

# Introduction to Orbital-Free Density-Functional Theory

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# Outline

## Basics of functional derivatives

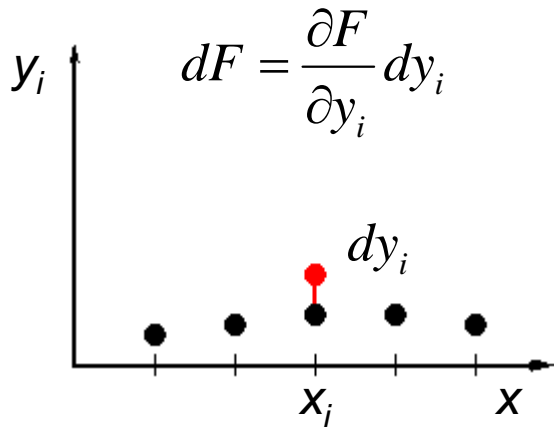
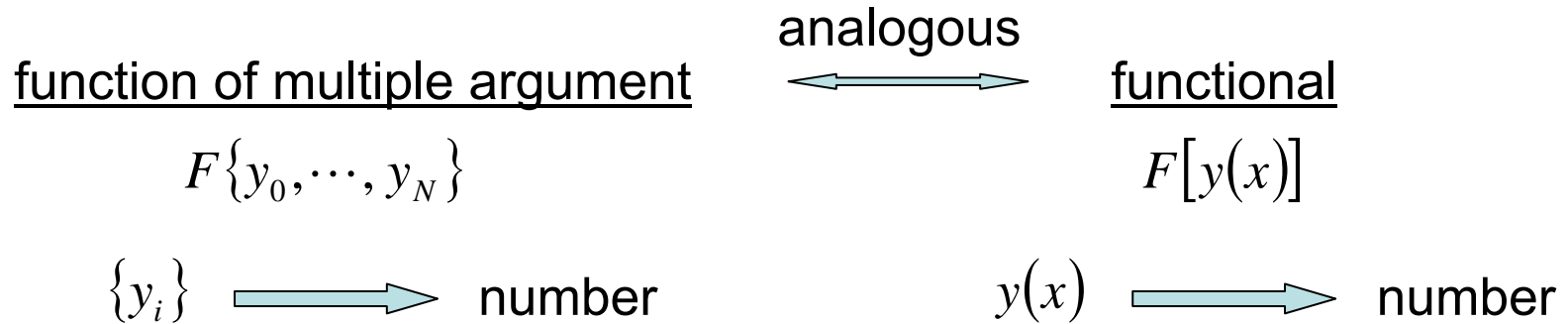
### I Principles of Orbital-free Density-Functional Theory

- basics of Density-Functional Theory
- motivation for OF-DFT
- basics of the numerical implementation

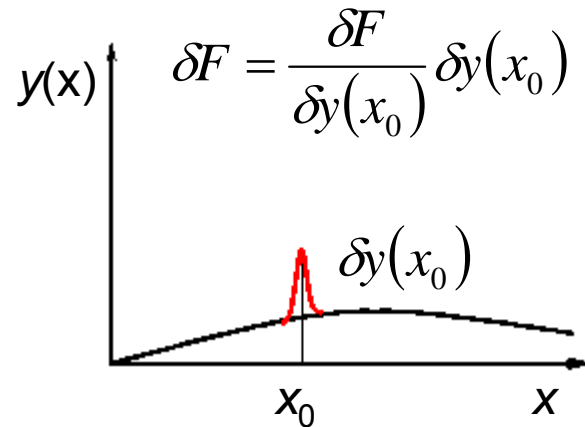
### II Approximations to the kinetic-energy functional

- The Thomas-Fermi Approximation
- The von-Weizsäcker term
- Linear-Response Theory
- Combination of TF and vW
- The Conventional Gradient Expansion
- Average-Density Approximation

# Basics of functional derivatives



$$dF = \sum_i \frac{\partial F}{\partial y_i} dy_i$$



$$\delta F = F[y + \delta y] - F[y] = \int dx \frac{\delta F}{\delta y(x)} \delta y(x)$$

# Basics of functional derivatives

some rules

$$F[y(x)] = \int dx f(y(x)) \quad \longrightarrow \quad \frac{\delta F[y]}{\delta y(x)} = \frac{\partial f}{\partial y}$$

„Proof“:

$$\begin{aligned} \delta F[y] &= F[y + \delta y] - F[y] \\ &= \int dx \underbrace{f(y + \delta y)}_{f(y) + \frac{\partial f}{\partial y} \delta y + O(\delta y^2)} - \int dx f(y) = \int dx \underbrace{\frac{\partial f}{\partial y}}_{\frac{\delta F}{\delta y(x)}} \delta y(x) \end{aligned}$$

$$F[y(x)] = \int dx f(y(x), y'(x)) \quad \longrightarrow \quad \frac{\delta F[y]}{\delta y(x)} = \frac{\partial f}{\partial y} - \frac{d}{dx} \frac{\partial f}{\partial y'}$$

$$\left( \frac{\delta F[y]}{\delta y(\vec{r})} = \frac{\partial f}{\partial y} - \nabla \frac{\partial f}{\partial \nabla y} = \frac{\partial f}{\partial y} - \frac{d}{dx_1} \frac{\partial f}{\partial (\partial y / \partial x_1)} - \frac{d}{dx_2} \frac{\partial f}{\partial (\partial y / \partial x_2)} - \frac{d}{dx_3} \frac{\partial f}{\partial (\partial y / \partial x_3)} \right)$$

# Basics of functional derivatives

some rules

„Proof“:

$$\begin{aligned}
 F[y + \delta y] &= \int dx f(y + \delta y, y' + \delta y') \\
 &= \int dx \left( f(y) + \frac{\partial f}{\partial y} \delta y + \frac{\partial f}{\partial y'} \delta y' \right) = F[y] + \int dx \frac{\partial f}{\partial y} \delta y + \underbrace{\int dx \frac{\partial f}{\partial y'} \delta y'}_{\substack{(y(x) \xrightarrow{x \rightarrow \pm \infty} 0) \quad - \int dx \frac{d}{dx} \left( \frac{\partial f}{\partial y'} \right) \delta y}}
 \end{aligned}$$

$$\delta F = \int dx \underbrace{\left( \frac{\partial f}{\partial y} - \frac{d}{dx} \frac{\partial f}{\partial y'} \right)}_{\frac{\delta F[y]}{\delta y(x)}} \delta y(x)$$

# Basics of functional derivatives

some rules

„chain rule“

$$F[G([y(x)], x)] \quad \longrightarrow \quad \frac{\delta F}{\delta y(x)} = \int dx' \frac{\delta F}{\delta G([y], x')} \frac{\delta G([y], x')}{\delta y(x)}$$

some examples

$$J[\rho] = \frac{1}{2} \iint d^3\vec{r} d^3\vec{r}' \frac{\rho(\vec{r})\rho(\vec{r}')}{|\vec{r} - \vec{r}'|}$$

$$V_H([\rho], \vec{r}) = \frac{\delta J[\rho]}{\delta \rho(\vec{r})} = \int d^3\vec{r}' \frac{\rho(\vec{r}')}{|\vec{r} - \vec{r}'|}$$

$$\frac{\delta^2 J[\rho]}{\delta \rho(\vec{r}) \delta \rho(\vec{r}')} = \frac{1}{|\vec{r} - \vec{r}'|}$$

# Basics of DFT

## First Hohenberg-Kohn-Theorem

Energy of groundstate is a mere function of the electron density  $\rho$

$$E[\rho] = F[\rho] + \int d^3\vec{r} V_{\text{ext}}(\vec{r})\rho(\vec{r})$$

$$F[\rho] = T[\rho] + E_{\text{ee}}[\rho] = T_s[\rho] + J[\rho] + E_{\text{xc}}[\rho]$$

$$J[\rho] = \frac{1}{2} \iint d^3\vec{r} d^3\vec{r}' \frac{\rho(\vec{r})\rho(\vec{r}')}{|\vec{r} - \vec{r}'|}$$

classical coulomb interaction

$$T_s[\rho]$$

kinetic energy of a non-interacting system with density  $\rho$

$$E_{\text{xc}}[\rho]$$

exchange-correlation energy

# Basics of DFT

## Second Hohenberg-Kohn-Theorem (Variational Principle)

$$\frac{\delta}{\delta \rho(\vec{r})} \left( E[\rho] - \mu \left( \int d^3\vec{r} \rho(\vec{r}) - N \right) \right) = 0 \quad \Rightarrow \quad \frac{\delta E[\rho]}{\delta \rho(\vec{r})} = \mu$$

„Euler-Lagrange-Equation“

$\mu$  chemical potential (negative of first ionization energy of system)



# Basics of DFT

- What is the kinetic energy  $T_s[\rho]$ ?  
→ introduction of a reference-system of non-interacting particles

$$\langle \varphi_i | \varphi_j \rangle = \delta_{ij} \quad \sum_{i=0}^{q-1} |\varphi_i(\vec{r})|^2 = \rho(\vec{r}) \quad \Rightarrow \quad T_s = -\frac{1}{2} \sum_i \langle \varphi_i | \Delta | \varphi_i \rangle$$

- orbitals  $\{\varphi_i\}$  are solutions of single-particle Schrödinger-equations

$$\left( -\frac{1}{2} \Delta + V_{\text{eff}}^{\text{KS}} \right) \varphi_i = \varepsilon_i \varphi_i$$

(Kohn-Sham-equations)

- effective potential has to be determined self-consistently

$$V_{\text{eff}}^{\text{KS}}([\rho], \vec{r}) = \frac{\delta J[\rho]}{\delta \rho} + \frac{\delta E_{\text{XC}}[\rho]}{\delta \rho} + V_{\text{ext}} = V_{\text{H}} + V_{\text{XC}} + V_{\text{ext}}$$

# Motivation for OF-DFT

- Introduction of orbitals in DFT is not desirable
  - matrix diagonalization scales cubically with basis size
  - many data have to be stored during computation
- the goal is to get rid of KS-orbitals and to express each energy contribution in terms of the electron charge density

⇒ a functional  $T_s[\rho]$  has to be found

- high accuracy for  $T_s[\rho]$  is required since  $T_s[\rho]$  is of the same order as  $E[\rho]$  (virial theorem)  $\leftrightarrow E_{xc}[\rho]$  is much smaller than  $E[\rho]$ 
  - ⇒ many schemes for approximating  $E_{xc}[\rho]$  might be inappropriate for  $T_s[\rho]$

# Basics of numerical implementation

Once an appropriate approximation for  $T_s[\rho]$  exists, how can the total energy  $E[\rho]$  of the groundstate be calculated?

two different approaches:

- direct minimization of the total energy
- self-consistent calculation

# Basics of numerical implementation

## direct minimization

- energy has to be minimized under the constrained of constant particle numbers

$$\Pi[\rho] = E[\rho] - \mu \left( \int d^3\vec{r} \rho(\vec{r}) - N \right)$$

- variable substitution to ensure positivity of electron density  $\rho$

$$\varphi(\vec{r}) = \sqrt{\rho(\vec{r})}$$

- minimization of  $\Pi$  with steepest descend, conjugate-gradients, etc.

$$\frac{\delta \Pi[\rho]}{\delta \varphi(\vec{r})} = 0$$

$$\varphi_{n+1}(\vec{r}) = \varphi_n(\vec{r}) - \tau \frac{\delta \Pi[\rho]}{\delta \varphi(\vec{r})} \Big|_{\varphi_n(\vec{r})}$$

# Basics of numerical implementation

## self-consistent calculation

- add and subtract kinetic energy of a bosonic system

$$E[\rho] = T_B[\rho] + T_S[\rho] + J[\rho] + E_{\text{xc}}[\rho] + \int d^3\vec{r} V_{\text{ext}}(\vec{r})\rho(\vec{r}) - T_B[\rho]$$

$$T_B[\rho] = -\frac{1}{2} \int d^3\vec{r} \sqrt{\rho(\vec{r})} \Delta \sqrt{\rho(\vec{r})}$$

- insert total energy expression in Euler-Lagrange-equation

integration by parts and chain rule  $\Rightarrow \frac{\delta T_B[\rho]}{\delta \rho(\vec{r})} = \dots = -\frac{1}{2} \frac{\Delta \varphi(\vec{r})}{\varphi(\vec{r})}$

# Basics of numerical implementation

## self-consistent calculation

- Euler-Lagrange-equation is transferred to a Kohn-Sham-like equation with an additional potential term

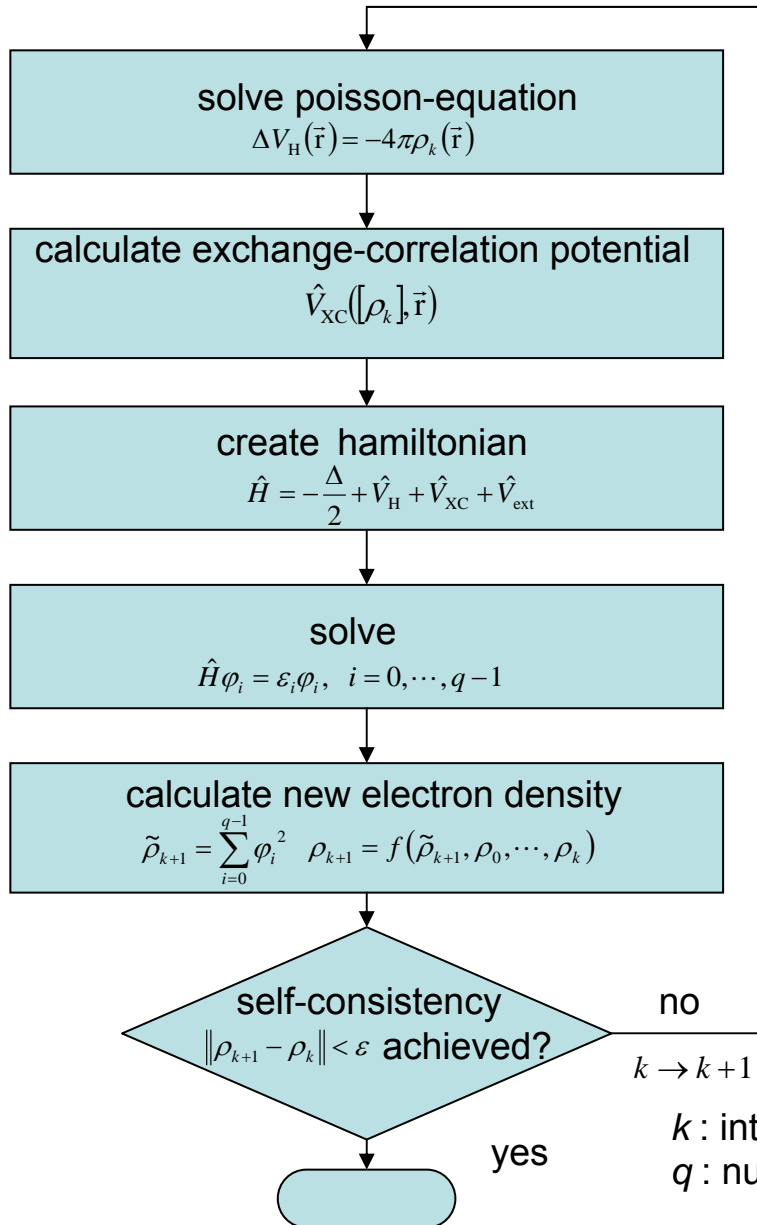
$$\frac{\delta E[\rho]}{\delta \rho(\vec{r})} = \mu \quad \Rightarrow \quad -\frac{1}{2} \frac{\Delta \varphi(\vec{r})}{\varphi(\vec{r})} + V_H + V_{XC} + V_{\text{ext}} + \frac{\delta T_S}{\delta \rho(\vec{r})} - \frac{\delta T_B}{\delta \rho(\vec{r})} = \mu$$

$$\hat{H}\varphi = \mu\varphi$$

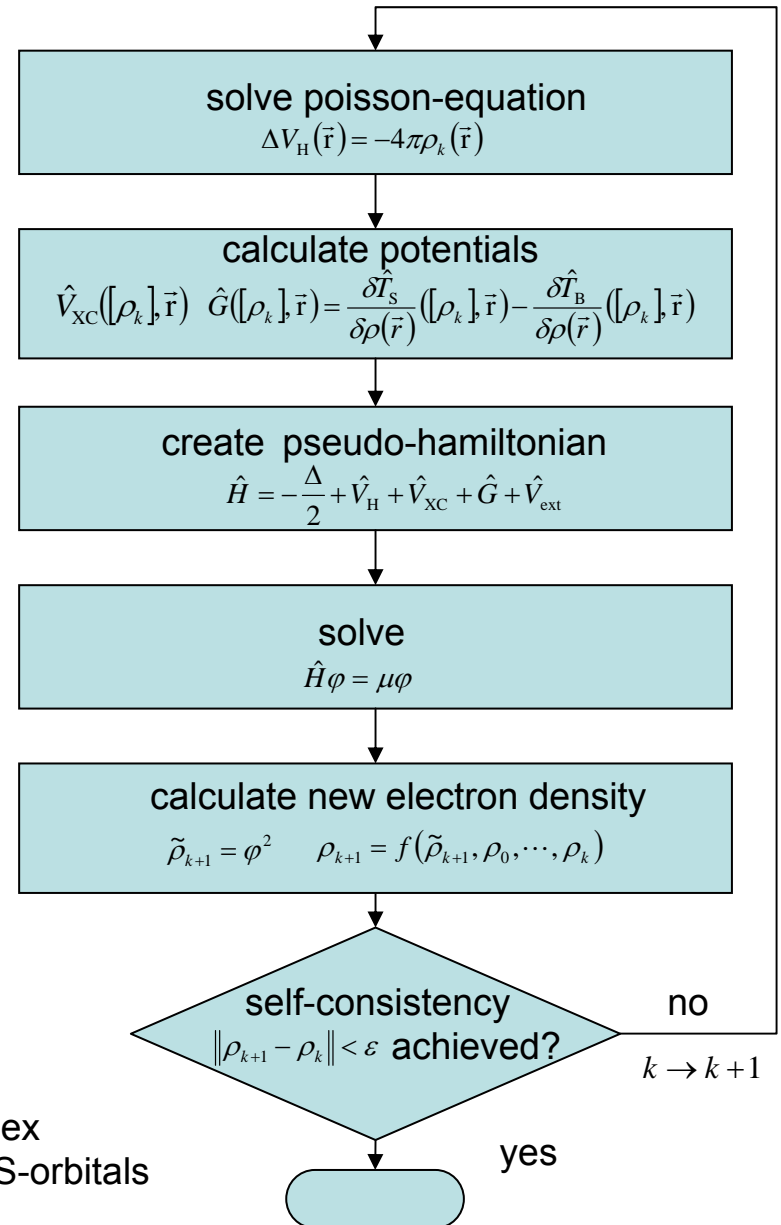
$$\hat{H} = -\frac{\Delta}{2} + V_H + V_{XC} + V_{\text{ext}} + \boxed{\frac{\delta T_S}{\delta \rho(\vec{r})} - \frac{\delta T_B}{\delta \rho(\vec{r})}}$$

- same solution methods can be used as in the case of the KS-scheme, but only with one orbital  $\Rightarrow$  no orthogonalization

## KS-scheme



## OF-scheme

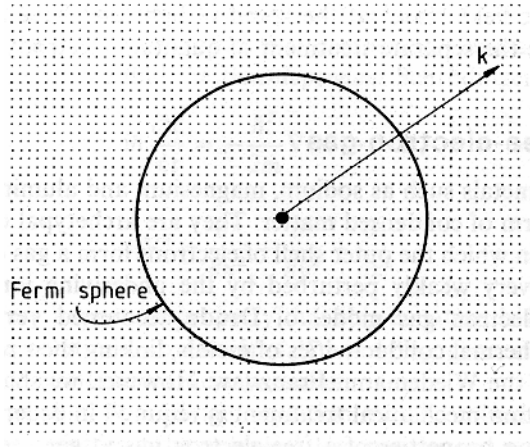


# The Thomas-Fermi approximation

- consider a system, consisting of non-interacting, free electrons

$$\hat{H} = -\frac{1}{2} \sum_i \Delta_i \quad \varphi_{\mathbf{k}}(\vec{r}) = C \exp(i\vec{k}\vec{r}) \quad (\rho_{\mathbf{k}}(\vec{r}) = C^2 = \text{const.})$$

- introducing periodic boundary conditions



$$k_i = n_i \frac{2\pi}{L_i}, i = x, y, z$$

$$\Delta^3 \vec{k} = \Delta k_x \Delta k_y \Delta k_z \frac{8\pi^3}{V}$$

$$k_F = (3\pi^2 \rho)^{1/3}$$



# The Thomas-Fermi approximation

- kinetic energy can be calculated exactly

$$T = 2 \sum_{\vec{k}} \frac{k^2}{2} = \frac{1}{\Delta^3 \vec{k}} \sum_{\vec{k}} \Delta^3 \vec{k} k^2 \approx \frac{V}{8\pi^3} \int_0^{k_F} d^3 \vec{k} k^2 = \frac{V}{2\pi^2} \int_0^{k_F} dk k^4 = \frac{V}{2\pi^2} \frac{k_F^5}{5}$$

$$T = V \cdot C \cdot \rho^{5/3}, C = \frac{3}{10} (3\pi^2)^{2/3}$$

- kinetic energy density  $t = T / V$  may be used to approximate the kinetic energy of a non-homogenous system with sufficiently slowly varying electron density

$$t = \frac{T}{V} = C \rho^{5/3} \quad T = \int d^3 \vec{r} t[\rho(\vec{r})]$$

# The Thomas-Fermi approximation

- by construction, the TF approximation is correct in the limit of a homogenous electron gas
- TF is correct in the limit of infinite nuclear charge ( $Z \rightarrow \infty$ )

## flaws

- infinite charge density at the nucleus
- bad total energies compared to Kohn-Sham
- algebraical decay of charge density ( $\propto r^{-6}$ ) instead of exponential ( $\propto \exp(-2\sqrt{-2\mu}r)$ )
- no binding of atoms to form molecules or solids
- no shell structure in atoms

# The von-Weizsäcker term

- originally, von-Weizsäcker derived intuitively a correction to the Thomas-Fermi approximation to describe the kinetic energy of core particles to explain mass defects

$$T = T_{\text{TF}} + T_{\text{vW}}$$

$$T_{\text{vW}} = \int d^3\vec{r} \, t(\rho, \nabla\rho)$$

- the von-Weizsäcker term is exact for one-orbital systems (e.g. bosonic systems, one or two electrons)

# The von-Weizsäcker term

## derivation

- for a one-orbital system, the kinetic energy can be calculated exactly

$$T_{\text{vW}} = -\frac{1}{2} \int d^3\vec{r} \varphi^*(\vec{r}) \Delta \varphi(\vec{r})$$

integration by parts  $(\varphi(\vec{r}) \xrightarrow{r \rightarrow \infty} 0)$

$$= \frac{1}{2} \int d^3\vec{r} |\nabla \varphi(\vec{r})|^2 = \frac{1}{2} \int d^3\vec{r} |\nabla \sqrt{\rho(\vec{r})}|^2$$

$$\nabla f(g(\vec{r})) = \frac{\partial f}{\partial g} \nabla g(\vec{r})$$

$$\nabla \sqrt{\rho(\vec{r})} = \frac{1}{2\sqrt{\rho(\vec{r})}} \nabla \rho(\vec{r})$$



$$T_{\text{vW}} = \frac{1}{8} \int d^3\vec{r} \frac{|\nabla \rho(\vec{r})|^2}{\rho(\vec{r})}$$

# The von-Weizsäcker term

## improvements compared to TF

- exponential decay of electronic density
- finite charge at the nucleus

## flaws

- in a homogenous system  $T_{\text{vW}} = 0$ , but for a one-orbital system  $T_{\text{TF}} \neq 0$   
 $\Rightarrow T_{\text{S}} = T_{\text{TF}} + T_{\text{vW}}$  does not reproduce the two limits

attempts to improve the bridge between the two extremes:

$$T_{\text{S}} = G(N)T_{\text{TF}} + T_{\text{vW}}$$

number of electrons  $\nearrow$

$$G(N) = (1 - \delta_{1N} - \delta_{2N}) \left( 1 - \frac{A_1}{N^{1/3}} + \frac{A_2}{N^{2/3}} \right)$$

$\nwarrow$  empirical parameters

- experiences indicated that the prefactor of the vW-Term might be too large

# Linear-Response Theory

## Why Linear-Response Theory?

- relationship between Linear Response and functional derivative of  $T_S$  can be derived
- correct Linear Response is important to describe charge oscillations in solids

## definition

- small change in potential causes a first-order change of the charge density


$$\delta\rho(\vec{r}) = \int d^3\vec{r}' \underbrace{\chi(\vec{r} - \vec{r}')}_{\frac{\delta\rho(\vec{r})}{\delta\nu(\vec{r}')}} \delta\nu(\vec{r}') \quad \longrightarrow \quad \delta\rho(\vec{q}) = \chi(\vec{q})\delta\nu(\vec{q})$$

fourier transformation

# Linear-Response Theory

## The Linear-Response Function

„inversion“ theorem of functional derivatives:

$$\delta(\vec{r}'' - \vec{r}') = \int d^3\vec{r} \frac{\delta\rho(\vec{r}'')}{\delta v(\vec{r})} \frac{\delta v(\vec{r})}{\delta\rho(\vec{r}')} = \int d^3\vec{r} \chi(\vec{r}'' - \vec{r}) \underbrace{\frac{\delta v(\vec{r})}{\delta\rho(\vec{r}')}}_{f(\vec{r}-\vec{r}')}$$


fourier transformation:

$$1 = \chi(\vec{q}) \hat{F} \left( \frac{\delta v(\vec{r})}{\delta\rho(\vec{r}')} \right) \Rightarrow \boxed{\hat{F} \left( \frac{\delta v(\vec{r})}{\delta\rho(\vec{r}')} \right) = \frac{1}{\chi(\vec{q})}}$$

# Linear-Response Theory

## Linear-Response in the DFT scheme

$$\hat{H} = -\frac{\Delta}{2} + V_{\text{eff}}$$

$$E = T_S + E_{\text{eff}}$$

$$V_{\text{eff}} = \frac{\delta E_{\text{eff}}}{\delta \rho(\mathbf{r})}$$

$$\frac{\delta V_{\text{eff}}}{\delta \rho(\mathbf{r}')} = \frac{\delta^2 E_{\text{eff}}}{\delta \rho(\mathbf{r}) \delta \rho(\mathbf{r}')} = \frac{\delta^2 (E - T_S)}{\delta \rho(\mathbf{r}) \delta \rho(\mathbf{r}')} \overset{\uparrow}{=} - \frac{\delta^2 T_S}{\delta \rho(\mathbf{r}) \delta \rho(\mathbf{r}')}$$

$$\left\{ \frac{\delta E}{\delta \rho(\vec{\mathbf{r}})} = \mu = \text{const.} \right.$$

→

$$\frac{1}{\chi(\vec{\mathbf{q}})} = -\hat{F} \left( \left. \frac{\delta^2 T_S}{\delta \rho(\vec{\mathbf{r}}) \delta \rho(\vec{\mathbf{r}}')} \right|_{\text{groundstate}} \right)$$

unknown !



# Linear-Response Theory

## The Free-Electron-Gas limit of the LR-function

$$\hat{H}_0 = -\frac{\Delta}{2}$$

$$\chi_{\text{Lindhard}} = -\frac{k_F}{\pi^2} \left( \frac{1}{2} + \frac{1-\eta^2}{4\eta} \ln \left( \frac{1+\eta}{1-\eta} \right) \right), \quad \eta = \frac{q}{2k_F}$$

Diagram illustrating the derivation of the Lindhard function from a general expression for a homogeneous system.

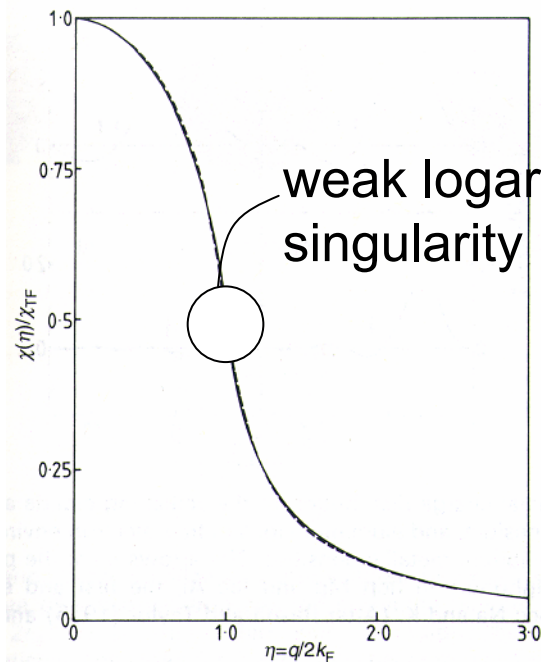
The diagram shows a light blue rectangular box containing the following expression:

$$\hat{F} \left( \underbrace{\frac{\delta^2 T_s}{\delta \rho(\vec{r}) \delta \rho(\vec{r}')}}_{f(|\vec{r}-\vec{r}'|)} \right) \bigg|_{\rho_0} = -\frac{1}{\chi_{\text{Lindhard}}(q)}$$

Annotations and arrows:

- An arrow points from the left towards the box.
- An arrow points from the term  $f(|\vec{r}-\vec{r}'|)$  to the text "due to symmetry..." below the box.
- An arrow points from the term  $\chi_{\text{Lindhard}}(q)$  to the text "homogenous system" to the right of the box.

# Linear-Response Theory



fourier transformation

$$\lim_{r \rightarrow \infty} \delta\rho(r) \propto \frac{\cos(2k_F r)}{r^3}$$

„Friedel oscillations“

⇒ singularity is important to describe the physics of a solid properly

# Combination of TF and vW

- goal is to put the combination of TF and vW on a physical basis by considering the linear-response

$$T_S = T_{\text{TF}} + \lambda T_{\text{vW}}$$

- consider a nearly homogeneous electron gas with small fluctuations

$$\rho(\vec{r}) = \rho_0 + \Delta\rho(\vec{r})$$

$$\int d^3\vec{r} \Delta\rho(\vec{r}) = 0$$

- kinetic energy may be expanded around the average density

$$T_S[\rho] \approx \underbrace{T_S[\rho_0]}_{T_{\text{TF}}} + \int d^3\vec{r} \underbrace{\frac{\delta T_S}{\delta \rho(\vec{r})}}_{\text{const.}} \bigg|_{\rho_0} \Delta\rho(\vec{r}) + \frac{1}{2} \iint d^3\vec{r} d^3\vec{r}' \underbrace{\frac{\delta^2 T_S}{\delta \rho(\vec{r}) \delta \rho(\vec{r}')}}_{-\hat{F}\left(\frac{1}{\chi_{\text{Lindhard}}(q)}\right)} \bigg|_{\rho_0} \Delta\rho(\vec{r}) \Delta\rho(\vec{r}')$$

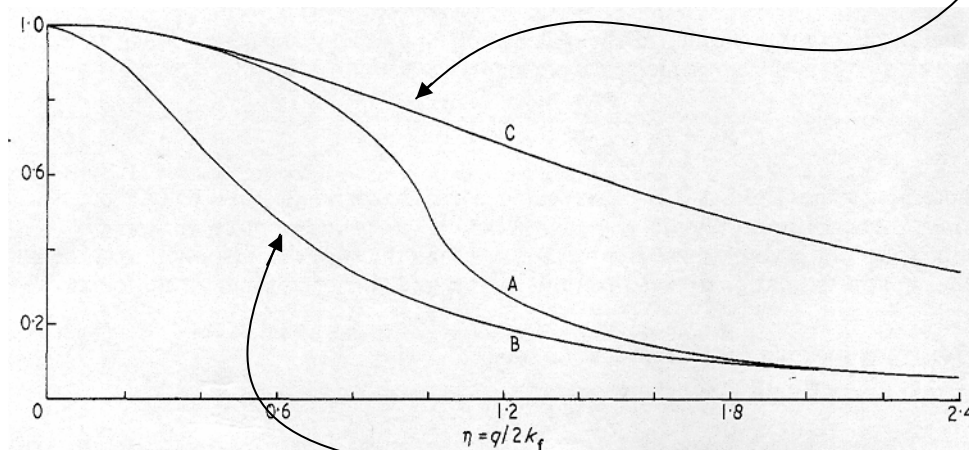
$\Rightarrow$  linear term vanishes

# Combination of TF and vW

$$\chi_{\text{Lindhard}} \approx -\frac{k_F}{\pi^2} \begin{cases} 1 - \frac{\eta^2}{3} \dots, & \text{small } \eta = \frac{q}{2k_F} \\ \frac{1}{3\eta^2} \dots, & \text{large } \eta \end{cases}$$

- Kompaneets, Pavlovskii (1957)
- Kirzhnits (1957)
- Le Couteur (1964)
- Stoddart, Beattie, March (1970)

$$\chi_{\text{TF}\lambda\text{vW}} = -\frac{k_F}{\pi^2} \frac{1}{1+3\lambda\eta^2} \approx -\frac{k_F}{\pi^2} \begin{cases} 1-3\lambda\eta^2 & , \text{small } \eta \Rightarrow \lambda = 1/9 \\ \frac{1}{3\lambda\eta^2} & , \text{large } \eta \Rightarrow \lambda = 1 \end{cases}$$



# Combination of TF and vW

- $\lambda = 1/9$  valid for long wavelength perturbation  
→ e.g. appropriate for impurity problems where long wavelength components of potential are dominant
- $\lambda = 1$  valid for short wavelength perturbation  
→ e.g. appropriate for perfect lattices

## flaws

- bad estimation of total energy:  
 $\lambda = 1 \rightarrow$  overestimation,  $\lambda = 1/9 \rightarrow$  underestimation

(interpolation leads to  $\lambda = 1/5$ )

- still no shell structures in atoms

# Conventional Gradient Expansion

## Basic Idea

- include higher order gradient corrections to the kinetic energy functional by expanding the Lindhard function to higher orders

$$\chi_{\text{Lindhard}} \approx -\frac{k_F}{\pi^2} \left( \underbrace{1}_{T_{\text{TF}}} - \underbrace{\frac{\eta^2}{3}}_{T_2} - \frac{\eta^4}{15} - \dots \right)$$

$$T = \underbrace{T_0}_{T_{\text{TF}}} + \underbrace{T_2}_{\frac{1}{9}T_{\text{vW}}} + T_4 + \dots$$

$$T_4[\rho] = \frac{1}{540(3\pi^2)^{2/3}} \int d^3\vec{r} \, \rho^{1/3} \left( \frac{(\nabla^2 \rho)^2}{\rho^2} - \frac{9\nabla^2 \rho (\nabla \rho)^2}{8\rho^3} + \frac{(\nabla \rho)^4}{3\rho^4} \right)$$

(Hodges, 1973)

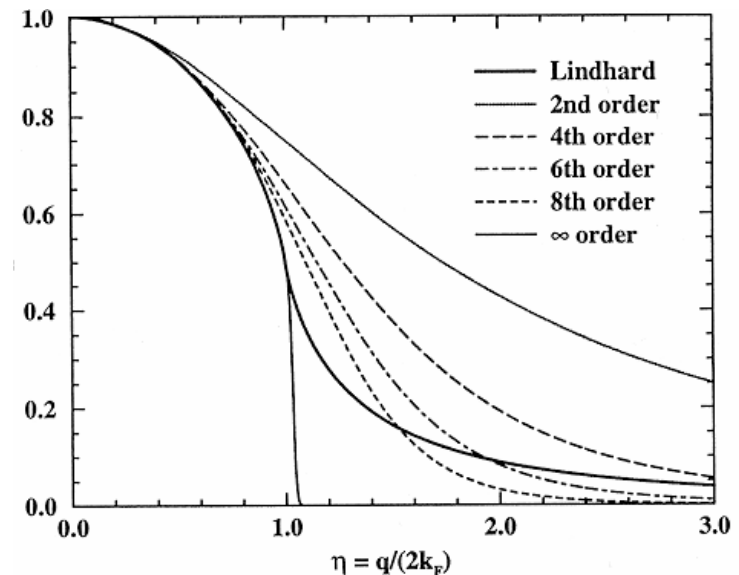
$$T_6[\rho] = \dots \quad (\text{extremely complicated...})$$

(Murphy, 1981)

# Conventional Gradient Expansion

## flaws

- not suitable for isolated systems with exponential decay of charge density  
→ kinetic energy potential  $\frac{\delta T}{\delta \rho}$  diverges for order four and  $\delta \rho$  higher  
→  $T$  diverges for order six  
  
⇒ in self-consistent calculations, charge density shows wrong decay behaviour
- linear response is wrong, since expansion does only converge for  $\eta < 1$



⇒ CGE is of no practical use

# Average-Density Approximation

## Basic idea

- include non-local effects to the kinetic energy functional

example: (Garcia-Gonzales et al., PRA 54, 1897 (1996) )

$$T_S[\rho] = -\frac{3}{5}T_{\text{TF}}[\rho] + T_{\text{vw}}[\rho] + \frac{8}{5} \int d^3\vec{r} \, \rho(\vec{r}) t_0(\tilde{\rho}(\vec{r}))$$

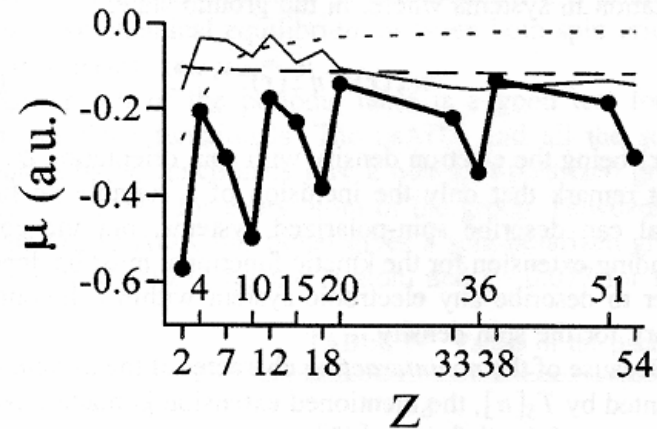
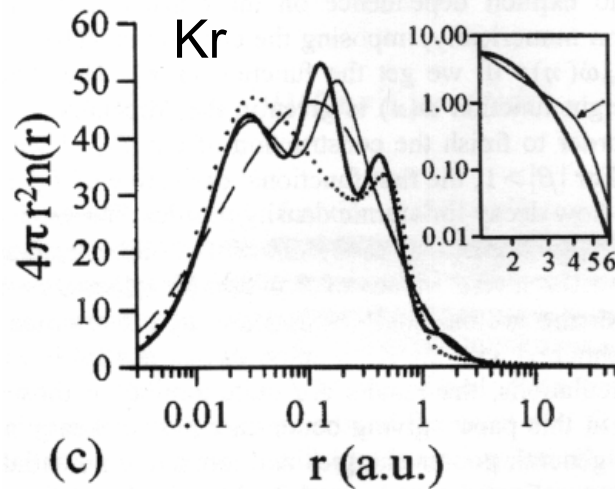
$$T_{\text{TF}}[\rho] = \int d^3\vec{r} \, \rho(\vec{r}) t_0(\rho(\vec{r})) \qquad \tilde{\rho}(\vec{r}) = \int d^3\vec{r}' \, \rho(\vec{r}') \Omega(\vec{r}, \vec{r}')$$


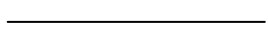
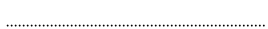

- correct linear-response behaviour is enforced by appropriate choice of the weight function  $\Omega(\vec{r}, \vec{r}')$

$$\hat{F} \left( \left. \frac{\delta^2 T_S}{\delta \rho(\vec{r}) \delta \rho(\vec{r}')} \right|_{\rho_0} \right) = - \frac{1}{\chi_{\text{Lindhard}}(q)}$$



# Average-Density Approximation



	Kohn-Sham	
	symmetric ADA	$\Omega(\vec{r}, \vec{r}') = \Omega(\vec{r}', \vec{r})$
	non-symmetric ADA	$\Omega(\vec{r}, \vec{r}') \neq \Omega(\vec{r}', \vec{r})$
	TFλvW	

⇒ non-local functionals can improve numerical results significantly

(Garcia-Gonzales et al., PRA 54, 1897 (1996) )

# Summary

- goal is to get rid of the Kohn-Sham-orbitals to reduce the computational time
- trade-off are less accurate results due to the necessity of approximating the kinetic energy functional
- state-of-the-art are non-local functionals which improve the results of the classical functionals significantly

# Literature

- Wang, Y.A., Carter, E.A. 2000, „Orbital-free kinetic energy density functional theory“, *Theoretical Methods in Condensed Phase Chemistry*, S.D. Schwartz, Ed. Kluwer, 117-184
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