Physics 514 – Density functional theory

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Chapter 1

Density functional theory

1.1 Introduction

Density functional theory is one of the most frequently used methods for simulating fermionic quantum many-body systems. It has been used in quantum chemistry and physics since the early 1970ies, for the simulation of weakly correlated molecules and solids. The 1998 nobel prize in Chemistry was awarded to Walter Kohn 'for the development of density functional theory'

1.2 Hohenberg-Kohn theorem

In 1963, Pierre Hohenberg and Walter Kohn proved that the density $n(r)$ completely characterizes a quantum mechanical system, so that an exact description of the ground state properties in therms of $n(r)$ is, at least in principle, possible. The general proof is remarkably simple, and we present it here for a non-degenerate ground state.[1]

Let $n(r)$ be the ground state density for N electrons in an external potential $v_1(r)$, corresponding to the ground state wave function ψ_1 and ground state energy E_1. Then

$$E_1 = \langle \psi_1 | H_1 | \psi_1 \rangle = \int d^3 r v_1(r) n(r) + \langle \psi_1 | T + V | \psi_1 \rangle. \qquad (1.1)$$

here H_1 is the total Hamilton operator corresponding to the potential v_1, T is the kinetic energy operator, and U the interaction energy operator describing the electron-electron interaction. Now assume that there exists a second potential $v_2(r) \neq v_1(r) + const$ with the ground state wave function $\psi_2(r) \neq e^{-\phi}\psi_1(r)$, corresponding to the same density $n(r)$ (with some arbitrary phase ϕ). Then

$$E_2 = \langle \psi_2 | H_2 | \psi_2 \rangle = \int d^3 r v_2(r) n(r) + \langle \psi_2 | T + V | \psi_2 \rangle. \qquad (1.2)$$

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[1] See also the 1998 nobel lecture of Walter Kohn, which provides a nice overview of density functional theory: http://nobelprize.org/chemistry/laureates/1998/kohn-lecture.pdf

Since ψ_1 is assumed to be non-degenerate,

$$E_1 < \langle\psi_2|H_1|\psi_2\rangle = \int d^3 r v_1(r)n(r) + \langle\psi_2|T+U|\psi_2\rangle \tag{1.3}$$

$$= E_2 + \int d^3 r(v_1(r) - v_2(r))n(r).$$

Similarly,

$$E_2 \leq \langle\psi_1|H_2|\psi_1\rangle = \int d^3 r v_2(r)n(r) + \langle\psi_1|T+U|\psi_1\rangle \tag{1.4}$$

$$= E_1 + \int d^3 r(v_2(r) - v_1(r))n(r).$$

Adding these two equations leads to the contradiction

$$E_1 + E_2 < E_2 + E_1 \tag{1.5}$$

and we must conclude that the assumption of the existence of a second potential $v_2 \neq v_1 + const$ giving the same $n(r)$ must be wrong.

Since $n(r)$ determines both the total particle number N and (up to an irrelevant constant) $v(r)$ it provides the Hamiltonian and particle number of the system. Therefore, $n(r)$ implicitly determines all the properties which can be derived from H via the solution of the Schrödinger equation.

1.3   Hohenberg-Kohn variational principle

The ground state energy can be calculated by finding the $\tilde{\psi}$ that minimizes the energy E:

$$E = \min_{\tilde{\psi}}\langle\tilde{\psi}|H|\tilde{\psi}\rangle \tag{1.6}$$

where $\tilde{\psi}$ is a normalized trial wave function corresponding to N electrons. Following Levy and Lieb, we can carry out this minimization in two steps: First, we fix a trial density $\tilde{n}(r)$ and denote by $\tilde{\psi}_{\tilde{n}}^{\alpha}$ the trial functions corresponding to this $\tilde{n}(r)$, with α a parameter enumerating all possible trial wave functions for that $\tilde{n}(r)$. The constrained energy minimum, with $\tilde{n}$ fixed, is then defined as

$$E^{LL}[\tilde{n}] \equiv \min_{\alpha}\langle\tilde{\psi}_{\tilde{n}}^{\alpha}|H|\tilde{\psi}_{\tilde{n}}^{\alpha}\rangle = \int d^3 r v(r)\tilde{n}(r) + F[\tilde{n}], \tag{1.7}$$

$$F[\tilde{n}] \equiv \min_{\alpha}\langle\tilde{\psi}_{\tilde{n}}^{\alpha}|T+U|\tilde{\psi}_{\tilde{n}}^{\alpha}\rangle. \tag{1.8}$$

In a second step, E^{LL} is mimimized over all $\tilde{n}$:

$$E = \min_{\tilde{n}} E^{LL}[\tilde{n}] = \min_{\tilde{n}}\left[\int d^3 r v(r)\tilde{n}(r) + F[\tilde{n}(r)]\right] \tag{1.9}$$

Equation 1.8 gives a definition of the *universal* functional of the density $F[\tilde{n}]$ as the sum of the kinetic and the interaction energy associated with $\tilde{n}$. F is universal in the sense that $F[\tilde{n}]$ does not contain any information on the external potential $v(r)$. While this definition involving an integration over a $3N$ dimensional trial wave function leads back to the unsolvable Schödinger equation, important formal progress has nevertheless been made. We now have an *exact* formulation of the ground state densities and energies entirely in terms of the density distribution $\tilde{n}(r)$ and of a unique, though not explicitly known functional of the density $F[\tilde{n}]$. The practical relevance of this formulation will depend on whether useful approximate forms of $F[\tilde{n}]$ can be found.

1.4 Kohn-Sham equations

In 1965, W. Kohn and his postdoc L. Sham extracted a set of Hartree-like, but formally exact equations from the Hohenberg-Kohn variational principle. The Hartree-Fock equations have the form of a Schrödinger equation for non-interacting particles moving in an effective external potential v_{eff}. A simple derivation of the Kohn-Sham equations makes use of the analogy to the non-interacting model to define v_{eff}.

In the non-interacting case ($U = 0$), the ground state energy and density of N particles moving in an external potential $v(r)$ can be obtained by calculating the eigenfunctions ϕ_j and eigenvalues ϵ_j of the non-interacting single-particle equation

$$\left(-\frac{1}{2}\nabla^2 + v(r) \right) \phi_j = \epsilon_j \phi_j \tag{1.10}$$

Taking into account the spin of electrons (and assuming a closed shell configuration, i.e. even number of particles), we obtain the energy and density

$$E = 2\sum_{j=1}^{N/2} \epsilon_j, \tag{1.11}$$

$$n(r) = 2\sum_{j=1}^{N/2} |\psi_j|^2 \tag{1.12}$$

On the other hand, for the non-interacting system, the Hohenberg-Kohn variational principle reads

$$E \leq E^{LL}[\tilde{n}] = \int d^3r\, v(r)\tilde{n}(r) + T^{\text{non-int}}[\tilde{n}], \tag{1.13}$$

where $T^{\text{non-int}}$ is the kinetic energy of the ground state of non-interacting fermions with density $\tilde{n}$. The minimum of E^{LL} under the constraint

$$\int d^3r\, \tilde{n}(r) = N \tag{1.14}$$

is computed using a Lagrange multiplier ϵ. The stationary point with respect to variations in $\tilde{n}(r)$ satisfies

$$v(r) + \left.\frac{\delta}{\delta \tilde{n}(r)} T^{\text{non-int}}[\tilde{n}(r)]\right|_{\tilde{n}=n} - \epsilon = 0. \tag{1.15}$$

We now return to the interacting problem and express the universal functional $F[\tilde{n}]$ in the form

$$F[\tilde{n}(r)] \equiv T^{\text{non-int}}[\tilde{n}(r)] + \frac{1}{2} \iint d^3r d^3r' \frac{n(r)n(r')}{|r-r'|} + E_{\text{xc}}[\tilde{n}(r)]. \tag{1.16}$$

This equation, in which we have separated the kinetic energy functional for the non-interacting electrons and the Hartree energy, *defines* the so-called exchange correlation functional $E_{\text{xc}}[\tilde{n}]$. The Hohenberg-Kohn variational principle for interacting electrons then takes the form

$$E \leq E^{LL}[\tilde{n}] = \int d^3r v(r)n(r) + T^{\text{non-int}}[\tilde{n}] + \frac{1}{2} \iint d^3r d^3r' \frac{n(r)n(r')}{|r-r'|} + E_{\text{xc}}[\tilde{n}(r)] \tag{1.17}$$

and the Euler-Lagrange equation is satisfied for

$$v_{\text{eff}}(r) + \left.\frac{\delta}{\delta \tilde{n}(r)} T^{\text{non-int}}[\tilde{n}(r)]\right|_{\tilde{n}=n} - \epsilon = 0 \tag{1.18}$$

where

$$v_{\text{eff}}(r) = v(r) + \int d^3r' \frac{n(r')}{|r-r'|} + v_{xc}(r), \tag{1.19}$$

$$v_{xc}(r) \equiv \left.\frac{\delta}{\delta \tilde{n}(r)} E_{\text{xc}}[\tilde{n}(r)]\right|_{\tilde{n}=n} \tag{1.20}$$

Note here that the form of the interacting equation Eq. 1.18 is identical to the non-interacting one, Eq. 1.15, except that the external potential $v(r)$ is replaced by some effective potential Eq. 1.19. Therefore the ground state density $n(r)$ can be obtained by solving the single particle equation

$$\left(-\frac{1}{2}\nabla^2 + v_{\text{eff}} - \epsilon_j\right)\phi_j = 0, \tag{1.21}$$

$$n(r) = 2\sum_{j=1}^{N/2} |\phi_j(r)|^2, \tag{1.22}$$

$$v_{\text{eff}} = v(r) + \int dr' \frac{n(r')}{|r-r'|} + v_{\text{xc}}(r). \tag{1.23}$$

The self-consistent equations Eq. 1.21, 1.22, and 1.23 are called the Kohn-Sham equations. They build the basis of all practical implementations of density functional theory. Note that the exchange-correlation potential defined in Eq. 1.19 depends on the entire density distribution and is still unknown.

Neither the wave functions ϕ_j nor the eigenenergies ϵ_j have any obvious physical interpretation, except that the ϕ_j give the true ground state energy via Eq. 1.22, and that the highest occupied ϵ_j is related to the ionization energy. Nevertheless, in solid-state physics the ϵ_j are often used to obtain an approximate band structure.

1.5 Local density approximation (LDA)

The real importance of the Kohn-Sham formulation of the many-body problem in terms of an auxiliary independent particle problem lies in the fact that it enables useful approximations. The kinetic energy term (of the non-interacting effective model) is taken care of explicitly, so the approximations can be limited to the exchange-correlation functional $E_{\text{xc}}[n]$ or the corresponding exchange-correlation potential v_{xc}. The most important approximations have a quasi-local form:

$$E_{\text{xc}}[n(r)] = \int d^3r\, e_{\text{xc}}(r; n[\tilde{r}])n(r), \tag{1.24}$$

where $e_{\text{xc}}(r; n[\tilde{r}])$ denotes an exchange-correlation energy per particle at r which is a functional of the density distribution $n(\tilde{r})$ in the vicinity of r.

The simplest approximation is the so-called *local density approximation* or LDA, which was introduced in the original paper by Kohn and Sham. Here, one uses the exchange correlation energy of a uniform electron gas of density n, $e_{\text{xc}}^{\text{uniform}}(n(r))$, which is function (rather than a functional) of $n(r)$:

$$E_{\text{xc}}^{LDA}[n(r)] \equiv \int d^3r\, e_{\text{xc}}^{\text{uniform}}(n(r))n(r). \tag{1.25}$$

The exchange energy of the uniform electron gas can be calculated analytically and evaluates to:

$$e_x^{\text{uniform}}(n) = -\frac{3}{4\pi}k_F(n) = -\frac{3}{4\pi}\left(\frac{9\pi}{4}\right)^{1/3}\frac{1}{r_s} = \frac{-0.458}{r_s} \tag{1.26}$$

where the density is expressed in terms of the radius r_s of a sphere containing one electron: $(4\pi/3)r_s^3 = 1/n$. The correlation energy has to be obtained by fitting to quantum Monte Carlo results for several values of n. A widely used form is due to Perdew and Zunger,

$$e_c^{\text{uniform}} \approx \begin{cases} -0.048 + 0.031\ln(r_s) - 0.0116r_s + 0.0002r_s\ln(r_s), & r_s < 1 \\ -0.142/(1 + 1.953\sqrt{r_s} + 0.333r_s), & r_s > 1 \end{cases} \tag{1.27}$$

LDA is exact for the uniform electron gas and one might expect that its application is restricted to systems characterized by a slowly varying density. However, it seems that this approximation works much better than anyone (including its creators) anticipated, and gives reasonable results even in atomic

systems with large density variations. Today, LDA is the basis of most of the material science, solid state, and quantum chemistry density functional simulations.

1.5.1   Beyond LDA

Improvements of the LDA have been an intense field of research in quantum chemistry and materials science. The 'local spin density approximation' (LSDA) uses separate densities for electrons with spin up and down. The 'generalized gradient approximation' (GGA) and its variants use functions that depend both on the local density and on the density derivative:

$$E_{xc}^{LDA}[n(r)] = \int dr e_{xc}^{\mathrm{uniform}}(n(r))n(r), \tag{1.28}$$

$$E_{xc}^{GGA}[n(r)] = \int dr f^{(1)}(n(r), |\nabla n(r)|)n(r). \tag{1.29}$$

The GGA functional is still a function, not a functional, of n and ∇n. It increases bonding energies for small molecules by a factor of 3-5.

Despite the success of LDA and its generalizations, one must keep in mind that these approximations can fail completely in situations which lack any resemblance to a non-interacting electron gas. This is the case for strongly correlated electron systems (e.g. transition metal compounds or actinides, as well as many low-dimensional systems), where electrons often occupy partially filled, narrow d and f orbitals. These must then be treated with other methods.