Thinking about foundations pays off in the long run.  
— Lucien Hardy[20]

2.1 PRELIMINARIES

The main focus of Quantum Chemistry is the non relativistic $N$-electron Hamiltonian

\[
\hat{H}[v] := -\frac{1}{2} \sum_{i=1}^{N} \nabla_{i}^2 + \frac{1}{2} \sum_{j=1 \neq i}^{N} v_{\text{ee}}(|\mathbf{r}_i - \mathbf{r}_j|) + \sum_{i=1}^{N} v_{\text{ext}}^{\text{ext}}(\mathbf{r}_i). \tag{2.1}
\]

The kinetic energy operator $\hat{T}$ and the electron-electron repulsion operator $\hat{V}_{\text{ee}}$ are the same for all complexes with the same number of particles $N$. Therefore, the Hamiltonian in eq. (2.1) describes different systems by varying the external potential, as indicated by the square brackets on the right hand side.

In Chemistry, Atomic Physics, and Solid State Physics the external potential represents typically the attraction to $M$ nuclei located at a fixed position $\mathbf{R}_a$:

\[
v_{\text{ext}}(\mathbf{r}_i) = -\sum_{\alpha=1}^{M} \frac{Z_{\alpha}}{|\mathbf{r}_i - \mathbf{R}_\alpha|}, \tag{2.2}
\]

while the electron-electron interaction is given by the Coulomb term

\[
v_{\text{ee}}(|\mathbf{r}_i - \mathbf{r}_j|) = \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|}. \tag{2.3}
\]

Via the Schrödinger equation

\[
\hat{H}[v] \Psi_0 = E_0[v] \Psi_0 \tag{2.4}
\]

the external potential determines the ground state function $\Psi_0$, the corresponding ground state energy $E_0[v]$ and all the ground state observables of the system (in absence of degeneracies). In particular, it fixes the ground state one-electron density, defined as

\[
\rho_0(\mathbf{r}) := \sum_{i=1}^{N} \langle \Psi_0 | \delta(\mathbf{r} - \mathbf{r}_i) | \Psi_0 \rangle = N \int_{\Omega} |\Psi_0(\mathbf{r}, \mathbf{r}_2, \ldots, \mathbf{r}_N)|^2 d\mathbf{r}_2 \ldots d\mathbf{r}_N. \tag{2.5}
\]
Equivalently to eq. (2.4), one can obtain the ground state energy applying the Rayleigh-Ritz variational principle:

$$E_0[v] = \inf_{\Psi \in \mathcal{W}_N} \langle \Psi | \hat{H} | \Psi \rangle,$$

(2.6)

with

$$\mathcal{W}_N = \{ \Psi \in H^1_N | \| \Psi \|_2 = 1, \Psi \text{ antisymmetric} \},$$

(2.7)

where $H^1_N$ denotes the first order Sobolev space, an Hilbert space with inner product given by

$$\langle \Psi_1 | \Psi_2 \rangle = \langle \Psi_1 | \Psi_2 \rangle + \sum_{i=1}^{N} \langle \nabla_i \Psi_1 | \nabla_i \Psi_2 \rangle.$$

(2.8)

2.2 THE HOHENBERG-KOHN THEOREM AND THE LEVY-LIEB CONSTRAINED FORMULATION

A direct consequence of eq. (2.6), together with the fact that potentials that differ for more than a constant yield to different ground states\(^1\), is the concavity of the ground state energy $E_0[v]$ as a functional of the external potential. In other words, if $\rho$ is the ground state density associated with the potential $\rho$, for any potential $v \neq \rho + c$, $c \in \mathbb{R}$ we have

$$E_0[v] = \langle \rho | \hat{H} | \rho \rangle < \langle \rho | \hat{H} | \rho \rangle = E_0[\rho] + \int (v(r) - \rho(r))\rho(r)dr.$$  

(2.9)

Considering two potentials $v_1$ and $v_2 \neq v_1 + c$ and the corresponding ground state densities $\rho_1$ and $\rho_2$, we can use eq. (2.9) twice to get

$$\int (v_1(r) - v_2(r)) (\rho_1(r) - \rho_2(r))dr < 0$$

(2.10)

which implies

$$v_1 \neq v_2 + c \Rightarrow \rho_1 \neq \rho_2.$$  

(2.11)

That is to say, potentials that differs for more than a constant $c$ must yield different ground state densities. This is the content of the Hohenberg and Kohn theorem: there is a one-to-one correspondence between the potential and its ground state density. Defining the sets

$$\mathcal{V}_N := \{ v | \hat{H}[v] \text{ has an N-electron ground state} \},$$

(2.12)

$$\mathcal{A}_N := \{ \rho | \rho \text{ is obtained from an N-electron ground state of } \hat{H}[v], v \in \mathcal{V}_N \},$$

(2.13)

we introduce the Hohenberg-Kohn universal functional as the Legendre transform of the functional $E_0[v]$:

$$F_{HK}[\rho] := \max_{v \in \mathcal{V}_N} \left\{ E_0[v] - \int v(r)\rho(r)dr \right\}, \quad \rho \in \mathcal{A}_N.$$  

(2.14)

\(^1\)This is sometimes addressed as the first Hohenberg-Kohn theorem. The original work\(^5\), does not contain a demonstration of this fact, being presented as self-evident.
2.2 THE HK THEOREM AND THE LL CONSTRANDED FORMULATION

Figure 2.1: Schematic representation of the relation between the ground state density, the external potential and the (possibly $k$-degenerate) ground state.

By "universal" we mean that it is the same for every system with a given number of particles. Since also the ground state wavefunction is a functional of the ground state density (see fig. 2.1), we can write

$$E_0[v] = \inf_{\varrho \in \mathcal{A}_N} \left\{ F_{HK}[\varrho] + \int v(r) \varrho(r) \, dr \right\}, \quad v \in \mathcal{V}_N. \quad (2.15)$$

Unfortunately, the sets $\mathcal{A}_N$ and $\mathcal{V}_N$ are not known a priori. To overcome this issue, the Levy-Lieb constrained approach redefines the universal functional as

$$F_{LL}[\varrho] = \min_{\Psi \rightarrow \Psi_0} \langle \Psi | \hat{T} + \hat{V}_{ee} | \Psi \rangle \quad (2.16)$$

and obtain the ground state energy by

$$E_0[v] = \inf_{\varrho \in \mathcal{I}_N} \left\{ F_{LL}[\varrho] + \int v(r) \varrho(r) \, dr \right\}, \quad v \in \mathcal{V}_C, \quad (2.17)$$

where the minimization is carried over the N-representable densities

$$\mathcal{I}_N := \{ \varrho \geq 0 | \int \varrho = N, \sqrt{\varrho} \in H_1^1 \}. \quad (2.18)$$

Notice that, since $\mathcal{A}_N \subseteq \mathcal{I}_N$, we have $F_{HK}[\varrho] = F_{LL}[\varrho]|_{\mathcal{A}_N}$.

Moreover, the potential $v$ is not required any more to support a $N$ particles ground state function as in eq. (2.12). We denoted the set of such potentials as $\mathcal{V}_C$.

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2 It is important to stress that it is not forbidden, for an Hamiltonian with a different kinetic energy operator $\hat{T}$ or different electron-electron operator $\hat{V}_{ee}$, to have the same ground state density of Hamiltonian (2.1).
2.3 The Lieb Density Matrix Constrained-Search Functional

The functional $F_{LL}[\psi]$ is not convex, implying that the mapping $\psi \to F_{LL}[\psi] + \int v \psi$ could have non-global minima that hamper the minimization in eq. (2.17). Extending the Levy-Lieb constrained-search formalism to ensembles of states allows to introduce a convex functional $F_{DM}$ that bypasses this difficulty. The extension to density-matrices is straightforward, and the derivation largely follows the one in sec. 2.2.

To start with, we introduce the set of all N-electron ensemble density matrices as:

$$D_N := \{ \hat{\chi} | \hat{\chi} = \sum_{i=1}^{N} p_i |\Psi_i \rangle \langle \Psi_i|, \ p_i \geq 0, \sum_{i=1}^{N} p_i = 1, \ |\Psi_i \rangle \in \mathcal{W}_N \}, \ (2.19)$$

and recast eq. (2.6) as

$$E_0[v] = \inf_{\hat{\chi} \in D_N} \text{Tr} \{ \hat{\chi} \hat{H} |v| \}. \quad (2.20)$$

Next, we define the convex set

$$B_N = \{ |\psi \rangle | \psi \text{ is obtained from an N-electron ground state density matrix} \}$$

with $A_N \subsetneq B_N$. In analogy with eqs. (2.14), (2.15) we introduce the extended Hohenberg-Kohn functional as

$$F_{eHK}[\psi] = \max_{v \in \mathcal{V}_N} \{ E_0[v] - \int v(\mathbf{r}) \psi(\mathbf{r}) d\mathbf{r} \}, \ \psi \in B_N, \quad (2.22)$$

and the Hohenberg-Kohn variational principle now reads as

$$E_0[v] = \min_{\psi \in B_N} \{ F_{eHK}[\psi] + \int v(\mathbf{r}) \psi(\mathbf{r}) d\mathbf{r} \}, \ \psi \in \mathcal{V}_N. \quad (2.23)$$

It is clear, however, that this generalization suffers from the same flaws as the ones in sec. 2.2, namely the resort to a priori unknown domains $\mathcal{V}_N$ and $B_N$. The two-step minimization procedure used in sec. 2.3 comes to our help again: first extend the set

$$I_N := \{ |\psi \rangle | |\psi \rangle = \text{Tr} \{ \hat{\psi} \hat{\chi} \}, \ \hat{\chi} \in D_N \}. \quad (2.24)$$

Next, introduce the Lieb density matrix constrained functional as

$$F_{DM}[\psi] = \inf_{\hat{\chi} \rightarrow \psi} \text{Tr} \{ \hat{\chi} \left( \hat{T} + \hat{V}_{ee} \right) \}, \ \psi \in I_N, \quad (2.25)$$

from which the Hohenberg Kohn minimisation principle now reads

$$E_0[v] = \inf_{\psi \in I_N} \{ F_{DM}[\psi] + \int v(\mathbf{r}) \psi(\mathbf{r}) d\mathbf{r} \}, \ \psi \in L^{3/2} + L^\infty. \quad (2.26)$$

The following inclusion relations hold for the sets introduced so far:

$$A_N \subsetneq B_N \subsetneq I_N, \quad (2.27)$$

$$\mathcal{V}_N \subsetneq \mathcal{V}_C \subsetneq L^{3/2} + L^\infty. \quad (2.28)$$
As a consequence, the relation between the universal functionals introduced hitherto reads

\[ F_{\text{HK}} = F_{\text{eHK}}|_{A_N} = F_{\text{LL}}|_{A_N} = F_{\text{DM}}|_{A_N}, \]
\[ F_{\text{eHK}} = F_{\text{LL}}|_{B_N} = F_{\text{DM}}|_{B_N}. \]

In what follows we shall mostly refer to the Levy-Lieb constrained search functional \( F_{\text{LL}}[\phi] \), which shall be denoted for simplicity \( F[\phi] \). The concepts outlined in the following sections can be extended to density matrices in a straightforward manner\[21\].

### 2.4 The Kohn-Sham Self-Consistent Scheme

Despite its apparent simplicity, the approach outlined in eq. (2.15) is not easy to pursue, since the explicit form of the universal functional \( F[\phi] \) is not known in general. Therefore, one needs to introduce approximations that allow to apply the variational principle effectively.

The most popular strategy, devised by Kohn and Sham in 1965\[6\], consists in introducing an auxiliary non-interacting system that has the same ground-state density as the interacting one

\[ E_0[\psi] := \min_{\psi} \langle \psi | \hat{T} + \hat{V}_s[\phi] | \psi \rangle = \min_{\psi \rightarrow \uparrow \downarrow} \langle \psi | \hat{T} | \psi \rangle + \int \nu_s[\phi](r) \phi(r) dr. \]

The Kohn Sham potential \( \hat{V}_s[\phi] := \sum_{i=1}^{N} \nu_s[\phi](r_i) \), defined by eq. (2.31), is a one-body operator that acts as an effective potential that mimics the effect of the electron-electron repulsion \( \hat{V}_{ee} \) in eq. (2.1) to provide the same physical density \( \phi \) of the original interacting system. It is an unproved assumption that the KS potential always exists for a well-behaved density. In other words, a non-interacting Hamiltonian which reproduces the ground state density of the true interacting one might not exist. Nevertheless, as discussed in ref. \[22\], it is always possible for a KS system to produce a non interacting \( \nu \)-representable density which approximate an interacting \( \nu \)-representable density to arbitrary accuracy. Alternative ways around the so-called "non interacting \( \nu \)-representability problem" include Moreau-Yosida regularization\[23\] or coarse graining techniques\[24\].

The ground state associated with eq. (2.31) is a Slater determinant of \( N \) orbitals which satisfy

\[ -\frac{1}{2} \nabla^2 + \nu_s[\phi](r) \phi_i(r, \sigma) = \epsilon_i \phi(r, \sigma), \]

\[ \sum_{\sigma} |\phi_i(r, \sigma)|^2 = \phi(r), \]
Table 2.1: Exact kinetic energy and KS kinetic energy for different atoms\[25–27].

<table>
<thead>
<tr>
<th>Atom</th>
<th>T[q]</th>
<th>T[s][q]</th>
</tr>
</thead>
<tbody>
<tr>
<td>He</td>
<td>2.904</td>
<td>2.867</td>
</tr>
<tr>
<td>Be</td>
<td>14.667</td>
<td>14.594</td>
</tr>
<tr>
<td>Ne</td>
<td>128.94</td>
<td>128.1</td>
</tr>
</tbody>
</table>

and from which the non-interacting KS kinetic energy can be readily written down:

\[
T_{s}[q] = -\frac{1}{2} \sum_{i} \sum_{\sigma} \int \phi_{i}^{*}(r,\sigma) \nabla^{2} \phi_{i}(r,\sigma) dr. \quad (2.33)
\]

To unravel the problem of constructing the KS potential, first define the exchange-correlation energy \(E_{xc}[\rho]\):

\[
E_{xc}[\rho] := F[\rho] - \frac{1}{2} \int \frac{\rho(r)\rho(r')}{|r-r'|} dr dr' - T_{s}[\rho]. \quad (2.34)
\]

To within a constant, the Euler Lagrange equations for eqs. (2.31), (2.15) yield

\[
v_{s}[\rho](r) = v(r) + \int \frac{\rho'(r')}{|r-r'|} dr' + \frac{\delta E_{xc}[\rho]}{\delta \rho(r)} \quad (2.35)
\]

where we introduced the exchange correlation potential \(v_{xc}\).

It might seem at first that no progress has been made, as the ignorance of the explicit form of the universal functional \(F[\rho]\) transfers to the exchange correlation energy functional \(E_{xc}[\rho]\).

However, one has to keep in mind that the kinetic energy is typically the main contributor to the total energy, and it is extremely difficult to design explicit and accurate kinetic functionals of the density.

The KS scheme allows to bypass the construction of the kinetic energy \(T[\rho]\), by introducing the functional \(T_{s}[\rho]\), which is implicit in the density but explicit in the KS orbitals \(\phi_{i}\). It turns out that in most cases the KS kinetic energy is a very good approximation to the real one (see table 2.1 for a few examples).

As a consequence, the yet unknown functional \(E_{xc}[\rho]\), which encloses all the energetic contributions beyond the mean field approximation, is a very small fraction of the total energy. In KS Density Functional Theory it is only this small fraction that requires approximations. Given an approximate form for \(v_{xc}\) as a functional of \(\rho\), the eqs. (2.32) can be solved self-consistently starting from an initial guess.
for \( \varrho \). Once \( \varrho \) converges to the ground state density \( \varrho_0 \), the total energy reads

\[
E_0 = \sum_{i=1}^{N} e_i - U_H[\varrho_0] - \int \varrho_0(r) v_{xc}[\varrho_0](r) d\mathbf{r} + E_{xc}[\varrho_0].
\]  

(2.36)

### 2.5 Adiabatic Connection Formalism

The exchange correlation energy \( E_{xc}[\varrho] \) can be written explicitly as a one-dimensional integral on the expectation value of the Coulomb interaction energy \[28\]. To show this, we first introduce the generalized Levy-Lieb universal functional

\[
F_\lambda[\varrho] = \min_{\Psi} \langle \Psi | \hat{T} + \lambda \hat{V}_{ee} | \Psi \rangle := \langle \Psi_\lambda[\varrho] | \hat{T} + \lambda \hat{V}_{ee} | \Psi_\lambda[\varrho] \rangle = T^\lambda[\varrho] + \lambda V_{ee}^\lambda[\varrho].
\]  

(2.37)

Let \( \hat{V}^\lambda[\varrho] = \sum_{i=1}^{N} v^\lambda[\varrho](\mathbf{r}_i) \) be the Lagrange multiplier that guarantees

\[
\langle \Psi_\lambda[\varrho] | \sum_{i=1}^{N} \delta(\mathbf{r} - \mathbf{r}_i) | \Psi_\lambda[\varrho] \rangle = \langle \Psi_{\lambda=1}[\varrho] | \sum_{i=1}^{N} \delta(\mathbf{r} - \mathbf{r}_i) | \Psi_{\lambda=1}[\varrho] \rangle \quad \forall \lambda \in \mathbb{R}.
\]

(2.38)

Under the assumptions that \( \hat{V}^\lambda[\varrho] \) exists for every \( \lambda \), the minimizing wavefunction in eq. (2.37) is also an eigenstate of the Hamiltonian \[29, 30\]:

\[
\hat{H}_\lambda[\varrho] := \hat{T} + \lambda \hat{V}_{ee} + \hat{V}^\lambda[\varrho].
\]

(2.39)

Furthermore, notice eq. (2.37) and \( v^\lambda[\varrho](\mathbf{r}) \) are connected by \[31\]

\[
\frac{\delta F_\lambda[\varrho]}{\delta \varrho(\mathbf{r})}_{\varrho=\varrho^\lambda} = -v^\lambda[\varrho](\mathbf{r}),
\]

(2.40)

as a consequence of the variational principle.

Eq (2.39) connects the physical system (\( \lambda = 1 \)) to the non-interacting KS system (\( \lambda = 0 \)). In particular, \( F_0[\varrho] = T_s[\varrho] \) and \( \hat{V}^0[\varrho] = \hat{V}_s[\varrho] \). As a consequence, defining \( E_0[\varrho](\lambda) = \langle \Psi_\lambda[\varrho] | \hat{H}_\lambda[\varrho] | \Psi_\lambda[\varrho] \rangle \), we have

\[
\begin{align*}
E_0[\varrho](0) &= T_s[\varrho] + \int v_s[\varrho](\mathbf{r}) \varrho(\mathbf{r}) d\mathbf{r} \\
E_0[\varrho](1) &= F[\varrho] + \int v[\varrho](\mathbf{r}) \varrho(\mathbf{r}) d\mathbf{r}.
\end{align*}
\]

(2.41)

Using eqs. (2.34), (2.35), we get

\[
E_{xc}[\varrho] + U_H[\varrho] = E_0[\varrho](1) - E_0[\varrho](0).
\]

(2.42)

On the other hand, since \( \Psi_\lambda[\varrho] \) is an eigenstate of \( \hat{H}_\lambda[\varrho] \), the Hellman-Feynman theorem implies

\[
E_0[\varrho](1) - E_0[\varrho](0) = \int_0^1 \langle \Psi_\lambda[\varrho] | \hat{V}_{ee} | \Psi_\lambda[\varrho] \rangle d\lambda.
\]

(2.43)
Introducing the *Adiabatic Connection integrand*

\[ W_\lambda[q] := \langle \Psi_\lambda[q] | \hat{V}_{ee} | \Psi_\lambda[q] \rangle - U_H[q], \quad (2.44) \]

the exchange correlation energy can be expressed in closed form as

\[ E_{xc}[q] = \int_0^1 W_\lambda[q] d\lambda. \quad (2.45) \]

A sketch of \( W_\lambda[q] \) can be found in fig. 2.2, which shows some of the exact properties that \( W_\lambda[q] \) must satisfy:

- \( W_\lambda[q] \) is negative, monotonically decreasing\[30\].
- The point \( \lambda = 0 \) defines the *exchange* functional \( E_x[q] := W_0[q] \) and reads explicitly in terms of the occupied KS orbitals:

\[ E_x[q] = -\frac{1}{2} \sum_{ij} \int \frac{\phi_i(r')\phi_j(r')\phi_i(r)\phi_j(r)}{|r-r'|} dr dr'. \quad (2.46) \]

- For small values of \( \lambda \), the Görling-Levy perturbation theory\[32, 33\] provides

\[ W_\lambda[q] \sim E_x[q] + \lambda \cdot 2E^{GL2}[q] + \mathcal{O}(\lambda^2), \quad \lambda \ll 1. \quad (2.47) \]

- The high coupling limit defines the functional \( W_{\infty}[q] \), which plays a crucial role in the so-called *Strong Interacting Limit* of Density Functional Theory (see the next chapter):

\[ \lim_{\lambda \to \infty} W_\lambda[q] = W_{\infty}[q]. \quad (2.48) \]

Other more subtle properties of \( W_\lambda[q] \) cannot be guessed by an inspection of a simple blueprint, including:

- The *Lieb-Oxford inequality*\[34, 35\]:

\[ W_\lambda[q] \geq -C_{LO} \int q(r)^{4/3} dr, \quad \forall \lambda > 0. \quad (2.49) \]

Despite the fact that the constant \( C_{LO} \) is not known yet, it is ascertained that \( 1.4442 \leq C_{LO} \leq 1.6358 \)[36–38].

- \( W_\lambda[q] \) satisfies the following scaling property\[39\]:

\[ W_\lambda[q] = \lambda W_1 \left[ \theta_1^\lambda \right], \quad \theta_1^\lambda(r) = \frac{1}{\lambda^3} \theta \left( \frac{r}{\lambda} \right). \quad (2.50) \]

In particular the lower bound \( W_{\infty}[q] \) satisfies\[40\]:

\[ W_{\infty}[q] = \lim_{\lambda \to \infty} \lambda E_{xc} \left[ \theta_1^\lambda \right]. \quad (2.51) \]
In the next chapter we will deepen the properties of $W_\lambda[e]$ at high couplings, starting from its leading term of the expansion in the $\lambda \to \infty$ limit, $W_\infty[e]$. We will then move to the inspection of the subleading orders, their analytical properties and the possible implications for building useful approximations for the exchange correlation functional $E_{xc}[e]$: in fact, they can be used in an interpolation scheme, e.g. the one first presented in ref. [41, 42]. The idea is to fillet the expansions at the two extremes of the domain of the Adiabatic Connection integrand to obtain a global expression that can be used directly in expression (2.43).