

Ground-state DFT

Outline

1st part

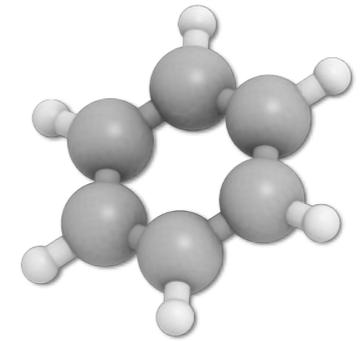
- Basics of DFT
 - the Hohenberg-Kohn theorem
 - the Kohn-Sham equations
 - xc-functionals

2nd part

- Basics of TDDFT
 - the Runge-Gross theorem
 - td xc-functionals
 - applications

The Many-body Schrödinger equation

$$\hat{H}\Psi(\underline{r}, \underline{R}) = E\hat{H}\Psi(\underline{r}, \underline{R})$$



Hamiltonian (atomic units) for a systems of N_e electrons with coordinates $(\vec{r}_1, \dots, \vec{r}_{N_e}) = \underline{r}$ and N_n nuclei with coordinates $(\vec{R}_1, \dots, \vec{R}_{N_n}) = \underline{R}$ masses $\bar{M}_1, \dots, M_{N_n}$ and charges Z_1, \dots, Z_{N_n}

$$\hat{H} = \hat{T}_n(\underline{R}) + \hat{W}_{nn}(\underline{R}) + \hat{T}_e(\underline{r}) + \hat{W}_{ee}(\underline{r}) + \hat{U}_{en}(\underline{R}, \underline{r})$$

$$\hat{T}_e = \sum_i^{N_e} -\frac{\nabla_i^2}{2m_i} \quad \hat{W}_{ee} = \frac{1}{2} \sum_{\substack{j,k \\ j \neq k}}^{N_e} \frac{1}{|r_j - r_k|}$$

$$\hat{T}_n = \sum_\nu^{N_n} -\frac{\nabla_\nu^2}{2M_\nu} \quad \hat{W}_{nn} = \frac{1}{2} \sum_{\substack{\mu,\nu \\ \mu \neq \nu}}^{N_n} \frac{Z_\mu Z_\nu}{|R_\mu - R_\nu|}$$

$$\hat{U}_{en} = \sum_{j=1}^{N_e} \sum_{\nu=1}^{N_n} -\frac{Z_\nu}{|r_j - R_\nu|}$$

Why don't we just solve the many-body SE?

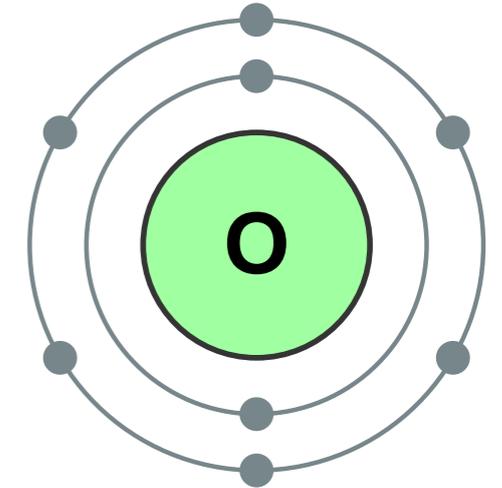


The underlying physical laws necessary for the mathematical theory of a large part of physics and the whole of chemistry are thus completely known, and **the difficulty is only that the exact application of these laws leads to equations much too complicated to be soluble.** It therefore becomes desirable that approximate practical methods of applying quantum mechanics should be developed, which can lead to an explanation of the main features of complex atomic systems without too much computation.

P.A.M. Dirac, Proceedings of the Royal Society of London. Series A 123, 792 (1929)

Why don't we just solve the many-body SE?

Example: Oxygen atom (8 electrons)



$\Psi(\vec{r}_1, \dots, \vec{r}_8)$ depends on 24 (3x8) coordinates

Storage rough estimate

10 entries per coordinates:



10^{24} entries

1 byte per entry:
(single precision float is 4 bytes - 32 bit)



10^{24} bytes

10^{10} bytes per DVD:

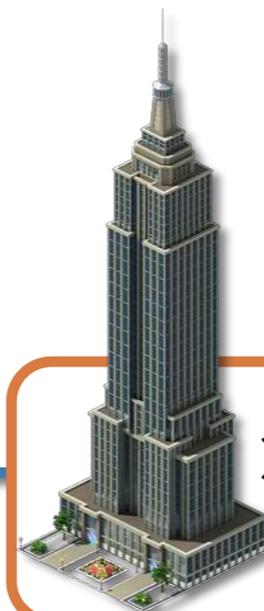


10^{14} DVDs

10 g per DVD:



10^9 tons



$\times 250$

estimated mass of the empire state building
tons
 4×10^6 tons



Ab-initio solution of the many-body SE

Wavefunction methods

- Quantum Montecarlo
- Configuration interaction family (Full CI, CI-singles and doubles, CASSCF, Hartree Fock, etc.)
- Tensor networks

Functional theories

Total energy expressed as a functional of a quantity simpler than the total wavefunction

Ab-initio solution of the many-body SE

Functional theories

MBPT

$$G(\mathbf{r}, \mathbf{r}', t - t')$$

RDMFT

$$\gamma(\mathbf{r}, \mathbf{r}') = G(\mathbf{r}, \mathbf{r}', 0^+)$$

DFT

$$\rho(\mathbf{r}) = \gamma(\mathbf{r}, \mathbf{r})$$

Functional

$$\Sigma_{xc}[G]$$

$$\Phi_{xc}[G]$$

$$E_{xc}[\gamma]$$

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

$$v_{xc}[\rho]$$

Approx.

Easy
e.g. GW

hard

very hard

Comp.

heavy

moderate

light

Ab-initio solution of the many-body SE

Functional theories

MBPT

$$G(\mathbf{r}, \mathbf{r}', t - t')$$

RDMFT

$$\gamma(\mathbf{r}, \mathbf{r}') = G(\mathbf{r}, \mathbf{r}', 0^+)$$

DFT

$$\rho(\mathbf{r}) = \gamma(\mathbf{r}, \mathbf{r})$$

Each of these functional theories comes in two versions:

- a ground-state (equilibrium) version
- a time-depedent (non-equilibrium) version

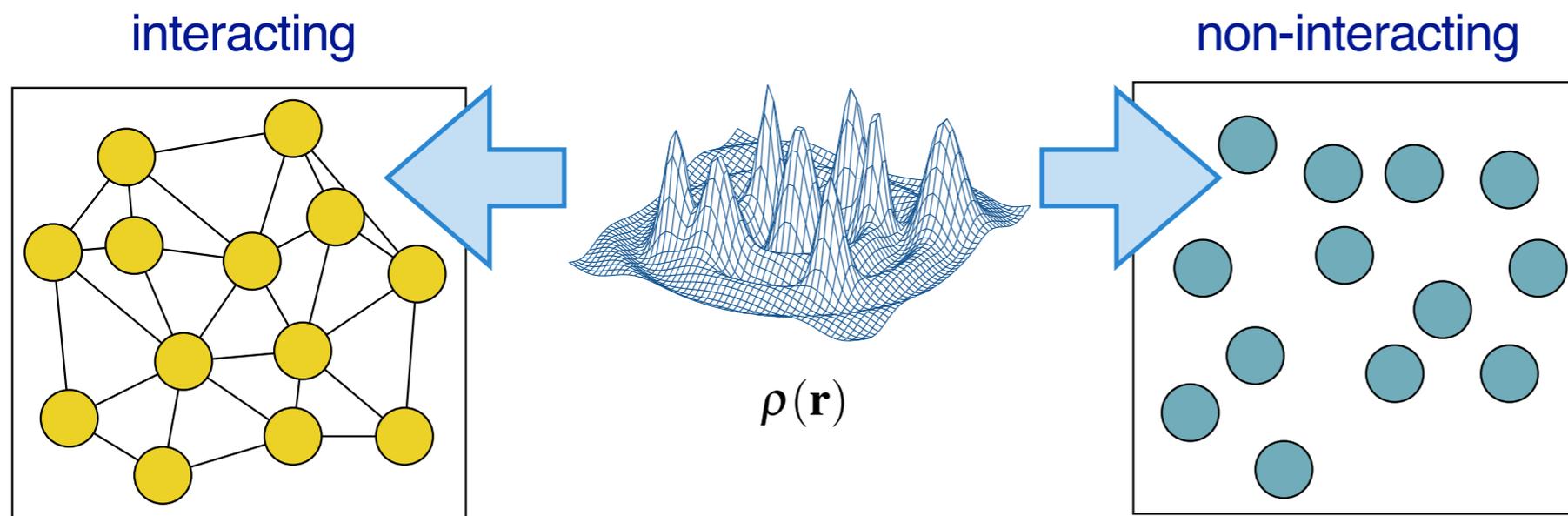
The foundations of Density Functional Theory (DFT)

Every observable quantity of a quantum system can be calculated from the density of the system alone

Hohenberg-Kohn theorem (1964)



Walter Kohn
Nobel prize in
chemistry (1998)



The density of particles interacting with each other can be calculated as the density of an auxiliary system of non interacting particles

Kohn-Sham theorem (1965)

DFT is a theory for the electrons. We consider the nuclei fixed.

The electronic many-body problem

The Schrödinger equation

$$\hat{H}\Psi_0(\mathbf{r}_1, \dots, \mathbf{r}_N) = E_0\Psi_0(\mathbf{r}_1, \dots, \mathbf{r}_N)$$

The Hamiltonian

$$\hat{H} = \hat{T} + \hat{V} + \hat{W}$$

kinetic operator

$$\hat{T} = \sum_{j=1}^N -\frac{\nabla_j^2}{2}$$

external potential

$$\hat{V} = \sum_{j=1}^N v(\mathbf{r}_j)$$

system
dependence

electron-electron interaction

$$\hat{W} = \frac{1}{2} \sum_{j \neq k}^N w(|\mathbf{r}_j - \mathbf{r}_k|)$$

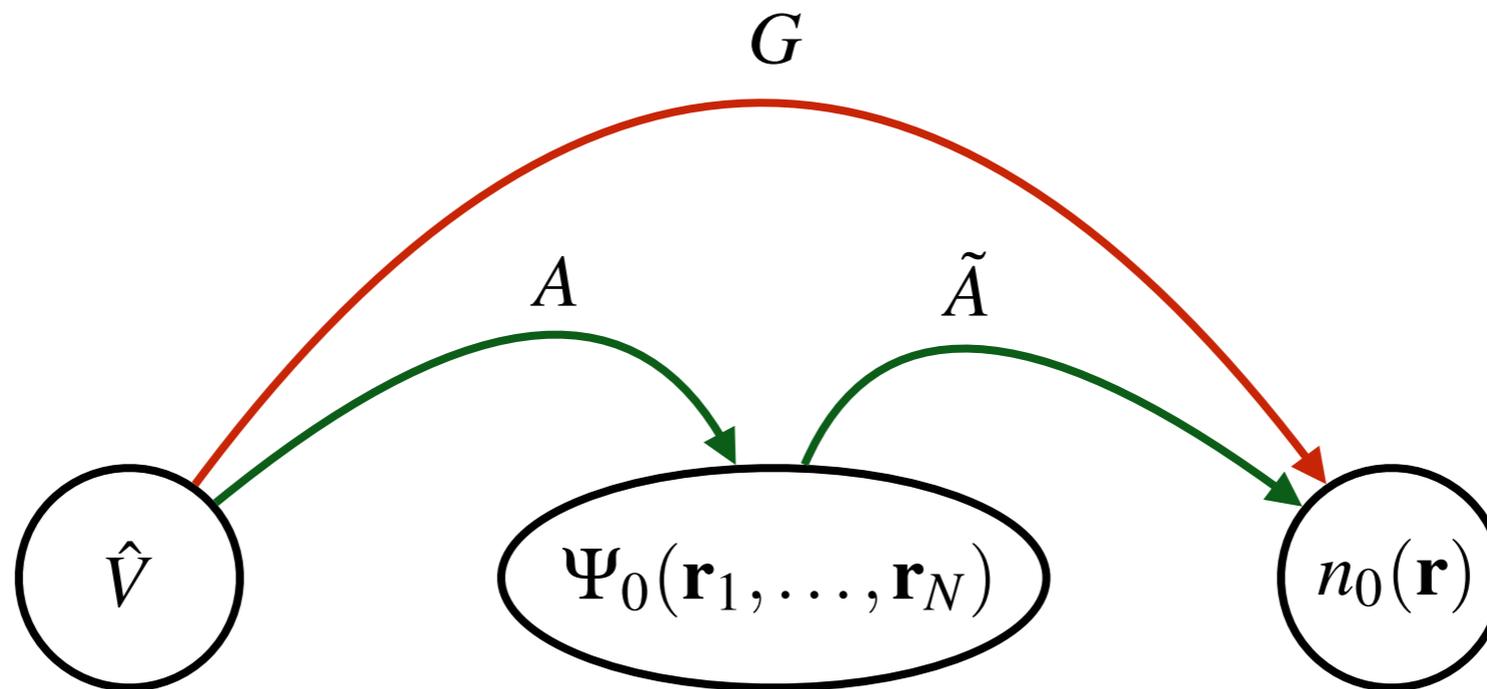
The density is obtained by integrating the wf
(implicit summation over spin)

$$n_0(\mathbf{r}) = N \int d\mathbf{r}_2 \dots \int d\mathbf{r}_N \Psi_0(\mathbf{r}, \mathbf{r}_2, \dots, \mathbf{r}_N)$$

Change of
notation

$$n(\mathbf{r}) = \rho(\mathbf{r})$$

Are the ground-state densities of different potentials always different?



Hohenberg-Kohn theorem. In a finite, interacting N-electron system with a given particle–particle interaction there exists a one-to-one correspondence between the external potential $v(r)$ and the ground-state density $n(r)$. In other words, the external potential is a unique functional of the ground-state density, $v[n](r)$, up to an arbitrary additive constant.

P. Hohenberg and W. Kohn Physical Review 136 B864 (1964)

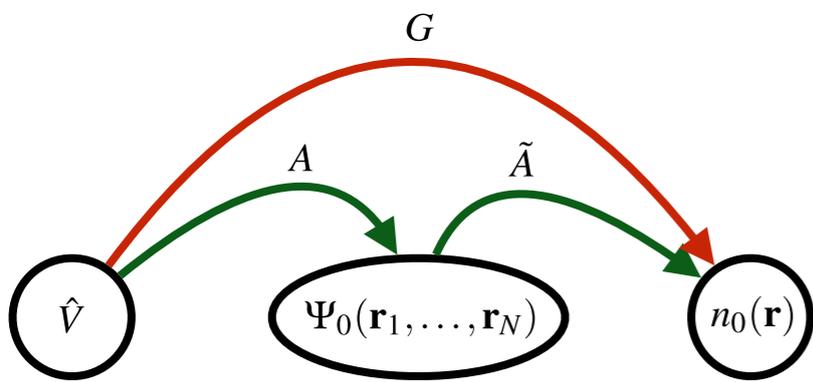
... or equivalently

$$G : \hat{V} \rightarrow n_0(\mathbf{r}) \text{ is invertible}$$

Proof

A and \tilde{A} are invertible

$$\hat{H}\Psi_0 = E_0\Psi_0$$
$$\hat{H} = \hat{T} + \hat{V} + \hat{W}$$



Step I: invertibility of A

Solve the Schrödinger equation for the external potential \hat{V}

$$\hat{V} = \frac{(E_0 - \hat{T} - \hat{W})\Psi_0}{\Psi_0}$$

$$\hat{V} = \frac{(\hat{T}\Psi_0)}{\Psi_0} - \hat{W} - \text{constant}$$

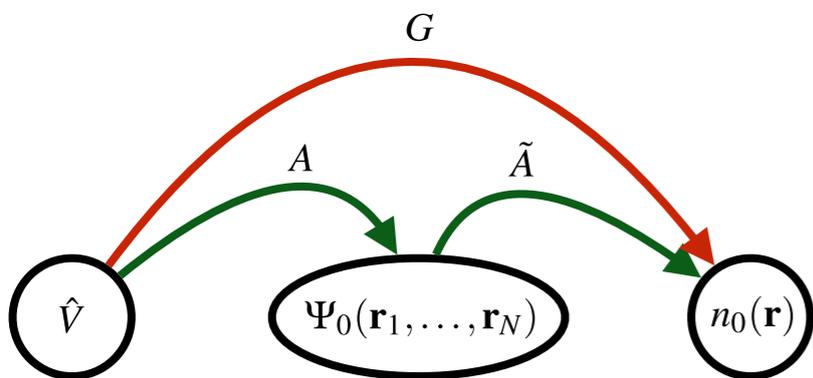
This is clearly the inverse map.

Therefore the relationship between external potential and the ground-state wavefunction is unique (up to a constant)

Proof

A and \tilde{A} are invertible

$$\hat{H}\Psi_0 = E_0\Psi_0$$
$$\hat{H} = \hat{T} + \hat{V} + \hat{W}$$



Step II: invertibility of \tilde{A}

Given two non-degenerate ground states such that:

$$\hat{H}\Psi_0 = E_0\Psi_0$$

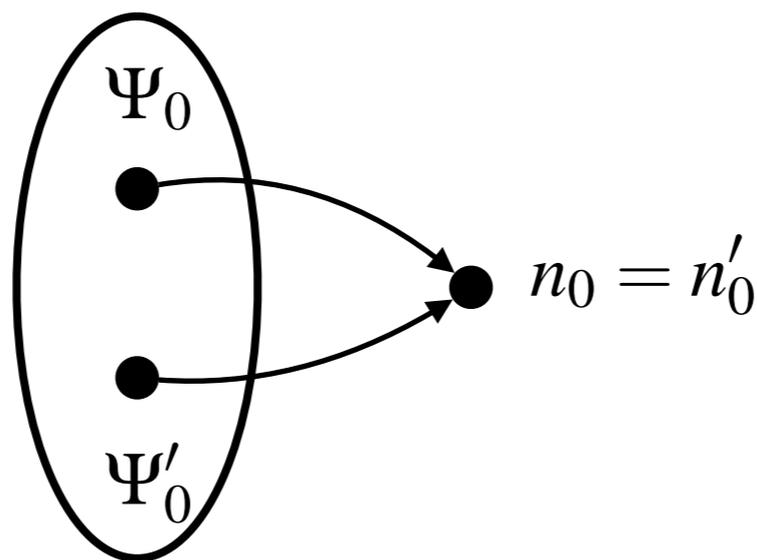
$$\hat{H} = \hat{T} + \hat{V} + \hat{W}$$

$$\hat{H}'\Psi'_0 = E'_0\Psi'_0$$

$$\hat{H}' = \hat{T} + \hat{V}' + \hat{W}$$

from step I

we want to show that

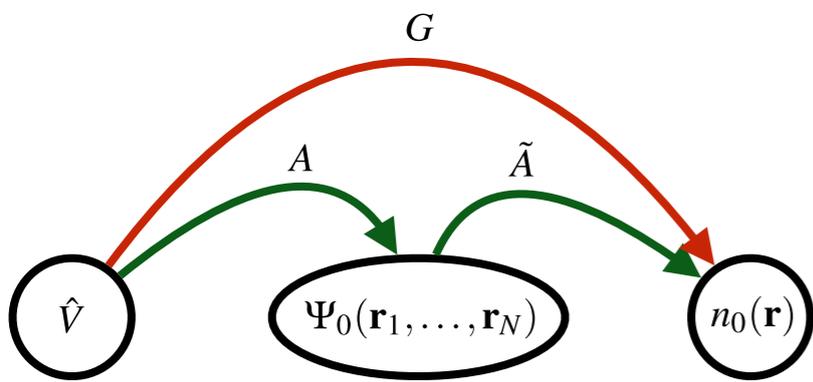


cannot happen

Proof

A and \tilde{A} are invertible

$$\hat{H}\Psi_0 = E_0\Psi_0$$
$$\hat{H} = \hat{T} + \hat{V} + \hat{W}$$



Step II: invertibility of \tilde{A}

Use Rayleigh-Ritz variational principle:

$$(1) \quad E'_0 < \langle \Psi_0 | \hat{H}' | \Psi_0 \rangle = \langle \Psi_0 | \hat{H} + \hat{V}' - \hat{V} | \Psi_0 \rangle = E_0 + \int d\mathbf{r} [v'(\mathbf{r}) - v(\mathbf{r})] n_0(\mathbf{r})$$

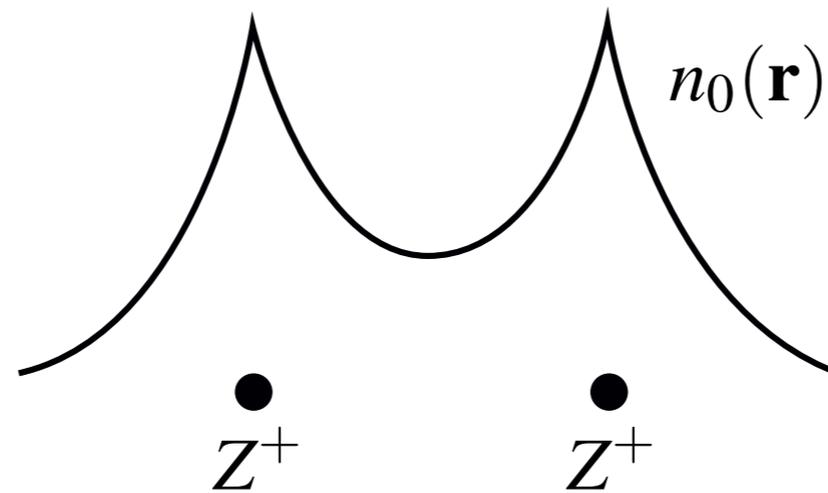
$$(2) \quad E_0 < \langle \Psi'_0 | \hat{H} | \Psi'_0 \rangle = \langle \Psi'_0 | \hat{H}' + \hat{V} - \hat{V}' | \Psi'_0 \rangle = E'_0 + \int d\mathbf{r} [v(\mathbf{r}) - v(\mathbf{r})'] n'_0(\mathbf{r})$$

Reductio and absurdum:

If $n_0 = n'_0$ and sum (1) and (2) I get that: $E_0 + E'_0 < E_0 + E'_0$

q.e.d.

Example



spherical average
of the density
around the cusp

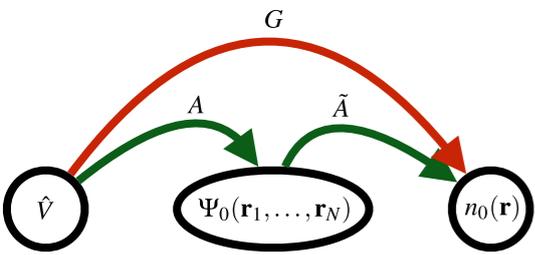
Kato's theorem

$$Z_i = \frac{1}{2n(\mathbf{r})} \left. \frac{\partial \bar{n}(\mathbf{r})}{\partial r} \right|_{r=R_i}$$

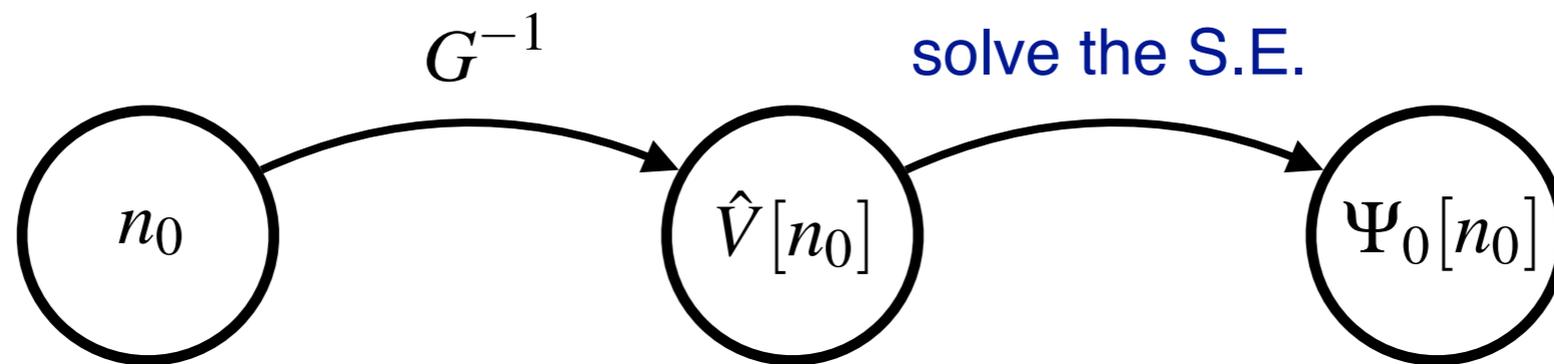
The density **uniquely** defines the potential

- the position of the cusps determine the location of the nuclei
- the magnitude and the slope of the density determine the nuclear charges
- the integral over the density gives the total number of electrons

Consequences of the HK theorem I



Every quantum mechanical observable is completely determined by the ground state density. In other words it is a functional of the gs density.



square bracket notation indicates functional dependence

Given an observable expressed by an Hermitian operator \hat{O} :

$$O[n_0] = \langle \Psi_0[n_0] | \hat{O} | \Psi_0[n_0] \rangle$$

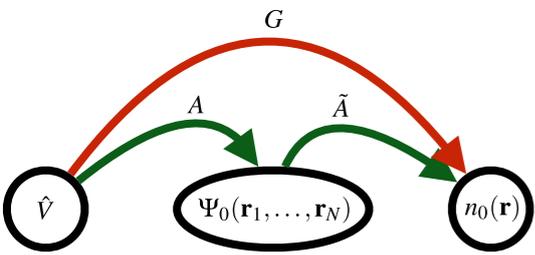
also excited states!!

The Hamiltonian itself is a functional of the gs density $\hat{H}[n_0]$



All the ground and excited state properties of an N-electron system are entirely determined by the ground state density

Consequences of the HK theorem II

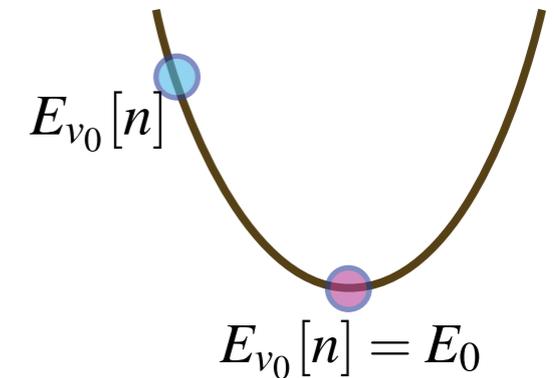


For a given external potential we can express the total energy functional as

$$E_{v_0}[n] = \langle \Psi[n] | \hat{T} + \hat{V}_0 + \hat{W} | \Psi[n] \rangle$$

$$E_{v_0}[n] > E_0 \quad \text{for } n \neq n_0$$

$$E_{v_0}[n] = E_0 \quad \text{for } n = n_0$$

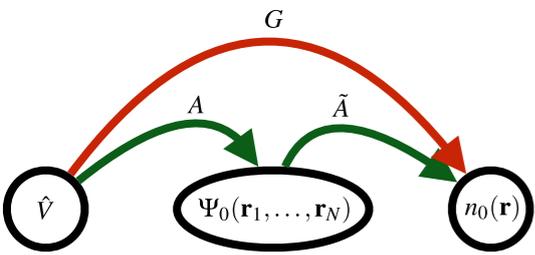


The exact ground state density can be found from the Euler equation

$$\frac{\delta}{\delta n(\mathbf{r})} \left[E_{v_0}[n] - \mu \int d\mathbf{r}' n(\mathbf{r}') \right] = 0$$

Lagrange multiplier
to ensure the correct
total number
of electrons

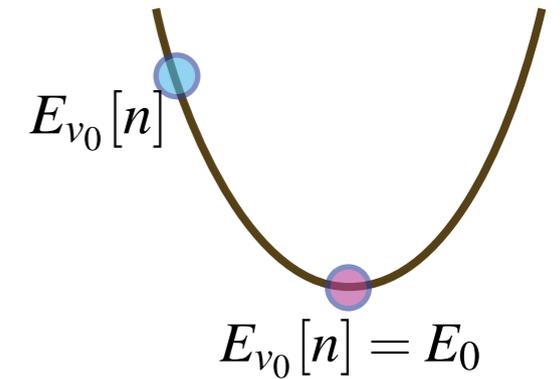
Consequences of the HK theorem II



the total energy functional

$$E_{v_0}[n] = \langle \Psi[n] | \hat{T} + \hat{V}_0 + \hat{W} | \Psi[n] \rangle$$

$$E_{v_0}[n] = F[n] + \int d\mathbf{r} n(\mathbf{r}) v_0(\mathbf{r})$$



universal
(same for any system)

$$F[n] = \langle \Psi[n] | \hat{T} + \hat{W} | \Psi[n] \rangle = \hat{T}[n] + \hat{W}[n]$$

the Euler equation

$$\frac{\delta}{\delta n(\mathbf{r})} \left[E_{v_0}[n] - \mu \int d\mathbf{r}' n(\mathbf{r}') \right] = 0$$

$$\frac{\delta F[n]}{\delta n(\mathbf{r})} + v_0(\mathbf{r}) = \mu$$

The HK theorem in summary

1. One to one mapping between density and external potential

$$v(\mathbf{r}) \longleftrightarrow n_0(\mathbf{r})$$

2. Any observable is a density functional

$$O[n_0] = \langle \Psi_0[n_0] | \hat{O} | \Psi_0[n_0] \rangle$$

3. Total energy expressed as a density functional

$$E_{v_0}[n] = F[n] + \int d\mathbf{r} n(\mathbf{r}) v_0(\mathbf{r})$$

$F[n]$ is universal. In practice needs to be approximated

4. Variational principle

$$\frac{\delta}{\delta n(\mathbf{r})} \left[E_{v_0}[n] - \mu \int d\mathbf{r}' n(\mathbf{r}') \right] = 0 \quad \text{or} \quad \frac{\delta F[n]}{\delta n(\mathbf{r})} + v_0(\mathbf{r}) = \mu$$

The HK theorem imply a complete paradigm shift of the many-electron problem where the wf is replaced with the ground state **density** as **fundamental** quantity to calculate

Expansion of $F[n]$ in powers of e^2

$$F[n] = F^{(0)}[n] + e^2 F^{(1)}[n] + e^4 F^{(1)}[n] + \dots$$

kinetic energy of non-interacting electrons

$$F^{(0)}[n] = T_S[n]$$

Hartree + exchange energies

$$e^2 F^{(1)}[n] = \frac{e^2}{2} \iint d\mathbf{r} d\mathbf{r}' \frac{n(\mathbf{r})n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} + E_x[n]$$

Correlation energy

$$\sum_{i=2}^{\infty} (e^2)^i F^{(i)}[n] = E_c[n]$$

$$F[n] = T_S[n] + \frac{e^2}{2} \iint d\mathbf{r} d\mathbf{r}' \frac{n(\mathbf{r})n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} + E_x[n] + E_c[n]$$

Towards the exact functional

$$F[n] = T_S[n] + \frac{e^2}{2} \iint d\mathbf{r}d\mathbf{r}' \frac{n(\mathbf{r})n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} + E_x[n] + E_c[n]$$

1st generation DFT

2nd generation DFT

3rd generation DFT

approximated: LDA/GGA
e.g. Thomas-Fermi

exact: Kohn-Sham (see later)

exact: Kohn-Sham

T_S

$$T_S[n] = \int d\mathbf{r} \left(an^{5/3} + b \frac{(\nabla n)^2}{n} + \dots \right)$$

$$T_S^{exact}[n] = \sum_j \int d\mathbf{r} \varphi^*[n](\mathbf{r}) \left(-\frac{\nabla^2}{2} \right) \varphi[n](\mathbf{r})$$

$$T_S^{exact}[n] = \sum_j \int d\mathbf{r} \varphi^*[n](\mathbf{r}) \left(-\frac{\nabla^2}{2} \right) \varphi[n](\mathbf{r})$$

E_x

approximated: LDA/GGA

approximated: LDA/GGA

exact: orbital functional

$$E_x^{exact}[n] = \sum_{j,k} \int d\mathbf{r}d\mathbf{r}' \frac{\varphi_k^*[n](\mathbf{r}') \varphi_k[n](\mathbf{r}) \varphi_j^*[n](\mathbf{r}) \varphi_j[n](\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|}$$

E_c

approximated: LDA/GGA

approximated: LDA/GGA

approximated: orbital functional

V-representability

By construction, the HK theorem is defined for all those densities $n(r)$ that are ground-state density of some potential. These functions are called V-representable

are all densities $n(r)$ V-representable?

V-representability theorem

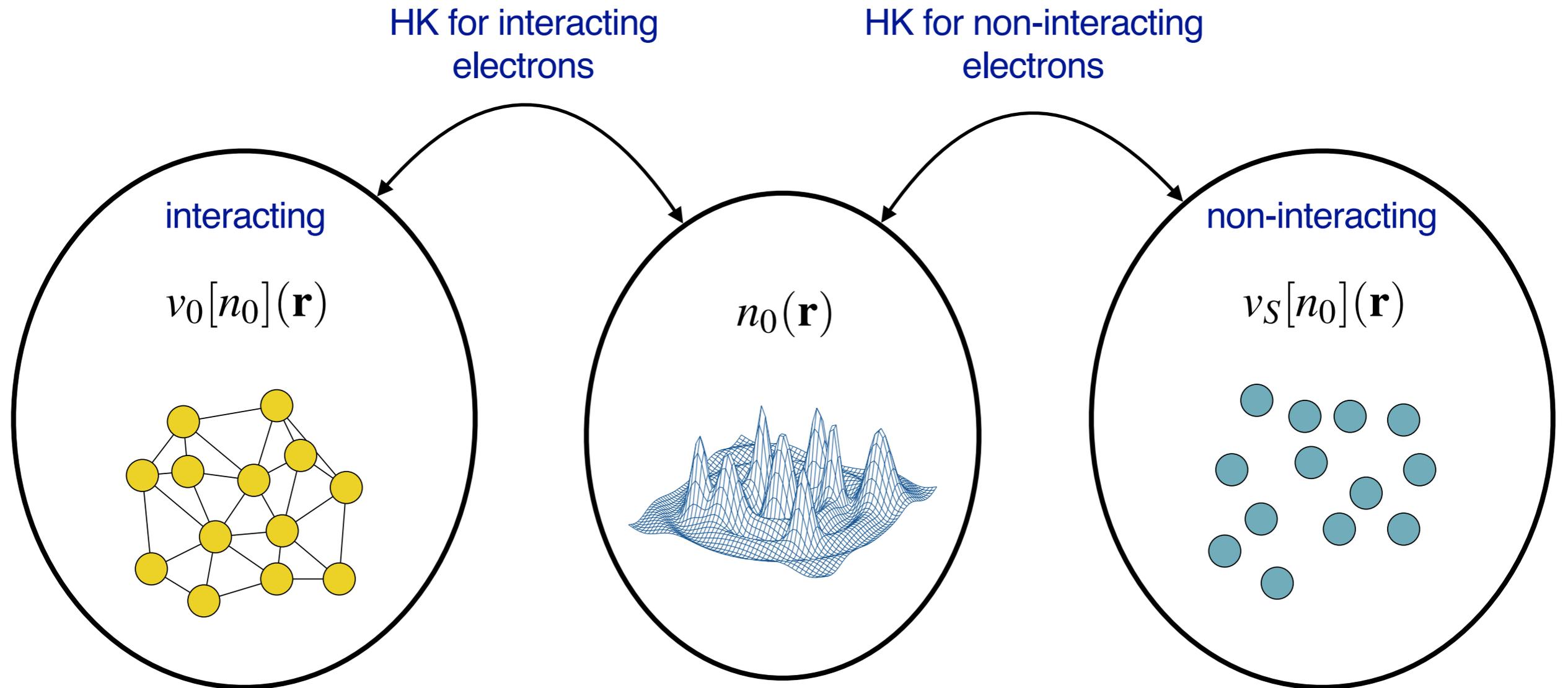
On a lattice (finite or infinite), any normalizable positive function $n(r)$, that is compatible with the Pauli principle, is (both interacting and non-interacting) ensemble-V-representable

J. T. Chayes, et al J. Stat. Phys., 38, 497 (1985)

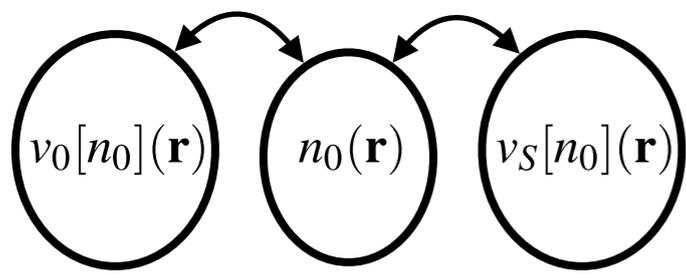
In other words: for any given $n(r)$ (normalizable, positive and compatible with Pauli principle), there exist a potential, $v_{\text{exp}}[n](r)$, yielding $n(r)$ as interacting groundstate density, and there exist another potential, $v_{\text{s}}[n](r)$, yielding $n(r)$ as non-interacting ground state density.

In the worst case, the potential has degenerate ground states such that the given $n(r)$ is representable as a linear combination of the degenerate ground-state densities (ensemble-V-representable).

The Kohn-Sham equations



The Kohn-Sham equations



the Hamiltonian

non-interacting system

$$\hat{H}' = \hat{T} + \hat{V}_S = \sum_{j=1}^N \left(-\frac{\nabla_j^2}{2} + v_S(\mathbf{r}_j) \right)$$

the energy functional

$$E_{v_S}[n] = T_S[n] + \int d\mathbf{r} n(\mathbf{r}) v_S(\mathbf{r})$$

the variational principle

$$\frac{\delta E_{v_S}[n]}{\delta n(\mathbf{r})} = \frac{\delta T_S[n]}{\delta n(\mathbf{r})} + v_S(\mathbf{r}) = \mu$$

the wavefunction is a SD

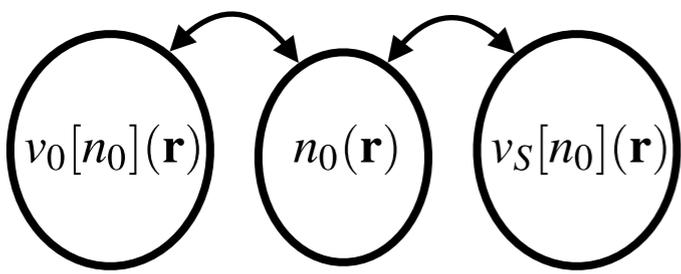
$$\Psi_S(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N) = \frac{1}{\sqrt{N!}} \begin{vmatrix} \varphi_1(\mathbf{r}_1) & \varphi_2(\mathbf{r}_1) & \dots & \varphi_N(\mathbf{r}_1) \\ \varphi_1(\mathbf{r}_2) & \varphi_2(\mathbf{r}_2) & \dots & \varphi_N(\mathbf{r}_2) \\ \dots & \dots & \dots & \dots \\ \varphi_1(\mathbf{r}_N) & \varphi_2(\mathbf{r}_N) & \dots & \varphi_N(\mathbf{r}_N) \end{vmatrix}$$

the Schrödinger equation

$$\left(-\frac{\nabla^2}{2} + v_S(\mathbf{r}) \right) \varphi_j(\mathbf{r}) = \varepsilon_j \varphi_j(\mathbf{r})$$

the density

$$n_S(\mathbf{r}) = \sum_j^N |\varphi_j(\mathbf{r})|^2$$



The Kohn-Sham equations

$$\frac{\delta E_{v_S}[n]}{\delta n(\mathbf{r})} = \frac{\delta T_S[n]}{\delta n(\mathbf{r})} + v_S(\mathbf{r}) = \mu$$

interacting system

rewrite the total energy

$$\begin{aligned} E_{v_0}[n] &= F[n] + \int d\mathbf{r} n(\mathbf{r}) v_0(\mathbf{r}) \\ &= T_S[n] + \int d\mathbf{r} n(\mathbf{r}) v_0(\mathbf{r}) + \frac{1}{2} \iint d\mathbf{r} d\mathbf{r}' \frac{n(\mathbf{r})n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} + E_{xc}[n] \end{aligned}$$

$$E_H[n] = \frac{1}{2} \iint d\mathbf{r} d\mathbf{r}' \frac{n(\mathbf{r})n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|}$$

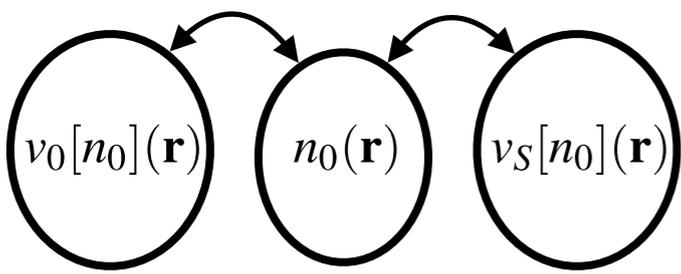
classical Coulomb energy

$$E_{xc}[n] = T[n] - T_S[n] + W[n] - \frac{1}{2} \iint d\mathbf{r} d\mathbf{r}' \frac{n(\mathbf{r})n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|}$$

exchange and correlation energy

together with the variational formulation

$$\frac{\delta}{\delta n(\mathbf{r})} \left[E_{v_0}[n] - \mu \int d\mathbf{r}' n(\mathbf{r}') \right] = 0 \quad \Rightarrow \quad \frac{\delta T_S[n]}{n(\mathbf{r})} + v_0(\mathbf{r}) + \int d\mathbf{r}' \frac{n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} + \frac{\delta E_{xc}[n]}{n(\mathbf{r})} = \mu$$



The Kohn-Sham equations

interacting system

$$\frac{\delta T_S[n]}{\delta n(\mathbf{r})} + v_0(\mathbf{r}) + \int d\mathbf{r}' \frac{n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} + \frac{\delta E_{xc}[n]}{\delta n(\mathbf{r})} = \mu \quad \frac{\delta E_{v_S}[n]}{\delta n(\mathbf{r})} = \frac{\delta T_S[n]}{\delta n(\mathbf{r})} + v_S(\mathbf{r}) = \mu$$



Kohn-Sham equations

$$v_S[n](\mathbf{r}) = v_0(\mathbf{r}) + \int d\mathbf{r}' \frac{n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} + v_{xc}(\mathbf{r})$$

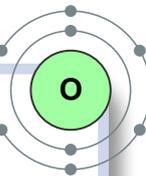
$$\left(-\frac{\nabla^2}{2} + v_S[n](\mathbf{r}) \right) \varphi_j(\mathbf{r}) = \epsilon_j \varphi_j(\mathbf{r})$$

$$n_0(\mathbf{r}) = \sum_j^N |\varphi_j(\mathbf{r})|^2$$

Oxygen

Need to account only for N orbitals $\varphi_i(\mathbf{r})$

$8 \times 10^3 \approx 8 \text{ Kb}$



The local density approximation (LDA)

It expresses the xc energy of an inhomogeneous system as the integral over the xc energy density of a homogeneous electron liquid, evaluated at the local density

$$E_{\text{xc}}^{\text{LDA}}[n] = \int d^3r e_{\text{xc}}^h(\bar{n}) \Big|_{\bar{n}=n(\mathbf{r})} \implies v_{\text{xc}}^{\text{LDA}}(\mathbf{r}) = \frac{de_{\text{xc}}^h(\bar{n})}{d\bar{n}} \Big|_{\bar{n}=n(\mathbf{r})}$$

e_x^h

e_c^h

the homogeneous electron gas

Exchange

$$e_x^h(n, \zeta) = e_x^h(n, 0) + [e_x^h(n, 1) - e_x^h(n, 0)]f(\zeta)$$

$$e_x^h(n, 0) = -\frac{3}{4} \left(\frac{3}{\pi}\right)^{1/3} n^{4/3}, \quad e_x^h(n, 1) = -\frac{3}{4} \left(\frac{6}{\pi}\right)^{1/3} n^{4/3}$$

$$f(\zeta) = \frac{(1 + \zeta)^{4/3} + (1 - \zeta)^{4/3} - 2}{2(2^{1/3} - 1)}$$

Correlation

(Perdew-Wang interpolation)

$$\tilde{e}_c^h(r_s, \zeta) = \tilde{e}_c^h(r_s, 0) + \alpha_c(r_s) \frac{f(\zeta)}{f''(0)} (1 - \zeta^4) + [\tilde{e}_c^h(r_s, 1) - \tilde{e}_c^h(r_s, 0)]f(\zeta)\zeta^4$$

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

	$e_c(r_s, 0)$	$e_c(r_s, 1)$	$-\alpha_c(r_s)$
A	0.031091	0.015545	0.016887
α_1	0.21370	0.20548	0.11125
β_1	7.5957	14.1189	10.357
β_2	3.5876	6.1977	3.6231
β_3	1.6382	3.3662	0.88026
β_4	0.49294	0.62517	0.49671

The local density approximation (LDA)

It expresses the xc energy of an inhomogeneous system as the integral over the xc energy density of a homogeneous electron liquid, evaluated at the local density

$$E_{\text{xc}}^{\text{LDA}}[n] = \int d^3r e_{\text{xc}}^h(\bar{n}) \Big|_{\bar{n}=n(\mathbf{r})} \quad \Longrightarrow \quad v_{\text{xc}}^{\text{LDA}}(\mathbf{r}) = \frac{de_{\text{xc}}^h(\bar{n})}{d\bar{n}} \Big|_{\bar{n}=n(\mathbf{r})}$$

Upsides

- Total atomic and molecular ground-state energies typically within 1–5% of the experimental values
- Molecular equilibrium distances and geometries reproduced within ~3%
- Fermi surfaces of bulk metals reproduced within a few percent
- Lattice constants of solids typically reproduced within 2%
- Vibrational frequencies and phonon energies excellent within a few percent

The local density approximation (LDA)

Limitations (also GGA)

- Not free from spurious self-interaction: KS potential decays faster than r^{-1}
 - no Rydber series
 - no bound negative atomic ions
 - ionization potential underestimated

- Cannot describe dispersion forces

$$W_{\text{int}}(\mathbf{R}) \rightarrow e^{-\mathbf{R}} \text{ rather than } \mathbf{R}^{-6}$$

- Too small band-gap

$$E_{\text{gap}}^{\text{LDA}} \approx 0.5 E_{\text{gap}}^{\text{exp}}$$

- Cohesive energy for bulk metals too small

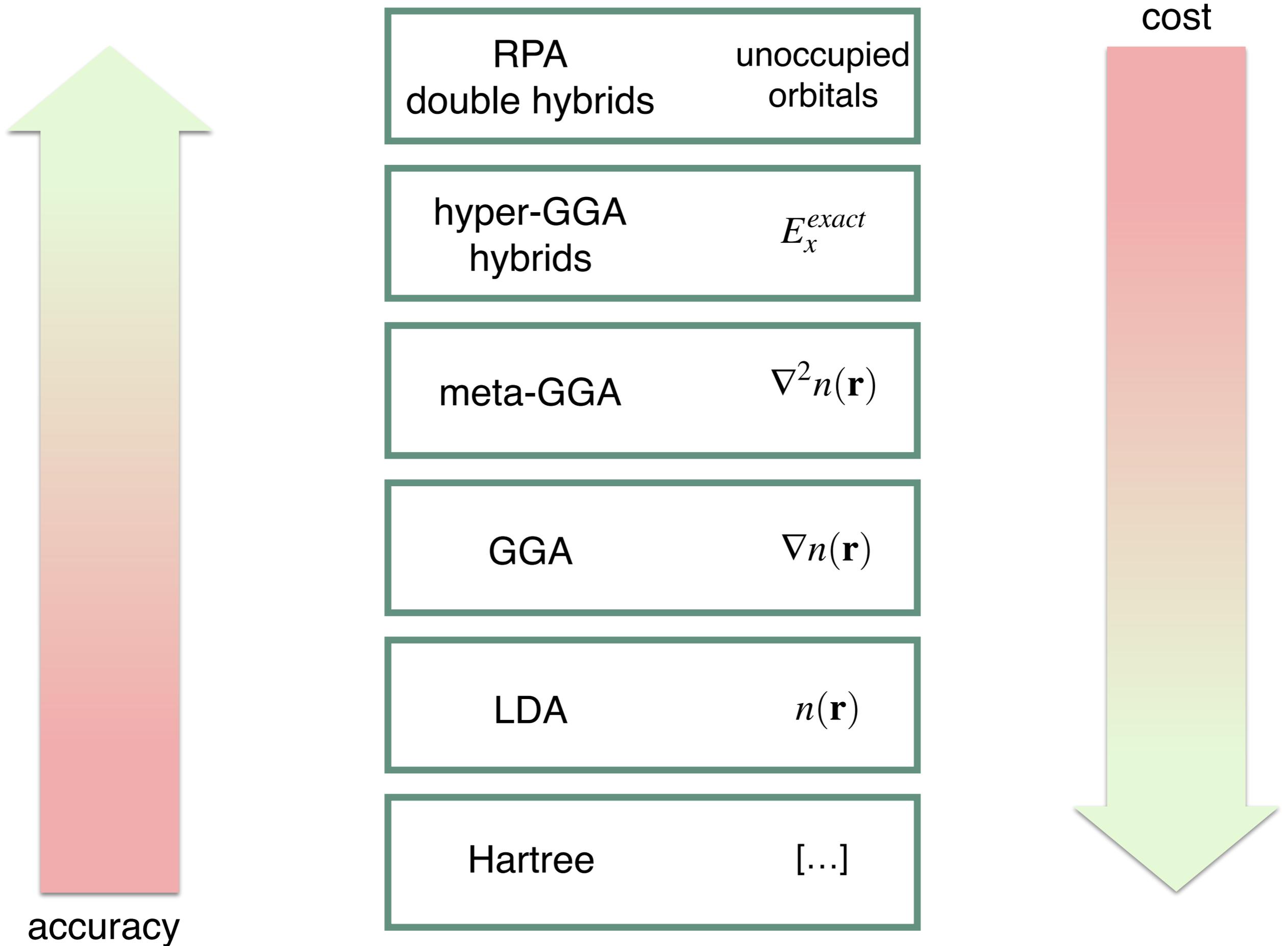
LDA overestimated

GGA underestimated

- Wrong gs for strongly correlated solids

e.g. FeO, La₂CuO₄ predicted as metals

Approximations of the xc-functional



Mean absolute errors for molecular properties

	Formation enthalpy ^a	Ionization potential ^b	Equilibrium bond length ^c	Vibrational frequency ^d	H-bonded complexes ^e
HF	211.54	1.028	0.0249	136.2	2.77
LSDA	121.85	0.232	0.0131	48.9	5.78
BLYP	9.49	0.286	0.0223	55.2	0.64
BPW91	9.04	0.241	0.0168	41.4	0.99
BP86	26.33	0.215	0.0175	45.5	0.76
PW91	23.59	0.221	0.0145	39.8	1.43
PBE	22.22	0.235	0.0159	42.0	1.00
HCTH	7.17	0.232	0.0145	39.9	0.91
OLYP	5.88	0.288	0.0177	40.2	2.18
B3LYP	4.93	0.184	0.0104	33.5	0.43
B3PW91	3.90	0.190	0.0093	36.2	0.88
B3P86	26.14	0.551	0.0084	37.0	0.73
PBE0	6.66	0.199	0.0097	43.6	0.66
VSXC	3.46	0.226	0.0131	33.9	1.34
PKZB	6.98	0.310	0.0269	51.7	2.90
TPSS	5.81	0.242	0.0142	30.4	0.59
TPSSh	3.90	0.229	0.0101	26.9	0.78

^a For a test set of 223 molecules (in kcal/mol).

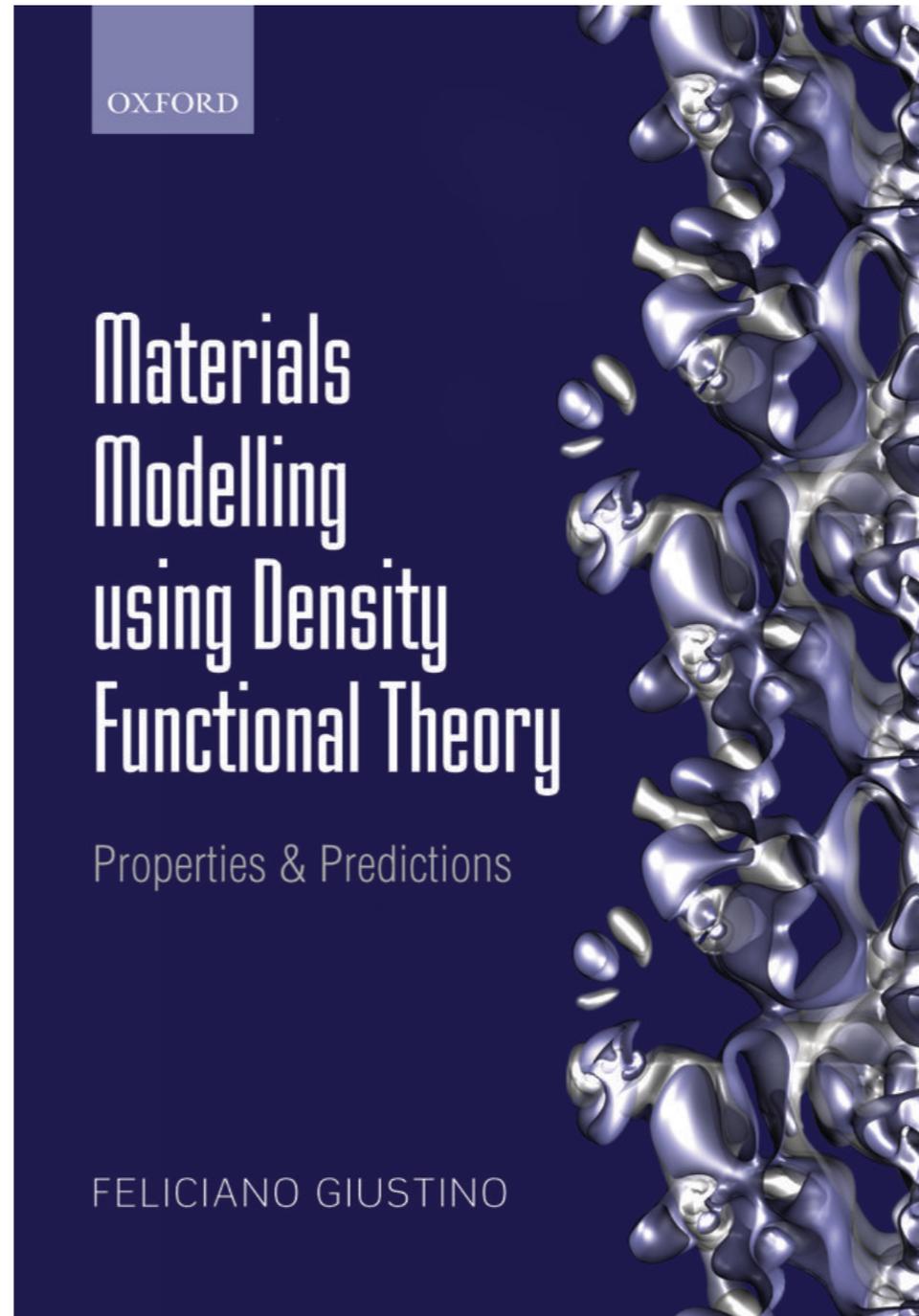
^b For a test set of 223 molecules (in eV), evaluated from the total-energy differences between the cation and the corresponding neutral, for their respective geometries.

^c For a test set of 96 diatomic molecules (in Å).

^d For a test set of 82 diatomic molecules (in cm⁻¹).

^e For a test set of 10 hydrogen-bonded complexes (dissociation energies in kcal/mol).

More on DFT



F. Giustino,
Materials Modelling Using Density Functional Theory: Properties and Predictions
(Oxford University Press, 2014).