10.675 LECTURE 12

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1. Today

→ LSD
→ Functionals
→ Correlation Methods
→ CI, Partial CI
→ G1, G2, G3
→ Coupled Cluster, CCD, CCSD, QCISD

2. LSD - Local Spin DFT

Thomas Fermi is too hard to correct wave function, as $T^T F|\rho|$ would completely change it.

LSD - Electrons can be unpaired here, as opposed to ground state paired methods.

In the following derivations, $\sigma$ means either the $\alpha$ or $\beta$ spin.

$$E[\rho_\alpha, \rho_\beta] = \sum_\phi \int \Psi^*_\rho \left( -\frac{1}{2} \nabla^2 \right) \Psi_\rho \, dr + \int (\rho_\alpha + \rho_\beta) + E_{xc}[\rho_\alpha, \rho_\beta] + \int v(r)(\rho_\alpha - \rho_\beta)dr + \int \beta_b(r)\rho_\alpha - \beta_e b(r)\rho_\beta)dr$$

Where $b(r)$ is the magnetic field.

set $n_{\rho_\sigma}$'s to 1 for the lowest KS orbitals w/normalization.

Solve 2 KS equations

$$\left( -\frac{1}{2} \nabla^2 + V_{eff}^{\alpha} \right) \Psi_{\rho_\alpha} = \epsilon_{\rho_\alpha} \Psi_{\rho_\alpha}$$

$$\left( -\frac{1}{2} \nabla^2 + V_{eff}^{\beta} \right) \Psi_{\rho_\beta} = \epsilon_{\rho_\beta} \Psi_{\rho_\beta}$$

For $q = 1, 2, 3, 4 \ldots N$

$V_{eff}^q = V(r) + \int \frac{\rho(r)dr}{|r-r'|} + \frac{iE_{xc}[\rho_\alpha, \rho_\beta]}{2\rho_\sigma}$ which are the coupling terms.

same for $V_{eff}^\beta$, substitute and solve for $\alpha$ and $\beta$

NOW, all we need is an accurate $E_{xc}[\rho]$

3. Functionals

LSDA - Local Spin Density Approximation.

→ choose form of $E_x$ and $E_c$ from that of a homogenous electron gas

$$E_x[\rho_\alpha, \rho_\beta] = E_x[\rho_\alpha, 0] + E_x[0, \rho_\beta]$$

→ $E_x$ only depends on the same $\rho_\sigma$

→ for the spin compensated case, $\rho_\alpha = \rho_\beta = \frac{1}{2}\rho$

$$E_x[\frac{1}{2}\rho, \frac{1}{2}\rho] = E_x[\frac{1}{2}, 0] + E_x[0, \frac{1}{2}\rho] = 2E_x[\frac{1}{2}\rho, 0]$$

⇒ $E_x[\rho]$

For the case when spins are not compensated.

$$E_x[\rho_\alpha, \rho_\beta] = \frac{1}{2}E_x[2\rho_\alpha] + \frac{1}{2}E_x[2\rho_\beta]$$

Date: Fall 2004.
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.

$E_{loc}^{WN}$ “local” thus developed.

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

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

$E_{loc}^{c}$ give $E_c$ about 2x to high. $E_{loc}^{x}$ gives $E_x$ about 10% too low.

$E_x 10 \times E_c$ and thus the errors cancel.

4. Corrections to Local Density Approximation

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

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

Where CGA means the generalized gradient approximation.

Becke’s correction to $E_x^{LSD}$

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

$x_\sigma = |\nabla \rho_\sigma| \rho_\sigma$

$\beta$ 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.

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

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

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

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

→ incorporation of the electron exchange at the cost of a HF calculation.

→ BUT, no a priori rule for knowing what function is more accurate than another.

→ No method for getting more and more accurate correlation.