

# Density Functional Theory

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Theory and Computation for Interface Science and Catalysis:  
Fundamentals, Research and Hands on Engagement using VASP  
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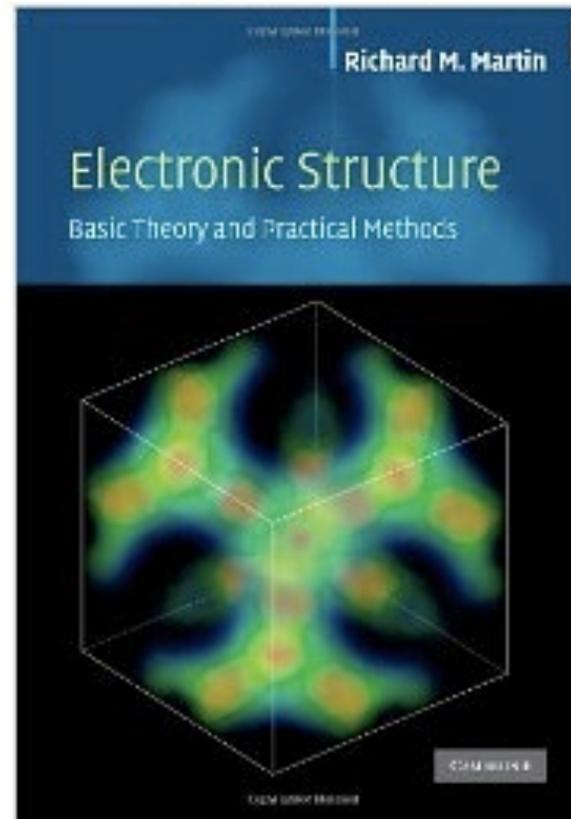
# Outline

- Hohenberg-Kohn theorems (I & II)
- Thomas Fermi approximation
- Kohn-Sham ansatz
- Exchange-correlation functionals
  - LDA
  - GGA
  - Hybrid

# Reference

Electronic Structure:  
Basic Theory and  
Practical Methods

Richard M. Martin,  
Cambridge  
University Press

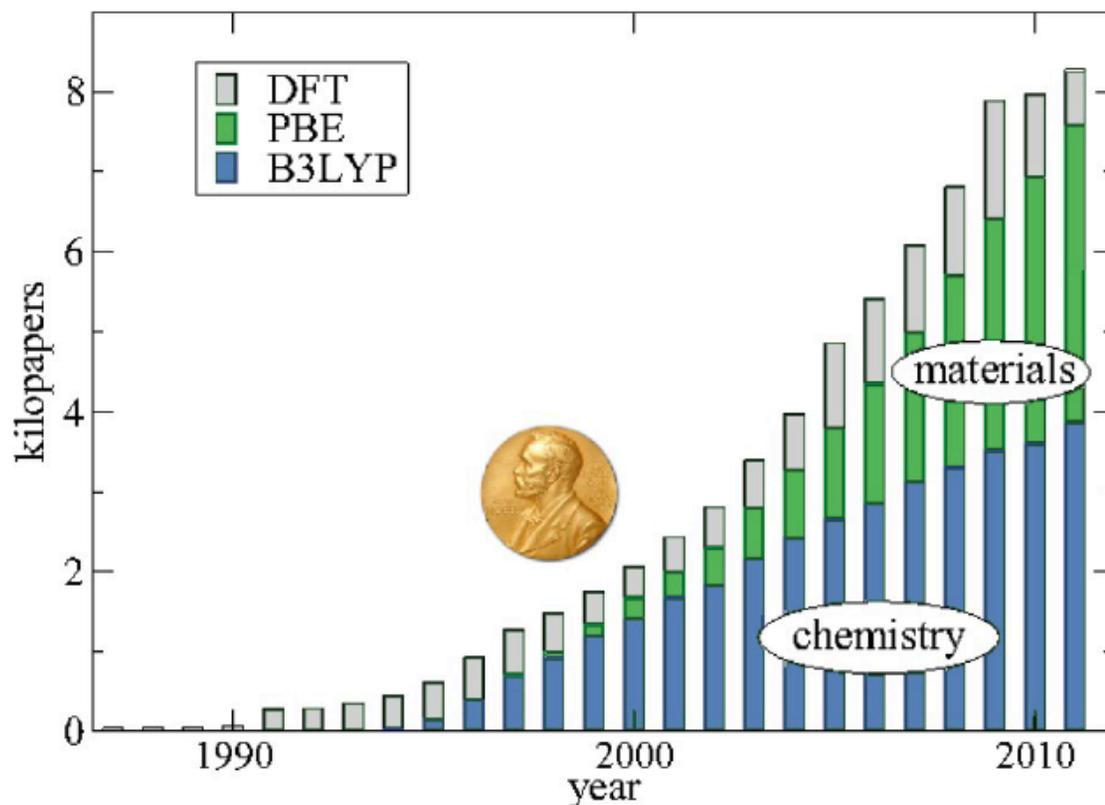


# Further reading

- “The ABC of DFT”, Kieron Burke
- “Perspective on density functional theory”, Kieron Burke, *J. Chem. Phys.* 136, 150901 (2012)
- “Progress in the development of exchange-correlation functionals” in *Theory and Applications of Computational Chemistry: The First Forty Years*, Gustavo E. Scuseria and Viktor N. Staroverov, 2005.
- Table of “EXCHANGE-CORRELATION FUNCTIONALS, Exc”, Mark E. Casida (<https://sites.google.com/site/markcasida/dft>)

# DFT applications

- Condensed matter physics
- Chemistry
- Material sciences
- Biology
- Geophysics
- Astrophysics
- ...



Numbers of papers when DFT is searched as a topic in Web of Knowledge (grey), B3LYP citations (blue), and PBE citations (green, on top of blue).

Kieron Burke, *J. Chem. Phys.* 136, 150901 (2012)

# Density functional theory



Walter Kohn

Nobel Prize in Chemistry 1998

exponential  
wall ( $p^{3N}$ )

$$\left\{ -\frac{\hbar^2}{2m} \sum_j \nabla_j^2 - \sum_{j,\ell} \frac{Z_\ell e^2}{|r_j - R_\ell|} + \frac{1}{2} \sum_{j \neq j'} \frac{e^2}{|r_j - r_{j'}|} - E \right\} \Psi = 0$$

The fundamental laws necessary for the mathematical treatment of large parts of physics and the whole of chemistry are thus fully known, and the difficulty lies only in the fact that application of these laws leads to equations that are **too complex to be solved.** ----- Paul Dirac

$$\Psi(\vec{r}_1, \vec{r}_2, \dots, \vec{r}_N) \quad \Rightarrow \quad n(\vec{r})$$

The density of particles in the ground state of quantum many body system is a basic variable, i.e., all properties of the system can be considered unique functionals of the **ground state density.**

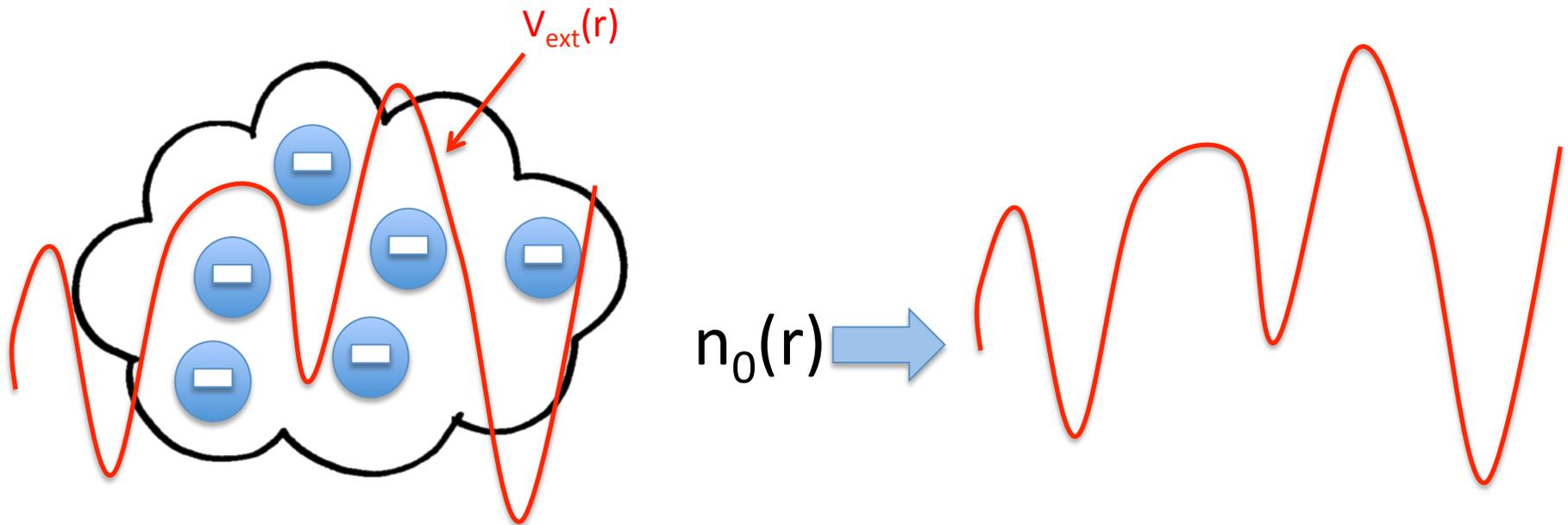
The **Kohn-Sham ansatz** assumes that the ground state density of the original system is equal to an auxiliary **non-interacting system.**

P. Hohenberg and W. Kohn, *Phys. Rev. B*, **136**: 864, 1964.

W. Kohn and L. Sham, *Phys. Rev. A*, **140**: 1133, 1965.

# Hohenberg-Kohn theorem I

Theorem I: For any system of interacting particles in an external potential  $V_{\text{ext}}(r)$ , the potential  $V_{\text{ext}}(r)$  is determined uniquely, except for a constant, by the ground state particle density  $n_0(r)$ .



# Proof of theorem I

Assume two external potentials,  $V_{ext}^{(1)}(\mathbf{r})$  and  $V_{ext}^{(2)}(\mathbf{r})$ , exist that differ by more than a constant and correspond to the same GS density.

$$\begin{array}{l} V_{ext}^{(1)}(\mathbf{r}) \Rightarrow \hat{H}^{(1)} \Rightarrow \Psi^{(1)} \\ V_{ext}^{(2)}(\mathbf{r}) \Rightarrow \hat{H}^{(2)} \Rightarrow \Psi^{(2)} \end{array} \begin{array}{l} \searrow \\ \nearrow \end{array} n_0(\mathbf{r})$$

Assume the ground state is not degenerate. Variational principle dictates

$$E^{(1)} = \langle \Psi^{(1)} | \hat{H}^{(1)} | \Psi^{(1)} \rangle < \langle \Psi^{(2)} | \hat{H}^{(1)} | \Psi^{(2)} \rangle$$

$$E^{(2)} = \langle \Psi^{(2)} | \hat{H}^{(2)} | \Psi^{(2)} \rangle < \langle \Psi^{(1)} | \hat{H}^{(2)} | \Psi^{(1)} \rangle$$

Rewrite the last term:

$$\langle \Psi^{(2)} | \hat{H}^{(1)} | \Psi^{(2)} \rangle = \langle \Psi^{(2)} | \hat{H}^{(2)} | \Psi^{(2)} \rangle + \int d\vec{r} \left[ V_{ext}^{(1)}(\vec{r}) - V_{ext}^{(2)}(\vec{r}) \right] n_0(\vec{r})$$

$$\langle \Psi^{(1)} | \hat{H}^{(2)} | \Psi^{(1)} \rangle = \langle \Psi^{(1)} | \hat{H}^{(1)} | \Psi^{(1)} \rangle + \int d\vec{r} \left[ V_{ext}^{(2)}(\vec{r}) - V_{ext}^{(1)}(\vec{r}) \right] n_0(\vec{r})$$

Add them together:  $E^{(1)} + E^{(2)} < E^{(2)} + E^{(1)}$

# Hohenberg-Kohn theorem I

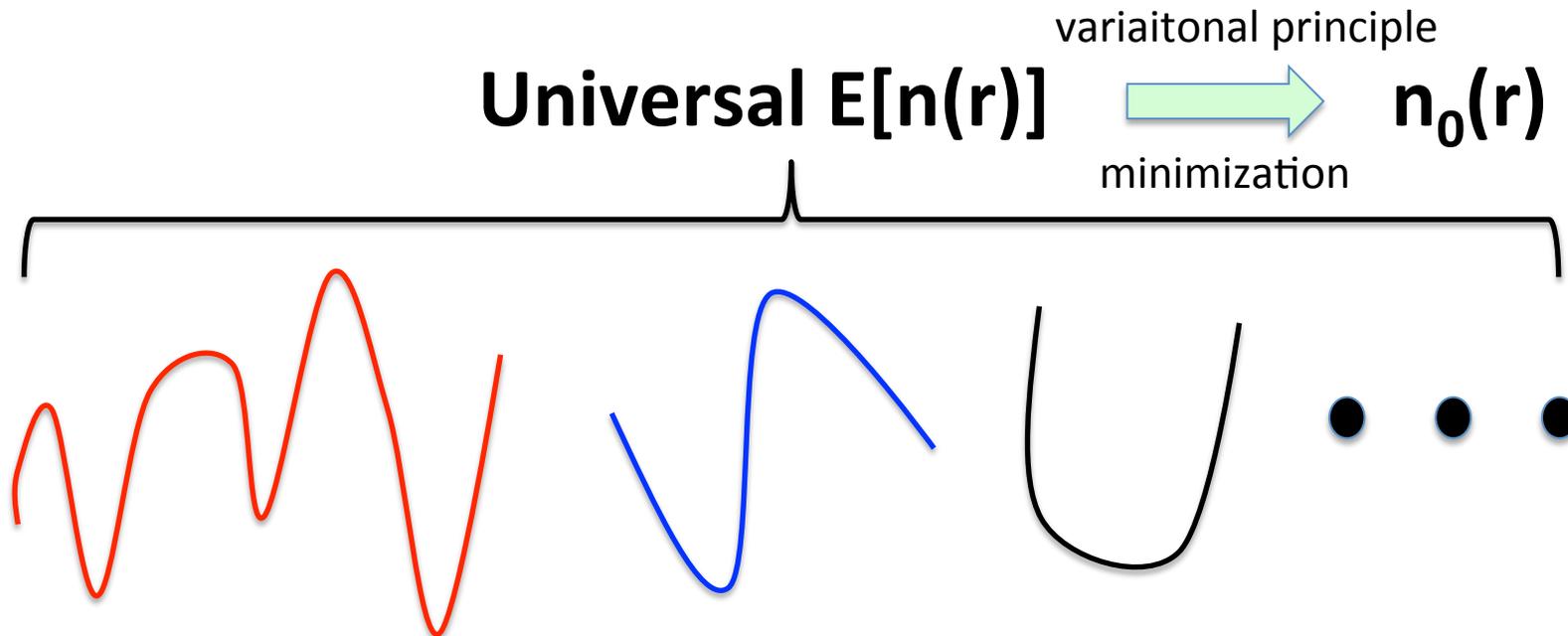
**Theorem I:** For any system of interacting particles in an external potential  $V_{\text{ext}}(r)$ , the potential  $V_{\text{ext}}(r)$  is determined uniquely, except for a constant, by the ground state particle density  $n_0(r)$ .

**Corollary I:** Since the Hamiltonian is fully determined, except for a constant shift of the energy, it follows that the many-body wavefunctions for all states (ground and excited) are determined. **Therefore all properties of the system are completely determined given only the ground state density  $n_0(r)$ .**

$$n_0(r) \Rightarrow V_{\text{ext}}(r) \Rightarrow H$$

# Hohenberg-Kohn theorem II

Theorem II: A **universal functional** for the energy  $E[n]$  in terms of the density  $n(r)$  can be defined, valid for any external potential  $V_{\text{ext}}(r)$ . For any particular  $V_{\text{ext}}(r)$ , the exact ground state energy of the system is the global minimum value of this functional, and the density  $n(r)$  that minimizes the functional is the exact ground state density  $n_0(r)$ .



# Proof of theorem II

**HK I:**

$$n_0(r) \Rightarrow V_{\text{ext}}(r) \Rightarrow H \Rightarrow E[n]$$

$n_1 \quad n_2 \quad n_3 \quad n_4 \quad n_5$

**V-representable**

For a given  $H$ , all properties, such as kinetic energy and interaction energy are uniquely determined.

$$n_0(r) \Rightarrow V_{\text{ext}}(r) \Rightarrow H \text{ and } H \Rightarrow \Psi$$

$$T = \left\langle \Psi \left| -\frac{\hbar^2}{2m} \sum_j \nabla_j^2 \right| \Psi \right\rangle \Rightarrow T[n]$$

$$E_{\text{int}} = \left\langle \Psi \left| \frac{1}{2} \sum_{j \neq j'} \frac{e^2}{|r_j - r_{j'}|} \right| \Psi \right\rangle \Rightarrow E_{\text{int}}[n]$$

$$E_{\text{HK}}[n] \equiv F_{\text{HK}}[n] + \int d^3r V_{\text{ext}}(r) n(r) + E_{\text{II}} \quad \text{where}$$

$$F_{\text{HK}}[n] = T[n] + E_{\text{int}}[n]$$

# Proof of theorem II

Consider ground state density  $n^{(1)}(r)$  corresponding to  $V_{\text{ext}}^{(1)}(r)$ . The ground state wavefunction of  $H^{(1)}$  can be solved as  $\Psi^{(1)}$ . It follows that

$$E^{(1)} = \langle \Psi^{(1)} | H^{(1)} | \Psi^{(1)} \rangle = E_{HK}[n^{(1)}]$$

Now consider a different wavefunction  $\Psi^{(2)}$  and density  $n^{(2)}(r)$

$$E^{(1)} = \langle \Psi^{(1)} | H^{(1)} | \Psi^{(1)} \rangle < \langle \Psi^{(2)} | H^{(1)} | \Psi^{(2)} \rangle = E^{(2)}$$

The density  $n(r)$  that minimizes the functional is the exact ground state density  $n_0(r)$ .

# Hohenberg-Kohn theorem II

Theorem II: A **universal functional** for the energy  $E[n]$  in terms of the density  $n(r)$  can be defined, valid for any external potential  $V_{\text{ext}}(r)$ . For any particular  $V_{\text{ext}}(r)$ , the exact ground state energy of the system is the global minimum value of this functional, and the density  $n(r)$  that minimizes the functional is the exact ground state density  $n_0(r)$ .

Corollary II: The functional  $E[n]$  alone is sufficient to determine the exact ground state energy and density. In addition, thermal equilibrium properties, e.g., specific heat, are determined directly by the free-energy functional of the density.

# Extensions of HK theorems

## ➤ Spin density functional theory

➤ Spin polarized systems

➤ Zeeman effect:  $H = H_0 + V_m$  with  $V_m = -\vec{\mu} \cdot \vec{B}$

$$E = E_{HK}[n, s] \quad \text{where} \quad n(r) = n(r, \sigma = \uparrow) + n(r, \sigma = \downarrow)$$
$$s(r) = n(r, \sigma = \uparrow) - n(r, \sigma = \downarrow)$$

## ➤ Time-dependent density functional theory (TDDFT)

“Given the initial wavefunction at one time, the evolution at all later times is a unique functional of the time-dependent density”, i.e.,  $n(r) \Rightarrow n(r, t)$ .

➤ Extension of HK to the time domain

➤ A formal theory to study excitations

Runge and Gross, *Phys. Rev. Lett.*, 52: 997-1000, 1984.

# Summary of HK theorems

**Interacting particles in an external potential:**

$$H = -\frac{\hbar^2}{2m} \sum_i \nabla_i^2 + \sum_i V_{ext}(r_i) + \frac{1}{2} \sum_{i \neq j} \frac{e^2}{|r_i - r_j|}$$

**Hohenberg-Kohn theorem I:**  $n_0(r) \Rightarrow V_{ext}(r)$

**Hohenberg-Kohn theorem II:**  $\delta E_{HK}(n) / \delta n \big|_{n_0} = 0$

$$\Psi(\{r_1, r_2, \dots, r_n\}) \Rightarrow n_0(r)$$

The HK theorems reformulate the problem of many interacting particles in terms of a *functional* of the ground state density. However, the exact form of the functional is unknown.

# Hohenberg-Kohn theorems

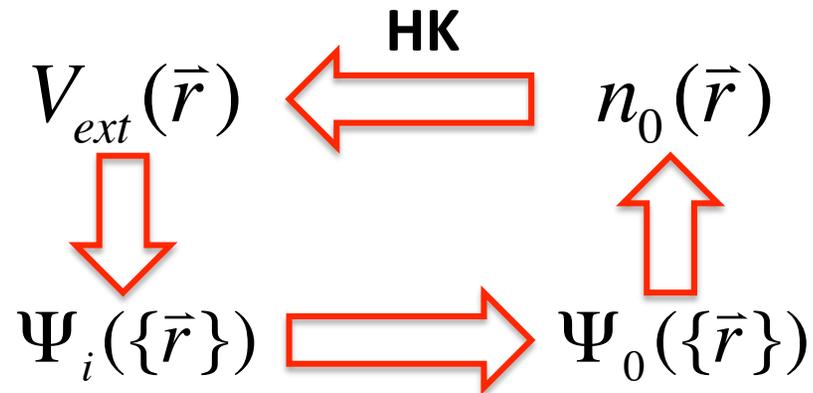
Interacting particles in  
an external potential:

$$H = -\frac{\hbar^2}{2m} \sum_i \nabla_i^2 + \frac{1}{2} \sum_{i \neq j} \frac{e^2}{|r_i - r_j|} + \sum_i V_{ext}(r_i)$$

$$\Psi(\{\vec{r}\}) \longrightarrow n(\vec{r})$$

Hohenberg-Kohn theorem I:  $n_0(r) \Rightarrow V_{ext}(r)$

Hohenberg-Kohn theorem II:  $\delta E_{HK}(n) / \delta n |_{n_0} = 0$



# Homogeneous Electron Gas

$$k_F = (3\pi^2)^{1/3} (n)^{1/3} \quad \text{or} \quad k_F^\sigma = (6\pi^2)^{1/3} (n^\sigma)^{1/3}$$

**Table 5.2.** Characteristic energies for each spin  $\sigma$  for the homogeneous electron gas in the Hartree–Fock approximation: the Fermi energy  $E_{F0}^\sigma$ ; kinetic energy  $T_0^\sigma$  and Hartree–Fock exchange energy per electron  $E_x^\sigma$  which is negative; and the increase in band width in the Hartree–Fock approximation  $\Delta W_{\text{HFA}}$ .

Quantity	Expression	Atomic units
$E_{F0}^\sigma$	$\frac{\hbar^2}{2m_e} (k_F^\sigma)^2$	$\frac{1}{2} (k_F^\sigma)^2$
$T_0^\sigma$	$\frac{3}{5} E_F^\sigma$	$\frac{3}{5} E_F^\sigma$
$-E_x^\sigma$	$\frac{3e^2}{4\pi} k_F^\sigma$	$\frac{3}{4\pi} k_F^\sigma$

# Thomas-Fermi-Dirac approximation: Example of a functional

## ➤ Local approximation

$$n \Rightarrow n(r) \quad r_s \Rightarrow r_s(r) \quad k_F \Rightarrow k_F(r)$$

## ➤ TF functional

$$E_{TF}[n] = C_1 \int d^3r n(r)^{5/3} + \int d^3r V_{ext}(r) n(r)$$

$$+ C_2 \int d^3r n(r)^{4/3} + \frac{1}{2} \int d^3r d^3r' \frac{n(r)n(r')}{|r-r'|}$$

Kinetic energy  
 $\sim k_F^2$  per electron

Local exchange energy  
 $\sim k_F$  per electron

Hartree energy

Minimize TFD functional against  $n(r)$  subject to the constrain of total number of electrons:

$$\int d^3 r n(r) = N.$$

The solution can be obtained from unconstrained minimization of the new functional,

$$\Omega_{TF}[n] = E_{TF}[n] - \mu \left\{ \int d^3 r n(r) - N \right\},$$

where the Lagrange multiplier  $\mu$  is the Fermi energy.

The variational principle requires  $\delta\Omega_{TF}[n]/\delta n = 0$ .

$$\delta\Omega_{TF}[n] = \int d^3 r \left\{ \frac{5}{3} C_1 n(r)^{2/3} + \underbrace{V_{ext}(r) + \frac{4}{3} C_2 n(r)^{1/3} + \int d^3 r' \frac{n(r')}{|r-r'|}}_{V_{eff}(r)} - \mu \right\} \delta n(r)$$

TF variational equation:

$$\frac{1}{2} (3\pi^2)^{2/3} n(r)^{2/3} + V_{eff}(r) - \mu = 0$$

# TF approximation

➤ Truly a density functional

➤ Weizsacker gradient correction

$$\frac{1}{4}(\nabla n^\sigma(r))^2/n^\sigma(r) \quad \text{or} \quad \frac{1}{36}(\nabla n^\sigma(r))^2/n^\sigma(r)$$

C. F. von Weizsacker, *Z. Phys.* 96: 431, 1935

➤ TF in practice

➤ The approximations are too crude

➤ Missing essential physics and chemistry, e.g., shell structure of atoms and binding of molecules

# Hartree approximation

$$\left\{ -\frac{1}{2} \nabla^2 + v_H(r) \right\} \varphi_j(r) = \epsilon_j \varphi_j(r)$$

$$v_H(r) = -\frac{Z}{r} + \int \frac{n(r')}{|r - r'|} dr'$$

$$n(r) = \sum_{j=1}^N |\varphi_j(r)|^2$$

- A set of self-consistent single particle equations to treat atoms
- Kinetic energy derived from the non-interacting system
- Much better description of the atomic ground state than TF

# Early DFT practice: TFD and Hartree App.

$$\frac{1}{2} (3\pi^2)^{2/3} n(r)^{2/3} + V_{\text{eff}}(r) - \mu = 0$$

$$V_{\text{ext}}(r) + \int d^3r' \frac{n(r')}{|r-r'|} + \frac{4}{3} C_2 n(r)^{1/3}$$

- Truly a density functional
- One equation solves the density
- It does not give the correct shell structure of atoms and binding of molecules

$$\left\{ -\frac{1}{2} \nabla^2 + v_H(r) \right\} \varphi_j(r) = \epsilon_j \varphi_j(r)$$

$$v_H(r) = -\frac{Z}{r} + \int \frac{n(r')}{|r-r'|} dr'$$

$$n(r) = \sum_{j=1}^N |\varphi_j(r)|^2$$

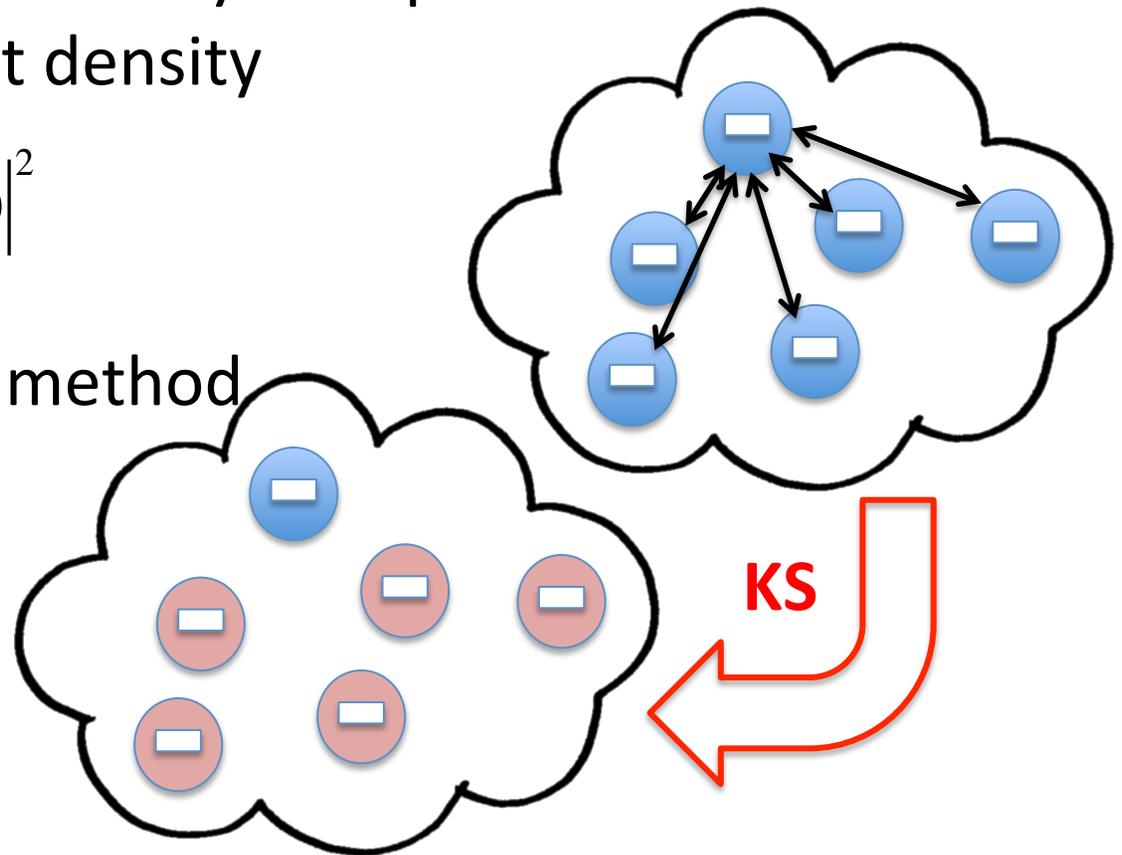
- A set of self-consistent single particle equations to treat atoms
- Kinetic energy derived from the non-interacting system
- Much better description of the atomic ground state than TF

# The Kohn-Sham ansatz

- Replace the original many-body problem by an auxiliary **independent-particle problem**
  - The ground state density is required to be the same as the exact density

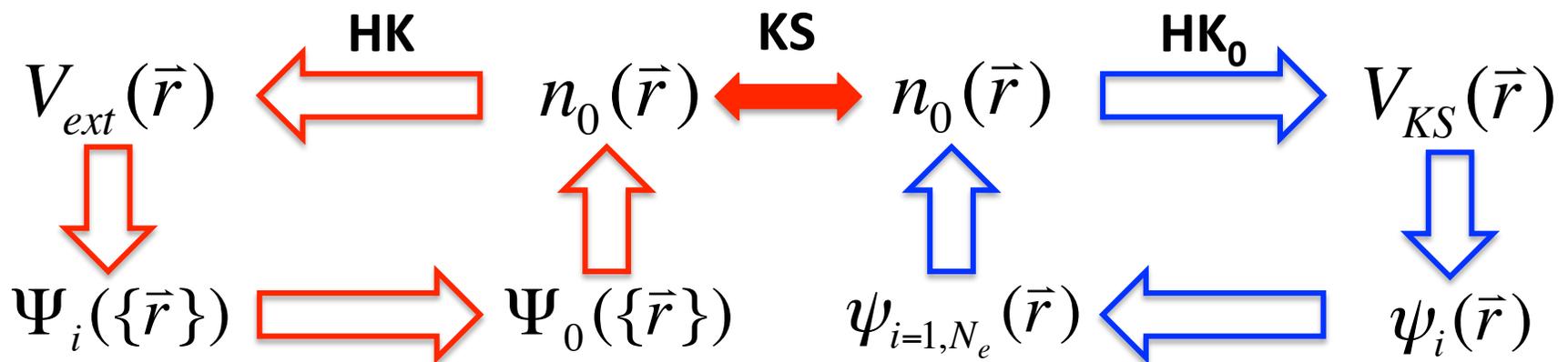
$$n_0(\mathbf{r}) = \sum_{\sigma} \sum_i |\psi_i^{\sigma}(\mathbf{r})|^2$$

- A self-consistent method
- Easy to solve



# The Kohn-Sham ansatz

- There is no rigorous proof for real systems.
  - Weakly correlated systems
  - Strongly correlated systems
- In principle the solution of the auxiliary independent particle system determines all properties of the full many-body system.



# Kohn-Sham energy functional

$$E_{KS}[n] = T_s[n] + \int d^3r V_{ext}(r) n(r) + E_{Hartree}[n] + E_{II} + E_{xc}[n]$$

where

$$T_s[n] = -\frac{1}{2} \sum_{\sigma} \sum_{i=1}^{N_{\sigma}} \langle \psi_i^{\sigma} | \nabla^2 | \psi_i^{\sigma} \rangle = \frac{1}{2} \sum_{\sigma} \sum_{i=1}^{N_{\sigma}} \int d^3r |\nabla \psi_i^{\sigma}|^2$$

$$E_{Hartree}[n] = \frac{1}{2} \int d^3r d^3r' \frac{n(r)n(r')}{|r-r'|}$$

**All the many-body effects are embedded in  $E_{xc}[n]$ , whose exact expression is unknown.**

# Kohn-Sham variational equation

$T_S$  is a functional of  $\psi_i^\sigma$  and all other terms are functionals of density. One can apply variational principle to  $\psi_i^\sigma$

$$\delta E_{KS} / \delta \psi_i^{\sigma*}(r) = 0$$

under the orthonormalization constrains  $\langle \psi_i^\sigma | \psi_j^{\sigma'} \rangle = \delta_{ij} \delta_{\sigma\sigma'}$

$$\frac{\delta}{\delta \psi_i^{\sigma*}} \left\{ E_{KS} - \varepsilon_i^\sigma \sum_{ij} \left( \langle \psi_i^\sigma | \psi_j^{\sigma'} \rangle - \delta_{ij} \delta_{\sigma\sigma'} \right) \right\} = 0$$

Using the results

$$\delta T_S / \delta \psi_i^{\sigma*}(r) = -\frac{1}{2} \nabla^2 \psi_i^\sigma(r) \text{ and } \delta n^\sigma(r) / \delta \psi_i^{\sigma*}(r) = \psi_i^\sigma(r),$$

# Kohn-Sham variational equation

the Kohn-Sham equation is derived as:

$$\left( H_{KS}^{\sigma} - \varepsilon_i^{\sigma} \right) \psi_i^{\sigma}(r) = 0,$$

where

$$H_{KS}^{\sigma}(r) = -\frac{1}{2} \nabla^2 + V_{KS}^{\sigma}(r)$$

and

$$\begin{aligned} V_{KS}^{\sigma}(r) &= V_{ext}(r) + \frac{\delta E_{Hartree}}{\delta n(r, \sigma)} + \frac{\delta E_{xc}}{\delta n(r, \sigma)} \\ &= V_{ext}(r) + V_{Hartree}(r) + V_{xc}^{\sigma}(r). \end{aligned}$$

$$V_{xc}^{\sigma} = \frac{\delta E_{xc}}{\delta n(r, \sigma)} \text{ has to be approximated!}$$

# Local density approximation

- Approximation to  $E_{xc}[n]$  requires information from reference many-body systems of interacting electrons
- Local density approximation (LDA)

$$E_{xc}[n] = \int d^3r n(r) \varepsilon_{xc}([n], r)$$

$$V_{xc}(r) = \frac{\delta E_{xc}([n], r)}{\delta n(r)} = \varepsilon_{xc}([n], r) + n(r) \frac{\delta \varepsilon_{xc}([n], r)}{\delta n(r)}$$

- Approximate  $\varepsilon_{xc}$  based on HEG

$$\varepsilon_{xc}([n], r) \approx \varepsilon_x^{HEG}([n], r) + \varepsilon_c^{HEG}([n], r)$$

# Exchange correlation in HEG

- Solvable model

$$r_s = \left( \frac{3}{4\pi n} \right)^{1/3}$$

$$\mathcal{E}_x^{HEG}(r_s) = -\frac{3}{4\pi} \left( \frac{9\pi}{4} \right)^{1/3} r_s^{-1}$$

known exactly

$$\mathcal{E}_c^{HEG}(r_s) \rightarrow \begin{cases} \frac{a_1}{r_s} + \frac{a_2}{r_s^{3/2}} + \frac{a_3}{r_s^2} + \dots & \text{low density} \\ 0.311 \ln(r_s) - 0.048 + r_s (A \ln(r_s) + C) + \dots & \end{cases}$$

high density: perturbation theory fails

- In between, the correlation energy is obtained by fitting to the QMC data of Ceperley-Alder (1980).

# Local spin density approximation

Functional of  $n(r)$ , fully local:

$$E_{xc}^{\text{LSDA}}[n^\uparrow, n^\downarrow] = \int d^3r n(r) \varepsilon_{xc}(n^\uparrow(r), n^\downarrow(r))$$

Define

$$n = n^\uparrow + n^\downarrow, \xi = \frac{n^\uparrow - n^\downarrow}{n} \quad f_x(\xi) = \frac{1}{2} \frac{(1+\xi)^{4/3} + (1-\xi)^{4/3} - 2}{2^{1/3} - 1}$$

$$\varepsilon_x(n, \xi) = \varepsilon_x(n, 0) + [\varepsilon_x(n, 1) - \varepsilon_x(n, 0)] f_x(\xi)$$

fully polarized    unpolarized

$$\varepsilon_c(n, \xi) = \varepsilon_c(n, 0) + [\varepsilon_c(n, 1) - \varepsilon_c(n, 0)] f_x(\xi)$$

- Different parameterizations in use:
  - PW92, Perdew and Wang, Phys. Rev. B 45, 13244 (1992)
  - PZ, Perdew and Zunger, Phys. Rev. B 23, 5048 (1981)
  - VWN (SVWN5), S. H. Vosco, L. Wilk, and M. Nusair, Can. J. Phys. 58, 1200 (1980)
- See Appendix B1 of R.Martin's "Electronic Structures" for analytic forms for  $\varepsilon_c$ .

# Typical errors for atoms, molecules, and solids

J. Perdew and S. Kurth, “Density Functionals for Non-relativistic Coulomb Systems in the New Century” (2003)

Property	LSD
$E_x$	5% (not negative enough)
$E_c$	100% (too negative)
bond length	1% (too short)
structure	overly favors close packing
energy barrier	100% (too low)

- Despite being a relatively small fraction of  $E_{\text{tot}}$ ,  $E_{xc}$  contributes significantly (about 100%) to the chemical bonding or atomization energy.
- $E_x$  is much larger than  $E_c$  → error cancellation in prediction of  $E_{xc}$  (5-10%).
- Small errors in bond length: Geometry and vibration (phonons) are usually good.
- Large errors in energy barrier and dissociation energies: Not good for thermochemistry.



# Generalized gradient approximation (GGA)

Functional of  $n(\mathbf{r})$  and  $|\nabla n(\mathbf{r})|$ , **semilocal**

$$E_{\text{xc}}^{\text{GGA}}[n^\uparrow, n^\downarrow] = \int d^3r n(r) \varepsilon_{\text{xc}}(n^\uparrow, n^\downarrow, |\nabla n^\uparrow|, |\nabla n^\downarrow|)$$

$$V_{\text{xc}}[n(\mathbf{r})] = \frac{\partial E_{\text{xc}}[n]}{\partial n(\mathbf{r})} - \nabla \cdot \frac{\partial E_{\text{xc}}[n]}{\partial(\nabla n(\mathbf{r}))}$$

Use exact conditions to constrain construction

- PW91, PBE (non-empirical), B88, BLYP (empirical)
- Accuracy (for chosen sets) versus transferability (outside the sets)
- See Appendix B2 of R.Martin's "Electronic Structures" for analytic forms of PBE

# Comparison of LSDA and GGA

Typical errors for atoms, molecules, and solids

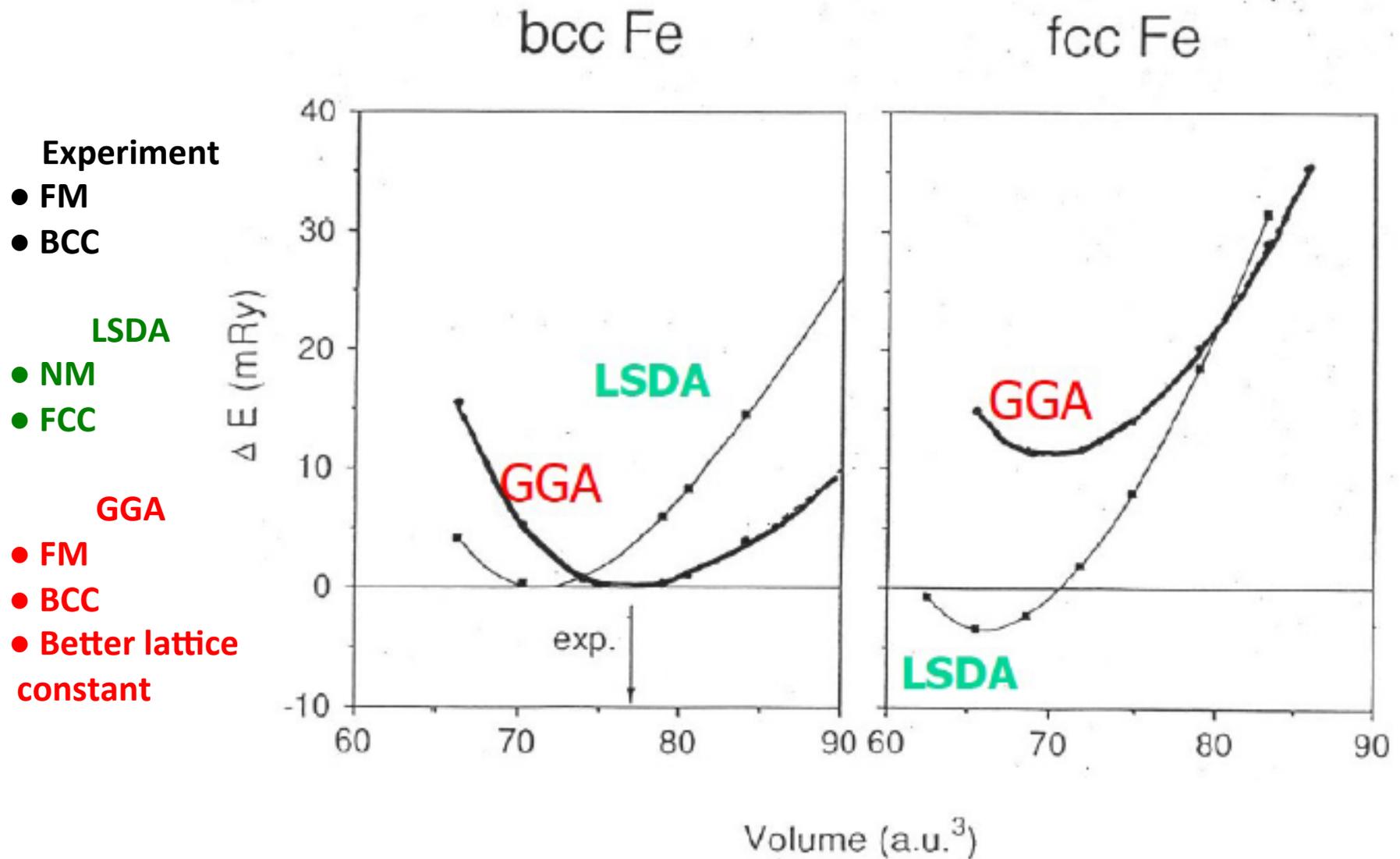
Property	LSD	GGA
$E_x$	5% (not negative enough)	0.5%
$E_c$	100% (too negative)	5%
bond length	1% (too short)	1% (too long)
structure	overly favors close packing	more correct
energy barrier	100% (too low)	30% (too low)

Mean absolute error of the atomization energies for 20 molecules

Approximation	Mean absolute error (eV)
LSD	1.3 (overbinding)
GGA	0.3 (mostly overbinding)
Desired “chemical accuracy”	0.05

J. Perdew and S. Kurth, “Density Functionals for Non-relativistic Coulomb Systems in the New Century” (2003)

# Example: Ground state of solid Fe



# Hybrid Functionals

- Mix in some fraction ( $a$ ) of HF exchange

$$E_{xc}^{\text{hyb}}[n] = a(E_x - E_x^{\text{GGA}}) + E_{xc}^{\text{GGA}}[n]$$

- B3LYP: Most widely used functional in chemistry

$$E_{xc} = (1 - a_0)E_x^{\text{LSDA}} + a_0E_x^{\text{exact}} + a_x\Delta E_x^{\text{B88}} + a_cE_c^{\text{LYP}} + (1 - a_c)E_c^{\text{VWN}}$$

$$a_0 = 0.20, a_x = 0.72, \text{ and } a_c = 0.81.$$

- HSE [ $\alpha=1/4$ ]: range-separated, with adjustable parameters

$$E_{xc}^{\text{PBE0}} = \alpha E_x^{\text{HF}} + (1 - \alpha)E_x^{\text{PBE}} + E_c^{\text{PBE}}$$

$$E_{xc}^{\text{HSE}} = \alpha E_x^{\text{HF,SR}}(\omega) + (1 - \alpha)E_x^{\text{PBE,SR}}(\omega) + E_x^{\text{PBE,LR}}(\omega) + E_c^{\text{PBE}}$$

# Assessment of functionals using G2 test sets

- G2 and extended G2 test sets are often used to assess and improve new theoretical models.
- Original G2 test set: 55 molecules used for comparing theoretical and experimental molecular energies (atomization energies, ionization potentials, electron affinities, and proton affinities) .

L. A. Curtiss, K. Raghavachari, G. W. Trucks, and J. A. Pople, *J. Chem. Phys.* 94, 7221 (1991).

- Extended G2 set (G2 neutral test set): 148 molecules with well-established enthalpies of formation at 298 K, including 29 radicals, 35 nonhydrogen systems, 22 hydrocarbons, 47 substituted hydrocarbons, and 15 inorganic hydrides.

L. A. Curtiss, K. Raghavachari, P. C. Redfern, and J. A. Pople, *J. Chem. Phys.* 106, 1063 ~1997!.

# Test of XC functionals with G2 sets

## Atomization energies (kcal/mol)

Emerhof and Scuseria, JCP , 110, 5029 (1999)

		Mae (G2)	Mae (G2-1)	Max ae (G2)	Max ae (G2-1)
LDA	SVWN <sup>a</sup>	121.2	39.6	229	94
	LSD(SVWN5)	83.7	36.4	216	84
GGA	PBE	17.1	8.6	52	26
	BLYP <sup>a</sup>	7.1	4.7	28	15
meta-GGA	VSXC <sup>b</sup>	2.7	2.5	12	8
hybrid	B3LYP <sup>a</sup>	3.1	2.4	20	10
	PBE1PBE	4.8	3.5	24	10

$$\Delta E = \left| E_{\text{tot}}(\text{mol}) - \sum_{i=1}^{N_{\text{atom}}} E_{\text{tot}}(\text{atom}) \right|$$

## Bond length (Angstrom)

	Mae	Max ae
LSD (SVWN5)	0.016	0.095
PBE	0.014	0.054
BLYP <sup>a</sup>	0.019	0.045
VSXC <sup>a</sup>	0.013	0.075
B3LYP <sup>a</sup>	0.009	0.039
PBE1PBE	0.009	0.055

# Test of XC functionals with G2 sets

Ermerhof and Scuseria, JCP , 110, 5029 (1999)

## Ionization energies (eV)

	Mae (G2-1)	Max ae(G2-1)
SVWN	0.69	1.2
LSD(SVWN5)	0.22	0.6
PBE	0.16	0.5
BLYP <sup>a</sup>	0.20	0.6
VSXC <sup>b</sup>	0.13	0.4
B3LYP <sup>a</sup>	0.17	0.8
PBE1PBE	0.16	0.7

$$I = E(N-1) - E(N)$$

## Electron affinity (eV)

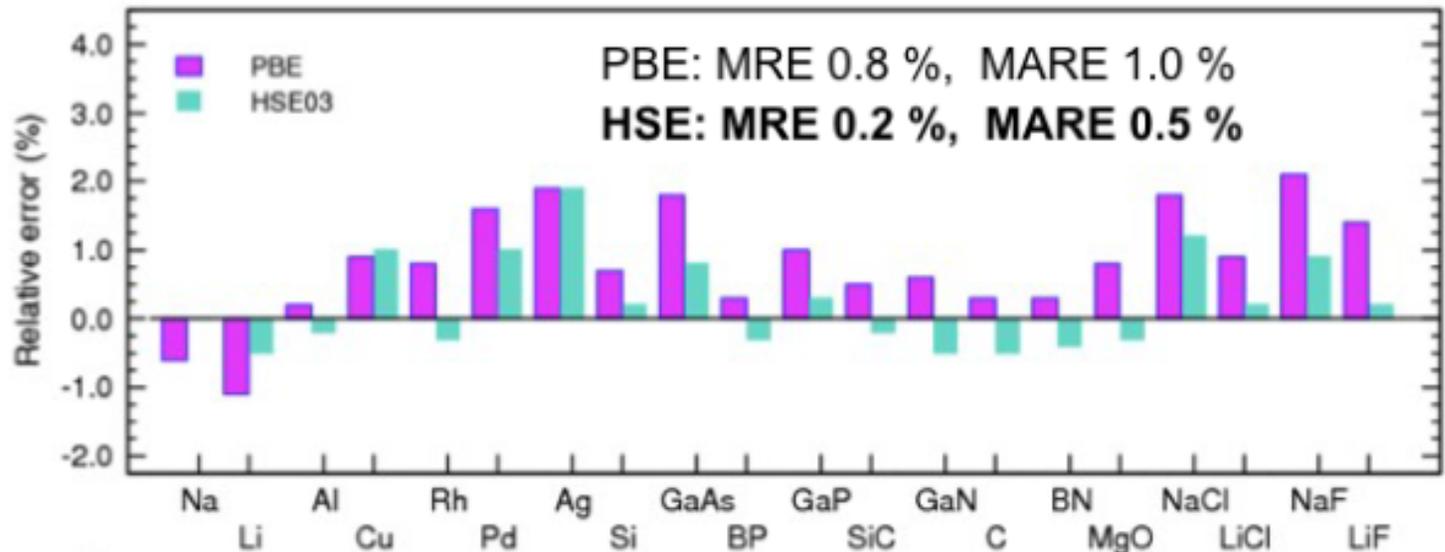
	Mae (G2-1)	Max ae(G2-1)
SVWN <sup>a</sup>	0.74	1.2
LSD (SVWN5)	0.30	0.7
PBE	0.11	0.3
BLYP <sup>a</sup>	0.11	0.4
B3LYP <sup>a</sup>	0.11	0.5
PBE1PBE	0.13	0.3

Hybrid functionals do not improve over GGA for IP and EA.

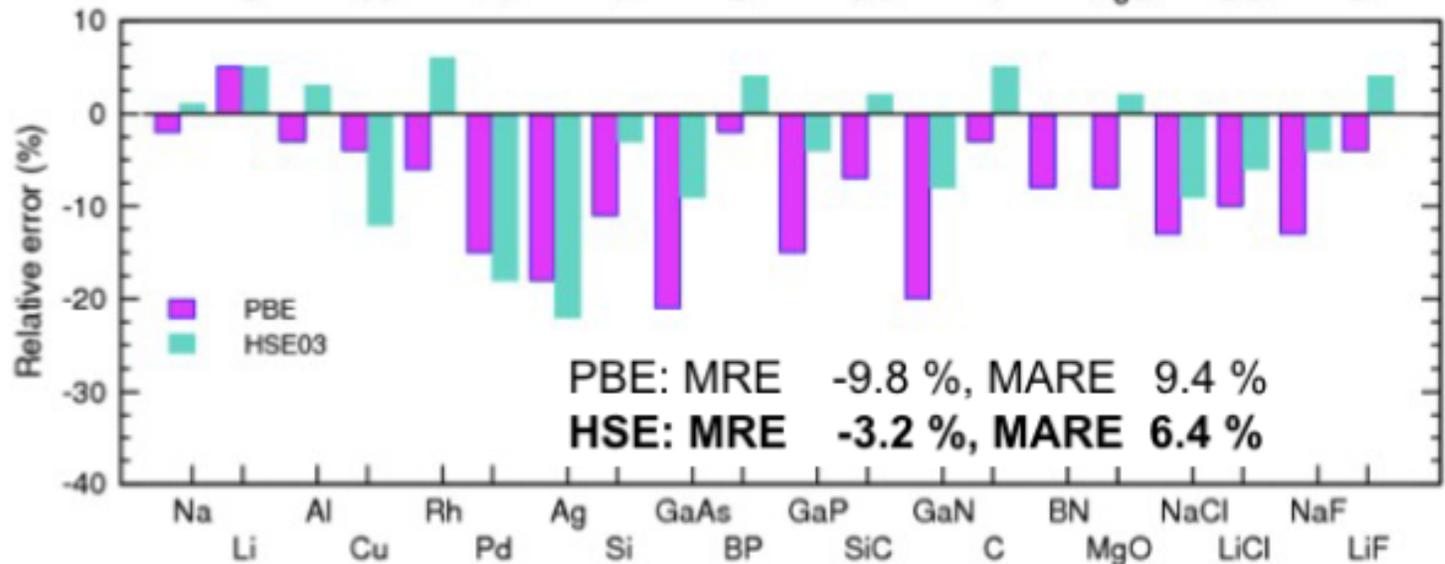
$$A = E(N) - E(N+1)$$

# Test of XC functionals for solids

Lattice constant



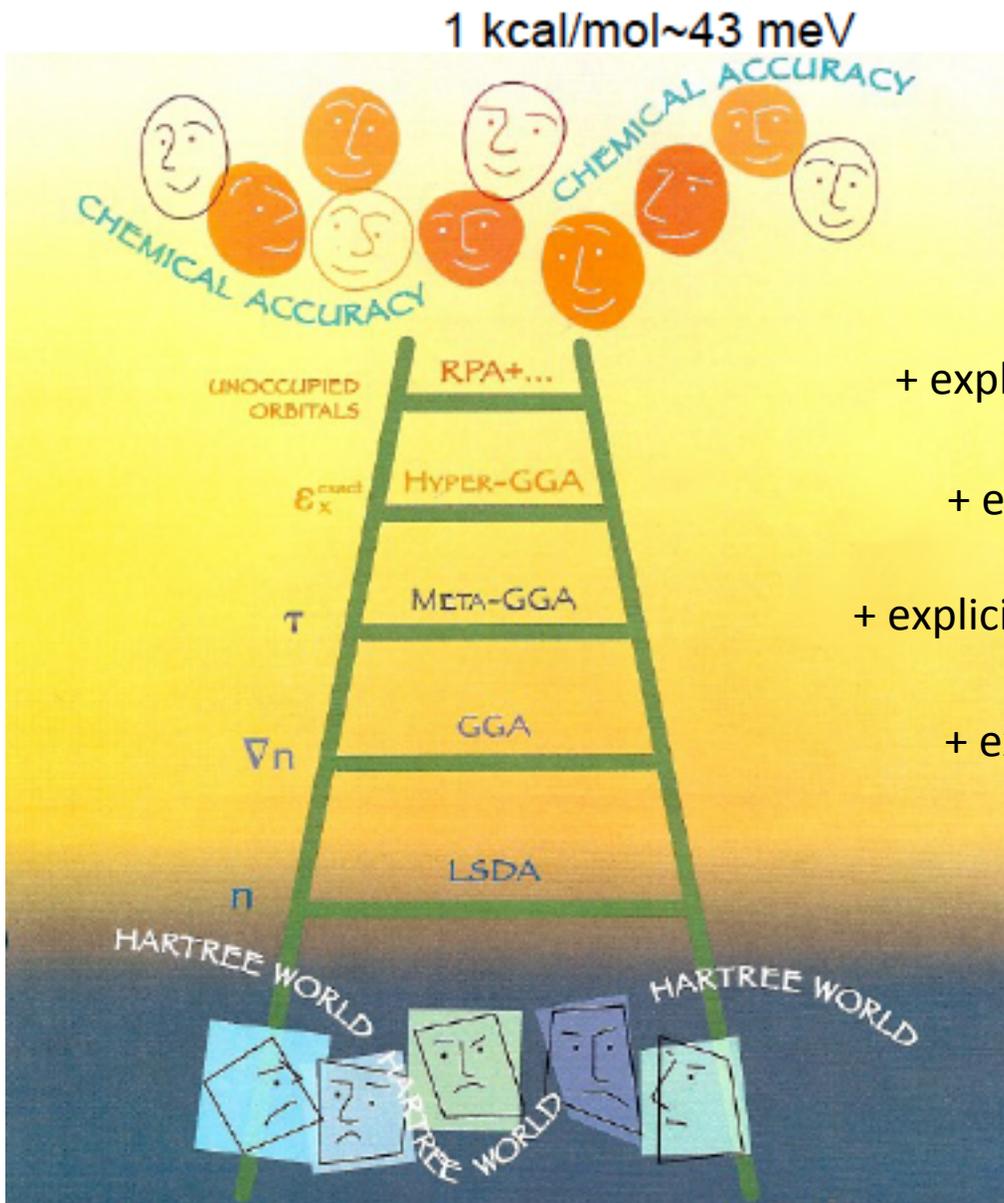
Bulk modulus



# Challenges in DFT

- Self-interaction error (SIE)
  - One electron interacts with its own mean-field
  - incomplete cancellation of self-interactions in Coulomb and exchange terms
  - Self-interaction correction (SIC)  
J. Perdew and Z. Zunger, Phys. Rev. B 23, 5048 (1981)
  - Optimized effective potential (OEP)
- “Band-gap” problem
- van der Waals dispersion is not properly described

# John Perdew's Jacob' ladder to “DFT heaven”



+ explicit dependence on **unoccupied orbitals**

+ explicit dependence on **occupied orbitals**

+ explicit dependence on **kinetic energy density**

+ explicit dependence on **density gradients**

**Local density only**

John P. Perdew and Karla Schmidt, in Density Functional Theory and Its Applications to Materials, AIP Conference Proceedings, Vol. 577, page 1-20.