DENSITY FUNCTIONAL THEORY

Hohenberg & Kohn (1964)

$$\hat{H} = \hat{T} + V_{ee} + \sum_{i=1}^{N} V(i)$$

$$E[\rho] = F[\rho] + \int \rho(\vec{r}) V(\vec{r}) dV$$

$$V(\vec{r}) = -\sum_{K=1}^{NUCLEI} \frac{Z_K}{\left| \vec{r} - \vec{R}_K \right|}$$

$$F[\rho] = T_S[\rho] + J[\rho] + E_{XC}[\rho]$$

where

$$E_{XC} = T - T_S + V_{ee} - J$$

DFT continued

The electronic energy may be written

$$E[\rho] = T_S + J + \int \rho(\vec{r})V(\vec{r})dV + E_{XC}[\rho]$$

Where J is the classical electron-electron repulsion energy

$$J[\rho] = \frac{1}{2}\int \frac{\rho(\vec{r})\rho(\vec{r}')dVdV'}{|\vec{r} - \vec{r}'|}$$

T_S is the kinetic energy of a system of non-interacting electrons

E_{xc} is the (UNKNOWN) exchange-correlation energy

Kohn-Sham (1965)

Method of constructing the <u>exact density</u> from a <u>finite number</u> of one electron functions called the Kohn-Sham orbitals

one can write $$\rho(\vec{r}) = \sum_{i=1}^{N} \varphi_i^2(\vec{r})$$

whrere the $\varphi_i(\vec{r})$ ***are obtained as solutions of the equations***

$$(-\frac{1}{2}\nabla^2 + V_{eff})\varphi_i = \varepsilon_i \varphi_i$$

with $\langle \varphi_i | \varphi_j \rangle = \delta_{ij}$ ***and***

$$V_{eff} = V(\vec{r}) + \int \frac{\rho(\vec{r}\,')dV'}{|\vec{r} - \vec{r}\,'|} + V_{XC}$$

$$V_{XC} = \frac{\delta E_{XC}}{\delta \rho}$$

DFT continued

Presently, the Exchange-Correlation energy E_{xc} is presumed to have the form

$$E_{XC} = \int f(\rho, \nabla\rho) dV$$

The integrand is written as the sum of an exchange and correlation contribution

$$f(\rho, \nabla\rho) = f_X(\rho, \nabla\rho) + f_C(\rho, \nabla\rho)$$

These in turn are written as the sum of local and non-local or gradient containing terms

$$f_X(\rho, \nabla\rho) = f_{XL}(\rho) + f_{XNL}(\rho, \nabla\rho)$$

&

$$f_C(\rho, \nabla\rho) = f_{CL}(\rho) + f_{CNL}(\rho, \nabla\rho)$$