# Density Functional Theory

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## 1 Introduction

These notes intrduce the ideas underlying electronic structure calculations via density functional theory (DFT). You should be familiar Schrödinger equation in some form: our purpose here is to use it to describe many interacting electrons in a solid. We will show how the intractable problem of solving the many-body problem for interacting electrons can be put in to a much more approachable form by a mean-field approach considering the electrons as interacting only via an effective potential resulting from their total density.

DFT has for some time been dominant approach in the electronic structure field, with literally thousands of people using it every day in research around the world, particularly when you consider that many quantitative higher-level theory approaches are built on it in some way (eg LDA+DMFT, QMC, GW, GW+BSE). Its reasonable balance of accuracy and computational cost is perfect for many applications, and DFT is thus a mainstay of modern condensed matter theory. It is therefore worth some time to understand it properly: it is an extremely subtle and elegant theory.

A broad overview of electronic structure theory can fall into the trap of writing down a whole host of complicated-looking Hamiltonians and introducing a raft of different approximations to different parts of it without good justification. Seen in this way, DFT can seem rather counter-intuitive, and the approximations may seem unfounded. I will work through a very brief explanation of the way Kohn-Sham DFT can be justified first, to show where it all leads, then I will go back and re-introduce some ideas a little more carefully afterwards.

## 2 Density Functionals

DFT is easy to explain badly. That is to say, it not that hard to explain how in practice the method simplifies the intractable problem of many-electron quantum mechanics into something that can be feasibly handled by a computer. However, if you pay close attention you will notice there are several stages at which approximations are made which don't look like they ought to work, and indeed sometimes (often) they don't... and that is why practical methods have limited accuracy. The skill in being a DFT practioner lies in understanding when it can be expected to work reasonably well, and when it definitely won't work, and thus what level of approximation is sufficient for a given problem.

Let us first consider the full quantum mechanical description of electrons in a solid. We will assume the ions are fixed: this means we have already invoked the 'Born-Oppenheimer approximation', which separates out nuclear and electronic motion. The Hamiltonian below can be derived by starting from a full QM description of both the electrons and the ions as QM particles, and noting the very significantly different timescales associated with the motion of each, resulting from their very different masses.

Within the Born-Oppenheimer approximation, the Hamiltonian of a system with electrons labelled $i$ of charge $-e$ at positions $\mathbf{r}_i$ and frozen classical nuclei, labelled $\alpha$, of charge $Z_\alpha e$ at positions $\mathbf{R}_\alpha$ is

$$\hat{H} = \sum_i \frac{\mathbf{p}_i^2}{2m_e} + \sum_{i>j} \frac{e^2}{4\pi\varepsilon_0|\mathbf{r}_i - \mathbf{r}_j|} - \sum_i \sum_\alpha \frac{Z_\alpha e^2}{4\pi\varepsilon_0|\mathbf{r}_i - \mathbf{R}_\alpha|} + \sum_{\alpha>\beta} \frac{Z_\alpha Z_\beta e^2}{4\pi\varepsilon_0|\mathbf{R}_\alpha - \mathbf{R}_\beta|} \ . \quad (1)$$

We could say we would like to solve the full many-body Schrödinger equation in the form:

$$\hat{H}\Psi(\mathbf{r}_1, \ldots, \mathbf{r}_N) = E\Psi(\mathbf{r}_1, \ldots, \mathbf{r}_N) \ ,. \quad (2)$$

to find the exact many-body wavefunction $\Psi(\mathbf{r}_1, \ldots, \mathbf{r}_N)$. As anyone who has ever tried to run large quantum chemistry or quantum Monte Carlo calculations will tell you, this is *hard work!* The computational effort involved in any exact solution will explode exponentially with the number of electrons. Even the amount of data required for a solution on a $3N$-dimensional grid becomes totally unfeasible much beyond $N = 2$.

Instead, let's skip to the end and pretend we have already convinced ourselves that we don't need the wavefunction, and that in fact all the properties of the quantum mechanical ground state of a system of interacting electrons that we might want can in fact be determined without knowing it. We will assume that the electron density $n(\mathbf{r})$ everywhere in space uniquely determines the system. In fact, we can prove this later, and discuss how the electron density relates to the many-body wavefunction) [1]. For the moment the nuclei just produce a classical Coulomb potential, we will forget about spin and relativity, and we will work with atomic units such that $e = m_e = 4\pi\epsilon_0 = a_0 = \hbar = 1$. The ion-ion energy is just a constant $E_{II}$ within the Born-Oppenheimer approximation and plays no interesting role.

If the electron density specfies all properties, including the energy, then we could imagine expressing the ground state total energy of this system as a *functional* of the electron density, denoted $E_{\mathrm{HK}}[n(\mathbf{r})]$ after Hohenberg and Kohn, who first proposed this approach back in 1964. To solve for the ground state of a system, we want to minimise this energy with respect to the density, subject to the requirement that the density represent a certain number of electrons $N_e$.

We can imagine, on the basis of Eq. 1 that we can divide up this total energy functional into a sum of terms each with similar meanings to the corresponding term of the Hamiltonian. This would result in terms for the kinetic energy of the electrons, the Coulomb interaction of the electrons with each other, and the interaction of the electrons with the nuclei, each individually functionals of the density:

$$E_{\mathrm{HK}}[n] = T[n] + E_{\mathrm{int}}[n] + E_{\mathrm{ext}}[n] + E_{II} \quad (3)$$

We will find, shortly, that the first two terms in fact constitute a *universal* functional of the density, in that while of course the energies themselves depend on the density, and thus on the external potential, the *form* of the functional for e-e interactions and kinetic energy does not need to depend on the details of the nuclei for a particular system: only the $E_{\text{ext}}$ and $E_{II}$ terms actually depend explicitly on the nuclear coordinates.

The external potential term is simple to evaluate for a local potential:

$$E_{\text{ext}}[n] = \int \mathrm{d}\mathbf{r} V_{\text{ext}}(\mathbf{r}) n(\mathbf{r}) \ , \tag{4}$$

where $V_{\text{ext}}(\mathbf{r})$ is the external potential created by the nuclei. The ion-ion term is simply a constant:

$$E_{II} = \sum_{\alpha > \beta} \frac{Z_\alpha Z_\beta e^2}{4\pi\varepsilon_0 |\mathbf{R}_\alpha - \mathbf{R}_\beta|} \ , \tag{5}$$

though evaluating this for an infinite periodic solid is not so simple (the Ewald construction is widely used).

## 2.1 Kohn-Sham Density Functional Theory

To get any further, we need tractable forms of $T[n]$ and $E_{\text{int}}[n]$. We must therefore invent the key substitution that lies at the heart of the Kohn-Sham approach density functional theory [2]. We *replace* the full interacting system of electrons with a *fictitious*, non-interacting system *which has the same density* $n(\mathbf{r})$. By definition, we invent a functional for this new system whose energy equals that of the original Hohenberg-Kohn system:

$$E_{\text{KS}}[n] = E_{\text{HK}}[n] \tag{6}$$

However, this new system is much more tractable than the full one: because it is non-interacting, we can imagine constructing a wavefunction for it as a Slater determinant of single-particle orbitals $\psi_i(\mathbf{r})$. A Slater determinant can be seen as the minimal form of many-body wavefunction that fits with the idea that electrons are indistinguishable fermions (i.e. the wavefunction is antisymmetric under exchange of any two particles).

This Slater determinant is associated with an electron density given by:

$$n(\mathbf{r}) = \sum_{i=1}^{N_e} |\psi_i(\mathbf{r})|^2 \tag{7}$$

We can write a ‘Kohn-Sham total energy’ for this non-interacting system as follows:

$$E_{\text{KS}}[n] = T_s[n] + E_{\text{H}}[n] + E_{\text{xc}}[n] + E_{\text{ext}}[n] + E_{II} \ , \tag{8}$$

where we have defined several new terms: $T_s$, $E_{\text{H}}$ and $E_{\text{xc}}$. $T_s$ is non-interacting kinetic energy, given by

$$T_s = -\frac{1}{2} \sum_{i=1}^{N_e} \langle \psi_i | \nabla^2 | \psi_i \rangle . \tag{9}$$

$E_{\mathrm{H}}$ is the Hartree energy, representing the Coulombic interaction of the density with itself, given by

$$E_{\mathrm{H}} = \frac{1}{2}\int \mathrm{d}\mathbf{r}\,\mathrm{d}\mathbf{r}'\frac{n(\mathbf{r})n(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}. \tag{10}$$

$E_{\mathrm{xc}}$ is the 'Exchange-Correlation' energy, which is supposed to ensure exact equality of $E_{\mathrm{KS}}[n]$ and $E_{\mathrm{HK}}[n]$, hence is defined as:

$$E_{\mathrm{xc}}[n] = T[n] - T_s[n] + E_{\mathrm{int}}[n] - E_{\mathrm{H}}[n]\ . \tag{11}$$

It should be easy to see that with this definition $E_{\mathrm{KS}}[n] = E_{\mathrm{HK}}[n]$. But what have we actually done here? Effectively we have taken a problem we did not know how to solve, because we could not hope to evaluate accurate functionals of the density for $T[n]$ and $E_{\mathrm{int}}[n]$, with a problem where a lot of the main elements, namely $T_s[n]$ and $E_{\mathrm{H}}[n]$, are easy to calculate exactly, and we have shoved all the terms we do not know, but might have some hope of approximating, into $E_{\mathrm{xc}}[n]$. This has at least some chance of working even with a relatively crude approximation as long as $E_{\mathrm{xc}}[n]$ is fairly small compared to the other parts. This will be the case if the electrons are relatively weakly interacting, i.e. if to a reasonably good approximation they do indeed behave as independent particles.

To find the ground state, we need to minimise $E_{\mathrm{KS}}$ with respect to the single-particle orbitals $\psi_i(\mathbf{r})$, subject to the constraint that, since the fictitious independent electrons are Fermions each occupying a different normalised state, we must have $\langle\psi_i|\psi_j\rangle = \delta_{ij}$.

We can use the chain rule on Eq.8 to take the derivative of $E_{\mathrm{KS}}$ with respect to $\psi_i^*(\mathbf{r})$, to give

$$\frac{\delta E_{\mathrm{KS}}}{\delta\psi_i^*(\mathbf{r})} = \frac{\delta T_s}{\delta\psi_i^*(\mathbf{r})} + \left[\frac{\delta E_{\mathrm{ext}}}{\delta n(\mathbf{r})} + \frac{\delta E_{\mathrm{H}}}{\delta n(\mathbf{r})} + \frac{\delta E_{\mathrm{xc}}}{\delta n(\mathbf{r})}\right]\frac{\delta n(\mathbf{r})}{\delta\psi_i^*(\mathbf{r})}\ . \tag{12}$$

Eq.9 tells us that $\frac{\delta T_s}{\delta\psi_i^*(\mathbf{r})} = -\frac{1}{2}\nabla^2\psi_i(\mathbf{r})$, Eq.7 tells us that $\frac{\delta n(\mathbf{r})}{\delta\psi_i^*(\mathbf{r})} = \psi_i(\mathbf{r})$, Eq.4 tells us that $\frac{\delta E_{\mathrm{ext}}}{\delta n(\mathbf{r})} = V_{\mathrm{ext}}(\mathbf{r})$, Eq.10 tells us that $\frac{\delta E_{\mathrm{H}}}{\delta n(\mathbf{r})} = V_{\mathrm{H}}(\mathbf{r})$, and we finally we simply define the XC potential as $V_{\mathrm{xc}}(\mathbf{r}) = \frac{\delta E_{\mathrm{xc}}}{\delta n(\mathbf{r})}$.

We can now minimise $E_{\mathrm{KS}}$ subject to the constraint that the single particle orbitals are normalised: we add a set of Lagrange multipliers $\epsilon_i$, by inserting the expression $\epsilon_i\delta(\langle\psi_i|\psi_i\rangle - 1)$ before taking the derivative.

Using the aforementioned substitutions, we get a set of Schrödinger-like equations for $\psi_i(\mathbf{r})$:

$$\left[-\frac{1}{2}\nabla^2 + V_{\mathrm{ext}}(\mathbf{r}) + V_{\mathrm{H}}(\mathbf{r}) + V_{\mathrm{xc}}(\mathbf{r})\right]\psi_i(\mathbf{r}) \quad = \quad \epsilon_i\psi_i(\mathbf{r}) \tag{13}$$

or equivalently

$$\hat{H}_{\mathrm{KS}}\psi_i(\mathbf{r}) = \epsilon_i\psi_i(\mathbf{r})$$

where

$$\hat{H}_{\mathrm{KS}} = -\frac{1}{2}\nabla^2 + V_{\mathrm{ext}}(\mathbf{r}) + V_{\mathrm{H}}(\mathbf{r}) + V_{\mathrm{xc}}(\mathbf{r})$$

is the Kohn-Sham Hamiltonian and Eq.13 is the Kohn-Sham Equation.

## 2.2 The Local Density Approximation

To proceed, we need a simple functional of the density to represent the effect of exchange and correlation. A careful analysis of the *interacting electron gas* reveals useful information. For the homogeneous gas, the electron-background, background-background, and the direct electron-electron term all cancel, so only the kinetic energy and the effects of exchange and correlation contribute to the total energy:

$$\epsilon_{HF}(n) = t(n) + \epsilon_x(n) + \epsilon_c(n)$$

Ignoring correlation initially, we can proceed based on Hartree-Fock theory. The orbitals will still be plane waves, filled up to a Fermi level $k_F$. However, the analysis is too long to present here: an excellent presentation can be found in Roi Baer's lectures on density functional theory, available online here: http://www.fh.huji.ac.il/~roib/LectureNotes/DFT/

The end result is orbital energies for the HEG, given by:

$$\epsilon_k = \frac{k^2}{2} - \frac{2k_F}{\pi} F\left(\frac{k_F}{k}\right)$$

where $F(x) = 1 + \frac{1}{2}(x - 1/x)\ln\left|\frac{x+1}{x-1}\right|$. The first term clearly represents the kinetic energy, whereas the second contributes the exchange energy. After some further manipulations, we obtain the exchange energy per particle:

$$\epsilon_x = -\frac{3k_F}{4\pi} = -C_X n^{1/3}$$

where $C_x = \frac{3}{4}\left(\frac{3}{\pi}\right)^{1/3} = 0.73856$. This simple expression turns out to be a respectable approximation, if taken point-wise, even in situations which are not homogeneous!

Since the average number of electrons in the volume $\mathrm{d}^3\mathbf{r}_0$ is $n(\mathbf{r}_0)\mathrm{d}^3\mathbf{r}_0$, this suggests approximating the total XC energy using the formula:

$$E_{\mathrm{xc}}[n] \approx \int_{\mathrm{system}} \varepsilon_{\mathrm{xc}}(n(\mathbf{r}_0))n(\mathbf{r}_0)\mathrm{d}^3\mathbf{r}_0 \ , \tag{14}$$

where $\varepsilon_{\mathrm{xc}}(n)$ is the XC energy per electron in a uniform electron gas of density $n$. Note that $\varepsilon_{\mathrm{xc}}(n)$ is a simple function of its argument $n$ (a number), *not* a functional of the full non-uniform electron density $n(\mathbf{r})$. To work out $\varepsilon_{\mathrm{xc}}(n(\mathbf{r}_0))$, all you need to know is the value of the electron density $n(\mathbf{r}_0)$ at the single point $\mathbf{r}_0$.

This approximation, which is known as the local density approximation (LDA), has proved astonishingly successful (the reasons for this success are still not completely understood). Density-functional calculations based on the LDA can reproduce many of the physical properties (phonon frequencies, bond lengths, bond energies, ...) of real solids and molecules to within a few percent.

Early attempts at parameterising the correlation energy centred on interpolation between the high- and low-density limits we encountered previously. The high-density limit gives us:

$$\epsilon_c = A\ln(r_s) + B + r_s(C\ln(r_s) + D)$$

(see for example Parr and Yang, 1994), whereas the low-density limit gives us

$$\epsilon_c = \frac{1}{2}\left(\frac{g_0}{r_s} + \frac{g_1}{r_s^{3/2}} + \dots\right)$$

However, for real materials, which exist between the high- and low-density limits, this approach is found to be insufficiently accurate for real calculations without precise parameters. The breakthrough came at the start of the 1980's, when Ceperly and Alder performed groundbreaking Quantum Monte Carlo calculations of the Homogeneous Electron Gas for a range of densities. From their data it was possible to parameterize a form of the correlation energy per electron $\epsilon_c(n)$ based on exact limits which was surprisingly accurate.

Given the success of the LDA, and the fact that densities are reasonably smooth, one can imagine constructing higher-order functionals as a Taylor expansion in terms the density and its gradients. Generalised Gradient Approximations (GGAs), such as the widely used Perdew-Burke-Ernzerhof approximation (PBE), are in many cases rather more accurate than the LDA, with lattice parameters notably improved in covalent and ionic solids and binding energies rather better represented. They also have certain rather less desirable properties, for example they underestimate energy gaps even worse than LDA, and perform even worse in vdW-bonded materials than LDA (though that performs well for the wrong reasons in such materials). It turns out not to be profitable to use further gradients of the density as the series expansion is not convergent: instead 'meta-GGAs' utilise the local kinetic energy density, and are becoming increasingly popular.

Over the last decade, 'hybrid functionals', mixing in a component of exact exchange calculated as in Hartree-Fock theory, have become very widespread. These perform well at energy gaps, and improve quasiparticle energies considerably, at the cost of considerably increased computational complexity. In recent years, fully-nonlocal functionals such as the vdW-DF have had great success in representing weakly-bonded interactions.

## 2.3 Pseudopotentials

In the context of electronic structure calculations, a pseudopotential is a substitution of the Coulomb potential for a bare atomic nucleus by a less rapidly varying 'pseudo' potential representing the nucleus and its tightly-bound core electrons. The motivations behind introducing pseudopotentials into a calculation are a) the simplification of the problem by removing many or most of the electrons from the system, hence a reduction in the number of orbitals that must be calculated, and b) the reduction in the size of the basis set needed to represent those orbitals, due to the less rapid spatial variation of the wavefunctions when they are solutions to a less rapidly varying potential. The idea is founded on the principle that the scattering properties of a localised spherical potential for a plane wave at energy $\varepsilon$ can be described in terms of a phase shift $\eta_l(\varepsilon)$, which determines the scattering cross section and all properties of the wavefunction outside the localised region. Therefore, by replacing one potential with undesirable properties with another one where the same phase shifts modulo $2\pi$ are reproduced but with more favourable properties, one can replace a complicated problem with a much more tractable one.

Generally, one generates *ab initio* pseudopotentials in a stand-alone prior calculation, by solving for the electronic structure of an isolated atom or ion in some particular reference configuration, using the same level of theory as one wishes to use in the full calculation.

The outline of the procedure is as follows:

- Calculate the single-particle orbitals $\psi_i^{AE}(\mathbf{r})$ and effective potential $V_{\text{eff}}(\mathbf{r})$ for the all-electron atom for a chosen reference configuration of the all-electron atom.
- Choose the electrons to be retained as valence electrons. This normally comprises the outermost shell (eg $2s^2 2p^4$ for oxygen) but may include lower subshells if required (such as the $4d$ electrons in titanium).
- From the all-electron orbitals, construct pseudo-orbitals with more favourable properties according to the criteria discussed below.
- 'Invert' the Schrödinger equation to find the Hamiltonian, and thus the effective potential, to which the pseudo-orbitals are solutions. This will now be angular-momentum dependent.

Sounds simple enough, but the difficulty lies in the fact that the choice of how to construct pseudo-orbitals from the all-electron ones is far from unique.

## 2.4 Single Point Energies

We now know that the exact ground-state density of the interacting system may be obtained by solving a non-interacting problem in which the potential $V_{\text{eff}}(\mathbf{r})$ depends self-consistently on the electron density $n(\mathbf{r})$, and we have examined some approaches to representing the single-particle orbitals with which one solves such a problem. Now let us examine the full procedure for a working calculation proceeding via density mixing:

1. Start with a reasonable guess, $n^{\text{in}}(\mathbf{r})$, for the ground-state electron density.
2. Work out the Hartree and XC potentials (within the LDA) for that input density, and hence obtain the effective potential:

$$V_{\text{eff}}([n^{\text{in}}],\mathbf{r}) = V_{\text{nuc}}(\mathbf{r}) + V_{\text{H}}([n^{\text{in}}],\mathbf{r}) + V_{\text{xc}}([n^{\text{in}}],\mathbf{r}) \; . \tag{15}$$

3. Solve the non-interacting Schrödinger equation,

$$\left(-\frac{1}{2}\nabla^2 + V_{\text{eff}}([n^{\text{in}}],\mathbf{r})\right)\psi_i^{\text{out}}(\mathbf{r}) = \epsilon_i \psi_i^{\text{out}}(\mathbf{r}) \; , \tag{16}$$

   to obtain the wavefunctions $\psi_i^{\text{out}}(\mathbf{r})$ and the output density

$$n^{\text{out}}(\mathbf{r}) = \sum_{i\ \text{occ}} |\psi_i^{\text{out}}(\mathbf{r})|^2 \; . \tag{17}$$

   The value of $T[n^{\text{out}}]$ is then given by

$$T[n^{\text{out}}] = \sum_{i\ \text{occ}} \int \left(\psi_i^{\text{out}}(\mathbf{r})\right)^* \left(-\frac{1}{2}\nabla^2\right)\psi_i^{\text{out}}(\mathbf{r}) d\mathbf{r} \; . \tag{18}$$

4. In general, you will find that $n^{\text{out}} \neq n^{\text{in}}$. Set $n^{\text{in}} = n^{\text{out}}$ and return to step 2.
5. Repeat steps 2–4 until the iteration converges and $n^{\text{out}}(\mathbf{r}) = n^{\text{in}}(\mathbf{r})$.
6. Once the iteration has converged, evaluate the energy functional $E[n]$. Gradients of the energy functional with respect to nuclear positions give the forces on the nuclei.

In practice, this simple iteration does not always converge and it is often necessary to use more sophisticated iterative schemes (analogous to the Newton-Raphson method). Once convergence (self-consistency) has been attained, however, the identical input and output densities are both equal to the ground-state density of the interacting system $n_0(\mathbf{r})$.

An alternative approach, more widely used these days, considers how the value of the total energy functional changes as the one-electron orbitals $\psi_i^{\text{out}}(\mathbf{r})$ (and hence the density $n^{\text{out}}(\mathbf{r})$) are varied. Since $E[n^{\text{out}}]$ is minimised when $n^{\text{out}}(\mathbf{r})$ is the true ground-state density, we can seek the ground state directly by varying the members of a set of $N$ orthonormal orbitals until the minimum is found. The minimisation is tackled using a standard downhill optimisation method such as the conjugate gradients algorithm. In effect, when using this approach, the orbitabls $\psi_i^{\text{out}}(\mathbf{r})$ replace the density $n^{\text{out}}(\mathbf{r})$ as the fundamental quantities of the theory.

It can easily be shown that the ground-state energy may also be written as

$$E \;=\; \sum_{i\ \text{occ}} \epsilon_i - \int V_{\text{eff}}(\mathbf{r}) n_0(\mathbf{r})\, d^3r + E_{\text{en}}[n_0] + E_H[n_0] + E_{\text{nn}} + E_{\text{xc}}[n_0]\ . \tag{19}$$

This form is interesting because of what it has to say about the KS energy functional. The total ground-state energy is not just the sum of the one-electron eigenvalues, as might be expected, but includes additional density-dependent terms. Because these involve the density directly, rather than the individual one-electron orbitals, they turn out to be simpler than the sum of eigenvalues and can often be approximated using a pair potential. The non-pairwise chemical bonding contributions mainly arise from the sum of eigenvalues.

## 2.5 Forces

Once a self-consistent energy and a set of single-particle wavefunctions have been determined, calculations of forces in DFT (as in any electronic structure method) usually proceed by application of the Hellmann-Feynman theorem. The Hellmann-Feynman theorem is a particularly elegant description of the force conjugate to any variation in the Hamiltonian. The force $\mathbf{F}_I$ on nucleus $I$, at position $\mathbf{R}_I$, can always be written

$$\mathbf{F}_I = -\frac{\partial E}{\partial \mathbf{R}_I}\ .$$

For a ground state wavefunction $\Psi$, first order perturbation theory lets us write this force in the form

$$\mathbf{F}_I = -\langle\Psi|\frac{\partial \hat{H}}{\partial \mathbf{R}_I}|\Psi\rangle - \langle\frac{\partial \Psi}{\partial \mathbf{R}_I}|\hat{H}|\Psi\rangle - \langle\Psi|\hat{H}|\frac{\partial \Psi}{\partial \mathbf{R}_I}\rangle\ .$$

At the ground state $\Psi$, the energy $E$ is already minimised w.r.t. any variations in$\Psi$, so the linear terms $\partial\Psi/\partial\mathbf{R}_I$ must be zero, giving the appealing result that the force depends solely on the change in the Hamiltonian:

$$\mathbf{F}_I = -\langle\Psi|\frac{\partial\hat{H}}{\partial\mathbf{R}_I}|\Psi\rangle \ . \tag{20}$$

Similar results can be obtained for other parameterizations of the Hamiltonian. Furthermore, if we can decompose the energy in the usual way (i.e. in the presence of local potentials only):

$$E = \langle\Psi|\hat{H}|\Psi\rangle = \langle\hat{T}\rangle + \langle\hat{V}_{\mathrm{ee}}\rangle + \int V_{\mathrm{ext}}(\mathbf{r})n(\mathbf{r})\,\mathrm{d}\mathbf{r} + E_{II} \ ,$$

then the change in the Hamiltonian only affects the latter two terms, and thus only on the density and the nuclear positions

$$\mathbf{F}_I = -\int \frac{\partial V_{\mathrm{ext}}(\mathbf{r})}{\partial\mathbf{R}_I}n(\mathbf{r})\mathrm{d}\mathbf{r} - \frac{\partial E_{II}}{\partial\mathbf{R}_I} \ ,$$

not on the details of the wavefunction. Unfortunately, in the presence of nonlocal pseudopotentials this is no longer true, but Eq.20 still holds and the nonlocal terms are relatively simple to evaluate with most choices of basis set. These forces provide the vital information required for almost all the real-world uses of DFT, including geometry optimisation, molecular dynamics, phonon calculations, transition state searches and many more.

## 2.6 The Hohenberg-Kohn Theorems

The foundation that density functional theory is build upon is an *exact* mapping from a system of interacting electrons to a system of non-interacting electrons moving in an effective potential which is a functional of the electron density [1]. The explanation given above is founded on a pair of theorems by Hohenberg and Kohn, which state that for a given external potential $v_{\mathrm{ext}}(\mathbf{r})$ acting on a many-electron system, it is possible to define a functional $E_{\mathrm{HK}}[n]$ of the electron density $n(\mathbf{r})$ which is minimized and equal to the exact ground state energy when $n(\mathbf{r})$ is the ground state electron density, and that for a given number of interacting particles in an external potential $v_{\mathrm{ext}}(\mathbf{r})$, this potential is uniquely determined by the ground state density $n(\mathbf{r})$. The theory was extended to spin polarized systems by von Barth and Hedin, in terms of a unique functional of the spin density $E\left[n^{\uparrow}(\mathbf{r}), n^{\downarrow}(\mathbf{r})\right]$. Reviews of density functional theory focusing on different areas can be found by, among others: Jones and Gunnarsson, 1989; Dreizler and Gross, 1990; and Gross, Runge, and Heinonen, 1991.

Proof that $n(\mathbf{r})$ uniquely determines $v_{ext}(\mathbf{r})$ proceeds by contradiction: assume that there are two external potentials $v_{ext}^{(1)}(\mathbf{r})$ and $v_{ext}^{(2)}(\mathbf{r})$ which differ by more than a constant, producing different Hamiltonians $\hat{H}^{(1)}$ and $\hat{H}^{(2)}$, which thus have different ground state wavefunctions $\Psi^{(1)}$ and $\Psi^{(2)}$. Then, because $\Psi^{(2)}$ is not the ground state of $\hat{H}^{(1)}$, the variational principle demands that

$$E^{(1)} = \langle\Psi^{(1)}|\hat{H}^{(1)}|\Psi^{(1)}\rangle < \langle\Psi^{(2)}|\hat{H}^{(1)}|\Psi^{(2)}\rangle \ . \tag{21}$$

The assumption of strict inequality is discussed further in [**?**], and the result can be generalized to degenerate cases where this cannot be assumed. We write the last term of Eq. 21 as

$$\langle \Psi^{(2)} | \hat{H}^{(1)} | \Psi^{(2)} \rangle = \langle \Psi^{(2)} | \hat{H}^{(2)} | \Psi^{(2)} \rangle - \langle \Psi^{(2)} | \hat{H}^{(2)} - \hat{H}^{(1)} | \Psi^{(2)} \rangle \ . \tag{22}$$

The interactions between particles are identical in both Hamiltonians, so only the interaction of the density with the external potential differs, giving

$$E^{(1)} < E^{(2)} + \int \mathrm{d}^3\mathbf{r} \ \left[ v_{\mathrm{ext}}^{(1)}(\mathbf{r}) - v_{\mathrm{ext}}^{(2)}(\mathbf{r}) \right] n(\mathbf{r}) \tag{23}$$

Interchanging the subscripts also gives us

$$E^{(2)} < E^{(1)} + \int \mathrm{d}^3\mathbf{r} \ \left[ v_{\mathrm{ext}}^{(2)}(\mathbf{r}) - v_{\mathrm{ext}}^{(1)}(\mathbf{r}) \right] n(\mathbf{r}) \tag{24}$$

Adding the two together gives the evidently contradictory result $E^{(1)}+E^{(2)} < E^{(1)}+E^{(2)}$, completing the proof. Crucially, this also ensures that the ground state wavefunction itself, and thus all the properties of the system, are uniquely determined by $n(\mathbf{r})$.

Proof of the second theorem, that there exists a universal functional for the energy $E[n(\mathbf{r})]$, proceeds by a similar approach: Since all properties are uniquely determined by $n(\mathbf{r})$, then individually each property, such as kinetic energy, total energy, must also be individually functionals of $n(\mathbf{r})$, so we can write:

$$E_{\mathrm{HK}}[n] = T[n] + E_{\mathrm{int}}[n] + E_{\mathrm{ext}}[n] + E_{II} \ .$$

Because $T[n]+E_{\mathrm{int}}[n]$ have no dependence on the external potential, they must constitute a *universal* functional of $n$, $F_{\mathrm{HK}}[n] = T[n] + E_{\mathrm{int}}[n]$, the same for all possible electron systems. Now consider a system with density $n^{(1)}(\mathbf{r})$ corresponding to $v_{\mathrm{ext}}^{(1)}(\mathbf{r})$: the expectation value of the Hamiltonian in the unique ground state of this potential has wavefunction $\Psi^{(1)}$ and energy

$$E^{(1)} = E_{\mathrm{HK}}[n^{(1)}] = \langle \Psi^{(1)} | \hat{H}^{(1)} | \Psi^{(1)} \rangle$$

Now consider a different density $n^{(2)}$ corresponding to a different wavefunction $\Psi^{(2)}$. We can see immediately that the energy of this state is greater than $E^{(1)}$, because

$$E^{(1)} = \langle \Psi^{(1)} | \hat{H}^{(1)} | \Psi^{(1)} \rangle < \langle \Psi^{(2)} | \hat{H}^{(1)} | \Psi^{(2)} \rangle = E^{(2)}$$

The original Hohenberg-Kohn proof only applied to a certain subset of possible densities: those that are the ground state density of the electron Hamiltonian with some external potential $v_{\mathrm{ext}}(\mathbf{r})$, also known as “V-representable”. It was later extended to the more general class of “N-representable” densities — those that are derivable from any valid $N$-electron wavefunction $\Psi_N$ — by the approach of Levy and Lieb involving a constrained search over the space of wavefunctions that produce a particular density.

# References

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[2] W. Kohn and L.J. Sham, Phys. Rev. **140**, 1133 (1965).