

# Density-functional theory for beginners

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## **Abstract**

Density-functional theory is today one of the most important tools for calculating the ground-state properties of electronic systems. However, most texts on the subject are written by experienced researchers in the field, and are therefore somewhat inaccessible to beginners, especially undergraduate students. Intended to bridge this gap, this presentation is written by and for a beginner in the field. All fundamental concepts are introduced at their most basic level, and almost all expressions are derived explicitly. Several references are given to more or less advanced review articles. Limited experience within the field of many-body theory as well as basic training in quantum mechanics is assumed. The text is primarily based on other sources, in particular lecture notes by Carl-Olof Almbladh and Ulf von Barth, who kindly allowed me to use them as the fundament of this presentation.

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# 1 Introduction

The principal goal of any many-body theory is to reduce the number of parameters needed to describe the many-body system. In such a system, which may contain anywhere between 2 and  $10^{23}$  particles, each particle is described by its three coordinates in space, which may be time-dependent, plus possibly a spin coordinate. Obviously, it is a hopeless task to solve the equations of motion of such a system. Furthermore, since in quantum mechanics the particles are indistinguishable – whether they are fermions (which are furthermore subject to the Pauli exclusion principle) or bosons – we are not even able to say which particle is where, only that *some* particle is at a given position.

We thus realize, that it is utterly futile to try to keep track of each individual particle. The classical counterpart of this arises in *statistical mechanics*, where the solution is given by *thermodynamics*. Instead of determining the trajectory of each individual molecule or atom in a gas, we describe the system by *macroscopic equilibrium parameters*, such as temperature, density and entropy.

It is this idea we try to introduce in quantum many-body theory with *density-functional theory* (DFT), which, as the name implies, treats the *particle density* as the fundamental variable. As always in physics, the goal is to derive the energy of the system, so our task primarily becomes expressing all contributions to the energy in terms of the density. It is imperative to note that, by definition, density-functional theory is only able to predict the *ground-state* energy and properties, even though there are certain theories about how to treat excitation energies. Furthermore, since the ground-state energy is a function of a number of parameters of the system, we may also use DFT to find other ground-state properties – such as equilibrium bond-lengths – by minimizing the ground-state energy with respect to these parameters.

In principle, the theory is able to produce these quantities exactly, but in practice it is necessary to introduce some *approximations*. Fortunately, even the simplest conceivable approximation – the local density approximation, LDA – gives remarkably accurate results, even for systems in which this approximation doesn't even seem to be valid. One of the main reasons for this success is that the large kinetic energy is treated exactly, unlike in the Thomas–Fermi model which we will review briefly in the next section. This accuracy, alongside the fact that DFT transforms the many-body problem into an equivalent single-particle problem, are the major appealing features of the theory.

Throughout this text is used *atomic units*, in which  $e^2 = m_e = \hbar = 4\pi\epsilon_0 = 1$  and the unit of length is the Bohr radius  $a_0 = 0.529 \text{ \AA}$  and the unit of energy is Hartree,  $1 \text{ H} = 2 \text{ Ry} = 27.2 \text{ eV}$ . All integrations are assumed, unless otherwise indicated, to run over all space. The fact that  $e^2 = 1$  makes the particle and charge densities equal, with only a possible sign difference. Spin will not be considered explicitly (the reader is referred to cited review articles for treatment of e.g. spin-polarized system), but will still play an important role in the underlying many-body results, in particular via the Pauli principle to generate exchange and correlation contributions to the energy. Bosons are not considered at all, so by "particles" we shall mean fermions by default.

## 2 Historical background

Density-functional theory has a long history, which goes back to the *Thomas–Fermi theory* for a many-body system. This assumes a homogeneous system of  $N$  independent fermions. The kinetic energy per particle is then given simply by

$$\frac{T}{N} = t(n) = \frac{3}{5}\mathcal{E}_F(n), \quad (2.1)$$

where  $\mathcal{E}_F$  is the Fermi energy, which depends on the number density  $n$  of particles.

If we assume that the density  $n(\mathbf{r})$  is slowly varying in space, we may express the total kinetic energy as

$$T[n] \approx \int t(n) n(\mathbf{r}) d^3r, \quad (2.2)$$

which is a *functional* of the density, since the density is a function. Adding to this the electrostatic potential energy and interaction with some external potential  $w$ , we get the total energy expressed as

$$E[w, n] \approx \int t(n) n(\mathbf{r}) d^3r + \frac{1}{2} \iint \frac{n(\mathbf{r})n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d^3r d^3r' + \int n(\mathbf{r}) w(\mathbf{r}) d^3r. \quad (2.3)$$

The approximations made in this expression are rather severe, and for instance we do not get shell structure in atoms. The largest approximation is actually made in the kinetic term, which in itself often is the largest term, whereas the last term is exact. In the middle term we have ignored effects of exchange or correlation.

In 1964, P. Hohenberg and W. Kohn [1] showed that the exact ground-state energy can be expressed entirely in terms of functionals of the particle density. The original arguments only applied to non-degenerate ground-states, which imposes rather strict limitations on the applicability of the theory. The real breakthrough then came the year after, when Kohn and L. Sham [2, 3] showed how the variational problem could be solved via an effective one-particle scheme. This step was crucial to making DFT a usable tool. Later, in 1979, M. Levy [4] was able to define the necessary functionals without the restrictions of the original Hohenberg–Kohn scheme, via a so-called restricted search.

From then on, much effort has been devoted to DFT as a field, and many review articles are available [5–13]. This paper will only treat the fundament of the theory, so the reader is referred to these reviews and references therein for discussions on various more or less elaborate approximations, as well as successes and failures of DFT within different fields of physics and chemistry. Relativistic extensions have been made by Rajagopal and Callaway [14], and the extension into finite temperatures is originally due to Mermin [15].

### 3 Some useful definitions from many-body theory

Consider a system of  $N$  particles under the external potential  $w$ . The total Hamiltonian is then

$$\begin{aligned}
 H &= \sum_{i=1}^N \left( -\frac{1}{2} \nabla_i^2 \right) + \frac{1}{2} \sum_{i \neq j}^N v(\mathbf{r}_i - \mathbf{r}_j) + \sum_{i=1}^N w(\mathbf{r}_i) \\
 &\equiv \hat{T} + \hat{U} + \hat{W},
 \end{aligned}
 \tag{3.1}$$

where the interaction potential  $v$  for instance is the Coulomb potential for electron–electron interaction.

The second line of the equation above defines three energy operators, which in turn define three contributions to the total energy,

$$E = \langle \Psi | H | \Psi \rangle = T + U + W. \tag{3.2}$$

Using basic many-body theory, it is straightforward to show that we may rewrite

$$U = \frac{1}{2} \iint n(\mathbf{r}) n(\mathbf{r}') v(\mathbf{r} - \mathbf{r}') g(\mathbf{r}, \mathbf{r}') d^3r d^3r', \tag{3.3}$$

$$W = \int n(\mathbf{r}) w(\mathbf{r}) d^3r, \tag{3.4}$$

where  $n(\mathbf{r})$  is the *particle density*, and  $g(\mathbf{r}, \mathbf{r}')$  is the *pair-correlation function*, which is complicated – or even impossible – to evaluate.

It is possible to derive similar many-body expressions for the kinetic term  $T$ , but since we will not use them in the following – but instead derive a completely different way of calculating the ground-state energy –, the reader is referred to standard texts on many-body theory [16–18].

The pair-correlation function satisfies the very important *sum-rule*

$$\int n(\mathbf{r}) (g(\mathbf{r}, \mathbf{r}') - 1) d^3r' = -1, \tag{3.5}$$

valid for all positions  $\mathbf{r}$ . Simply stated, the pair-correlation function gives the probability of finding an electron at position  $r'$ , given that there already is an electron at  $r$ . See further discussions on the sum-rule in Section 6, and also below.

The effect of the pair-correlation function is to keep the particles apart by virtue of the interaction and the *Pauli exclusion principle*. Of these, we expect the interaction – in the case of electrons given by Coulomb repulsion – to give the larger contribution. In fact, setting  $g \equiv 1$  amounts to the *Hartree approximation*, which neglects all effects of exchange and correlation, but still takes the Coulomb repulsion into account. Furthermore, we expect that at large distances the particles must interact very weakly, thus  $g(\mathbf{r}, \mathbf{r}') \rightarrow 1$  as  $|\mathbf{r} - \mathbf{r}'| \rightarrow \infty$ . These two observations inspire us to separate  $U$  into two parts by rewriting  $g = 1 + (g - 1)$ , which will give one pure interaction term – or Hartree term, if we wish

– from the 1, expected to be the larger one, and one hopefully small exchange-correlation term from  $g - 1$ :

$$U = \frac{1}{2} \iint n(\mathbf{r}) n(\mathbf{r}') v(\mathbf{r} - \mathbf{r}') d^3r d^3r' + \frac{1}{2} \iint n(\mathbf{r}) n(\mathbf{r}') v(\mathbf{r} - \mathbf{r}') (g(\mathbf{r}, \mathbf{r}') - 1) d^3r d^3r'. \quad (3.6)$$

At this point it is appropriate to say a few words about the *Hartree-Fock approximation*, in which *exchange* – that is, the Pauli principle – is taken into account by requiring all wavefunctions to be *Slater determinants*. It still ignores the *correlation energy*<sup>1</sup>, which can be defined as exactly that: everything ignored in Hartree-Fock. As Ashcroft and Mermin [19] puts it, "the correlation energy is not a quantity with physical significance; it merely represents the error induced in making a fairly crude first-order approximation" (viz. Hartree-Fock).

We also define the *density operator*  $\hat{n}$ , defined and related to the particle density  $n(\mathbf{r})$  and total particle number  $N$  by

$$\hat{n}(\mathbf{r}) \equiv \sum_{i=1}^N \delta(\mathbf{r} - \mathbf{r}_i), \quad (3.7)$$

$$n(\mathbf{r}) = \langle \Psi | \hat{n}(\mathbf{r}) | \Psi \rangle, \quad (3.8)$$

$$N = \int n(\mathbf{r}) d^3r, \quad (3.9)$$

where  $\mathbf{r}_i$  is the position of the  $i$ :th particle.

## 4 Basics of DFT

Using the definitions of the previous section, we write the Hamiltonian generally as

$$H = \hat{T} + \hat{U} + \hat{W}, \quad (4.1)$$

where  $\hat{T}$  is the kinetic energy operator, which we expect will not be trivial to evaluate,  $\hat{U}$  is the operator describing the interaction between the particles, and  $\hat{W}$  is the interaction with the external potential, as given in the previous section.

It is clear that for different external potentials  $w$ , the ground-state energy is, in general, different. Hence the ground-state energy is a functional of  $w$ ,  $E = E[w]$ . Furthermore, we showed above, in Section 2, that in the Thomas–Fermi approximation the energy was a functional of the density, and we expect this to be the case also in the more general situation. The density itself is also a functional of  $w$ , since changing the external potential obviously affects the particle distribution.

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<sup>1</sup> Hartree-Fock does take correlations into account in the sense that the particles obey the Pauli principle; hence the term correlation energy is not exactly accurate [19].

Thus the ground-state energy is, at first glance, a functional of *both* the density and the external potential,  $E = E[w, n]$ , which makes things complicated. It is nevertheless rather simple to prove, that if two densities based on two different ground-state potentials are equal,  $n(r, w) = n'(r, w')$ , then the potentials  $w$  and  $w'$  can at most differ by a constant. This enables us to establish a *unique correspondence* between the ground-state density and the external potential, which in turn makes the energy only a functional of the density.

To prove this, we assume that the ground-state is *non-degenerate*, and that  $w(\mathbf{r}) - w'(\mathbf{r}) \neq \text{constant}$ . Then the two ground-state wavefunctions  $\Psi$  and  $\Psi'$ , corresponding to the two different potentials, cannot be identical,  $\Psi \neq \Psi'$ . Now, the ground-state energy corresponding to  $w$  is

$$\begin{aligned} E &= \langle \Psi | H_w | \Psi \rangle \\ &< \langle \Psi' | H_w | \Psi' \rangle = \langle \Psi' | H_{w'} | \Psi' \rangle + \int (w - w') n d^3r \\ &= E' + \int (w - w') n d^3r, \end{aligned} \tag{4.2}$$

where the inequality follows from the *variational principle* since  $\Psi$  is the true ground-state wavefunction, and the next step follows from the definition of the Hamiltonian (4.1). Since we also have the same relation for the ground-state  $E'$  of  $w'$ ,

$$\begin{aligned} E' &= \langle \Psi' | H_{w'} | \Psi' \rangle \\ &< \langle \Psi | H_{w'} | \Psi \rangle = \langle \Psi | H_w | \Psi \rangle + \int (w' - w) n d^3r \\ &= E + \int (w' - w) n d^3r, \end{aligned} \tag{4.3}$$

we may add these equations to get  $E + E' < E + E'$ , which is a contradiction. Thus our assumption was false. Hence it must be possible to unambiguously invert the relation  $n(\mathbf{r}) = n[w, \mathbf{r}] \rightarrow w(\mathbf{r}) = w[n, \mathbf{r}]$ , and thus *the total energy may be expressed as a unique functional of the density alone*. This is the first of the two fundamental DFT theorems of Hohenberg, Kohn and Sham.

To formally construct the energy functional of the density, it becomes necessary to differentiate functionals with respect to the functional argument. A brief presentation of *functional derivatives*, with some examples, is given in Appendix A. With those results, we may immediately infer from the first order perturbation theory result

$$\begin{aligned} \delta E[w] &= \langle \Psi | \delta H_w | \Psi \rangle = \int \delta w(\mathbf{r}) \langle \Psi | \hat{n}(\mathbf{r}) | \Psi \rangle d^3r \\ &= \int \delta w(\mathbf{r}) n(\mathbf{r}) d^3r \end{aligned} \tag{4.4}$$

that the functional derivative of  $E[w]$  is

$$\frac{\delta E[w]}{\delta w(\mathbf{r})} = n(\mathbf{r}). \tag{4.5}$$

Let us now compare with thermodynamics. There, the energy is an explicit function of both the entropy and the volume,  $E = E(S, V)$ . However, it is much more convenient to express the energy in terms of the measurable quantity temperature. Entropy and temperature are related by  $T = \left(\frac{\partial E}{\partial S}\right)_V$ , so if we define, via a *Legendre transformation*,

$$F(T, V) \equiv E - ST = E - S \left(\frac{\partial E}{\partial S}\right)_V,$$

we arrive at the well known expression for the Helmholtz free energy, which is a very useful potential in thermodynamics.

In our present case, we have a similar problem: we have the energy expressed as a functional of the density and the external potential,  $E = E[n, w]$ , but we wish to express it only in  $n$ . The density and the potential are related by (4.5), so if we define

$$\begin{aligned} F[n] &\equiv E[n] - \int \frac{\delta E[w]}{\delta w(\mathbf{r})} w(\mathbf{r}) d^3r \\ &= E[n] - \int n(\mathbf{r}) w(\mathbf{r}) d^3r, \end{aligned} \tag{4.6}$$

we have a new dependent variable, which depends only on the independent variable  $n$ .

The second theorem of DFT asserts, that the total energy functional

$$E[n] = F[n] + \int n(\mathbf{r}) w(\mathbf{r}) d^3r \tag{4.7}$$

has a *minimum* equal to the ground-state energy at the ground-state density of the system.

The original proof, by Hohenberg and Kohn [1], is rather abstract and further makes some, as is turned out later, unnecessary assumptions regarding the non-degeneracy of the ground-state and *w-representability* of the particle density<sup>2</sup>. The approach by Levy [4], using a so-called *restricted search*, is not only more intuitive, but also provides explicit definitions of the functionals.

## 4.1 Proof by Hohenberg and Kohn

Put simply, the proof amounts to restating the traditional variational principle for wave-functions in the same inequality expressed in densities, the minimum being given by the correct ground-state density.

We are studying a system of  $N$  particles under the external potential  $w$ . The system is assumed to have a non-degenerate ground-state  $\Psi$  with a corresponding density  $n(\mathbf{r})$ . We now *define* the functional  $F[n]$  by

$$F[n] \equiv \langle \Psi | \hat{T} + \hat{U} | \Psi \rangle, \tag{4.8}$$

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<sup>2</sup> A density  $n$  is *w-representable* if it is the ground-state of a many-body system subject to *some* external potential  $w$ . We will return to this issue several times in the following.

which is a unique functional of the density, since from the first theorem  $\Psi$  is uniquely defined by  $n$ . Note that the  $\Psi$  in the definition of  $F[n]$  is necessarily the ground-state. We also define an energy functional of *any* arbitrary density  $n'(\mathbf{r})$ ,

$$E_w[n'] \equiv F[n'] + \int n'(\mathbf{r}) w(\mathbf{r}) d^3r. \quad (4.9)$$

The task becomes to show, that the functional  $E_w$  assumes its minimum value for the correct ground-state density  $n$  corresponding to  $w$ .

Now consider a different wavefunction  $\Psi'$ , which is assumed to be the ground-state obtained from solving the Schrödinger equation with a *different* external potential  $w'$ , and let  $n'$  be the density associated with  $\Psi'$ .

The traditional Rayleigh–Ritz functional of an arbitrary wavefunction  $\Psi'$

$$\mathcal{E}_w[\Psi'] \equiv \langle \Psi' | H | \Psi' \rangle = \int n'(\mathbf{r}) w(\mathbf{r}) d^3r + \langle \Psi' | \hat{T} + \hat{U} | \Psi' \rangle \quad (4.10)$$

has, from the variational principle, a lower value for the correct ground-state wavefunction  $\Psi$  than for any other wavefunction (according to the assumption of non-degeneracy the inequality is strict), and thus<sup>3</sup>

$$\begin{aligned} \mathcal{E}_w[\Psi'] &= \langle \Psi' | \hat{T} + \hat{U} | \Psi' \rangle + \langle \Psi' | \hat{W} | \Psi' \rangle \\ &= F[n'] + \int n'(\mathbf{r}) w(\mathbf{r}) d^3r \\ &> \mathcal{E}_w[\Psi] = F[n] + \int n(\mathbf{r}) w(\mathbf{r}) d^3r. \end{aligned} \quad (4.11)$$

The inequality immediately gives the desired result

$$E_w[n] < E_w[n'], \quad (4.12)$$

and from the definitions (4.8) and (4.9) it is obvious that the minimum value is the ground-state energy, and that the minimizing density is the correct ground-state density associated with  $w$ .

## 4.2 Levy’s restricted search

In Levy’s approach, we introduce a *restricted search* over a subspace of the Hilbert space, namely over those wavefunctions which give a certain density. By doing so we avoid any assumptions of  $w$ -representability and non-degeneracy of the ground-state, and it also enables us to define the functionals which give the ground-state energy in an explicit way.

It is instructive to study the non-interacting case first, and we then move on to the interacting system.

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<sup>3</sup> Note that we can identify  $\langle \Psi' | \hat{T} + \hat{U} | \Psi' \rangle = F[n']$  only because  $\Psi'$  is the ground-state corresponding to *some* density  $n'$ . This is where the  $w$ -representability comes in.

### 4.2.1 Non-interacting system

For non-interacting fermions, without approximations, all many-body wavefunctions are Slater determinants, made up of *orbitals*  $\{\phi_i\}_{i=1}^N$ , and we are always able to find "exact" solutions for the ground-state wavefunction – which in turn gives the ground-state density – by some standard numerical method.

Consider *all* Slater determinants  $\Psi$  which produce a given density  $n(\mathbf{r})$ ,

$$n(\mathbf{r}) = \langle \Psi | \hat{n} | \Psi \rangle = \sum_{i=1}^N |\phi_i|^2. \quad (4.13)$$

For each of these, we may calculate the kinetic energy

$$T(\Psi) = \langle \Psi | \hat{T} | \Psi \rangle = \sum_{i=1}^N \left\langle \phi_i \left| -\frac{\nabla^2}{2} \right| \phi_i \right\rangle. \quad (4.14)$$

Now *define* the minimum<sup>4</sup> of  $T$ ,

$$T_0[n] \equiv \inf_{\Psi: \langle \Psi | \hat{n} | \Psi \rangle = n(\mathbf{r})} \langle \Psi | \hat{T} | \Psi \rangle. \quad (4.15)$$

We wish to show, that this is the independent particle kinetic energy of the ground-state for a certain many-body system. Let us therefore assume<sup>5</sup>, that  $n_0(\mathbf{r})$  is the ground-state density of a non-interacting system under the external potential  $w$ . The energy  $E_0$  of the ground-state  $\Psi_0$  is

$$\begin{aligned} E_0 &= \langle \Psi_0 | H | \Psi_0 \rangle = \langle \Psi_0 | \hat{T} | \Psi_0 \rangle + \int n_0(\mathbf{r}) w(\mathbf{r}) d^3r \\ &> T_0[n] + \int n_0(\mathbf{r}) w(\mathbf{r}) d^3r, \end{aligned} \quad (4.16)$$

where the inequality follows from (4.15), and thus

$$\min T(\Psi) = E_0 - \int n_0(\mathbf{r}) w(\mathbf{r}) d^3r. \quad (4.17)$$

In our present case of non-interacting fermions, when the density by construction is  $w$ -representable, we have a well-defined minimum (not only infimum), which of course is given by

$$\sum_{i=1}^N \left\langle \phi_i^{(0)} \left| -\frac{\nabla^2}{2} \right| \phi_i^{(0)} \right\rangle,$$

where the  $\phi_i^{(0)}$  are the orbitals of the ground-state Slater determinant.

It is noteworthy to point out that we need not actually require that  $\Psi$  varies only over Slater determinants, but of course the ground-state will eventually turn out to be one.

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<sup>4</sup> In functional theory, we should avoid demanding  $T_0$  to be the minimum, but instead use the infimum, since this always exists, which need not be the case for the minimum.

<sup>5</sup> Note that we do not assume  $w$ -representability of  $n_0$ ; instead it is the potential which is *given*, and  $n_0$  is the ground-state density corresponding to it.

### 4.2.2 Interacting system

Again, consider all many-body wavefunctions  $\Psi$ , which we no longer can limit to be Slater determinants, which all produce a given density  $n(\mathbf{r}) = \langle \Psi | \hat{n}(\mathbf{r}) | \Psi \rangle$ .

For each wavefunction we calculate the sum  $\langle \Psi | \hat{T} + \hat{U} | \Psi \rangle$  of the kinetic and interaction energies. Different wavefunctions give different values of this sum, and we now define the functional  $F[n]$  as the smallest (possibly the infimum) of these:

$$F[n] \equiv \inf_{\Psi: \langle \Psi | \hat{n} | \Psi \rangle = n(\mathbf{r})} \langle \Psi | \hat{T} + \hat{U} | \Psi \rangle. \quad (4.18)$$

Our attention is on the ground-state  $\Psi_0$  of the Hamiltonian (4.1), with the energy

$$E_0 = \langle \Psi_0 | H | \Psi_0 \rangle = \langle \Psi_0 | \hat{T} + \hat{U} | \Psi_0 \rangle + \int n_0(\mathbf{r}) w(\mathbf{r}) d^3r, \quad (4.19)$$

where  $n_0(\mathbf{r}) = \langle \Psi_0 | \hat{n}(\mathbf{r}) | \Psi_0 \rangle$  is the ground-state density. From the definition (4.18) of  $F[n]$  follows immediately

$$\langle \Psi_0 | \hat{T} + \hat{U} | \Psi_0 \rangle \geq F[n_0], \quad (4.20)$$

and thus

$$E_0 \geq F[n_0] + \int n_0(\mathbf{r}) w(\mathbf{r}) d^3r. \quad (4.21)$$

Moreover, by the variational theorem we have

$$E_0 \leq \langle \Psi | \hat{T} + \hat{U} | \Psi \rangle + \int n(\mathbf{r}) w(\mathbf{r}) d^3r \quad (4.22)$$

for any  $N$ -representable density  $n(\mathbf{r})$ , i.e. a density which is the expectation value of the density operator (3.7) for some  $N$ -particle wavefunction  $\Psi$ .

Now, let us perform Levy's restricted search: search for the  $\Psi$  which minimizes the right hand side of (4.22), while keeping the density  $n$  fixed. Obviously we then get

$$E_0 \leq F[n] + \int n(\mathbf{r}) w(\mathbf{r}) d^3r. \quad (4.23)$$

Next, find the minimum of this with respect to  $n$ , and call this minimizing density  $n'$ . Thus

$$E_0 \leq \min_n \left( F[n] + \int n(\mathbf{r}) w(\mathbf{r}) d^3r \right) = F[n'] + \int n'(\mathbf{r}) w(\mathbf{r}) d^3r. \quad (4.24)$$

Comparing Eqs. (4.21) and (4.24) gives

$$F[n_0] + \int n_0(\mathbf{r}) w(\mathbf{r}) d^3r \leq E_0 \leq F[n'] + \int n'(\mathbf{r}) w(\mathbf{r}) d^3r, \quad (4.25)$$

and by letting  $n' \rightarrow n_0$  we realize that we must have equality.

We have thus shown, that if we define the functional

$$E_w[n] = F[n] + \int n(\mathbf{r}) w(\mathbf{r}) d^3r \quad (4.26)$$

for a fixed potential  $w$ , we find the ground-state energy and density by letting the density in (4.26) vary<sup>6</sup> and search for the minimum for  $E_w[n]$ . The minimizing density is the ground-state density  $n_0$ , and the ground-state energy is given by  $E_w[n_0]$ :

$$E_0 = \min_{w \text{ fix}} E_w[n]. \quad (4.27)$$

For a degenerate ground-state, the minimizing density can be any of the ground-state densities.

Finally, since we have shown that we must have equality in (4.21), we have demonstrated the equivalence between Levy's functionals and those defined in the Hohenberg–Kohn scheme. However, the Levy functionals are defined also for functionals which are not  $w$ -representable. Furthermore, in contrast to Hohenberg and Kohn's method, the approach by Levy is readily generalized to spin-polarized systems [20].

### 4.3 Exchange-correlation potential

We are, despite the formal success contained in the results of the previous section, a long way from actually calculating the ground-state energy; for this we need a more practical approach. This was supplied by Kohn and Sham [2,3], who showed how to turn the evaluation of the functionals into an *equivalent one-particle problem*.

Since it is the interaction which complicates things, we now introduce an artificial way to gradually (or *adiabatically*) "turn on" the interaction, by letting

$$\hat{U} \rightarrow \lambda \hat{U},$$

where  $0 \leq \lambda \leq 1$  is a real parameter.  $\lambda = 0$  means we are studying the corresponding non-interacting system, and  $\lambda = 1$  gives us back our original interacting system.

By changing the interaction, we indirectly change the particle density, which is not desirable. Therefore we concurrently let the external potential vary,  $w \rightarrow w_\lambda$ , in such way that the particle density  $n(\mathbf{r})$  remains the same. *The assumption that this is always possible lies at the heart of density-functional theory*, and is tantamount to requiring  $n$  to be  $w$ -representable, which we have already encountered. It has yet not been proven generally that all physically valid densities are  $w$ -representable, but it has nevertheless been seen to work in all practical cases tested, where solutions to the problem may be obtained by other methods.

By performing these changes, the Hamiltonian and the energy are transformed as

$$\begin{aligned} H &\rightarrow H_\lambda = \hat{T} + \lambda \hat{U} + \hat{W}_\lambda, \\ E &\rightarrow E_\lambda, \end{aligned}$$

where

$$\hat{W}_\lambda = \int w_\lambda(\mathbf{r}) \hat{n}(\mathbf{r}) d^3r. \quad (4.28)$$

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<sup>6</sup> The variation is performed under the constraint of conserved number of particles,  $N = \int n(\mathbf{r}) d^3r$ .

Using the Hellman–Feynman theorem (see Appendix B), we now get

$$\begin{aligned}
\frac{\partial E_\lambda}{\partial \lambda} &= \left\langle \Psi_\lambda \left| \frac{\partial H_\lambda}{\partial \lambda} \right| \Psi_\lambda \right\rangle \\
&= \left\langle \Psi_\lambda \left| \hat{U} \right| \Psi_\lambda \right\rangle + \int n(\mathbf{r}) \frac{\partial w_\lambda}{\partial \lambda} d^3r \\
&= \frac{1}{2} \iint n(\mathbf{r}) n(\mathbf{r}') g_\lambda(\mathbf{r}, \mathbf{r}') v(\mathbf{r} - \mathbf{r}') d^3r d^3r' + \int n(\mathbf{r}) \frac{\partial w_\lambda}{\partial \lambda} d^3r.
\end{aligned} \tag{4.29}$$

For  $\lambda = 0$  we get back the non-interacting case, and so

$$E_{\lambda=0} = T_0 + \int w_0(\mathbf{r}) n(\mathbf{r}) d^3r, \tag{4.30}$$

where  $w_0$  is the potential which, in the non-interacting case, gives the same density as  $w$  does in the interacting case, and  $T_0$  is the corresponding kinetic energy for this non-interacting system.

To get the corresponding expression for  $\lambda = 1$ , i.e. our original interacting system, we integrate back over the derivative<sup>7</sup> to get

$$\begin{aligned}
E[n] = E_{\lambda=1} &= E_{\lambda=0} + \int_0^1 \frac{\partial E_\lambda}{\partial \lambda} d\lambda \\
&= T_0[n] + \int w_0(\mathbf{r}) n(\mathbf{r}) d^3r + \\
&\quad + \frac{1}{2} \iint n(\mathbf{r}) n(\mathbf{r}') v(\mathbf{r} - \mathbf{r}') \left( \int_0^1 g_\lambda(\mathbf{r}, \mathbf{r}') d\lambda \right) d^3r d^3r' + \\
&\quad + \int n(\mathbf{r}) \left( \int_0^1 \frac{\partial w_\lambda}{\partial \lambda} d\lambda \right) d^3r \\
&= T_0[n] + \frac{1}{2} \iint n(\mathbf{r}) n(\mathbf{r}') v(\mathbf{r} - \mathbf{r}') \tilde{g}(\mathbf{r}, \mathbf{r}') d^3r d^3r' + \int n(\mathbf{r}) w(\mathbf{r}) d^3r,
\end{aligned} \tag{4.31}$$

where  $\tilde{g}$  is defined as the integral of  $g_\lambda$  over  $\lambda$ .

Like we did on page 4, we also here separate out the large contribution from the Coulomb interaction by writing  $\tilde{g} = 1 + (\tilde{g} - 1)$ , and we get

$$E[n] = T_0[n] + \frac{1}{2} \iint n(\mathbf{r}) n(\mathbf{r}') v(\mathbf{r} - \mathbf{r}') d^3r d^3r' + \int n(\mathbf{r}) w(\mathbf{r}) d^3r + E_{\text{xc}}[n], \tag{4.32}$$

where the *exchange-correlation energy*  $E_{\text{xc}}[n]$  is thus *implicitly defined*. As a very important consequence of this rewrite, the energy contribution from the exchange-correlation is small compared to the other terms in (4.32), and those other terms are calculated *exactly*.

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<sup>7</sup> This may seem pointless, as we just differentiated, but in between we have made use of the Hellman–Feynman theorem.

We remind ourselves that the term  $T_0[n]$  is the ground-state kinetic energy of the *non-interacting*  $N$ -particle system, subject to some potential which reproduces, in the non-interacting system, the same ground-state particle density as the true ground-state density of the interacting system. This means that the extremely complicated many-body problem has been reduced to: a) solving an equivalent one-particle (i.e. non-interacting) system, and b) determining  $E_{xc}[n]$ .

The exchange-correlation energy is given in more detail by

$$E_{xc}[n] = \frac{1}{2} \iint n(\mathbf{r}) n(\mathbf{r}') (\tilde{g}(\mathbf{r}, \mathbf{r}') - 1) v(\mathbf{r} - \mathbf{r}') d^3r d^3r', \quad (4.33)$$

from which we also may define an *exchange-correlation potential*

$$v_{xc}(\mathbf{r}) \equiv \frac{\delta E_{xc}[n]}{\delta n(\mathbf{r})} = \int n(\mathbf{r}') (\tilde{g}(\mathbf{r}, \mathbf{r}') - 1) v(\mathbf{r} - \mathbf{r}') d^3r' + \frac{1}{2} \iint n(\mathbf{r}') n(\mathbf{r}'') \frac{\delta \tilde{g}(\mathbf{r}', \mathbf{r}'')}{\delta n(\mathbf{r})} v(\mathbf{r}' - \mathbf{r}'') d^3r' d^3r'', \quad (4.34)$$

where  $\delta \tilde{g}/\delta n$  is named the three-particle correlation function.

However, we still have no idea how to actually calculate  $\tilde{g}(\mathbf{r}, \mathbf{r}')$ . So it remains to approximate  $E_{xc}$  with more or less sophisticated methods. But since the approximation is made on the smallest term, we still can expect good results to emerge from these approximations. In fact, even the simplest approximation imaginable gives astonishingly good results. This is to be compared with the Thomas–Fermi model, where the largest term, viz. the kinetic energy, was grossly approximated.

## 5 Effective one-particle scheme

We showed in the previous section how the many-body problem could be reduced to an effective one-particle problem by separating out the large kinetic and long range Coulomb energy contributions. We have for the ground-state energy of a system subjected to the external potential  $w$

$$E_w[n] = F[n] + \int n(\mathbf{r}) w(\mathbf{r}) d^3r, \quad (5.1)$$

where

$$F[n] = T_0[n] + \frac{1}{2} \iint n(\mathbf{r}) n(\mathbf{r}') v(\mathbf{r} - \mathbf{r}') d^3r d^3r' + E_{xc}[n]. \quad (5.2)$$

$T_0[n]$  is the kinetic energy of a non-interacting system, and the exchange-correlation energy will need to be approximated, which we will deal with in the following section.

As demonstrated by Levy, we find the ground-state density and energy by minimizing  $E_w[n]$  when the density varies under the constraint of conserved number of particles. At the minimum<sup>8</sup>,  $E_w[n]$  must be stationary or, equivalently, the variation of  $E_w[n]$  must vanish.

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<sup>8</sup> Of course, also a maximum has this property, so in a real calculation we need to pay some attention so that we really obtain the minimum.

Introducing the constraint  $\delta N = 0$  via a Lagrangian multiplier, we get

$$\delta \left( E_w[n] - \mu \int n(\mathbf{r}) d^3r \right) = 0. \quad (5.3)$$

Performing the free variations, we get (c.f. Eq. (4.34))

$$\frac{\delta T_0[n]}{\delta n(\mathbf{r})} + V_H(\mathbf{r}) + v_{xc}(\mathbf{r}) + w(\mathbf{r}) - \mu = 0, \quad (\text{interacting}) \quad (5.4)$$

where

$$V_H(\mathbf{r}) = \int n(\mathbf{r}') v(\mathbf{r} - \mathbf{r}') d^3r' \quad (5.5)$$

is the Hartree potential.

Let us now turn to the problem of non-interacting particles, which we assume move in an effective potential  $w_{\text{eff}}$  which reproduces *the same density*  $n(\mathbf{r})$  as in the interacting case. The Hamiltonian is then

$$H_0 = \hat{T}_0 + \int \hat{n}(\mathbf{r}) w_{\text{eff}}(\mathbf{r}) d^3r. \quad (5.6)$$

By performing the same variation as in the interacting case, we get

$$\frac{\delta T_0[n]}{\delta n(\mathbf{r})} + w_{\text{eff}}(\mathbf{r}) - \mu = 0. \quad (\text{non-interacting}) \quad (5.7)$$

In principle we should use a different Lagrangian multiplier in the two cases (5.4) and (5.7), but it is readily realized that they may differ by at most a constant, which is assumed to be absorbed into  $w_{\text{eff}}$ .

Now the first term in (5.4) and (5.7) is still unknown. However, for the non-interacting case we have an alternative way of solving the problem: by numerical methods we may solve  $N$  single-particle equations

$$\left[ -\frac{\nabla^2}{2} + w_{\text{eff}}(\mathbf{r}) \right] \phi_i(\mathbf{r}) = \epsilon_i \phi_i(\mathbf{r}), \quad (5.8)$$

from which we get both the kinetic term

$$T_0[n] = -\frac{1}{2} \sum_{i=1}^N \int \nabla^2 \phi_i(\mathbf{r}) \phi_i(\mathbf{r}) d^3r = \sum_{i=1}^N \epsilon_i - \int n(\mathbf{r}) w_{\text{eff}}(\mathbf{r}) d^3r \quad (5.9)$$

and the density

$$n(\mathbf{r}) = \sum_{i=1}^N |\phi_i(\mathbf{r})|^2. \quad (5.10)$$

It is very important to be careful when considering the individual "eigenenergies"  $\epsilon_i$ . In general, they can *not* be attributed with any physical relevance, such as being excitation energies, which would be a natural interpretation. There are nevertheless situations in which they have some significance, at least approximately (sometimes in the sense that they are the only available results).

The question now becomes how to relate the two potentials  $w_{\text{eff}}$  and  $w$ . The condition is, as mentioned already several times, that  $w_{\text{eff}}$  should generate the same ground-state density in the non-interacting case, as  $w$  does in the interacting. By comparing Eqs. (5.4) and (5.7) we see that if we use

$$w_{\text{eff}}(\mathbf{r}) = V_{\text{H}}(\mathbf{r}) + v_{\text{xc}}(\mathbf{r}) + w(\mathbf{r}), \quad (5.11)$$

this is fulfilled, and we finally have an expression for the kinetic part of the total energy,

$$\frac{\delta T_0[n]}{\delta n(\mathbf{r})} = -w_{\text{eff}}(\mathbf{r}) + \mu. \quad (5.12)$$

Since both the Hartree potential and, in some complicated way, the exchange-correlation potential depend on the density, which in turn is given by  $w_{\text{eff}}$ , we immediately realize that the whole process must be implemented as a *self-consistent iteration scheme*. Further we have yet to discuss how to approximate  $v_{\text{xc}}$ .

We conclude this section by again mentioning that this whole procedure is based on the fundamental assumption that for all densities  $n$ , there is a corresponding potential  $w_{\text{eff}}$ , i.e.  $w$ -representability.

## 6 Approximation schemes; LDA

The one remaining problem before we can calculate the ground-state energy of the many-body system is to determine the exchange-correlation potential  $v_{\text{xc}}$ . In theory, we actually have explicit expressions for it by Eq. (4.34). But since the purpose of our derivations in the previous sections has been to postpone all the troublesome many-body exchange and correlation effects, we can expect that trying to use this expression is tantamount to treating the original interaction operator, which all along has been our intention to eliminate. Indeed, (4.34) contains the integrated pair-correlation function  $\tilde{g}$  which we have no explicit expression for. Instead, approximations of  $v_{\text{xc}}$  are necessary.

The criterion for the *local density approximation* or LDA [1, 2] – which is the only one we will treat in any detail here – is, as the name implies, that the density locally varies slowly. The precise definition of "slowly" is that over distances comparable to the inverse Fermi wavevector, the density should vary smoothly. In this case, we may consider the whole inhomogeneous and interacting system as consisting of a large number of boxes, each containing a *homogeneous but interacting* electron gas. Then we may approximate the total exchange-correlation energy as the sum (integral) of the contributions of all such boxes,

$$E_{\text{xc}} = \int n(\mathbf{r}) \epsilon_{\text{xc}}(n) d^3r, \quad (6.1)$$

where  $\epsilon_{\text{xc}}$  is the exchange-correlation energy per particle of a homogeneous electron gas. This energy can be measured experimentally, and over the years successively more accurate results have been obtained. To be useful in theoretical calculations, such data must be parametrized, and the most commonly used parametrization today is due to Hedin and Lundqvist [21] for density dependence and von Barth and Hedin [20] for spin dependence. Gupta and Rajagopal have derived corresponding results for finite temperatures [22].

In fact, when used in practice, LDA gives surprisingly good results, even for systems far outside the formal range of validity for the approximation, such as atoms and molecules. Naturally this is to large extent an effect of the exchange term being the smallest contribution to the energy, and the largest term, the kinetic, is treated exactly. But that is certainly not the whole truth.

In Section 3 we discussed the sum-rule (3.5) for the pair-correlation function, which of course also is valid after the integration over the interaction strength. We also stated that the interpretation of the pair-correlation function  $g$  is, that the electrons avoid each other.

If we define [23] a new quantity

$$n_{xc}(\mathbf{r}, \mathbf{r}') \equiv n(\mathbf{r}') (\tilde{g}(\mathbf{r}, \mathbf{r}') - 1) \quad (6.2)$$

and compare with Eq. (4.33), we find that the exchange-correlation energy may be written

$$E_{xc}[n] = \frac{1}{2} \iint n(\mathbf{r}) n_{xc}(\mathbf{r}, \mathbf{r}') v(\mathbf{r} - \mathbf{r}') d^3r d^3r'. \quad (6.3)$$

This is the Coulomb interaction of each electron (at position  $\mathbf{r}$ ) with a charge distribution  $n_{xc}(\mathbf{r}, \mathbf{r}')$ , which then may be interpreted as the *conditional density*<sup>9</sup>. The conditional density vanishes as the distance between the particles goes to zero, and may be interpreted as a "hole", surrounding each particle, and it is named *exchange-correlation hole*. The hole keeps the particles apart, due to Coulomb repulsion and the Pauli principle.

Thus Eq. (6.2) expresses how each electron interacts with its own exchange-correlation hole. The hole is the manifestation of charge depletion due to exchange and Coulomb repulsion, and the fact that this depletion corresponds to one unit of charge is expressed by the sum-rule, which now becomes

$$\int n_{xc}(\mathbf{r}, \mathbf{r}') d^3r = -1, \quad \forall \mathbf{r}. \quad (6.4)$$

From this discussion, we may actually give an equivalent definition of LDA, from which we conclude that the exchange-correlation hole in LDA fulfills the sum-rule, as it should.

Ever more importantly, it supplies the explanation for the possibly most important factor underlying the success of LDA [24]. An outstanding feature – and often a source of great nuisance – of the Coulomb interaction is its long range. This means, among other things, that the interaction energy between two charge distributions is rather insensitive to the shapes of the distributions, but only of their total charges. Hence even if our approximation is not able to reproduce the detailed spatial shape of the hole, as long as the sum rule is fulfilled (which gives the total charge) the errors involved will be small, and LDA will produce good results.

Inspired by this, we may define the spherical average  $\bar{n}_{xc}(\mathbf{r}, R)$  of the exchange-correlation hole with respect to the point  $\mathbf{r}$ ,

$$\bar{n}_{xc}(\mathbf{r}, R) \equiv \int n_{xc}(\mathbf{r}, \mathbf{r} + \mathbf{R}) \frac{1}{4\pi} d\Omega_{\mathbf{R}}, \quad (6.5)$$

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<sup>9</sup> The probability of having an electron at some position, given that another electron is at another

from which we see that

$$E_{\text{xc}}[n] = \frac{1}{2} \int n(\mathbf{r}) d^3r \int v(R) \bar{n}_{\text{xc}}(\mathbf{r}, R) v(R) d^3R. \quad (6.6)$$

Hence the exchange-correlation energy will depend only on the spherical average of the hole. An interesting feature is also that the exact hole is centered on the nucleus, whereas the LDA hole is spherically symmetric and centered on the electron. The LDA hole will also be more extended compared to the exact hole, which is rather localized [24].

Finally, we should mention that more elaborate approximations and corrections to LDA have been constructed, for which the reader is referred to references in the cited review articles.

## Appendix A: Functional derivatives

Given a functional  $F[w]$  of some function  $w$ , we make a small change  $w \rightarrow w + \delta w$ . What is the change  $\delta F$  in  $F[w]$ ? Assume we can write

$$\delta F = \int \lambda(\mathbf{r}) \delta w(\mathbf{r}) d^3r + \mathcal{O}(\delta w^2). \quad (\text{A.1})$$

If this is possible, then we say that the functional  $F$  is differentiable, and the *functional derivative* is defined as  $\lambda(\mathbf{r})$ . Formally, we may write

$$\frac{\delta F[w]}{\delta w(\mathbf{r})} = \lambda(\mathbf{r}). \quad (\text{A.2})$$

Note that the dimension of the functional derivative is not that of  $F$  divided by that of  $w$  (see the Hartree example just below). Hence the symbol  $\frac{\delta F[w]}{\delta w(\mathbf{r})}$  is not to be interpreted strictly as a ratio of quantities (as the usual derivative can be seen as, in the proper limit). Further insight into this issue can be found from the discussion at the end of this Appendix.

A simple one-dimensional example of a functional derivative can be found from the functional

$$F[n] = \int \left( \frac{dn}{dx} \right)^2 dx. \quad (\text{A.3})$$

Functionals which appear in physical applications are usually of this form, where the functional is a scalar, although it is equally possible to define vector functionals, or even functional functionals. Upon varying our functional (A.3) we get

$$\begin{aligned} F[n] + \delta F[n] &= \int \left( \frac{d(n + \delta n)}{dx} \right)^2 dx \\ &= \int \left[ \left( \frac{dn}{dx} \right)^2 + 2 \frac{dn}{dx} \frac{d}{dx} \delta n \right] dx \\ &= F[n] + 2 \int \frac{dn}{dx} \frac{d}{dx} \delta n dx \\ &= F[n] - 2 \int \frac{d^2 n}{dx^2} \delta n dx \end{aligned} \quad (\text{A.4})$$

to linear order in  $\delta n$ . In the last step we have partially integrated and used the fact that the density must vanish at infinity for the functional to be finite. Hence we have

$$\frac{\delta F[n]}{\delta n} = -2 \frac{d^2 n}{dx^2}. \quad (\text{A.5})$$

For a more physically relevant example, we may study the Hartree energy  $E_H[n]$  as a functional of the particle density  $n(\mathbf{r})$ , which may be written as (c.f. Eq. (3.3) with  $g \equiv 1$ )

$$E_H[n] = \frac{1}{2} \iint n(\mathbf{r}) n(\mathbf{r}') v(\mathbf{r} - \mathbf{r}') d^3r d^3r'. \quad (\text{A.6})$$

Make a small change in the density,  $n \rightarrow n + \delta n$ . Then, if we abbreviate and let  $n \equiv n(\mathbf{r})$  and  $n' \equiv n(\mathbf{r}')$ , we have

$$\begin{aligned} E_{\text{H}} + \delta E_{\text{H}} &= \frac{1}{2} \int (n + \delta n) (n' + \delta n') v(\mathbf{r} - \mathbf{r}') d^3 r d^3 r' + \mathcal{O}(\delta n^2) \\ &= E_{\text{H}} + 2 \frac{1}{2} \iint n' \delta n v(\mathbf{r} - \mathbf{r}') d^3 r d^3 r' + \mathcal{O}(\delta n^2), \end{aligned} \quad (\text{A.7})$$

where the factor 2 is from the two integrals with the prime switched between the  $n$ 's; the expression is obviously symmetric in  $n$  and  $n'$ . From the definition in (A.1) we may now conclude that

$$\frac{\delta E_{\text{H}}[n]}{\delta n(\mathbf{r})} = \int n(\mathbf{r}') v(\mathbf{r} - \mathbf{r}') d^3 r', \quad (\text{A.8})$$

which we recognize as the Hartree potential  $V_{\text{H}}(\mathbf{r})$ .

From a numerical point of view, we can regard (A.1) as a generalization of the chain-rule for differentiating a function  $f$  of several variables,

$$\frac{df(a_1, a_2, \dots)}{dt} = \sum_i \frac{\partial f}{\partial a_i} \frac{\partial a_i}{\partial t}. \quad (\text{A.9})$$

A functional  $F[n]$  depends on the function values  $n(x)$  in each point  $x$ . If we discretize our (for simplicity one-dimensional) space into  $N$  equidistant points  $x_i$  with spacing  $h$ , the functional actually becomes a function  $F(n_i)$  where  $n_i = n(x_i)$ . The function values can all be varied independently, and hence

$$dF(n_1, n_2, \dots) = \sum_{i=1}^N h \left( \frac{1}{h} \frac{\partial F}{\partial n_i} \Big|_{n^0} \right) dn_i, \quad (\text{A.10})$$

where the factors  $h$  are introduced in anticipation of the limit  $h \rightarrow 0$ . In the limit  $N \rightarrow \infty$  (and  $h \rightarrow 0$ ), we can identify the definition of a Riemann integral, and with  $\delta n(x) = dy_n$  arrive at

$$dF = \int \frac{\delta F}{\delta n(x)} \Big|_{n^0(x)} \delta n(x) dx. \quad (\text{A.11})$$

$n^0(x)$  is the function  $n(x)$  which is the starting point of the variation  $\delta n(x)$ . The step-size  $h$  has been absorbed into  $\frac{\delta F}{\delta n(x)}$ , and the expression (A.11) can then be taken as the definition of (and together with (A.10) a method for numerically evaluating) the functional derivative. We also see where the unexpected dimensionality of the functional derivative, discussed above, appears from, namely the incorporated step-size (in three dimensions this is a volume element).

To see how this works, let us consider the same functional as above, Eq. (A.3). The discretized version reads

$$F(n_1, n_2, \dots) = \sum_i h \frac{(n_{i+1} - n_i)^2}{h^2}, \quad (\text{A.12})$$

and

$$\frac{\partial F}{\partial n_i} = -\frac{2}{h}(n_{i+1} - n_i) + \frac{2}{h}(n_i - n_{i-1}) = -2h \frac{n_{i+1} + n_{i-1} - 2n_i}{h^2}. \quad (\text{A.13})$$

Summing over all  $i$ , we get

$$dF = \sum_i h \left( \frac{1}{h} \frac{\partial F}{\partial n_i} \right) dn_i = -2 \sum_i h \left( \frac{n_{i+1} + n_{i-1} - 2n_i}{h^2} \right) dn_i. \quad (\text{A.14})$$

Now in the limit  $h \rightarrow 0$  the quantity in parenthesis is exactly  $\frac{d^2 n}{dx^2}$  and hence

$$\delta F = \int -2 \frac{d^2 n}{dx^2} \delta n(x) dx \quad (\text{A.15})$$

in complete accordance with the results above.

## Appendix B: The Hellman–Feynman theorem

Suppose the Hamiltonian  $H$ , in addition to whatever dependence on spatial coordinates and so on, depends on some real parameter  $\lambda$ . Then, of course, the ground-state energy and the ground-state wavefunction (which we assume remains normalized for all values of  $\lambda$ ) will also be dependent on this parameter. The Hellman–Feynman theorem then states that

$$\frac{\partial E_\lambda}{\partial \lambda} = \left\langle \Psi_\lambda \left| \frac{\partial H_\lambda}{\partial \lambda} \right| \Psi_\lambda \right\rangle. \quad (\text{B.1})$$

*Proof:* Since  $\Psi_\lambda$  is the eigenstate of  $H_\lambda$ , we naturally have  $H_\lambda |\Psi_\lambda\rangle = E_\lambda |\Psi_\lambda\rangle$ , and  $E_\lambda = \langle \Psi_\lambda | H_\lambda | \Psi_\lambda \rangle$ . We use this to write

$$\begin{aligned} \frac{\partial E_\lambda}{\partial \lambda} &= \left\langle \frac{\partial \Psi_\lambda}{\partial \lambda} \left| H_\lambda \right| \Psi_\lambda \right\rangle + \left\langle \Psi_\lambda \left| \frac{\partial H_\lambda}{\partial \lambda} \right| \Psi_\lambda \right\rangle + \left\langle \Psi_\lambda \left| H_\lambda \right| \frac{\partial \Psi_\lambda}{\partial \lambda} \right\rangle \\ &= E_\lambda \left[ \left\langle \frac{\partial \Psi_\lambda}{\partial \lambda} \left| \frac{\partial \Psi_\lambda}{\partial \lambda} \right\rangle + \left\langle \frac{\partial \Psi_\lambda}{\partial \lambda} \left| \Psi_\lambda \right\rangle \right] + \left\langle \Psi_\lambda \left| \frac{\partial H_\lambda}{\partial \lambda} \right| \Psi_\lambda \right\rangle \\ &= E_\lambda \frac{\partial}{\partial \lambda} \langle \Psi_\lambda | \Psi_\lambda \rangle + \left\langle \Psi_\lambda \left| \frac{\partial H_\lambda}{\partial \lambda} \right| \Psi_\lambda \right\rangle. \end{aligned} \quad (\text{B.2})$$

But since we assumed the wavefunction to stay normalized, we have  $\langle \Psi_\lambda | \Psi_\lambda \rangle = 1$ , which concludes the proof.

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