

10.675 LECTURE 11

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1. TODAY

- 2nd Hohenberg-Kohn Theorem
- Kinetic Energy
- Thomas Fermi
- Kohn-Sham Orbitals
- Spin DFT
- Gradient Corrected "Non-Local" Functionals

2. 2ND THEREOM

Variational principle as applied to DFT, for trial density $\rho^T(r)$

such that $\int \rho^T(r) dr = N$ electrons

$$E_o \leq E_v[\rho^T(r)]$$

$$E_v[\rho] = \int v(r)\rho(r)dr + F[\rho]$$

where $v(r)$ are the nuc-elec interactions, $F[\rho]$ is the electron KE + elec-elec interactions

$$F[\rho] = \int \Psi^*(T + U)\Psi dr$$

Where T = KE, U = elec-elec

$$E_v[\Psi^T] = \int \Psi^{T*}(T + U + V)\Psi^T dr > E_o[\Psi]$$

$$\rho(r) = |\Psi(r)|^2$$

So far, all we've dealt with is the ground state energy... Only HF can deal with excited states.

$$E[\rho] = T[\rho] + N[\rho] + U[\rho] + (Nuc/Nuc)$$

T is KE, N is Nuc-elec, U is elec-elec.

$T[\rho]$ is the Thomas fermi theory \Rightarrow choose the form of $T[\rho]$ to be that of a gas of free homogenous electrons.

for no potential (particle in a box) $\Psi = \frac{1}{v^{1/3}} e^{ikr}$, $k_x = \frac{2\pi}{l_x} n_x$

$$\Rightarrow T^{TF}[\rho] = C_f \int \rho(r)^{5/3} dr$$

$$C_f = \frac{3}{10} (3\pi^2)^{2/3}$$

"local" functional.

$$E[\rho] = T[\rho] + N[\rho] + J[\rho] + X[\rho] + C'[\rho]$$

J is the "mean field" coulombic interaction term, X is exchange, C is correlation.

It doesn't work well, using local functionals is disastrous. $T^{TF}[\rho]$

→ No covalent bonding ever occurs in this model, "Teller" theorem... because bonding for the most part is determined by changes in T.

Similarly, Dirac developed a "local" functional for electron exchange.

$$X^\rho[\rho] = C_x \int \rho^{4/3}(r) dr$$

$$C_x = \frac{3}{4} \left(\frac{3}{\pi}\right)^{1/3}$$

Date: Fall 2004.

X_α theory, is similar but additional $3/2$ constant

3. KOHN-SHAM ORBITALS

$$T = \sum_p^N n_p \int \Psi_p^*(1) \left(\frac{-1}{2} \nabla_i^2 \right) \Psi_p dr$$

$$\rho(r) = \sum_p n_p \int \Psi_p^*(1) \Psi_p(1) dr$$

Rigorously, for any interacting systems. \sum contains ∞ # of terms

Clever idea from K-S \rightarrow choose a non-interacting reference system.

$n'_p s \Rightarrow 1$ for the lowest n orbitals, all other $n'_p s = 0$, still fermions can't occupy the same orbital

$$T_S = \sum_{p=1}^N \int \Psi_p^*(1) \left(-\frac{1}{2} \vec{\nabla}^2 \right) \Psi_p(1) dr$$

$$\rho(r) = \sum_p^N \int \Psi_p^*(1) \Psi_p(1) dr$$

$$E[\rho] = T_S[\rho] + N[\rho] + J + X + C' + (T - T_x)$$

$$\text{Let } C = C' + T - T_S$$

Let $E_{xc} \rightarrow$ exchange correlation functional, $E_{xc} = X + C$

$$E[\rho] = \sum_{p=1}^N \int |Psi_p^* - \frac{1}{2} \nabla^2 Psi_p + J + E_{xc} + \int v(r) \rho(r) dr$$

Kohn-Sham orbitals are auxilliary, needed to solved but they don't really have a physical meaning.

If there exists a non-interacting reference state w/density $\rho(r)$

How can we calculate Ψ_p 's. Analogous to HF equations.

$$\text{define } \Omega[\Psi_p, s] = E[\rho] - \sum_p^N \sum_q^N \epsilon_{pq} \int \Psi_p^* \Psi_q$$

where ϵ_{pq} is the lagrange multiplier, set $d\Omega = 0$

$$\left[-\frac{1}{2} \nabla^2 + V_{eff} \right] \Psi_r = \sum_q^N \epsilon_{pq} \Psi_q \text{ where } V_{eff} = v(r) + \frac{\delta J[\rho]}{\delta \rho} + \frac{\delta E_{xc}[\rho]}{\delta \rho}$$

$$\left[-\frac{1}{2} \nabla^2 + v(r) + \frac{\int \rho(r) dr}{|r-r'|} + V_{xc}(r) \right] \Psi_p = \epsilon_p \Psi_p$$

Choose a basis expansion for KS orbitals $\Rightarrow V_{eff}$ solve iteratively.

$$E = \sum_p^N \epsilon_p - \frac{1}{2} \int \int \frac{\rho(r) \rho(r')}{|r-r'|} + E_{xc}[\rho] - \int v_{xc}(r) \rho(r) dr$$

DFT is highly dependent on having an accurate E_{xc} functional.