Density Functional Theory

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Key concepts, a.k.a. Slang

*Fundamental challenges: **your** chance!*

- Schrödinger Equation
  - Fundamental challenges
  - Mean-field theory
  - Nearsightedness & Exponential Wall Problem
  - Dephasing
- Density Functional Theory and Alternatives
  - Hohenberg-Kohn Theorem(s)
  - Pre-HK: gradient expansion, TFDW,…
  - Kohn-Sham equations
  - Post-HK: ”functional” theories
  - Today’s challenges and developments

Point of departure

Single-particle Schrödinger equation

$$
\begin{aligned}
E\,\psi(\boldsymbol{r}) &= \hat{H}\,\psi(\boldsymbol{r}) \\
\hat{H} &= \hat{t} + \hat{v} = -\frac{\hbar^2}{2m}\,\Delta + v(\boldsymbol{r})
\end{aligned}
$$

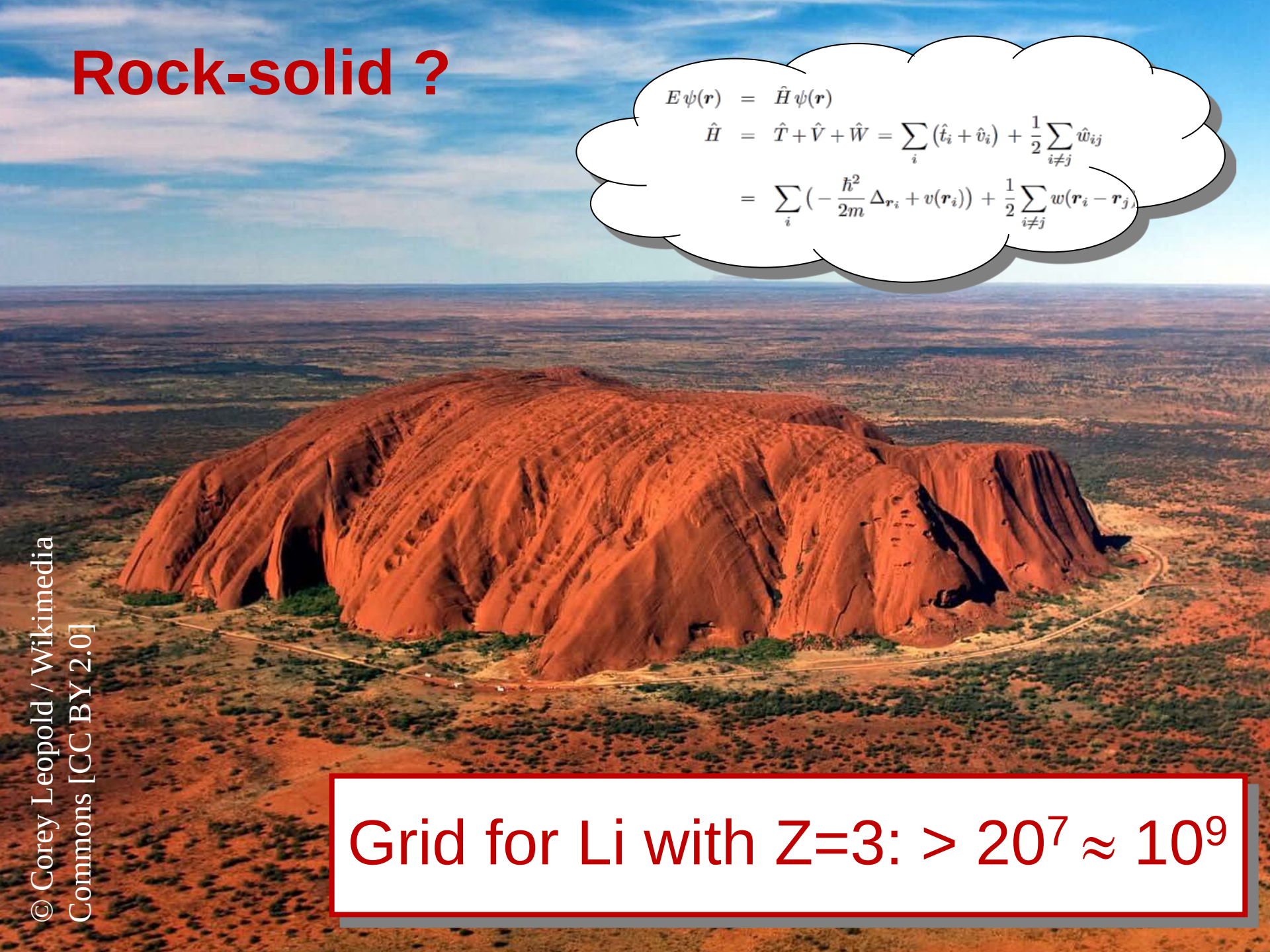
- Hydrogen atom, double slit, Aharonov Bohm effect..
- Spin..., relativistic effects...,

Many-particle Schrödinger equation

$$
\begin{aligned}
E\,\psi(\boldsymbol{r}) &= \hat{H}\,\psi(\boldsymbol{r}) \\
\hat{H} &= \hat{T} + \hat{V} + \hat{W} = \sum_i \left(\hat{t}_i + \hat{v}_i\right) + \frac{1}{2}\sum_{i\neq j} \hat{w}_{ij} \\
&= \sum_i \left(-\frac{\hbar^2}{2m}\,\Delta_{\boldsymbol{r}_i} + v(\boldsymbol{r}_i)\right) + \frac{1}{2}\sum_{i\neq j} w(\boldsymbol{r}_i - \boldsymbol{r}_j)
\end{aligned}
$$

Rock-solid ?

$$
\begin{aligned}
E\,\psi(\boldsymbol{r}) &= \hat{H}\,\psi(\boldsymbol{r}) \\
\hat{H} &= \hat{T}+\hat{V}+\hat{W} = \sum_i \left(\hat{t}_i+\hat{v}_i\right) + \frac{1}{2}\sum_{i\neq j}\hat{w}_{ij} \\
&= \sum_i \left(-\frac{\hbar^2}{2m}\Delta_{\boldsymbol{r}_i} + v(\boldsymbol{r}_i)\right) + \frac{1}{2}\sum_{i\neq j} w(\boldsymbol{r}_i-\boldsymbol{r}_j)
\end{aligned}
$$



Grid for Li with Z=3: > $20^7 \approx 10^9$

Mean-field theory: “Hartree”

$$\epsilon_\nu \, \varphi_\nu(\boldsymbol{r}) = \hat{h}_{Hartree} \, \varphi_\nu(\boldsymbol{r})$$

$$\hat{h}_{Hartree} = -\frac{\hbar^2}{2m}\Delta + v_{\text{external}}(\boldsymbol{r}) + \int d^3\boldsymbol{r}' \, \frac{e^2 \, \rho(\boldsymbol{r}')}{4\pi\varepsilon_0 \, |\boldsymbol{r} - \boldsymbol{r}'|}$$

$$\rho(\boldsymbol{r}) = \sum_{occ.} \left|\varphi_\nu(\boldsymbol{r})\right|^2$$

$$\Psi_{Hartree}(\boldsymbol{r}_1, \boldsymbol{r}_2, \ldots, \boldsymbol{r}_N) \sim \prod_{\nu \in occ.} \varphi_\nu(\boldsymbol{r}_\nu)$$

Popular vote: ~ 100% YES

… but: *“invalid wavefunction”* (Pauli!)

$$\Psi_{HF}(\boldsymbol{r}_1, \boldsymbol{r}_2, \ldots, \boldsymbol{r}_N) \sim \sum_{P=\text{permutation}} \text{sign}(P) \prod_{\nu \in occ.} \varphi_{P(\nu)}(\boldsymbol{r}_\nu)$$

$$= \sum_{P=\text{permutation}} \text{sign}(P) \prod_{\nu \in occ.} \varphi_\nu(\boldsymbol{r}_{P(\nu)})$$

Mean-field theory: ☺ “Hartree-Fock”

$$\hat{h}_{HF} = \hat{h}_{Hartree} + \hat{h}_{Fock}$$

$$\left(\hat{h}_{electro\text{-}static}\varphi_\nu\right)_{\boldsymbol{r}} = +\int d^3\boldsymbol{r}' \, \frac{e^2\,\rho(\boldsymbol{r}',\boldsymbol{r}')}{4\pi\varepsilon_0\,|\boldsymbol{r}-\boldsymbol{r}'|}\,\varphi_\nu(\boldsymbol{r})$$

$$\left(\hat{h}_{Fock}\varphi_\nu\right)_{\boldsymbol{r}} = -\int d^3\boldsymbol{r}' \, \frac{e^2\,\rho_{s_\nu}(\boldsymbol{r},\boldsymbol{r}')}{4\pi\varepsilon_0\,|\boldsymbol{r}-\boldsymbol{r}'|}\,\varphi_\nu(\boldsymbol{r}')$$

$$\rho_{\sigma=\uparrow\downarrow}(\boldsymbol{r},\boldsymbol{r}') = \sum_{\nu\in occ.,\, s_\nu=\sigma} \varphi_\nu(\boldsymbol{r})\,\varphi_\nu^\star(\boldsymbol{r}')$$

Fock- / Exchange term:

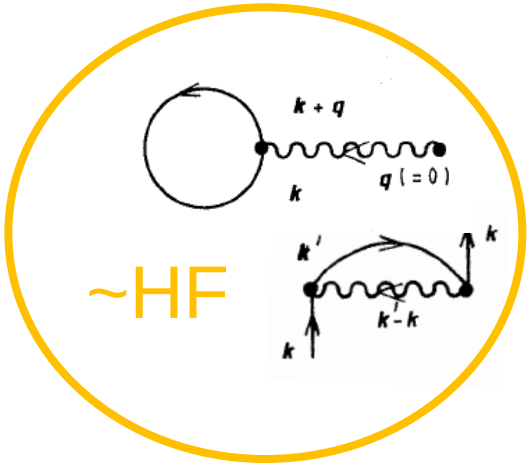
- still: ‘single-particle’
- integral operator
- ‘correction’, thus ‘-’
- HF (like all MFT) biased towards symmetry-breaking
- $E_{exact} - E_{HF} = E_{correlation}$

$$\epsilon_\nu\,\varphi_\nu(\boldsymbol{r}) = \hat{h}_{HF}\,\varphi_\nu(\boldsymbol{r})$$

Perturbation theory

Two major paradigms:

1.) Feynman Diagrams



~HF

… and all the Rest …

2.) Configuration interaction

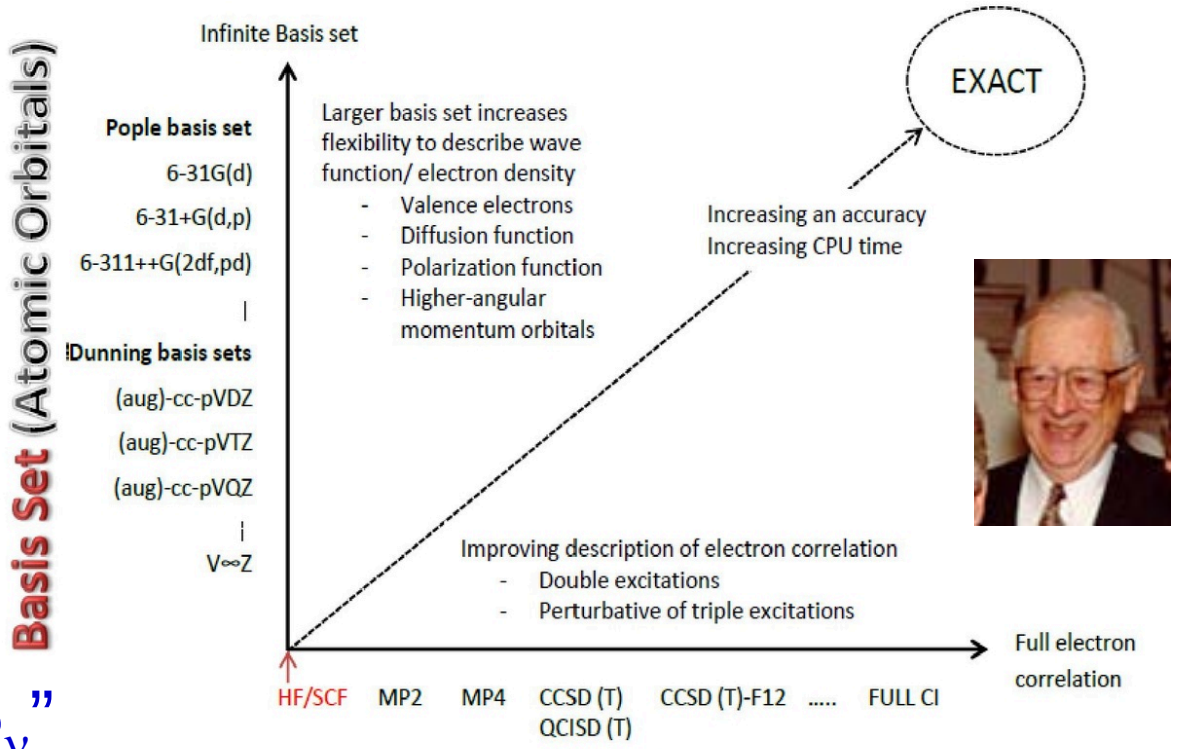
$$\Psi_{CI}(\boldsymbol{r}_1, \boldsymbol{r}_2, \ldots, \boldsymbol{r}_N) \sim \sum_{P=\text{permutation}} \text{sign}(P) \left\{CI\right\}$$

$$\left\{CI\right\} = \alpha \prod_{\nu \in occ.} \varphi_{P(\nu)}(\boldsymbol{r}_\nu) + \sum_{\mu_1 \nu_j} \alpha_{\mu_1,\nu_j} \prod_{\substack{\nu \in occ. \\ \nu_j \to \mu_1}} \varphi_{P(\nu)}(\boldsymbol{r}_\nu)$$

$$+ \sum_{\mu_1 \mu_2 \nu_j \nu_k} \alpha_{\mu_1 \mu_2, \nu_j \nu_k} \prod_{\substack{\nu \in occ. \\ \nu_j \to \mu_1, \nu_k \to \mu_2}} \varphi_{P(\nu)}(\boldsymbol{r}_\nu) + \ldots$$

≡ traditional quantum chemistry

"Pople diagram"



"better φ_ν"

"more μ_μ"

Food for thought:

Walter Kohn's "exponential wall"

Nobel Lecture: Electronic structure of matter—wave functions and density functionals*

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CONTENTS

In the intervening more than six decades enormous progress has been made in finding approximate solutions of Schrödinger's wave equation for systems with several electrons, decisively aided by modern electronic computers. The outstanding contributions of my Nobel Prize co-winner John Pople are in this area. The main objective of the present account is to explicate DFT, which is an alternative approach to the theory of electronic structure, in which the electron density distribution $n(r)$

$$\Psi = \Psi_{\text{system 1}} = \sum_P \prod_\nu \varphi_\nu^{(1)} \times \Psi_{\text{system 2}} = \sum_P \prod_\rho \varphi_\rho^{(2)} \times \Psi_{\text{system 3}} = \sum_P \prod_\kappa \varphi_\kappa^{(3)} \times \ldots$$

Food for thought:

Walter Kohn's "nearsightedness"

VOLUME 76, NUMBER 17 PHYSICAL REVIEW LETTERS

Density Functional and Density Matrix Method Scaling Linearly with the Number of Atoms

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(Received 21 August 1995)

A widely applicable "nearsightedness" principle is first discussed as the physical basis for the existence of computational methods scaling linearly with the number of atoms. This principle applies to

A few remarks about this principle:

(1) The principle is generally a consequence of wave-mechanical destructive interference. It requires the presence of many particles, which need not be interacting.

(2) It is not universally valid. [superconductivity,…].

(3) The principle is tacitly assumed in much of chemistry and materials science.

(4) .. long range electric fields, as in ionic crystals, … must be self-consistently [treated]…

Food for thought:

Peter Fulde's "local correlators"

The Journal of Chemical Physics PERSPECTIVE

Wavefunctions of macroscopic electron systems

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ABSTRACT

Wavefunctions for large electron numbers N are plagued by the Exponential Wall Problem (EWP), i.e., an exponential increase in the dimensions of Hilbert space with N. Therefore, they lose their meaning for macroscopic systems, a point stressed, in particular, by Kohn. The EWP has to be resolved in order to provide a solid basis for wavefunction based electronic structure calculations of macroscopic systems, e.g., solids. The origin of the EWP is the multiplicative property of wavefunctions when independent subsystems are considered. Therefore, it can only be avoided when wavefunctions are formulated so that they are additive instead, in particular, when matrix elements involving them are calculated. We describe how this is done for the ground state of a macroscopic electron system. Going over from a multiplicative to an additive quantity requires taking a logarithm. Here it implies going over from Hilbert space to the operator- or Liouville space with a metric based on

Food for thought:

Peter Fulde's "local correlators"

The Journal of Chemical Physics PERSPECTIVE

Wavefunctions of macroscopic electron systems

$$\Psi_{\text{corr}} \sim \exp(-\sum_{\alpha} \hat{O}_{\alpha})\, \psi_{\text{mean-field}}$$

e.g. cusp condition

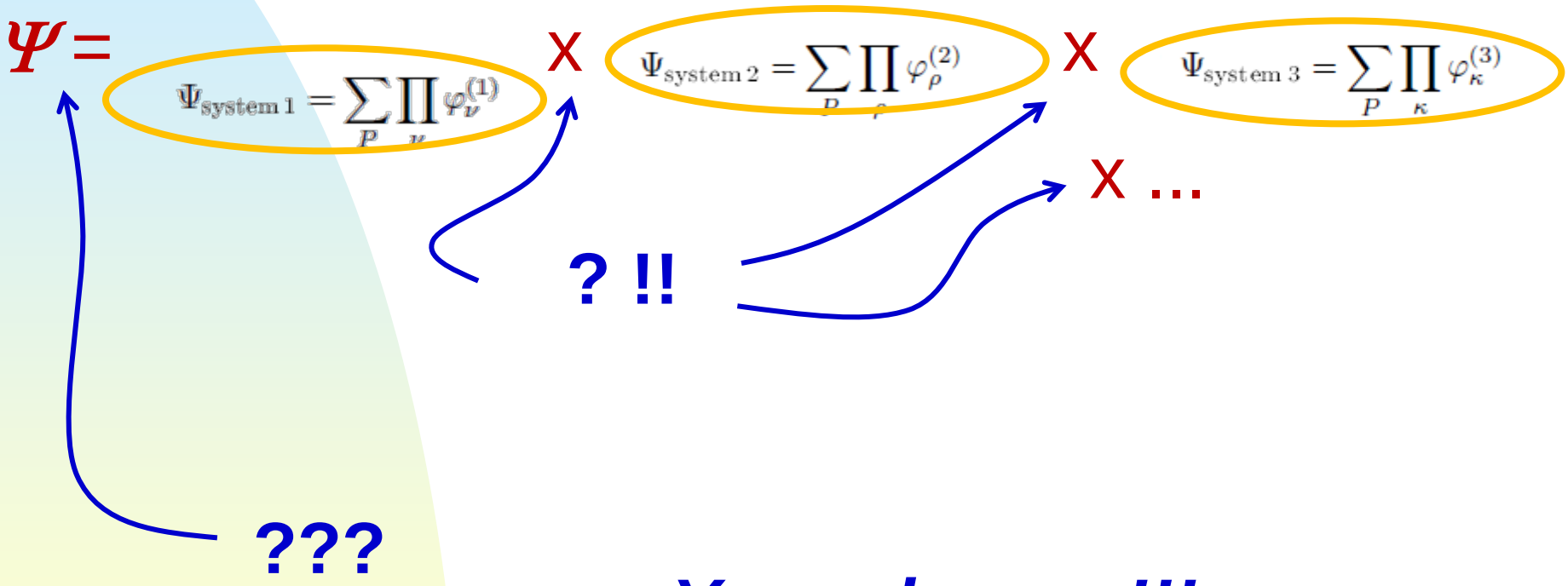
$$\hat{O}_{\alpha} \sim f(|\boldsymbol{r}_i - \boldsymbol{r}_j|)$$

$$\left\langle \Psi_{\text{corr}} \middle| \hat{A} \middle| \Psi_{\text{corr}} \right\rangle = \sum_{\alpha_\ell \alpha'_m} \langle \hat{O}_{\alpha_1} \hat{O}_{\alpha_2} \ldots \hat{A} \hat{O}_{\alpha'_1} \hat{O}_{\alpha'_2} \rangle^{\text{cumulant}}_{\text{mean-field}}$$

- O(N)
- cf. nearsightedness

Food for thought:

The role of “dephasing / de-correlating”



Your chance !!!

Hohenberg-Kohn Theorem(s)

$f_{v\to\psi}$ solve S.-Eq.

$f_{\psi\to v}$ apply *E-T-W*

set of all "reasonable" potentials v

set of all groundstate wavefunctions ψ

$f_{\psi\to\rho}(f_{v\to\psi}(v))$

$f_{\psi\to\rho}$ integrate

???

set of all "reasonable" groundstate density profiles ρ

$$\exists\, v(.) = F_{HK}[\rho(.)] \quad \text{iff} \quad \left(v_1\to\rho \text{ and } v_2\to\rho \Leftrightarrow v_1(r) = v_2(r) + const\right)$$

"functional"

Hohenberg-Kohn Theorem (1964)

Consider Hamiltonians of the form (fixed interaction W)

$$\hat{H} = \hat{T} + \hat{W} + \hat{V}_{\text{extern}}$$

$\exists$ v(.) = $F_{HK}[\rho(.)]$ iff ($v_1 \to \rho$ and $v_2 \to \rho \Leftrightarrow v_1(r) = v_2(r) + const$)

Ritz principle (assume non-degenerate ground states ;-)

$$\begin{aligned} E_{gs}^{(1)} &= \langle \psi^{(1)} | \hat{T} + \hat{W} + \hat{V}^{(1)} | \psi^{(1)} \rangle \overset{!}{<} \langle \psi^{(2)} | \hat{T} + \hat{W} + \hat{V}^{(1)} | \psi^{(2)} \rangle \\ &= \langle \psi^{(2)} | \hat{T} + \hat{W} + \hat{V}^{(2)} | \psi^{(2)} \rangle + \int \left(v^{(1)}(\boldsymbol{r}) - v^{(2)}(\boldsymbol{r}) \right) \rho(\boldsymbol{r}) \, d^3\boldsymbol{r} \\ &= E_{gs}^{(2)} + \int \left(v^{(1)}(\boldsymbol{r}) - v^{(2)}(\boldsymbol{r}) \right) \rho(\boldsymbol{r}) \, d^3\boldsymbol{r} \end{aligned}$$

Analogously

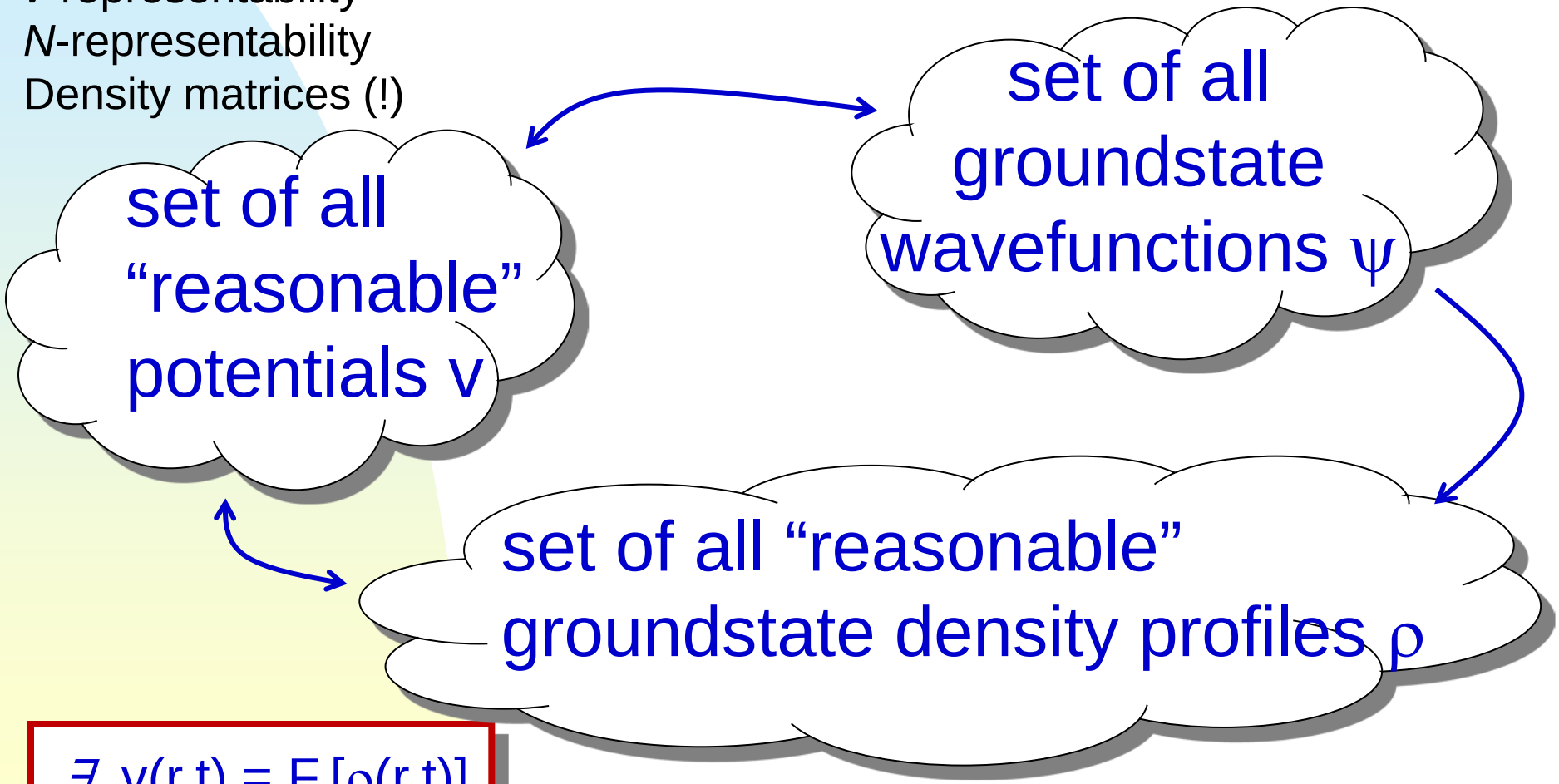
$$E_{gs}^{(2)} < E_{gs}^{(1)} + \int \left(v^{(2)}(\boldsymbol{r}) - v^{(1)}(\boldsymbol{r}) \right) \rho(\boldsymbol{r}) \, d^3\boldsymbol{r}$$

And finally

$$E_{gs}^{(1)} + E_{gs}^{(2)} < E_{gs}^{(1)} + E_{gs}^{(2)}$$

Hohenberg-Kohn Theorem (DFT, 1964), Runge-Gross Theorem (td-DFT 1984) … and much more (temperature, fields&currents, superconductivity, relativity, classical systems,…)

Issues:
v-representability
N-representability
Density matrices (!)



$\exists\ v(r,t) = F[\rho(r,t)]$

Slang and nomenclature

Homogeneous Fermi gas / electron gas (equation of state):

Energy densities are functions of the particle density, …

$$\frac{\langle \hat{H} \rangle}{\Omega} = e_{\text{e-gas}}(\rho, T) \approx e_{\text{e-gas}}(\rho)$$

$$\frac{\langle \hat{T} \rangle}{\Omega} = \tau_{\text{e-gas}}(\rho, T) \approx \tau_{\text{e-gas}}(\rho)$$

… which are easily evaluated for non-interacting fermions

$$\frac{\langle \Phi_0 | \hat{T} | \Phi_0 \rangle}{\Omega} = \tau_0(\rho) = \frac{\hbar^2 k_F^5}{10 m_e \pi^2}$$

$$\frac{\langle \Phi_0 | (\hat{W} - \hat{V}_{\text{jellium}}) | \Phi_0 \rangle}{\Omega} = e_{x,0}(\rho) = -\frac{e^2 k_F^4}{16 \epsilon_0 \pi^4}$$

For PR reasons, the "unkown rest" is called "correlation energy" ;-)

$$e_{xc}(\rho) = e_{\text{e-gas}}(\rho) - \tau_0(\rho)$$

- **e.g. Quantum MC $\Rightarrow$ $e_{xc}(\rho)$**
- **Application, e.g.: stability of neutron stars**

Inhomogeneous Fermi gas / electron gas: Gradient expansion

We need expectation values of functions of the Hamiltonian, e.g.,

$$\tau(x) = -\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2}\,\rho(x,y)_{y=x}$$

$$\rho(x,y) = \sum_{\nu\in occ.,\, s_\nu=\sigma} \varphi_\nu(x)\,\varphi_\nu^\star(y) = \left\langle x\right|\theta\Big(E_F - \frac{\hat{p}^2}{2m} - \hat{v}\Big)\left|y\right\rangle$$

$$= \int \left\langle x\right|\theta\Big(E_F - \frac{\hat{p}^2}{2m} - \hat{v}\Big)\left|k\right\rangle \underbrace{e^{-iky}}_{\langle k|y\rangle}\, dk$$

Gradient expansion [see: D. A. Kirzhnits, A.J. Meadows, Field Theoretical Methods in Many-body Systems]

$$f(\hat{A}+\hat{B})\,|a\rangle = \sum_{n=0}^{\infty} f^{(n)}(\alpha+\hat{B})\,\hat{O}_n\,|\alpha\rangle$$

$$\hat{O}_1 = 1\,,\ \hat{O}_1 = 0\,,\ \hat{O}_2 = \left[\hat{A},\hat{B}\right],\ \ldots$$

.. yields terms like

$$\hat{A}\equiv\boldsymbol{\nabla}^2\,,\ \hat{B}\equiv E_F - v(\boldsymbol{r}) = \frac{\hbar^2}{2m}\,k_F^2(\boldsymbol{r})\boldsymbol{\nabla}^2 \quad\Rightarrow\quad \hat{O}_2 \sim (\boldsymbol{\nabla}k_F(\boldsymbol{r}))^2\,\text{etc.}$$

Gradient expansion

Straightforward evaluations

$$\rho(\boldsymbol{r}) = \frac{k_F^3(\boldsymbol{r})}{3\pi^2} + \frac{1}{24\pi^2}\frac{\Delta k_F^2(\boldsymbol{r})}{k_F(\boldsymbol{r})} - \frac{1}{96\pi^2}\frac{(\nabla k_F^2(\boldsymbol{r}))^2}{k_F^3(\boldsymbol{r})} + \dots$$

$$\tau(\boldsymbol{r}) = \frac{\hbar^2}{m_e}\left(\frac{k_F^5(\boldsymbol{r})}{10\pi^2} - \frac{k_F(\boldsymbol{r})\left(\Delta k_F^2(\boldsymbol{r})\right)}{48\pi^2} - \frac{1}{64\pi^2}\frac{(\nabla k_F^2(\boldsymbol{r}))^2}{k_F(\boldsymbol{r})} + \dots\right)$$

$$e_x(\boldsymbol{r}) = -\frac{e^2}{4\pi\epsilon_0}\left(\frac{k_F^4(\boldsymbol{r})}{4\pi^3} - \frac{1}{576\pi^3}\frac{(\nabla k_F^2(\boldsymbol{r}))^2}{k_F^2(\boldsymbol{r})} + \dots\right)$$

and term-wise inversion

$$k_F^5(\boldsymbol{r}) = (3\pi^2)^{5/3}\rho(\boldsymbol{r}) - \frac{5}{3}\frac{(3\pi^2)^2}{36\pi^2}\Delta\rho(\boldsymbol{r}) + \dots$$

yields **our first non-trivial density functional :-) a.k.a TFDW theory**

$$\tau[\rho(.)] = \tau(\rho, \boldsymbol{\nabla}\rho, \dots) = \frac{\hbar^2}{m_e}\left(\frac{3(3\pi^2)^{2/3}}{10\pi^2}\rho^{5/3}(\boldsymbol{r}) + \frac{1}{72}\frac{(\nabla\rho(\boldsymbol{r}))^2}{\rho(\boldsymbol{r})} \underbrace{-\frac{1}{12}\Delta\rho(\boldsymbol{r})}_{\text{no contribution}} + \dots\right)$$

$$e_x[\rho(.)] = e_x(\rho, \boldsymbol{\nabla}\rho, \dots) = -\frac{e^2}{4\pi\epsilon_0}\left(\frac{3\sqrt[3]{3}}{4\sqrt[3]{\pi}}\rho^{4/3}(\boldsymbol{r}) + \frac{7}{432\pi\sqrt[3]{3\pi^2}}\frac{(\nabla\rho(\boldsymbol{r}))^2}{\rho^{4/3}(\boldsymbol{r})} + \dots\right)$$

TFDW theory of the neutral atom

$$E = E[\rho(.)] = \int_0^\infty \Big(-\frac{Ze^2}{4\pi\varepsilon_0}\frac{\rho(r)}{r} + v_{\mathrm{Hartree}}(r)\,\rho(r) \Big)\, 4\pi r^2 dr$$
$$\int_0^\infty \Big(\tau_0\big(\rho(r), \frac{d\rho(r)}{dr}, \dots\big) + e_x\big(\rho(r), \frac{d\rho(r)}{dr}, \dots\big) \Big)\, 4\pi r^2 dr - \lambda \int_0^\infty \rho(r)\, 4\pi r^2 dr$$

Minimize

More slang: LDA

gradient corrections

Works quite well

Z	$-E_{HF}$ (2Ry)	$-E_{TFDW}$ (2Ry)	error (%)	$-E_{0.024}$ (2Ry)	error (%)
Ne(10)	128.6	140	8.8	129.56	0.78
Xe (54)	7232	7559	4.5	7253	0.01
U (92)	25664	26618	3.7	25656	0.03
(120)	48203	49838	3.4	48191	0.02

The “original sin of DFT”

0.014..* $\dfrac{(\nabla\rho(\boldsymbol{r}))^2}{\rho(\boldsymbol{r})}$ → 0.024* $\dfrac{(\nabla\rho(\boldsymbol{r}))^2}{\rho(\boldsymbol{r})}$

Works amazingly well !!!

Construction principle:
Satisfaction of exact constraints

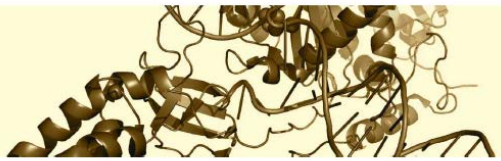
“The original sin of DFT” and “the character of DFT”

Is this “theoretical physics” ?

Slang:
“ab-initio” and “first principles”

DFT2018 poll

organized by:
marcel swart
f. matthias bickelhaupt
miquel duran



The annual popularity poll for density functionals:
edition 2018

contents

Primera Divisió 2019

B2PLYP, B3LYP, B3LYP-D, B97-D, CAM-B3LYP, DSD-PBEP86, HSE, LDA, M06, M06-2X, M06-L, PBE, PBE-D, PBE0 (PBE1PBE), PW91, revPBE, SCAN, TPSSh, wB97X-D, wB97X-V

Segona Divisió 2019

B3PW91, B97M-V, BEEF-vdW, BHandH, BLYP, BP86, DSD-BLYP, LC-PBE, LC-wPBE, OLYP, optB88-vdW, PBEsol, PW6B95, PWPB95-D3, revTPSS, revTPSS-D, RPA, RPBE, S12g, SAOP, SSB-D, wB97M-V

Suggestions

PBEsol, BEEF-vdW, 8 additional slots

Send message to marcel.swart@udg.edu for additional suggestions

“The character of DFT”…

… as formulated by Hardy Gross

The functional $E_{xc}[\rho]$ is <u>universal:</u>

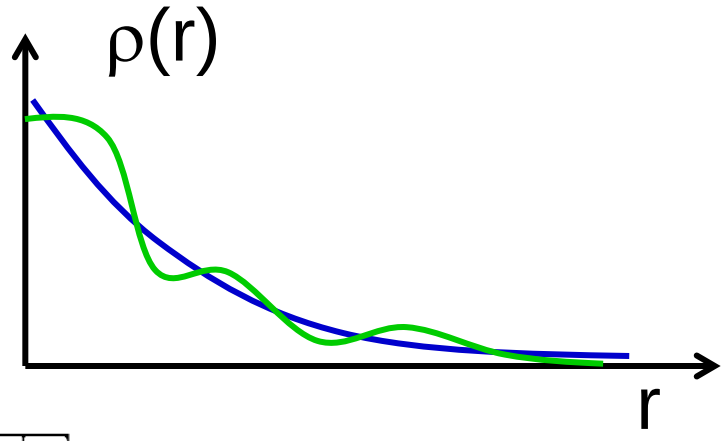
Curse or blessing?

Only **<u>ONE</u>** functional needs to be approximated.

Functional can be systematically improved, i.e. results will improve - on average - for all systems.
Systematic improvement for a single given system is not possible.

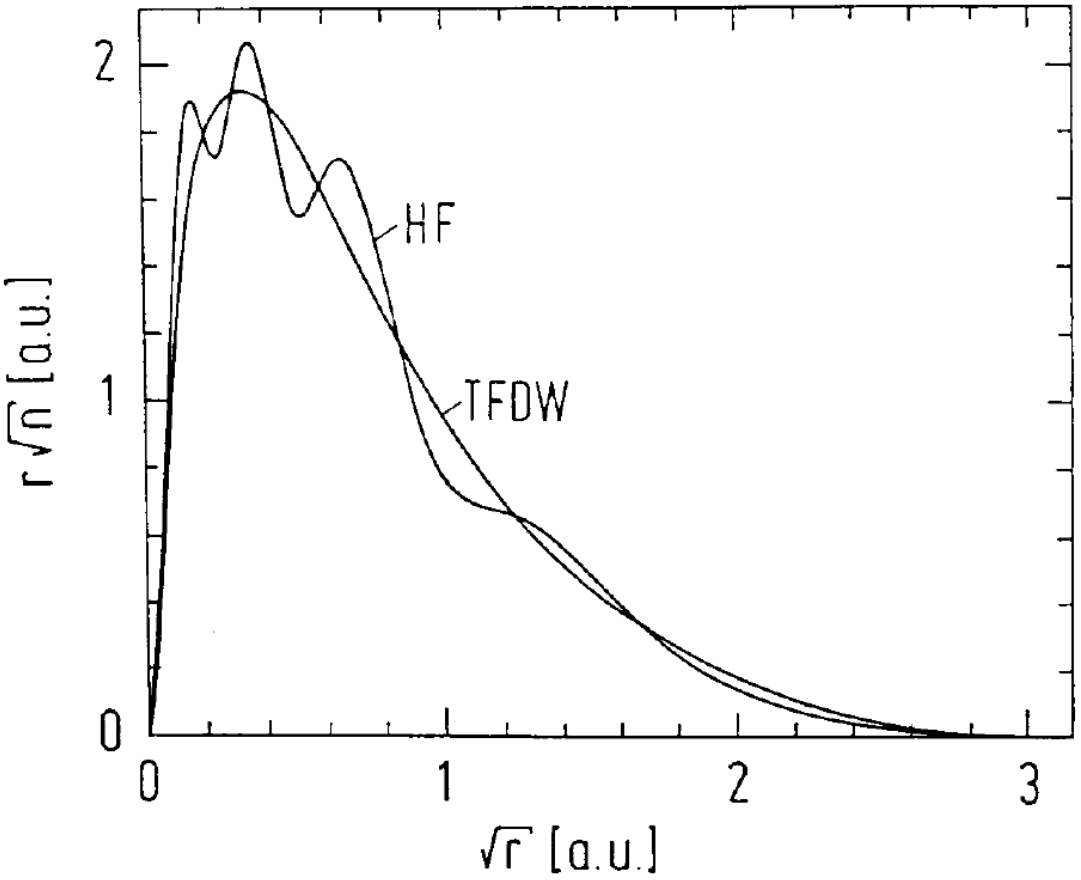
TFDW vs. shell structure

Recall QM 101's hydrogen atom and the shell structure



Quiz: Which one is better, blue or green ?

Answer:

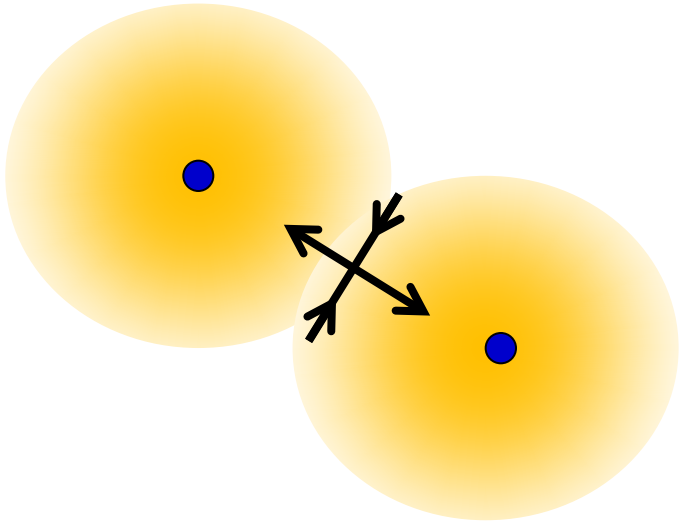


The important point: This type of DFT does not yield shells!

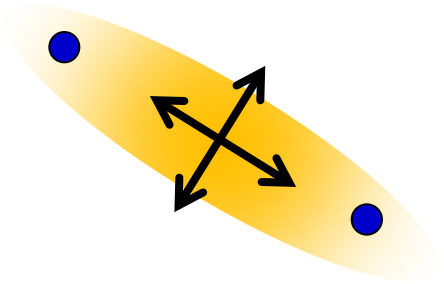
My own guess: develop density-matrix theory $E=E[\rho(x,y)]$, but…

A side remark: Electron density vs. valence-electron density

Electron density



Valence electron density



Keep your eyes and ears open during the summer school ;-)

Kohn-Sham equations

"Parametrize" density in terms of (fictitious) **KS orbitals**:

$$\rho(\boldsymbol{r}) = \sum_{occ.} \left|\phi_\nu(\boldsymbol{r})\right|^2$$

Define "ad-hoc"

$$\tau_{KS}(\boldsymbol{r}) = \sum_{occ.} \frac{\hbar^2}{2m_e} \left|\boldsymbol{\nabla}\phi_\nu(\boldsymbol{r})\right|^2$$

Evaluate $\dfrac{\delta E}{\delta\rho(\boldsymbol{r}')}\dfrac{\delta\rho(\boldsymbol{r}')}{\delta\phi_\nu(\boldsymbol{r})}$ Slang: xc potential $v_{xc} = \dfrac{\delta E_{xc}}{\delta\rho}$

$$\begin{aligned}\epsilon_\nu\,\phi_\nu(\boldsymbol{r}) &= \left(-\frac{\hbar^2}{2m}\Delta + v_{\text{external}}(\boldsymbol{r}) + v_{\text{Hartree}}(\boldsymbol{r}) + v_{xc}\big(\rho(\boldsymbol{r}), \boldsymbol{\nabla}\rho(\boldsymbol{r}), \ldots\big)\right)\phi_\nu(\boldsymbol{r}) \\ &= \hat{h}_{KS}\big(\rho(\boldsymbol{r}), \boldsymbol{\nabla}\rho(\boldsymbol{r}), \ldots\big)\,\phi_\nu(\boldsymbol{r})\end{aligned}$$

- Shell structure issue: settled almost automatically!
- Is there any physics in ϕ_ν and ε_ν ??!!???...

Keep your eyes and ears open during the summer school ;-)

Slang: "interacting" and "KS" Green's functions & response functions

$$\{\epsilon_\nu, \phi_\nu(\boldsymbol{r})\} \;\Leftrightarrow\; iG_{KS}(\boldsymbol{r},\boldsymbol{r}';E) = \sum_\nu \frac{\phi_\nu(\boldsymbol{r})\phi_\nu^\star(\boldsymbol{r}')}{E-\varepsilon_\nu - i0+}$$

$$\Leftrightarrow\; G_{KS}(\boldsymbol{r},\boldsymbol{r}';t) = \theta(t)\sum_\nu \phi_\nu(\boldsymbol{r})\phi_\nu^\star(\boldsymbol{r}')e^{-i\epsilon_\nu t/\hbar}$$

$$G(\boldsymbol{r},\boldsymbol{r}';t) = \langle \Psi_{\text{exact}}|\hat{\psi}^+_{\boldsymbol{r}t}\hat{\psi}_{\boldsymbol{r}'0}|\Psi_{\text{exact}}\rangle$$

$$\rho(\boldsymbol{r},\boldsymbol{r}') = G(\boldsymbol{r},\boldsymbol{r}';t=0)$$

less "complex"

$$\rho(\boldsymbol{r},\boldsymbol{r}') = G(\boldsymbol{r},\boldsymbol{r}';t=0)$$

$$\rho(\boldsymbol{r}) = \rho(\boldsymbol{r},\boldsymbol{r}')$$

HK: no loss of "information"

“Functional Theories”

Exact

Many-body perturbation theory

DFT

Correlated wavefunctions

Density-matrix-based theories

$G(\boldsymbol{r}, \boldsymbol{r}'; t)$ $\rho(\boldsymbol{r}, \boldsymbol{r}')$ $\rho(\boldsymbol{r})$

Good functionals:

rather easy, e.g. GW approximation

very, very difficult

$$\Sigma(\boldsymbol{k}, E) = G(\boldsymbol{k} - q, E - E')\, W(q, E')$$

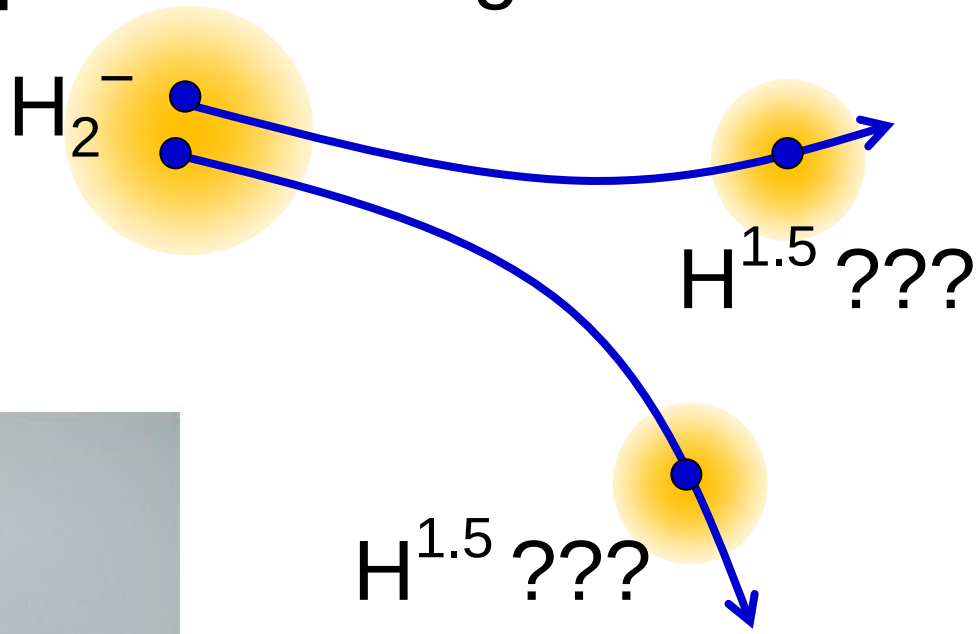
Numerics:

Very, very hard

rather easy

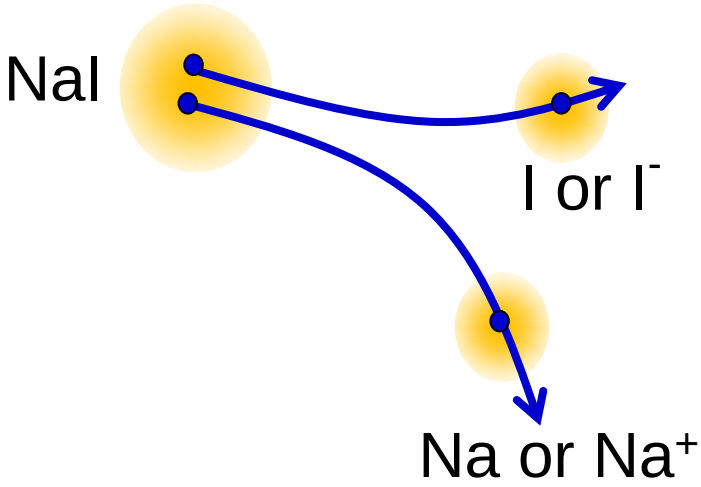
DFT is “damned useful” ⇔ Nobel Prize 1998 for W. Kohn

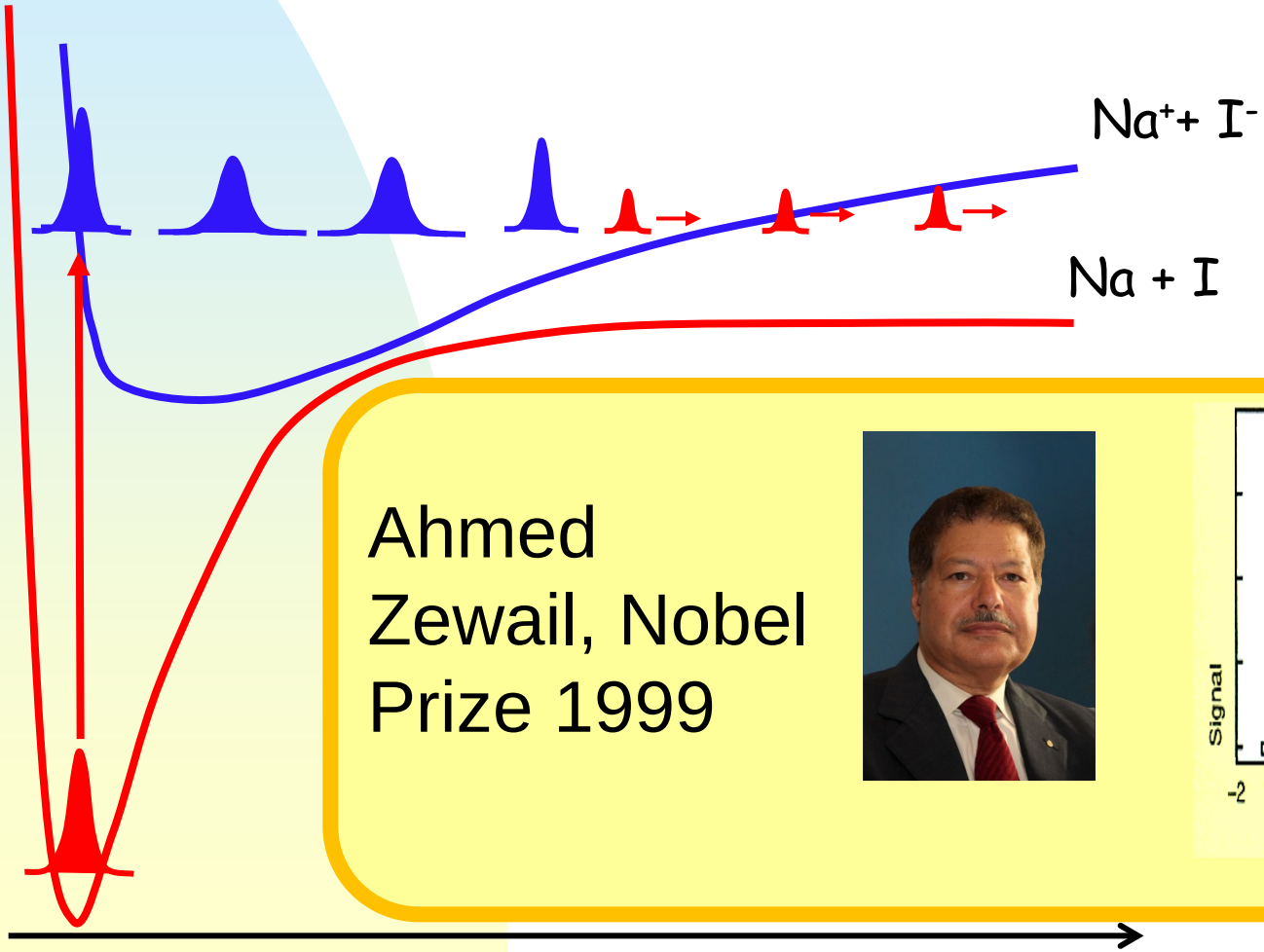
.. but there are conceptual challenges



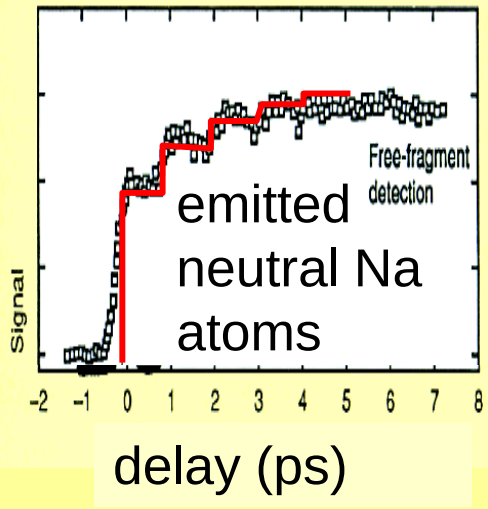
Ask yourself:
What ***should*** be DFT’s answer ?

A conceptual challenge: What should be DFT's answer ?





Ahmed Zewail, Nobel Prize 1999



A big step towards answers: Hardy Gross' theory of nonadiabatic and quantum nuclear effects

N.I. Gidopoulos, E.K.U. Gross,
Phil. Trans. R. Soc. 372, 20130059 (2014)

Theorem: The exact wave function

$$\hat{H}\Psi(\{\boldsymbol{r}_j\},\{\boldsymbol{R}_I\}) \;=\; E\,\Psi(\{\boldsymbol{r}_j\},\{\boldsymbol{R}_I\})$$

can be factorized in a unique way into

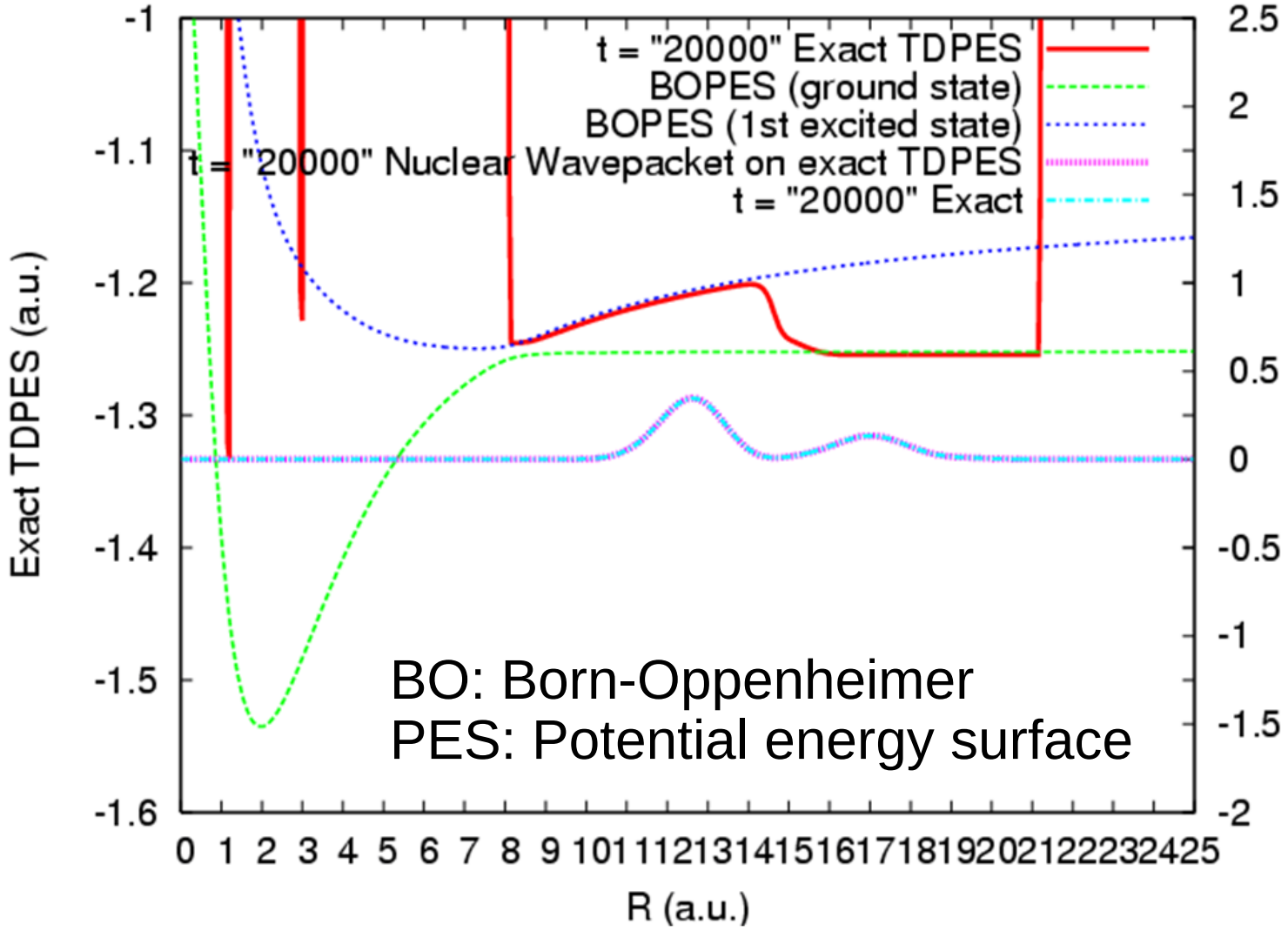
$$\Psi(\{\boldsymbol{r}_j\},\{\boldsymbol{R}_I\}) \;=\; \Phi_{\{\boldsymbol{R}_I\}}(\{\boldsymbol{r}_j\})\cdot\chi(\{\boldsymbol{R}_I\})$$

with

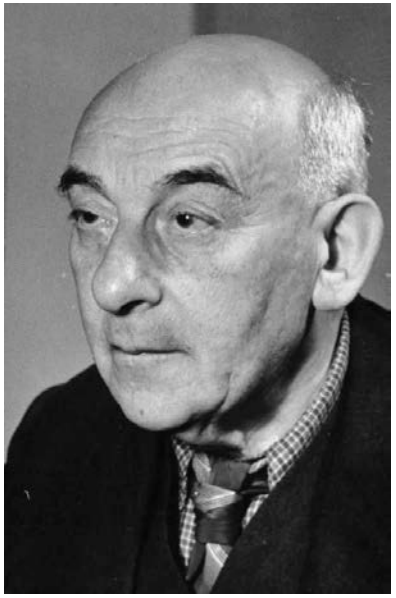
$$\int\cdots\int \left|\Phi_{\{\boldsymbol{R}_I\}}(\{\boldsymbol{r}_j\})\right|^2 d\boldsymbol{r}_1\ldots d\boldsymbol{r}_n \;=\; 1 \;\;\forall\{\boldsymbol{R}_I\}$$

Equations of motion have been derived.

Hardy Gross' theory of nonadiabatic and quantum nuclear effects



Progress in science: 4th paradigm, data science, AI,…



Victor Klemperer (9 October 1881 – 11 February 1960) was a Romance languages scholar who also became known as a diarist. His journals, published in Germany in 1995, detailed his life under the German Empire, the Weimar Republic, the Third Reich, and the German Democratic Republic. Those covering the period of the Third Reich have since become standard sources and have been extensively quoted by Saul Friedländer,[1] Michael Burleigh,[2] Richard J. Evans,[3] and Max Hastings.[4] (from Wikipedia)

Sprache, die für dich dichtet und denkt…

(Language, that thinks for you...)

Evolution, Ferns, Reptiles, Viruses, Entropie, Adiabaticity, Mean-field vs. Correlations, …

Thank you for your attention!
Enjoy the Summer School, enjoy DFT!

Density Functional Theory

- Schrödinger Equation
  - Fundamental challenges
  - Mean-field theory
  - Nearsightedness & Exponential Wall Problem
  - Dephasing

- Density Functional Theory and Alternatives
  - Hohenberg-Kohn Theorem(s)
  - Pre-HK: gradient expansion, TFDW,…
  - Kohn-Sham equations:
  - Post-HK: ”functional” theories
  - Today’s challenges and developments