

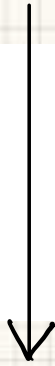
# **Introduction to Ground State Density Functional Theory**

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Ground-state DFT



Time-dependent DFT

## Eleven references for basics of ground-state DFT

1. K. Burke, *ABC of DFT* ; <http://dft.uci.edu>
2. J.P. Perdew and S. Kurth, *Density Functionals for Non-relativistic Coulomb Systems in the New Century*, in *A Primer in Density Functional Theory*, edited by C. Fiolhais et al. (Springer-Verlag, NY, 2003).
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5. J.P. Perdew, *What do the Kohn-Sham energies mean? How do atoms dissociate?*, in NATO ASI Ser., Ser.B 123 (Density Funct. Methods Phys.), 265 (1985).
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8. E.J. Baerends, *Chemical Potential, etc.* Phys. Chem. Chem. Phys. **24**, 12745 (2022).
9. A. Ruzsinsky and J.P. Perdew, *Twelve outstanding problems in ground-state density functional theory: A bouquet of puzzles*, Comp. Theor. Chem. **963**, 2 (2011).
10. A.J. Cohen, P. Mori-Sanchez, and W. Yang, *Challenges for Density Functional Theory*, Chem. Rev. **112**, 289 (2012).
11. A. Wasserman, J. Nafziger, K. Jiang, M-C.Kim, E. Sim, and K. Burke, *The Importance of Being Inconsistent*, Ann. Rev. Phys. Chem. **68**, 555 (2017).

From Perdew's 2019 lecture notes:

**MANTRA OF CORRELATED-WAVEFUNCTION THEORY:**

**THE RIGHT ANSWER FOR THE RIGHT REASON  
(BUT AT A HIGH PRICE, AND ONLY FOR FEW-  
ELECTRON SYSTEMS.)**

**MANTRA OF DENSITY FUNCTIONAL THEORY:**

**ALMOST THE RIGHT ANSWER FOR ALMOST THE  
RIGHT REASON AT ALMOST THE RIGHT PRICE  
FOR ALMOST ALL SYSTEMS OF INTEREST.**

**THE HISTORY OF DFT SHOWS THE POWER OF AN  
EXISTENCE THEOREM.**

## Outline

1. Basic definitions
2. Hohenberg-Kohn theorem
3. The XC energy
4. KS equations
5. Exact conditions
6. Local Density Approximation



Hamiltonian of interest:

$N$  electrons  
( $\hbar = m_e = e = 1$ )

$$\hat{H} = \hat{T} + \hat{V}_{ee} + \int d^3r v(\vec{r}) \hat{n}(\vec{r})$$

"external potential"

$$-\frac{1}{2} \sum_i^N \nabla_i^2 \quad \frac{1}{2} \sum_i^N \sum_j^N \frac{1}{|\vec{r}_i - \vec{r}_j|} \quad \sum_i^N \delta(\vec{r} - \vec{r}_i)$$

Ground-state wavefunction:

$$\Psi_0(\vec{r}_1 \sigma_1, \vec{r}_2 \sigma_2, \dots, \vec{r}_N \sigma_N)$$

Normalized:

$$\sum_{\sigma_1 \dots \sigma_N} \int d^3r_1 \dots d^3r_N |\Psi_0|^2 = 1$$

Antisymmetric:

$$\Psi_0(\dots \vec{r}_i \sigma_i \dots \vec{r}_j \sigma_j \dots) = -\Psi_0(\dots \vec{r}_j \sigma_j \dots \vec{r}_i \sigma_i \dots)$$

Ground-state density:

$$n_0(\vec{r}) = N \sum_{\sigma_1 \dots \sigma_N} \int d^3r_2 \dots d^3r_N |\Psi_0|^2$$

Integrates to  $N$  electrons:

$$\int d^3r n_0(\vec{r}) = N$$

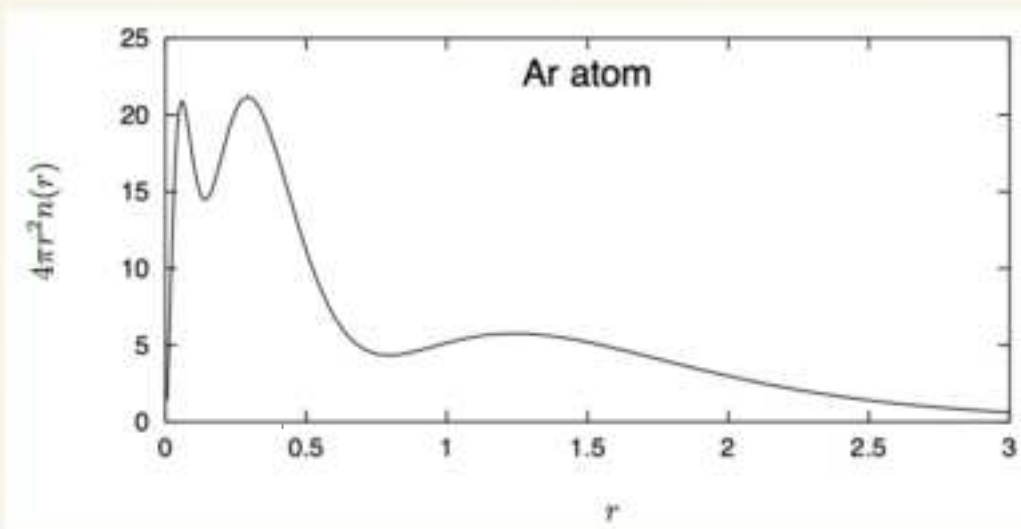
Ground-state energy:

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

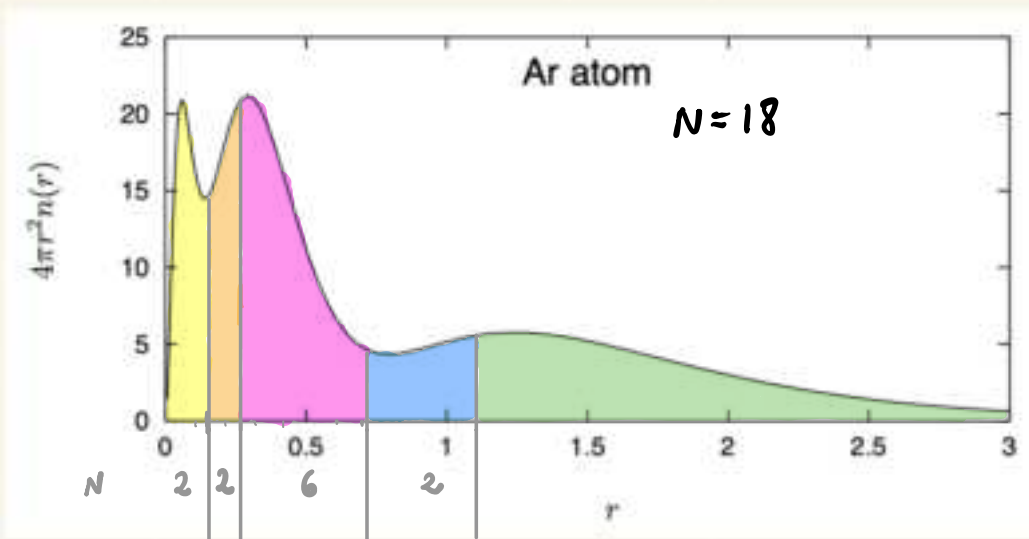
From the variational principle:

$$E_0 = \min_{\Psi} \langle \Psi | \hat{H} | \Psi \rangle$$

All possible  $N$ -electron normalized antisymmetric wavefunctions.



(From K. Burke, "The ABC of DFT")



## Hohenberg-Kohn theorem (1964):

$n_0(\mathbf{r}) \xrightarrow{\text{uniquely determines}} \psi(\mathbf{r}) \xrightarrow{\text{"in principle"}} \text{All properties can be calculated from } \psi(\mathbf{r})$

### Proof of Hohenberg-Kohn theorem

Assume  $\left. \begin{matrix} v_{\text{ext}}^{(1)}(\mathbf{r}) \\ v_{\text{ext}}^{(2)}(\mathbf{r}) \end{matrix} \right\} \rightarrow n_0(\mathbf{r}) ; v_{\text{ext}}^{(1)}(\mathbf{r}) \neq v_{\text{ext}}^{(2)}(\mathbf{r}) + C$   
 (non-degenerate ground state)

$$\begin{aligned}
 E_1 &= \langle \Psi_1 | \hat{H}^{(1)} | \Psi_1 \rangle = \langle \Psi_1 | \hat{T} + \hat{V}_{ee} | \Psi_1 \rangle + \int d\mathbf{r} n_0(\mathbf{r}) v_{\text{ext}}^{(1)}(\mathbf{r}) \\
 &< \langle \Psi_2 | \hat{H}^{(1)} | \Psi_2 \rangle = \langle \Psi_2 | \hat{T} + \hat{V}_{ee} | \Psi_2 \rangle + \int d\mathbf{r} n_0(\mathbf{r}) v_{\text{ext}}^{(1)}(\mathbf{r})
 \end{aligned}$$

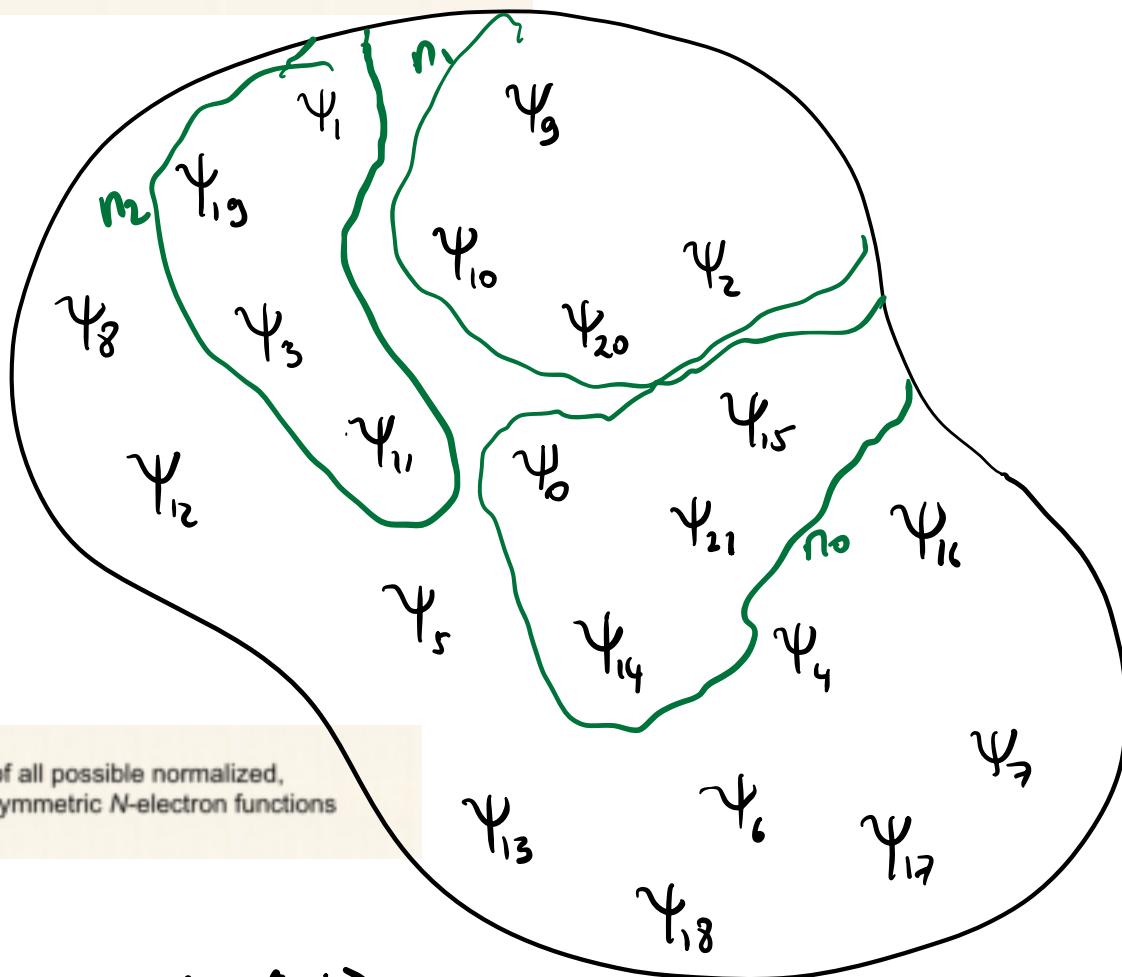
$$\rightarrow \langle \Psi_1 | \hat{T} + \hat{V}_{ee} | \Psi_1 \rangle < \langle \Psi_2 | \hat{T} + \hat{V}_{ee} | \Psi_2 \rangle$$

But switching indices...

$$\langle \Psi_2 | \hat{T} + \hat{V}_{ee} | \Psi_2 \rangle < \langle \Psi_1 | \hat{T} + \hat{V}_{ee} | \Psi_1 \rangle$$



Levy's constrained-search proof (1979):



Set of all possible normalized, antisymmetric  $N$ -electron functions

$$E_0 = \min_{\Psi} \langle \Psi | \hat{H} | \Psi \rangle$$

$$= \min_n \min_{\Psi \rightarrow n} \langle \Psi | \hat{H} | \Psi \rangle$$

$$= \min_n \left\{ \min_{\Psi \rightarrow n} \langle \Psi | \hat{T} + \hat{V}_{ee} | \Psi \rangle + \int d^3r v(r)n(r) \right\}$$

universal

$$E_0 = \min_n \left\{ F[n] + \int d^3r v(r)n(r) \right\}$$

$$E_0[n]$$

Euler-Lagrange equation:

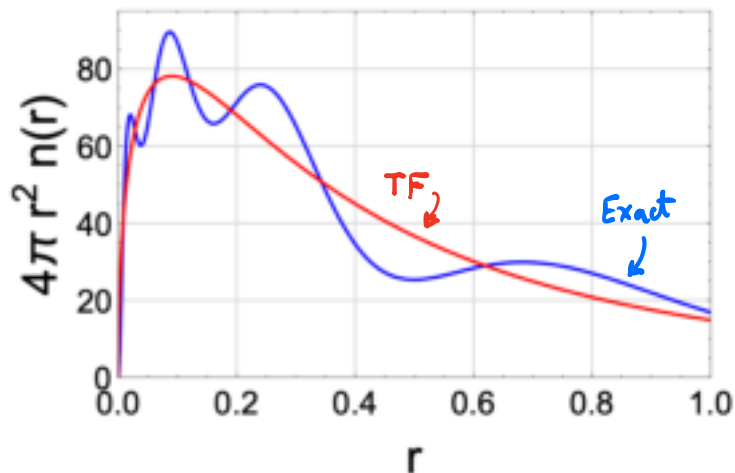
$$\frac{\delta E_v[n]}{\delta n(\vec{r})} - \mu = 0 \rightarrow \frac{\delta F[n]}{\delta n(\vec{r})} + v(\vec{r}) - \mu = 0$$

For a given external potential, the solution to this equation yields the correct ground-state density. But we need to know  $F[n]$ ...

Approximations for  $F[n]$  that are explicit functionals of the density are generally too crude to be very useful.

e.g. Thomas-Fermi approximation:

$$F^{\text{TF}}[n] = \frac{3}{10}(3\pi^2)^{2/3} \int d^3r n^{5/3}(\mathbf{r}) + \frac{1}{2} \int d^3r \int d^3r' \frac{n(\mathbf{r})n(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}$$



From P. Okun and K. Burke, *Semiclassics Book Chapter* (2023).

Kohn-Sham (1965):

$$F[n] = T_s[n] + E_H[n] + E_{XC}[n]$$

Kinetic energy for system of non-interacting electrons

Hartree energy

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



The Kohn-Sham wavefunction  $\Phi_n$  is the wavefunction for non-interacting electrons yielding density  $n(\mathbf{r})$  and minimizing  $\langle \hat{T} \rangle$

Kohn-Sham Hamiltonian:

$$\hat{H}_S = \hat{T} + \int d^3r v_S(\mathbf{r}) \hat{n}(\mathbf{r})$$

↑  
KS potential

Kohn-Sham Energy:

$$E_S \neq E_0$$

Euler-Lagrange equation for the KS system:

$$\frac{\delta T_S[n]}{\delta n(\mathbf{r})} + v_s(\mathbf{r}) - \mu = 0$$

$$\int \delta n(\mathbf{r}) d^3r = 0$$

$\mu$ , "tricky point"

$$\frac{\delta F[n]}{\delta n(\mathbf{r})} + v_s(\mathbf{r}) - \mu = 0 = \frac{\delta T_S[n]}{\delta n(\mathbf{r})} + \frac{\delta E_H(\mathbf{r})}{\delta n(\mathbf{r})} + \frac{\delta E_{xc}[n]}{\delta n(\mathbf{r})}$$

$$+ v_s(\mathbf{r}) - \mu = 0$$

KS equations:

$$\left( -\frac{1}{2} \nabla^2 + v_s(\mathbf{r}) \right) \phi_i(\mathbf{r}) = \epsilon_i \phi_i(\mathbf{r})$$

$$v_s(\mathbf{r}) = v(\mathbf{r}) + \int d\mathbf{r}' \frac{n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} + v_{xc}(\mathbf{r})$$

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

Solve these self-consistently:

- (1) Guess an initial density
- (2) Solve the equations to get initial set of KS orbitals
- (3) Construct new density
- (4) Iterate until the new density matches the one from previous iteration

Note: If  $E_{xc}[n]$  were "exact", you would be guaranteed the exact  $n(\mathbf{r})$  and the exact ground-state energy.

Definition of Correlation Energy:

$$E_c[n] = \underbrace{\langle \Psi_n | \hat{T} + \hat{V}_{ee} | \Psi_n \rangle}_{F[n]} - \langle \Phi_n | \hat{T} + \hat{V}_{ee} | \Phi_n \rangle$$

$\Psi$  that minimizes  $\hat{T} + \hat{V}_{ee}$

Definition of Exchange Energy:

$$E_x[n] = \langle \Phi_n | \hat{V}_{ee} | \Phi_n \rangle - E_H[n]$$

Approximating the Exchange-Correlation Energy:

$$E_{xc}[n] \approx E_x[n] + E_c[n]$$

= ?

The first approximation one could think of is setting  $E_{xc}[n] = 0$

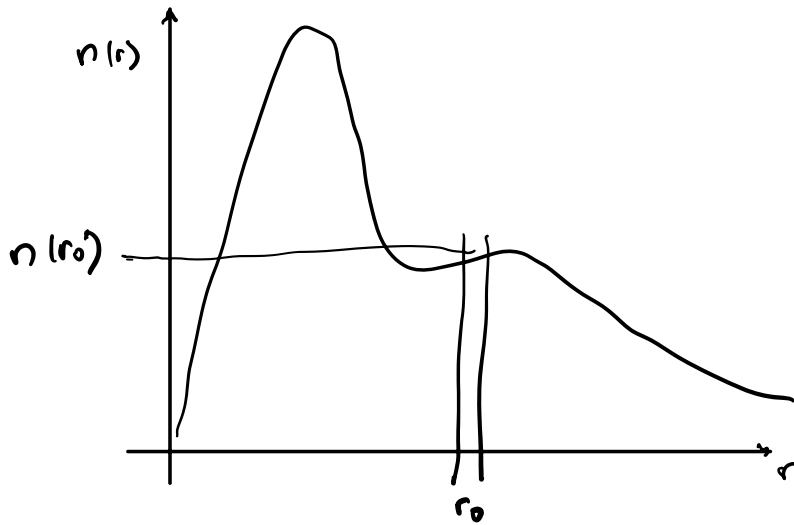
The results of this "simplified Hartree approximation" are not very good: Bond lengths are typically ~20% too large, and binding energies way too small.

Local Density Approximation (LDA, Kohn-Sham 1965):

$$E_{xc}[n] \approx E_{xc}^{LDA}[n] = \int d^3r n(\vec{r}) \epsilon_{xc}^{unif}(n(\vec{r}))$$

$$\epsilon_x^{unif}(n) = -\frac{3}{4\pi} (3\pi^2 n)^{1/3}$$

XC energy per particle of an interacting electron gas of uniform density

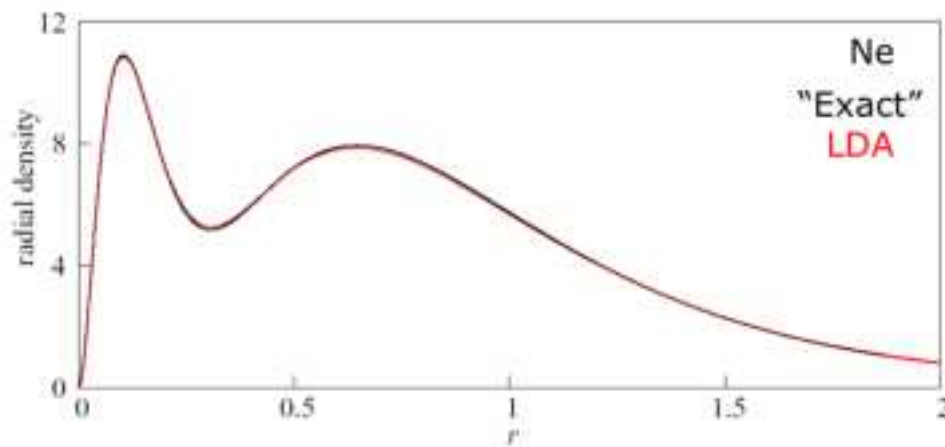


LDA gives the exact answer for the uniform electron gas

In practice, use the Local Spin Density Approximation, LSDA

$$E_{XC}^{LSDA}[n_{\uparrow}, n_{\downarrow}] = \int d^3r n(\mathbf{r}) \epsilon_{XC}^{unif}(n_{\uparrow}(\mathbf{r}), n_{\downarrow}(\mathbf{r}))$$

LSDA yields much better results than the simplified Hartree approximation: Bond lengths and binding energies are just a few % off.





Why does the LSDA work as well as it does?

Coupling-constant integral for  $E_{xc}[n]$  (Langreth and Perdew, 1975):

$\lambda$ -dependent Hamiltonian:

$$\hat{H}_\lambda = \hat{T} + \lambda \hat{V}_{ee} + \int d^3r v_\lambda(\mathbf{r}) \hat{n}(\mathbf{r}) \quad 0 \leq \lambda \leq 1$$

Adjust  $v_\lambda(\mathbf{r})$  to hold the ground-state density fixed at its  $\lambda = 1$  value.

$$v_\lambda(\mathbf{r}) = \begin{cases} v(\mathbf{r}), & \lambda = 1 \\ v_s(\mathbf{r}), & \lambda = 0 \end{cases}$$

$$E_{xc}[n] = \langle \Psi_n | \hat{T} + \hat{V}_{ee} | \Psi_n \rangle - \langle \Phi_n | \hat{T} + \hat{V}_{ee} | \Phi_n \rangle \\ + \langle \Phi_n | \hat{V}_{ee} | \Phi_n \rangle - E_H[n]$$

$$\begin{aligned} &= \langle \Psi_n^\lambda | \hat{T} + \lambda \hat{V}_{ee} | \Psi_n^\lambda \rangle \Big|_0^1 - E_H[n] \\ &= \int_0^1 d\lambda \frac{d}{d\lambda} \langle \Psi_n^\lambda | \hat{T} + \lambda \hat{V}_{ee} | \Psi_n^\lambda \rangle - E_H[n] \\ &= \int_0^1 d\lambda \langle \Psi_n^\lambda | \hat{V}_{ee} | \Psi_n^\lambda \rangle - E_H[n] \\ &= \frac{1}{2} \int_0^1 d\lambda \frac{\rho_2^\lambda(\mathbf{r}, \mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} - E_H[n] \end{aligned}$$

$(\Psi_n^{\lambda=0} = \Phi_n)$

Two-particle density matrix:

$$\rho_2^\lambda(\mathbf{r}, \mathbf{r}') = N(N-1) \sum_{\sigma_1} \dots \sum_{\sigma_N} \int d^3r_3 \dots \int d^3r_N |\Psi_n^\lambda(\mathbf{r}\sigma_1, \mathbf{r}'\sigma_2, \mathbf{r}_3\sigma_3, \dots, \mathbf{r}_N\sigma_N)|^2$$

Joint probability density

$$\rho_2^\lambda(\mathbf{r}, \mathbf{r}') = n(\mathbf{r}) \left[ n(\mathbf{r}') + n_{XC}^\lambda(\mathbf{r}, \mathbf{r}') \right]$$

Density at  $\mathbf{r}'$  of the XC hole around an electron at  $\mathbf{r}$ .

Sum rule:

$$\int n_{XC}^\lambda(\mathbf{r}, \mathbf{r}') d^3r' = -1 \quad \forall \mathbf{r}$$

Around an electron at  $\mathbf{r}$ , one electron is missing from the space  $\mathbf{r}' \neq \mathbf{r}$

Why does the LSDA work as well as it does?

Coupling-constant averaged XC hole density.

$$E_{XC}[n] = \frac{1}{2} \int d^3r \int d^3r' \frac{n(\mathbf{r}) \bar{n}_{XC}(\mathbf{r}, \mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|}$$

Other exact conditions:

e.g. Uniform coordinate scaling:

$$\text{e.g. } E_x [n_\delta] = \delta E_x [n]$$

$$n_\delta(\vec{r}) = \delta^3 n(r\vec{r})$$

To make progress, Perdeu's Golden Rules:

(1) Get the uniform gas limit right.

(2) Satisfy more exact constraints.

(3) Add more ingredients that provide more information.

# Modern DFT



Kieron Burke



Hardy Gross



John Perdew

