

4. Likewise the orbital energies ϵ_j have, in general, no physical meaning.
5. The density dependence of $v_s[s]$ is non-local, i.e. the potential $v_s(\vec{r})$ at point \vec{r} is determined by the density at all points $s(\vec{r}')$.

4. Local Density Approximation (LDA)

(Phys. Rev. 140,
A 1133 (1965))

4.1. The homogeneous electron gas

We use a simple system, namely the homogeneous electron gas (HEG), to construct an approximation for $E_{xc}[s]$.

What is the HEG?

- electron density $s(\vec{r})$ is constant over space, therefore the electron number is infinite
- negative charge is compensated by a rigid uniform positive background

KS system of the HEG:

- by symmetry the KS potential $v_s(\vec{r})$ must be constant over space $\Rightarrow v_s(\vec{r}) \equiv 0$
- we impose periodic boundary conditions over a volume V and then consider the limit $V \rightarrow \infty$
- KS orbitals are plane waves $\varphi(\vec{r}) = \frac{1}{\sqrt{V}} e^{i\vec{k}\vec{r}}$ with momentum \vec{k} and KS energy $\frac{k^2}{2}$
- number of electrons in volume V

$$N = s \cdot V = 2 \cdot \sum_{\vec{k}} \Theta(k_F - k) = 2 \cdot \frac{V}{(2\pi)^3} \int_0^{k_F} dk 4\pi k^2 \quad k_F: \text{Fermi vector}$$

$$= \frac{V}{3\pi^2} k_F^3$$

$$\Rightarrow s = \frac{k_F^3}{3\pi^2} = \frac{3}{4\pi r_s^3}$$

r_s : Seitz radius
= radius of sphere that on average contains one electron

- kinetic energy per particle

$$t_s(s) = \frac{T_s[s]}{N} = \frac{2}{N} \sum_{\vec{k}} \Theta(k_F - k) \frac{k^2}{2} = \frac{2V}{N(2\pi)^3} \int_0^{k_F} dk 4\pi k^2 \frac{k^2}{2}$$

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$$t_s(s) = \frac{3}{5} \frac{k_F^2}{2} = \frac{3}{10} (3\pi^2 s)^{2/3}$$

- exchange correlation energy per particle

$$\text{exchange part: } e_x(s) = -\frac{3}{4\pi} k_F = -\frac{3}{4\pi} (3\pi^2 s)^{1/3} = -\frac{3}{4\pi} \frac{(9\pi/4)^{1/3}}{s}$$

correlation part: only some limits are known

$$\text{for } r_s \rightarrow 0 \quad e_c(s) = c_0 \ln r_s - c_1 + c_2 r_s \ln r_s - c_3 r_s + \dots$$

$$\text{with } c_0 = 0.031091 \\ c_1 = 0.046644$$

$$\text{for } r_s \rightarrow \infty \quad e_c(s) = -\frac{d_0}{r_s} + \frac{d_1}{r_s^{3/2}} + \dots$$

Quantum Monte Carlo calculations for the gs energy

at different r_s : D.M. Ceperley, B.J. Alder Phys. Rev. Lett. 45, 566 (1980)

r_s	1.0	2.0	5.0	10.0	20.0
E	1.174	0.0041	-0.1512	-0.10675	-0.06329

r_s	50.0	100.0
E	-0.02884	-0.015321

collect all available information and parametrize

for example J.P. Perdew, Y. Wang Phys. Rev. B 45, 13244 (1992)

$$e_c(s) = -2c_0 (1 + \alpha_1 r_s) \ln \left[1 + \frac{1}{2c_0 (\beta_1 r_s^{1/2} + \beta_2 r_s + \beta_3 r_s^{3/2} + \beta_4 r_s^2)} \right]$$

$$\text{with } \beta_1 = \frac{1}{2c_0} \exp\left(-\frac{c_1}{2c_0}\right), \quad \beta_2 = 2c_0 \beta_1^2$$

$$\alpha_1 = 0.21370, \quad \beta_3 = 1.6382, \quad \beta_4 = 0.49294$$

other parametrizations

S.H. Vosko, L. Wilk, M. Nusair Can. J. Phys. 58, 1200 (1980)

J.P. Perdew, A. Zunger Phys. Rev. B 23, 5048 (1981)

At this point we have a formula for the xc energy per particle of the HEG.

How do we use this knowledge for inhomogeneous systems?

idea of the LDA: at each point in space \vec{r} we use e_{xc} of the HEG evaluated at the density $s(\vec{r})$

$$E_{xc}^{LDA}[s] = \int d^3r s(\vec{r}) e_{xc}(s(\vec{r}))$$

4.2. Quality of the LDA

From its construction we expect the LDA to work well for systems where the density varies slowly over space.

For atoms we get:

	E_{xc}^{LDA}	E_{xc}^{exact}	
He	-1.00	-1.09	LDA works extremely well in these cases
Be	-2.54	-2.76	
Ne	-11.78	-12.50	

Why is the LDA so good?

4.3. Coupling constant integration

Original many-body Hamiltonian

$$H_\lambda = \sum_{j=1}^N \left(-\frac{\nabla_j^2}{2} + v_\lambda(\vec{r}_j) \right) + \frac{1}{2} \lambda \sum_{\substack{j,k=1 \\ j \neq k}}^N \frac{1}{|\vec{r}_j - \vec{r}_k|}$$

add a parameter λ , $0 \leq \lambda \leq 1$

$v_\lambda(\vec{r})$ is chosen in such a way that the gs density of H_λ remains the same: $s_\lambda(\vec{r}) = s_{\lambda=1}(\vec{r}) = s(\vec{r})$.

Note: v_λ is unique because one can prove a HK theorem for each λ .

By going to $\lambda=0$, $H_{\lambda=0}$ describes non-interacting electrons moving in the external potential $v_{\lambda=0}(\vec{r})$.

Since $s_{\lambda=0}(\vec{r}) = s_{\lambda=1}(\vec{r})$ the potential $v_{\lambda=0}(\vec{r})$ must be the KS potential $v_s(\vec{r})$.

$$H_\lambda \Psi_\lambda(\vec{r}_1, \dots, \vec{r}_N) = E_\lambda \Psi_\lambda(\vec{r}_1, \dots, \vec{r}_N)$$

$$E_\lambda = \langle \Psi_\lambda | H_\lambda | \Psi_\lambda \rangle$$

How does the energy change with λ ?

$$\begin{aligned} \frac{dE_\lambda}{d\lambda} &= \langle \frac{d\Psi_\lambda}{d\lambda} | H_\lambda | \Psi_\lambda \rangle + \langle \Psi_\lambda | \frac{dH_\lambda}{d\lambda} | \Psi_\lambda \rangle + \langle \Psi_\lambda | H_\lambda | \frac{d\Psi_\lambda}{d\lambda} \rangle \\ &= E_\lambda \langle \frac{d\Psi_\lambda}{d\lambda} | \Psi_\lambda \rangle + \langle \Psi_\lambda | \frac{dV_\lambda}{d\lambda} + W | \Psi_\lambda \rangle + E_\lambda \langle \Psi_\lambda | \frac{d\Psi_\lambda}{d\lambda} \rangle \\ &= E_\lambda \frac{d}{d\lambda} \underbrace{\langle \Psi_\lambda | \Psi_\lambda \rangle}_{=1} + \langle \Psi_\lambda | \frac{dV_\lambda}{d\lambda} + W | \Psi_\lambda \rangle \end{aligned}$$

$$\begin{aligned} \langle \Psi_\lambda | W | \Psi_\lambda \rangle &= \frac{1}{2} \int d^3r_1 \dots d^3r_N \Psi_\lambda^*(\vec{r}_1, \dots, \vec{r}_N) \sum_{\substack{j,k=1 \\ j \neq k}}^N \frac{1}{|\vec{r}_j - \vec{r}_k|} \Psi_\lambda(\vec{r}_1, \dots, \vec{r}_N) \\ &= \int d^3r_1 \dots d^3r_N \Psi_\lambda^*(\vec{r}_1, \dots, \vec{r}_N) \frac{1}{|\vec{r}_1 - \vec{r}_2|} \Psi_\lambda(\vec{r}_1, \dots, \vec{r}_N) \\ &\quad + \int d^3r_1 \dots d^3r_N \Psi_\lambda^*(\vec{r}_1, \dots, \vec{r}_N) \frac{1}{|\vec{r}_2 - \vec{r}_3|} \Psi_\lambda(\vec{r}_1, \dots, \vec{r}_N) + \dots \\ &= \int d^3r_1 d^3r_2 \frac{1}{|\vec{r}_1 - \vec{r}_2|} \cdot \int d^3r_3 \dots d^3r_N \Psi_\lambda^*(\vec{r}_1, \dots, \vec{r}_N) \Psi_\lambda(\vec{r}_1, \dots, \vec{r}_N) \\ &\quad + \int d^3r_1 \dots d^3r_N \Psi_\lambda^*(\vec{r}_3, \vec{r}_1, \vec{r}_2, \dots, \vec{r}_N) \frac{1}{|\vec{r}_1 - \vec{r}_2|} \Psi_\lambda(\vec{r}_3, \vec{r}_1, \vec{r}_2, \dots, \vec{r}_N) + \dots \\ &= \frac{1}{2} \int d^3r_1 d^3r_2 \frac{T_\lambda(\vec{r}_1, \vec{r}_2)}{|\vec{r}_1 - \vec{r}_2|} \end{aligned}$$

with

$$T_\lambda(\vec{r}_1, \vec{r}_2) = N(N-1) \int d^3r_3 \dots d^3r_N |\Psi_\lambda(\vec{r}_1, \dots, \vec{r}_N)|^2$$

$$\frac{dE_\lambda}{d\lambda} = \int d^3r s(\vec{r}) \frac{dV_\lambda(\vec{r})}{d\lambda} + \frac{1}{2} \int d^3r_1 d^3r_2 \frac{T_\lambda(\vec{r}_1, \vec{r}_2)}{|\vec{r}_1 - \vec{r}_2|}$$

$$E_{\lambda=1} - E_{\lambda=0} = \int_0^1 d\lambda \frac{dE_\lambda}{d\lambda}$$

$$\begin{aligned} &= \int d^3r s(\vec{r}) \underbrace{\int_0^1 d\lambda \frac{dV_\lambda(\vec{r})}{d\lambda}}_{=V_{\lambda=1}(\vec{r}) - V_{\lambda=0}(\vec{r})} + \frac{1}{2} \int d^3r_1 d^3r_2 \int_0^1 d\lambda \frac{T_\lambda(\vec{r}_1, \vec{r}_2)}{|\vec{r}_1 - \vec{r}_2|} \quad (*) \\ &= V(\vec{r}) - V_0(\vec{r}) \end{aligned}$$

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remember: $\lambda=1$ is the full interacting system $\lambda=0$ is the KS system

$$E_{\lambda=1} = T_s[s] + E_H[s] + \int d^3r v(\vec{r}) s(\vec{r}) + E_{xc}[s]$$

$$E_{\lambda=0} = T_s[s] + \int d^3r v_s(\vec{r}) s(\vec{r})$$

$$\Rightarrow E_{\lambda=1} - E_{\lambda=0} = \int d^3r [v(\vec{r}) - v_s(\vec{r})] s(\vec{r}) + E_H[s] + E_{xc}[s]$$

$$\begin{aligned} (*) \Rightarrow E_{xc}[s] &= \frac{1}{2} \int d^3r_1 d^3r_2 \int_0^1 d\lambda \frac{T_\lambda(\vec{r}_1, \vec{r}_2)}{|\vec{r}_1 - \vec{r}_2|} - E_H[s] \\ &= \frac{1}{2} \int d^3r_1 d^3r_2 \left[\int_0^1 d\lambda \frac{T_\lambda(\vec{r}_1, \vec{r}_2) - s(\vec{r}_1) s(\vec{r}_2)}{|\vec{r}_1 - \vec{r}_2|} \right] \\ &= \frac{1}{2} \int d^3r_1 s(\vec{r}_1) \int d^3r_2 \left[\int_0^1 d\lambda \frac{T_\lambda(\vec{r}_1, \vec{r}_2) / s(\vec{r}_1) - s(\vec{r}_2)}{|\vec{r}_1 - \vec{r}_2|} \right] \end{aligned}$$

define exchange-correlation hole

$$s_{xc}(\vec{r}_2 | \vec{r}_1) = \underbrace{\frac{\int_0^1 d\lambda T_\lambda(\vec{r}_1, \vec{r}_2)}{s(\vec{r}_1)}}_{\text{Conditional probability to find an electron at } \vec{r}_2 \text{ given there is an electron at } \vec{r}_1} - s(\vec{r}_2)$$

2 Unconditional probability to find an electron at \vec{r}_2

Why is this called a hole?

$$\begin{aligned} \int d^3r_2 s(\vec{r}_2 | \vec{r}_1) &= \frac{1}{s(\vec{r}_1)} \int_0^1 d\lambda \int d^3r_2 T_\lambda(\vec{r}_1, \vec{r}_2) - \int d^3r_2 s(\vec{r}_2) \\ &= \frac{1}{s(\vec{r}_1)} (N-1) N \int_0^1 d\lambda \int d^3r_2 \dots d^3r_N |\Psi_\lambda(\vec{r}_1 \dots \vec{r}_N)|^2 - N \\ &= \frac{1}{s(\vec{r}_1)} (N-1) \int_0^1 d\lambda \underbrace{s_\lambda(\vec{r}_1)}_{s(\vec{r}_1)} - N \\ &= N-1 - N \\ &= -1 \end{aligned}$$

$$E_{xc}[s] = \frac{1}{2} \int d^3r_1 s(\vec{r}_1) \int d^3r_2 \frac{s_{xc}(\vec{r}_2 | \vec{r}_1)}{|\vec{r}_1 - \vec{r}_2|}$$

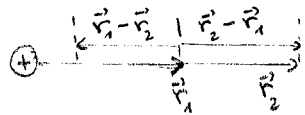
$$E_{xc}^{LDA}[s] = \frac{1}{2} \int d^3r_1 s(\vec{r}_1) \int d^3r_2 \frac{s_{xc}^{HEG}(\vec{r}_2 | \vec{r}_1)}{|\vec{r}_1 - \vec{r}_2|}$$

16- Since s_{xc}^{HEG} is the xc-hole of a physical system it obeys the sum rule $\int d^3r_2 s_{xc}^{HEG}(\vec{r}_2 | \vec{r}_1) = -1$.

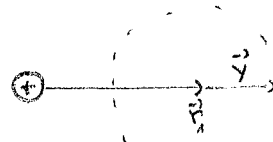
$$\begin{aligned} \frac{1}{2} \int d^3r_2 \frac{s_{xc}(\vec{r}_2 | \vec{r}_1)}{|\vec{r}_1 - \vec{r}_2|} &= \frac{1}{2} \int d^3y \frac{s_{xc}(\vec{r}_1 + \vec{y} | \vec{r}_1)}{|\vec{y}|} & \vec{r}_2 &= \vec{r}_1 + \vec{y} \\ &= \frac{1}{2} \int_0^\infty dy y^2 \frac{1}{|y|} \int d\Omega_y s_{xc}(\vec{r}_1 + \vec{y} | \vec{r}_1) \\ &= \frac{1}{2} \int_0^\infty dy y s_{xc,av.}(y, \vec{r}_1) \end{aligned}$$

$s_{xc,av.}$: average xc-hole (averaged over an angle)

See plots on next page for a comparison of the exchange and averaged exchange holes of the neon atom (from Phys. Rev. B 20, 3136 (1979)).



We need to integrate over all \vec{r}_2



Rearrange integration to

$$\vec{y} = \vec{r}_2 - \vec{r}_1$$

→ Collect all points with the same $|\vec{y}|$ = integration over $d\Omega_y$

A few words on the hole:

$P(\vec{r}_1, \vec{r}_2)$: probability to find an electron at \vec{r}_1 and one at \vec{r}_2

If the electrons are independent $P(\vec{r}_1, \vec{r}_2) = s(\vec{r}_1) \cdot s(\vec{r}_2)$ otherwise $P(\vec{r}_1, \vec{r}_2)$ is the product of $s(\vec{r}_1)$ times the conditional probability, i.e. the probability of finding a second electron at \vec{r}_2 if we know that there is one electron at \vec{r}_1 . $s_{xc}(\vec{r}_2 | \vec{r}_1)$ describes the difference between these two cases. The sum rule $\int d^3r_2 s_{xc}(\vec{r}_2 | \vec{r}_1) = -1$ means that if an electron is definitely at \vec{r}_1 it is missing from the rest of the cloud...

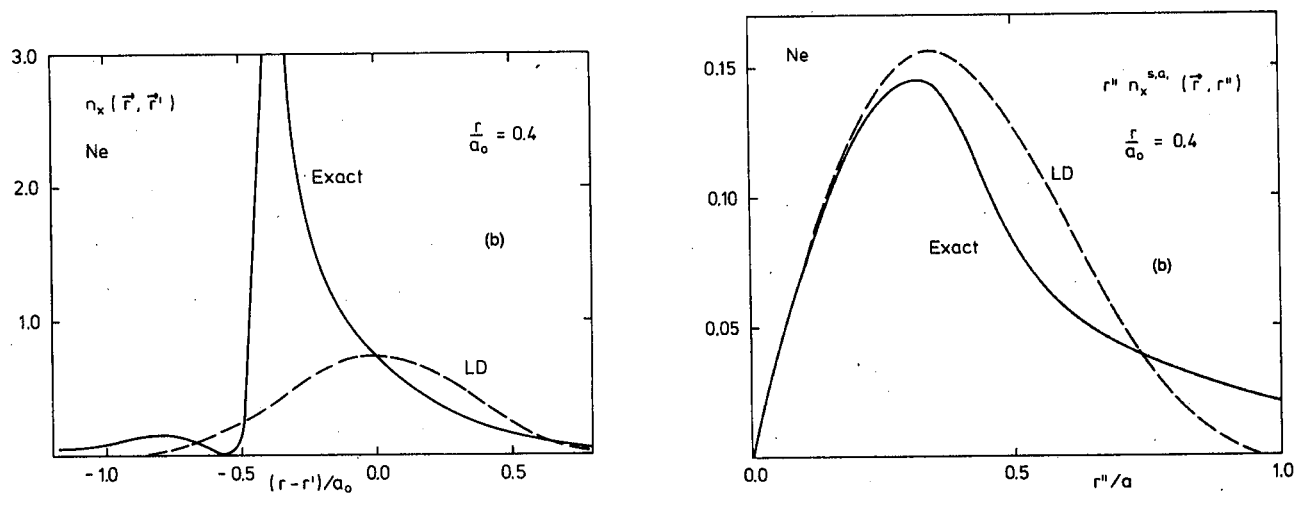


Figure 1: Exchange hole of the neon atom for $r = 0.4a_0$, exact and LDA. Total hole (left) and averaged hole (right)

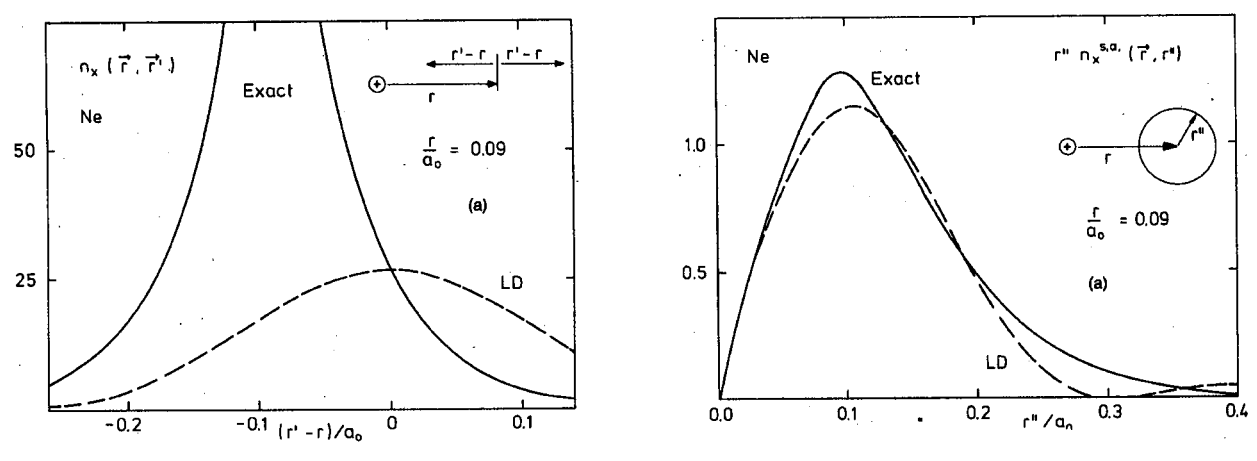


Figure 2: Exchange hole of the neon atom for $r = 0.9a_0$, exact and LDA. Total hole (left) and averaged hole (right)

5. Gradient expansion and generalized gradient approximations (GEA and GGA)

idea: correct LDA with terms depending on $\nabla s, \nabla^2 s \dots$

$$E_{xc}[s] = E_{xc}^{LDA}[s] + \int d^3r f(s, \nabla s, \nabla^2 s, \dots)$$

To determine f we perturb a system with constant density with an external potential $\delta v(\vec{r})$

$$\text{density of perturbed system: } s(\vec{r}) = s_0 + \delta s(\vec{r})$$

$$\text{with } \int d^3r s(\vec{r}) = N \Rightarrow \int d^3r \delta s(\vec{r}) = 0$$

$$\begin{aligned} E_{xc}[s_0 + \delta s] &= E_{xc}[s_0] + \int d^3r \left. \frac{\delta E_{xc}}{\delta s(\vec{r})} \right|_{s_0} \delta s(\vec{r}) \\ &\quad + \frac{1}{2} \iint d^3r d^3r' \left. \frac{\delta^2 E_{xc}}{\delta s(\vec{r}) \delta s(\vec{r}')} \right|_{s_0} \delta s(\vec{r}) \delta s(\vec{r}') + \dots \end{aligned}$$

$$\left. \frac{\delta E_{xc}}{\delta s(\vec{r})} \right|_{s_0} = v_{xc}(s_0) \Rightarrow \int d^3r v_{xc}(s_0) \delta s(\vec{r}) = 0$$

$$\left. \frac{\delta^2 E_{xc}}{\delta s(\vec{r}) \delta s(\vec{r}')} \right|_{s_0} = K_{xc}(\vec{r}, \vec{r}') \Big|_{s_0}^{HEG} = K_{xc}(|\vec{r} - \vec{r}'|, s_0)$$

$$\Rightarrow E_{xc}[s_0 + \delta s] = E_{xc}[s_0] + \frac{1}{2} \iint d^3r d^3r' K_{xc}(|\vec{r} - \vec{r}'|, s_0) \delta s(\vec{r}) \delta s(\vec{r}') + \dots$$

for the LDA functional

$$E_{xc}^{LDA}[s] = \int d^3r e_{xc}(s(\vec{r})) \cdot s(\vec{r})$$

$$\begin{aligned} E_{xc}^{LDA}[s_0 + \delta s] &= E_{xc}^{LDA}[s_0] + \underbrace{\frac{\partial(e_{xc} \cdot s)}{\partial s} \Big|_{s_0}}_{=0} \int d^3r \delta s(\vec{r}) \\ &\quad + \frac{1}{2} \frac{\partial^2(e_{xc} \cdot s)}{\partial s^2} \Big|_{s_0} \int d^3r \delta s^2(\vec{r}) + \dots \\ &= E_{xc}^{LDA}[s_0] + \frac{1}{2} \frac{\partial v_{xc}}{\partial s} \Big|_{s_0} \int d^3r \delta s^2(\vec{r}) + \dots \end{aligned}$$

$$\begin{aligned} E_{xc}[s_0 + \delta s] - E_{xc}^{LDA}[s_0 + \delta s] &= \frac{1}{2} \iint d^3r d^3r' \left[K_{xc}(|\vec{r} - \vec{r}'|, s_0) - \frac{\partial v_{xc}}{\partial s} \Big|_{s_0} \delta(|\vec{r} - \vec{r}'|) \right] \\ &\quad \cdot \delta s(\vec{r}) \delta s(\vec{r}') \\ &\quad + \mathcal{O}(\delta s^3) \end{aligned}$$

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$$V_{xc} [s_0 + \delta s] (\vec{r}) = V_{xc}(s_0) + \int d^3 r' \left. \frac{\partial V_{xc}(\vec{r})}{\partial s(\vec{r}')} \right|_{s_0} \delta s(\vec{r}') + \dots$$

suppose $\delta s(\vec{r}) = \delta s_0 = \text{constant}$

$$\begin{aligned} \Rightarrow \frac{V_{xc}(s_0 + \delta s_0) - V_{xc}(s_0)}{\delta s_0} &= \int d^3 r' K_{xc}(|\vec{r} - \vec{r}'|, s_0) + \dots \\ &= \left. \frac{\partial V_{xc}}{\partial s} \right|_{s_0} \quad (*) \end{aligned}$$

Fourier transformation

$$\delta \tilde{g}(\vec{k}) = \int d^3 r e^{i\vec{k}\vec{r}} \delta s(\vec{r})$$

$$\delta s(\vec{r}) = \int \frac{d^3 k}{(2\pi)^3} e^{-i\vec{k}\vec{r}} \delta \tilde{g}(\vec{k})$$

$$\begin{aligned} &\frac{1}{2} \iint d^3 r d^3 r' K_{xc}(|\vec{r} - \vec{r}'|, s_0) \delta s(\vec{r}) \delta s(\vec{r}') \\ &= \frac{1}{2} \iint d^3 r d^3 r' \delta s(\vec{r}) \delta s(\vec{r}') \int \frac{d^3 k}{(2\pi)^3} \tilde{K}_{xc}(k, s_0) e^{-i\vec{k}(\vec{r} - \vec{r}')} \\ &= \frac{1}{2} \int \frac{d^3 k}{(2\pi)^3} \tilde{K}_{xc}(k, s_0) \underbrace{\int d^3 r \delta s(\vec{r}) e^{-i\vec{k}\vec{r}}}_{\delta \tilde{g}(-\vec{k})} \underbrace{\int d^3 r' \delta s(\vec{r}') e^{i\vec{k}\vec{r}'}_{\delta \tilde{g}(\vec{k})} \\ &= \frac{1}{2} \int \frac{d^3 k}{(2\pi)^3} \tilde{K}_{xc}(k, s_0) \delta s(-\vec{k}) \delta s(\vec{k}) \end{aligned}$$

$$\left. \frac{\partial V_{xc}}{\partial s} \right|_{s_0} \stackrel{(*)}{=} \int d^3 r K_{xc}(|\vec{r}|, s_0) = \tilde{K}_{xc}(k=0, s_0)$$

$$\begin{aligned} &\frac{1}{2} \iint d^3 r d^3 r' \left. \frac{\partial V_{xc}}{\partial s} \right|_{s_0} \underbrace{\delta(\vec{r} - \vec{r}')}_{= \int \frac{d^3 k}{(2\pi)^3} e^{i\vec{k}(\vec{r} - \vec{r}')}} \delta s(\vec{r}) \delta s(\vec{r}') \\ &= \frac{1}{2} \int \frac{d^3 k}{(2\pi)^3} \tilde{K}_{xc}(k=0, s_0) \underbrace{\int d^3 r \delta s(\vec{r}) e^{i\vec{k}\vec{r}}}_{\delta \tilde{g}(\vec{k})} \underbrace{\int d^3 r' \delta s(\vec{r}') e^{-i\vec{k}\vec{r}'}_{\delta \tilde{g}(-\vec{k})} \\ &= \frac{1}{2} \int \frac{d^3 k}{(2\pi)^3} \tilde{K}_{xc}(k=0, s_0) \delta \tilde{g}(\vec{k}) \delta \tilde{g}(-\vec{k}) \end{aligned}$$

$$\begin{aligned} \Rightarrow E_{xc}[s + \delta s] - E_{xc}^{LDA}[s + \delta s] &= \frac{1}{2} \int \frac{d^3 k}{(2\pi)^3} \delta \tilde{g}(\vec{k}) \delta \tilde{g}(-\vec{k}) [\tilde{K}_{xc}(k, s_0) - \tilde{K}_{xc}(k=0, s_0)] \\ &\quad + \mathcal{O}(\delta s^3) \end{aligned}$$

20.

$\tilde{K}_{xc}(k, s_0) = \tilde{K}_{xc}(-k, s_0)$ from inversion symmetry of the HEG

$$\rightarrow \tilde{K}_{xc}(k, s_0) = \tilde{K}_{xc}(k=0, s_0) + \alpha(s_0) k^2 + \beta(s_0) k^4 + \dots$$

$$E_{xc}[s_0 + \delta s] - E_{xc}^{LDA}[s_0 + \delta s] = \frac{1}{2} \alpha(s_0) \int \frac{d^3k}{(2\pi)^3} k^2 \delta \hat{s}(\vec{k}') \delta \hat{s}(-\vec{k}') \\ + \frac{1}{2} \beta(s_0) \int \frac{d^3k}{(2\pi)^3} k^4 \delta \hat{s}(\vec{k}') \delta \hat{s}(-\vec{k}') + \dots$$

$$\int \frac{d^3k}{(2\pi)^3} k^2 \delta \hat{s}(\vec{k}') \delta \hat{s}(-\vec{k}') = \int d^3r (\nabla \delta s(\vec{r}'))^2 = \int d^3r (\nabla s(\vec{r}'))^2$$

$$\int \frac{d^3k}{(2\pi)^3} k^4 \delta \hat{s}(\vec{k}') \delta \hat{s}(-\vec{k}') = \int d^3r (\nabla^2 \delta s(\vec{r}'))^2 = \int d^3r (\nabla^2 s(\vec{r}'))^2$$

$$\nabla s(\vec{r}') = \nabla (s_0 + \delta s(\vec{r}')) = \nabla \delta s(\vec{r}')$$

\tilde{K}_{xc} is known for the HEG \rightarrow calculate $\alpha(s_0)$ and $\beta(s_0)$

For inhomogeneous systems there is no s_0

$\Rightarrow \alpha(s(\vec{r}'))$ and $\beta(s(\vec{r}'))$ are functions of $s(\vec{r}')$

$$\text{expansion } \alpha(s(\vec{r}')) = \alpha(s_0 + \delta s(\vec{r}')) = \alpha(s_0) + \left. \frac{\partial \alpha}{\partial s} \right|_{s_0} \delta s(\vec{r}') + \dots$$

end result (GEA):

$$E_{xc}[s] = E_{xc}^{LDA}[s] + \frac{1}{2} \int d^3r \alpha(s(\vec{r}')) (\nabla s(\vec{r}'))^2 + \frac{1}{2} \int d^3r \beta(s(\vec{r}')) (\nabla^2 s(\vec{r}'))^2 + \dots$$

all other 2nd order terms cancel
(not trivial)

Problem: numerical tests show that GEA is significantly worse than LDA, particularly the correlation energy is positive.

The gradient expansion approximation for the xc hole does not correspond to the hole of any physical system, contrary to its LDA counterpart. Therefore, it might violate any number of exact properties. For example, it violates the sum rule.

$s_{xc}^{GEA}(\vec{r}_1 + \vec{y} | \vec{r}_1)$ improves over s_{xc}^{LDA} for small $|\vec{y}|$ but worsens things at large $|\vec{y}|$. Since the Coulomb interaction $-1/y$ is long range this has major effects on