

## Chapter 5 continued - approximating $E_{xc}[n]$

Kohn-Sham:

$$E[n] = T_S[n] + \int d^3r v^{nuc}(\mathbf{r}) n(\mathbf{r}) + \frac{1}{2} \int d^3r d^3r' \frac{n(\mathbf{r}) n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} + E_{xc}[n]$$

$T_S$  via

$$\left[ -\frac{\nabla^2}{2} + v^{nuc}(\mathbf{r}) + v_{es}^e(\mathbf{r}) + v_{xc}(\mathbf{r}) \right] \phi_{ok}(\mathbf{r}) = \epsilon_{ok} \phi_{ok}(\mathbf{r})$$

$$v_{xc}(\mathbf{r}) = \frac{\delta E_{xc}[n]}{\delta n(\mathbf{r})}$$

Local-density approximation (LDA):  $E_{xc}[n] \approx E_{xc}^{LDA}[n] = \int d^3r n(\mathbf{r}) \epsilon_{xc}^{HEG}(n(\mathbf{r}))$

energy density (i.e. energy per volume and particle) of the homogeneous electron gas

### 5.3 LDA in practice - How and why it works

Some facts:

- Overall: "well-behaved" systems (covalently bonded, ionic, metallic, semiconducting bonded):

Remarkably good "chemical trends"

"First principles" - no adjustable parameters!

- A) "Over-binding":
- Lattice parameters too short by few %
  - Cohesive energies somewhat too large

B) Error cancellation:

Atoms & molecules [also solids]:

$E_x$  typ. underestimated  $\sim 10\%$

$E_c$  typ. overestimated  $\sim 100\% - 200\%$

but  $E_x \sim 4 E_c$

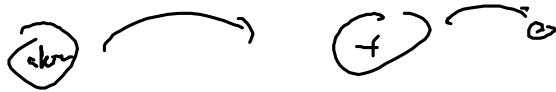
$\Rightarrow$  errors cancel (e.g., better than

wisely  $E_{HF}^x[\rho] + E_c[\rho]$ )

D) Ionization energies  $E(N) - E(N-1)$

better than HF, but still typ.  $\sim 0.25$  eV off

incorrect potential decay i-to vacuum: should be  $-\frac{1}{r}$   
is exponential decay



E) Lack of self-interaction cancellation:

In HF, for any systems, self-interaction in  $E^{\text{Hartree}}$  is cancelled by  $E^x$

In LDA ( $1e^-$ ), we have

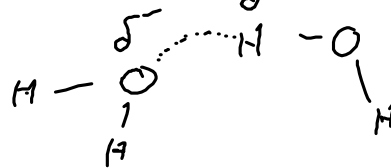
$$V^{\text{nuc}} + \underbrace{V_{\text{el}}^e + V_{\text{xc}}(\rho)}_{\text{LDA for HEG is not built to correct exactly the es. energy of a single-electron wave fun.}}$$

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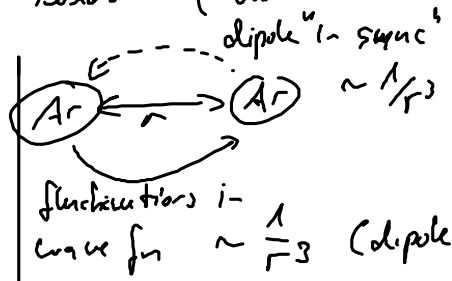
F) Weak bonds, for example

"Hydrogen bonds" in soft matter not well described

small inhomogeneous densities in bonding regions



6) Even "weaker" bonds (van der Waals, dispersion) not captured



no reason for chemical bond (closed-shell)

↳ total effective interaction  $\sim \frac{C_6}{r^6}$  completely non-local

(LDA thinks

$$E(\text{Ar}, \text{Ar}) = 2E(\text{Ar})$$

$$\rightarrow E_5(\text{Ar}-\text{Ar}) = 0$$

Why does LDA work as far it does?

→ "Exchange-correlation hole"

Remember HF

$$\left[ -\frac{\nabla^2}{2} + V^{\text{ext}}(\mathbf{r}) + V_{\text{es}}^e(\mathbf{r}) + V_k^x(\mathbf{r}) \right] \phi_{0k}(\mathbf{r}) = \epsilon_{0k} \phi_{0k}(\mathbf{r})$$

$V_k^x(\mathbf{r})$  formally defined as

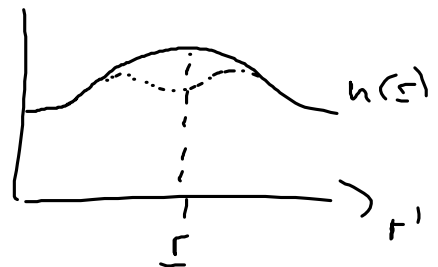
$$V_k^x(\mathbf{r}) = - \int d^3r' \frac{w_{\text{HF},k}(\mathbf{r}, \mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|}$$

$$w_{\text{HF}}(\mathbf{r}, \mathbf{r}') = \sum_{k \neq i} \frac{\phi_{0i}^*(\mathbf{r}') \phi_{0k}(\mathbf{r}') \phi_{0k}(\mathbf{r})}{\phi_{0i}(\mathbf{r})}$$

If we forced an electron to sit at  $\mathbf{r}$

then it would "see" an effective density  $[n(\mathbf{r}) - w_{\text{HF}}^k(\mathbf{r}, \mathbf{r}')] ]$  around itself

"exchange hole"  
(here state-dep.)



In total energy expression, what matters is

$$\bar{E}_x \sim - \sum_{k=1}^N \int d^3r \phi_{0k}^*(\mathbf{r}) \int d^3r' \frac{n_k^{\text{HF}}(\mathbf{r}, \mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} \phi_{0k}(\mathbf{r})$$

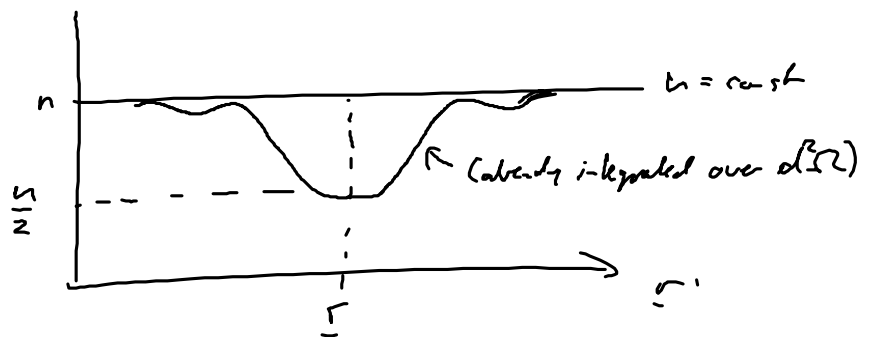
$$=: \int d^3r d^3r' \frac{n(\mathbf{r}) n^{\text{HF}}(\mathbf{r}, \mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|}$$

$$n^{\text{HF}}(\mathbf{r}, \mathbf{r}') = \sum_k \frac{1}{n(\mathbf{r})} \phi_{0k}^*(\mathbf{r}) n_k^{\text{HF}}(\mathbf{r}, \mathbf{r}') \phi_{0k}(\mathbf{r})$$

HEG:  $n(\mathbf{r}) = \frac{N}{V_{\text{box}}}$ ,  $\phi_k(\mathbf{r}) = \frac{1}{\sqrt{V_{\text{box}}}} e^{i\mathbf{k}\cdot\mathbf{r}}$

direct i-sobin yields average X hole of HEG

$$n_{\text{HEG}}^{\text{HF}}(\mathbf{r}, \mathbf{r}') = n_{\text{HEG}}^{\text{HF}}(|\mathbf{r} - \mathbf{r}'|) = \frac{g}{2} \frac{N}{V} \left( \frac{k_F |\mathbf{r} - \mathbf{r}'| \cos k_F |\mathbf{r} - \mathbf{r}'| - \sin k_F |\mathbf{r} - \mathbf{r}'|}{(k_F |\mathbf{r} - \mathbf{r}'|)^2} \right)$$



X hole: - positive everywhere

- contains exactly 1 electron  $\int d^3r' n_{\text{HEG}}^{\text{HF}}(\mathbf{r}, \mathbf{r}') = 1$

In general,  $E[n]$  can always be written by defining an XC hole for any system, even for "exact" functional

$$E[n] = T_S[n] + \int d^3r v^{\text{ext}}(\mathbf{r}) n(\mathbf{r}) + \frac{1}{2} \int d^3r d^3r' n(\mathbf{r}) \frac{n(\mathbf{r}') - n_{\text{xc}}(\mathbf{r}, \mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|}$$

by formal definitions (note  $T - T_s$ !)

But note: only average  $\int d^3r' \frac{n_{xc}(\underline{r}, \underline{r}')}{|\underline{r} - \underline{r}'|}$  enters  $E_{xc}[n]$

in particular:  $\int d^3r u \cdot \frac{1}{u} \int d^3r' \frac{n_{xc}(\underline{r}, \underline{r}')}{|\underline{r} - \underline{r}'|}$

gives  $\underline{\hat{n}}_{xc}(\underline{r}, u)$

Spherically averaged xc hole number for  $E_{xc}$ !

Note: Spherically symmetric LDA xc hole has the right average properties overall (normalization!)

### 5.4 Beyond LDA - Gradient expansion approximations

Kohn-Sham 1965: If LDA not enough, why not write

$$E_{xc}[n] \approx E_{xc}^{GFA}[n, |\nabla n|]$$

usually written as

$$E_{xc}^{GFA}[n] = \int d^3r n(\underline{r}) \epsilon_{xc}^{HEG}[n(\underline{r})] \cdot F_{xc}(n(\underline{r}), |\nabla n(\underline{r})|)$$

In practice (exchange), conventional to use "scaled gradient"

$$s = \frac{|\nabla n(\underline{r})|}{2k_F(\underline{r}) n(\underline{r})}$$

then  $F_x \approx 1 + C s^2(\underline{r}) \dots$

$$\hookrightarrow \left(\frac{10}{81}\right)$$

can be analyzed, similar (and more complicated) for correlation

But limit of small scaled gradients is not enough!

Essentially: XC hole does not correspond to physical system,  
not properly normalized!

Fix: Use properties of XC hole to define the right form  $F_{xc}[n, |\nabla n(r)|]$ .

## 5.5 Generalized gradient approximations

- 1981 Langreth-Meld "Real-space cutoff" GGA
- Perdew and others: parameterize " $F_{xc}$ " to fulfill known exact constraints  
→ get GGA form based only on fundamental constraints ("first principles")
- Becke, many others: Lots of empirical GGA forms.

(Probably) most successful in physics "PBE" GGA  
(Perdew, Burke, Ernzerhoff 1996)

as conventional  $E_{xc}^{PBE}[n, \eta] = E_x^{PBE}[n, \eta] + E_c^{PBE}[n, \eta]$

$$E_x^{PBE}[n] = \int d^3r n(r) E_x^{HEG}(n(r)) \cdot F_x(s)$$

$$\text{Use: } F_x(s) = 1 + \kappa - \frac{\kappa}{1 + \frac{\mu s^2}{\kappa}}$$

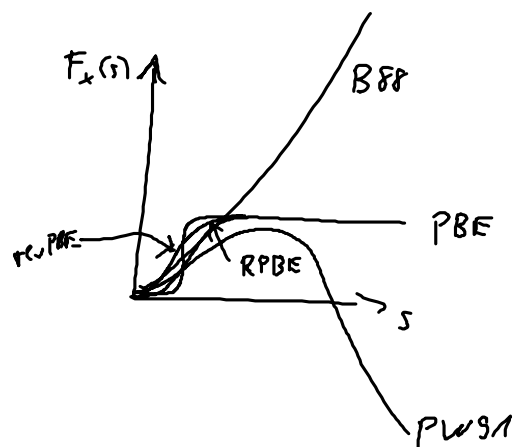
(and note spin scaling  $E_x[n_\uparrow, n_\downarrow] = \frac{1}{2} E_x[2n_\uparrow] + \frac{1}{2} E_x[2n_\downarrow]$ )

-  $\mu, \kappa$  can be obtained from fundamental limits

1) Known linear response of the GEA

$$F_x(s) \rightarrow 1 + C s^2 \rightarrow \text{Taylor: } \mu = C!$$

2) "Lieb-Oxford" bound: Showed that  $F_x(s) \leq 1.804$  everywhere.  
 if we take  $1.804 \rightarrow k = 0.804$ .



Correlation: Essentially similar game

$$E_x^{\text{PBE}}[u] = \int d^3r u(r) [e_c(u, \eta) + H(r_s, \eta, t)]$$

$$t = \frac{|\nabla u|}{2\phi k_s u}$$

$$k_s = \sqrt{\frac{4k_F}{\pi}}$$

$$\phi = [(1+\eta)^{2/3} + (1-\eta)^{2/3}] / 2$$

and functional form

$$H = \eta \phi^3 \ln \left[ 1 + \frac{\beta}{\eta} t^2 \left( \frac{1+A t^2}{1+A t^2 + A^2 t^4} \right) \right]$$

$$A(u, \eta) = \frac{\beta}{\eta} \left[ e^{-\epsilon_c^{\text{HEG}} / \eta \phi} - 1 \right]^{-1}$$

• Recovers GEA for  $t \rightarrow 0$   $H \sim \beta \phi^3 t^2$

•  $t \rightarrow \infty$  (rapid variation)  $\Rightarrow H \rightarrow -\epsilon_c^{\text{HEG}}$

• Scaling properties of  $\epsilon_c$ :  $u(r) \rightarrow \lambda^3 u(\lambda r)$

UGA  $\rightarrow$  a lot of basic theory went in

... but the result looks simple!

General remarks, GGA:

• Clearly improved cohesive energies, lattice parameters are now slightly too large  
works well for most well-balanced systems (now includes hydrogen-bonded systems)

• ... no van der Waals

• ... no exact self-interaction cancellation

• ... still no analytically correct  $V_{\text{ec}}$  as  $r \rightarrow \infty$  for atoms  
surface

Recent: There seems to be a "demonstrable" limit to repairing GGA's  
to cover (especially) self-interaction, must go beyond...

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Exercises (tentative): Tue 29.6. 14<sup>00</sup>-18<sup>00</sup>  
6.7.  
or Tue 29.6., Thu 1.7 (tbd)