# Chem 580: DFT

# Density Functional Theory (Chapter 6, Jensen)

Hohenberg-Kohn Theorem (Phys. Rev., 136,B864 (1964)): For molecules with a non degenerate ground state, the ground state molecular energy and all other electronic properties are uniquely determined by the ground state density $\rho_0$.

Appealing since density depends on 3 coordinates whereas wave function depends on 3N coordinates.

Problem: Don't know the density.

Also, need to know the density at every point in 3N-dimensional space.

Functional: Function of a function. $E[\rho_0 (x,y,z)]$

# Density functional theory

Goal of DFT development: Find exact energy functional that expresses the ground state energy in terms of the density: $E=E[\rho (x,y,z)]$

$$E[\rho] = T[\rho] + V_{ne}[\rho] + V_{ee}[\rho] = T[\rho] + V_{ne}[\rho] + J[\rho] + K[\rho]$$

In the limit of the exact density, $J[\rho]$ and $K[\rho]$ should implicitly include correlation. $V_{ne}[\rho]$ and $J[\rho]$ are treated normally.

$$V_{ne}[\rho] = -\sum_A \int \frac{Z_A \rho(r)}{r} dV$$

$$J[\rho] = \int\int \frac{\rho(r)\rho(r')}{|r-r'|} dV$$

# Density functional theory

$$E[\rho] = T[\rho] + V_{ne}[\rho] + V_{ee}[\rho] = T[\rho] + V_{ne}[\rho] + J[\rho] + K[\rho]$$

How do we determine T[ρ] and K[ρ]?

Thomas-Fermi theory (Physics): Provides T[ρ] of a uniform, non-interacting electron gas.

Problem: Does not work for chemistry since chemical bonds don't exist in this model.

$$T_{TF} = C_F \int \rho^{5/3}(r) dr$$

$$K_{TF} = -C_X \int \rho^{4/3}(r) dr \longrightarrow \text{Dirac}$$

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

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

# Density functional theory

- Kohn & Sham (KS) proposed using <u>orbitals</u> to construct functional. (Phys. Rev., 140, A1133 (1965)).

- Similar to HF independent particle model

Kohn & Sham considered a fictitious reference system of $n$ non-interacting electrons experiencing the same potential $v_s$.

This potential is such that the density of this fictitious system is equal to the ground state density of the system of interest: $\rho_s(x, y, z) = \rho_0(x, y, z)$

The Hamiltonian of the reference system is given by:

$$\hat{H}_s = \sum_{i=1}^{n} \hat{h}_i^{KS} \qquad\qquad \hat{h}_i^{KS} = -\frac{1}{2}\nabla_i^2 + v_s(\boldsymbol{r}_i)$$

The Hamiltonian of the real system can be related to the Hamiltonian of the fictitious system using the parameter λ:

$$\hat{H}_\lambda = \hat{T} + \hat{V}_{ext}(\lambda) + \lambda\hat{V}_{ee}$$

# Kohn-Sham (KS) Density functional theory

$$\hat{H}_\lambda = \hat{T} + V_{ext}(\lambda) + \lambda \hat{V}_{ee}$$

- If $\lambda = 0$ there is no electron-electron interaction: independent particle model

- If $\lambda = 1$ (the real molecule), the external potential $V_{ext} = V_{Ne}$

- What is the wave function for the reference system ($\lambda=0$)?

- Independent particle model: Must be a Slater determinant!

$$\psi_{s,0} = \left| \phi_1^\alpha \phi_1^\beta ... \phi_N^\alpha \phi_N^\beta \right|$$

The molecular orbitals $\phi_i$ are called **Kohn-Sham orbitals** with orbital energies $\varepsilon_i$

# KS Density functional theory

- The exact kinetic energy functional for the reference system is:

$$T_s[\rho] = \sum_i \left\langle \phi_i \left| -\frac{1}{2}\nabla_i^2 \right| \phi_i \right\rangle$$

- For interacting electrons, this is only an approximation (similar to HF). Since the density is still not known, Kohn-Sham calculated the density as:

$$\rho(r) = \rho_s(r) = \sum_i \left| \phi_i(r) \right|^2 \qquad \text{Same as for HF}$$

- Then, we have: $\quad E_{DFT}[\rho] = T_S[\rho] + V_{Ne}[\rho] + J[\rho] + E_{xc}[\rho]$

Contains exchange and correlation. Exchange is the largest part

# KS Density functional theory

- Major problem and effort is to find a reasonable expression for $E_{xc}[\rho]$.
- The KS procedure:

$$\hat{h}^{KS}(1)\phi_i(1) = \varepsilon_i\phi_i(1)$$

$$\left[-\frac{1}{2}\nabla_1^2 - \sum_A \frac{Z_A}{r_{1A}} + \int \frac{\rho(\boldsymbol{r}_2)}{r_{12}} d\boldsymbol{r}_2 + v_{xc}(1)\right]\phi_i(1) = \varepsilon_i\phi_i(1)$$

- Solved iteratively as in HF
- The exchange-correlation potential $v_{xc}$ is given by:

$$v_{xc}(\boldsymbol{r}) = \frac{\partial E_{xc}\left[\rho(\boldsymbol{r})\right]}{\partial\rho(\boldsymbol{r})}$$
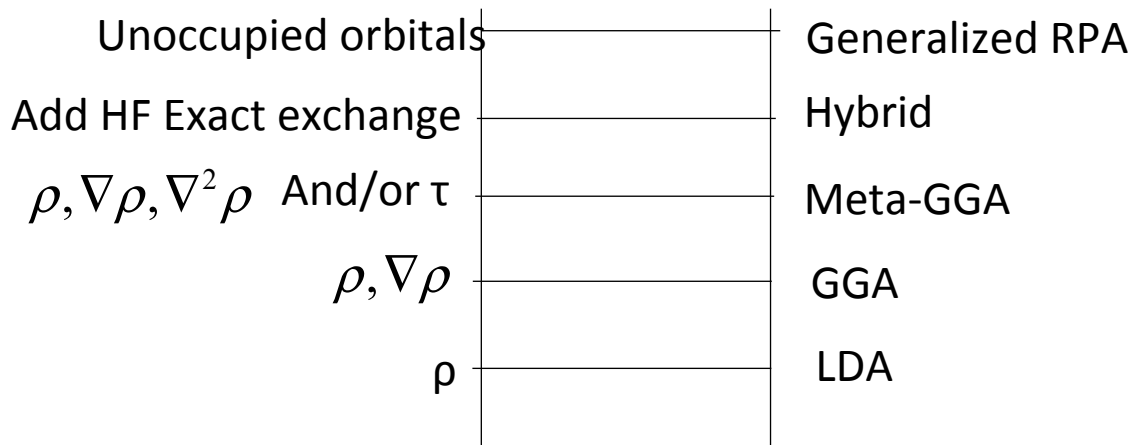
# KS Density functional theory

- There are MANY choices of exchange-correlation functionals. One approach, so far not broadly successful, is to use very high level of ab initio theory to get density, then use it to determine $E_{xc}[\rho]$. This approach is difficult to generalize.

- Very common to separate into two independent parts:

$$E_{xc}\left[\rho\right] = E_{x}\left[\rho\right] + E_{c}\left[\rho\right]$$

- Jacob's ladder:

| | |
|---|---|
| Unoccupied orbitals | Generalized RPA |
| Add HF Exact exchange | Hybrid |
| $\rho, \nabla\rho, \nabla^2\rho$ And/or τ | Meta-GGA |
| $\rho, \nabla\rho$ | GGA |
| ρ | LDA |

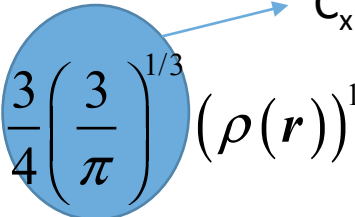**All levels build upon LDA as the base: House of cards**

- Local density approximation (LDA):
  The local density can be treated as a uniform electron gas. Basically Thomas-Fermi Theory

$$E_{xc}^{LDA}[\rho] = \int \varepsilon_{xc}(\rho)\rho(\boldsymbol{r})d\boldsymbol{r}$$

$$\varepsilon_{xc}(\rho) = \varepsilon_x(\rho) + \varepsilon_c(\rho)$$

$C_x$

- The exchange part: $\quad \varepsilon_x(\rho) = -\dfrac{3}{4}\left(\dfrac{3}{\pi}\right)^{1/3}\left(\rho(\boldsymbol{r})\right)^{1/3}$

Early variant was Xα method devised by Slater where correlation is ignored.

$$\varepsilon_{x\alpha}(\rho) = -\dfrac{3}{2}\alpha C_x\left(\rho(\boldsymbol{r})\right)^{1/3}$$

α is a parameter (usually 0.75)

# LDA

- Correlation functional calculated ad hoc, often determined using Monte Carlo methods and then fitted to analytic formula. The two most common correlation functionals:

    1) Vosko-Wilk-Nusair (VWN): *Can. J. Phys*,58,1200 (1980)
    2) Perdew-Wang: *Phys. Chem Rev. B*, 45,13244(1994)

Both formulas given in Jensen. **Lots of fitted parameters**.

- LDA tends to overestimate binding energies, does not describe hydrogen bonds properly.

- **Gradient corrected methods**:

  - <u>Generalized gradient approximation (GGA):</u> Non-uniform electron gas. Both exchange and correlation energies dependent on the gradient of the density.

  These functionals are sometimes called non-local: <u>Wrong</u> since they depend on the density at a point in space (unlike HF exchange).

  Exchange part: Best seems to be PW91 (Phys. Rev. B, 46,6671 (1992))
  **<u>Formula in Jensen, lots of parameters</u>. <u>Built on LDA</u>**

  <u>Correlation part</u>: Most popular by Lee, Yang, Parr (LYP). Contains 4 parameters determined by fitting to date on He atom. (Phys. Rev. B, 37, 785 (1988).

  Note: LYP provides no correlation for parallel spins.

- <u>Meta-GGA</u>: Include either (or both) the second derivative of the density or the orbital kinetic energy density.

$$\tau = \frac{1}{2}\sum_i \left|\nabla\phi_i^{KS}\right|^2$$

Most popular functionals: TPSS, B95, M06-L

Most popular new functionals are meta-GGAs. Most promising are set of M06 functionals from Truhlar group, but seem to need a different one for different problems. One size does not fit all.

- <u>Hybrid functionals</u>: Mix LDA, GGA (or meta-GGA) and exact HF exchange: Called "exact exchange"

Becke proposed (JCP, 98, 5648(1993)):

$$E_{xc}^{B3} = (1-a)E_x^{LDA} + aE_x^{exact} + b\Delta E_x^{B88} + E_c^{LDA} + c\Delta E_c^{GGA}$$

**Built on LDA** If we use the LYP correlation functional, we get B3LYP. Parameters a, b and c fitted to reproduce the G2 test set. Semi-empirical

| Method | Mean absolute deviation (kcal/mol) | Maximum Absolute deviation (kcal/mol) |
|---|---|---|
| G2 | 1.6 | 8.2 |
| G2(MP2) | 2.0 | 10.1 |
| G2(MP2, SVP) | 1.9 | 12.5 |
| B3LYP | 3.1 | 20.1 |
| B3PW91 | 3.5 | 21.8 |
| SVWN | 90.9 | 228.7 |

- <u>Hybrid functionals:</u>

Different hybrid functionals use different amounts of "exact exchange".

Works reasonably well for organic

Different hybrids work often better for different properties.

Often better barrier heights than HF or GGA.

Built on a house of cards

# Advantages and disadvantages of DFT

- DFT in GAMESS: $CONTRL DFTTYP=… $END and $DFT

- Can be run with SCFTYP= RHF, UHF, ROHF

- Numerical grids, cannot integrate analytically: Can make grid denser (better) or sparser using:

    NRAD= (Number of radial points, default=96)

    NTHE= (Number of angle theta grids, default=12)

    NPHI=  (Number of angle phi grids, default=24, must be twice NTHE)

**Larger values= finer grid**

Can avoid grid by using resolution of the identity to simplify integrals:

$$\left\langle \phi_i \left| x.y \right| \phi_j \right\rangle = \sum_m \left\langle \phi_i \left| x \right| \chi_m \right\rangle \left\langle \chi_m \left| y \right| \phi_j \right\rangle$$

Exact if $\{\chi_m\}$= complete basis. Can develop auxiliary basis set for this purpose. First suggested by Almlof, implemented by Glaesemann & Gordon. J. Chem. Phys., 112, 10738 (2000).

# Advantages and disadvantages of DFT

- Summary of scaling:

| CCSD(T) | $N^7$ |
|---------|-------|
| MP2 | $N^5$ |
| Full CI | $e^N$ |
| MRCI | $e^N$ |
| DFT | $N^4$ |
| HF | $N^4$ |

DFT and HF cost can be reduced by manipulating long-range: Make linear scaling at very long distances using multipolar expansion.

Very demanding methods can be reduced in scaling using localized orbitals: reduces range of interaction.

Semi-empirical methods ~ $N^2$-$N^3$: N grows less quickly. Bottleneck is matrix diagonalization.

Formal linear scaling method: MM

# Advantages and disadvantages of DFT

- Some problems:
  - Weak interactions due to dispersion. No dispersion in HF or DFT: No bonding between two Ar atoms or benzenes. <u>Solution</u>: Add dispersion ad hoc (Grimme)

  - Self-interaction error: Density of a single electron interacts with itself. Leads to underestimation of band gaps. Some functionals correct for self-interaction.

  - Range separated functionals

  - Poor charge transfer predictions.

  - Ground state theory (need TDDFT for excited states)

# Further Information

- http://www.phy.mtu.edu/pandey/talks/trickey_dft-course_2008-07.pdf