APPENDIX A

FUNCTIONAL.

A function is a rule for taking a number as an input and giving a number as an output. Likewise a functional is a rule for taking a function as an input and giving a number as output. An example of a functional is the particle number

$$N[\rho(r)] = \int \rho(r) dr \tag{1}$$

The particle number functional, $N[\rho(r)]$, takes a function (the electron density) as its input and gives a number (the number of particles) as its output. Other good examples of functional might be the average temperature during a day.

$$\langle T \rangle [T(t)] = \int_{t=0}^{t=24hr} \frac{T(t)}{24h} dt \tag{2}$$

And the expectation value of the kinetic energy for a quantum system

$$K[\psi(r)] = \int \psi(r)^* \left(-\frac{1}{2} \nabla^2 \right) \psi(r) dr \tag{3}$$

Functionals have their own type of differentiation rule. The functional derivative $\frac{\delta F[\rho(r)]}{\delta \rho(r)}$ of the function $F[\rho(r)]$ is defined as

$$\Delta F[\rho(r)] \equiv \int \frac{\delta F[\rho(r)]}{\delta \rho(r)} \Delta \rho(r) dr \tag{4}$$

where Δ represents an infinitesimally small change (Δ was chosen instead of δ to avoid confusion with the δ's used in the notation for the functional derivative). As an example we know that the particle number N is given as

$$N[\rho(r)] = \int \rho(r) dr \tag{5}$$

So,

$$\Delta N[\rho(r)] = \int ((\rho(r) + \Delta\rho(r)) - \rho(r)) dr = \int \Delta\rho(r) dr \tag{6}$$

and

$$\frac{\delta N[\rho(r)]}{\delta\rho(r)} = 1 \tag{7}$$

Likewise the contribution to the energy eigenvalue from the external potential is

$$V_{ne}[\rho(r)] = \int \rho(r)\upsilon(r) dr \tag{8}$$

so,

$$\Delta V_{ne}[\rho(r)] = \int [(\rho(r) + \Delta\rho(r)) - \rho(r)]\upsilon(r) dr = \int \Delta\rho(r)\upsilon(r) dr$$
(9)

$$\frac{\delta V_{ne}[\rho(r)]}{\delta\rho(r)} = \upsilon(r) \tag{10}$$

As we can see from the last example and the definition (4), the functional derivative does not have to be constant with respect to position. Additionally, it may also depend on the function, $\rho(\vec{r})$, at which it is evaluated. For instance if we have a functional

$$A[\rho(r)] = \int f(r)[\rho(r)]^2 dr$$

then,

$$\Delta A[\rho(r)] = \int f(r)([\rho(r)]^2 + 2\rho(r)[\Delta\rho(r)] + [\Delta\rho(r)]^2 - [\rho(r)]^2) d\vec{r}$$

So the functional becomes,

$$\frac{\delta A}{\delta\rho} = 2\rho(r)f(r)$$

As we saw in the previous section, a density can only be the ground state density of maximum one external potential. If $\rho(r)$ corresponds to the ground state we can therefore unambiguously define the energy functional

$$E[\rho(r)] \equiv \langle \psi \mid \widehat{H} \mid \psi \rangle$$

Where ψ denotes the ground state corresponding $\rho(r)$ and $\widehat{H}$ is the Hamiltonian yielding this ground state.

APPENDIX B

PROOF OF HOHENBERG AND KOHN THEOREMS

THEOREM 1. The external potential is determined by the electron density and for a given density there will be a single external potential.

Proof:

Let us assume that $\rho(r)$ is the ground state density of a system of electrons. Let us also assume that there are two potentials V_1 and V_2 which produces two different Hamiltonian H_1 and H_2 respectively as

$$H_1 = V_1 + T + V_{ee}$$

and,

$$H_2 = V_2 + T + V_{ee}$$

Again we assume that there are two wave functions ψ_1 and ψ_2 that produce the same density $\rho(r)$. Therefore,

$$E_1 = \langle \psi_1 \mid H \mid \psi_1 \rangle \langle \psi_2 \mid H \mid \psi_2 \rangle \tag{1}$$

Now, we consider the term,

$$\langle \psi_2 \mid H_1 \mid \psi_2 \rangle = \langle \psi_2 \mid H_2 - H_2 + H_1 \mid \psi_2 \rangle$$

$$\langle \psi_2 \mid H_1 \mid \psi_2 \rangle = \langle \psi_2 \mid H_2 \mid \psi_2 \rangle + \langle \psi_2 \mid H_1 - H_2 \mid \psi_2 \rangle$$

$$\langle \psi_2 \mid H_1 \mid \psi_2 \rangle = E_2 + \langle \psi_2 \mid V_1 - V_2 \mid \psi_2 \rangle \tag{2}$$

Thus equation (1) becomes,

$$E_1 < E_2 + \int \rho(r)[V_1 - V_2] d^3 r \tag{3}$$

Similarly,

$$E_2 = \langle \psi_2 | H_2 | \psi_2 \rangle < \langle \psi_1 | H_2 | \psi_1 \rangle$$

Considering the term,

$$\langle \psi_1 | H_2 | \psi_1 \rangle = \langle \psi_1 | H_1 - H_1 + H_2 | \psi_1 \rangle$$

$$\langle \psi_1 | H_2 | \psi_1 \rangle = \langle \psi_1 | H_1 | \psi_1 \rangle + \langle \psi_1 | H_2 - H_1 | \psi_1 \rangle$$

$$\langle \psi_1 | H_2 | \psi_1 \rangle = E_1 + \int \rho(r) [V_2 - V_1] d^3 r$$

$$\langle \psi_1 | H_2 | \psi_1 \rangle = E_1 - \int \rho(r) [V_1 - V_2] d^3 r$$

Thus equation (3) becomes,

$$E_2 < E_1 - \int \rho(r) [V_1 - V_2] d^3 r \tag{4}$$

Adding equation (2) and (4) we get,

$$E_1 + E_2 < E_2 + E_1 \tag{5}$$

This equation is naturally not correct and contradictory to each other. This is due to the fact that we considered two potential V_1 and V_2 for a given potential $\rho(r)$.

Hence we conclude that there cannot be two external potential for a single $\rho(r)$.

Theorem 2. The functional $F_{HK}[\rho] = T[\rho] + V_{ee}[\rho]$ determines the ground state energy if and only if the input density is the true ground state density.

Proof:

Let us assume that $\rho(r)$ is the ground state density for the system of electron. Then the ground state energy functional is

$$E[\rho] = \int \rho(r) V_{ext}(r) d^3 r + F_{HK}[\rho]$$

Here, $F_{HK}[\rho] = T[\rho] + V_{ee}[\rho]$ is the universal functional.

Let us consider a trial density $\tilde{\rho}(r)$ that determines its own $\tilde{V}_{ext}(r)$, the Hamiltonian $\tilde{H}$ and $\tilde{\psi}$.

Let us take $\widetilde{\psi}$ as trial function of the Hamiltonian H of the ground state density $\rho(r)$.

Then, $E[\rho] \le \left\langle \widetilde{\psi} \mid H \mid \widetilde{\psi} \right\rangle$

Now,

$$\left\langle \widetilde{\psi} \mid H \mid \widetilde{\psi} \mid \right\rangle = \left\langle \widetilde{\psi} \mid V_{ext}(r) \mid \widetilde{\psi} \right\rangle + \left\langle \widetilde{\psi} \mid -\frac{1}{2}\nabla^2 + V_{ee} \mid \widetilde{\psi} \right\rangle$$

$$\left\langle \widetilde{\psi} \mid H \mid \widetilde{\psi} \mid \right\rangle = \int \widetilde{\rho} V_{ext}(r) d^3 r + T[\widetilde{\rho}] + V_{ee}[\widetilde{\rho}]$$

$$\left\langle \widetilde{\psi} \mid H \mid \widetilde{\psi} \mid \right\rangle = \int \widetilde{\rho} V_{ext}(r) d^3 + F_{HK}[\widetilde{\rho}]$$

$$\left\langle \widetilde{\psi} \mid H \mid \widetilde{\psi} \mid \right\rangle = E[\widetilde{\rho}]$$

where, $F_{HK}[\widetilde{\rho}] = T[\widetilde{\rho}] + V_{ee}[\widetilde{\rho}]$

so, $E[\rho] \le E[\widetilde{\rho}]$

Thus, the functional $F_{HK}[\rho]$ delivers the ground state energy if and only if input density is the true ground state density.

APPENDIX C

DEDUCTION OF KOHN SHAM EQUATION

The total energy,

$$E[\rho] = \frac{1}{2}\sum_i \langle \phi_i \mid \nabla^2 \mid \phi_i \rangle + \frac{1}{2}\iint \frac{\rho(r)\rho(r')}{|r-r'|}drdr' + \int \upsilon_{ext}\rho dr + E_{XC}[\rho] \tag{1}$$

Let us apply the variational principle with the constraints that all the integrals,

$$I_K = \int \phi_i^*(r)\phi_i(r)dr = 1 \tag{2}$$

For this we follow the following steps:

Step 1:

First term in equation 1

$$-\frac{1}{2}\sum_i \langle \phi_i \mid \nabla^2 \mid \phi_i \rangle$$

The orbital function ϕ_K tem in this summation is

$$-\frac{1}{2}\langle \phi_K(r) \mid \nabla^2 \mid \phi_K(r)\rangle$$

$$= -\frac{1}{2}\int \phi_K^*(r)\nabla^2\phi_K(r)dr$$

$$= \int \phi_K^*(r)\left(-\frac{1}{2}\nabla^2\right)\phi_K(r)dr$$

Second term in equation (1):

$$\frac{1}{2}\iint \frac{\rho(r)\rho(r')}{|r-r'|}drdr'$$

$$= \frac{1}{2} \sum_i \iint \frac{\phi_i^*(r)\phi_i(r)\rho(r')}{|r-r'|} dr dr'$$

The orbital function $\phi_K(r) \dfrac{\rho(r')}{|r-r'|} \phi_K(r) dr dr'$

3rd term in the equation (1)

$$\int \upsilon_{ext}(r)\rho(r)dr$$

$$= \sum_i \int \upsilon_{ext}(r)\phi_i^*(r)\phi_i(r)dr$$

The orbital function $\phi_K(r)$ term in this summation is

$$\int \phi_K^*(r)\upsilon_{ext}(r)\phi_K(r)dr$$

Fourth term equation (1) is

$$E_{XC}[\rho] = \int \upsilon_{XC}(r)\rho(r)dr$$

$$= \sum_i \upsilon_{exc}(r)\phi_i^*(r)\phi_i(r)dr$$

The orbital function $\phi_K(r)$ term in the summation is

$$\int \phi_K^*(r)\upsilon_{exc}(r)\phi_K(r)dr$$

Step 2:

By variational principle,

$$\delta[E[\rho] - E_K I_K] = 0$$

Where E_K are Lagrange multipliers which is to be determined.

$$\delta E[\rho] - E_K \delta I_K = 0$$

Step 3:

$$I_K = \int \phi_K^*(r)\phi_k(r)dr$$

$$I_K + \delta I_K = \int \left(\phi_K^* + \delta\phi_K^*\right)\left(\phi_K + \delta\phi_K\right)dr$$

$$= I_K + \delta I_K = \int \phi_K^*(r)\phi_K(r)dr + \int \phi_K^*(r)\delta\phi_K(r)dr + \int \delta\phi_K^*(r)\phi_K(r)dr + \int \delta\phi_K^*(r)\delta\phi_K(r)$$

i.e. $\delta I_K = \int \delta\phi_K^*(r)\phi_K(r)dr + \int \phi_K^*(r)\delta\phi_K(r)dr$

Step 4:

Considering the variation in $\phi_K(r)$ and the term containing $\phi_K^*(r)$, we can write,

$\delta E[\rho] - E_K\delta I_K = 0$ as,

$$\int \delta\phi_K(r)\left(-\frac{1}{2}\nabla^2\right)\phi_K(r)dr$$

The term containing $\delta\phi_K^*(r)$ in the second term variation is,

$$\frac{1}{2}\iint \delta\phi_K^*(r)\frac{\rho(r')}{|r-r'|}\phi_K(r)drdr' + \frac{1}{2}\iint \delta\phi_K^*(r')\frac{\rho(r)}{|r-r'|}\phi_K(r')drdr'$$

It can be written as,

$$\int \delta\phi_K^*(r)\frac{\rho(r)}{|r-r'|}\phi_K(r)drdr'$$

The term containing $\delta\phi_K^*(r)$ in the third term variation is,

$$\int \delta\phi_K^*(r)\upsilon_{ext}(r)\phi_K(r)dr$$

The term containing $\delta\phi_K^*(r)$ in the fourth term variation is,

$$\int \delta\phi_K^*(r)\upsilon_{exc}(r)\phi_K(r)dr$$

And the term containing $\delta\phi_K^*(r)$ in the constraint variation is,

$$\delta I_K = \int \delta\phi_K^*(r)\phi_K(r)dr$$

Thus, we can write the equation of variation,

$$\delta E[\rho] - E_K \delta I_K = 0 .$$

Hence $\delta\phi_K^*(r)$ can be written as,

$$\int \delta\phi_K^*(r)\left(-\frac{1}{2}\nabla^2\right)\phi_K(r)dr + \iint \delta\phi_K^*(r)\frac{\rho(r')}{|r-r'|}\phi_K(r)drdr' + \int \delta\phi_K^*(r)\upsilon_{exc}(r)\phi_K(r)dr - \int \delta\phi_K^*(r)E_K\phi_K(r)dr = 0$$

$$\int \delta\phi_K^*(r)\left[-\frac{1}{2}\nabla^2 + \int \frac{\rho(r')}{|r-r'|}dr' + \upsilon_{ext}(r) + \upsilon_{exc}(r) + E_K\right]\phi_K(r)dr = 0$$

This implies,

$$\left[-\frac{1}{2}\nabla^2 + \int \frac{\rho(r')}{|r-r'|}dr' + \upsilon_{ext}(r) + \upsilon_{exc}(r) - E_K\right]\phi_K(r) = 0$$

$$\left[-\frac{1}{2}\nabla^2 + \int \frac{\rho(r')}{|r-r'|}dr' + \upsilon_{ext}(r) + \upsilon_{exc}(r)\right]\phi_K(r) = -E_K\phi_K(r)$$