r_{N_e}) \equiv \gamma^{3N_e/2} \Psi(\gamma r_1, \gamma r_2, \ldots, \gamma r_{N_e})
\]

\[
n_{\gamma}(r) \equiv \gamma^3 n(\gamma r)
\]

It is quite straightforward to show the following relations:

**Exercise**

Derive the following relation

\[
\langle \Psi_{\gamma} | \hat{n}(r) | \Psi_{\gamma} \rangle = \gamma^3 \langle \Psi | \hat{n}(\gamma r) | \Psi \rangle
\]

\[
\langle \Psi_{\gamma} | \hat{T} | \Psi_{\gamma} \rangle = \gamma^2 \langle \Psi | \hat{T} | \Psi \rangle
\]

\[
\langle \Psi_{\gamma} | \hat{\mathcal{U}} | \Psi_{\gamma} \rangle = \gamma \langle \Psi | \hat{\mathcal{U}} | \Psi \rangle
\]

From the first relation in this equation, one can deduce that if $\Psi \rightarrow n(r)$ (i.e. $\Psi$ is a many-electron wave function exhibiting the spatial density $n(r)$) then:

\[
\langle \Psi_{\gamma} | \hat{n}(r) | \Psi_{\gamma} \rangle = \gamma^3 \langle \Psi | \hat{n}(\gamma r) | \Psi \rangle = \gamma^3 n(\gamma r) = n_{\gamma}(r)
\]

One can now also use this relation to get a dilation inequality. Indeed, since $\Psi_{gs}(n)_{\gamma}$ realizes the density $n_{\gamma}(r)$ (see the first of Eqs. (6.6.2)): $F_{HK}[n_{\gamma}] \leq$
\(\langle \psi_{gs}[n]|\hat{T} + \mathcal{O}|\psi_{gs}[n]\rangle = \gamma^2 \langle \psi_{gs}[n]|\hat{T}|\psi_{gs}[n]\rangle + \gamma \langle \psi_{gs}[n]|\mathcal{O}|\psi_{gs}[n]\rangle\), thus we find the following exact dilation inequality:

\[
F_{HK}[n_\gamma] \leq \gamma^2 T[n] + \gamma U[n] = \gamma^2 F_{HK}[n] + \gamma (1 - \gamma)U[n] \tag{6.6.4}
\]

In particular, when \(\gamma = \frac{1}{2}\) we have:

\[
4F_{HK}[n_{1/2}] \leq T[n] + 2U[n] = F_{HK}[n] + U[n] \tag{6.6.5}
\]