10.675 LECTURE 12

RICK RAJTER

1. TODAY

$\rightarrow$ LSD
$\rightarrow$ Functionals
$\rightarrow$ Correlation Methods
$\rightarrow$ CI, Partial CI
$\rightarrow$ G1, G2, G3
$\rightarrow$ Coupled Cluster, CCD, CCSD, QCISD

2. LSD - LOCAL SPIN DFT

Thomas Fermi is too hard to correct wave function, as $T^{TF}[\rho]$ would completely change it.
LSD - Electrons can be unpaired here, as opposed to ground state paired methods.
$\rho_\alpha, \rho_\beta \rightarrow$ densities of the α, β spins, either +/- 1/2.
In the following derivations, σ is means either the α or β spin.
$E[\rho_\alpha, \rho_\beta] = \sum_{\phi_\sigma} n_{\rho_\sigma} \int \Psi^*_{\rho_\sigma}(-\frac{1}{2}\vec{\nabla}^2)\Psi_{\rho_\sigma} dr + J[\rho_\alpha + \rho_\beta] + E_{xc}[\rho_\alpha, \rho_\beta] + \int v(r)(\rho_\alpha - \rho_\beta)dr + \int \beta_e b(r)\rho_\alpha - \beta_e b(r)\rho_\beta)dr$
Where $b(r)$ is the magnetic field.
set n_{ρ_α}'s to 1 for the lowest KS orbitals w/normalization.
Solve 2 KS equations
$(-\frac{1}{2}\nabla^2 + V^\alpha_{eff})\Psi_{rho_\alpha} = \epsilon_{\rho_\alpha}\Psi_{\rho_\alpha}$
$(-\frac{1}{2}\nabla^2 + V^\beta_{eff})\Psi_{rho_\beta} = \epsilon_{\rho_\beta}\Psi_{\rho_\beta}$
For q = 1,2,3,4 ... N
$V^\alpha_{eff} = V(r) + \int \frac{\rho(r)dr}{|r-r'|} + \frac{\delta E_{xc}[\rho_\alpha, \rho_\beta]}{\delta \rho_\alpha}$ which are the coupling terms.
same for V^β_{eff}, substitute and solve for α and β
NOW, all we need is an accurate $E_{xc}[\rho]$

3. FUNCTIONALS

LSDA - Local Spin Density Approximation.
$\rightarrow$ choose form of E_x and E_c from that of a homogenous electron gas
$\rightarrow E_x[\rho_\alpha, \rho_\beta] = E_x[\rho_\alpha, 0] + E_x[0, \rho_\beta]$
$\rightarrow E_x only depends on the same spings$
$\rightarrow$for the spin compensated case, $\rho_\alpha = \rho_\beta = \frac{1}{2}\rho$
$E_x[\frac{1}{2}\rho, \frac{1}{2}\rho] = E_x[\frac{1}{2}, 0] + E_x[0, \frac{1}{2}\rho] = 2E_x[\frac{1}{2}\rho, 0]$
$\Rightarrow E_x[\rho]$
For the case when spins are not compensated.
$E_x[\rho_\alpha, \rho_\beta] = \frac{1}{2}E_x[2\rho_\alpha] + \frac{1}{2}E_x[2\rho_\beta]$

Recall Slater $E_x[\rho] = C_x \int \rho^{4/3} dr$

LSDA $E_x^{LSDA}[\rho_\alpha, \rho_\beta] = 2^{1/3} C_x \int (\rho_\alpha^{4/3} + \rho_\beta^{4/3}) dr$

Can take functional derivatives of E_x^{LSD}

Vosko, Wilk, and Nasair parameterized a form for E_c from monte carlo data from a homogenous electron gas.

E_C^{VWN} "local" thus developed.

Perdew and Zunger developed another correlation functional taking into account self interaction E_c^{pz}

Errors as high as 30-100 Kcal/mole. Local functional worked better than we might expect due to cancelation of errors.

E_c^{local} give E_c about 2x to high. E_x^{local} gives E_x about 10% too low.

E_x $10 * E_c$ and thus the errors cancel.

4. Corrections to local density approximation

$E_{xc}^{LSD}[\rho_\alpha, \rho_\beta] = \int dr \rho \epsilon_{xc}(\rho_\alpha, \rho_\beta)$

$E_{xc}^{LSD}[\rho_\alpha, \rho_\beta] = \int dr \rho \cdot f(\rho_\alpha, \rho_\beta) \nabla \rho_\alpha, \nabla \rho_\beta$

Where CGA means the generalized gradient approximation.

Becke's correction to E_x^{LSD}

$E_x^B = E_x^{LSD} - \beta \sum_\alpha \int \rho_\sigma^{4/3} \frac{x_\sigma^2 \, dr}{1 + 6\beta x_o \sinh^{-1}(x_\sigma)}$

$x_\sigma = \frac{|\nabla \rho_\sigma|}{\rho_\sigma^{4/3}}$

β is fit to "exact HF exchange" energies of 6 noble gas atoms from He to Ne.

Becke chose $\beta = 0.0042$

Other functionals: BLYP, PW91, PB (exchange and correlation)

5. Adiabatic Correction Method

Incorporation of the "exact" exchange.

$E_{xc} = \int_0^1 U_{xc}(\lambda) d\lambda$ $\lambda = 0$ no interaction $\lambda = 1$ full interaction.

$E_{xc} = C_o E_x^{exact} + C_1 U_{xc}^{LSDA}$

$U_{xc}^{LSDA} = \int U_{xc}[\rho_\alpha, \rho_\beta] dr$

Find coefficients by fitting eg atomization energies of small molecules

B3LYP

B represents the type of exchange

3 represents the number of parameters used

LYP is the correlation method used.

6. DFT

$\rightarrow$ incorporation of the electron exchange at the cost of a HF calculation.

$\rightarrow$ BUT, no *a priori* rule for knowing what function is more accurate than another.

$\rightarrow$ No method for getting more and more accurate correlation.