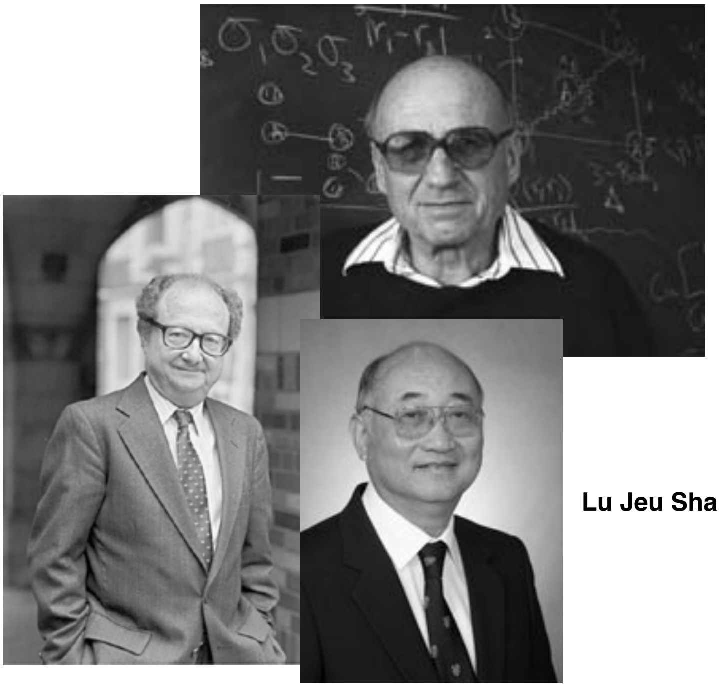
MSE 468 Lecture 5

FROM HF TO DFT - PART I



Walter Kohn

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The self-consistent field

- The single-particle Hartree operator is self-consistent! It depends on the orbitals that are the solution of all other Hartree equations
- We have *n* simultaneous integro-differential equations for the *n* orbitals
- Solution is achieved iteratively

$$\left[-\frac{1}{2}\nabla_i^2+\sum_I V(\vec{R}_I-\vec{r}_i)+\sum_{j\neq i}\int|\varphi_j(\vec{r}_j)|^2\frac{1}{|\vec{r}_j-\vec{r}_i|}d\vec{r}_j\right]\varphi_i(\vec{r}_i)=\varepsilon\varphi_i(\vec{r}_i)$$

What is missing?

- **Correlation**
  - One electron only sees the *average density of another*, not its instantaneous position
  - Too much electrostatic repulsion on average
- **Exchange**
  - The wavefunction is *not* anti-symmetric (for particle exchange)
  - Wrong particle statistics (no Pauli exclusion principle)

Spin-Statistics

- All elementary particles are either fermions (half-integer spins) or bosons (integer)
- A set of identical (*indistinguishable*) fermions has a wavefunction that is antisymmetric by exchange

$$\psi(\vec{r}_1,\vec{r}_2,\ldots,\vec{r}_j,\ldots,\vec{r}_k,\ldots,\vec{r}_n) = -\psi(\vec{r}_1,\vec{r}_2,\ldots,r_k,\ldots,\vec{r}_j,\ldots,\vec{r}_n)$$

- For bosons it is symmetric

Slater determinant

- An antisymmetric wavefunction is constructed via a Slater determinant of the individual orbitals
  (instead of just a product, as in the Hartree approach)

$$\psi(\vec{r}_1,\vec{r}_2,\dots,\vec{r}_n)=\frac{1}{\sqrt{n!}}\begin{array}{cc} \text{Orbitals} & \\ \begin{Vmatrix} \varphi_\alpha(\vec{r}_1) & \varphi_\beta(\vec{r}_1) & \cdots & \varphi_\nu(\vec{r}_1) \\ \varphi_\alpha(\vec{r}_2) & \varphi_\beta(\vec{r}_2) & \cdots & \varphi_\nu(\vec{r}_2) \\ \vdots & \vdots & \ddots & \vdots \\ \varphi_\alpha(\vec{r}_n) & \varphi_\beta(\vec{r}_n) & \cdots & \varphi_\nu(\vec{r}_n) \end{Vmatrix} & \text{Electrons} \end{array}$$

$$\boxed{\frac{1}{\sqrt{2}}\begin{Vmatrix} \varphi_\alpha(\vec{r}_1) & \varphi_\beta(\vec{r}_1) \\ \varphi_\alpha(\vec{r}_2) & \varphi_\beta(\vec{r}_2) \end{Vmatrix} = \frac{1}{\sqrt{2}}\left[\varphi_\alpha(\vec{r}_1)\varphi_\beta(\vec{r}_2)-\varphi_\beta(\vec{r}_1)\varphi_\alpha(\vec{r}_2)\right]}$$

Pauli principle

$$\psi(\vec{r}_1,\vec{r}_2,\dots,\vec{r}_n)=\frac{1}{\sqrt{n!}}\begin{Vmatrix} \varphi_\alpha(\vec{r}_1) & \varphi_\beta(\vec{r}_1) & \cdots & \varphi_\nu(\vec{r}_1) \\ \varphi_\alpha(\vec{r}_2) & \varphi_\beta(\vec{r}_2) & \cdots & \varphi_\nu(\vec{r}_2) \\ \vdots & \vdots & \ddots & \vdots \\ \varphi_\alpha(\vec{r}_n) & \varphi_\beta(\vec{r}_n) & \cdots & \varphi_\nu(\vec{r}_n) \end{Vmatrix}$$

- Changes sign when swapping rows (electrons)
  (**antisymmetric by exchange of identical particles**)
- Is zero if two rows are identical (**Pauli principle**:
  we can't have two electrons in the same quantum state)

Hartree-Fock Equations

The Hartree-Fock equations are, again, obtained from the variational principle: we look for the minimum of the many-electron Schrödinger equation in the class of all wavefunctions that are written as a **single Slater determinant**

$$\psi(\vec{r}_1,\ldots,\vec{r}_n) = \left\| Slater \right\|$$

Kinetic and potential energy

$$\left[-\frac{1}{2}\nabla_i^2 + \sum_I V(\vec{R}_I - \vec{r}_i)\right]\varphi_\lambda(\vec{r}_i) +$$

Hartree electrostatics

$$\left[\sum_\mu \int \varphi_\mu^*(\vec{r}_j)\frac{1}{|\vec{r}_j - \vec{r}_i|}\varphi_\mu(\vec{r}_j)\,d\vec{r}_j\right]\varphi_\lambda(\vec{r}_i) -$$

Exchange term

$$\sum_\mu \left[\int \varphi_\mu^*(\vec{r}_j)\frac{1}{|\vec{r}_j - \vec{r}_i|}\varphi_\lambda(\vec{r}_j)\,d\vec{r}_j\right]\varphi_\mu(\vec{r}_i) = \varepsilon\varphi_\lambda(\vec{r}_i)$$

Shell structure of atoms

- Self-interaction free
- Good for atomic properties
- Starting point of higher-order perturbation theory
- Exchange is now in, correlation still out

Dealing with electron spin

- We not only have a position for each electron, but also a spin variable (α, β)
- When swapping electrons, we swap both positions and spins

$$\Psi(\vec{r}_1\alpha, \vec{r}_2\beta) = -\Psi(\vec{r}_2\beta, \vec{r}_1\alpha)$$

- 2-electron wavefunction with **same space and spin will vanish**

$$\Psi(\vec{r}_1\alpha, \vec{r}_1\alpha) = -\Psi(\vec{r}_1\alpha, \vec{r}_1\alpha) = 0$$

- Wavefunction with same space, but different spin will not

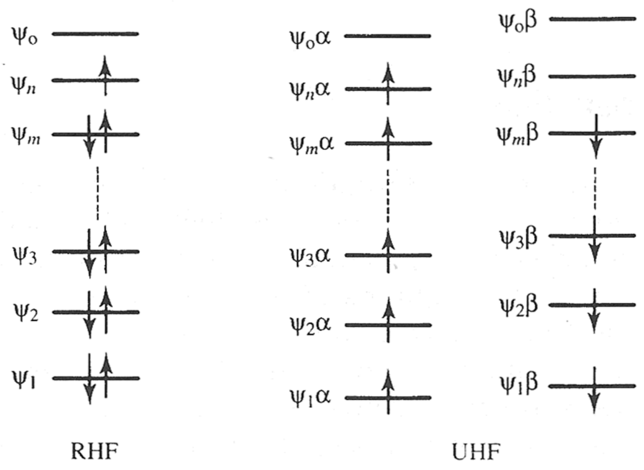
$$\Psi(\vec{r}_1\alpha, \vec{r}_1\beta) = -\Psi(\vec{r}_1\beta, \vec{r}_1\alpha)$$

Dealing with electron spin

- For each spatial orbital, there are two spin orbitals
- A system is **open shell** if it contains one or more unpaired electrons
- Restricted Hartree-Fock (RHF)
  Combinations of singly and doubly occupied molecular orbitals. *Doubly occupied orbitals use the same spatial functions* for electrons of both spins
- Unrestricted Hartree-Fock (UHF)
  Two distinct sets of orbitals used: one for spin-up electrons, one for spin-down electrons.
  Result: effectively two densities are used, one for each spin

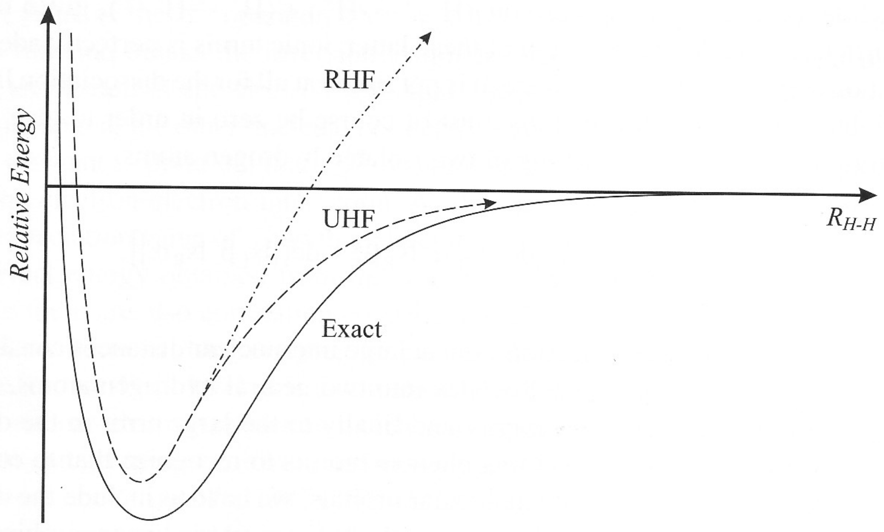
Restricted vs. unrestricted

- UHF approach is more general than RHF
- In a variational approach, it will have lower energy



$$\Psi_i\alpha(\vec{r}) \neq \Psi_i\beta(\vec{r})$$

The Dissociation of H_2



- RHF fails to describe dissociation; doubly-occupies the same bonding orbital
- Unphysical at far separation; UHF better for bond-breaking

What is missing

- Correlations (by definition!)
  - Dynamical correlations: HF describes electrons as moving in the average potential of the others, instantaneous influence of electrons coming close together not taken into account
  - Static correlations: a single determinant variational class in not good enough
- Spin contamination: even if the energy is correct (variational, quadratic) other properties might not (e.g. the UHF spin is an equal mixture of singlet and triplet, not an eigenvector of the total spin operator S^2)

What is missing

- Performs poorly for the homogenous electron gas

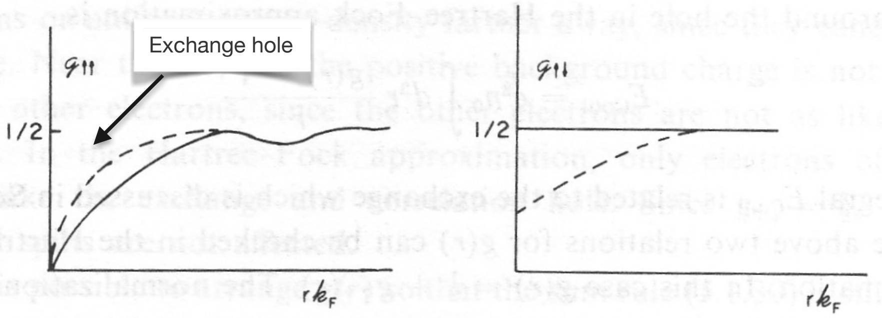


FIGURE 5.5. The pair distribution functions for parallel (left) and antiparallel (right) spins. The solid line is the Hartree–Fock approximation, while the dashed line includes correlation.

Faster, or better

- The exchange integrals are the "hidden" cost (fourth power).
- Semi-empirical methods (ZDO, NDDO, INDO, CNDO, MINDO): neglect certain multi-center integrals
- Configuration interaction (CI): variational method, linear combination of Slater determinants
- Møller-Plesset (perturbation theory)

Configuration Interaction (CI)

In normal Hartree Fock, the HF determinant is built from the lowest energy single-electron states.

$$\Psi^0_{HF} = \left|\varphi_1\ \varphi_2\ \cdots\ \varphi_K\right|$$

E.g. $1s^2 2s^2 2p^6$

Rationale of CI is to mix in “excited” states (e.g. exchange state i with K+1)

$$\Psi^1_{HF} = \left|\varphi_1\ \varphi_2\ \cdots\ \varphi_{K+1}\ \cdots\ \varphi_K\right|$$

E.g. $1s^2 2s^2 2p^5 3s^1$

Define new variational wave function:

$$\Psi = c_0\Psi_0 + c_1\Psi_1 + c_2\Psi_2 + \dots$$

Issues: Many possible excitations (combinatorial problem)

Time consuming (scaling N^6 or worse)

Variants of CI: **Full CI** (all configurations, scales like N! i.e. exponential), **truncated CI** (CIS: only single excitations; CID: only double excitations; CISD; CISDT; ...)

Coupled Cluster (CC)

Exponential operator used to combine Slater determinants

$$|\Psi\rangle = e^{T}|\Phi_0\rangle = (1 + T + T^2/2 + \cdots)|\Phi_0\rangle$$

where T is the cluster operator, e.g. $T = T_1 + T_2 + T_3 + \ldots$, where T_1 creates single excitations, T_2 double excitations, ...

Leads to wave function expansions with accurate energies for small molecules

Common variants:
CCD (only double excitations, $T=T_2$);
CCSD: single and double occupations ($T=T_1+T_2$)
CCSD(T): CCSD + perturbative treatment of triple excitations; when using a large basis set, is very accurate but scales as N^7

Time is precious

Method	**E_{coh} (% error)**	**Scaling with # electrons**	**Time for 50 atoms (if time for 1 atom is 1 second)**
HF	~50%	N^3-N^4	2.5 months
DFT (LDA)	15-25%	N^2-N^3	34 hours
CCSD(T)	10-15%	N^7	24,000 years

Adapted from Foulkes et al., RMP 73, 33 (2001)

Towards DFT:
density-matrix formulation

Reduced density matrices: definition

$$\gamma_1(\mathbf{r}_1, \mathbf{r}_1') = N \int \cdots \int \Psi^*(\mathbf{r}_1', \mathbf{r}_2, \ldots, \mathbf{r}_N)\Psi(\mathbf{r}_1, \mathbf{r}_2, \ldots, \mathbf{r}_N) d\mathbf{r}_2 \cdots d\mathbf{r}_N$$

$$\gamma_2(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_1', \mathbf{r}_2') = \frac{N(N-1)}{2} \int \cdots \int \Psi^*(\mathbf{r}_1', \mathbf{r}_2', \ldots, \mathbf{r}_N)\Psi(\mathbf{r}_1, \mathbf{r}_2, \ldots, \mathbf{r}_N) d\mathbf{r}_3 \cdots d\mathbf{r}_N$$

Note! $\gamma_1(\mathbf{r}, \mathbf{r}) = \rho(\mathbf{r})$ (The "trace")

Hence the name "density matrices"

A variation principle for RDMs

$$E = \int \left[\left(-\frac{1}{2}\nabla_1^2 + v(\mathbf{r}_1) \right) \gamma_1(\mathbf{r}_1', \mathbf{r}_1) \right]_{\mathbf{r}_1 = \mathbf{r}_1} d\mathbf{r}_1 +$$
$$\int \int \frac{1}{r_{12}} \gamma_2(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_1, \mathbf{r}_2) d\mathbf{r}_1 d\mathbf{r}_2$$

- As a function of the reduced density matrices, we have many less variables.
- However: **N-representability problem!**
  We don't know the domain - we don't know the conditions for a function γ_2 to be a valid RDM
  (while we know e.g. conditions for ψ: continuous, square-integrable)

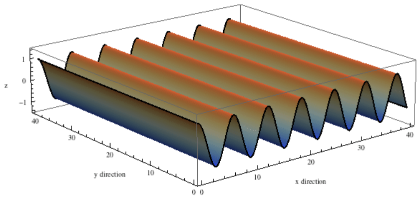
Density-functional theory
(first observations)

- The external potential V_{ext} and the number N of electrons completely define the quantum problem
- The wavefunctions are – in principle – uniquely determined, via the Schrödinger Equation
  (but we cannot compute them easily)
- All system properties follow from the wavefunctions
- The energy (and everything else) is thus a functional of V_{ext} and N

Can we reverse the relation?
The Thomas-Fermi approach (pre-DFT)

- Let's try to find out an expression for the **energy as a function of the charge density**
- E= kinetic + external + el.-el.
- Kinetic is the tricky term: second derivative (curvature) of wave functions

PLANE WAVE



$$\Psi \propto e^{i\vec{k}\cdot\vec{r}} \qquad \text{Kinetic energy} = \frac{\hbar^2 k^2}{2m}$$

$$\text{BUT } \rho = |\Psi|^2 \propto \text{constant!}$$

Local Density Approximation

- How do we get the curvature of a wavefunction from the charge density? Local density approximation
- We take the kinetic energy density at every point to correspond to the kinetic energy density of the **non-interacting homogenous** electron gas (exactly solvable)

$$\boxed{T(\vec{r}) = A\rho^{\frac{5}{3}}(\vec{r})}$$

$$E_{Th-Fe}[\rho] = \boxed{A\int \rho^{\frac{5}{3}}(\vec{r})d\vec{r}} + \int \rho(\vec{r})v_{ext}(\vec{r})d\vec{r} + \frac{1}{2}\iint \frac{\rho(\vec{r}_1)\rho(\vec{r}_2)}{|\vec{r}_1 - \vec{r}_2|}d\vec{r}_1 d\vec{r}_2$$

It’s a poor-man Hartree…

- The idea of an energy functional is not justified
- It does not include exchange effects - but Dirac proposed to add the LDA exchange energy:

$$-C\int \rho(\vec{r})^{\frac{4}{3}}\, d\vec{r}$$

- *Easy to compute*: It scales linearly, and we deal with 1 function of three coordinates!

The Argon atom

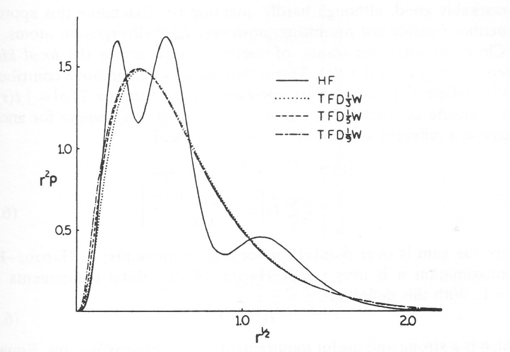


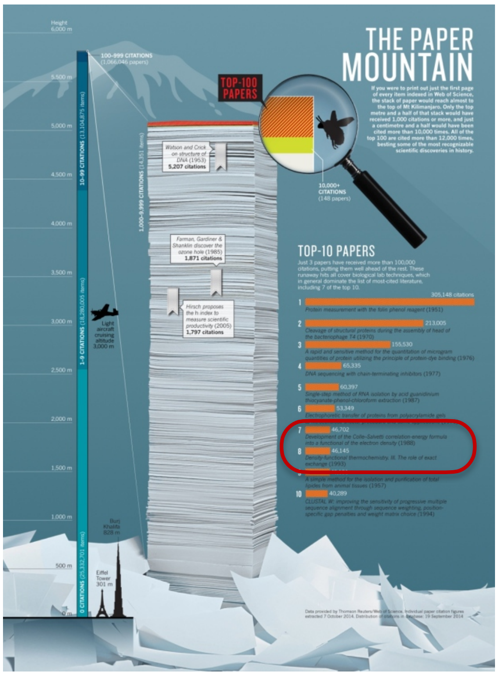
Figure 6.3 Electron density for argon from various models (after Yang 1986.)

- Not too bad despite its simplicity, BUT it misses e.g. shell structure of atoms (captured by HF instead)
- Not good for bonds and molecules, acceptable for metals

Towards DFT

- 30+ more years before theorems at the basis of DFT
- 15+ more years before actual use in materials

- Nowadays, however, it's widely used!



First Hohenberg-Kohn theorem

The density as the basic variable:

- external potential and the number of electrons determine uniquely the charge density, and
- **charge density (in the ground state) determines uniquely (1:1 correspondence) the external potential and the number of electrons**

$$\begin{tikzcd}
N, V_{ext} \arrow[r, "\text{Solve Schrödinger}", "\text{equation}"'] & \boxed{\Psi_i(\vec{r}_1, \ldots, \vec{r}_N)} \arrow[d, "\text{Pick lowest-energy solution}"] \\
n_0(\vec{r}) \arrow[u, "\text{1st HK theorem}"] & \Psi_0(\vec{r}_1, \ldots, \vec{r}_N) \arrow[l, "\text{Integrate}", "\text{square modulus}"']
\end{tikzcd}$$

All properties can be derived

Proof (ad absurdum)

- Let us consider a potential v(**r**) for a Hamiltonian *H*, with ground state ψ
- Let us assume (**ad absurdum**) that there exists a **different** potential *v*'(**r**) (Hamiltonian *H*') with ground state ψ', with *same* charge density *n*(**r**)
- Let call E and E' the respective ground-state energies
- We consider ψ' as **trial solution** for the Hamiltonian *H* and use the **variational principle**, we have a **strict** inequality:

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

- Now we do the same considering ψ as **trial solution** for the Hamiltonian *H':*

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

- We now sum the two expressions and get: *E*+*E*' < *E*'+*E*, which is impossible.

Note: in the next slides I will use interchangeably *n* or ρ to indicate the same quantity, the charge density

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The universal functional *F*[ρ]

- The ground state density determines the potential V_{ext} of the Schrödinger equation, and thus we could solve it and get the ground-state wavefunctions ψ
- We can then define this functional of the charge density:

$$F[\rho(\vec{r})] = \left\langle \Psi \middle| \hat{T} + \hat{V}_{e-e} \middle| \Psi \right\rangle$$

- It contains exact many-body interactions for any system, does not explicitly depend on external potential

Second Hohenberg-Kohn theorem

The variational principle – we have an alternative to Schrödinger, expressed in terms of the charge density only

$$E_v[\rho(\vec{r})] = F[\rho(\vec{r})] + \int v_{ext}(\vec{r})\rho(\vec{r})d\vec{r} \geq E_0$$

(ρ determines its ground-state wavefunctions, that can be taken as a trial wavefunctions in this external potential)

$$\langle\Psi|\hat{H}|\Psi\rangle = \langle\Psi|\hat{T} + \hat{V}_{e-e} + v_{ext}|\Psi\rangle = \int \rho v_{ext} + F[\rho]$$

=> It is E_0 at the minimum

If I *minimise* this expression to find the EXACT solution!

Euler-Lagrange equations

The minimum is obtained when a infinitesimal perturbation does not change the value

Lagrange multiplier
(to fix *N*)

$$\delta\left(F[n(\vec{r})] + \int v_{ext}(\vec{r})n(\vec{r})d\vec{r} - \mu\left(\int n(\vec{r})\,d\vec{r} - N\right)\right) = 0$$

$$\frac{\delta F[n(\vec{r})]}{\delta n(\vec{r})} + v_{ext}(\vec{r}) = \mu$$

Functional derivative
(extension of derivative to functionals, i.e. functions that take a function and return a number)

Still not very useful: I don't know F, I need to solve the Schrödinger equation to obtain it!

The non-interacting unique mapping

- **The Kohn-Sham system:** a reference system is introduced (the Kohn-Sham electrons)
- These electrons **do not interact**
- They live in an external potential (the Kohn-Sham potential) such that their ground-state charge density is **IDENTICAL to the charge density** of the interacting system

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Rewrite the unknown term...

- Now: for a system of **non-interacting electrons**, the Slater determinant is the **EXACT** many-body wavefunction
- The kinetic energy of the non interacting system is well defined

$$F[n(\mathbf{r})] = \boxed{T_s[n(\mathbf{r})]} + E_H[n(\mathbf{r})] + E_{xc}[n(\mathbf{r})],$$

Hartree electrostatic interaction

$$E_H[n(\mathbf{r})] = \frac{1}{2}\int\int \frac{n(\mathbf{r}_1)n(\mathbf{r}_2)}{|\mathbf{r}_1 - \mathbf{r}_2|} d\mathbf{r}_1 d\mathbf{r}_2.$$

- **This expression is DEFINING E_{xc}**; we've just rewritten F (unknown) as the sum of two terms we know (kinetic energy of non-interacting KS electrons, and Hartree term), plus...
- ...we *moved all we don't know in an exchange-correlation (xc) term* (not only xc, it actually also includes a correction for the kinetic energy of the *interacting* electrons)

Electronic total energy

From the 2nd
HK theorem:

$$E_v[\rho(\vec{r})] = F[\rho(\vec{r})] + \underline{\int v_{ext}(\vec{r})\rho(\vec{r})d\vec{r} \geq E_0}$$

$$\Big\downarrow$$

$$E[\{\psi_i\}] = \sum_{i=1}^{N} -\frac{1}{2}\int \psi_i^\star(\mathbf{r})\nabla^2\psi_i(\mathbf{r})\ d\mathbf{r} + E_H[n(\mathbf{r})] +$$

$$+E_{xc}[n(\mathbf{r})] + \underline{\int v_{ext}(\mathbf{r})n(\mathbf{r})\ d\mathbf{r}}$$

Kohn-Sham
wavefunctions

The Kohn-Sham equations

- Rewrite as an "eigenvector" equation for the KS wave functions: (it's a set of *N* independent single-particle Schrödinger equations)

$$\left[-\frac{1}{2}\nabla^2 + v_H(\mathbf{r}) + v_{xc}(\mathbf{r}) + v_{ext}(\mathbf{r})\right]\psi_i(\mathbf{r}) = \hat{H}_{KS}\ \psi_i(\mathbf{r}) = \epsilon_i\ \psi_i(\mathbf{r})$$

$$v_H(\mathbf{r}) = \int \frac{n(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}\,d\mathbf{r}', \qquad v_{xc}(\mathbf{r}) = \frac{\delta E_{xc}}{\delta n(\mathbf{r})}$$

$$n(\mathbf{r}) = \sum_{i=1}^{N} |\psi_i(\mathbf{r})|^2.$$