

Notes on Density Functional Theory

1 Basic Theorems

The energy, E , of a system with a given Hamiltonian H is a *functional* of the (normalized, many-particle) wave function Ψ . We write this functional as

$$E[\{\psi\}] = \langle \Psi | H | \Psi \rangle \quad (1)$$

and you recall that the meaning of Eq 1 is "take Ψ , act on it with H , multiply by the complex conjugate of Ψ and integrate over all space".

Consider now a system of N electrons moving in a fixed potential $V(r)$ defined for example by some atomic nuclei, and interacting with each other via the Coulomb interaction. The Hamiltonian is then

$$H = \sum_{i=1\dots N} \frac{\hat{p}_i^2}{2m} + \frac{1}{2} \sum_{i \neq j} \frac{e^2}{|r_i - r_j|} + \sum_{i=1\dots N} V(r_i) \quad (2)$$

$$= H_{electron-gas} + \sum_{i=1\dots N} V(r_i) \quad (3)$$

where $H_{electron-gas}$ is the part which is independent of V .

Observe that the *ground state* energy E_{GS} is a well-defined functional of $V(r)$: $E_{GS} = \Phi_V[\{V(r)\}]$. The slightly convoluted definition is: take V , solve the Schroedinger equation for the ground state Ψ , and put this ψ in Eq 1. Thus, you give me V and this uniquely (up to obvious degeneracies) fixes E_{GS} .

The particle density is defined by

$$n(r) = \int d^3r_1 \dots d^3r_N \Psi^*(r_1, \dots, r_N) \left(\sum_{i=1\dots N} \delta(r - r_i) \right) \Psi(r_1, \dots, r_N) \quad (4)$$

and using this definition we have

$$E[\{\psi\}] = \langle \Psi | \sum_{i=1\dots N} \frac{\hat{p}_i^2}{2m} + \frac{1}{2} \sum_{i \neq j} \frac{e^2}{|r_i - r_j|} | \Psi \rangle + \int d^3r V(r) n(r) \quad (5)$$

Hohenberg and Kohn showed that E_{GS} is a unique functional $n(r)$. The argument is deceptively simple: assume the contrary: then there must be two energies corresponding to the same $n(r)$; in other words there must exist two Ψ 's, which are different (by more than an overall phase), hence have different energies, but lead to the same particle density. Call these Ψ_1 and Ψ_2 . Because they are different they must solve the Schroedinger equation with different V 's, say V_1 and V_2 , thus

$$(H_{electron-gas} + V_1) \Psi_1 = E_1 \Psi_1 \quad (6)$$

$$(H_{electron-gas} + V_2) \Psi_2 = E_2 \Psi_2 \quad (7)$$

Now consider the energy you would get if you used Ψ_2 as a variational wave function for $H_{electron-gas} + V_1$. Because Ψ_2 is not the ground state of this Hamiltonian you must get an energy greater than E_1 , thus

$$\langle \Psi_2 | H_{electron-gas} + V_1 | \Psi_2 \rangle = E_1^2 > E_1 \quad (8)$$

But by writing $V_1 = V_2 + (V_1 - V_2)$ and using Eqs 5,7 and the assumption that the two wave functions lead to the same density one finds

$$E_1^2 = E_2 + \int d^3r (V_1(r) - V_2(r)) n(r)$$

so that

$$E_2 - E_1 > \int d^3r (V_2(r) - V_1(r)) n(r) \quad (9)$$

Now repeat the argument, interchanging the roles of 1 and 2. One obtains

$$E_2^1 = E_1 + \int d^3r (V_2(r) - V_1(r)) n(r) > E_2$$

in other words

$$\int d^3r (V_2(r) - V_1(r)) n(r) > E_2 - E_1 \quad (10)$$

Eqs 9, 10 cannot both be true unless $V_2 = V_1$; QED.

We have thus established that the ground state energy is a functional of the density $n(r)$: $E_{GS} = \Phi[\{n(r)\}]$. Again the recipe for finding Φ is rather convoluted: for given $n(r)$ find the $V(r)$ which leads to a ground state with this density, solve the Schroedinger equation, and insert the resulting wave function into Eq 1. This 'definition' makes it obvious that in fact Φ is minimized when $n(r)$ is the ground state density: a density other than the ground state density would lead to a wave function other than the ground state wave function and therefore to an energy higher than the ground state energy—for a given external potential.

Summary: the ground state energy of a system of N electrons in an external potential $V(r)$ is determined by minimizing a functional $\Phi[\{n(r)\}]$. This functional may be written

$$\Phi[\{n(r)\}] = \Phi_{electron-gas}[\{n(r)\}] + \int d^3r V(r) n(r) \quad (11)$$

with $\Phi_{electron-gas}$ given by

$$\Phi_{electron-gas}[\{n(r)\}] = \langle \Psi | \sum_{i=1\dots N} \frac{\hat{p}_i^2}{2m} + \frac{1}{2} \sum_{i \neq j} \frac{e^2}{|r_i - r_j|} | \Psi \rangle \quad (12)$$

with Ψ the exact ground state wave function for the given V .

The virtue of Eq 11 is that $\Phi_{electron-gas}$ makes no explicit reference to $V(r)$: it is a universal functional determined only by the properties of the electron gas. If one can obtain a reasonable approximation to it, and carry out the minimization, then one can use it with *any* $V(r)$.

2 Application

The actual applications of the formalism follow from a second brilliant insight of Kohn, this time with Lu Sham. To understand it, it is helpful to step away from the problem briefly and consider a problem of N noninteracting electrons moving in some potential $V_{KS}(r) = V(r) + V_{eff}(r)$. Because it is noninteracting electrons we know exactly what to do: solve the Schroedinger equation

$$-\frac{\hbar^2}{2m}\nabla^2\psi_i(r) + (V(r) + V_{eff}(r))\psi_i(r) = E_i\psi_i(r) \quad (13)$$

and find the N lowest eigenvalues and eigenfunctions. The wave function Ψ_{KS} is then the properly antisymmetrized product of the N lowest eigenfunctions, the charge density is the sum of the charge density in each occupied eigenfunction

$$n(r) = \sum_{i=1..N} \psi_i^*(r)\psi_i(r) \quad (14)$$

the energy is

$$E_{tot} = \sum_{i=1..N} E_i \quad (15)$$

The key insights of Kohn and Sham are

(1) there exists some $V_{eff}(r)$ which is a property only of the electron gas (and which of course is a functional of $n(r)$), and which, when used in 13, reproduces the exact ground state density and energy for each external potential V .

(2) reasonable approximations to V_{eff} may be constructed.

The simplest such approximation is the 'local density approximation', in which V_{eff} is approximated by the value which would give the right answer for a uniform electron gas at density $n(r)$. The answer for the uniform electron gas is known from detailed numerical studies. The simplest approximation, which describes the electron gas at moderate densities, is

$$V_{LDA-1}(r) = \left(\int d^3r' \frac{e^2 n(r')}{|r - r'|} \right) - V_{XC}(n(r)) \quad (16)$$

The first term in Eq V_{LDA-1} is simply the electric potential which would be produced by the charge density $n(r)$. The second term is a correction coming from more complicated interacting-electron physics.

Much effort over the years has gone into developing improved functionals, both to more accurately represent the energy of the uniform electron gas, and to produce functionals account for non-uniform densities.

3 The algorithm

The algorithm, adapted to the units we have used in class for solving the hydrogen atom, is

For a system of N electrons moving in the external potential

$$V(u) = -\frac{2Z}{u} \quad (17)$$

- (1) Guess a density $n(u)$
- (2) Compute the potential

$$V_{eff}(u) = \left(2 \int d^3u' \frac{e^2 n(u')}{|u - u'|} \right) + V_{XC}(n(u)) \quad (18)$$

Because we will deal only with spherically symmetric distributions of charge, we know that the electrostatic potential at radius u is given by taking the charge at $u' < u$ and concentrating it at the origin, so

$$V_{eff}(u) = \left(\frac{2}{u} \int_0^u u'^2 du' n(u') \right) - V_{XC}(n(u)) \quad (19)$$

You will use two choices of $V_{XC}(n(u))$. One based an old (pre-density functional theory) approximation of Slater is very simple to write down and is

$$V_{slater} = -3 \left[\frac{3}{\pi} n(u) \right]^{1/3} \quad (20)$$

The other is based on a more detailed parametrization of the properties of the uniform electron gas and requires a bit of notation. Define

$$r_s = \left(\frac{4\pi n(u)}{3} \right)^{-1/3} \quad (21)$$

(recall we measured distances in units of the Bohr radius).

Then

$$V_{Perdew} = \frac{0.5 * \gamma_u}{1 + \beta_1 \sqrt{r_s} + \beta_2 r_s} \left[\frac{1 + \frac{7}{6} \beta_1 \sqrt{r_s} + \frac{4}{3} \beta_2 r_s}{1 + \beta_1 \sqrt{r_s} + \beta_2 r_s} \right] \quad (r_s > 1) \quad (22)$$

$$V_{Perdew} = 0.5 \left(A \ln(r_s) + \left(B - \frac{A}{3} \right) + \frac{2}{3} C r_s \ln(r_s) + \frac{2D - C}{3} r_s \right) \quad (r_s < 1) \quad (23)$$

with numbers

$$\gamma = -0.1423 \quad (24)$$

$$\beta_1 = 1.029 \quad (25)$$

$$\beta_2 = 0.3334 \quad (26)$$

$$A = 0.0311 \quad (27)$$

$$B = -0.048 \quad (28)$$

$$C = 0.0020 \quad (29)$$

$$D = -0.0116 \quad (30)$$

(3) Obtain the radial eigenfunctions g_i corresponding to the N lowest eigenvalues of the radial schroedinger equation

$$-\frac{d^2 g_i(u)}{du^2} + (V(u) + V_{eff}(u)) g_i(u) = E_i g_i(u) \quad (31)$$

(4) Get the density (recall $g = r\psi/\sqrt{4\pi}$)

$$n(u) = \sum_{i=1..N} \frac{g_i^*(u)g_i(u)}{u^2} \quad (32)$$

(5) go back to (2) and repeat until the density and ground state energy cease to change significantly.

(6) Compute the ground state energy from

$$E = \sum_{i=1..N} E_i \quad (33)$$