

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

$$\left[-\frac{\nabla^2}{2} + v^{nuc}(\mathbf{r}) + v_{es}^e(\mathbf{r}) + v_{xc}(\mathbf{r}) \right] \phi_{0k}(\mathbf{r}) = \epsilon_{0k} \phi_{0k}(\mathbf{r})$$

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

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) "Overbinding":
- 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

w/ w/ $E_{HF}^x[\varphi] + E_c[\varphi]$

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 $E^{HF}[\varphi]$ is cancelled by E^x

In LDA (ρ^{γ}), we have

$$V_{nuc} + V_{ex}^c + V_{xc}(\rho)$$

LDA for NEG is not built to correct exactly the es. energy of a single-electron wave fun.

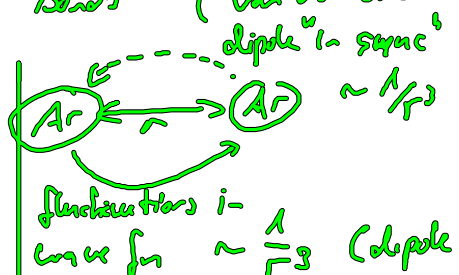
F) Weak bands, for example

"Hydrogen bonds" in soft matter not well described

small inhomogeneous densities in bonding regions



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



no reason for clustered bands (band-structure)

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

(LDA thinks

$$E(Ar, Ar) = 2E(Ar)$$

$$\rightarrow E_5(Ar-Ar) = 0$$

Why does LDA work as far it does?

→ "Exchange-correlation hole"

Remember HF

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

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

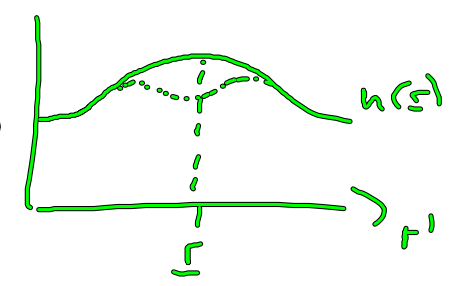
$$V_k^x(\mathbf{r}) = - \int d^3r' \frac{v_{HF,k}(\mathbf{r}, \mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|}$$

$$v_{HF}(\mathbf{r}, \mathbf{r}') = \sum_{k'n'} \delta_{s_k, s_{k'}} \frac{\phi_{k'n'}^*(\mathbf{r}') \phi_{k'}(\mathbf{r}') \phi_{k'n}(\mathbf{r})}{\phi_{k'}(\mathbf{r})}$$

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

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

"exchange hole"
(here state-dep.)



In total energy expression, what matters is

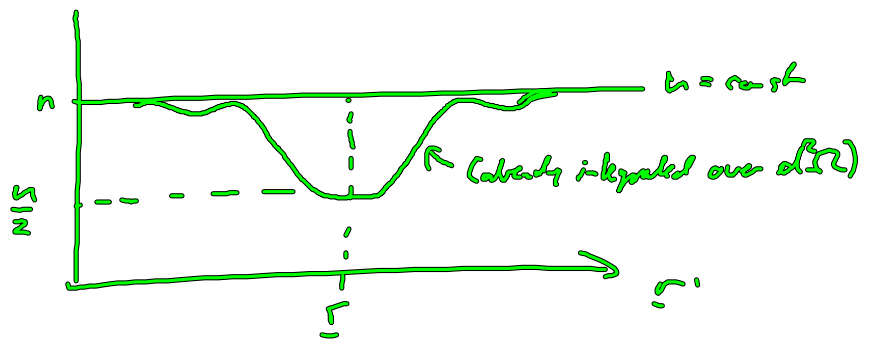
$$\begin{aligned} E_x &\sim - \sum_{k=1}^N \int d^3r \phi_{0k}^*(r) \int d^3r' \frac{v_k^{\text{HF}}(r, r')}{|r-r'|} \phi_{0k}(r) \\ &= \int d^3r d^3r' \frac{n(r) v^{\text{HF}}(r, r')}{|r-r'|} \end{aligned}$$

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

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

direct insertion yields average X hole of HEG

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



X hole: - positive everywhere

- carries exactly 1 electron $\int d^3r' v_{\text{HEG}}^{\text{HF}}(r, r') \stackrel{!}{=} 1$

In general, $E[n]$ can always be written by definition as XC

hole for any system, even for "exact" functional

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

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 $E_{xc}[\psi]$

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

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

$$E_{xc}[\psi] \approx E_{xc}^{GGA}[\psi, |\nabla\psi|]$$

usually written as

$$E_{xc}^{GGA}[\psi] = \int d^3r \psi(\underline{r}) E_{xc}^{HFB}[\psi(\underline{r})] \cdot F_{xc}(\psi(\underline{r}), |\nabla\psi(\underline{r})|)$$

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

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

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

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

can be analyzed, similar (much 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!

Fu: Use properties of XC hole to derive 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 constants ("first principles")
- Becke, many others: Lots of empirical GGA forms.

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

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

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

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

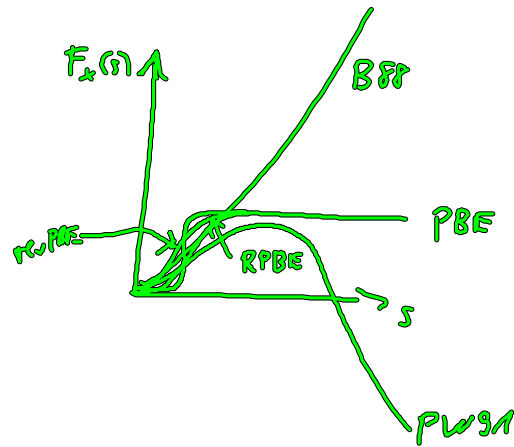
(and note spin scaling $E_x[n_\uparrow, n_\downarrow] = \frac{1}{2} E_x[2n_\uparrow] + \frac{1}{2} E_x[2n_\downarrow]$)

- μ, κ 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: Show that $F_x(s) \leq 1.804$ everywhere.
 if κ like 1.804 $\rightarrow \kappa = 0.804$.



Correlation: Essentially similar game

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

$$t = \frac{|\psi(\psi)|}{2\phi k_s \psi}$$

$$k_s = \sqrt{\frac{4k_F}{\pi}} \quad \phi = [(1+\eta)^{2/3} + (1-\eta)^{2/3}] / 2$$

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

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

• 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 ϵ_c : $\psi(r) \rightarrow \lambda^3 \psi(\lambda r)$

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 coll.-balanced systems (now includes hydrogen-bonded systems)

• ... no van der Waals

• ... no exact self-interaction cancellation

• ... still no analytically correct V_{ic} 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...

Exercises (tentative): Tue 29.6. 14⁰⁰-18⁰⁰
6.7.
or Tue 29.6., Thu 1.7 (tbd)