

**Density Functional Theory**

Parr&amp;Yang 3,7&amp;8

$$\hat{H}_{el} \equiv -\frac{1}{2} \sum_{i=1}^M \nabla_i^2 + \sum_{i<j}^M \frac{1}{|\hat{\mathbf{r}}_i - \hat{\mathbf{r}}_j|} + v(\mathbf{r})$$

only  $v$  changes

**Theorem (Hohenberg-Kohn):** If the ground state is not degenerate, the ground state density,  $\rho(\mathbf{r})$ , determines the potential,  $v(\mathbf{r})$ , up to an additive constant and vice versa.

Proof:  $v(\mathbf{r}) \rightarrow \rho(\mathbf{r})$ .  $v$  determines  $H$ .  $H$  determines  $\Psi_0$ , since the ground state is not degenerate.  $\Psi_0$  determines  $\rho$ :

$\rho(\mathbf{r}) \rightarrow v(\mathbf{r})$ . Assume the contrary and look for a contradiction. Then there are two potentials,  $v_1$  and  $v_2$ , that differ by more than an additive constant but give the same ground state density. Call the associated wave functions  $\Psi_1$  and  $\Psi_2$ . Then, consider  $\langle \Psi_1 | \hat{H}_2 | \Psi_1 \rangle$ . By the variational theorem, this must be  $\geq E_0^{[2]}$  (the ground state energy of  $H_2$ ). But:

$$\begin{aligned} \langle \Psi_1 | \hat{H}_2 | \Psi_1 \rangle &= \langle \Psi_1 | -\frac{1}{2} \sum_{i=1}^M \nabla_i^2 + \sum_{i<j}^M \frac{1}{|\hat{\mathbf{r}}_i - \hat{\mathbf{r}}_j|} + v_2(\mathbf{r}) | \Psi_1 \rangle \\ &= \langle \Psi_1 | -\frac{1}{2} \sum_{i=1}^M \nabla_i^2 + \sum_{i<j}^M \frac{1}{|\hat{\mathbf{r}}_i - \hat{\mathbf{r}}_j|} + v_1(\mathbf{r}) + (v_2(\mathbf{r}) - v_1(\mathbf{r})) | \Psi_1 \rangle \\ &= E_0^{[1]} + \langle \Psi_1 | (v_2(\mathbf{r}) - v_1(\mathbf{r})) | \Psi_1 \rangle \\ &= E_0^{[1]} + \int \rho(\mathbf{r}) (v_2(\mathbf{r}) - v_1(\mathbf{r})) d^3\mathbf{r} > E_0^{[2]} \end{aligned}$$

Here, the strict inequality holds because the potentials differ by more than a constant (so that the wave functions are not the same) and we know that the ground state is unique. Similarly:

$$\langle \Psi_2 | \hat{H}_1 | \Psi_2 \rangle = \dots = E_0^{[2]} + \int \rho(\mathbf{r}) (v_1(\mathbf{r}) - v_2(\mathbf{r})) d^3\mathbf{r} > E_0^{[1]}$$

Combining the two inequalities, we must then have

$$\int \rho(\mathbf{r}) (v_2(\mathbf{r}) - v_1(\mathbf{r})) d^3\mathbf{r} > E_0^{[2]} - E_0^{[1]}$$

and

$$E_0^{[2]} - E_0^{[1]} > \int \rho(\mathbf{r}) (v_2(\mathbf{r}) - v_1(\mathbf{r})) d^3\mathbf{r}$$

These inequalities cannot both be true and so we have reached a contradiction.

$\rho \rightarrow \text{everything!}$

The Kohn-Sham Idea:

$$\rho(x) \equiv \sum_{i=1}^N |\phi_i(x)|^2 \leftarrow \text{single determinant}$$

$$E[\rho(x)] = \sum_{i=1}^N \langle \phi_i | -\frac{1}{2} \nabla^2 + v(\mathbf{r}) | \phi_i \rangle + \int \frac{\rho(\mathbf{r}_1)\rho(\mathbf{r}_2)}{r_{12}} d\mathbf{r}_1 d\mathbf{r}_2 + E_{xc}[\rho(r)]$$

$\nwarrow$  K.E.     $\nwarrow$  e.N. att.     $\nwarrow$  Coulomb Repulsion     $\nwarrow$  xc functional

~~$$\frac{\delta E}{\delta \rho} = 0$$~~

$$L[\rho, x] = E[\rho] + \text{Tr}(\underline{x} \underline{P} \underline{P} - \underline{x} \underline{P})$$

$$\frac{\delta L}{\delta \rho} = 0 \dots$$

$$\underline{F} \rightarrow H_{\text{KS}}^{\text{KS}} = h_{\text{KS}} + \sum_{\lambda\sigma} P_{\lambda\sigma} \langle \chi_{\lambda} | v_{\text{KS}} | \chi_{\sigma} \rangle \rightarrow v_{\text{KS}}(\vec{r})$$

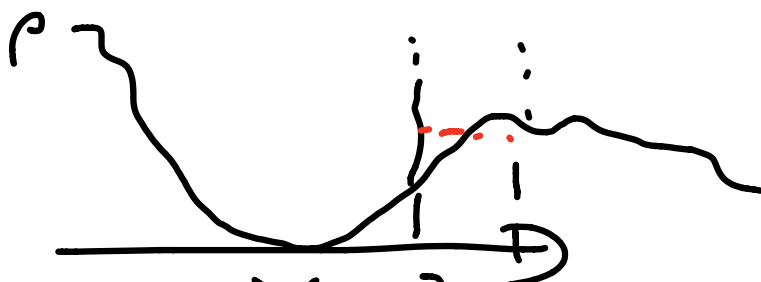
$$+ \int \chi_{\mu}^*(\mathbf{r}) \frac{\delta E_{xc}}{\delta \rho(\mathbf{r})} \chi_{\nu}(\mathbf{r}) d^3r$$

$$\langle \chi_{\mu} | v_{xc} | \chi_{\nu} \rangle$$

Looks Like HF!

What is  $E_{xc}$ ?

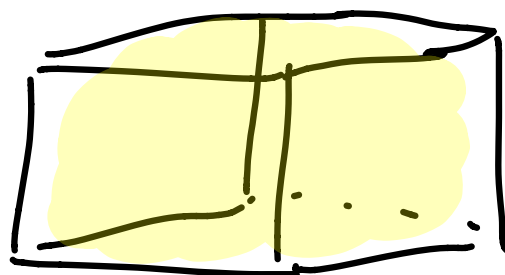
Idea: Uniform Electron Gas



What is  $E_{xc}$  here  $\rightarrow E_{xc}^{\text{UEG}}?$

Local Density Approx

$$E_{xc}[\rho] = \int \epsilon_{xc}^{\text{UEG}}(\rho(\mathbf{r})) d^3r$$



periodic, uniform  $\rho(r)$

$$E_{xc}[\rho(r)] \rightarrow E_{xc}^{\text{UEG}}(\rho)$$

QMC for UEG

$$E_{xc}^{\text{UEG}}[\rho] = \int \epsilon_{xc}^{\text{UEG}}(\rho) d^3r$$

Property	HF	LDA
IPs and EAs	$\pm 0.5$ eV	$\pm 0.5$ eV
Bond Lengths	-1%	+2%
Vibrational Frequencies	+10%	-20%
Barrier Heights	+30-50%	-75%
Bond Energies	-50%	+100%

### Generalized Gradient Approximation

$$E_{xc}^{GGA}[\rho] = \int F(\rho, \nabla \rho) d\mathbf{r}$$

Better Physics for varying  $\rho$ 's  
BLYP, PBE

How do we get  $F(\rho, \nabla \rho)$ ?

1) Nearly Uniform Gas  $\rightarrow \rho(r) = \rho + \delta \rho(r)$

$\hookrightarrow$  Recover UEG when  $\nabla \rho \rightarrow 0$

2) Atomic data  $\rho(r) \sim e^{-\alpha r}$

3) Physical Constraints

$\hookrightarrow$  Dimensional Scaling

$\hookrightarrow$  Sum rules (xc hole)

4) Empiricism

Property	HF	GGA	MP2	CCSD(T)
IPs and EAs	±0.5 eV	± 0.2 eV	±0.2 eV	±0.05 eV
Bond Lengths	-1%	+ 1%	±1 pm	±0.5 pm
Vibrational Frequencies	+10%	- 5%	+3%	±5 cm <sup>-1</sup>
Barrier Heights	+30-50%	- 50%	+10%	±2 kcal/mol
Bond Energies	-50%	+ 10 $\frac{\text{kcal}}{\text{mol}}$	±10 kcal/mol	±1 kcal/mol

Obvious next step: Meta (or hyper-) GGAs

$$E_{xc}^{GGA}[\rho] = \int F(\rho, \nabla\rho, \nabla^2\rho, \tau, \dots) d\mathbf{r}$$

$$\tau(\mathbf{r}) \equiv \sum_{i=1}^N |\nabla\phi_i(\mathbf{r})|^2$$

Doesn't improve much.

TPSS, M06, VSXC

Hybrids

$$E_{xc}[\rho] = \langle h \rangle + \int \frac{\rho(\mathbf{r}_1)\rho(\mathbf{r}_2)}{r_{12}} d\mathbf{r}_1 d\mathbf{r}_2 + c_x E_x^{GGA} + E_c^{GGA} + c_K E_K^{HF}$$

B3LYP

Why?