

## Intro to DFT

for a N-el system  $\Psi = \Psi(\tau_1, \dots, \tau_N)$

depends on coordinates of all N electrons

$$E = \frac{\langle \Psi | H | \Psi \rangle}{\langle \Psi | \Psi \rangle}$$

since H contains, at most, 2-body operators, we are integrating out the coordinates of N-2 electrons

Actually, one can prove that one can get the energy from the density

$$\gamma(\tau_1 | \tau_1') = N \int \Psi^*(\tau_1', \tau_2, \dots, \tau_N) \Psi(\tau_1, \tau_2, \dots, \tau_N) d\tau_2 \dots d\tau_n$$

first order density matrix

$$\psi = \frac{1s(r_1)1s(r_2)(\alpha\beta - \beta\alpha)}{\sqrt{2}}$$

$$\gamma(r_1' | r_1) = 2 \int 1s(r_1')1s(r_2)1s(r_1)1s(r_2)dr_2 = 2[1s(r')1s(r)]$$

$$\psi = \frac{[1s(r_1)2s(r_2) - 2s(r_1)1s(r_2)]}{\sqrt{2}} \alpha\alpha$$

$$\gamma(r_1' | r_1) = \int 1s(r_1')1s(r_1)2s(r_2)2s(r_2)dr_2 + \int 2s(r_1')2s(r_1)1s(r_2)1s(r_2)dr_2$$

$$\rho(r) = \gamma(r | r) = |1s(r)|^2 + |2s(r)|^2$$

So in the Hartree-Fock approximation,  $\rho$  is just a sum over the densities associated with the individual occupied orbitals



If one knew the exact density matrix, one can construct the natural orbitals (these diagonalize the density matrix)

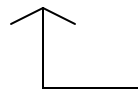
$$\rho_{exact} = \sum_{i=1}^{\infty} n_i |\varphi_i^{NO}|^2 \quad 0 \leq n_i \leq 1$$

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

But one does not know the exact  $\rho$

Kohn + Sham suggested using

$$\rho_{ks} = \sum_{i=1}^N |\varphi_i^{ks}|^2$$



precisely what one gets from a single Slater determinant

This gives

$$E[\{\varphi_i\}] = 2 \sum_i \langle \varphi_i | -\frac{1}{2} \nabla^2 | \varphi_i \rangle + \int V_{ion}(r) \rho(r) d^3 r$$
$$+ \frac{1}{2} \int \frac{\rho(r) \rho(r')}{|r - r'|} d^3 r d^3 r' + E_{xc}[\rho(r)] + E_{nuc}[\{R_I\}]$$

The KE term is no longer exact.

What is missing is absorbed into  $E_{xc}$ .

# Ne atom

$$E_{\text{exch}} = -12.11 \text{ au}$$

$$E_{\text{comel}} = -0.39 \text{ au}$$

$$E_{\text{exch}} = E_{\text{exch}}^{\text{SR}} + E_{\text{exch}}^{\text{LR}}$$

$$E_{\text{corr}} = E_{\text{corr}}^{\text{SR}} + E_{\text{corr}}^{\text{LR}}$$

dynamical

static  
(multiref)

SR = short-range

LR = long-range

In wavefunction theory the two LR contributions approximately cancel.

(obviously not true for dispersion).

In standard DFT approaches, the functional describes the short-range part of  $E_{\text{exch}}$  and  $E_{\text{corr}}$ .

If one replaces  $E_{\text{exch}}$  with the exact exchange (say from Hartree-Fock theory), the cancellation between the long-range exchange and correlation no longer occurs.

Vary the energy wrt changes in the density gives → Kohn-Sham equations

$$\left[-\frac{1}{2}\nabla^2 + V_{e-n}(r) + \int \frac{\rho(r')dr'}{|r-r'|} + V_{xc}(r)\right]\varphi_i(r) = \varepsilon_i\varphi_i$$

where 
$$V_{xc}(r) = \frac{\delta E_{xc}[\rho(r)]}{\delta\rho(r)}$$

$\varepsilon_i$  are actually derivatives of E wrt occupation #'s.

The problem is the exact  $E_{xc}[\rho]$  is not known.

There are probably on the order of 100 different approximations to  $E_{xc}[\rho]$ .

The earliest and simplest of these is the **local density approximation [LDA]**

$$E_{xc}(r) = E_{xc}^{\text{homog}}[\rho(r)]$$



homogeneous electron gas of the same density

$$E_x = \int \rho \varepsilon_x[\rho] dr \quad , \quad E_c = \int \rho \varepsilon_c[\rho(r)] dr \quad ,$$

$\varepsilon_x, \varepsilon_c$  = exchange + correlation energy per electron

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

$$\varepsilon_x[\rho] = -C_x \rho^{1/3}$$

$$E_x^{LSDA}[\rho] = -2^{1/3} C_x \int [\rho_a^{4/3} + \rho_b^{4/3}] dr \quad , \quad \text{to account for unpaired spins}$$

$\varepsilon_c^{LDA}[\rho]$  is obtained from Ceperly + Alder's quantum Monte Carlo simulations of a **uniform electron gas** as a function of density.

- LDA - exchange energies underestimated by ~10%
- correl. energy overestimated by ~2x

⇒ Generally strongly overbinds

GGA's – include gradient corrections

exchange  $\epsilon_x^{PW86} = E_x^{LDA} (1 + ax^2 + bx^4 + cx^6)^{1/15}$

$$x = \frac{|\nabla\rho|}{\rho^{4/3}}$$

$$\epsilon_x^{B88} = E_x^{LDA} - \beta\rho^{1/3} \frac{x^2}{1 + 6\beta x \sinh^{-1} x}$$

$\epsilon_x^{PW91}$  : even more complicated

correlation

$$\epsilon_c^{P86} = E_c^{LDA} + \frac{e^\Phi C(\rho) |\nabla\rho|^2}{f(\xi)\rho^{7/3}} \quad (\text{see Jensen book for definition of variables})$$

other commonly used correlation functionals

$$\epsilon_c^{PW91}, \epsilon_c^{LYP}$$

hybrid methods – include some exact exchange

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

$$a \sim .2, b \sim .7, c \sim .8$$

B3LYP is of this form with the LYP GGA used for the last term

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$V_{xc}$  integrals cannot be evaluated analytically  
Integration is done over a grid (spherical + radial)  
typically  $10^3$ - $10^4$  points per atom

The default in Gaussian –

Coulomb integrals done over orbitals  $\rightarrow N^4$  scaling

$$\text{Fit } \rho = \sum_i^m c_i \varphi_i \quad \text{4 - center integral} \rightarrow \text{3 center} \rightarrow N^3 \text{ scaling}$$

However, in hybrid schemes one needs the exact exchange integrals  $\rightarrow N^4$  scaling unless other approximations are made.

## Gradient-corrected functionals

Highly successful for a wide range of problems  
often of MP2 quality or even slightly better at lower  
computational cost

Extensively used throughout chemistry and materials sciences

There are some major limitations

- Do not treat long-range dispersion
- Self interaction error (can see by calculating  $H_2^+$  potential)
- Biased toward charge delocalization

### Application to excited states

Directly application to very few excited states (same  
issues as Hartree-Fock)

### TDDFT

essentially the same equations as TDHF  
often more reliable than TDHF  
problems with charge-transfer states