Chapter 37
Density Functional Theory of Atoms and Molecules

The Schrödinger equation is a (linear) partial differential equation that can be solved exactly only in very few special cases such as the Coulomb potential or the harmonic oscillator potential. For more general potentials or for problems with more than two particles, the quantum mechanical problem is no easier to solve than the corresponding classical one. In these situations, variational methods are one of the most powerful tools for deriving approximate eigenvalues E and eigenfunctions ψ. These approximations are done in terms of a theory of density functionals as proposed by Thomas, Fermi, Hohenberg and Kohn. This chapter explains briefly the basic facts of this theory.

37.1 Introduction

Suppose that the spectrum $\sigma(H)$ of a Hamilton operator H is purely discrete and can be ordered according to the size of the eigenvalues, i.e., $E_1 < E_2 < E_3 < \cdots$. The corresponding eigenfunctions ψ_i form an orthonormal basis of the Hilbert space $\mathcal{H}$. Consider a trial function

$$\overline{\psi} = \sum_{i=1}^{\infty} c_i \psi_i, \qquad \sum_{i=1}^{\infty} |c_i|^2 = 1.$$

The expectation value of H in the mixed state $\overline{\psi}$ is

$$\overline{E} = \langle \overline{\psi}, H\overline{\psi} \rangle = \sum_{i=1}^{\infty} |c_i|^2 E_i.$$

It can be rewritten as

$$\overline{E} = E_1 + |c_2|^2 (E_2 - E_1) + |c_3|^2 (E_3 - E_1) + \cdots \geq E_1.$$

Hence, $\overline{E}$ is an upper bound for the eigenvalue E_1 which corresponds to the ground state of the system. One basic idea of the variational calculations concerning spectral

properties of atoms and molecules is to choose trial functions depending on some parameters and then to adjust the parameters so that the corresponding expectation value $\overline{E}$ is minimized.

Application of this method to the helium atom by Hylleras played an important role in 1928–1929 when it provided the first test of the Schrödinger equation for a system that is more complicated than the hydrogen atom. In the limit of infinite nuclear mass, the Hamilton operator for the helium atom is

$$H = -\frac{\hbar^2}{2m}(\triangle_1 + \triangle_2) - \frac{e^2}{r_1} - \frac{e^2}{r_2} + \frac{e^2}{r_{12}},$$

where $r_i = |x_i|$ and where $r_{12} = |x_1 - x_2|$ is the electron–electron separation. The term $\frac{e^2}{r_{12}}$ describes the Coulomb repulsion between two electrons. Hylleras introduced trial functions of the form $\overline{\psi} = \sum_{i,j,k} a_{ijk} r_1^i r_2^j r_{12}^k \, e^{-\alpha r_1 - \beta r_2}$ depending on the parameters a_{ijk}, α and β.

The history of the density functional theory dates back to the pioneering work of Thomas [1] and Fermi [2]. In the 1960s, Hohenberg and Kohn [3] and Kohn and Sham [4] made substantial progress to give the density functional theory a foundation based on the quantum mechanics of atoms and molecules. Since then an enormous number of results has been obtained, and this method of studying solutions of many electron problems for atoms and molecules has become competitive in accuracy with up to date quantum chemical methods.

The following section gives a survey of the most prominent of these density functional theories. These density functional theories are of considerable mathematical interest since they present challenging minimization problems of a type which has not been attended to before. In these problems, one has to minimize certain functionals over spaces of functions defined on unbounded domains (typically on $\mathbb{R}^3$) and where nonreflexive Banach spaces are involved.

The last section reports on the progress in relating these density functional theories to the quantum mechanical theory of many electron systems for atoms and molecules. Here the results on self-adjoint Schrödinger operators obtained in Part B will be the mathematical basis. The results on the foundation of density functional theories are mainly due to Hohenberg–Kohn [3] and Kohn–Sham [4]. The original paper by Hohenberg–Kohn has generated a vast literature, see, for instance, [5–9].

Fifty years after the starting point of density functional theory its applications in chemistry and the study of electronic structures have been growing steadily, but the precise form of the energy functional is still elusive. Recently, in the same spirit, a formulation with phase space variables and Wigner functions has been suggested in [10].

37.2 Semiclassical Theories of Density Functionals

The main goal of these semiempirical models is to describe correctly the ground state energy by minimizing various types of density functionals.

In all these density functional theories, we are looking for the energy and the charge density of the ground state by solving directly a minimization problem of the form

$$\min \left\{ F(\rho) + \int \rho(x)v(x)\,\mathrm{d}\,x : \rho \in D_F \right\}.$$

Here, F is a functional of the charge density and depends only on the number N of electrons but not on the potential v generated by the nuclei. The minimum has to be calculated over a set D_F of densities which is either equal to or a subset of $D_N = \left\{ \rho \in L^1(\mathbb{R}^3) : 0 \le \rho, \|\rho\|_1 = N \right\}$ depending on the specific theory considered. Let us mention some of the prominent models.

- The model of *Thomas and Fermi* uses the functional

$$F_{TF}(\rho) = c_{TF} \int_{\mathbb{R}^3} \rho(x)^{5/3}\,\mathrm{d}\,x + D(\rho,\rho)$$

  on the domain $D_{TF} = D_N \cap L^{5/3}(\mathbb{R}^3)$. In the simplest models of this theory, the potential v is given by $v(x) = -\frac{Z}{|x|}$, where $Z > 0$ is a fixed parameter representing the charge of the atomic nucleus and

$$D(\rho,\rho) = \frac{1}{2} \int_{\mathbb{R}^3} \int_{\mathbb{R}^3} \frac{\rho(x)\rho(y)}{|x-y|}\,\mathrm{d}\,x\,\mathrm{d}\,y$$

  is nothing else than the Coulomb energy for the charge density ρ. The constant c_{TF} has the value $3/5$.
- The model of *Thomas–Fermi–von Weizsäcker* is associated with the functional

$$F_{TFW}(\rho) = c_W \int_{\mathbb{R}^3} (\nabla \rho(x)^{1/2})^2\,\mathrm{d}\,x + F_{TF}(\rho)$$

  on the domain $D_{TFW} = D_{TF} \cap H^1(\mathbb{R}^3)$.
- The model of *Thomas–Fermi–Dirac–von Weizsäcker* leads to the functional

$$F_{TFDW}(\rho) = F_{TFW}(\rho) - c_D \int_{\mathbb{R}^3} \rho(x)^{4/3}\,\mathrm{d}\,x$$

  on the same domain D_{TFW}. Note that for $1 \le p_1 < q < p_2$ one has $L^q(\mathbb{R}^3) \subset L^{p_1}(\mathbb{R}^3) \cap L^{p_2}(\mathbb{R}^3)$ and $\|u\|_q \le \|u\|_{p_1}^t \|u\|_{p_2}^{1-t}$ with $t = \frac{\frac{1}{q} - \frac{1}{p_2}}{\frac{1}{p_1} - \frac{1}{p_2}}$ which we apply for $p_1 = 1$, $p_2 = 5/3$ and $q = 4/3$. It follows that $\|\rho\|_{4/3}$ is finite on D_{TFW}. Therefore, the domain of F_{TFDW} is D_{TFW}.

All these models describe partially some observed natural phenomena but are nevertheless rather rudimentary and are no longer in use in the practice of quantum

chemistry. From a theoretical point of view these models are quite interesting since we are confronted with the same type of (mathematical) difficulties as in more realistic approaches.

Though the Thomas–Fermi theory is quite old, a mathematically rigorous solution of the minimization problem has been found only in 1977 by Lieb and Simon [11]. The basic aspects of this solution are discussed in [12, 13].

37.3   Hohenberg–Kohn Theory

The Hohenberg–Kohn theory is a successful attempt to link these semiclassical density functional theories to the quantum mechanics of atoms and molecules. Nevertheless from a mathematical point of view there remain several challenging problems as we will see later.

The N-particle Hamilton operators which are considered are assumed to be of the form

$$H_N = H_N(v) = -\sum_{j=1}^{N} \triangle_j + \sum_{j<k} u(x_j - x_k) + \sum_{j=1}^{N} v(x_j) \equiv H_0 + V, \qquad (37.1)$$

where $v(x)$ is a real-valued function on $\mathbb{R}^3$ and $V = \sum_{j=1}^{N} v(x_j)$. In typical situations u denotes the Coulomb interaction, but many other interactions can be used in this approach too. We restrict ourselves to the Coulomb case $u(x_j - x_k) = \frac{e^2}{|x_j - x_k|}$. In this case, the operator H_0 is well defined and self-adjoint on the domain $D(T)$ of operator $T = -\sum_{j=1}^{N} \triangle_j$ of the kinetic energy (compare Theorem 23.9 and the exercises for this theorem). For the one-particle potential v we assume in the following always $v \in L^2(\mathbb{R}^3) + L^\infty(\mathbb{R}^3)$ so that for these potentials too Kato's perturbation theory applies and assures that H_N is self-adjoint on $D(T)$. Note that $L^2(\mathbb{R}^3) + L^\infty(\mathbb{R}^3)$ is a Banach space when equipped with the norm

$$\|v\| = \inf \left\{ \|v_1\|_2 + \|v_2\|_\infty : v_1 \in L^2(\mathbb{R}^3), v_2 \in L^\infty(\mathbb{R}^3), v = v_1 + v_2 \right\}.$$

However, this Banach space is not reflexive. It is actually the topological dual of the Banach space $X = L^1(\mathbb{R}^3) \cap L^2(\mathbb{R}^3)$ for the norm $\|u\| = \|u\|_1 + \|u\|_3$, i.e.,

$$X' = L^2(\mathbb{R}^3) + L^\infty(\mathbb{R}^3).$$

In 1964, Hohenberg and Kohn proposed a method to solve the problem of finding the ground state energy of H_N through a varational principle. To explain this method we need some preparation. The single-particle reduced density matrix γ of an N-particle wave function ψ is given by the kernel

$$\gamma(z, z') = \int \overline{\psi}(z, z_2, \ldots, z_N) \psi(z', z_2, \ldots, z_N) \, d z_2 \cdots d z_N, \qquad (37.2)$$

where $z_i = (x_i, \sigma_i)$ denotes the space variable x_i and the spin variable σ_i. This formula defines a mapping $\psi \to \gamma$. This density matrix allows us to express the single particle density as

$$\rho(x) = N \sum_\sigma \gamma((x, \sigma), (x, \sigma)) \tag{37.3}$$

which defines a mapping $\gamma \to \rho$ and thus a mapping $v \to \rho_v = R(v)$ from potentials v to one-particle densities ρ when ψ is a ground state of $H_N(v)$. This mapping R plays a fundamental role in the Hohenberg–Kohn theory. Denote by G_N the set of all those potentials v for which the Hamiltonian $H_N(v)$ has a (unique) ground state $\psi \in D(T)$. Then we consider R as a mapping

$$R : G_N \cap X' \to \left\{ \rho \in L^1(\mathbb{R}^3) : 0 \le \rho \right\}, \tag{37.4}$$

and one wants to know when this mapping has an inverse. In order to be able to make progress in this problem one has to have a characterization of the range of the mapping R, i.e., one has to know: Under which conditions on ρ there is a potential $v \in G_N \cap X'$ such that the Hamilton operator $H_N(v)$ has a ground state ψ which defines $\rho = \rho_\psi$ through Eqs. (37.2) and (37.3).

Up to now this problem has found only a partial solution which nevertheless allows us to proceed. There are two conditions which are obviously necessary, namely $0 \le \rho(x)$ for all $x \in \mathbb{R}^3$ and $\|\rho\|_1 = N$, i.e., $\rho \in L^1(\mathbb{R}^3)$. The following lemma gives additional necessary conditions.

Lemma 37.1 *Suppose $\rho = \rho_\psi$ is obtained by Eqs. (37.2) and (37.3) from a state ψ the kinetic energy T. Then*

a) $\rho^{1/2} \in H^1(\mathbb{R}^3)$ and $\left\| \nabla \rho^{1/2} \right\|_2^2 \le T(\psi)$
b) $\rho \in L^3(\mathbb{R}^3) \cap L^1(\mathbb{R}^3)$ and $\left\| \rho_\psi \right\|_3 \le$ constant $T(\psi)$

Proof The kinetic energy is defined by

$$T(\psi) = \sum_{i=1}^N \int |\nabla_i \psi(x_1, \ldots, x_i, \ldots, x_N)|^2 \, dx_1 \cdots dx_N$$

$$= N \int |\nabla_1 \psi(x_1, \ldots, x_N)|^2 \, dx_1 \cdots dx_N.$$

For the density we calculate

$$\nabla \rho(x) = N \left(\int [(\overline{\nabla \psi} \psi)(x, x_2, \ldots, x_N) + (\overline{\psi} \nabla \psi)(x, x_2, \ldots, x_N)] \, dx_2 \cdots dx_N, \right.$$

and Schwarz' inequality implies

$$|\nabla \rho(x)|^2 \le 4N \int |(\nabla_1 \psi)(x, x_2, \ldots, x_N)|^2 \, dx_2 \cdots dx_N \rho(x).$$

We deduce

$$\left\|\nabla\rho^{1/2}\right\|_2^2 = \frac{1}{4}\int(\nabla\rho(x))^2\frac{\mathrm{d}x}{\rho(x)} \leq T(\psi).$$

This implies Part a).

Sobolev's inequality in $\mathbb{R}^3$ states (see (36.9)) $\|u\|_6^2 \leq S\|\nabla u\|_2^2$ which we apply for $u = \rho^{1/2}$ to get $\|\rho\|_3 = \left\|\rho^{1/2}\right\|_6^2 \leq S\left\|\nabla\rho^{1/2}\right\|_2^2 \leq ST(\psi) < \infty$. Thus, the statement of part b) follows. $\square$

Corollary 37.1

$$\operatorname{ran} R \subseteq \left\{\rho \in L^1(\mathbb{R}^3) \cap L^3(\mathbb{R}^3) : 0 \leq \rho,\ \rho^{1/2} \in H^1(\mathbb{R}^3)\right\} \equiv \mathbb{D}$$

and for $\rho \in \mathbb{D}$ there is a state ψ in the domain $D(T)$ such that $\rho = \rho_\psi$.

Proof The first part of the corollary is just a summary of the previous lemma. Given $\rho \in \mathbb{D}$ define ψ as a normalized symmetric N-fold tensor product of $\rho^{1/2}$. Since $\int(\nabla\rho(x))^2\frac{\mathrm{d}x}{\rho(x)} < \infty$ it follows that $\psi \in D(T)$. $\square$

Note that this corollary only gives some estimate of the set of those densities ρ for which there is $v \in G_N \cap X'$ such that ρ is the density of a ground state ψ of $H_N(v)$. The problem is that the set G_N is not known explicitly and thus the range of the map R is not known precisely.

The map $\psi \mapsto \rho$ is clearly not bijective and different ψ can give the same ρ. However, one can prove continuity though the proof is not too easy (see the appendix of [14]). Part of the difficulty comes from the fact that this map is not linear. Observe that the space $H^1(\mathbb{R}^{3N})$ is the form domain of the kinetic energy T.

Theorem 37.1 $\psi \mapsto \rho^{1/2}$ *is a continuous map $H^1(\mathbb{R}^{3N}) \to H^1(\mathbb{R}^3)$.*

Recall that we only consider one-particle potentials $v \in X'$ so that the domain of the N-particle Hamiltonian $H_N(v)$ is the domain

$$W_N = \left\{\psi \in L^2(\mathbb{R}^{3N}) : T(\psi) < \infty\right\} = D(T)$$

of the kinetic energy T. This allows us to determine the ground state energy of $H_N(v)$ as the solution of a minimization problem:

$$E(v) = \inf_{\psi\in W_N\setminus\{0\}} \frac{\langle\psi, H_N(v)\psi\rangle}{\langle\psi, \psi\rangle}. \tag{37.5}$$

There may or may not be a minimizing element ψ for the minimization problem (37.5) for the ground state energy. And if there exists one we do not always have uniqueness. Accordingly, any minimizing element ψ of (37.5) is called a ground state of $H_N(v)$. It satisfies $H_N(v)\psi = E(v)\psi$ at least in the sense of distributions. $E(v)$ has some important properties.

Theorem 37.2 *The ground state energy $E(v)$ defined by (37.5) has the following properties.*

a) *$E(v)$ is concave in $v \in X'$, i.e., for all $v_1, v_2 \in X'$ and all $0 \leq t \leq 1$ one has*
   $E(tv_1 + (1 - t)v_2) \geq t E(v_1) + (1 - t)E(v_2)$
b) *$E(v)$ is monotone increasing, i.e., if $v_1, v_2 \in X'$ and $v_1(x) \leq v_2(x)$ for all $x \in \mathbb{R}^3$, then $E(v_1) \leq E(v_2)$*
c) *$E(v)$ is continuous with respect to the norm of X' and it is locally Lipschitz.*

Proof See the Exercises.   □

The key result of the Hohenberg–Kohn theory is the observation that under certain conditions different potentials $v_1, v_2 \in G_N \cap X'$ lead to different densities ρ_1, ρ_2, thus proving injectivity of the map R.

Theorem 37.3 (Uniqueness Theorem) *Suppose $v_1, v_2 \in G_N \cap X'$ are potentials for which the Hamilton operators $H_N(v_1)$ and $H_N(v_2)$, respectively, have different ground states ψ_1, ψ_2. Then the densities $\rho_{\psi_1}, \rho_{\psi_2}$ defined by these states are different, $\rho_{\psi_1}(x) \neq \rho_{\psi_2}(x)$ for all points x in a set of positive Lebesgue measure.*

Proof We give the proof for the case where the ground state energies for both operators $H_N(v_1)$ and $H_N(v_2)$ are not degenerate. For the general case, we refer to the literature [7].

According to our definitions, we know $E(v_i) = \langle \psi_i, H_N(v_i)\psi_i \rangle$, $\psi_i \in W_N$, $\|\psi_i\| = 1$ and $E(v_i) \leq \langle \psi, H_N(v_i)\psi \rangle$ for all $\psi \in W_N$, $\|\psi\| = 1$ and $E(v_i) < \langle \psi, H_N(v_i)\psi \rangle$ for all $\psi \in W_N$, $\|\psi\| = 1$, $\psi \neq \psi_i$, $i = 1, 2$. Equations (37.1)–(37.3) imply $\langle \psi, H_N(v_i)\psi \rangle = \langle \psi, H_0\psi \rangle + N \int v_i(x)\rho_\psi(x)\,dx$, hence

$$E(v_1) = \langle \psi_1, H_0\psi_1 \rangle + N \int v_2(x)\rho_{\psi_1}(x)\,dx + N \int (v_1(x) - v_2(x))\rho_{\psi_1}(x)\,dx$$

$$> E(v_2) + N \int (v_1(x) - v_2(x))\rho_{\psi_1}(x)\,dx$$

and similarly $E(v_2) > E(v_1) + N \int (v_2(x) - v_1(x))\rho_{\psi_2}(x)\,dx$. By adding these two inequalities we get

$$0 > N \int (v_1(x) - v_2(x))(\rho_{\psi_1}(x) - \rho_{\psi_1}(x))\,dx.$$

All the above integrals are well defined because of part b) of Lemma 37.1 and the interpolation estimate $\|\rho\|_2 \leq \|\rho\|_1^{1/4} \|\rho\|_3^{3/4}$.   □

Note that the assumption that $H_N(v_1)$ and $H_N(v_2)$ have different ground states excludes the case that the potentials differ by a constant. This assumption was originally used by Hohenberg–Kohn.

Certainly one would like to have stronger results based on conditions on the potentials v_1, v_2 which imply that the Hamilton operators $H_N(v_1)$ and $H_N(v_2)$ have different ground states ψ_1 and ψ_2. But such conditions are not available here.

The basic Hohenberg–Kohn uniqueness theorem is an existence theorem. It claims that there exists a bijective map $R : v \to \rho$ between an unknown set of potentials

v and a corresponding set of densities which is unknown as well. Nevertheless, this result implies that the ground state energy E can in principle be obtained by using $v = R^{-1}(\rho)$, i.e., the potential v as a functional of the ground state density ρ. However, there is a serious problem since nobody knows this map explicitly.

37.3.1 Hohenberg–Kohn Variational Principle

Hohenberg and Kohn assume that every one-particle density ρ is defined in terms of a ground state ψ for some potential v, i.e., $H_N(v)\psi = E(v)\psi$. Accordingly, they introduce the set

$$A_N = \left\{ \rho \in L^1 \cap L^3(\mathbb{R}^3) : 0 \le \rho, \sqrt{\rho} \in H^1(\mathbb{R}^3), \exists \text{ ground state } \psi : \psi \mapsto \rho \right\}$$

and on A_N they considered the functional

$$F_{HK}(\rho) = E(v) - \int v(x)\rho(x)\,\mathrm{d}x. \tag{37.6}$$

This definition of F_{HK} requires Theorem 37.3 according to which there is a one-particle potential v associated with ρ, $v = R^{-1}(\rho)$. Using this functional the Hohenberg–Kohn variational principle reads

Theorem 37.4 (Hohenberg–Kohn Variational Principle) *For any $v \in G_N \cap X'$, the ground state energy is*

$$E(v) = \min_{\rho \in A_N} [F_{HK}(\rho) + \int v(x)\rho(x)\,d\,x]. \tag{37.7}$$

It must be emphasized that this variational principle holds only for $v \in G_N \cap X'$ and $\rho \in A_N$. But we have three major problems: The sets G_N and A_N and the form of the functional F_{HK} are unknown. On one hand the Hohenberg–Kohn theory is an enormous conceptual simplification since it gives some hints that the semiclassical density functional theories are reasonable approximations. On the other hand, the existence Theorem 37.3 does not provide any practical method for calculating physical properties of the ground state from the one electron density ρ. In experiments we measure ρ but we do not know what Hamilton operator $H_N(v)$ it belongs to.

The contents of the uniqueness theorem can be illustrated by an example. Consider the N_2 and CO molecules. They have exactly the same numbers of electrons and nuclei, but whereas the former has a symmetric electron density this is not the case for the latter. We are, therefore, able to distinguish between the molecules. Imagine now that we add an external electrostatic potential along the bond for the N_2 molecule. The electron density becomes polarized and it is no more obvious to distinguish between N_2 and CO. But according to the Hohenberg–Kohn uniqueness theorem it is possible to distinguish between the two molecules in a unique way.

The Hohenberg–Kohn variational principle provides the justification for the variational principle of Thomas Fermi in the sense that $E_{TF}(\rho)$ is an approximation to the functional $E(\rho)$ associated with the total energy. Let us consider the

functional $E_v(\rho) = F_{HK}(\rho) + \int v(x)\rho(x)\,dx$. The Hohenberg–Kohn variational principle requires that the ground state density is a stationary point of the functional $E_v(\rho) - \mu[\int \rho(x)\,dx - N]$ which gives the Euler–Lagrange equation (assuming differentiability)

$$\mu = DE_v(\rho) = v + DF_{HK}(\rho), \tag{37.8}$$

where μ denotes the chemical potential of the system.

If we were able to know the exact functional $F_{HK}(\rho)$ we would obtain by this method an exact solution for the ground state electron density. It must be noted that $F_{HK}(\rho)$ is defined independently of the external potential v; this property means that $F_{HK}(\rho)$ is a universal functional of ρ. As soon as we have an explicit form (approximate or exact) for $F_{HK}(\rho)$ we can apply this method to any system and the Euler–Lagrange Eq. (37.8) will be the basic working equation of the Hohenberg–Kohn density functional theory. A serious difficulty here is that the functional $F_{HK}(\rho)$ is defined only for those densities which are in the range of the map R, a condition which, as already explained, is still unknown.

37.3.2 The Kohn–Sham Equations

The Hohenberg–Kohn uniqueness theorem states that all the physical properties of a system of N interacting electrons are uniquely determined by its one-electron ground state density ρ. This property holds independently of the precise form of the electron–electron interaction. In particular when the strength of this interaction vanishes the functional $F_{HK}(\rho)$ defines the ground state kinetic energy of a system of noninteracting electrons as a functional of its ground state density $T_0(\rho)$. This fact was used by Kohn and Sham [4] in 1965 to map the problem of interacting electrons for which the form of the functional $F_{HK}(\rho)$ is unknown onto an equivalent problem for noninteracting particles. To this end $F_{HK}(\rho)$ is written in the form

$$F_{HK}(\rho) = T_0(\rho) + \frac{1}{2} \int \frac{\rho(x)\rho(y)}{|x-y|}\,dx\,dy + E_{xc}(\rho). \tag{37.9}$$

The second term is nothing else than the classical electrostatic self-interaction, and the term $E_{xc}(\rho)$ is called the exchange–correlation energy.

Variations with respect to ρ under the constraint $\|\rho\|_1 = N$ leads formally to the same equation which holds for a system of N noninteracting electrons under the influence of an effective potential V_{scf}, also called the self-consistent field potential whose form is explicitly given by

$$v_{scf}(x) = v(x) + \left(\rho * \frac{1}{|x|}\right)(x) + v_{xc}(x), \tag{37.10}$$

where the term $v_{xc}(x) = D_\rho E_{xc}(\rho)$ is called the exchange–correlation potential, as the functional derivative of the exchange–correlation energy.

There have been a number of attempts to remedy the shortcomings of the Hohenberg–Kohn theory. One of the earliest and best known is due to E. Lieb [14]. The literature we have mentioned before offers a variety of others. Though some progress is achieved major problems are still unresolved. Therefore we cannot discuss them here in our short introduction.

A promising direction seems to be the following. By Theorem 37.2 we know that $-E(v)$ is a convex continuous functional on X'. Hence (see [15]), it can be represented as the polar functional of its polar functional $(-E)^*$:

$$-E(v) = \sup_{u \in X''} [\langle v, u \rangle - (-E)^*(u)] \qquad \forall \, v \in X'], \qquad (37.11)$$

where the polar functional $(-E)^*$ is defined on X'' by

$$(-E)^*(u) = \sup_{v \in X'} [\langle v, u \rangle - (-E)(v)] \qquad \forall \, u \in X''. \qquad (37.12)$$

Now $X = L^2(\mathbb{R}^3) \cap L^1(\mathbb{R}^3)$ is contained in the bi-dual X'' but this bi-dual is much larger ($L^1(\mathbb{R}^3)$ is not a reflexive Banach space) and $L^3(\mathbb{R}^3) \cap L^1(\mathbb{R}^3) \subset L^2(\mathbb{R}^3) \cap L^1(\mathbb{R}^3)$. But one would like to have a representation of this form in terms of densities $\rho \in A_N \subset L^3(\mathbb{R}^3) \cap L^1(\mathbb{R}^3)$, not in terms of $u \in X''$.

Remark 37.1 In Theorem 37.4, the densities are integrable functions on all of $\mathbb{R}^3$ which complicates the minimization problem in this theorem considerably, as we had mentioned before in connection with global boundary and eigenvalue problems. However having the physical interpretation of the functions ρ in mind as one-particle densities of atoms or molecules, it is safe to assume that all the relevant densities have a compact support contained in some finite ball in $\mathbb{R}^3$. Thus, in practice, one considers this minimization problem over a bounded domain B with the benefit that compact Sobolev embeddings are available. As an additional advantage we can then work in the reflexive Banach space $L^3(B)$ since $L^1(B) \subset L^3(B)$ instead of $L^1(\mathbb{R}^3) \cap L^3(\mathbb{R}^3)$.

37.4 Exercises

1. Prove Theorem 37.2.
   Hints: For $v_1, v_2 \in X'$ and $0 \le t \le 1$ show first that $H_N(tv_1 + (1-t)v_2) = t H_N(v_1) + (1-t)H_N(v_2)$. Part a) now follows easily. For part b) consider $v_1, v_2 \in X'$ such that $v_1(x) \le v_2(x)$ for almost all $x \in \mathbb{R}^3$ and show as a first step: $\langle \psi, H_N(v_1)\psi \rangle \le \langle \psi, H_N(v_2)\psi \rangle$ for all $\psi \in W_N, \|\psi\| = 1$.
   For part c) proceed similarly and show $|\langle \psi, (H_N(v_1) - H_N(v_2))\psi \rangle| \le N \|v_1 - v_2\|_\infty$ for all $\psi \in W_N, \|\psi\| = 1$. This implies $\pm(E(v_1) - E(v_2)) \le N \|v_1 - v_2\|_\infty$.
2. Show that the Coulomb energy functional D is weakly lower semi-continuous on the Banach space $L^{6/5}(\mathbb{R}^3)$.
3. Prove: The Thomas–Fermi energy functional E_{TF} is well defined on the cone $D_{TF} = \{\rho \in L^{5/3} \cap L^1(\mathbb{R}^3) : \rho \ge 0\}$.

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