

Density functional theory in solid state physics

Lecture 4

- HPC-accounts have been applied for and (apparently) been already created
- An e-mail asking to set a password should come soon (if it has not already)
- I will prepare a tutorial document about how to login to the HPC from windows over the course of the week

- Hohenberg-Kohn theorems: ground-state electron density uniquely defines Hamiltonian and ground-state energy. Theoretical basis to an exact density functional theory
- Kohn-Sham approach: mapping of system of interacting electrons onto to fictitious system of non-interacting electrons moving in an auxiliary effective potential v_{KS}

$$\left(-\frac{1}{2} \nabla^2 + \underbrace{v_{KS}(\vec{r})}_{v(\vec{r}) + v_H(\vec{r}) + v_{xc}(\vec{r})} \right) \varphi_i(\vec{r}) = \varepsilon_i \varphi_i(\vec{r})$$

- Central approximation in DFT: Exchange-correlation potential v_{xc} , contains all electron-electron interaction missing in the other terms.

$$E_{xc}[n] = \int n(\vec{r}) \varepsilon_{xc}[n(\vec{r})] d\vec{r}$$

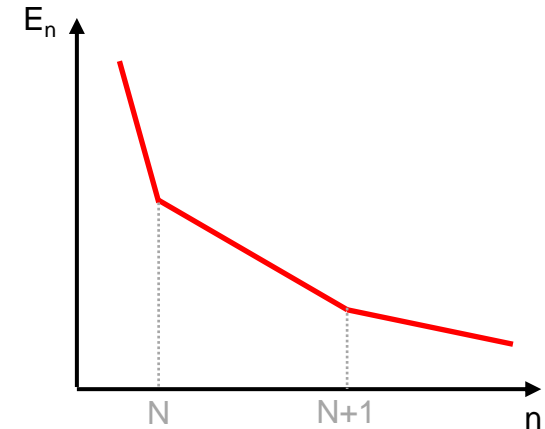
$$v_{xc}(\vec{r}) = \frac{dE_{xc}}{dn(\vec{r})} = \varepsilon_{xc} + n(\vec{r}) \frac{d\varepsilon_{xc}}{dn(\vec{r})}$$

- Known properties of exact exchange-correlation functional:

- Asymptotic decay of v_{XC} in finite systems, $v_{XC} \sim \frac{1}{r}$ for $r \rightarrow \infty$
- Derivative discontinuity of v_{XC} with respect to particle numbers. For $\eta \rightarrow 0$:

$$v_{xc}^{N-\eta}(\vec{r}) = v_{xc}^N(\vec{r})$$

$$v_{xc}^{N+\eta}(\vec{r}) = v_{xc}^N(\vec{r}) + C$$



- Write $E_{XC}[n]$ in terms of exchange-correlation hole $n_{XC} = n_X + n_C$

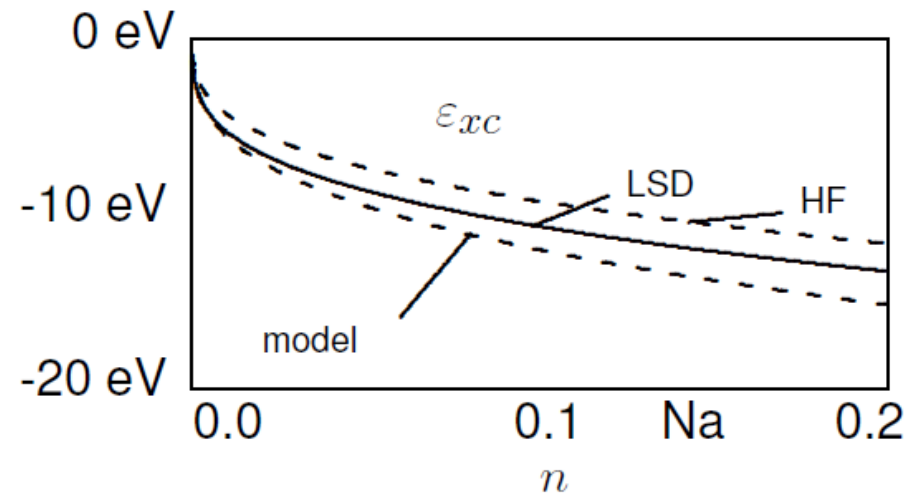
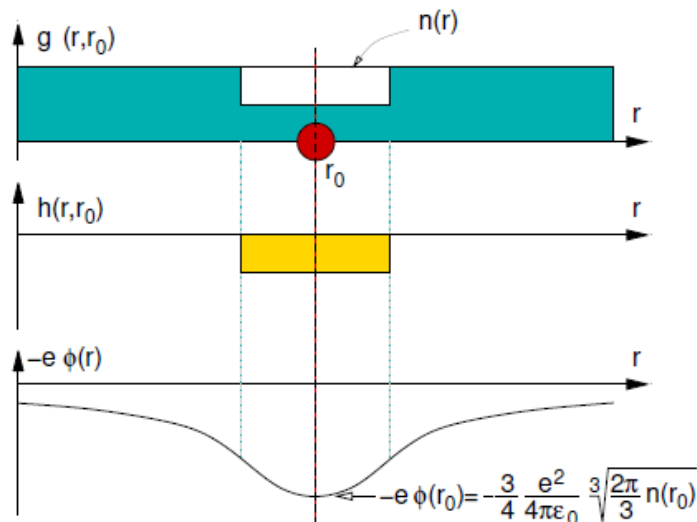
$$E_{XC} = \iint n(\vec{r}) \frac{n_{XC}(\vec{r}, \vec{r}')}{|\vec{r} - \vec{r}'|} d\vec{r} d\vec{r}'$$

Sum rules: $\int n_X(\vec{r}, \vec{r}') d\vec{r}' = -1$ $\int n_C(\vec{r}, \vec{r}') d\vec{r}' = 0$

Also: $n_X(\vec{r}, \vec{r}') \leq 0$

Simple XC functional

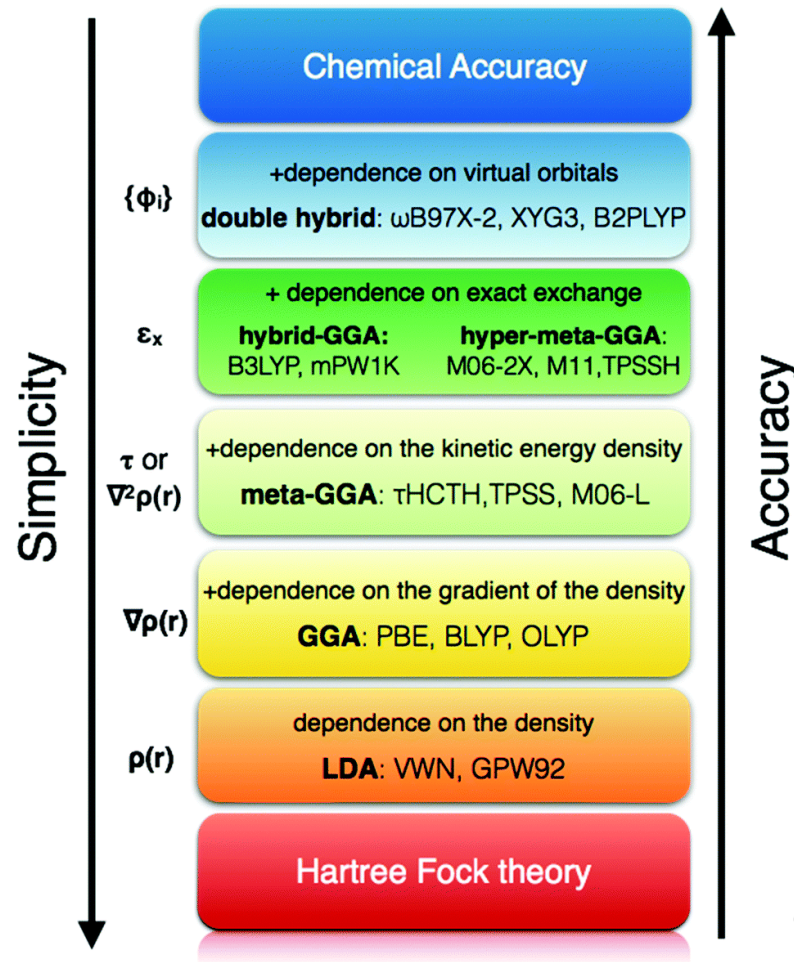
- In principle simple to come up with new exchange-correlation functionals:
 - Model exchange-correlation hole, for example with a simple shape
 - Scale the model XC hole such that it contains exactly one electronic charge
 - Derive the corresponding exchange-correlation energy



Taken from <https://www.cond-mat.de/events/correl11/manuscripts/bloechl.pdf>

Jacob's ladder of XC approximations

- A variety of exchange-correlation approximations with different degrees of accuracy and simplicity have been proposed
- „Jacob's ladder“ of exchange-correlation functionals:



AIP Conf. Proc. 577, 1 (2001)

Chem. Soc. Rev., 45, 6093 (2016)

The uniform electron gas

- The simplest model system to derive an expression for the exchange-correlation functional is the uniform (homogeneous) electron gas with density n .

„Zero rung approximation“

- All properties only depend on the electron density of the system

- Useful concept: Wigner radius r_s with $\frac{4}{3}\pi r_s^3 = \frac{1}{n}$

- Hartree-Fock approach: describe electrons as independent particles. Can be described by plane waves

$$\varphi_{j,s_j}(\vec{r}) = \frac{1}{\sqrt{V}} e^{i\vec{k}_j \cdot \vec{r}}$$

- The positive potential from the nuclei is approximated as a homogeneous positive background charge density $p(\vec{R})=\text{const}$:

$$v^{e-n}(\vec{r}) = \iint \frac{p(\vec{R})}{|\vec{r} - \vec{R}|} dR = -v_H(\vec{r})$$

The uniform electron gas: Exchange

- Energy of an electron with wavenumber k :

$$\begin{aligned}\varepsilon_k^{HEG} &= \varepsilon_{kin,k}^{HEG} + \varepsilon_k^x + \varepsilon_k^c \\ &= \frac{1}{2}k^2 + \varepsilon_k^x + \varepsilon_k^c\end{aligned}\quad (\text{again in atomic units})$$

- Exchange part is simple, see $X\alpha$ method. The Hartree-Fock approximation yields for the exchange energy of an electron in state i with wavevector k :

$$\varepsilon_i^x = - \int \varphi_{i,s_i}^*(\vec{r}) \int \sum_j^N \delta_{s_i,s_j} \frac{\varphi_{j,s_j}^*(\vec{r}') \varphi_{i,s_i}(\vec{r}') \varphi_{j,s_j}(\vec{r})}{|\vec{r} - \vec{r}'|} d\vec{r}' d\vec{r}$$

∴ algebra

$$\varepsilon_{k,s_i}^x = - \frac{2k_F}{\pi} F(x) \quad \text{with } F(x) = \frac{1}{2} + \frac{1-x^2}{4x} \ln \left| \frac{1+x}{1-x} \right| \text{ and } x = \frac{k}{k_F}$$

- Averaged over all occupied states, $\bar{F} = 0.75$

The uniform electron gas, extra slide I

- Derivation of the Hartree-Fock exchange energy per electron shown on the previous slide
- Hartree-Fock approach:

$$\left(-\sum_i^N \nabla_i^2 + v(\vec{r}) + v_H(\vec{r}) \right) \varphi_{i,s_i}(\vec{r}) - \underbrace{\sum_j \delta_{s_i,s_j} \int \frac{\varphi_{j,s_j}^*(\vec{r}') \varphi_{i,s_i}(\vec{r}') \varphi_{j,s_j}(\vec{r})}{|\vec{r} - \vec{r}'|} d\vec{r}'}_{\varepsilon_i^{x,HF} \varphi_{i,s_i}(\vec{r})} = \varepsilon_{i,s_i} \varphi_{i,s_i}(\vec{r})$$

$$\rightarrow \varepsilon_i^{x,HF} = - \int \varphi_{i,s_i}^*(\vec{r}) \int \sum_j^N \delta_{s_i,s_j} \frac{\varphi_{j,s_j}^*(\vec{r}') \varphi_{i,s_i}(\vec{r}') \varphi_{j,s_j}(\vec{r})}{|\vec{r} - \vec{r}'|} d\vec{r}' d\vec{r}$$

$$= -\frac{1}{V^2} \int e^{-i\vec{k}\cdot\vec{r}} \int \sum_j^N \delta_{s_i,s_j} \frac{e^{-i\vec{k}'\cdot\vec{r}'} e^{i\vec{k}\cdot\vec{r}'} e^{i\vec{k}'\cdot\vec{r}}}{|\vec{r} - \vec{r}'|} d\vec{r}' d\vec{r} \quad \text{with } \vec{k} = \vec{k}_i, \vec{k}' = \vec{k}_j$$

$$= -\frac{1}{V(2\pi)^3} \int_0^{k_F} \left(\iint \frac{e^{i(\vec{k}' - \vec{k}) \cdot (\vec{r}' - \vec{r})}}{|\vec{r} - \vec{r}'|} d\vec{r}' d\vec{r} \right) d\Omega_{k'}, \quad \text{with } \sum_j^N \delta_{s_i,s_j} \rightarrow \frac{V}{(2\pi)^3} \int_0^{k_F} d\Omega_{k'}$$

Integral over sphere surface with radius k'

The uniform electron gas, extra slide II

$$\begin{aligned}
 &= -\frac{1}{V(2\pi)^3} \int_0^{k_F} \int dr \left(\iint \frac{e^{i(\vec{k}' - \vec{k}) \cdot \vec{u}}}{u} du \right) dk' \\
 &= -\frac{1}{(2\pi)^3} \int_0^{k_F} \frac{4\pi}{|\vec{k}' - \vec{k}|^2} dk' = -\frac{2}{(2\pi)^2} \int_0^{k_F} \frac{1}{k^2 - 2kk' + k'^2} d\Omega_{k'} = -\frac{1}{(2\pi)^3} \int_0^{k_F} \frac{4\pi}{|\vec{k}' - \vec{k}|^2} d\Omega_{k'} \\
 &= -\frac{2}{(2\pi)^2} \int_0^{2\pi} d\varphi \int_0^{k_F} \int_0^\pi \frac{k'^2 \sin(\Theta)}{k^2 - 2kk' \cos(\Theta) + k'^2} d\Theta dk' \quad \text{with } \sin(\Theta) d\Theta = -d(\underbrace{\cos(\Theta)}_y) \\
 &= -\frac{1}{\pi} \int_0^{k_F} \left(\int_{-1}^1 \frac{k'^2}{k^2 - 2kk'y + k'^2} dy \right) dk' = -\frac{1}{\pi} \int_0^{k_F} \frac{k'}{k} \ln \left| \frac{k+k'}{k-k'} \right| dk'
 \end{aligned}$$

∴ Somewhat lengthy Integration by parts,

$$\varepsilon_{k,si}^x = -\frac{k_F}{\pi} \left[1 + \frac{1-x^2}{2x} \ln \left| \frac{1+x}{1-x} \right| \right] \quad \text{with } x = \frac{k}{k_F}$$

The uniform electron gas: Exchange

- Together with a factor $\frac{1}{2}$ to remove double counting, this leads to the exchange energy density

$$\varepsilon_x^{HEG}(n) = \frac{E_x^{HEG}(n)}{N} = -\frac{3}{4\pi} k_F$$

- For a spin-polarized system: $n = n^\uparrow + n^\downarrow$

$$\varepsilon_x^{HEG,\sigma}(n^\sigma) = -\frac{3}{4\pi} (6\pi^2 n^\sigma)^{\frac{1}{3}} = -\frac{3}{4\pi} \left(\frac{9}{4}\pi\right)^2 / r_s^\sigma$$

Density of electrons with spin σ

- For spin-unpolarized system: $n^\uparrow = n^\downarrow = \frac{1}{2}n$

$$\begin{aligned}\varepsilon_x^{HEG,\uparrow}(n^\uparrow) &= \varepsilon_x^{HEG,\downarrow}(n^\downarrow) = -\frac{3}{4\pi} \left(6\pi^2 \frac{1}{2}n\right)^{\frac{1}{3}} \\ &= -\frac{3}{4\pi} (3\pi^2 n)^{\frac{1}{3}} = \varepsilon_x^{HEG}(n)\end{aligned}$$

- The correlation energy can only be determined analytically for the limiting cases of low- and high electron density. The relevant range for realistic materials is $1 < r_s < 6$.
- Several propositions:

- Low density-limit ($r_s \gg 1$):

$$\varepsilon_c^{HEG}(r_s) = -\frac{0.438}{r_s} + \frac{1.33}{r_s^{3/2}} + \frac{1.47}{r_s^2} + \dots$$

- Wigner proposed an interpolation formula between a Wigner crystal in the low-density limit and a constant high-density limit

$$\varepsilon_c^{HEG} \approx \frac{0.44}{r_s + 7.8} \quad (\text{in units of Hartree}) \quad \text{Phys. Rev 46, 1002 (1934)}$$

- Gell-Mann&Brueckner summed over an infinite series of Feynman diagrams, exact expression for high-density ($r_s \rightarrow 0$) limit:

$$\varepsilon_c^{HEG}(r_s) = 0.0311 \ln(r_s) - 0.047 + r_s(A \ln(r_s) + C) + \dots$$

Phys. Rev 106, 364 (1957)

The uniform electron gas: Correlation

- Accurate Monte Carlo calculations over a relevant range of r_s values and subsequent analytical fits to the QMC data *Phys Rev Lett* 45, 566 (1980)

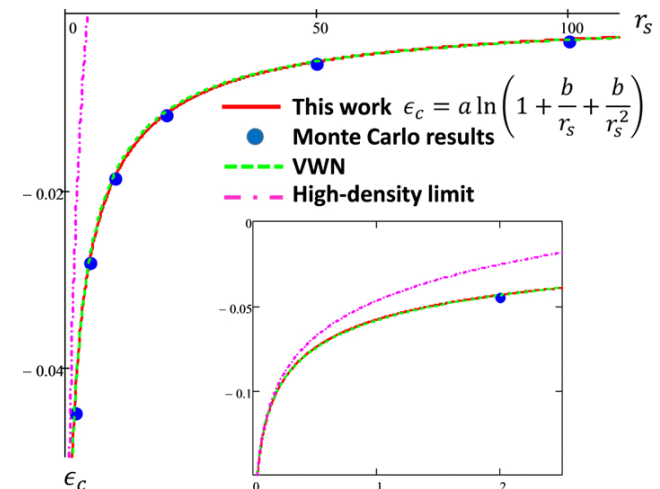
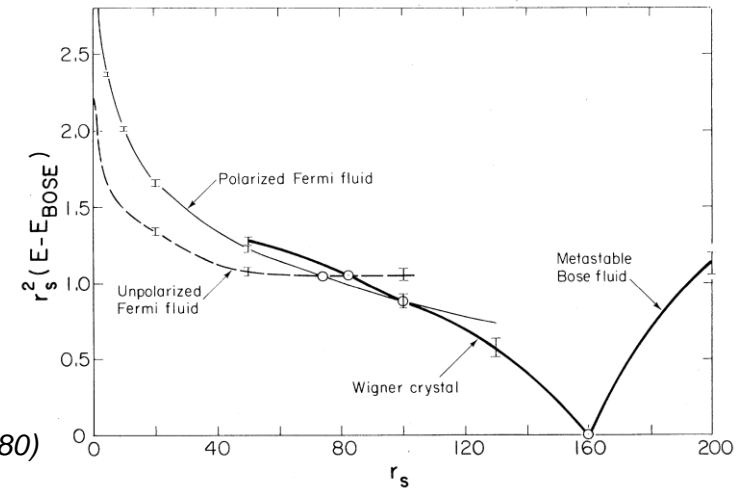
Parametrizations

- Perdew-Wang: *Phys Rev B* 45, 13244 (1992)
- Perdew-Zunger: *Phys. Rev. B* 23, 5048 (1981)
- Lee-Yang-Parr (LYP): *Phys. Rev. B* 37, 785 (1988)
- Vosko-Wild-Nusair (VWN): *Can. J. Phys.* 58, 1200 (1980)

$$\epsilon_c(r_s) = A \left\{ \ln \frac{x^2}{X(x)} + \frac{2b}{Q} \tan^{-1} \frac{Q}{2x+b} - \frac{bx_0}{X(x_0)} \left[\ln \frac{(x-x_0)^2}{X(x)} + \frac{2(b+2x_0)}{Q} \tan^{-1} \frac{Q}{2x+b} \right] \right\}$$

- Chachiyo: Simple interpolation formula with very small errors compared to QMC over the whole range of relevant densities

J. Chem. Phys. 145, 021101 (2016)



Local-density approximation (LDA)

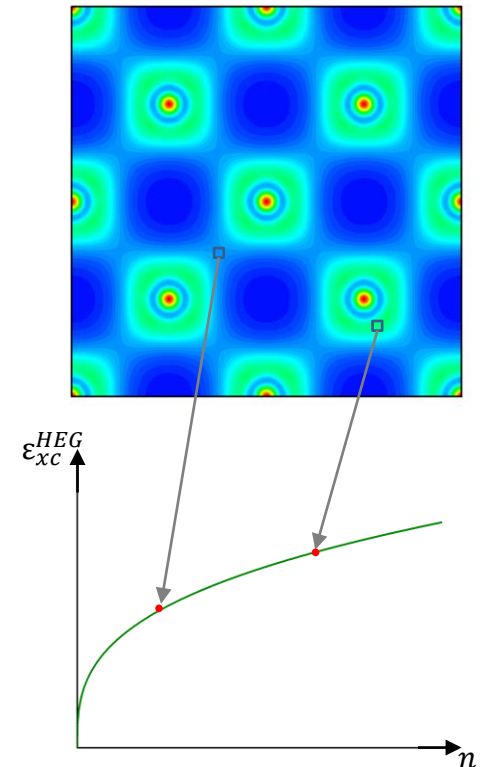
- Local-density approximation (LDA): A simple approach for electronic systems with a non-uniform electron density. First rung of Jacob's Ladder
- Idea: Use homogeneous electron gas to estimate exchange interaction of electron at position \vec{r}
- For a spin-unpolarized system;

$$E_{xc}^{LDA} = \int n(\vec{r}) \varepsilon_{xc}^{LDA}(n(\vec{r})) d\vec{r}$$

$$\varepsilon_{xc}^{LDA}(n, \vec{r}) = \varepsilon_{xc}^{HEG}(n(\vec{r})) = -\frac{3}{4\pi} (3\pi^2 n(\vec{r}))^{\frac{1}{3}} + \varepsilon_c^{HEG}(n(\vec{r}))$$

$$v_{xc}^{LDA}(\vec{r}) = \frac{d}{dn} E_{xc}^{LDA} = -\frac{1}{\pi} (3\pi^2 n(\vec{r}))^{\frac{1}{3}} + v_c^{HEG}(n(\vec{r}))$$

- Exchange component is always fixed („Dirac“ or „Slater exchange“), but different flavours of LDA exist depending on the used parametrization of the correlation energy



Local-density approximation (LDA)

- Local spin density approximation (LSDA): Generalization of LDA to (possibly) spin-polarized systems (*J. Phys. C: Solid State Phys.* 5, 1629 (1972))

- Exchange-correlation energy: $E_{xc}^{LSDA} = \int n(\vec{r}) \epsilon_{xc}^{LSDA}(n(\vec{r}), \zeta(\vec{r})) dr$

with the fractional spin-polarization $\zeta(\vec{r}) = \frac{n^\uparrow(\vec{r}) - n^\downarrow(\vec{r})}{n(\vec{r})}$

$\zeta = 0$: paramagnetic, spin-unpolarized conditions

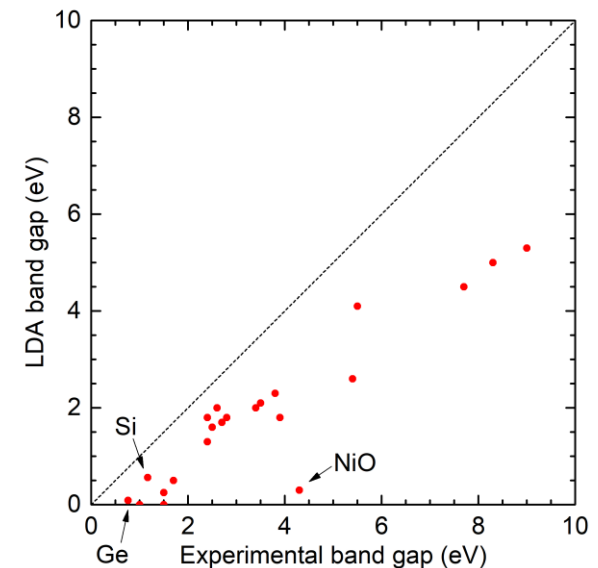
$\zeta = \pm 1$: purely ferro- or antiferromagnetic conditions

- LSDA XC energy density: $\epsilon_x^{LSDA}(n(\vec{r}), \zeta(\vec{r})) = \frac{1}{2} \left((1 + \zeta(\vec{r})) \epsilon_x^{HEG, \uparrow} + (1 - \zeta(\vec{r})) \epsilon_x^{HEG, \downarrow} \right)$

Local-density approximation (LDA)

- LDA works surprisingly well for realistic systems, particularly solids
- Structural properties are quite good
 - Typical underestimation of bond lengths, lattice constants and covalent binding energies by a few percent („overbinding“)
 - Phonon frequencies are (typically) overestimated
 - Usually better than Hartree-Fock results
- LDA favours homogeneous electron densities
- LDA lacks a derivative discontinuity; electronic band gaps are underestimated or plainly wrong
- Not very good with magnetic systems

	exp	LDA	Δ
Si	5.43	5.4	-0.55%
Ge	5.65	5.63	-0.3%
GaAs	5.65	5.63	-0.3%
La ₂ O ₃	3.95, 6.15	3.92, 6.04	-0.76%, -1.79%
Al	4.03	3.98	-1.25%
Cu	3.6	3.52	-2.17%
W	3.16	3.13	-0.88%



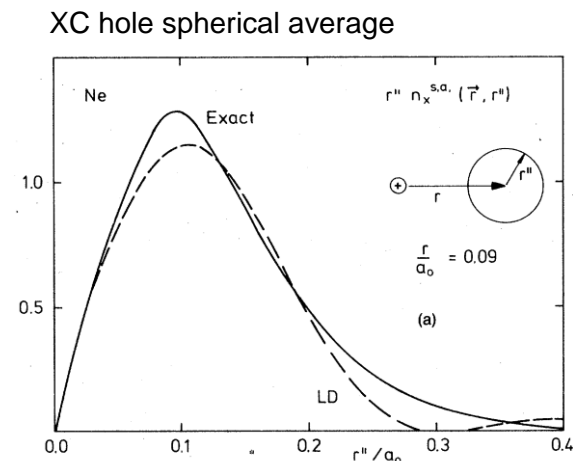
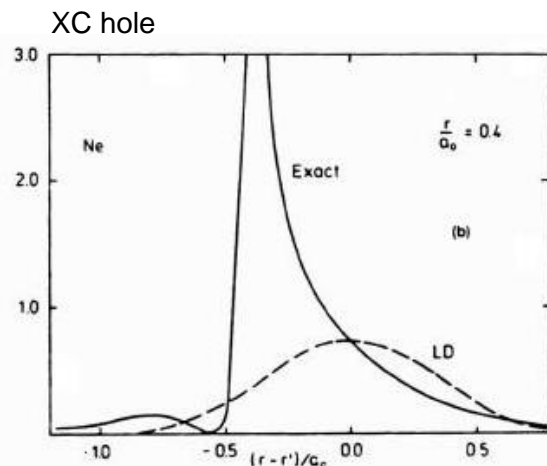
Int J. Quant. Chem. 19, 497 (1986)

Local-density approximation (LDA)

- LDA is exact treatment for a specific system: the homogeneous electron gas
- As such, it satisfies many constraints of the exact exchange-correlation functional
- LDA exchange-correlation hole is bad, but spherical average is a reasonable estimate

$$E_{xc} = \frac{1}{2} \iint n(\vec{r}) \frac{n_{xc}(\vec{r}, \vec{r}')}{|\vec{r} - \vec{r}'|} d\vec{r} d\vec{r}' = \frac{1}{2} \int n(\vec{r}) \left[\int 4\pi u^2 \frac{n_{xc}(\vec{r}, \vec{r} + \vec{u})}{u} \frac{d\Omega_u}{4\pi} \right] dr$$

- Error cancellation between underestimated exchange energies and overestimated correlation energies



Phys Rev B 20, 3136 (1979)

- Natural next step (?) for systematically improving on LDA: Gradient expansion of exchange-correlation potential of slowly varying electron density
- For example: introduce a weak and slowly varying external potential and derive the resulting XC energy
- Measure of inhomogeneity: reduced density gradients

$$s(\vec{r}) = \frac{|\nabla n|}{2k_F n} \quad t(\vec{r}) = \frac{|\nabla n|}{2k_s n} \quad \text{with } k_s = \left(\frac{4k_F}{\pi} \right)^{1/2}$$

How fast and how much does the density vary on the scale of the local k_F ? Relevant range: $0 \leq s \leq 3$

- Second-order gradient expansion („Gradient expansion approximation“):

$$E_x[n, s] = A_x \int n^{4/3} [1 + \mu s^2 + \dots] dr$$

Known: $\mu = \frac{10}{81}$

$$E_c[n, s] = \int n [\epsilon_c^{HEG} + \beta(n)t^2 + \dots] dr$$

- Coefficients are tedious to obtain

- Paradox: LDA works rather well for atoms, molecules, solids. GEA usually does not
- GEA correlation energy is positive for atoms
- Electron densities in real materials are usually not slowly varying
- GEA exchange and correlation holes are more realistic around the electron than LDA holes, but bad at larger distances due to truncated expansion.

- „Sum rules“ of exchange and correlation holes are not fulfilled:

$$\int n_x^{GEA}(\vec{r}, \vec{r}') dr' \neq -1 \quad \cancel{n_x^{GEA}(\vec{r}, \vec{r}') \leq 0}$$

$$\int n_c^{GEA}(\vec{r}, \vec{r}') dr' \sim s^2 \neq 0$$

- LDA is the exchange-correlation for a possible physical system, while GEA is not. Hence, GEA violates several exact properties of the exact XC functional that LDA satisfies.

- A remedy: Generalized gradient approximation (GGA). Second rung of Jacob's Ladder
- Task: Include the density gradient in a way that the exact properties of LDA remain satisfied
- Generalized form: $E_{xc}^{GGA}[n^\uparrow, n^\downarrow, \nabla n^\uparrow, \nabla n^\downarrow] = \int n(\vec{r}) \varepsilon_{xc}^{GGA}(n^\uparrow, n^\downarrow, \nabla n^\uparrow, \nabla n^\downarrow) d\vec{r}$
- ε_{xc}^{GGA} is chosen to satisfy desired properties of the exact XC functional in the s-range of interest
- Satisfaction of the exchange and correlation hole sum rules through real-space cutoffs, only include contributions of gradient expansion that are negative
- Ideal case: finding a ε_{xc} that is simple, accurate and transferable for system with different bonding characteristics

- Large number of GGAs with different ϵ_{xc}^{GGA} available today, both derived from first principles and using empirical parameters
- Most widely used approximation today: Perdew-Burke-Ernzerhof (PBE)

Phys. Rev. Lett. 77, 3865 (1996)

$$E_{xc}^{PBE} = E_x^{PBE} + E_c^{PBE}$$

$$E_x^{PBE} = \int n(\vec{r}) \epsilon_x^{HEG}(n) F_x^{PBE}(s) dr$$

$$E_c^{PBE} = \int n(\vec{r}) [\epsilon_c^{HEG}(n) + H(n, t)] dr$$

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

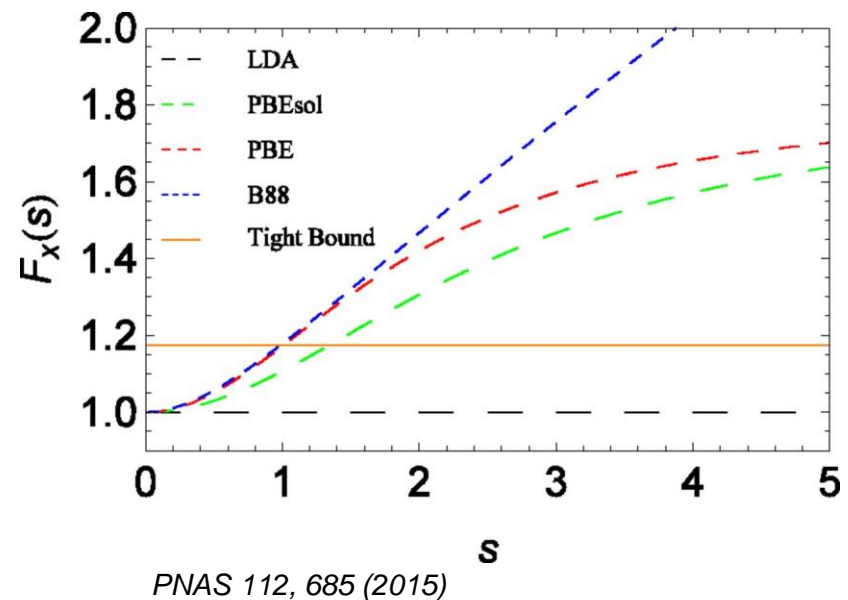
$$H(n, t) = \frac{\beta^2}{2\alpha} \ln \left[1 + \frac{2\alpha}{\beta} \frac{t^2 + At^4}{1 + At^2 + A^2 t^4} \right]$$

with $\kappa = 0.804, \mu = 0.22$

with $A = 2\alpha / (\beta \exp[-2\alpha \epsilon_c^{HEG}(n) / \beta^2] - 1)$
 $\alpha = 0.0716, \beta = 0.066725$

- General spin-scaling relation: $E_x[n^\uparrow, n^\downarrow] = \frac{1}{2} [E_x[2n^\uparrow] + E_x[2n^\downarrow]]$
- LDA is recovered for $|\nabla n| \rightarrow 0$

- Other important implementations:
 - B88: correct asymptotic behavior of the XC energy for atoms/molecules, single empirical parameter fitted to XC energies of six noble gas atoms
Phys. Rev. A 38, 3098 (1988)
 - PW91: analytical fit to a corrected GEA exchange-correlation hole
Phys. Rev. B 43, 8911 (1991)
 - PBEsol: reparametrization of PBE to yield better results for solids and surfaces
Phys. Rev. B 79, 075126 (2009)
- $F_x \geq 1$ for all s and all GGAs
- It appears to be impossible to find a single implementation of the enhancement factor that works equally well for finite systems (atoms, molecules) and extended systems (solids)



Generalized gradient approximation (GGA)

- In general improvement over LDA
- Structural properties and energies often better than LDA, but „underbinding“ tendency

Functional	a_0					B_0					E_{coh}				
	ME	MAE	MRE	MARE	MAXRE	ME	MAE	MRE	MARE	MAXRE	ME	MAE	MRE	MARE	MAXRE
LDA															
LDA ⁸⁰	-0.071	0.071	-1.5	1.5	-4.9 (Ba)	10.1	11.5	8.1	9.4	32.8 (Ni)	0.77	0.77	17.2	17.2	38.7 (Ni)
GGA															
SG4 ⁶⁰	0.005	0.026	0.0	0.6	-1.9 (V)	1.7	7.9	-2.2	7.8	-25.9 (Rb)	0.19	0.28	3.5	7.0	19.5 (Ni)
WC ⁸¹	0.002	0.029	0.0	0.6	-2.5 (Ba)	-0.2	7.6	-2.6	7.4	-23.8 (Rb)	0.22	0.26	4.2	6.2	20.1 (Ni)
SOGGA ⁸²	-0.012	0.027	-0.3	0.6	-2.3 (Ba)	4.1	8.9	0.6	7.4	23.6 (Ni)	0.39	0.41	8.8	9.2	26.8 (Ni)
PBEsol ⁸³	-0.005	0.030	-0.1	0.6	-2.3 (Sr)	0.7	7.8	-1.4	7.0	19.5 (Ni)	0.29	0.31	6.1	6.9	22.8 (Ni)
AM05 ⁸⁴	0.014	0.037	0.2	0.8	2.1 (NaF)	-0.3	8.8	-4.0	9.2	-25.9 (Rb)	0.30	0.45	7.6	12.6	90.4 (LiH)
PBEint ⁸⁵	0.026	0.039	0.5	0.8	2.5 (NaF)	-3.0	8.4	-5.3	8.7	-25.5 (Rb)	0.10	0.20	1.5	4.7	16.4 (Ni)
PBEalpha ⁸⁶	0.021	0.042	0.4	0.9	2.0 (Sn)	-6.0	8.4	-5.0	7.6	-21.2 (Ge)	0.10	0.18	1.8	4.1	14.5 (Ni)
RGE2 ⁸⁷	0.043	0.051	0.8	1.0	3.6 (Cs)	-4.3	9.0	-7.3	10.2	-31.5 (Rb)	0.00	0.20	-1.2	5.0	-14.9 (Au)
PW91 ⁸⁸	0.053	0.059	1.1	1.2	2.6 (Sn)	-11.0	12.1	-9.8	10.9	-25.3 (Ge)	-0.12	0.18	-3.5	4.6	-20.1 (Au)
PBE ⁷³	0.056	0.061	1.1	1.2	2.8 (Sn)	-11.2	12.2	-9.8	11.0	-25.5 (Ge)	-0.13	0.19	-3.9	5.0	-21.0 (Au)
HTBS ⁸⁹	0.068	0.077	1.3	1.6	8.1 (Cs)	-4.0	9.9	-9.4	12.7	-47.7 (Rb)	-0.14	0.23	-4.5	6.2	-20.1 (Cs)
PBEfe ⁹⁰	0.002	0.082	0.1	1.7	-4.9 (Cs)	-10.0	12.6	-3.3	11.2	-27.1 (Ge)	0.15	0.22	3.4	5.0	13.5 (Sn)
revPBE ⁹¹	0.106	0.107	2.2	2.2	5.4 (Cs)	-17.1	17.5	-16.0	16.4	-34.3 (Rb)	-0.48	0.48	-12.6	12.6	-34.2 (Au)
RPBE ⁹²	0.119	0.119	2.4	2.4	6.1 (Cs)	-19.0	19.3	-17.2	17.5	-35.1 (Au)	-0.52	0.52	-13.2	13.2	-36.7 (Au)
BLYP ^{93,94}	0.118	0.120	2.5	2.5	5.2 (Sn)	-25.1	25.2	-19.9	20.3	-44.6 (Au)	-0.69	0.69	-20.3	20.3	-52.8 (Cs)

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- Band gaps are similar to LDA, lack of derivative discontinuity
- Better treatment of magnetic systems, better magnetic momenta compared to LDA

- Third rung: metaGGAs. More generalized form of GGAs with additional degrees-of-freedom
- Observation: Taylor expansion of the exchange hole n_x for small $|\vec{r} - \vec{r}'|$ depends on $n^\sigma, \nabla n^\sigma, \nabla^2 n^\sigma$, but also on the *kinetic energy density*

$$\tau^\sigma(\vec{r}) = \frac{1}{2} \sum_{\alpha} f_{F-D}^{\alpha} |\nabla \varphi_{\alpha}^{\sigma}|^2$$

- metaGGA functional form:

$$E_{xc}^{metaGGA} = \int n(\vec{r}) \varepsilon_{xc}^{metaGGA}(n^{\uparrow}, n^{\downarrow}, \nabla n^{\uparrow}, \nabla n^{\downarrow}, \nabla^2 n^{\uparrow}, \nabla^2 n^{\downarrow}, \tau^{\uparrow}, \tau^{\downarrow}) dr$$

- Additional degrees-of-freedom allows for the satisfaction of additional exact constraints that go beyond the capabilities of pure GGAs
- Example: One-electron regions can be recognized by the condition

$$\tau^\sigma(\vec{r}) = \frac{|\nabla n^\sigma|^2}{8n^\sigma}$$

and the correlation part of can be set to zero in these regions.