

Chapter 2

Foundations of Density Functional Theory: Existence Theorems

2.1 Hohenberg-Kohn Theorem

The starting point of any discussion of DFT is the Hohenberg-Kohn (HK) theorem [6]. It represents the most basic of a number of existence theorems which ensure that stationary many-particle systems can be characterized (fully) by the ground state density and closely related quantities. As the reasoning leading to the HK theorem is quite instructive, it is worthwhile to study this prototype of an existence theorem in some detail (the discussion of the HK theorem follows [7]).

Let us consider the standard Hamiltonian of a stationary system of N interacting spin-1/2 particles (typically electrons),

$$\hat{H} = \hat{T} + \hat{V}_{\text{ext}} + \hat{W}, \quad (2.1)$$

which consists of the kinetic energy operator \hat{T} ,

$$\hat{T} = \sum_{i=1}^N \frac{(-i\hbar\nabla_i)^2}{2m} = -\frac{\hbar^2}{2m} \sum_{\sigma=\uparrow,\downarrow} \int d^3r \hat{\psi}^\dagger(\mathbf{r}\sigma) \nabla^2 \hat{\psi}(\mathbf{r}\sigma), \quad (2.2)$$

the interaction of the particles with external sources characterized by a given, time-independent potential $v_{\text{ext}}(\mathbf{r})$,

$$\hat{V}_{\text{ext}} = \sum_{i=1}^N v_{\text{ext}}(\mathbf{r}_i) = \int d^3r v_{\text{ext}}(\mathbf{r}) \hat{n}(\mathbf{r}) \quad (2.3)$$

$$\hat{n}(\mathbf{r}) = \sum_{i=1}^N \delta^{(3)}(\mathbf{r} - \mathbf{r}_i) = \sum_{\sigma=\uparrow,\downarrow} \hat{\psi}^\dagger(\mathbf{r}\sigma) \hat{\psi}(\mathbf{r}\sigma), \quad (2.4)$$

and a particle–particle interaction \hat{W} ,

$$\begin{aligned}
\hat{W} &= \sum_{i,j=1; i < j}^N w(\mathbf{r}_i, \mathbf{r}_j) = \frac{1}{2} \sum_{i,j=1; i \neq j}^N w(\mathbf{r}_i, \mathbf{r}_j) \\
&= \frac{1}{2} \sum_{\sigma, \sigma'=\uparrow, \downarrow} \int d^3r \int d^3r' \hat{\psi}^\dagger(\mathbf{r}\sigma) \hat{\psi}^\dagger(\mathbf{r}'\sigma') w(\mathbf{r}, \mathbf{r}') \hat{\psi}(\mathbf{r}'\sigma') \hat{\psi}(\mathbf{r}\sigma). \quad (2.5)
\end{aligned}$$

In Eqs. (2.2)–(2.5) \mathbf{r}_i represents the position of particle i , σ_i is its spin projection in z -direction (the two possible orientations of σ_i will be either denoted as \uparrow, \downarrow or by $\pm 1/2$). $\hat{\psi}^{(\dagger)}(\mathbf{r}\sigma)$ is the field operator which describes the creation/annihilation of one particle with spin σ at point \mathbf{r} . As we are dealing with spin-1/2 particles, $\hat{\psi}^{(\dagger)}(\mathbf{r}\sigma)$ satisfies anticommutation rules,

$$\{\hat{\psi}(\mathbf{r}\sigma), \hat{\psi}(\mathbf{r}'\sigma')\} = \{\hat{\psi}^\dagger(\mathbf{r}\sigma), \hat{\psi}^\dagger(\mathbf{r}'\sigma')\} = 0 \quad (2.6)$$

$$\{\hat{\psi}(\mathbf{r}\sigma), \hat{\psi}^\dagger(\mathbf{r}'\sigma')\} = \delta^{(3)}(\mathbf{r} - \mathbf{r}') \delta_{\sigma\sigma'}. \quad (2.7)$$

At this point it is not necessary to specify the interaction $w(\mathbf{r}, \mathbf{r}')$ in detail. The basic DFT formalism is independent of the form of w , as long as w is kept the same throughout the complete discussion. It is only assumed that w is symmetric, $w(\mathbf{r}, \mathbf{r}') = w(\mathbf{r}', \mathbf{r})$ and independent of spin. In practice, of course, one is primarily interested in electrons with their Coulomb interaction. Similarly, the external potential v_{ext} which is of particular interest in practical applications is given by Eq. (1.6). For the present discussion, however, v_{ext} is considered to be an arbitrary function of \mathbf{r} .

Some further comments on Eqs. (2.1)–(2.5) seem appropriate.

- (a) The Hamiltonian (2.1) is strictly nonrelativistic. The complete formalism presented in this chapter can, however, be extended to the relativistic domain on the basis of quantum electrodynamics. A detailed account of relativistic DFT is given in Chap. 8.
- (b) For the time being, the Hamiltonian does not include the presence of external magnetic fields. This extension will be discussed in Sects. 2.5 and 2.6. The absence of magnetic fields does not imply, however, that the eigenstates of (2.1), and in particular the ground state, can not exhibit magnetic properties.
- (c) Although it is not obvious from Eqs. (2.1)–(2.5), the following discussion will be restricted to the zero temperature formalism. An extension to systems with $T \neq 0$ may be found in [8, 7].
- (d) All energy contributions, which do not depend on the electron degrees of freedom, as the interaction among atomic nuclei (1.4), are irrelevant in the present context. They can be added to the electron part of the Hamiltonian when needed.
- (e) An important property of the operator (2.3) is its local (that is multiplicative) character. The potential (1.6) has this character, but the class of legitimate potentials also includes additional electrostatic fields applied to the many-particle system. It does not include, however, the standard type of pseudopotentials utilized in the context of DFT (see e.g. [9, 10]). In order to introduce these

nonlocal pseudopotentials one first establishes DFT on the all-electron level, before making the transition to the pseudopotential description.

It is worthwhile to note at this point that there also exists an extension of the HK-theorem to nonlocal potentials [11, 12]. In this approach the 1-particle density matrix

$$\gamma(\mathbf{r}\sigma, \mathbf{r}'\sigma') = \sum_{\sigma_2, \dots, \sigma_N} \int d^3r_2 \dots d^3r_N \Psi_0(\mathbf{r}\sigma, \mathbf{r}_2\sigma_2, \dots, \mathbf{r}_N\sigma_N) \\ \times \Psi_0^*(\mathbf{r}'\sigma', \mathbf{r}_2\sigma_2, \dots, \mathbf{r}_N\sigma_N),$$

where Ψ_0 denotes the non-degenerate ground state wavefunction corresponding to the nonlocal external potential, plays the role that the density plays in DFT. The arguments behind this extension follow closely the lines given below.

- (f) As indicated in Eqs. (2.1)–(2.5) we will frequently switch between the first and second quantized formalism, depending on which is more appropriate for a given problem. An introduction to the language of second quantization may be found in Appendix B.

The many-body eigenstates $|\Psi_k\rangle$ corresponding to the Hamiltonian (2.1) are obtained by solution of the stationary Schrödinger equation,

$$\hat{H}|\Psi_k\rangle = E_k|\Psi_k\rangle. \quad (2.8)$$

This is true in particular for the ground state $|\Psi_0\rangle$, on which we will focus attention in the following.

Now consider the set of all Hamiltonians of the form (2.1) with non-degenerate ground states, i.e. the set of all local potentials v_{ext} for which (2.8) leads to a non-degenerate $|\Psi_0\rangle$, while the interaction (2.5) is kept fixed. This set does not only contain physically realizable potentials, but also an infinite number of purely mathematical constructs. In addition, it contains an infinite number of trivial copies of any given $v_{\text{ext}}(\mathbf{r})$, which are obtained by simply adding an arbitrary constant to $v_{\text{ext}}(\mathbf{r})$. These trivial copies, of course, lead to the same ground state, so that they are physically equivalent to $v_{\text{ext}}(\mathbf{r})$. On the other hand, there exist physical systems with degenerate ground states which are not included in the present discussion—the restriction to non-degenerate ground states will be removed later.

One can then interpret the solution of the Schrödinger equation as a map between the set \mathcal{V} of external potentials which differ by more than a constant,

$$\mathcal{V} = \{v_{\text{ext}} \mid \text{with: } v_{\text{ext}} \text{ multiplicative, corresponding } |\Psi_0\rangle \text{ exists and} \\ \text{is non-degenerate, } v'_{\text{ext}}(\mathbf{r}) \neq v_{\text{ext}}(\mathbf{r}) + \text{const}\}. \quad (2.9)$$

and the set \mathcal{G} of resulting ground states,

$$\mathcal{G} = \{|\Psi_0\rangle \mid \text{with: } |\Psi_0\rangle \text{ ground state corresponding to one element of } \mathcal{V}, \\ |\Psi'_0\rangle \neq e^{i\varphi}|\Psi_0\rangle \text{ with } \varphi \text{ being some global phase}\}. \quad (2.10)$$

Let us denote the map from \mathcal{V} to \mathcal{G} as A ,

$$A: \mathcal{V} \longrightarrow \mathcal{G}.$$

Introducing the ground state density n_0 ,

$$\begin{aligned} n_0(\mathbf{r}) &= \langle \Psi_0 | \hat{n}(\mathbf{r}) | \Psi_0 \rangle \\ &= N \sum_{\sigma_1, \dots, \sigma_N} \int d^3 r_2 \dots d^3 r_N |(\mathbf{r} \sigma_1, \mathbf{r}_2 \sigma_2 \dots \mathbf{r}_N \sigma_N | \Psi_0 \rangle|^2, \end{aligned} \quad (2.11)$$

one can furthermore define a second map B between the set \mathcal{G} and the set \mathcal{N} of all ground state densities obtained from some element of \mathcal{G} via (2.11),

$$\begin{aligned} \mathcal{N} &= \{n_0 \mid n_0(\mathbf{r}) = \langle \Psi_0 | \hat{n}(\mathbf{r}) | \Psi_0 \rangle, |\Psi_0\rangle \in \mathcal{G}\} \\ B: \mathcal{G} &\longrightarrow \mathcal{N}. \end{aligned} \quad (2.12)$$

The two maps are illustrated in Fig. 2.1. By construction both maps are surjective.

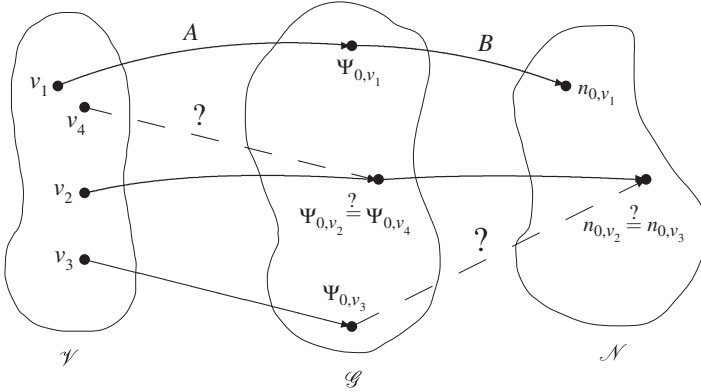


Fig. 2.1 Correspondence between external potentials v_i , associated ground states Ψ_{0,v_i} and ground state densities n_{0,v_i} in the case of non-degenerate ground states.

The question then is: can it happen that the same $|\Psi_0\rangle$ is obtained as ground state for two different potentials or that the same n_0 results from two different ground states? These possibilities are indicated by the dashed lines in Fig. 2.1.

The crucial observation of HK was: both maps are also injective and thus unique. The proof of this statement for map A consists in demonstrating the validity of the following two statements:

- (i) For given v_{ext} there exists only one $|\Psi_0\rangle$ in \mathcal{G} , i.e. there is no v_{ext} which is mapped onto two elements of \mathcal{G} .
- (ii) There is no $|\Psi_0\rangle$ which is simultaneously ground state for two different potentials v_{ext} and v'_{ext} which differ by more than a constant.

Statement (i) is trivial due to the restriction to non-degenerate ground states. It remains to prove statement (ii).

The standard proof of (ii) is based on a *reductio ad absurdum*. Let us assume that $|\Psi_0\rangle$ is simultaneously ground state for two different potentials v_{ext} and $v'_{\text{ext}} \neq v_{\text{ext}} + \text{const.}$ $|\Psi_0\rangle$ thus satisfies two Schrödinger equations,

$$\hat{H}|\Psi_0\rangle = [\hat{T} + \hat{V}_{\text{ext}} + \hat{W}]|\Psi_0\rangle = E_0|\Psi_0\rangle \quad (2.13)$$

$$\hat{H}'|\Psi_0\rangle = [\hat{T} + \hat{V}'_{\text{ext}} + \hat{W}]|\Psi_0\rangle = E'_0|\Psi_0\rangle. \quad (2.14)$$

Upon subtraction of (2.13) and (2.14) one obtains

$$[\hat{V}_{\text{ext}} - \hat{V}'_{\text{ext}}]|\Psi_0\rangle = [E_0 - E'_0]|\Psi_0\rangle. \quad (2.15)$$

Equation (2.15) is best written in first quantized form, in which, due to the multiplicative character of the potentials, one can divide by the ground state wavefunction

$$(\mathbf{r}_1\sigma_1, \dots, \mathbf{r}_N\sigma_N|\Psi_0\rangle = \Psi_0(\mathbf{r}_1\sigma_1, \dots, \mathbf{r}_N\sigma_N). \quad (2.16)$$

One thus finds

$$\sum_{i=1}^N [v_{\text{ext}}(\mathbf{r}_i) - v'_{\text{ext}}(\mathbf{r}_i)] = E_0 - E'_0 \quad (2.17)$$

for all points \mathbf{r}_i for which the wavefunction $\Psi_0(\mathbf{r}_1\sigma_1, \dots, \mathbf{r}_N\sigma_N)$ does not vanish. Keeping $N-1$ of the \mathbf{r}_i fixed and letting the remaining position vary, Eq. (2.17) leads to a contradiction (as the right-hand side is constant, while v_{ext} and v'_{ext} are assumed to differ by more than a constant). Consequently, the map A is unique: there is a one-to-one correspondence between the potential v_{ext} and the resulting ground state $|\Psi_0\rangle$ (up to some additive constant in v_{ext}).

Let us now turn to the map B . The definition of B via Eq. (2.11) implies that it is impossible that one $|\Psi_0\rangle$ is mapped onto two different densities n_0 and n'_0 . In order to demonstrate the injectivity of B , one has to show that two different $|\Psi_0\rangle \in \mathcal{G}$ can not lead to the same ground state density n_0 . The proof again relies on *reductio ad absurdum*. Assume that n_0 is obtained from two different elements $|\Psi_0\rangle$ and $|\Psi'_0\rangle$ of \mathcal{G} . From the Ritz variational principle one then obtains an inequality for the ground state energy,

$$E_0 = \langle \Psi_0 | \hat{H} | \Psi_0 \rangle < \langle \Psi'_0 | \hat{H} | \Psi'_0 \rangle, \quad (2.18)$$

where \hat{H} is the unique Hamiltonian leading to $|\Psi_0\rangle$ (due to the uniqueness of map A) and the strict inequality originates from the non-degeneracy of $|\Psi_0\rangle$ and $|\Psi'_0\rangle$. The right-hand side of (2.18) can be evaluated further by adding and subtracting the unique potential \hat{V}'_{ext} which corresponds to $|\Psi'_0\rangle$,

$$E_0 < E'_0 + \langle \Psi'_0 | \hat{V}_{\text{ext}} - \hat{V}'_{\text{ext}} | \Psi'_0 \rangle. \quad (2.19)$$

Using the multiplicative form of \hat{V}_{ext} , Eq. (2.3), and the assumption that both states lead to the same density n_0 , one obtains

$$E_0 < E'_0 + \int d^3r n_0(\mathbf{r}) [v_{\text{ext}}(\mathbf{r}) - v'_{\text{ext}}(\mathbf{r})]. \quad (2.20)$$

However, this argument can equally well be given with primed and unprimed quantities interchanged,

$$E'_0 < E_0 + \int d^3r n_0(\mathbf{r}) [v'_{\text{ext}}(\mathbf{r}) - v_{\text{ext}}(\mathbf{r})]. \quad (2.21)$$

Upon addition of Eqs. (2.20) and (2.21), one ends up with a contradiction,

$$E_0 + E'_0 < E'_0 + E_0. \quad (2.22)$$

One therefore concludes that the map B is also unique: there is a one-to-one correspondence between $|\Psi_0\rangle$ and n_0 .

On the basis of these arguments one can formulate the fundamental statements of the HK theorem.

- (a) Taking both maps together, one has a one-to-one correspondence between the external potential v_{ext} in the Hamiltonian, the (non-degenerate) ground state $|\Psi_0\rangle$ resulting from solution of the Schrödinger equation and the associated ground state density n_0 ,

$$v_{\text{ext}}(\mathbf{r}) \begin{array}{c} \longleftrightarrow \\ \uparrow \\ \text{unique (up to some constant in } v_{\text{ext}}) \end{array} |\Psi_0\rangle \begin{array}{c} \longleftrightarrow \\ \uparrow \\ \text{unique (up to some constant in } v_{\text{ext}}) \end{array} n_0(\mathbf{r}) = \langle \Psi_0 | \hat{n}(\mathbf{r}) | \Psi_0 \rangle. \quad (2.23)$$

Thus v_{ext} , $|\Psi_0\rangle$ and n_0 determine each other uniquely. In mathematical terms: the ground state is a unique functional of the ground state density, denoted as $|\Psi[n]\rangle$. Upon insertion of one element $n_0 \in \mathcal{N}$, this functional yields the ground state $|\Psi_0\rangle$ associated with this particular n_0 ,

$$|\Psi_0\rangle = |\Psi[n_0]\rangle. \quad (2.24)$$

The functional $|\Psi[n]\rangle$ is a realization of the map B^{-1} .

Note that no explicit information on v_{ext} is required to construct $|\Psi_0\rangle$ from n_0 : $|\Psi[n]\rangle$ has the same functional form for all kinds of many-particle systems with the same interaction (w was kept fixed throughout the complete discussion). The same functional $|\Psi[n]\rangle$ applies to atoms, molecules and solids. The particular geometry of the systems under consideration is mediated by the structure of the density. $|\Psi[n]\rangle$ is therefore called *universal*. Clearly, the functional dependence of $|\Psi[n]\rangle$ on n must be extremely complicated.

- (b) The existence of the functional $|\Psi[n]\rangle$ leads to the statement that any ground state observable is a density functional,

$$O[n] := \langle \Psi[n] | \hat{O} | \Psi[n] \rangle. \quad (2.25)$$

This is true, in particular, for the ground state energy, which turns out to be the most important density functional,

$$E[n] := \langle \Psi[n] | \hat{H} | \Psi[n] \rangle = F[n] + \int d^3r v_{\text{ext}}(\mathbf{r})n(\mathbf{r}) \quad (2.26)$$

$$F[n] := \langle \Psi[n] | \hat{T} + \hat{W} | \Psi[n] \rangle. \quad (2.27)$$

In (2.26) the universal part $F[n]$ has been extracted from the total energy functional $E[n]$, in order to emphasize the fact that v_{ext} enters $E[n]$ at only one point.

- (c) There exists a minimum principle for $E[n]$: if n_0 is the ground state density corresponding to v_{ext} , one has for all densities $n'_0(\mathbf{r}) \neq n_0(\mathbf{r})$

$$E[n_0] < E[n'_0] \quad \Longleftrightarrow \quad E_0 = \min_{n \in \mathcal{N}} E[n]. \quad (2.28)$$

This is a direct consequence of the unique relation between n_0 and $|\Psi_0\rangle$ and the Ritz variational principle (the ground state $|\Psi'_0\rangle$ associated with n'_0 differs from $|\Psi_0\rangle$). At this point it is worthwhile to emphasize the restricted domain of the functional $E[n]$: only densities in \mathcal{N} , i.e. ground state densities which are obtained by solution of the Schrödinger equation, are legitimate, but not arbitrary non-negative functions of \mathbf{r} with finite norm.

How can one interpret the last result physically? Obviously the particles react to any (arbitrarily small) change in v_{ext} , so that their total energy is minimized, and this response is unique. Due to the locality of the potential there is no modification of v_{ext} which does not require a readjustment of the electron wavefunction and, consequently, of the density distribution.¹ This response is very familiar in a number of cases. If, for instance, the nuclear charge is increased in an atom, the orbitals are contracted in a well-defined way. If the form of the nuclear charge distribution is changed from point-like to a finite shape, the density of the electrons in the vicinity of the nucleus reflects this change of v_{ext} . If the atoms in a molecule are taken apart, the wavefunction and the density follow this positional change. The basic result of the HK theorem is therefore intuitively plausible.

Of course, these statements are only correct if the particles actually experience the change in v_{ext} . If, for instance, some part of space is separated by a barrier of infinite height and non-vanishing width from the region in which the particles are moving, a modification of v_{ext} in this exterior region does not affect the particles

¹ This implies the uniqueness of the density–density response function of the system.

at all (as there is no communication between the two parts of space). Similarly, if the difference between v_{ext} and v'_{ext} is non-vanishing only at the nodes of $|\Psi_0\rangle$ ($v_{\text{ext}} - v'_{\text{ext}}$ would have a δ -type form), the proof of the uniqueness of map A breaks down. However, such situations are either trivial (as the case of an infinite barrier) or rather unphysical. Potentials with δ -like structures are not met in first-principles electron structure calculations. For this reason one can safely assume the validity of the HK theorem for all systems of practical interest.

In view of the intuitive physical background of the HK theorem it is not surprising that the first energy functionals were introduced long before HK's existence proof. Thomas [13] and Fermi [14] considered the kinetic energy of a noninteracting electron gas, which turns out to be a simple functional of the gas density—for a derivation see Appendix D. Using this functional with the actual inhomogeneous densities of systems like atoms or molecules (rather than just the uniform gas density) constitutes the so-called *Thomas-Fermi model*. A variety of extensions and properties of the Thomas-Fermi approach have been established with time. A complete review of these aspects of DFT is beyond the scope of this book. The basics are summarized in Appendix D, for further information the interested reader is referred to [15, 7] which provide a rather complete account of the TF approach and extensions.

2.2 Degenerate Ground States

The proof of the HK theorem presented in Sect. 2.1 relies crucially on the restriction to non-degenerate ground states. The argument has to be modified in the case of degenerate states. In this situation two or more ground states $|\Psi_{0,i}\rangle$ originate from the same potential v_{ext} . The first step thus is an appropriate redefinition of the set of legitimate potentials \mathcal{V} ,

$$\mathcal{V} = \{v_{\text{ext}} \mid \text{with: } v_{\text{ext}} \text{ multiplicative, } v'_{\text{ext}}(\mathbf{r}) \neq v_{\text{ext}}(\mathbf{r}) + \text{const}\}, \quad (2.29)$$

the set \mathcal{G} of resulting ground states,

$$\mathcal{G}_{v_{\text{ext}}} = \left\{ |\Psi\rangle \mid \text{with: } |\Psi\rangle = \sum_{i=1}^q c_i |\Psi_{0,i}\rangle, \right. \\ \left. |\Psi_{0,i}\rangle = \text{degenerate ground states to } v_{\text{ext}} \right\} \quad (2.30)$$

$$\mathcal{G} = \bigcup_{v_{\text{ext}}} \mathcal{G}_{v_{\text{ext}}}, \quad (2.31)$$

and the set \mathcal{N} of associated ground state densities,

$$\mathcal{N}_{v_{\text{ext}}} = \{n(\mathbf{r}) \mid \text{with: } n(\mathbf{r}) = \langle \Psi | \hat{n}(\mathbf{r}) | \Psi \rangle, |\Psi\rangle \in \mathcal{G}_{v_{\text{ext}}}\} \quad (2.32)$$

$$\mathcal{N} = \bigcup_{v_{\text{ext}}} \mathcal{N}_{v_{\text{ext}}}. \quad (2.33)$$

The definitions of $\mathcal{G}_{v_{\text{ext}}}$ and $\mathcal{N}_{v_{\text{ext}}}$ include the non-degenerate situation.

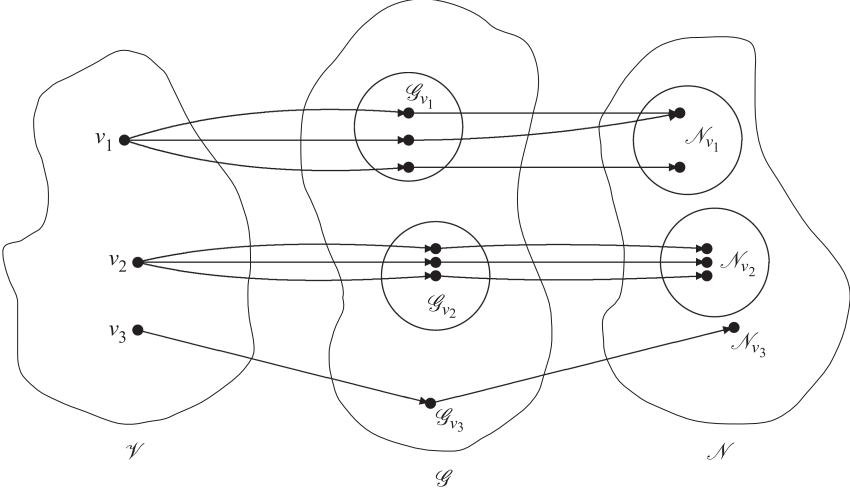


Fig. 2.2 Correspondence between external potentials v_i , associated subsets of ground states \mathcal{G}_{v_i} and subsets of ground state densities \mathcal{N}_{v_i} in the case of degeneracy.

One can then show [16] that there exists a one-to-one correspondence between the potential v_{ext} , the class $\mathcal{G}_{v_{\text{ext}}}$ of all possible ground states resulting from v_{ext} and the class $\mathcal{N}_{v_{\text{ext}}}$ of ground state densities obtained from these ground states and that the subsets $\mathcal{G}_{v_{\text{ext}}}$ and $\mathcal{N}_{v_{\text{ext}}}$ for different v_{ext} are disjoint,

$$\begin{array}{ccc}
 v_{\text{ext}}(\mathbf{r}) & \longleftrightarrow & \mathcal{G}_{v_{\text{ext}}} \longleftrightarrow \mathcal{N}_{v_{\text{ext}}} \\
 \uparrow & & \uparrow \\
 \text{unique (up to some constant in } v_{\text{ext}}) & &
 \end{array} \tag{2.34}$$

$|\Psi_0\rangle \neq |\Psi'_0\rangle$ and $n_0 = \langle \Psi_0 | \hat{n} | \Psi_0 \rangle \neq n'_0 = \langle \Psi'_0 | \hat{n} | \Psi'_0 \rangle$
 for all pairs $|\Psi_0\rangle \in \mathcal{G}_{v_{\text{ext}}}$, $|\Psi'_0\rangle \in \mathcal{G}_{v'_{\text{ext}}}$ with $v'_{\text{ext}} \neq v_{\text{ext}} + \text{const}$.

The proof of these statements proceeds as in the non-degenerate case: assuming that two potentials v_{ext} and $v'_{\text{ext}} \neq v_{\text{ext}} + \text{const}$ have a common ground state $|\Psi_0\rangle$, one can follow the arguments from (2.13) to (2.17) to end up with a contradiction. Two different v_{ext} always lead to two disjoint sets of ground states $\mathcal{G}_{v_{\text{ext}}}$ —a given $|\Psi_0\rangle \in \mathcal{G}$ can only belong to one particular $\mathcal{G}_{v_{\text{ext}}}$ and therefore to one particular v_{ext} . Similarly, one arrives at a contradiction if one assumes that two states $|\Psi_0\rangle \in \mathcal{G}_{v_{\text{ext}}}$ and $|\Psi'_0\rangle \in \mathcal{G}_{v'_{\text{ext}}}$ lead to the same density n_0 and then follows the arguments in Eqs. (2.18) to (2.22). A density $n_0 \in \mathcal{N}$ can only be an element of one single set $\mathcal{N}_{v_{\text{ext}}}$. Two densities from different $\mathcal{N}_{v_{\text{ext}}}$ necessarily correspond to two different

$\mathcal{G}_{v_{\text{ext}}}$ and two different v_{ext} and vice versa. A sketch of the situation is given in Fig. 2.2.

In other words: one needs only one element of $\mathcal{N}_{v_{\text{ext}}}$ to identify the corresponding $\mathcal{G}_{v_{\text{ext}}}$ and v_{ext} . On the other hand, it can happen that the same density is obtained for two different elements of one subset $\mathcal{G}_{v_{\text{ext}}}$. As a simple example one may consider the boron atom on the noninteracting level, i.e. in terms of a Hamiltonian with only a spherical Coulomb potential. As the $2p$ -states are degenerate, a possible classification of the $2p$ -states is

$$\begin{aligned} 2p^0 : \quad \phi_{2p}^0(\mathbf{r}) &= \frac{R_{21}(r)}{r} Y_{1,0}(\Omega) \\ 2p^\pm : \quad \phi_{2p}^\pm(\mathbf{r}) &= \frac{R_{21}(r)}{r} Y_{1,\pm 1}(\Omega), \end{aligned}$$

where $R_{nl}(r)$ denotes the standard radial orbitals of the hydrogen problem and $Y_{lm}(\Omega)$ the spherical harmonics. However, due to

$$|Y_{1,\pm 1}(\Omega)|^2 = \frac{3}{8\pi} \sin^2 \Theta,$$

one finds that the density

$$n(\mathbf{r}) = \sum_{i=1}^N |\phi_i(\mathbf{r})|^2$$

is identical for the following two 5-particle states (Slater determinants),

$$\begin{aligned} \Psi_+ &= \frac{1}{\sqrt{5!}} \det \left((1s)^2 (2s)^2 2p_+ \right) \\ \Psi_- &= \frac{1}{\sqrt{5!}} \det \left((1s)^2 (2s)^2 2p_- \right). \end{aligned}$$

A unique functional $|\Psi[n]\rangle$ does not exist in the case of degenerate ground states.

Fortunately, the existence of such a unique functional is not really required in order to extend the most important statement of the HK theorem to degenerate ground states: only the existence of $E[n]$ is of interest [16]. One first notes that, by definition, all the degenerate states $|\Psi_{0,i}\rangle$ lead to the same ground state energy. Even if two degenerate states $|\Psi_1\rangle = \sum_{i=1}^q a_i |\Psi_{0,i}\rangle$ and $|\Psi_2\rangle = \sum_{i=1}^q b_i |\Psi_{0,i}\rangle$ with $|\Psi_1\rangle \neq |\Psi_2\rangle$ lead to the same n , this density nevertheless determines the ground state energy uniquely,

$$E_0 = \langle \Psi_1 | \hat{H} | \Psi_1 \rangle = \langle \Psi_2 | \hat{H} | \Psi_2 \rangle, \quad (2.35)$$

as, by virtue of (2.34), both $|\Psi_1\rangle$ and $|\Psi_2\rangle$ originate from the same v_{ext} , i.e. the same Hamiltonian (up to the constant in v_{ext} which is always undetermined). Similarly, two different densities n_1, n_2 from the same $\mathcal{N}_{v_{\text{ext}}}$ give the same ground state energy. As a result, E_0 is a unique functional of n .

Choosing an arbitrary representative $|\Psi\rangle$ among all states which lead to the same given density n , one can define an energy functional $E[n]$ for degenerate states,

$$E[n] = \langle \Psi[n] | \hat{H} | \Psi[n] \rangle, \quad (2.36)$$

which is unambiguous for all n in the set (2.33). As in the case of the non-degenerate situation one can then verify the existence of a minimum principle,

$$E_0 = E[n_i] \quad \forall n_i \in \mathcal{N}_{v_{\text{ext}}} \quad , \quad E_0 < E[n] \quad \forall n \notin \mathcal{N}_{v_{\text{ext}}} . \quad (2.37)$$

2.3 Variational Equation, Interacting v -Representability, Functional Differentiability

The minimum principles (2.28) and (2.37) indicate the possibility to determine the ground state density of a many-particle system by a variational equation,

$$\frac{\delta}{\delta n(\mathbf{r})} \left\{ E[n] - \mu \left(\int d^3r n(\mathbf{r}) - N \right) \right\} \Big|_{n(\mathbf{r})=n_0(\mathbf{r})} = 0, \quad (2.38)$$

where the subsidiary condition is required to ensure the proper normalization of the density. Unfortunately, the transition from (2.28), (2.37) to Eq. (2.38) is not completely legitimate from a mathematical point of view. The existence of the variational derivative $\delta E[n]/\delta n$ requires the functional $E[n]$ to be defined on a sufficiently dense set of densities n (just as the differentiation of functions requires more than integer numbers as the domain of definition). So far, however, $E[n]$ is only defined for ground state densities resulting from the solution of the Schrödinger equation (2.8). One thus has to face the question whether there exists a potential v_{ext} for every given normalizable function $n(\mathbf{r})$, so that $n(\mathbf{r})$ is the ground state density corresponding to v_{ext} ? If such a potential can be found the density is termed *interacting v -representable*.

Unfortunately, one can give explicit counterexamples, which demonstrate that the issue of v -representability is non-trivial for the functionals (2.26) and (2.36). The discussion of this problem is, however, mathematically somewhat involved. The reader may thus wish to skip the remainder of Sect. 2.3 in a first reading and simply accept the (admittedly vague) statement that the functional derivative $\delta E[n]/\delta n$ exists for all practical purposes, if the definition of $E[n]$ is suitably extended.

1. The first counterexample is based on degeneracy. Let $|\Psi_{0,1}\rangle \dots |\Psi_{0,q}\rangle$ be q orthonormal degenerate ground states for some v_{ext} . One can then construct a statistical density matrix \hat{D} from these states,

$$\hat{D} = \sum_{i=1}^q c_i |\Psi_{0,i}\rangle \langle \Psi_{0,i}|; \quad c_i = c_i^* \geq 0; \quad \sum_{i=1}^q c_i = 1. \quad (2.39)$$

The corresponding (ensemble) density is obtained by

$$n_D(\mathbf{r}) = \text{tr} \{ \hat{D} \hat{n}(\mathbf{r}) \} = \sum_{i=1}^q c_i \langle \Psi_{0,i} | \hat{n}(\mathbf{r}) | \Psi_{0,i} \rangle. \quad (2.40)$$

The important observation is: a density of the form (2.40) can not be obtained from a single ground state $|\Psi_0\rangle$ [17, 18].

This statement is worth to be demonstrated explicitly. The most general ground state of the degenerate system has the form

$$|\Psi_0\rangle = \sum_{i=1}^q d_i |\Psi_{0,i}\rangle; \quad \sum_{i=1}^q |d_i|^2 = 1. \quad (2.41)$$

The corresponding density is

$$n_0(\mathbf{r}) = \sum_{i,j=1}^q d_i^* d_j \langle \Psi_{0,i} | \hat{n}(\mathbf{r}) | \Psi_{0,j} \rangle. \quad (2.42)$$

For the densities n_0 and n_D to be identical, the relation

$$\sum_{i,j=1}^q \left(c_i \delta_{ij} - d_i^* d_j \right) \langle \Psi_{0,i} | \hat{n}(\mathbf{r}) | \Psi_{0,j} \rangle = 0$$

has to be satisfied. As the matrix elements $\langle \Psi_{0,i} | \hat{n}(\mathbf{r}) | \Psi_{0,j} \rangle$ do not vanish and as they all exhibit a different \mathbf{r} -dependence, all prefactors must vanish individually,

$$c_i \delta_{ij} - d_i^* d_j = 0. \quad (2.43)$$

The q unknown complex numbers d_i have to satisfy $2q^2$ linearly independent equations. As there is in general no solution to (2.43), one can not find a linear combination of the $|\Psi_{0,i}\rangle$ with the density n_D .

For this reason one distinguishes between *pure-state* and *ensemble* v -representability,

pure-state $\equiv n(\mathbf{r})$ results from a single state $|\Psi_0\rangle$

ensemble $\equiv n(\mathbf{r})$ results from a density matrix, i.e. a statistical ensemble

Obviously the original HK energy functional is only defined for pure-state representable densities.

In order to cope with ensemble v -representable densities one replaces the set $\mathcal{G}_{\text{vext}}$ of pure states, Eq. (2.30), by the set of all density matrices which can be built on the basis of the potential v_{ext} ,

$$\mathcal{D}_{\text{vext}} = \left\{ \hat{D} \mid \text{with: } \hat{D} = \sum_{i=1}^q c_i |\Psi_{0,i}\rangle \langle \Psi_{0,i}|; \quad c_i = c_i^* \geq 0; \quad \sum_{i=1}^q c_i = 1; \right. \\ \left. |\Psi_{0,i}\rangle = \text{degenerate ground states to } v_{\text{ext}} \right\}. \quad (2.44)$$

One can then show that there is a one-to-one correspondence between v_{ext} , the set $\mathcal{D}_{v_{\text{ext}}}$ and the set of ensemble v -representable densities resulting from the elements of $\mathcal{D}_{v_{\text{ext}}}$ via Eq. (2.40) [17, 18]. The sets $\mathcal{D}_{v_{\text{ext}}}$ and v_{ext} are uniquely determined by any given ensemble v -representable n : a given n can not result from more than one $\mathcal{D}_{v_{\text{ext}}}$ and the $\mathcal{D}_{v_{\text{ext}}}$ are disjoint—the underlying argument is the same as in the case of degenerate ground states. This allows a redefinition of $E[n]$, Eq. (2.36), as

$$\begin{aligned} E_{\text{EHK}}[n] &:= \text{tr} \{ \hat{D}[n] \hat{H} \} \quad \text{with} \quad n = \text{tr} \{ \hat{D}[n] \hat{n} \} \\ &= \sum_{i=1}^q c_i \langle \Psi_{0,i} | \hat{H} | \Psi_{0,i} \rangle \\ &\text{with} \quad n(\mathbf{r}) = \sum_{i=1}^q c_i \langle \Psi_{0,i} | \hat{n}(\mathbf{r}) | \Psi_{0,i} \rangle; \quad c_i = c_i^* \geq 0; \quad \sum_{i=1}^q c_i = 1; \\ &|\Psi_{0,i}\rangle = \text{degenerate ground states to } \hat{H}. \end{aligned} \quad (2.45)$$

Any \hat{D} which corresponds to the potential v_{ext} , which in turn is determined by a given density n , yields the same energy value, so that $E_{\text{EHK}}[n]$ is a unique density functional. In this way the domain of $E[n]$ is extended to ensemble v -representable densities (for pure-state v -representable densities both functionals coincide, since the minimizing density matrix in (2.45) results from the non-degenerate ground state in this case).

2. The second counterexample [19] is of a more explicit nature: a single particle in one spatial dimension. There is nothing in the HK proof which requires the presence of more than one particle, an interaction or a three-dimensional system. All statements of the HK theorem are also valid in this special limit.

The Schrödinger equation then has the simple form

$$\left\{ -\frac{\hbar^2}{2m} \frac{d^2}{dx^2} + v_{\text{ext}}(x) \right\} \Psi(x) = E \Psi(x); \quad n(x) = |\Psi(x)|^2. \quad (2.46)$$

Equation (2.46) represents a direct map between n and v_{ext} , if one chooses $\Psi(x)$ to be real,

$$v_{\text{ext}}(x) = \frac{\hbar^2}{2m} \frac{1}{\sqrt{n(x)}} \frac{d^2}{dx^2} \sqrt{n(x)} + E. \quad (2.47)$$

A similar relation can be established for noninteracting particles in three dimensions.

One can now consider the density

$$n(x) = (a + b|x|^\alpha)^2 f(x)^2, \quad (2.48)$$

with

$$a, b > 0; \quad \frac{1}{2} < \alpha < 1; \quad f(x) = f_0 \quad \forall |x| \leq x_0. \quad (2.49)$$

The function $f(x)$ ensures the normalizability of $n(x)$, so that (2.48) represents a legitimate density for which $E[n]$ should exist (the precise form of $f(x)$ for $|x| > x_0$ is irrelevant at this point).

The derivative of $n(x)$ required for the determination of the corresponding $v_{\text{ext}}(x)$ via Eq. (2.47) can be evaluated by use of the general rule²

$$\begin{aligned} \frac{d}{dx} |x|^p &= \frac{d}{dx} \left\{ \Theta(x)x^p + \Theta(-x)(-x)^p \right\} \\ &= \delta(x) \left\{ x^p - (-x)^p \right\} + px|x|^{p-2} \end{aligned} \quad (2.50)$$

$$= px|x|^{p-2} \quad \text{for } p > 0. \quad (2.51)$$

If one assumes that $df/dx(x_0) = d^2f/dx^2(x_0) = 0$ (which is legitimate as a single counterexample is sufficient), one obtains in the interesting region $|x| \leq x_0$,

$$\frac{d}{dx} \sqrt{n(x)} = \frac{d}{dx} \Psi(x) = f_0 b \alpha x |x|^{\alpha-2} \quad (2.52)$$

$$\begin{aligned} \frac{d^2}{dx^2} \sqrt{n(x)} &= \frac{d^2}{dx^2} \Psi(x) = f_0 b \alpha (\alpha - 1) |x|^{\alpha-2} \\ &\quad + f_0 b \alpha \delta(x) \left[x^{\alpha-1} + (-x)^{\alpha-1} \right]. \end{aligned} \quad (2.53)$$

The kinetic energy associated with $\Psi(x)$ is finite,

$$\begin{aligned} T &= \frac{\hbar^2}{2m} \int_{-x_0}^{+x_0} dx \left(\frac{d}{dx} \Psi(x) \right)^2 + T_R \\ &= \frac{\hbar^2}{2m} f_0^2 b^2 \alpha^2 \int_{-x_0}^{+x_0} dx |x|^{2\alpha-2} + T_R < \infty, \end{aligned} \quad (2.54)$$

as $\alpha > 1/2$ has been chosen (T_R is the finite contribution from the exterior region $|x| > x_0$). The corresponding potential reads ($|x| \leq x_0$) [20]

$$v_{\text{ext}}(x) = \frac{\hbar^2}{2m} \frac{b\alpha}{a+b|x|} \left\{ (\alpha-1)|x|^{\alpha-2} + \delta(x) \left[x^{\alpha-1} + (-x)^{\alpha-1} \right] \right\} + E, \quad (2.55)$$

As could be expected, v_{ext} has a distributional character. The potential diverges more strongly than $|x|^{-1}$ in the limit $|x| \rightarrow 0$ for $\alpha < 1$. The corresponding potential energy,

$$V = \int_{-x_0}^{+x_0} dx v_{\text{ext}}(x) n(x) + V_R, \quad (2.56)$$

is not well-defined, the individual contributions being highly divergent. Obviously, potentials of the type (2.55) neither define a proper Hamiltonian, nor are

² Note that for $p > 0$ one has $\delta'(x)x^p f(x) = -\delta(x)px^{p-1}f(x)$ for any regular $f(x)$.

they particularly realistic. This example calls for a more stringent characterization of the sets of admissible densities and corresponding potentials.

3. The third counterexample [19] is even more simple. Consider a single (noninteracting) particle in a spherical potential. Then any density with a zero is not v -representable, as nodes can only show up for excited states (the ground state is nodeless [21]).

The examples show that the treatment of non- v -representable densities needs closer attention. A rigorous resolution of the problem of interacting v -representability can either be obtained by a more mathematical approach or with a more practically motivated argument.

1. In the practical variant one relies on the fact that any numerical realization of DFT requires the use of grids. On a (finite or infinite) spatial grid, however, any strictly positive ($n(\mathbf{r}) > 0$), normalizable density, which is compatible with the Pauli principle, is ensemble v -representable [20]. The crucial point is the representation of the Laplacian by a suitable finite difference formula, as e.g.

$$\nabla^2 f(\mathbf{r}) = \frac{1}{h^2} \sum_{i=1}^3 [f(\mathbf{r} + h\mathbf{e}_i) - 2f(\mathbf{r}) + f(\mathbf{r} - h\mathbf{e}_i)], \quad (2.57)$$

where an equidistant mesh and Cartesian coordinates have been used (with mesh spacing h ; \mathbf{e}_i denotes a Cartesian unit vector). The answer to the question of v -representability is in this line of argumentation associated with the finite resolution of the grid, which does not permit a representation of singular potentials: the finite grid spacing suppresses all singularities.

2. For the mathematical resolution of the v -representability problem one introduces a suitable redefinition of the energy functional [22, 17, 23]. The starting point of this generalization is the *Levy-Lieb functional*

$$E_{\text{LL}}[n] := F_{\text{LL}}[n] + \int d^3r v_{\text{ext}}(\mathbf{r}) n(\mathbf{r}) \quad (2.58)$$

$$F_{\text{LL}}[n] := \inf_{\Psi \rightarrow n} \langle \Psi | \hat{T} + \hat{W} | \Psi \rangle. \quad (2.59)$$

The notation $\Psi \rightarrow n$ indicates that the infimum has to be taken over all N -particle states Ψ which yield the given density n (in fact, the infimum is a minimum, i.e. there always exists some Ψ which minimizes $\langle \Psi | \hat{T} + \hat{W} | \Psi \rangle$ for given n [23]). This restricted minimization procedure is usually referred to as the *Levy-Lieb constrained search*.

The Levy-Lieb functional $E_{\text{LL}}[n]$ represents a consistent extension of the original HK functional: $E_{\text{LL}}[n]$ is identical with $E[n]$ for all pure-state v -representable n and has its minimum for exactly the same density as $E[n]$. This can be shown by use of the Ritz principle,

$$\begin{aligned}
E_0 &= \inf_{\Psi} \langle \Psi | \hat{H} | \Psi \rangle \\
&= \inf_n \left\{ \inf_{\Psi \rightarrow n} \langle \Psi | \hat{T} + \hat{W} + \hat{V}_{\text{ext}} | \Psi \rangle \right\} \\
&= \inf_n E_{\text{LL}}[n].
\end{aligned} \tag{2.60}$$

As the infimum is actually reached for the true ground state with the density n_0 , $E_{\text{LL}}[n]$ is minimized by this density and one has $E_{\text{LL}}[n_0] = E[n_0]$. Moreover, each state Ψ , which minimizes $\langle \Psi | \hat{H} | \Psi \rangle$ for some potential v_{ext} , is a ground state by construction and therefore leads to a pure-state v -representable density. As a consequence there are no additional densities n which are not pure-state v -representable, but nevertheless give the same energy as the true degenerate ground states. On the complete domain of $E[n]$ one thus finds

$$E_{\text{LL}}[n] = E[n] \quad \text{for all pure-state } v\text{-representable } n. \tag{2.61}$$

The same is true for F_{LL} : $F_{\text{LL}}[n] = F[n]$, if n is pure-state v -representable. So far, the problem of v -representability has, however, only been reformulated by the definition (2.59). The question, still to be answered, is: given some non-negative, normalizable function $n(\mathbf{r})$, is there always a suitable antisymmetric, normalizable N -particle function Ψ with $n(\mathbf{r}) = \langle \Psi | \hat{n}(\mathbf{r}) | \Psi \rangle$? If so, the function $n(\mathbf{r})$ is called (pure-state) *N -representable*. Fortunately, the answer is yes [11, 24–26]. In fact, one can explicitly construct such a wavefunction [24].

This construction, ignoring spin for simplicity, starts with the definition of suitable single-particle orbitals,

$$\phi_{\mathbf{k}}(\mathbf{r}) := \left(\frac{n(\mathbf{r})}{N} \right)^{1/2} e^{i[\mathbf{k} \cdot \mathbf{f}(\mathbf{r}) + \varphi(\mathbf{r})]}; \quad \mathbf{k} \in \mathbb{Z}^3, \tag{2.62}$$

with the Cartesian components of the vector field \mathbf{f} given by

$$f_1(\mathbf{r}) = 2\pi \frac{\int_{-\infty}^x dx' n(x', y, z)}{\int_{-\infty}^{\infty} dx' n(x', y, z)} \tag{2.63}$$

$$f_2(\mathbf{r}) = 2\pi \frac{\int_{-\infty}^{\infty} dx' \int_{-\infty}^y dy' n(x', y', z)}{\int_{-\infty}^{\infty} dx' \int_{-\infty}^{\infty} dy' n(x', y', z)} \tag{2.64}$$

$$f_3(\mathbf{r}) = 2\pi \frac{\int_{-\infty}^{\infty} dx' \int_{-\infty}^{\infty} dy' \int_{-\infty}^z dz' n(x', y', z')}{\int_{-\infty}^{\infty} dx' \int_{-\infty}^{\infty} dy' \int_{-\infty}^{\infty} dz' n(x', y', z')}, \tag{2.65}$$

and a real, but otherwise arbitrary scalar field $\varphi(\mathbf{r})$. Different choices of $\phi_{\mathbf{k}}$ are possible, uniqueness is not required at this point.

The functions $\phi_{\mathbf{k}}$ define an orthonormal and complete basis. Orthonormality is verified as follows. One starts with

$$\int d^3r \phi_{\mathbf{k}}^{\dagger}(\mathbf{r}) \phi_{\mathbf{q}}(\mathbf{r}) = \frac{1}{N} \int d^3r n(\mathbf{r}) e^{i(\mathbf{q}-\mathbf{k}) \cdot \mathbf{f}(\mathbf{r})}. \tag{2.66}$$

For the evaluation of (2.66) the integration over \mathbf{r} has to be replaced by one over \mathbf{f} . Consider first the x -coordinate. As long as $n(\mathbf{r})$ does not vanish identically in some finite region of space, f_1 is a monotonically increasing function of x (for fixed y and z). One can therefore substitute

$$\begin{aligned}
& \int_{-\infty}^{\infty} dz \int_{-\infty}^{\infty} dy \int_{-\infty}^{\infty} dx n(x, y, z) \\
&= \int_{-\infty}^{\infty} dz \int_{-\infty}^{\infty} dy \int_{f_1(-\infty)}^{f_1(+\infty)} df_1 \left(\frac{\partial f_1(x, y, z)}{\partial x} \right)^{-1} n(x, y, z) \\
&= \frac{1}{2\pi} \int_{-\infty}^{\infty} dz \int_{-\infty}^{\infty} dy \int_0^{2\pi} df_1 \int_{-\infty}^{\infty} dx' n(x', y, z).
\end{aligned}$$

This procedure can be repeated with y and f_2 . For fixed z , the function (2.64) is a monotonically increasing function of y ,

$$\begin{aligned}
& \int_{-\infty}^{\infty} dz \int_{-\infty}^{\infty} dy \int_{-\infty}^{\infty} dx n(x, y, z) \\
&= \frac{1}{2\pi} \int_0^{2\pi} df_1 \int_{-\infty}^{\infty} dz \int_{f_2(-\infty)}^{f_2(+\infty)} df_2 \left(\frac{\partial f_2(y, z)}{\partial y} \right)^{-1} \int_{-\infty}^{\infty} dx' n(x', y, z) \\
&= \frac{1}{(2\pi)^2} \int_0^{2\pi} df_1 \int_{-\infty}^{\infty} dz \int_0^{2\pi} df_2 \int_{-\infty}^{\infty} dx' \int_{-\infty}^{\infty} dy' n(x', y', z).
\end{aligned}$$

Finally, z is replaced by f_3 ,

$$\int_{-\infty}^{\infty} dz \int_{-\infty}^{\infty} dy \int_{-\infty}^{\infty} dx n(x, y, z) = \frac{N}{(2\pi)^3} \int_0^{2\pi} df_1 \int_0^{2\pi} df_2 \int_0^{2\pi} df_3. \quad (2.67)$$

Equation (2.67) allows a direct evaluation of (2.66),

$$\int d^3 r \phi_{\mathbf{k}}^{\dagger}(\mathbf{r}) \phi_{\mathbf{q}}(\mathbf{r}) = \frac{1}{(2\pi)^3} \prod_{j=1}^3 \int_0^{2\pi} df_j e^{i(q_j - k_j)f_j} = \delta_{\mathbf{k}, \mathbf{q}}. \quad (2.68)$$

Equation (2.68) is the desired orthonormality relation. In a similar fashion one can establish the completeness of the set of functions $\phi_{\mathbf{k}}$,

$$\begin{aligned}
\sum_{\mathbf{k} \in \mathbb{Z}^3} \phi_{\mathbf{k}}(\mathbf{r}) \phi_{\mathbf{k}}^{\dagger}(\mathbf{r}') &= \frac{\sqrt{n(\mathbf{r})n(\mathbf{r}')}}{N} e^{i\varphi(\mathbf{r}) - i\varphi(\mathbf{r}')} \sum_{\mathbf{k} \in \mathbb{Z}^3} e^{i\mathbf{k} \cdot [\mathbf{f}(\mathbf{r}) - \mathbf{f}(\mathbf{r}')] } \\
&= \frac{\sqrt{n(\mathbf{r})n(\mathbf{r}')}}{N} e^{i\varphi(\mathbf{r}) - i\varphi(\mathbf{r}')} (2\pi)^3 \delta^{(3)}(\mathbf{f}(\mathbf{r}) - \mathbf{f}(\mathbf{r}')) \\
&= \frac{\sqrt{n(\mathbf{r})n(\mathbf{r}')}}{N} e^{i\varphi(\mathbf{r}) - i\varphi(\mathbf{r}')} (2\pi)^3 \delta^{(3)}(\mathbf{r} - \mathbf{r}') \left| \frac{\partial(f_1, f_2, f_3)}{\partial(x, y, z)} \right|^{-1} \\
&= \delta^{(3)}(\mathbf{r} - \mathbf{r}'), \quad (2.69)
\end{aligned}$$

using the Jacobi determinant of (2.67).

With the $\phi_{\mathbf{k}}$ one can construct an antisymmetric N -particle state. The Slater determinant

$$\Phi_{\mathbf{k}_1 \dots \mathbf{k}_N} = \frac{1}{\sqrt{N}} \det(\phi_{\mathbf{k}_1} \dots \phi_{\mathbf{k}_N}) \quad (2.70)$$

has all the properties required for the Levy-Lieb construction (2.59). In particular, one obtains as the density corresponding to $\Phi_{\mathbf{k}_1 \dots \mathbf{k}_N}$ the desired result

$$n(\mathbf{r}) = \sum_{i=1}^N |\phi_{\mathbf{k}_i}(\mathbf{r})|^2 = \frac{n(\mathbf{r})}{N} \cdot N. \quad (2.71)$$

On the basis of this explicit construction of suitable N -particle states one concludes that the Levy-Lieb functional (2.58) is mathematically well-defined for arbitrary non-negative functions $n(\mathbf{r})$.

The Levy-Lieb construction solves the question of ν -representability: $E_{\text{LL}}[n]$ is well-defined for any density n in the vicinity of some ground state density n_0 . Unfortunately, this does not automatically imply that the functional derivative of $E_{\text{LL}}[n]$ at n_0 exists. This is analogous to the situation for ordinary functions, for which differentiability at some point x_0 requires more than the existence of the function in a neighborhood of x_0 .

In order to settle the question of functional differentiability an even more general extension of the HK functional $E[n]$ than $E_{\text{LL}}[n]$ has to be introduced. A complete and mathematically rigorous discussion of this extension, the *Lieb functional* [23], requires a substantial background in functional analysis. Therefore only the basic concepts and the main results will be outlined here (for an extended and coherent review of Lieb's work see [27]; a complementary approach, emphasizing the aspect of Legendre transforms and generalizing the Lieb functional to non-integer particle number, is presented in [28]). After a characterization of the admissible densities and potentials in section (a) the Lieb functional is defined in section (b). Its functional differentiability is discussed in section (c). Finally, in section (d) an alternative form of the Lieb functional is introduced, which turns out to be most useful for establishing the Kohn-Sham equations in a rigorous way. The hasty reader may proceed directly to the summarizing statement at the end of section (c).

(a) Admissible densities and potentials

In the first step of this extension the sets of admissible densities and potentials are specified more precisely, as differentiability can only be demonstrated for a mathematically well-defined domain. In fact, not every non-negative, normalizable function $n(\mathbf{r})$ is a reasonable candidate for which a ground state energy functional should be defined. Rather one requires the components of the ground state energy to be finite separately,

$$\langle \Psi | \hat{T} | \Psi \rangle < \infty \quad (2.72)$$

$$|\langle \Psi | \hat{V}_{\text{ext}} | \Psi \rangle| < \infty \quad (2.73)$$

$$\langle \Psi | \hat{W} | \Psi \rangle < \infty. \quad (2.74)$$

According to condition (2.72) the gradients of the admissible N -particle wavefunctions $\Psi(\mathbf{r}_1\sigma_1, \dots)$ have to be square-integrable,

$$T(\Psi) := \sum_{i=1}^N \sum_{\sigma_1, \dots, \sigma_N} \int d^3r_1 \dots d^3r_N |\nabla_i \Psi(\mathbf{r}_1\sigma_1, \dots, \mathbf{r}_N\sigma_N)|^2 \quad (2.75)$$

$$= N \sum_{\sigma_1, \dots, \sigma_N} \int d^3r_1 \dots d^3r_N |\nabla_1 \Psi(\mathbf{r}_1\sigma_1, \dots, \mathbf{r}_N\sigma_N)|^2 < \infty. \quad (2.76)$$

This condition leads to a constraint for the corresponding density [23],

$$\int d^3r \left[\nabla n^{1/2}(\mathbf{r}) \right]^2 < \infty. \quad (2.77)$$

In mathematical language, each component of $\nabla_i \Psi$ is in the set $\mathcal{L}^2(\mathbb{R}^{3N})$ of square-integrable functions over \mathbb{R}^{3N} , each component of $\nabla n(\mathbf{r})^{1/2}$ is in the set $\mathcal{L}^2(\mathbb{R}^3)$. Quite generally, $\mathcal{L}^p(\mathbb{R}^q)$ denotes the set of all functions of q real variables for which the norm

$$\|f\|_p := \left[\int dx_1 \dots dx_q |f(x_1, \dots, x_q)|^p \right]^{1/p} \quad (2.78)$$

is finite,

$$\mathcal{L}^p(\mathbb{R}^q) := \{f(x_1, \dots, x_q) \mid \|f\|_p < \infty\}. \quad (2.79)$$

If one combines (2.76) and (2.77) with the square-integrability of Ψ ,

$$\|\Psi\| := (\|\Psi\|_2)^2 = \sum_{\sigma_1, \dots, \sigma_N} \int d^3r_1 \dots d^3r_N |\Psi(\mathbf{r}_1 \sigma_1, \dots, \mathbf{r}_N \sigma_N)|^2 = 1 \quad (2.80)$$

$$\implies \Psi \in \mathcal{L}^2(\mathbb{R}^{3N}), \quad (2.81)$$

and of $n^{1/2}$,

$$\left(\|n^{1/2}\|_2 \right)^2 = \|n\|_1 = \int d^3r n(\mathbf{r}) = N \quad (2.82)$$

$$\implies n \in \mathcal{L}^1(\mathbb{R}^3); n^{1/2} \in \mathcal{L}^2(\mathbb{R}^3), \quad (2.83)$$

one arrives at the statement that both Ψ and $n^{1/2}$ belong to the Sobolev space \mathcal{H}^1 , $\Psi \in \mathcal{H}^1(\mathbb{R}^{3N})$ and $n^{1/2} \in \mathcal{H}^1(\mathbb{R}^3)$. This space,

$$\mathcal{H}^1 = \{f \mid f \in \mathcal{L}^2, \nabla f \in \mathcal{L}^2\},$$

is a Hilbert space with the inner product

$$\langle f | g \rangle = \int f^* g + \int \nabla f^* \cdot \nabla g.$$

As soon as $\Psi \in \mathcal{H}^1(\mathbb{R}^{3N})$ the constraint (2.74) is automatically satisfied [23]. The sets of relevant wavefunctions \mathcal{W} and densities \mathcal{S} are thus given by

$$\mathcal{W} = \{\Psi \mid \|\Psi\| = 1, T(\Psi) < \infty\} \quad (2.84)$$

$$\mathcal{S} = \left\{ n \mid n(\mathbf{r}) \geq 0, \int d^3r n(\mathbf{r}) = N, n^{1/2} \in \mathcal{H}^1(\mathbb{R}^3) \right\}. \quad (2.85)$$

\mathcal{S} has the important property that it is *convex*: with the densities n_1 and n_2 all densities on the “straight connection line” between the two densities are in \mathcal{S} ,

$$n_1, n_2 \in \mathcal{S}; \quad 0 \leq \lambda \leq 1 \quad \implies \quad n = [\lambda n_1 + (1 - \lambda)n_2] \in \mathcal{S}. \quad (2.86)$$

Since $\mathcal{S} \subset \mathcal{H}^1(\mathbb{R}^3)$, this result follows directly from the definition of the norm $\|f\| = \langle f|f \rangle^{1/2}$ in $\mathcal{H}^1(\mathbb{R}^3)$, if Schwartz’s inequality,

$$\begin{aligned} \left(\nabla n^{1/2} \right)^2 &= \frac{(\nabla n)^2}{4n} \\ &= \left[\lambda \frac{n_1^{1/2}}{n^{1/2}} \nabla n_1^{1/2} + (1 - \lambda) \frac{n_2^{1/2}}{n^{1/2}} \nabla n_2^{1/2} \right]^2 \\ &\leq \lambda \left(\frac{\lambda n_1}{n} \right) \left(\nabla n_1^{1/2} \right)^2 + (1 - \lambda) \left(\frac{(1 - \lambda)n_2}{n} \right) \left(\nabla n_2^{1/2} \right)^2 \\ &\leq \lambda \left(\nabla n_1^{1/2} \right)^2 + (1 - \lambda) \left(\nabla n_2^{1/2} \right)^2, \end{aligned}$$

is used.

On this basis one can now consider the constraint (2.73), which leads to a characterization of the set of admissible external potentials. One first has to realize that any density in \mathcal{S} also belongs to the larger space $\mathcal{L}^1(\mathbb{R}^3) \cap \mathcal{L}^3(\mathbb{R}^3)$, which is a Banach space (i.e. a complete normed vector space). This is a result of Sobolev’s inequality, which (in 3 dimensions) states

$$\|n\|_3 = \left[\int d^3r |n(\mathbf{r})|^3 \right]^{1/3} \leq \frac{1}{3} \left(\frac{2}{\pi} \right)^{4/3} \int d^3r \left[\nabla n^{1/2}(\mathbf{r}) \right]^2.$$

However, a function which belongs to both $\mathcal{L}^1(\mathbb{R}^3)$ and $\mathcal{L}^3(\mathbb{R}^3)$, also belongs to $\mathcal{L}^2(\mathbb{R}^3)$. The integral (2.73),

$$\langle \Psi | \hat{V}_{\text{ext}} | \Psi \rangle = \int d^3r n(\mathbf{r}) v_{\text{ext}}(\mathbf{r}) = \|n v_{\text{ext}}\|_1, \quad (2.87)$$

is thus finite, if

$$v_{\text{ext}} \in \mathcal{L}^{3/2}(\mathbb{R}^3) + \mathcal{L}^\infty(\mathbb{R}^3), \quad (2.88)$$

where $\mathcal{L}^\infty(\mathbb{R}^3)$ denotes the space of all bounded functions,

$$\|f\|_\infty := \sup_{(x_1, \dots, x_q) \in \mathbb{R}^q} |f(x_1, \dots, x_q)| \quad (2.89)$$

$$\mathcal{L}^\infty(\mathbb{R}^q) := \{f(x_1, \dots, x_q) \mid \|f\|_\infty < M\}. \quad (2.90)$$

It is immediately clear that potentials from the set \mathcal{L}^∞ (we will now drop the indication of the coordinate space over which the functions are defined, as it should be obvious at this point) yield a finite $\|n v_{\text{ext}}\|_1$. For the potentials from the set $\mathcal{L}^{3/2}$

one relies on the Hölder inequality [29],

$$\begin{aligned} \|fg\|_1 &\leq \|f\|_p \|g\|_q \quad \text{with} \quad \frac{1}{p} + \frac{1}{q} = 1 \\ \implies \|nv_{\text{ext}}\|_1 &\leq \|n\|_3 \|v_{\text{ext}}\|_{3/2} < \infty. \end{aligned} \quad (2.91)$$

The set $\mathcal{L}^{3/2} + \mathcal{L}^\infty$ includes in particular the Coulomb potential, which may be decomposed as³

$$\begin{aligned} \frac{1}{|\mathbf{r}|} &= \frac{\Theta(R - |\mathbf{r}|)}{|\mathbf{r}|} + \frac{1 - \Theta(R - |\mathbf{r}|)}{|\mathbf{r}|} \\ \frac{\Theta(R - |\mathbf{r}|)}{|\mathbf{r}|} &\in \mathcal{L}^{3/2} \\ \frac{1 - \Theta(R - |\mathbf{r}|)}{|\mathbf{r}|} &\in \mathcal{L}^\infty. \end{aligned}$$

$\mathcal{L}^{3/2} + \mathcal{L}^\infty$ is a Banach space with the norm

$$\|v_{\text{ext}}\| = \inf_{f \in \mathcal{L}^{3/2}, g \in \mathcal{L}^\infty} \{ \|f\|_{3/2} + \|g\|_\infty \mid v_{\text{ext}} = f + g \}. \quad (2.92)$$

The characterization of the spaces involved is completed by the observation that the dual space of $\mathcal{L}^1 \cap \mathcal{L}^3$, i.e. the space of all continuous linear functionals on the space of functions $\mathcal{L}^1 \cap \mathcal{L}^3$, is exactly $\mathcal{L}^{3/2} + \mathcal{L}^\infty$ —all continuous linear functionals on $\mathcal{L}^1 \cap \mathcal{L}^3$ have the form $\int d^3r v(\mathbf{r})n(\mathbf{r})$ with $v \in \mathcal{L}^{3/2} + \mathcal{L}^\infty$ [29].

(b) Definition of Lieb functional and basic properties

At this point one can start the discussion of energy functionals. One first defines the energy $E[v]$ of an N -particle system subject to the external potential v in the most natural way,

$$E[v] := \inf_{\Psi} \{ \langle \Psi | \hat{H}_v | \Psi \rangle \mid \Psi \in \mathcal{W} \}. \quad (2.93)$$

Here the index v at \hat{H}_v characterizes the external potential in \hat{V}_{ext} . This definition is obviously legitimate for all $v \in \mathcal{L}^{3/2} + \mathcal{L}^\infty$. Of course, the existence of $E[v]$ for some v does not imply that there is a minimizing state Ψ which satisfies a Schrödinger equation with the operator \hat{H}_v . This is only the case if v belongs to the set of potentials for which a ground state exists: the ground state then minimizes the right-hand side of (2.93). The set of all densities, for which one finds such a ground state is the domain of the original HK-functional,

³ On the other hand, unbounded potentials such as the harmonic oscillator require an additional restriction on the set of densities.

$$\mathcal{A} := \{n = \langle \Psi | \hat{n} | \Psi \rangle \mid \exists \Psi \in \mathcal{W} \text{ with } E[v] = \langle \Psi | \hat{H}_v | \Psi \rangle\} . \quad (2.94)$$

The second domain of interest is that of $E_{\text{EHK}}[n]$, i.e. the set of all ensemble v -representable densities,

$$\mathcal{B} := \left\{ n = \sum_{i=1}^q c_i \langle \Psi_{0,i} | \hat{n} | \Psi_{0,i} \rangle \mid c_i = c_i^* \geq 0; \sum_{i=1}^q c_i = 1; \right. \\ \left. |\Psi_{0,i}\rangle = \text{degenerate ground states for some } v \in \mathcal{L}^{3/2} + \mathcal{L}^\infty \right\}. \quad (2.95)$$

With the energy functional (2.93) the Lieb functional is then defined as [23]

$$F_L[n] := \sup_v \left\{ E[v] - \int d^3r v(\mathbf{r}) n(\mathbf{r}) \mid v \in \mathcal{L}^{3/2} + \mathcal{L}^\infty \right\} \quad \text{with } n \in \mathcal{S}. \quad (2.96)$$

The domain of this functional can be extended to the complete space $\mathcal{L}^1 \cap \mathcal{L}^3$, if one allows $F_L[n]$ to assume the value $+\infty$ (which is no problem in functional analysis). However, only the densities in \mathcal{S} are really relevant in the following. The energy (2.93) for any external potential $v \in \mathcal{L}^{3/2} + \mathcal{L}^\infty$ is then obtained by

$$E[v] = \inf_n \left\{ F_L[n] + \int d^3r v(\mathbf{r}) n(\mathbf{r}) \mid n \in \mathcal{S} \right\}, \quad (2.97)$$

which is a consequence of the definitions of $E[v]$ and $F_L[n]$ as mutual Legendre transforms.⁴

This identity can be verified by establishing two suitable inequalities. On the one hand, one has by definition of $F_L[n]$ for any given $v_0 \in \mathcal{L}^{3/2} + \mathcal{L}^\infty$

$$\begin{aligned} E[v_0] - \int d^3r v_0 n &\leq F_L[n] \quad \forall n \in \mathcal{S}, v_0 \in \mathcal{L}^{3/2} + \mathcal{L}^\infty \\ \Rightarrow \inf_n \left\{ \left[E[v_0] - \int d^3r v_0 n \right] + \int d^3r v n \mid n \in \mathcal{S} \right\} \\ &\leq \inf_n \left\{ F_L[n] + \int d^3r v n \mid n \in \mathcal{S} \right\} \quad \forall v, v_0 \in \mathcal{L}^{3/2} + \mathcal{L}^\infty \end{aligned}$$

⁴ An extended version of $F_L[n]$ in which the pure-state energy (2.93) is replaced by an ensemble energy,

$$\begin{aligned} F[n, N] &:= \sup_v \left\{ E[v, N] - \int d^3r v(\mathbf{r}) n(\mathbf{r}) \mid v \in \mathcal{L}^{3/2} + \mathcal{L}^\infty \right\} \\ E[v, N] &:= \inf_{\hat{D}} \left\{ \text{tr} \{ \hat{D} \hat{H} \} \mid \text{tr} \{ \hat{D} \hat{N} \} = N \right\}, \end{aligned}$$

has been introduced by Eschrig [28]. It shares many properties with $F_L[n]$ and allows a consistent handling of non-integer particle numbers. In accordance with the more general definition of $E[v, N]$, one finds

$$F[n, N] \leq F_L[n] = F_{\text{HK}}[n] \quad \text{for } n \in \mathcal{A}.$$

This inequality also holds for $v_0 = v$,

$$E[v] \leq \inf_n \left\{ F_L[n] + \int d^3 r v n \mid n \in \mathcal{S} \right\} \quad \forall v \in \mathcal{L}^{3/2} + \mathcal{L}^\infty. \quad (2.98)$$

On the other hand, one has by definition of $E[v]$

$$E[v] \leq \inf_{\Psi} \{ \langle \Psi | \hat{H}_v | \Psi \rangle \mid \Psi \in \mathcal{W}, \langle \Psi | \hat{n} | \Psi \rangle = n \} \quad \forall n \in \mathcal{S}, v \in \mathcal{L}^{3/2} + \mathcal{L}^\infty,$$

so that

$$\begin{aligned} & E[v] - \int d^3 r v n \\ & \leq \inf_{\Psi} \{ \langle \Psi | \hat{T} + \hat{W} | \Psi \rangle \mid \Psi \in \mathcal{W}, \langle \Psi | \hat{n} | \Psi \rangle = n \} \quad \forall n \in \mathcal{S}, v \in \mathcal{L}^{3/2} + \mathcal{L}^\infty \\ \Rightarrow & F_L[n] = \sup_v \left\{ E[v] - \int d^3 r v n \mid v \in \mathcal{L}^{3/2} + \mathcal{L}^\infty \right\} \\ & \leq \inf_{\Psi} \{ \langle \Psi | \hat{T} + \hat{W} | \Psi \rangle \mid \Psi \in \mathcal{W}, \langle \Psi | \hat{n} | \Psi \rangle = n \} \quad \forall n \in \mathcal{S} \\ \Rightarrow & F_L[n] + \int d^3 r v n \\ & \leq \inf_{\Psi} \{ \langle \Psi | \hat{H}_v | \Psi \rangle \mid \Psi \in \mathcal{W}, \langle \Psi | \hat{n} | \Psi \rangle = n \} \quad \forall n \in \mathcal{S}, v \in \mathcal{L}^{3/2} + \mathcal{L}^\infty. \end{aligned}$$

However, for any $\Psi \in \mathcal{W}$ the resulting expectation value $\langle \Psi | \hat{n} | \Psi \rangle$ is in \mathcal{S} , so that the infimum of the right-hand side of this inequality is exactly $E[v]$,

$$\begin{aligned} & \inf_n \left\{ F_L[n] + \int d^3 r v n \mid n \in \mathcal{S} \right\} \\ & \leq \inf_{\Psi} \{ \langle \Psi | \hat{H}_v | \Psi \rangle \mid \Psi \in \mathcal{W} \} = E[v] \quad \forall v \in \mathcal{L}^{3/2} + \mathcal{L}^\infty. \end{aligned} \quad (2.99)$$

Combination of this inequality with (2.98) proves (2.97).

As a direct consequence of (2.97) one obtains

$$F_L[n] = F_{LL}[n] = F_{HK}[n] \quad \forall n \in \mathcal{A}, \quad (2.100)$$

so that $F_L[n]$ is a consistent extension of the initial HK functional.

(c) Functional differentiability of Lieb functional

For the functional $F_L[n]$ one can prove the following properties [23, 30, 31]:

1. $F_L[n]$ is *convex*: for $n_0, n_1 \in \mathcal{S}$ and $0 \leq \lambda \leq 1$ one has

$$F_L[\lambda n_1 + (1 - \lambda) n_0] \leq \lambda F_L[n_1] + (1 - \lambda) F_L[n_0]. \quad (2.101)$$

Note that the convexity of \mathcal{S} ensures that $F_L[n]$ is defined (i.e. finite) for all $n = \lambda n_1 + (1 - \lambda) n_0$. The property (2.101) results from the linearity of $F_L[n]$ in n in combination with the definition of $F_L[n]$ as a supremum.

2. $F_L[n]$ is *weakly lower semicontinuous*: for any sequence n_k which converges weakly against a limit n , i.e. for which

$$\|(n_k - n)v\|_1 \xrightarrow{k \rightarrow \infty} 0 \quad \forall v \in \mathcal{L}^{3/2} + \mathcal{L}^\infty,$$

one has

$$F_L[n] \leq \lim_{k \rightarrow \infty} \inf_{l \geq k} F_L[n_l] = \liminf_{k \rightarrow \infty} F_L[n_k].$$

This relation is a “weak” version of the standard concept of continuity which requires that $|F_L[n] - F_L[n_k]| \xrightarrow{k \rightarrow \infty} 0$ if n_k is norm convergent against n (i.e. if $\|n_k - n\|_1 \xrightarrow{k \rightarrow \infty} 0$ and simultaneously $\|n_k - n\|_3 \xrightarrow{k \rightarrow \infty} 0$).

3. $F_L[n]$ has a *unique continuous tangent functional* on \mathcal{B} : for all $n_0 \in \mathcal{B}$ there exists a continuous linear functional $\delta F_{n_0}[n]$ with domain $\mathcal{L}^1 \cap \mathcal{L}^3$, i.e. a functional of the form

$$\delta F_{n_0}[n] = - \int d^3r v(\mathbf{r}) n(\mathbf{r}) \quad \text{with } v \in \mathcal{L}^{3/2} + \mathcal{L}^\infty, \quad (2.102)$$

so that

$$F_L[n] \geq F_L[n_0] + \delta F_{n_0}[n - n_0] \quad \forall n \in \mathcal{L}^1 \cap \mathcal{L}^3, \quad (2.103)$$

and the kernel v in $\delta F_{n_0}[n - n_0]$ is unique up to a constant (the uniqueness is a consequence of the HK theorem). The tangent functional vanishes for $n = n_0$, so that (2.103) becomes an equality at this density, which explains the name.

4. The *set of densities in \mathcal{B} is norm dense in \mathcal{S}* : for arbitrary $n_0 \in \mathcal{S}$ there exists a sequence $n_k \in \mathcal{B}$ such that $\|n_k - n_0\|_1 \xrightarrow{k \rightarrow \infty} 0$ and simultaneously $\|n_k - n_0\|_3 \xrightarrow{k \rightarrow \infty} 0$.

This statement ensures that for any $n_0 \in \mathcal{S}$ one can find a unique continuous tangent functional for a density n_1 which is infinitesimally close to n_0 , so that, from a practical point of view, continuous tangent functionals exist for all $n_0 \in \mathcal{S}$.

These properties finally allow a resolution of the initial question concerning functional differentiability. The point is: for any convex, finite, lower semicontinuous functional with a unique continuous tangent functional the existence of the functional derivative is guaranteed, the functional derivative being identical with the kernel $-v(\mathbf{r})$ of the tangent functional [30, 31, 29] (for a more precise formulation see in particular Corollary 2.5 and Proposition 5.3 of [32] or [27]). Since the first step of the proof of this statement is both simple and instructive, it is worthwhile to present it here. Consider the densities

$$n = n_0 + \lambda(n_1 - n_0) \quad \text{with } n_0 \in \mathcal{B}, n_1 \in \mathcal{S}, 0 \leq \lambda \leq 1.$$

Due to the convexity of \mathcal{S} the density n is also in \mathcal{S} . Now combine the convexity of $F_L[n]$ (property 1.) with the existence of the tangent functional (property 3.),

$$\lambda F_L[n_1] + (1 - \lambda)F_L[n_0] \geq F_L[n_0 + \lambda(n_1 - n_0)] \geq F_L[n_0] + \delta F_{n_0}[\lambda(n_1 - n_0)] .$$

If one subtracts $F_L[n_0]$, uses $\delta F_{n_0}[\lambda(n_1 - n_0)] = \lambda \delta F_{n_0}[n_1 - n_0]$ and divides by λ , one arrives at

$$F_L[n_1] - F_L[n_0] \geq \frac{F_L[n_0 + \lambda(n_1 - n_0)] - F_L[n_0]}{\lambda} \geq \delta F_{n_0}[n_1 - n_0] . \quad (2.104)$$

Both $F_L[n_1] - F_L[n_0]$ and $\delta F_{n_0}[n_1 - n_0]$ are well defined and finite, so that the so-called *Gâteaux differential*

$$F'[n_0, n_1] := \lim_{\lambda \rightarrow 0} \frac{F_L[n_0 + \lambda(n_1 - n_0)] - F_L[n_0]}{\lambda}$$

of $F_L[n]$ at $n = n_0$ exists.

In order to complete the proof of the existence of the functional derivative one has to demonstrate that the Gâteaux differential is linear and continuous in $(n_1 - n_0)$, i.e. that it is identical with $\delta F_{n_0}[n_1 - n_0]$. This second step of the proof is more involved, so that the reader is referred to the literature [32, 27] for a mathematically rigorous discussion. The linearity of the Gâteaux differential is, however, intuitively clear on geometrical grounds, if one interprets the functionals involved as simple functions as in Fig. 2.3: the right-hand inequality in (2.104) shows that the Gâteaux differential approaches the limit $n_1 = n_0$ at least as slowly as the linear functional $\delta F_{n_0}[n_1 - n_0]$ when n_1 approaches n_0 . So, $F'[n_0, n_1]$ can not vanish faster than $n_1 - n_0$

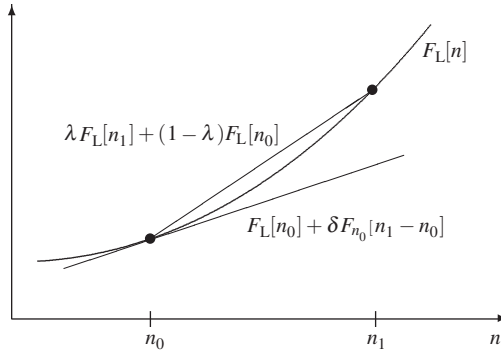


Fig. 2.3 Illustration of convex functional $F_L[n]$ with unique Gâteaux differential $\delta F_{n_0}[n_1 - n_0]$.

for $n_1 \rightarrow n_0$. On the other hand, the convexity of $F_L[n]$ does not allow $F'[n_0, n_1]$ to approach its limit zero more slowly than $n_1 - n_0$ (as the straight line between $F_L[n_1]$ and $F_L[n_0]$ must be above $F_L[n_0 + \lambda(n_1 - n_0)]$ for arbitrary n_1 —this excludes that $F_L[n_0 + \lambda(n_1 - n_0)]$ jumps above this line for some sequence of λ , so that semicontinuity implies continuity). Consequently, $F'[n_0, n_1]$ must be linear in $n_1 - n_0$. More-

over, as the direction of $n_1 - n_0$ is arbitrary and the tangent functional is unique, $F'[n_0, n_1]$ must coincide with $\delta F_{n_0}[n_1 - n_0]$.

In summary: The functional derivative of $F_L[n]$ exists for all ensemble ν -representable densities and is identical with a potential v_{ext} from the dual space $\mathcal{L}^{3/2} + \mathcal{L}^\infty$,

$$\left. \frac{F_L[n]}{\delta n(\mathbf{r})} \right|_{n=n_0} = -v_{\text{ext}}(\mathbf{r}) \quad \text{with} \quad v_{\text{ext}} \in \mathcal{L}^{3/2} + \mathcal{L}^\infty. \quad (2.105)$$

Moreover, for any other “reasonable” density n (i.e. for any $n \in \mathcal{S}$) one can find an ensemble ν -representable density which is arbitrarily close to n , so that the functional derivative of $F_L[n]$ again exists.

In order to complete the picture, it is worthwhile to reconsider the Levy-Lieb functional (2.59) at this point. The existence of a unique continuous tangent functional for all $n \in \mathcal{A}$ has also been demonstrated for $F_{\text{LL}}[n]$ [23]. However, this functional is not convex on \mathcal{S} [23]. Since convexity is crucial for establishing the existence of the functional derivative of $F_L[n]$ via Eq. (2.104), functional differentiability has not been rigorously proven for $F_{\text{LL}}[n]$ so far.

(d) Representation of Lieb functional in terms of density matrices

So, as a matter of principle, the subsequent development of the DFT formalism should therefore be based explicitly on the Lieb functional. We will nevertheless often ignore the issue of functional differentiability in the following and will not distinguish between the various flavors of the energy functional. A prominent exception is the derivation of the Kohn-Sham equations. For this purpose, an alternative form of $F_L[n]$ is most useful. In fact, for all $n \in \mathcal{S}$ the Lieb functional $F_L[n]$ can be recast in the form [23]

$$F_L[n] = \inf_{\hat{D} \rightarrow n} \text{tr} \{ \hat{D}(\hat{T} + \hat{W}) \}, \quad (2.106)$$

with the density matrices restricted to the form

$$\begin{aligned} \hat{D} &= \sum_k d_k |\Psi_k\rangle \langle \Psi_k|, \quad d_k^* = d_k \geq 0, \quad \sum_k d_k = 1, \quad \langle \Psi_k | \Psi_l \rangle = \delta_{kl}, \quad \Psi_k \in \mathcal{H}^1 \\ n(\mathbf{r}) &= \sum_k d_k \langle \Psi_k | \hat{n}(\mathbf{r}) | \Psi_k \rangle \end{aligned}$$

(the $|\Psi_k\rangle$ denote a set of orthonormal wavefunctions in the N -particle Hilbert space). One can also show that there always exists a minimizing \hat{D} for all $n \in \mathcal{S}$ [23]. The form (2.106) will be used in particular to establish the Kohn-Sham equations for degenerate systems (see Sect. 3.3).

2.4 Fractional Particle Numbers, Derivative Discontinuity

The variational equation (2.38) raises one further question: in this equation the particle number is determined via a subsidiary condition, which implies the existence of $E[n]$ for non-integer particle numbers. However, so far all energy functionals are only defined for integer N . Therefore the question has to be addressed, how to extend the energy functional to fractional particle numbers.

Assume that a density integrates up to $N + \eta$,

$$\int d^3r n(\mathbf{r}) = N + \eta; \quad N = 1, 2, \dots; \quad 0 \leq \eta < 1. \quad (2.107)$$

The simplest definition of an energy functional for such a density is a statistical superposition of the lowest possible energies of two states $|\Psi_N\rangle$ and $|\Psi_{N+1}\rangle$ with the neighboring integer particle numbers N and $N + 1$ [33],

$$E_f[n] := F_f[n] + \int d^3r v_{\text{ext}}(\mathbf{r}) n(\mathbf{r}) \quad (2.108)$$

$$F_f[n] := \min_{\Psi_N, \Psi_{N+1}} \{ (1 - \eta) \langle \Psi_N | \hat{T} + \hat{W} | \Psi_N \rangle + \eta \langle \Psi_{N+1} | \hat{T} + \hat{W} | \Psi_{N+1} \rangle \} \quad (2.109)$$

$$\text{with } n(\mathbf{r}) = (1 - \eta) \langle \Psi_N | \hat{n}(\mathbf{r}) | \Psi_N \rangle + \eta \langle \Psi_{N+1} | \hat{n}(\mathbf{r}) | \Psi_{N+1} \rangle \quad (2.110)$$

$$\langle \Psi_N | \Psi_N \rangle = \langle \Psi_{N+1} | \Psi_{N+1} \rangle = 1.$$

The condition (2.110) restricts the variational search for the minimum in (2.109) to those combinations of normalizable states $|\Psi_N\rangle$ and $|\Psi_{N+1}\rangle$, which yield the prescribed density n (constrained search). On the other hand, $|\Psi_N\rangle$ and $|\Psi_{N+1}\rangle$ need not be related to the potential v_{ext} in any way. Equation (2.110) automatically guarantees the desired particle number (2.107). The definition (2.109) is an obvious extension of the Levy-Lieb functional (2.59) to fractional particle numbers. Correspondingly, $F_f[n]$ becomes identical with the Levy-Lieb functional for $\eta = 0$. On the basis of $E_f[n]$ the variational equation (2.38) is also well-defined for fractional particle numbers,⁵

$$\frac{\delta E_f[n]}{\delta n(\mathbf{r})} = \mu_L, \quad (2.111)$$

as $F_f[n]$ exists for any non-negative $n(\mathbf{r})$ which integrates up to $N + \eta$. For any given particle number $N + \eta$ one finds a corresponding Lagrange multiplier $\mu_L(N + \eta)$.

For integer particle number this Lagrange multiplier is identical with the chemical potential

$$\mu(N) := \frac{\partial E}{\partial N}(N), \quad (2.112)$$

⁵ Precisely speaking, the extension of the Lieb functional to non-integer particle number [28] is required at this point. We will, however, not distinguish between the two functionals in the following.

where $E(N + \eta)$ denotes the minimum of the functional (2.108) for given, fractional particle number,

$$E(N + \eta) = \min_n E_f[n]. \quad (2.113)$$

Equation (2.112) can be verified by functional Taylor expansion of the total energy of a system with fractional particle number around the ground state density n_N of the N -particle system,

$$\begin{aligned} & \frac{\partial E}{\partial N}(N) \\ &= \lim_{\eta \rightarrow 0} \frac{1}{\eta} [E(N + \eta) - E(N)] \\ &= \lim_{\eta \rightarrow 0} \frac{1}{\eta} \left[E_f[n_N] + \int d^3r \left. \frac{\delta E_f[n]}{\delta n(\mathbf{r})} \right|_{n=n_N} [n_{N+\eta}(\mathbf{r}) - n_N(\mathbf{r})] + \dots - E(N) \right], \end{aligned}$$

where $n_{N+\eta}$ denotes the ground state density for particle number $N + \eta$ and $E_f[n_N] = E(N)$. One can now use (2.111) to identify the Lagrange multiplier with $\partial E / \partial N$,

$$\mu(N) = \frac{\partial E}{\partial N}(N) = \mu_L(N) \lim_{\eta \rightarrow 0} \frac{1}{\eta} \int d^3r [n_{N+\eta}(\mathbf{r}) - n_N(\mathbf{r})] = \mu_L(N). \quad (2.114)$$

It is worthwhile to examine $\mu(N)$ more closely. Consider the ground state energy of a system with $N + \eta$ particles,

$$\begin{aligned} E(N + \eta) &= \min_n E_f[n] \\ &= \min_n \min_{\Psi_N, \Psi_{N+1}} \{ (1 - \eta) \langle \Psi_N | \hat{H} | \Psi_N \rangle + \eta \langle \Psi_{N+1} | \hat{H} | \Psi_{N+1} \rangle \} \quad (2.115) \\ &\quad \text{with } n(\mathbf{r}) = (1 - \eta) \langle \Psi_N | \hat{n}(\mathbf{r}) | \Psi_N \rangle + \eta \langle \Psi_{N+1} | \hat{n}(\mathbf{r}) | \Psi_{N+1} \rangle, \end{aligned}$$

where the search for the minimum over n is restricted to densities with the fractional particle number $N + \eta$. However, the expression

$$(1 - \eta) \langle \Psi_N | \hat{H} | \Psi_N \rangle + \eta \langle \Psi_{N+1} | \hat{H} | \Psi_{N+1} \rangle$$

becomes minimal if $|\Psi_N\rangle$ is the ground state of the N particle system and $|\Psi_{N+1}\rangle$ is the ground state of the $N + 1$ particle system (for the same v_{ext} —one now assumes that the normalizable ground state $|\Psi_{N+1}\rangle$ exists, i.e. that v_{ext} is capable of binding $N + 1$ particles). The minimum of (2.115) is therefore obtained if n is given by a superposition of the ground state density n_N of the N -particle system and the ground state density n_{N+1} of the $(N + 1)$ -particle system,

$$n(\mathbf{r}) = (1 - \eta) n_N(\mathbf{r}) + \eta n_{N+1}(\mathbf{r}). \quad (2.116)$$

A similar superposition is found for the total energy of the system with $N + \eta$ particles,

$$E(N + \eta) = (1 - \eta)E(N) + \eta E(N + 1). \quad (2.117)$$

This dependence of the energy on the particle number is illustrated in Fig. 2.4. The

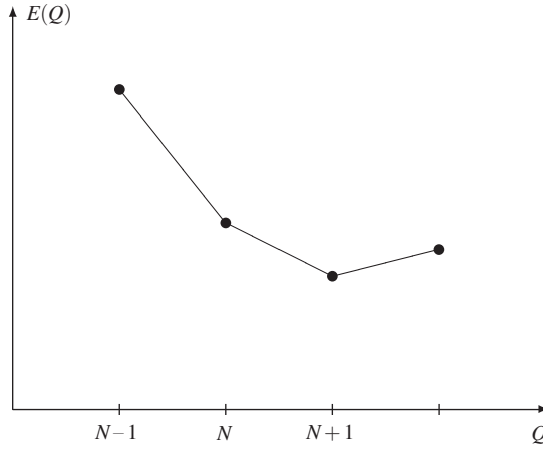


Fig. 2.4 Particle number dependence of the total energy $E(Q)$ for fractional particle number Q (the external potential v_{ext} is the same for all Q).

total energy is a linear function between two neighboring integer particle numbers. According to Eq. (2.114), $\mu(N)$ is the slope of this piecewise linear curve. One thus obtains

$$\mu(N - \eta) = E(N) - E(N - 1) = -\text{IP} \quad (\text{ionization potential}) \quad (2.118)$$

$$\mu(N + \eta) = E(N + 1) - E(N) = -\text{EA} \quad (\text{electron affinity}), \quad (2.119)$$

if N is the number of electrons required for charge neutrality (and $\eta > 0$). As a consequence, $\mu(N)$ is discontinuous at all integer particle numbers. In view of Eqs. (2.114) and (2.111) this implies that the functional derivative of the total energy functional $E_f[n]$ itself must have discontinuities at these particle numbers, the so-called *derivative discontinuities* (for an extended discussion of this and related aspects see [15]).

2.5 Spin-Polarized Systems

Up to now the discussion focused on systems of interacting particles moving in an electrostatic external potential. Density functional theory can, however, also be extended to systems in which the particles are subject to a static magnetic field [34, 35]. In the simplest version the corresponding Hamiltonian is given by

$$\hat{H} = \hat{T} + \hat{W} + \int d^3r \{ v_{\text{ext}}(\mathbf{r}) \hat{n}(\mathbf{r}) + \mathbf{B}_{\text{ext}}(\mathbf{r}) \cdot \hat{\mathbf{m}}(\mathbf{r}) \}. \quad (2.120)$$

Here $\hat{\mathbf{m}}$ is the operator of the magnetization density,⁶

$$\hat{\mathbf{m}}(\mathbf{r}) = \mu_B \sum_{i=1}^N \boldsymbol{\sigma}_i \delta^{(3)}(\mathbf{r} - \mathbf{r}_i) = \mu_B \sum_{\sigma, \sigma'=\uparrow, \downarrow} \hat{\psi}^\dagger(\mathbf{r}\sigma) \boldsymbol{\sigma}_{\sigma\sigma'} \hat{\psi}(\mathbf{r}\sigma'), \quad (2.121)$$

where $\boldsymbol{\sigma}$ denotes the 2×2 Pauli matrices,

$$\sigma_x = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} \iff \sigma_{x, \sigma\sigma'} = \delta_{\sigma', -\sigma} \quad (2.122)$$

$$\sigma_y = \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix} \iff \sigma_{y, \sigma\sigma'} = i \text{sign}(\sigma') \delta_{\sigma', -\sigma} \quad (2.123)$$

$$\sigma_z = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} \iff \sigma_{z, \sigma\sigma'} = \text{sign}(\sigma) \delta_{\sigma', \sigma} \quad , \quad (2.124)$$

and μ_B is the Bohr magneton, $\mu_B = e\hbar/(2mc)$ ($e = |e|$). In addition to the conventional single-particle density n_0 , now a second density variable, the ground state magnetization density

$$\mathbf{m}_0(\mathbf{r}) = \langle \Psi_0 | \hat{\mathbf{m}}(\mathbf{r}) | \Psi_0 \rangle, \quad (2.125)$$

offers itself for a characterization of the ground state $|\Psi_0\rangle$ of the Hamiltonian (2.120). And indeed, one can verify the following two statements [34, 35]:

- (a) Two different non-degenerate ground states $|\Psi_0\rangle$ and $|\Psi'_0\rangle$ from the set of all ground states resulting from Hamiltonians of type (2.120) always lead to two different sets of ground state densities (n_0, \mathbf{m}_0) and (n'_0, \mathbf{m}'_0) , i.e. at least one of the four density components differs. As a conse-

⁶ Both the components of bispinors and spin quantum numbers will be characterized by either the numerical values $\pm 1/2$ or, alternatively, the symbolic equivalents \uparrow, \downarrow , depending on which notation is more convenient or clear.

In Eqs. (2.120) and (2.121) the sign of the magnetization density has been chosen so that $\hat{\mathbf{m}}$ differs from the conventional magnetization density of electrons introduced in classical electrodynamics (see e.g. [36]) by a minus sign.

quence, $|\Psi_0\rangle$ is uniquely determined by the set (n_0, \mathbf{m}_0) , i.e. is a unique functional of (n, \mathbf{m}) ,

$$|\Psi_0\rangle \xleftrightarrow[\text{one-to-one}]{\quad} (n_0, \mathbf{m}_0) \quad \implies \quad |\Psi_0\rangle = |\Psi[n_0, \mathbf{m}_0]\rangle. \quad (2.126)$$

The proof via *reductio ad absurdum* proceeds as for the purely electrostatic potential. Assume that the ground states $|\Psi_0\rangle$ and $|\Psi'_0\rangle$ corresponding to the Hamiltonians \hat{H} and \hat{H}' yield the same set (n_0, \mathbf{m}_0) . Then consider the ground state energy and use both the Ritz variational principle and the fact that the two states are non-degenerate,

$$\begin{aligned} \langle \Psi_0 | \hat{H} | \Psi_0 \rangle &< \langle \Psi'_0 | \hat{H} | \Psi'_0 \rangle \\ &= \langle \Psi'_0 | \hat{H}' | \Psi'_0 \rangle + \int d^3r \{ [v_{\text{ext}} - v'_{\text{ext}}] n_0 + [\mathbf{B}_{\text{ext}} - \mathbf{B}'_{\text{ext}}] \cdot \mathbf{m}_0 \} \end{aligned} \quad (2.127)$$

(as $|\Psi_0\rangle \neq |\Psi'_0\rangle$ and both states are non-degenerate one necessarily has $\hat{H} \neq \hat{H}'$, i.e. $(v_{\text{ext}}, \mathbf{B}_{\text{ext}}) \neq (v'_{\text{ext}}, \mathbf{B}'_{\text{ext}})$). Interchanging primed and unprimed quantities one finds

$$\langle \Psi'_0 | \hat{H}' | \Psi'_0 \rangle < \langle \Psi_0 | \hat{H} | \Psi_0 \rangle + \int d^3r \{ [v'_{\text{ext}} - v_{\text{ext}}] n_0 + [\mathbf{B}'_{\text{ext}} - \mathbf{B}_{\text{ext}}] \cdot \mathbf{m}_0 \}. \quad (2.128)$$

Addition of (2.127) and (2.128) leads to the desired contradiction.

- (b) The functional $|\Psi[n, \mathbf{m}]\rangle$ allows the definition of a ground state energy functional,

$$E[n, \mathbf{m}] = F[n, \mathbf{m}] + \int d^3r \{ v_{\text{ext}}(\mathbf{r}) n(\mathbf{r}) + \mathbf{B}_{\text{ext}}(\mathbf{r}) \cdot \mathbf{m}(\mathbf{r}) \} \quad (2.129)$$

$$F[n, \mathbf{m}] = \langle \Psi[n, \mathbf{m}] | \hat{T} + \hat{W} | \Psi[n, \mathbf{m}] \rangle, \quad (2.130)$$

which satisfies a minimum principle,

$$E[n_0, \mathbf{m}_0] < E[n, \mathbf{m}] \quad \forall (n, \mathbf{m}) \neq (n_0, \mathbf{m}_0), \quad (2.131)$$

with (n_0, \mathbf{m}_0) being the ground state densities corresponding to $(v_{\text{ext}}, \mathbf{B}_{\text{ext}})$.

The proof follows the same pattern as in the original argument by HK. Note that it is usual to call $E[n, \mathbf{m}]$ a density functional, in spite of the fact that this functional not only depends on n , but also on the magnetization density. Ignoring the issue of v -representability, one can furthermore reformulate (2.131) as a set of four coupled

variational equations,⁷

$$\left. \frac{\delta E[n, \mathbf{m}]}{\delta n(\mathbf{r})} \right|_{n=n_0, \mathbf{m}=\mathbf{m}_0} = \mu ; \quad \left. \frac{\delta E[n, \mathbf{m}]}{\delta \mathbf{m}(\mathbf{r})} \right|_{n=n_0, \mathbf{m}=\mathbf{m}_0} = \mathbf{0}, \quad (2.132)$$

with the Lagrange parameter μ ensuring the correct particle number as in (2.38).

A number of points should be noted:

1. The reader will have noticed that the existence theorem formulated for systems subject to magnetic fields is much more restrictive than the original HK theorem. In particular, nothing has been said about the relation between the ground state $|\Psi_0\rangle$ and the set of external potentials $(v_{\text{ext}}, \mathbf{B}_{\text{ext}})$. Obviously, the corresponding proof used for the original HK theorem does not apply in the present situation, as the operator $\mathbf{B}_{\text{ext}} \cdot \hat{\mathbf{m}}$ does not allow a factorization of the ground state wavefunction (which was utilized in Eq. (2.17)).

In fact, one can give a rather simple argument that two different sets of $(v_{\text{ext}}, \mathbf{B}_{\text{ext}})$ can lead to the same ground state [34, 37, 38]: whenever one has a magnetic field of the *collinear* form

$$\mathbf{B}_{\text{ext}}(\mathbf{r}) = (0, 0, B)$$

with constant B , any ground state $|\Psi_0\rangle$ of some Hamiltonian \hat{H} ,

$$\hat{H}|\Psi_0\rangle = E_0|\Psi_0\rangle,$$

which is simultaneously an eigenstate of

$$\hat{S}_z = \sum_{i=1}^N \sigma_{i,z}; \quad \hat{S}_z|\Psi_0\rangle = S_z|\Psi_0\rangle,$$

is also an eigenstate of the extended Hamiltonian $\hat{H} + \mu_B B \hat{S}_z$,

$$(\hat{H} + \mu_B B \hat{S}_z)|\Psi_0\rangle = (E_0 + \mu_B B S_z)|\Psi_0\rangle,$$

irrespective of the magnitude of B . Moreover, as long as B is sufficiently small, $|\Psi_0\rangle$ remains the ground state of the system characterized by $\hat{H} + \mu_B B \hat{S}_z$, demonstrating the non-uniqueness of the map between all ground states and the set of external potentials $(v_{\text{ext}}, \mathbf{B}_{\text{ext}})$.

However, the above example obviously relies on the fact that B is constant. Correspondingly, one can show that two pairs of spin-dependent potentials,

$$v_{\pm}(\mathbf{r}) = v_{\text{ext}}(\mathbf{r}) \pm \mu_B B_{\text{ext}}(\mathbf{r}) \quad \text{and} \quad v'_{\pm}(\mathbf{r}) = v'_{\text{ext}}(\mathbf{r}) \pm \mu_B B'_{\text{ext}}(\mathbf{r}),$$

⁷ Here and in the following the derivative with respect to a vector is to be understood as the vector which results from differentiation with respect to the components,

$$\frac{\delta E[n, \mathbf{m}]}{\delta \mathbf{m}(\mathbf{r})} = \left(\frac{\delta E[n, \mathbf{m}]}{\delta m_1(\mathbf{r})}, \frac{\delta E[n, \mathbf{m}]}{\delta m_2(\mathbf{r})}, \frac{\delta E[n, \mathbf{m}]}{\delta m_3(\mathbf{r})} \right).$$

for which v_σ differs from v'_σ by more than a σ -dependent constant (for both $\sigma = \pm$) always have different ground states [38–40].

Returning to the general case of a magnetic field \mathbf{B}_{ext} with more than one non-vanishing component, the question of uniqueness then reduces to the question whether one can find a local rotation in spin space which transforms \mathbf{B}_{ext} to the collinear form $(0, 0, B_{\text{ext}})$? The answer is no [40] (with the exception of some rather special cases [41]), so that the map between the ground state $|\Psi_0\rangle$ and the set of external potentials $(v_{\text{ext}}, \mathbf{B}_{\text{ext}})$ is invertible in the general situation.

2. Often the actual magnetic field has only one non-vanishing component,

$$\mathbf{B}_{\text{ext}}(\mathbf{r}) = (0, 0, B_{\text{ext}}(\mathbf{r})). \quad (2.133)$$

Of course, one can go through the existence theorem for a field of the form (2.133) as in the general situation. One ends up with the statement that there is a one-to-one correspondence between $|\Psi_0\rangle$ and the set $(n_0, m_{z,0})$,

$$|\Psi_0\rangle \iff (n_0, m_{z,0}) \implies |\Psi_0\rangle = |\Psi[n_0, m_{z,0}]\rangle. \quad (2.134)$$

Correspondingly, the energy becomes a functional of n and the z -component of the magnetization density, m_z .

It is standard to reformulate this functional in terms of the spin-densities,

$$\hat{n}_\sigma(\mathbf{r}) = \frac{1}{2} \sum_{i=1}^N [1 + \text{sign}(\sigma) \sigma_{z,i}] \delta^{(3)}(\mathbf{r} - \mathbf{r}_i) = \hat{\psi}^\dagger(\mathbf{r}\sigma) \hat{\psi}(\mathbf{r}\sigma) \quad (2.135)$$

$$\hat{n}(\mathbf{r}) = \sum_{\sigma=\uparrow,\downarrow} \hat{n}_\sigma(\mathbf{r}). \quad (2.136)$$

In fact, for the z -component of Eq. (2.121) one immediately obtains

$$\hat{m}_z(\mathbf{r}) = \mu_B [\hat{\psi}^\dagger(\mathbf{r}\uparrow) \hat{\psi}(\mathbf{r}\uparrow) - \hat{\psi}^\dagger(\mathbf{r}\downarrow) \hat{\psi}(\mathbf{r}\downarrow)] = \mu_B [\hat{n}_\uparrow(\mathbf{r}) - \hat{n}_\downarrow(\mathbf{r})]. \quad (2.137)$$

Thus the set $(n_\uparrow, n_\downarrow)$ is completely equivalent to (n, m_z) . All statements can equally well be formulated in terms of $(n_\uparrow, n_\downarrow)$. The most frequently used form of the spin-density functional then reads

$$E[n_\uparrow, n_\downarrow] = F[n_\uparrow, n_\downarrow] + \int d^3r \{ v_{\text{ext}}[n_\uparrow + n_\downarrow] + \mu_B B_{\text{ext}}[n_\uparrow - n_\downarrow] \} \quad (2.138)$$

$$F[n_\uparrow, n_\downarrow] = \langle \Psi[n_\uparrow, n_\downarrow] | \hat{T} + \hat{W} | \Psi[n_\uparrow, n_\downarrow] \rangle. \quad (2.139)$$

The associated variational equations rely on the fact that in the case of the reduced magnetic field (2.133) the Hamiltonian (2.120) commutes with the total particle number for given spin,

$$\hat{N}_\sigma = \int d^3r \hat{n}_\sigma(\mathbf{r}) \implies [\hat{H}, \hat{N}_\sigma] = 0 \quad (2.140)$$

(for the basic commutators involved see Appendix L). It is thus possible to fix the individual numbers N_σ of particles with spin σ , as long as the total particle number is N ,

$$N_\sigma = \langle \Psi_0 | \hat{N}_\sigma | \Psi_0 \rangle ; \quad N_\uparrow + N_\downarrow = N. \quad (2.141)$$

Each pair N_\uparrow, N_\downarrow defines one sector of Fock space for which the Ritz variational principle is separately valid, so that the DFT minimum principle also applies to each sector separately. Consequently, the variational equations have the form

$$\left. \frac{\delta E[n_\uparrow, n_\downarrow]}{\delta n_\sigma(\mathbf{r})} \right|_{n_\sigma = n_{\sigma,0}} = \mu_\sigma, \quad (2.142)$$

with the Lagrange parameters μ_σ controlling the individual particle numbers N_σ . The true ground state then corresponds to the pair of N_σ which gives the minimum energy.

3. One can finally reconsider the many-particle problem without any magnetic field. For this problem it is nevertheless legitimate, though not formally necessary, to use the spin-dependent functional

$$E[n_\uparrow, n_\downarrow] = F[n_\uparrow, n_\downarrow] + \int d^3r v_{\text{ext}}[n_\uparrow + n_\downarrow],$$

rather than the original form (2.26): the class of systems discussed in the present section also contains the more restricted class considered in the original HK theorem. In practice, Eqs. (2.138)–(2.142) with $B_{\text{ext}} = 0$ represent the standard DFT approach to spin-polarized systems, i.e. systems with non-vanishing magnetic moment.

Why is this extended description of spin-polarized systems superior to the more direct approach in terms of only the density? In principle, n_\uparrow and n_\downarrow are functionals of the complete n as long as $B_{\text{ext}} = 0$. However, their functional dependence on n is definitely complicated. Consequently, it is advantageous to resolve this unknown functional dependence by explicit use of the spin-densities via the functional (2.138). In this way, one effectively introduces an exact symmetry of the system into the energy functional.

One can go even further and apply the full magnetization density formalism (2.129)–(2.132) for the description of systems without any external magnetic field. As a matter of fact, many systems, ranging from open subshell atoms to large classes of solids, show a local variation of the direction of \mathbf{m} , i.e. a *non-collinear* magnetization density.

The most prominent example for a system with non-collinear \mathbf{m} is γ -Fe, which crystallizes in the fcc structure.⁸ When γ -Fe is synthesized as precipitates in a Cu matrix, the local magnetic moments \mathbf{M}_i of the iron atoms, i.e. the integrals over \mathbf{m} around single sites,

$$\mathbf{M}_i = \int_{\Omega_i} d^3r \mathbf{m}(\mathbf{r}),$$

⁸ γ -Fe is the standard form of iron in the temperature range between 910°C and 1390°C.

do not align ferromagnetically, as one would expect from the bcc phase of iron and other 3d elements. Rather the local moments form a spiral wave [42], referred to as *spin-spiral* or spiral *spin-density wave* (SDW),

$$\mathbf{M}_i = M \left(\cos(\mathbf{Q} \cdot \mathbf{R}_i + \phi) \sin(\theta), \sin(\mathbf{Q} \cdot \mathbf{R}_i + \phi) \sin(\theta), \cos(\theta) \right),$$

in which the direction of the \mathbf{M}_i precesses around one of the cubic axes, if one proceeds from site to site along this axis (\mathbf{R}_i denotes the position of site i). Moreover, the spin-spiral is incommensurate with the crystal lattice, i.e. its wavelength can not be expressed as a rational number times the lattice constant a of the fcc lattice. Experimentally one observes a wave vector of $\mathbf{Q} \approx (0.1, 0, 1) (2\pi/a)$ and $\theta = \pi/2$ [42], corresponding to a planar spiral wave⁹ (helical SDW).

Early DFT calculations for γ -Fe (see e.g. [44]) relied on the inclusion of non-collinearity on an intermediate level: assuming \mathbf{m} to be collinear around the individual sites, only the spin-quantization axis was allowed to vary from site to site. A spin-density functional approach allowing for this inter-atomic non-collinearity has been formulated quite early [45, 46] (for a review see [47]). More recently, however, it became clear that the variation of \mathbf{m} on the intra-atomic scale (intra-atomic non-collinearity) plays an important role¹⁰ for γ -Fe [48, 43, 49, 50]. Non-collinearity has also been observed for the ground states of α -Mn (bulk Mn at room temperature and ambient pressure—see [51] and references therein), a number of Mn and Fe compounds (see e.g. [52]), several Uranium compounds (see [47] and references therein) as well as thin Cr and Fe films (see [53–55] and references therein). Mono-layers of Mn on a tungsten surface develop a cycloidal spin-spiral, resulting from the spin-orbit interaction in a system lacking inversion symmetry [56].

Finite systems exhibit non-collinear magnetism as well: for instance, non-collinear calculations for several low-lying states of free small iron clusters show a variation of the direction and size of \mathbf{m} on the constituent atoms [57]. A simple example is the ground state of Fe_5 . In this trigonal bipyramid structure the magnetic moments in the basis of the pyramids are aligned, the moments of the two tips, however, are tilted with respect to the majority spin direction defined by the atoms of the basis. When deposited on a Cu surface, on the other hand, iron clusters seem to prefer ferromagnetic ordering [58]. However, even for clusters on a surface geometric frustration can lead to non-collinear magnetic moments in the case of Mn and Cr clusters [58], consistent with the vanishing total magnetic moments observed in experiment [59, 60].

It is obvious that use of the non-collinear formalism (2.129)–(2.132) is mandatory for systems for which the non-collinearity of \mathbf{m} is an indispensable feature of the electronic structure, as, for instance, γ -Fe. For most problems, however, the corrections resulting from non-collinearity are rather small, in particular for open-subshell atoms [61] (compare also [62, 63]). For these systems the application of the more complicated calculational scheme resulting from Eqs. (2.129)–(2.132) is usually too high a price to be paid for the more accurate representation of \mathbf{m} . Spin-density functional theory in the form (2.138)–(2.142) represents the standard approach to magnetic systems for this reason. It seems worthwhile to emphasize that this approach rigorously covers antiferromagnetic ordering of

⁹ The value $\theta = \pi/2$ follows rigorously from symmetry constraints as long as spin-orbit coupling is neglected [43].

¹⁰ At the same time even the early calculations revealed a very high sensitivity of the magnetic structure of the ground state to the equilibrium volume.

magnetic moments, including situations as the linearly polarized spin-density wave observed for the ground state¹¹ of bulk Cr.

2.6 Current Density Functional Theory

The Hamiltonian (2.120) accounts for the dominant coupling mechanism between magnetic fields and electrons, at least for low electron velocities. It neglects, however, the Lorentz force exerted on the electrons by the magnetic field. This effect is included in *current density functional theory* (CDFT) and its extension, *current spin density functional theory* (CSDFT) [68–71]. The starting point for the discussion of CSDFT is the Pauli Hamiltonian,

$$\begin{aligned} \hat{H} = & \frac{1}{2m} \sum_{\sigma=\uparrow,\downarrow} \int d^3r \hat{\psi}^\dagger(\mathbf{r}\sigma) \left[-i\hbar\nabla + \frac{e}{c}\mathbf{A}_{\text{ext}}(\mathbf{r}) \right]^2 \hat{\psi}(\mathbf{r}\sigma) \\ & + \int d^3r \left[v_{\text{ext}}(\mathbf{r})\hat{n}(\mathbf{r}) + \mathbf{B}_{\text{ext}}(\mathbf{r}) \cdot \hat{\mathbf{m}}(\mathbf{r}) \right] + \hat{W}, \end{aligned} \quad (2.143)$$

where the magnetization density $\hat{\mathbf{m}}$ is defined as in Eq. (2.121) and \mathbf{A}_{ext} denotes the vector potential which generates the magnetic field,

$$\mathbf{B}_{\text{ext}}(\mathbf{r}) = \nabla \times \mathbf{A}_{\text{ext}}(\mathbf{r}). \quad (2.144)$$

The Hamiltonian (2.143) can be systematically derived from the fully relativistic Hamiltonian of Dirac theory,¹² either by an expansion in powers of $1/c$ or, alternatively, by a low order Foldy-Wouthuysen transformation.

The formulation of a density functional approach for the Hamiltonian (2.143) has to be preceded by some remarks on the issue of gauge transformations. The magnetic field (2.144) does not change under the gauge transformation¹³

¹¹ The ground state of bulk Cr (which crystallizes in the bcc structure) exhibits a static SDW along the (100) direction of the conventional cubic unit cell (for an overview see [64]): while the directions of the local magnetic moments on nearest neighbor sites (corner and body-center of the bcc structure) are antiparallel (corresponding to an anti-ferromagnetic ordering), the amplitudes μ_i of these local moments are modulated in an almost sinusoidal form, $\mu_i = M_1 \sin(\mathbf{Q} \cdot \mathbf{R}_i) + \dots$ (with $M_1 = 0.62 \mu_B$). Moreover, the wavelength of the SDW is incommensurate with the crystal lattice: the dominant wave vector in the SDW is found to be $|\mathbf{Q}| = 0.952 \frac{2\pi}{a}$, the period of the complete spin-density pattern is as long as $20.83 a$. A longitudinal SDW is observed below a spin-flip temperature of 123 K, a transverse SDW between this and the Néel temperature of 311 K. However, in both cases linear polarization is energetically favored over some helical SDW, so that \mathbf{m} remains collinear (for corresponding SDFT calculations see [65–67]).

¹² More precisely speaking, the Hamiltonian (2.143) is obtained from quantum electrodynamics, i.e. from the QED Hamiltonian (8.39). In the present context, however, only an expansion of the relativistic kinetic energy operator is relevant.

¹³ Quite generally, the electromagnetic fields (1.10), (1.11) do not change under the combined gauge transformation

$$\mathbf{A}'_{\text{ext}}(\mathbf{r}) = \mathbf{A}_{\text{ext}}(\mathbf{r}) - \nabla\lambda(\mathbf{r}). \quad (2.148)$$

On the other hand, the Hamiltonian (2.143), which depends on the vector potential itself, is not invariant under the transformation (2.148) (unlike the reduced Hamiltonian (2.120)). The same statement necessarily also applies to the ground state $|\Psi_0\rangle$ corresponding to (2.143),

$$\hat{H}|\Psi_0\rangle = E_0|\Psi_0\rangle. \quad (2.149)$$

However, it is easy to show that the transformation (2.148) simply leads to a phase transformation of the corresponding ground state: if the wavefunction

$$\Psi_0(\mathbf{r}_1\sigma_1, \dots, \mathbf{r}_N\sigma_N) \equiv (\mathbf{r}_1\sigma_1, \dots, \mathbf{r}_N\sigma_N|\Psi_0)$$

is a solution of (2.149) for the potential \mathbf{A}_{ext} , the gauge transformed wavefunction

$$\Psi'_0(\mathbf{r}_1\sigma_1, \dots, \mathbf{r}_N\sigma_N) = \exp\left[\frac{ie}{\hbar c} \sum_{k=1}^N \lambda(\mathbf{r}_k)\right] \Psi_0(\mathbf{r}_1\sigma_1, \dots, \mathbf{r}_N\sigma_N) \quad (2.150)$$

is a solution of (2.149) for the potential \mathbf{A}'_{ext} obtained by the gauge transformation (2.148)—this can be verified by insertion into (2.149) in first quantized form. All pairs $(\mathbf{A}_{\text{ext}}, \Psi_0)$ which differ by no more than the combined transformation (2.148), (2.150) are physically equivalent.¹⁴ As a result they lead to the same ground state energy E_0 , the same ground state density n_0 and the same ground state magnetization density \mathbf{m}_0 ,

$$E'_0 = E_0 \quad (2.152)$$

$$v'_{\text{ext}}(\mathbf{r}t) = v_{\text{ext}}(\mathbf{r}t) - \frac{e}{c} \frac{\partial}{\partial t} \Lambda(\mathbf{r}t) \quad (2.145)$$

$$\mathbf{A}'_{\text{ext}}(\mathbf{r}t) = \mathbf{A}_{\text{ext}}(\mathbf{r}t) - \nabla\Lambda(\mathbf{r}t) \quad (2.146)$$

of the set of potentials. As the present discussion is restricted to static external fields, the class of admissible gauge transformations is given by

$$\Lambda(\mathbf{r}t) = \lambda_0 t + \lambda(\mathbf{r}). \quad (2.147)$$

The first term corresponds to the addition of the constant λ_0 to the external potential v_{ext} . If only this potential is present, $\Lambda(\mathbf{r}t) = \lambda_0 t$ is the only legitimate gauge transformation. One can therefore identify the class of v_{ext} which differ by more than a constant with the class of potentials which differ by more than a (static) gauge transformation.

¹⁴ Note that this equivalence also manifests itself as the invariance of the Hamiltonian (2.143) under the simultaneous transformation of the vector potential by (2.148) and of the field operator by

$$\hat{\psi}'(\mathbf{r}\sigma) = e^{ie\lambda(\mathbf{r})/(\hbar c)} \hat{\psi}(\mathbf{r}\sigma). \quad (2.151)$$

In fact, this invariance of \hat{H} is sometimes even identified with the actual gauge invariance of the corresponding expectation value $\langle\Psi_0|\hat{H}|\Psi_0\rangle$. The same statements apply to the complete ground state current (2.156). Similarly, the gauge dependence of the paramagnetic current is reflected by the lack of invariance of \hat{j}_p under the combined transformations (2.148) and (2.151).

$$n'_0(\mathbf{r}) = n_0(\mathbf{r}) \quad (2.153)$$

$$\mathbf{m}'_0(\mathbf{r}) = \mathbf{m}_0(\mathbf{r}) . \quad (2.154)$$

As required, gauge invariance is also observed for the physical ground state current \mathbf{j}_0 ,

$$\mathbf{j}'_0(\mathbf{r}) = \mathbf{j}_0(\mathbf{r}) = \langle \Psi_0 | \hat{\mathbf{j}}(\mathbf{r}) | \Psi_0 \rangle , \quad (2.155)$$

which, in the case of the Hamiltonian (2.143), is obtained from the operator¹⁵

$$\hat{\mathbf{j}}(\mathbf{r}) = \hat{\mathbf{j}}_p(\mathbf{r}) + \frac{c}{e} \nabla \times \mathbf{m}(\mathbf{r}) + \frac{e}{mc} \mathbf{A}_{\text{ext}}(\mathbf{r}) \hat{n}(\mathbf{r}) . \quad (2.156)$$

Here $\hat{\mathbf{j}}_p$ denotes the (canonical) paramagnetic current density,¹⁶

$$\hat{\mathbf{j}}_p(\mathbf{r}) = \frac{-i\hbar}{2m} \sum_{i=1}^N \left[\nabla_i \delta^{(3)}(\mathbf{r} - \mathbf{r}_i) + \delta^{(3)}(\mathbf{r} - \mathbf{r}_i) \nabla_i \right] \quad (2.157)$$

$$= -\frac{i\hbar}{2m} \sum_{\sigma=\uparrow,\downarrow} \left[\hat{\psi}^\dagger(\mathbf{r}\sigma) (\nabla \hat{\psi}(\mathbf{r}\sigma)) - (\nabla \hat{\psi}^\dagger(\mathbf{r}\sigma)) \hat{\psi}(\mathbf{r}\sigma) \right] . \quad (2.158)$$

If one wants to set up a DFT scheme for the Hamiltonian (2.143), the first issue to be addressed is an appropriate choice of the basic variables. As usual, the coupling between densities and external potentials in the Hamiltonian allows the identification of the basic DFT variables. However, using (2.156), the Hamiltonian (2.143) can be rewritten in two alternative ways,

$$\hat{H} = \hat{T} + \hat{W} + \int d^3r \left\{ \frac{e}{c} \mathbf{A}_{\text{ext}} \cdot \hat{\mathbf{j}} + \left[v_{\text{ext}} - \frac{e^2}{2mc^2} \mathbf{A}_{\text{ext}}^2 \right] \hat{n} \right\} \quad (2.159)$$

$$= \hat{T} + \hat{W} + \int d^3r \left\{ \frac{e}{c} \mathbf{A}_{\text{ext}} \cdot \left[\hat{\mathbf{j}}_p + \frac{c}{e} \nabla \times \hat{\mathbf{m}} \right] + \left[v_{\text{ext}} + \frac{e^2}{2mc^2} \mathbf{A}_{\text{ext}}^2 \right] \hat{n} \right\} , \quad (2.160)$$

where \hat{T} is the standard kinetic energy operator (2.2). The form (2.159) suggests to employ the density plus the complete physical current as basic variables of a DFT scheme. However, the discussion of gauge transformations has shown that the set n_0, \mathbf{j}_0 does not determine the ground state uniquely. One is thus bound to base CSDFT on the combination of the density operator \hat{n} with the current operator [72, 73]

¹⁵ The operator (2.156) can either be derived by a Gordon decomposition of the fully relativistic current (compare Sect. 8.7), followed by the limit $c \rightarrow \infty$. Alternatively, $\hat{\mathbf{j}}$ can be identified by an analysis of the time-dependent Schrödinger equation obtained from the Hamiltonian (2.143) as the current for which a continuity equation holds.

¹⁶ For the transition from first to second quantized form note that

$$\langle \mathbf{r}' \sigma' | \hat{\mathbf{j}}_p(\mathbf{r}) | \mathbf{r}'' \sigma'' \rangle = \frac{-i\hbar}{2m} \delta_{\sigma' \sigma''} \delta^{(3)}(\mathbf{r}' - \mathbf{r}'') \left[\nabla'' \delta^{(3)}(\mathbf{r} - \mathbf{r}'') + \delta^{(3)}(\mathbf{r} - \mathbf{r}'') \nabla'' \right] .$$

$$\hat{\mathbf{j}}_{\mathbf{g}}(\mathbf{r}) = \hat{\mathbf{j}}_{\mathbf{p}}(\mathbf{r}) + \frac{c}{e} \nabla \times \hat{\mathbf{m}}(\mathbf{r}), \quad (2.161)$$

whose ground state expectation value

$$\mathbf{j}_{\mathbf{g},0}(\mathbf{r}) = \langle \Psi_0 | \hat{\mathbf{j}}_{\mathbf{g}}(\mathbf{r}) | \Psi_0 \rangle \quad (2.162)$$

is as gauge-dependent as the ground state itself: under the gauge transformation (2.150) the ground state current $\mathbf{j}_{\mathbf{g},0}$ transforms just as the paramagnetic current,

$$\mathbf{j}'_{\mathbf{p},0}(\mathbf{r}) = \mathbf{j}_{\mathbf{p},0}(\mathbf{r}) + \frac{e}{mc} n(\mathbf{r}) \nabla \lambda(\mathbf{r}), \quad (2.163)$$

since the magnetization density is gauge invariant, Eq. (2.154).

In the second step one has to prove an existence theorem for these variables. The core of the proof of the HK-theorem is the strict inequality (2.20). In order to derive an equivalent inequality for the Hamiltonian (2.160), one considers two different non-degenerate ground states $|\Psi_0\rangle$ and $|\Psi'_0\rangle$ with associated sets of potentials $v_{\text{ext}}, \mathbf{A}_{\text{ext}}$ and $v'_{\text{ext}}, \mathbf{A}'_{\text{ext}}$ (the sets $v_{\text{ext}}, \mathbf{A}_{\text{ext}}$ and $v'_{\text{ext}}, \mathbf{A}'_{\text{ext}}$ also differ, since $|\Psi_0\rangle$ and $|\Psi'_0\rangle$ are non-degenerate). Now assume that $|\Psi_0\rangle$ and $|\Psi'_0\rangle$ lead to the same ground state density n_0 and current

$$\mathbf{j}_{\mathbf{g},0}(\mathbf{r}) = \langle \Psi_0 | \hat{\mathbf{j}}_{\mathbf{g}}(\mathbf{r}) | \Psi_0 \rangle = \langle \Psi'_0 | \hat{\mathbf{j}}_{\mathbf{g}}(\mathbf{r}) | \Psi'_0 \rangle. \quad (2.164)$$

The expectation value of the Hamiltonian (2.160) with respect to the ground state $|\Psi'_0\rangle$ corresponding to $v'_{\text{ext}}, \mathbf{A}'_{\text{ext}}$ can then be expressed as

$$\begin{aligned} \langle \Psi'_0 | \hat{H} | \Psi'_0 \rangle &= \langle \Psi'_0 | \hat{H}' | \Psi'_0 \rangle + \int d^3r \left[v_{\text{ext}} - v'_{\text{ext}} + \frac{e^2}{2mc^2} (\mathbf{A}_{\text{ext}}^2 - \mathbf{A}'_{\text{ext}}{}^2) \right] n_0 \\ &\quad + \frac{e}{c} \int d^3r [\mathbf{A}_{\text{ext}} - \mathbf{A}'_{\text{ext}}] \cdot \mathbf{j}_{\mathbf{g},0}, \end{aligned} \quad (2.165)$$

where \hat{H}' is the Hamiltonian (2.160) with primed potentials. If one could now state that the unprimed ground state energy $\langle \Psi_0 | \hat{H} | \Psi_0 \rangle$ is strictly lower than $\langle \Psi'_0 | \hat{H} | \Psi'_0 \rangle$,

$$E_0 = \langle \Psi_0 | \hat{H} | \Psi_0 \rangle < \langle \Psi'_0 | \hat{H} | \Psi'_0 \rangle \quad \forall \quad |\Psi'_0\rangle \neq |\Psi_0\rangle, \quad (2.166)$$

the desired inequality of type (2.20) would have been found,

$$\begin{aligned} E_0 &< E'_0 + \int d^3r \left[v_{\text{ext}} - v'_{\text{ext}} + \frac{e^2}{2mc^2} (\mathbf{A}_{\text{ext}}^2 - \mathbf{A}'_{\text{ext}}{}^2) \right] n_0 \\ &\quad + \frac{e}{c} \int d^3r [\mathbf{A}_{\text{ext}} - \mathbf{A}'_{\text{ext}}] \cdot \mathbf{j}_{\mathbf{g},0}. \end{aligned} \quad (2.167)$$

However, $|\Psi_0\rangle$ and $|\Psi'_0\rangle$ can be related by a gauge transformation and the actual ground state energies associated with these states are identical, Eq. (2.152). This raises the question whether the strict inequality (2.166), i.e. the Ritz principle, still holds if $|\Psi'_0\rangle$ differs from $|\Psi_0\rangle$ only by the phase transformation (2.150). Let us con-

vince ourselves that this is indeed the case. If $|\Psi'_0\rangle$ and $|\Psi_0\rangle$ are related by (2.150), the difference between $\langle\Psi'_0|\hat{H}|\Psi'_0\rangle$ and the ground state energy is given by

$$\begin{aligned} & \langle\Psi'_0|\hat{H}|\Psi'_0\rangle - \langle\Psi_0|\hat{H}|\Psi_0\rangle \\ &= \frac{1}{2m} \sum_{\sigma_1, \dots, \sigma_N} \int d^3r_1 \dots d^3r_N \Psi_0^*(\mathbf{r}_1\sigma_1, \dots, \mathbf{r}_N\sigma_N) \\ & \quad \times \sum_{k=1}^N \left[e^{-\frac{ie}{\hbar c}\lambda(\mathbf{r}_k)} \left(-i\hbar\nabla_k + \frac{e}{c}\mathbf{A}_{\text{ext}}(\mathbf{r}_k) \right)^2 e^{\frac{ie}{\hbar c}\lambda(\mathbf{r}_k)} - \left(-i\hbar\nabla_k + \frac{e}{c}\mathbf{A}_{\text{ext}}(\mathbf{r}_k) \right)^2 \right] \\ & \quad \times \Psi_0(\mathbf{r}_1\sigma_1, \dots, \mathbf{r}_N\sigma_N), \end{aligned}$$

which is easily evaluated to

$$\begin{aligned} & \langle\Psi'_0|\hat{H}|\Psi'_0\rangle - \langle\Psi_0|\hat{H}|\Psi_0\rangle \\ &= \frac{1}{2m} \sum_{\sigma_1, \dots, \sigma_N} \int d^3r_1 \dots d^3r_N \Psi_0^*(\mathbf{r}_1\sigma_1, \dots, \mathbf{r}_N\sigma_N) \\ & \quad \times \sum_{k=1}^N \left[2\frac{e}{c} [\nabla_k\lambda(\mathbf{r}_k)] \cdot \left(-i\hbar\nabla_k + \frac{e}{c}\mathbf{A}_{\text{ext}}(\mathbf{r}_k) \right) - i\hbar\frac{e}{c} [\nabla_k^2\lambda(\mathbf{r}_k)] + \left(\frac{e}{c}\nabla_k\lambda(\mathbf{r}_k) \right)^2 \right] \\ & \quad \times \Psi_0(\mathbf{r}_1\sigma_1, \dots, \mathbf{r}_N\sigma_N). \end{aligned}$$

After partial integration of half of the first term in the square brackets one can rewrite this expression in terms of the paramagnetic current (2.158),

$$\begin{aligned} & \langle\Psi'_0|\hat{H}|\Psi'_0\rangle - \langle\Psi_0|\hat{H}|\Psi_0\rangle \\ &= \int d^3r \langle\Psi_0| \left[\frac{e}{c} [\nabla\lambda(\mathbf{r})] \cdot \left(\hat{\mathbf{j}}_p(\mathbf{r}) + \frac{e}{mc}\mathbf{A}_{\text{ext}}(\mathbf{r})\hat{n}(\mathbf{r}) \right) + \left(\frac{e}{c}\nabla\lambda(\mathbf{r}) \right)^2 \hat{n}(\mathbf{r}) \right] |\Psi_0\rangle. \end{aligned}$$

One can now use Eq. (2.156) to replace $\hat{\mathbf{j}}_p$ by the physical current,

$$\langle\Psi'_0|\hat{H}|\Psi'_0\rangle - \langle\Psi_0|\hat{H}|\Psi_0\rangle = \int d^3r \left[\frac{e}{c}(\nabla\lambda) \cdot \left(\mathbf{j}_0 - \frac{c}{e}\nabla \times \mathbf{m}_0 \right) + \left(\frac{e}{c}\nabla\lambda \right)^2 n_0 \right].$$

Finally, use of current conservation and Gauss' theorem leads to

$$\langle\Psi'_0|\hat{H}|\Psi'_0\rangle - \langle\Psi_0|\hat{H}|\Psi_0\rangle = \int d^3r \left(\frac{e}{c}\nabla\lambda(\mathbf{r}) \right)^2 n_0(\mathbf{r}) > 0. \quad (2.168)$$

This confirms the strict inequality (2.166) and thus Eq. (2.167) (provided that λ is not a simple constant and does not vanish wherever n_0 is non-zero).

The inequality (2.167) can then be used in the standard fashion (combination with the same relation with primed and unprimed quantities interchanged) to derive a contradiction of the type (2.22).

- (a) One concludes that there exists a one-to-one correspondence between the set of ground states and the set of densities $(n_0, \mathbf{j}_{g,0})$ [68],

$$|\Psi_0\rangle \iff \{n_0(\mathbf{r}), \mathbf{j}_{g,0}(\mathbf{r})\}. \quad (2.169)$$

This correspondence establishes the existence of a unique functional $|\Psi[n, \mathbf{j}_g]\rangle$, which, by insertion of the actual $(n_0, \mathbf{j}_{g,0})$, reproduces the ground state of the system, $|\Psi_0\rangle = |\Psi[n_0, \mathbf{j}_{g,0}]\rangle$.

An extended variant of CSDFT is obtained, if one gives up the relation (2.144) between \mathbf{B}_{ext} and \mathbf{A}_{ext} and considers these two fields as independent (which is legitimate from a mathematical point of view—for an even more general form of CSDFT see [68]). The Hamiltonian then contains three independent coupling terms,

$$\begin{aligned} \hat{H} = & \hat{T} + \hat{W} + \frac{e}{c} \int d^3r \hat{\mathbf{j}}_p(\mathbf{r}) \cdot \mathbf{A}_{\text{ext}}(\mathbf{r}) + \int d^3r \mathbf{B}_{\text{ext}}(\mathbf{r}) \cdot \hat{\mathbf{m}}(\mathbf{r}) \\ & + \int d^3r \left[v_{\text{ext}}(\mathbf{r}) + \frac{e^2}{2mc^2} \mathbf{A}_{\text{ext}}^2(\mathbf{r}) \right] \hat{n}(\mathbf{r}). \end{aligned} \quad (2.170)$$

In this case one finds (by the standard argument) an extended one-to-one correspondence [68],

$$|\Psi_0\rangle \iff \{n_0(\mathbf{r}), \mathbf{j}_{p,0}(\mathbf{r}), \mathbf{m}_0(\mathbf{r})\}, \quad (2.171)$$

i.e. a ground state functional of the form $|\Psi[n_0, \mathbf{j}_{p,0}, \mathbf{m}_0]\rangle$. This approach is particularly legitimate if the external magnetic field vanishes anyway, $\mathbf{B}_{\text{ext}} = \mathbf{A}_{\text{ext}} = \mathbf{0}$. The use of $\mathbf{j}_{p,0}$ and \mathbf{m}_0 as independent variables could potentially introduce additional flexibility into the representation of the ground state, compared to the reduced form (2.169). This point is further investigated in the context of the KS equations of CSDFT in Sect. 3.7.

If one neglects the coupling between \mathbf{m} and \mathbf{B}_{ext} completely, one arrives at the existence theorem of current density functional theory (CDFT) [74]: the ground state $|\Psi_0\rangle$ of a system governed by the Hamiltonian (2.170) with $\mathbf{B}_{\text{ext}} = \mathbf{0}$ is uniquely determined by the ground state density and the paramagnetic current density,

$$|\Psi_0\rangle \iff \{n_0(\mathbf{r}), \mathbf{j}_{p,0}(\mathbf{r})\}, \quad (2.172)$$

so that it can be written as a functional of these quantities, $|\Psi_0\rangle = |\Psi[n_0, \mathbf{j}_{p,0}]\rangle$.

Either of the correspondences (2.169), (2.171) and (2.172) allows a representation of the ground state expectation value of any operator \hat{O} as a functional of the corresponding independent combination of variables.¹⁷

¹⁷ For a constrained search formulation of CDFT see [75].

- (b) Restricting the explicit discussion to CSDFT in the form (2.169), one has

$$O[n, \mathbf{j}_g] = \langle \Psi[n, \mathbf{j}_g] | \hat{O} | \Psi[n, \mathbf{j}_g] \rangle . \quad (2.173)$$

In particular, one obtains for the ground state energy

$$\begin{aligned} E[n, \mathbf{j}_g] &= F[n, \mathbf{j}_g] + \frac{e}{c} \int d^3r \mathbf{j}_g(\mathbf{r}) \cdot \mathbf{A}_{\text{ext}}(\mathbf{r}) \\ &\quad + \int d^3r \left[v_{\text{ext}}(\mathbf{r}) + \frac{e^2}{2mc^2} \mathbf{A}_{\text{ext}}^2(\mathbf{r}) \right] n(\mathbf{r}) \end{aligned} \quad (2.174)$$

$$F[n, \mathbf{j}_g] = \langle \Psi[n, \mathbf{j}_g] | \hat{T} + \hat{W} | \Psi[n, \mathbf{j}_g] \rangle . \quad (2.175)$$

The basic variational principle of CSDFT then follows, as usual, from Ritz's principle. It states that the functional (2.174) has a minimum for the true current and density distributions $n_0, \mathbf{j}_{g,0}$ corresponding to the given external fields,

$$E[n_0, \mathbf{j}_{g,0}] < E[n, \mathbf{j}_g] \quad \forall (n, \mathbf{j}_g) \neq (n_0, \mathbf{j}_{g,0}) . \quad (2.176)$$

The resulting variational equations,

$$\left. \frac{\delta E[n, \mathbf{j}_g]}{\delta n(\mathbf{r})} \right|_{n_0, \mathbf{j}_{g,0}} = 0 \quad (2.177)$$

$$\left. \frac{\delta E[n, \mathbf{j}_g]}{\delta \mathbf{j}_g(\mathbf{r})} \right|_{n_0, \mathbf{j}_{g,0}} = \mathbf{0} , \quad (2.178)$$

have to be solved under the constraint of particle number conservation,

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

and a constraint expressing the (static) continuity equation for the physical current,

$$\nabla \cdot \mathbf{j}(\mathbf{r}) = 0 , \quad (2.179)$$

which may be resolved as

$$\nabla \cdot \mathbf{j}_p(\mathbf{r}) = -\frac{e}{mc} \nabla \cdot [\mathbf{A}_{\text{ext}}(\mathbf{r}) n(\mathbf{r})] . \quad (2.180)$$

As in the case of SDFT, the existence theorems of C(S)DFT only involve the relation between the current and density variables and the ground state. No statement is made concerning a possible unique correspondence between the external potentials and the ground state. The reason for this restriction is the same as for SDFT: one

can give explicit counterexamples which demonstrate that one can find more than one set of potentials which yield a given ground state [76]. In fact, two different types of counterexamples are available, an extension of the symmetry argument of Sect. 2.5 (which may be characterized as *systematic non-uniqueness*) and a second class (referred to as *accidental non-uniqueness*).

Let us first consider the symmetry-related counterexample for the case of CDFT, i.e. ignoring the spin degree of freedom for simplicity. Assume that $|\Psi_0\rangle$ is the ground state corresponding to the CDFT Hamiltonian

$$\hat{H} = \hat{T} + \hat{W} + \int d^3r \left\{ \hat{n}(\mathbf{r}) \left[v_{\text{ext}}(\mathbf{r}) + \frac{e^2}{2mc^2} \mathbf{A}_{\text{ext}}^2(\mathbf{r}) \right] + \frac{e}{c} \hat{\mathbf{j}}_p(\mathbf{r}) \cdot \mathbf{A}_{\text{ext}}(\mathbf{r}) \right\} \quad (2.181)$$

$$\hat{H} |\Psi_0\rangle = E_0 |\Psi_0\rangle . \quad (2.182)$$

The question then is: can $|\Psi_0\rangle$ also be the ground state of a CDFT Hamiltonian in which v_{ext} and \mathbf{A}_{ext} are replaced by two different potentials

$$v'_{\text{ext}} = v_{\text{ext}} + \Delta v_{\text{ext}} \quad (2.183)$$

$$\mathbf{A}'_{\text{ext}} = \mathbf{A}_{\text{ext}} + \Delta \mathbf{A}_{\text{ext}} . \quad (2.184)$$

In other words: can one find Δv_{ext} and $\Delta \mathbf{A}_{\text{ext}}$, so that

$$\Delta \hat{H} |\Psi_0\rangle = \Delta E_0 |\Psi_0\rangle , \quad (2.185)$$

with $\Delta \hat{H}$ given by

$$\Delta \hat{H} = \int d^3r \left\{ \hat{n} \left[\Delta v_{\text{ext}} + \frac{e^2}{2mc^2} (\Delta \mathbf{A}_{\text{ext}}^2 + 2\Delta \mathbf{A}_{\text{ext}} \cdot \mathbf{A}_{\text{ext}}) \right] + \frac{e}{c} \hat{\mathbf{j}}_p \cdot \Delta \mathbf{A}_{\text{ext}} \right\} ? \quad (2.186)$$

For Eq. (2.185) to hold, the operator $\Delta \hat{H}$ has to be a constant of motion, i.e. has to commute with the Hamiltonian (2.181). An explicit example for such a constant of motion is the angular momentum¹⁸ [76]

$$\hat{L}_z = m \int d^3r (\mathbf{e}_z \times \mathbf{r}) \cdot \hat{\mathbf{j}}_p(\mathbf{r}) \quad (2.187)$$

in the case of systems which are invariant under rotations about the z -axis. However, choosing

¹⁸ In second quantization the angular momentum operator is given by

$$\hat{\mathbf{L}} = -i\hbar \sum_{\sigma=\uparrow,\downarrow} \int d^3r [\hat{\psi}^\dagger(\mathbf{r}\sigma)(\mathbf{r} \times \nabla) \hat{\psi}(\mathbf{r}\sigma)] ,$$

which may be expressed in terms of the paramagnetic current after suitable partial integration,

$$\hat{\mathbf{L}} = m \int d^3r [\mathbf{r} \times \hat{\mathbf{j}}_p(\mathbf{r})] .$$

$$\Delta \mathbf{A}_{\text{ext}}(\mathbf{r}) = \frac{\Delta B}{2} (\mathbf{e}_z \times \mathbf{r}) \quad (2.188)$$

$$\Delta v_{\text{ext}}(\mathbf{r}) = -\frac{e^2}{2mc^2} (\Delta \mathbf{A}_{\text{ext}}^2(\mathbf{r}) + 2\Delta \mathbf{A}_{\text{ext}}(\mathbf{r}) \cdot \mathbf{A}_{\text{ext}}(\mathbf{r})) , \quad (2.189)$$

with constant ΔB , the operator (2.186) becomes a simple multiple of \hat{L}_z , so that Eq. (2.185) is satisfied for all Hamiltonians for which $[\hat{H}, \hat{L}_z] = 0$. Thus, as long as ΔE_0 is smaller than the energy gap between the ground and first excited state, $|\Psi_0\rangle$ remains the ground state corresponding to the primed potentials. The size of ΔE_0 , however, is easily controlled by the size of ΔB . Consequently, one finds a complete set of potentials which lead to the same ground state.

As an example for an accidental non-uniqueness consider a single particle within CDFT, again ignoring spin. Assume that the non-degenerate ground state orbital $\phi_0(\mathbf{r})$ satisfies the Schrödinger equation

$$\left\{ \frac{1}{2m} \left[-i\hbar \nabla + \frac{e}{c} \mathbf{A}_{\text{ext}}(\mathbf{r}) \right]^2 + v_{\text{ext}}(\mathbf{r}) \right\} \phi_0(\mathbf{r}) = \varepsilon_0 \phi_0(\mathbf{r}) \quad (2.190)$$

for

$$\mathbf{A}_{\text{ext}} = \mathbf{0}$$

(this example includes all vector potentials which differ from $\mathbf{0}$ by a gauge transformation, $\mathbf{A}_{\text{ext}} = -\nabla \lambda$). The (nodeless) orbital $\phi_0(\mathbf{r})$ can then be chosen real,

$$\phi_0^*(\mathbf{r}) = \phi_0(\mathbf{r}) . \quad (2.191)$$

Now one again asks the question whether one can find some further set of potentials $v'_{\text{ext}}, \mathbf{A}'_{\text{ext}}$ for which $\phi_0(\mathbf{r})$ remains the ground state? For this to be the case, Eq. (2.190) must also be valid with the unprimed potentials replaced by the primed ones. It is straightforward to show, however, that the Schrödinger equation with the potentials

$$\mathbf{A}'_{\text{ext}}(\mathbf{r}) = \frac{\nabla \times \mathbf{C}(\mathbf{r})}{\phi_0(\mathbf{r})^2} \quad (2.192)$$

$$v'_{\text{ext}}(\mathbf{r}) = v_{\text{ext}}(\mathbf{r}) - \frac{e^2}{2mc^2} (\mathbf{A}'_{\text{ext}}(\mathbf{r}))^2 \quad (2.193)$$

is satisfied by $\phi_0(\mathbf{r})$ for arbitrary $\mathbf{C}(\mathbf{r})$, provided that Eq. (2.190) holds for the unprimed potentials [76]. In fact, insertion of (2.193) into the Schrödinger equation (with primed potentials) and use of (2.190) for the unprimed potentials yields the condition

$$\left[(\nabla \cdot \mathbf{A}'_{\text{ext}}(\mathbf{r})) + 2\mathbf{A}'_{\text{ext}}(\mathbf{r}) \cdot \nabla \right] \phi_0(\mathbf{r}) = 0 , \quad (2.194)$$

which is trivially satisfied by the form (2.192). For given v_{ext} and thus ϕ_0 one has found an infinite number of potentials $v'_{\text{ext}}, \mathbf{A}'_{\text{ext}}$, for which ϕ_0 is an eigenstate. Again, if the magnitude of $\mathbf{C}(\mathbf{r})$ is chosen sufficiently small, ϕ_0 remains the ground state.

In order to provide some physical background of this accidental non-uniqueness let us fix the gauge of the potential (2.192): among all physically admissible vector potentials giving a particular magnetic field $\mathbf{B}(\mathbf{r}) = \nabla \times \mathbf{A}'_{\text{ext}}(\mathbf{r})$ one can always choose to work with the one which satisfies Coulomb gauge,

$$\nabla \cdot \mathbf{A}'_{\text{ext}}(\mathbf{r}) = 0. \quad (2.195)$$

All other potentials which give the same $\mathbf{B}(\mathbf{r})$ can only differ from this \mathbf{A}'_{ext} by gauge transformations. Restricting the set of potentials (2.192) to those which satisfy Eq. (2.195) requires

$$[\nabla \phi_0(\mathbf{r})] \cdot [\nabla \times \mathbf{C}(\mathbf{r})] = 0 \quad (2.196)$$

for all \mathbf{r} , so that the potentials of the type (2.192) ultimately also correspond to a specific symmetry of the ground state.

A final remark on C(S)DFT addresses the limit $\mathbf{A}_{\text{ext}} = \mathbf{0}$. In this limit all variants of C(S)DFT reduce to standard DFT, as all spin- and spin-current-densities are now unique functionals of n . For instance, one has for the approach (2.171),

$$\mathbf{j}_p(\mathbf{r}) = \mathbf{j}_p[n](\mathbf{r}); \quad \mathbf{m}(\mathbf{r}) = \mathbf{m}[n](\mathbf{r}) \quad \implies \quad E[n, \mathbf{j}_p, \mathbf{m}] = \tilde{E}[n].$$

In analogy to the improved description of spin-dependent systems with $\mathbf{B}_{\text{ext}} = \mathbf{0}$ by $E[n_{\uparrow}, n_{\downarrow}]$, there might be some advantage in retaining the more flexible form $E[n, \mathbf{j}_p, \mathbf{m}]$ also for $\mathbf{A}_{\text{ext}} = \mathbf{0}$. Similar statements apply to all other variants of C(S)DFT.

2.7 Excited States: Part 1

Let us return to the Hamiltonian (2.1) for which the original HK-theorem is valid. The ground state density n_0 does not only determine the ground state $|\Psi_0\rangle$ uniquely, but also all excited states $|\Psi_i\rangle$ ($i > 0$). The reason for this, at first glance surprising, statement is the one-to-one correspondence of n_0 and the external potential v_{ext} . Once v_{ext} is known, all excited states are unambiguously determined by solution of the Schrödinger equation,

$$\begin{array}{ccc} n_0 & \xRightarrow{\quad} & v_{\text{ext}} \xRightarrow{\quad} |\Psi_i\rangle; \quad i = 0, 1, \dots, \infty. \\ \uparrow & & \uparrow \\ \text{HK theorem} & & \text{solution of the Schrödinger equation} \end{array} \quad (2.197)$$

All matrix elements of excited states $|\Psi_i\rangle$ can, in view of this correspondence, be regarded as functionals of the ground state(!) density. This conclusion applies in particular to all excitation energies.

The practical exploitation of (2.197) is complicated by two aspects: it is more difficult to derive acceptable approximations for the energy functional of excited states and there exists no suitable variational principle for these states. An excep-

tion to the latter statement is found if the complete Fock space can be decomposed into subspaces with different symmetry, i.e. if the Hamiltonian commutes with some symmetry operator. In this case there exists a minimum principle for each of the subspaces with a given symmetry (an argument, which has already been used in the case of the spin). It is possible to formulate a HK theorem for the energetically lowest state of each subspace, in analogy to the original version [77]: there is a one-to-one correspondence between the energetically lowest state $|\Psi_i\rangle$ of the subspace and the associated density $n_i = \langle\Psi_i|\hat{n}|\Psi_i\rangle$, defining the functional $|\Psi_i[n_i]\rangle$ (the spaces \mathcal{G} and \mathcal{N} of the original HK proof have to be restricted to the symmetry under consideration). The functional dependence of $|\Psi_i\rangle$ on n_i , however, in general differs from that of the ground state functional $|\Psi[n]\rangle$. Lacking any alternative, ground state density functionals are nonetheless often used for the discussion of excited states as, for example, atomic states with different angular momenta. However, this approach runs into difficulties with the resolution of the individual states of multiplets, as long as the density functional does not reflect the specific symmetry under consideration (for a scheme to deal with multiplet states see [78, 79]).

Density Functional Theory

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