
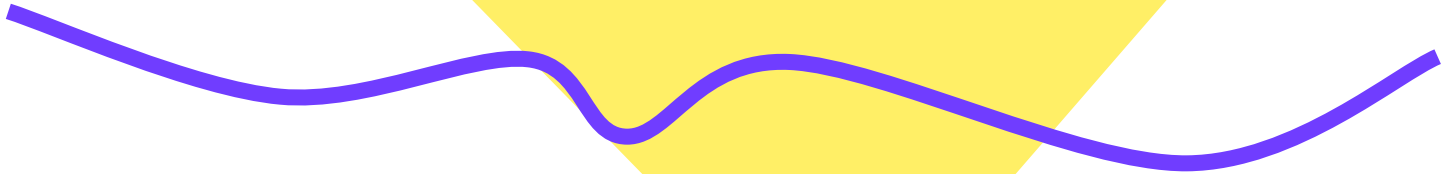
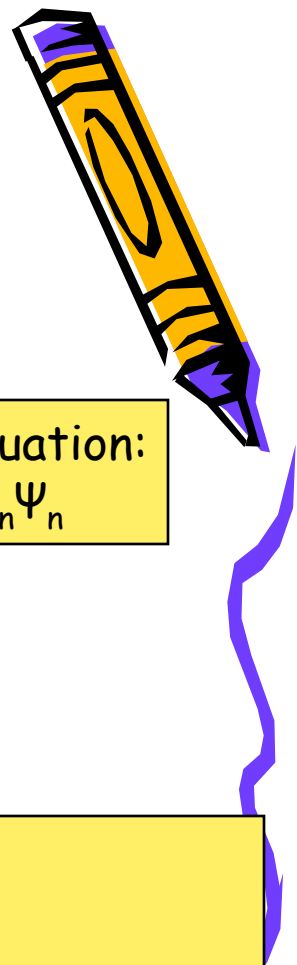


**Electron  
Correlation**



# Levels of QM Theory



$$H\Psi = E\Psi$$

Born-Oppenheimer approximation

$$\text{Nuclear equation: } H_n\Psi_n = E_n\Psi_n$$

$$\text{Electronic equation: } H_e\Psi_e = E_e\Psi_e$$

Single determinant SCF

**Correlation approaches:**

1. WF based. Multi-determinantal methods
  - variational (MCSCF, CI)
  - non-variational (MBPT, CC)
2. DFT:
  - "orbital free" ( $\rho$  - based)
  - Single determinantal (Kohn-Sham)

Semi-empirical methods



# Why "correlation" ?

The Hartree Product

$$\Phi^{\text{HP}}(x_1; x_2; \dots; x_n) = \varphi_1(x_1) \varphi_2(x_2) \dots \varphi_n(x_n)$$

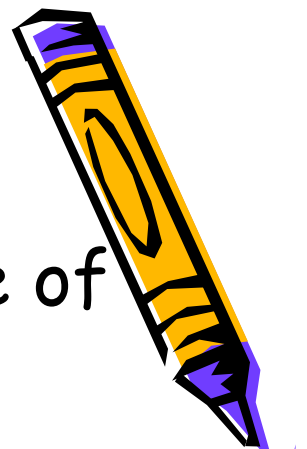
is completely uncorrelated, in the sense that the probability of simultaneously finding electron 1 at  $x_1$ , electron 2 at  $x_2$ , etc., is given by :

$$|\Phi^{\text{HP}}(x_1; x_2; \dots; x_n)|^2 dx_1 dx_2 \dots dx_n = |\varphi_1(x_1)|^2 |\varphi_2(x_2)|^2 \dots |\varphi_n(x_n)|^2 dx_1 dx_2 \dots dx_n$$

which is the probability of finding electron 1 at  $x_1$  times the probability of finding electron 2 at  $x_2$ , etc... the product of the probabilities. This makes the Hartree Product an independent particle model. Electrons move independently; their motion is **uncorrelated**



# The Hartree-Fock approximation



- The n-electronic wave function  $\psi$  in the case of Hartree-Fock (HF) approximation:

$$\Psi_{HF}(1, 2, \dots, n) = \det \begin{pmatrix} \phi_1(1) & \phi_2(1) \dots & \phi_n(1) \\ \phi_1(2) & \phi_2(2) \dots & \phi_n(2) \\ \dots & \dots & \dots \\ \phi_1(n) & \phi_2(n) \dots & \phi_n(n) \end{pmatrix}$$

- One-electron density:

$$\rho_{HF}(x, y, z) = \sum_j n_j |\phi_j|^2$$

$n_j$  is the “occupation number” ( $n_j = 0, 1, 2$ )



# Hartree-Fock Energy



$$E = \sum_{i=1}^n h_i + \frac{1}{2} \sum_{i=1}^n \sum_{j=1}^n (J_{ij} - K_{ij})$$

Sums run over occupied orbitals.  $h_i$  is the one-electron integral,  $J_{ij}$  is the Coulomb integral, and  $K_{ij}$  is the exchange integral.

$$h_i = \int dr \phi_i^*(r) \left[ -\frac{1}{2} \Delta - \sum_I \frac{Z_I e^2}{R_{I-e}} \right] \phi_i(r) = - \left( \int dr \left[ \frac{1}{2} \phi_i^*(r) \Delta \phi_i(r) + \frac{Z_I e^2}{R_{I-e}} \rho_i(r) \right] \right)$$

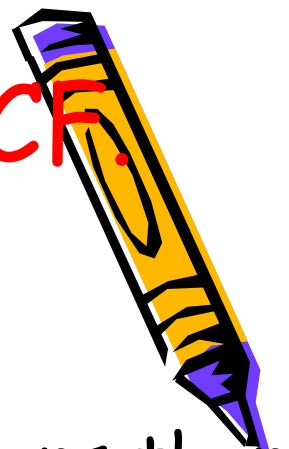
$$J_{ij} = \iint dr_1 dr_2 \phi_i^*(r_1) \phi_i(r_1) \frac{1}{r_{12}} \phi_j^*(r_2) \phi_j(r_2) = \iint dr_1 dr_2 \rho_i(r_1) \frac{1}{r_{12}} \rho_j(r_2)$$

$$K_{ij} = \iint dr_1 dr_2 \phi_i^*(r_1) \phi_j(r_1) \frac{1}{r_{12}} \phi_j^*(r_2) \phi_i(r_2)$$



# WF approaches beyond the SCF. Correlated Methods (CM)

- Include more explicit interaction of electrons than HF :  $E_{corr} = E - E_{HF}$  , where  $E\Psi = H\Psi$
- Most CMs begin with HF wavefunction, then incorporate varying amounts of electron-electron interaction by mixing in excited state determinants with ground state HF determinant
- The limit of infinite basis set & complete electron correlation is the exact solution of Schrödinger equation (which is still an approximation)



# The N-electron Basis

- A collection of atom-centered Gaussian functions can be used as a basis set for expanding one-electron functions (molecular orbitals)

$$\phi_j = \sum_{s=1}^b c_{sj} \chi_s = c_{1j} \chi_1 + c_{2j} \chi_2 + \dots + c_{bj} \chi_b$$

- We need to solve the electronic Schrodinger equation to get  $\Psi_e(r_1; r_2; \dots; r_n)$ , a function of n electrons.  
What can we use as a basis for expanding  $\Psi_e$ ?
- Slater determinants are proper n-electron basis functions: they are functions which can be used to expand any antisymmetric) n-electron function.
- In the limit of an infinite number of Slater determinants, any n-electron function can be expanded exactly.





# Configuration Interaction (CI) and other correlation methods

- CI method for many-electron WF

$$\Psi_e(r_1, r_2, \dots, r_n) = c_0 \Phi_0^{HF}(r_1, r_2, \dots, r_n) + \sum_{I=1}^N c_I \Phi_I(r_1, r_2, \dots, r_n)$$

where  $N$  is the number of "excited" determinants

Ways of Coefficients  $c_I$  definition:

1. Variations - CI

2. Perturbation expansions - MBPT

SCF-like iterations - Coupled Cluster





# Classification of CI methods



- The Hartree-Fock "reference" determinant  $\Phi_0$  should be the leading term. Expect the importance of other configurations to drop off rapidly as they substitute more orbitals.

Let denote a determinant  $\Phi_{ij\dots k}^{ab\dots c}$

which differs from  $\Phi_0$  by replacing **occupied** orbitals  $ij \dots k$  with **virtual** orbitals  $ab \dots c$ .

$$\Psi = c_0 \Phi_0^{HF} + \sum c_i^a \Phi_i^a + \sum c_{ij}^{ab} \Phi_{ij}^{ab} + \sum c_{ijk}^{abc} \Phi_{ijk}^{abc} + \dots$$

Reference

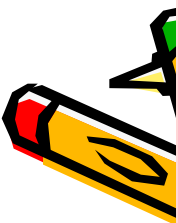
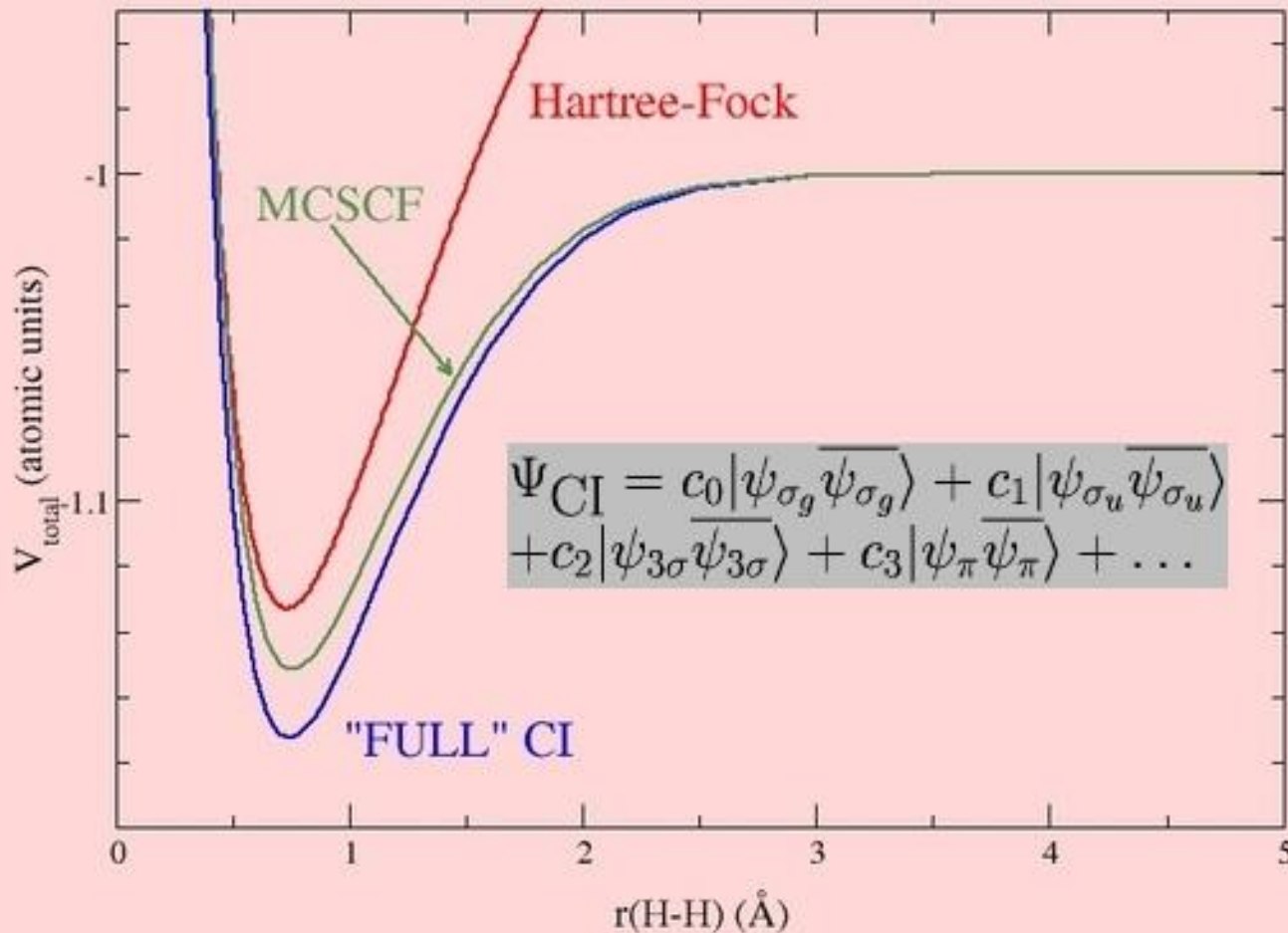
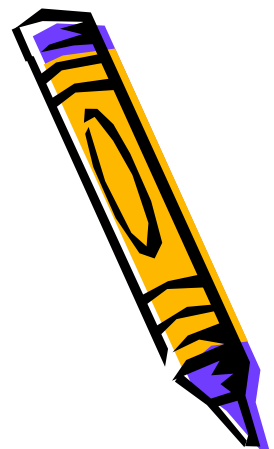
Singles  
**CIS**

Doubles  
**CISD**

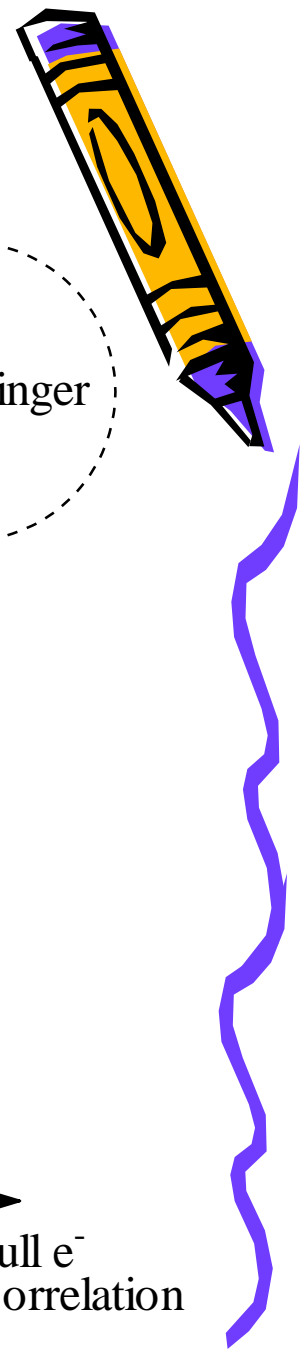
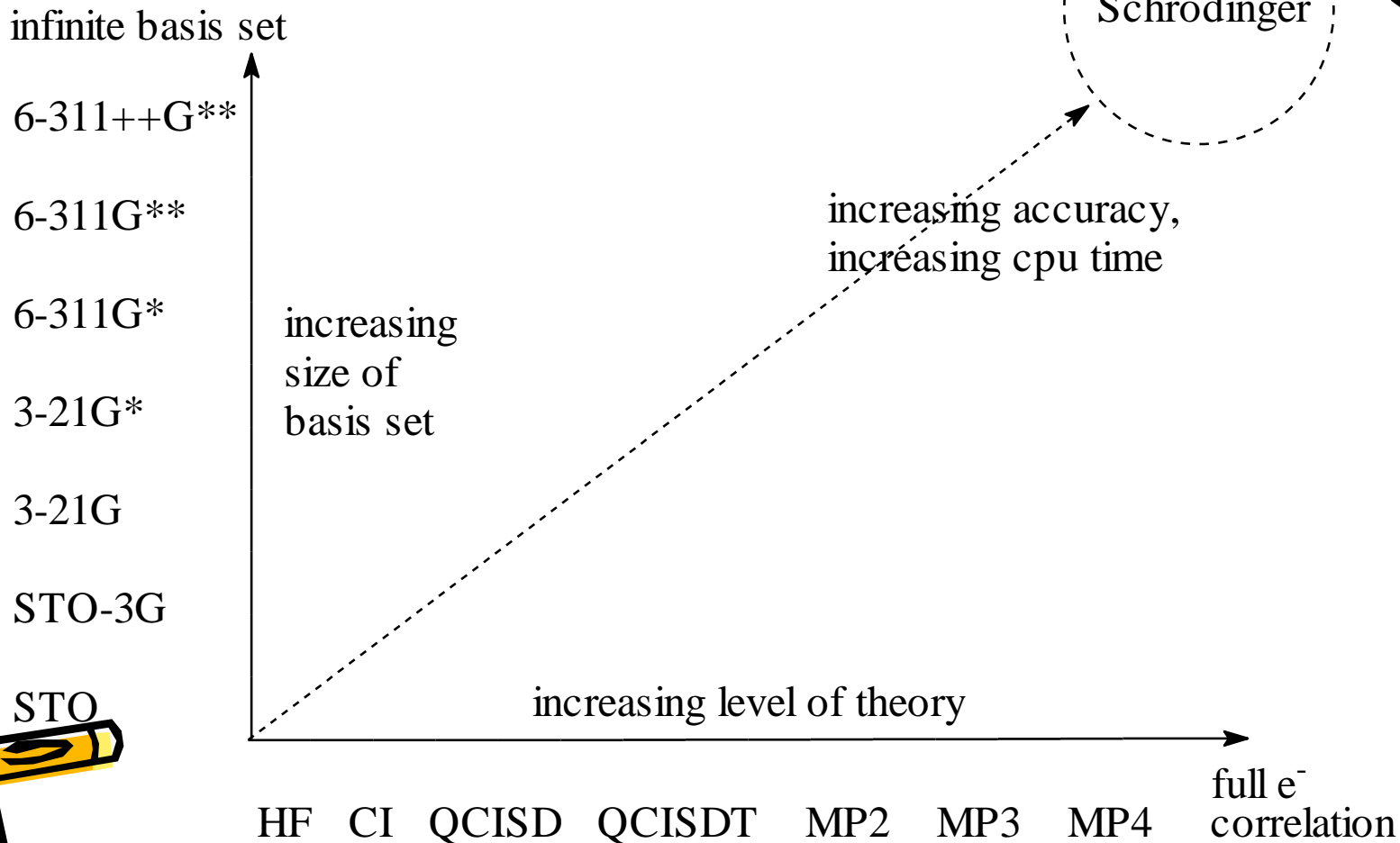
Triples  
**CISDT**



# Example of CI calculation: H<sub>2</sub> molecule



# WF methodology:



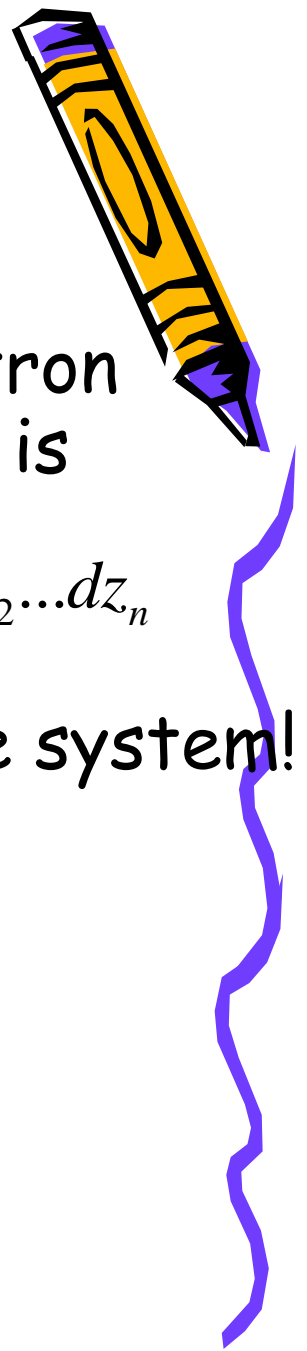
# Density Functional Theory

- 1998 Nobel Prize in Chemistry (Kohn and Pople) recognized work in this area.
- **Main idea:** Use the density instead of complicated many electron wavefunctions.
- **Basic approach:** minimize the energy with respect to the density.

Relationship of energy to density is the "functional"  $E[\rho]$  (true form of this functional is unknown: use approx.)



# One-electronic density



- The probability density  $\rho$  of finding an electron (**ANY!!!**) in the neighborhood of point  $(x, y, z)$  is

$$\rho(x, y, z) = n \sum_{\text{all } m_s} \int \dots \int |\psi(x, y, z, x_2, \dots, z_n, m_{s_1}, \dots, m_{s_n})|^2 dx_2 \dots dz_n$$

- In most cases - knowing the  $\rho$  is knowing the system!

$$\langle \hat{A} \rangle = \iiint A(x, y, z) \rho(x, y, z) dx dy dz$$

$$Z = \sum_{m_s} \iiint e \rho(x, y, z) dx dy dz = en$$

Main question –  
How does  $\rho$  look like?



# The energy functional $\equiv$ density functional (W. Kohn)



- Model Hamiltonian:  $H_\lambda = T + (1-\lambda)V_{\text{ext}}(\lambda) + \lambda V_{ee}$   
 $0 \leq \lambda \leq 1$ ;  $\rho_{\lambda=1} = \rho_{\lambda=0} = \rho$
- $H_{\lambda=1} = H$   $H_{\lambda=0} = T + V_{\text{ext}}(0)$  -single-e-H
- Kohn - Sham:  $E = E[\Psi] = \int \Psi^* \hat{H} \Psi dV = E[\rho] = ?$
- HF:  $E^{\text{HF}}[\rho] = T[\rho(\varphi)] + E_{\text{ne}}[\rho] + (J[\rho] + K[\rho(\varphi)])$
- DFT:  $E[\rho] = T[\rho] + E_{\text{ne}}[\rho] + (J[\rho] + K[\rho] + E_{\text{cor}}[\rho])$  -  
single-electron theory including correlation!

Alternatives:

$$\rho(x, y, z) = \sum_j n_j |\phi_j|^2$$

I

II



# Orbital-free DFT

$$E[\rho] = T[\rho] + E_{ne}[\rho] + J[\rho] + K[\rho] + E_{corr}[\rho]$$

- In the HF method  $E_{corr}[\rho]$  is missed

$$E_{ne}[\rho] = - \sum_a^{N_{\text{nuclei}}} \int \frac{Z_a(\mathbf{R}_a)\rho(\mathbf{r})}{|\mathbf{R}_a - \mathbf{r}|} d\mathbf{r}$$

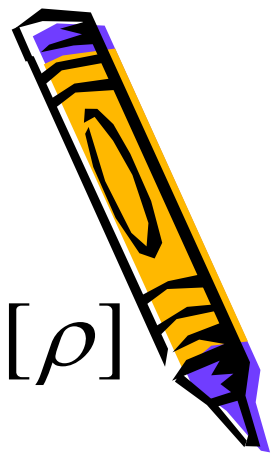
- General case:

$$J[\rho] = \frac{1}{2} \iint \frac{\rho(\mathbf{r})\rho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}d\mathbf{r}'$$

- Homogenous e-gas (Tomas-Fermi-Dirac) - simplest case:  $E_{TFD}[\rho] = T_{TF}[\rho] + E_{ne}[\rho] + J[\rho] + K_D[\rho]$

$$T_{TF}[\rho] = C_F \int \rho^{5/3}(\mathbf{r}) d\mathbf{r}$$

$$K_D[\rho] = -C_x \int \rho^{4/3}(\mathbf{r}) d\mathbf{r}$$



# Kinetic and exchange functionals' corrections



- Kinetic functional:

$$T[\rho] = T_{\text{TF}}[\rho] + T_2[\rho] + T_4[\rho] + T_6[\rho] + \dots$$

$$T_2[\rho] = \lambda \tau_{\text{w}}[\rho]; \quad \tau_{\text{w}}[\rho] = \int \frac{|\nabla \rho(\mathbf{r})|^2}{8\rho(\mathbf{r})} d\mathbf{r}$$

$$T_4[\rho] = \left(540(3\pi)^{2/3}\right)^{-1} \int \rho^{1/3}(\mathbf{r}) \left\{ \left( \frac{\nabla^2 \rho(\mathbf{r})}{\rho(\mathbf{r})} \right)^2 - \frac{9}{8} \left( \frac{\nabla^2 \rho(\mathbf{r})}{\rho(\mathbf{r})} \right) \left( \frac{\nabla \rho(\mathbf{r})}{\rho(\mathbf{r})} \right)^2 + \frac{1}{3} \left( \frac{\nabla \rho(\mathbf{r})}{\rho(\mathbf{r})} \right)^4 \right\} d\mathbf{r}$$

- Exchange functional:

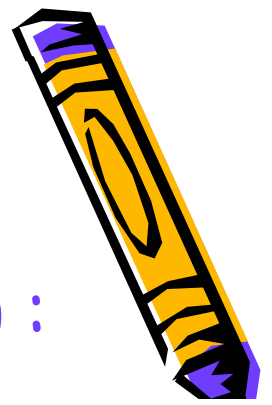
$$K[\rho] = K_{\text{D}}[\rho] + K_2[\rho] + K_4[\rho] + \dots$$

$$K_2[\rho] = -\frac{5}{216} (3\pi^5)^{-1/3} \int \frac{|\nabla \rho(\mathbf{r})|^2}{\rho^{4/3}(\mathbf{r})} d\mathbf{r}$$





# Correlation functionals



- An example Lee, Parr, Yang (LYP)  $E_{\text{corr}}[\rho]$  :

$$\varepsilon_c^{\text{LYP}} = -4a \frac{\rho_\alpha \rho_\beta}{\rho^2(1+d\rho^{-1/3})} -$$

$$ab\omega \left\{ \frac{\rho_\alpha \rho_\beta}{18} \left[ 144(2^{2/3})C_F(\rho_\alpha^{8/3} + \rho_\beta^{8/3}) + (47 - 7\delta)|\nabla\rho|^2 - \right. \right. \\ \left. \left. (45 - \delta)(|\nabla\rho_\sigma|^2 + |\nabla\rho_\beta|^2) + 2\rho^{-1}(11 - \delta)(\rho_\sigma|\nabla\rho_\sigma|^2 + \rho_\beta|\nabla\rho_\beta|^2) \right] \right. \\ \left. + \frac{2}{3}\rho^2(|\nabla\rho_\sigma|^2 + |\nabla\rho_\beta|^2 - |\nabla\rho|^2) - (\rho_\alpha^2|\nabla\rho_\beta|^2 + \rho_\beta^2|\nabla\rho_\alpha|^2) \right\}$$

$$\omega = \frac{e^{-c\rho^{-1/3}}}{\rho^{14/3}(1+d\rho^{-1/3})}$$

$$\delta = c\rho^{-1/3} + \frac{d\rho^{-1/3}}{(1+d\rho^{-1/3})}$$



# Kohn-Sham theory (DFT with orbitals)



- Exact WF:  $\rho(x, y, z) = \sum_j n_j |\phi_j|^2$
- $n_j$  is the “generalized occupation number” ( $n_j \cong 0$  or  $1$ );  
 $\phi_j$  - natural orbitals  $j=1, \dots, \infty$
- Kohn-Sham (KS) WF:

$$\Psi_{KS}(1, 2, \dots, n) = \det \begin{pmatrix} \phi_1(1) & \phi_2(1) \dots & \phi_n(1) \\ \phi_1(2) & \phi_2(2) \dots & \phi_n(2) \\ \dots & \dots & \dots \\ \phi_1(n) & \phi_2(n) \dots & \phi_n(n) \end{pmatrix}$$

- Exact exchange + KS kinetic functional  $T_S = \sum_{i=1}^{N_{elec}} \langle \phi_i | -\frac{1}{2} \nabla^2 | \phi_i \rangle$   
- very precise

$$T[\rho_{exact}] = \sum_{i=1}^{\infty} n_i \langle \phi_i^{NO} | -\frac{1}{2} \nabla^2 | \phi_i^{NO} \rangle$$



# Jacob's Ladder



Level	Name	Variables	Examples
1	Local density	$\rho$	LDA, LSDA, $X_\alpha$
2	GGA	$\rho, \nabla\rho$	BLYP, OPTX, OLYP, PW86, PW91, PBE, HCTH
3	Meta-GGA	$\rho, \nabla\rho, \nabla^2\rho$ or $\tau$	BR, B95, VSXC, PKZB, TPSS, $\tau$ -HCTH
4	Hyper-GGA	$\rho, \nabla\rho, \nabla^2\rho$ or $\tau$ <i>HF exchange</i>	H+H, ACM, B3LYP, B3PW91, O3LYP, PBE0, TPSSh, $\tau$ -HCTH-hybrid
5	Generalized RPA	$\rho, \nabla\rho, \nabla^2\rho$ or $\tau$ <i>HF exchange</i> <i>Virtual orbitals</i>	OEP2

