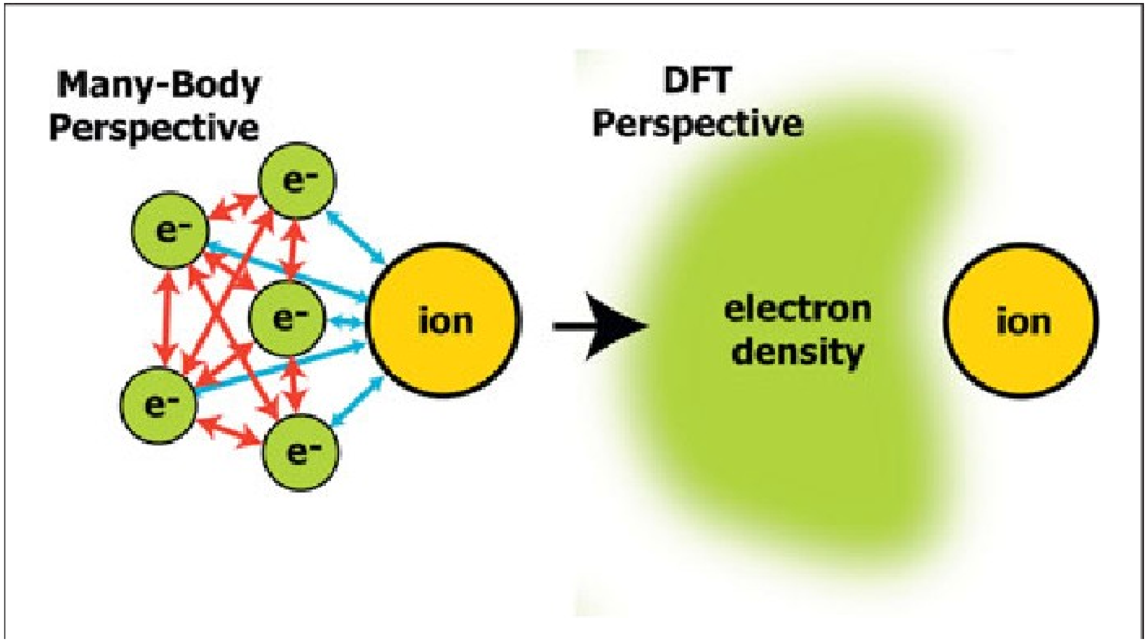
Approximations in DFT



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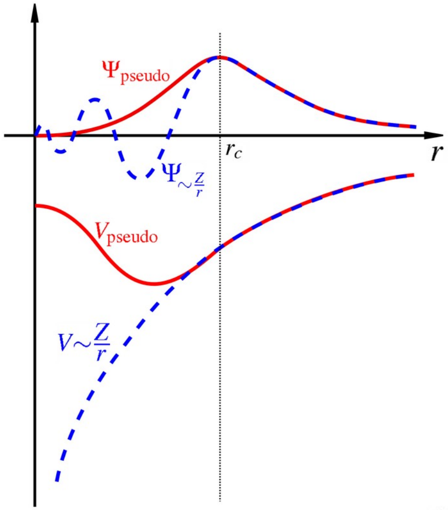
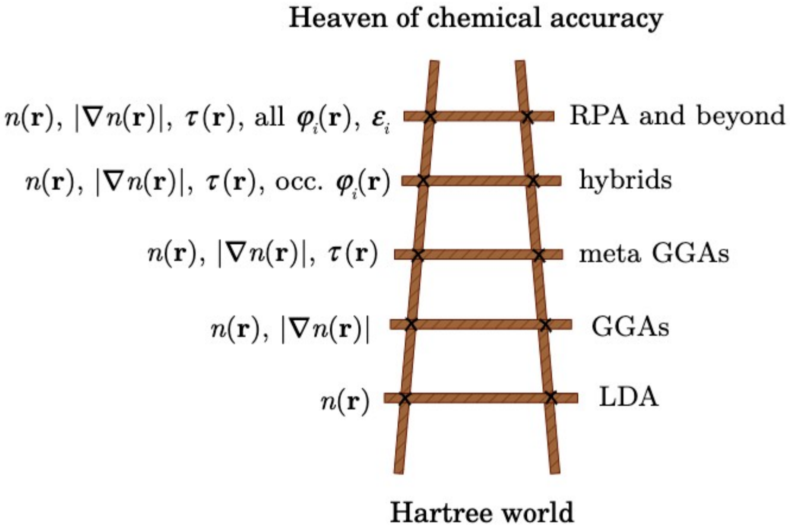
Outline

- Pseudo-potentials



- Exchange-correlation functions



- Miscellaneous

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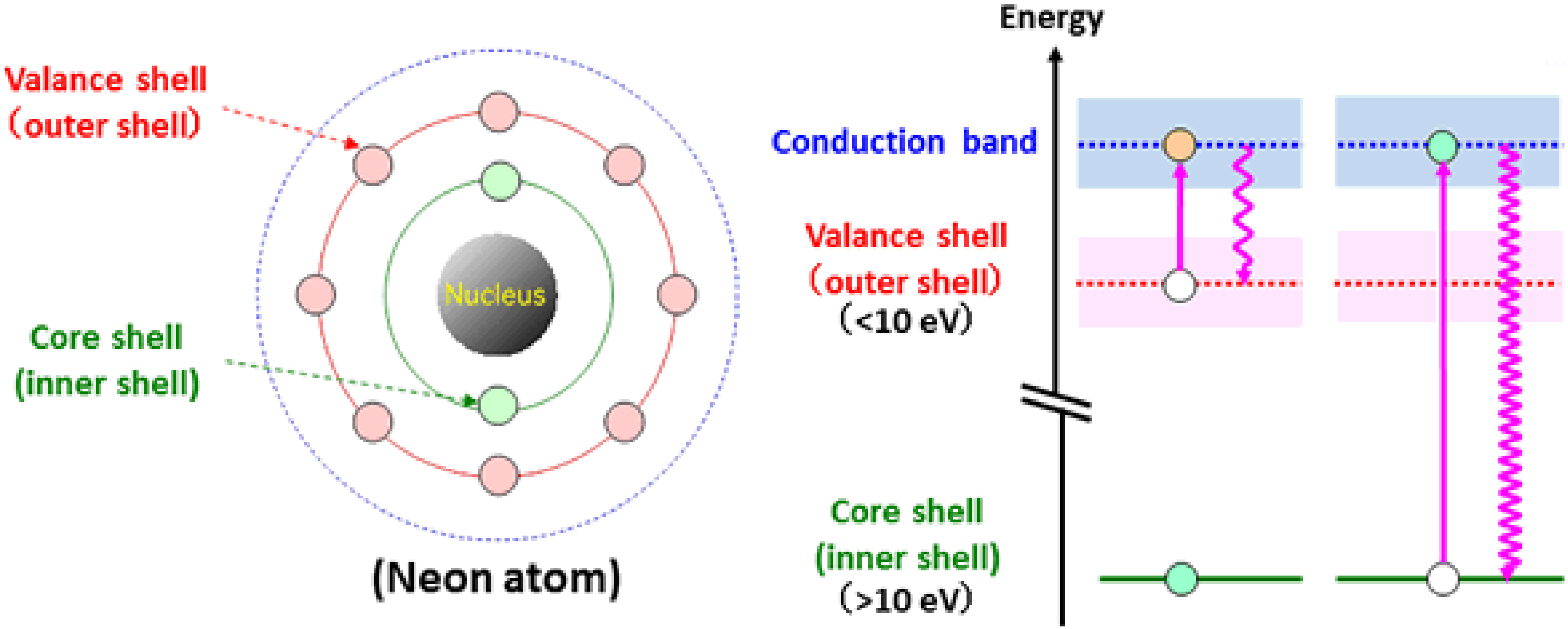
Pseudo-potentials



We do not want to simulate core electrons:

1) they do not participate to chemical reactions, atomic structures, etc..

2) including all electron in the simulations increase computational time/memory

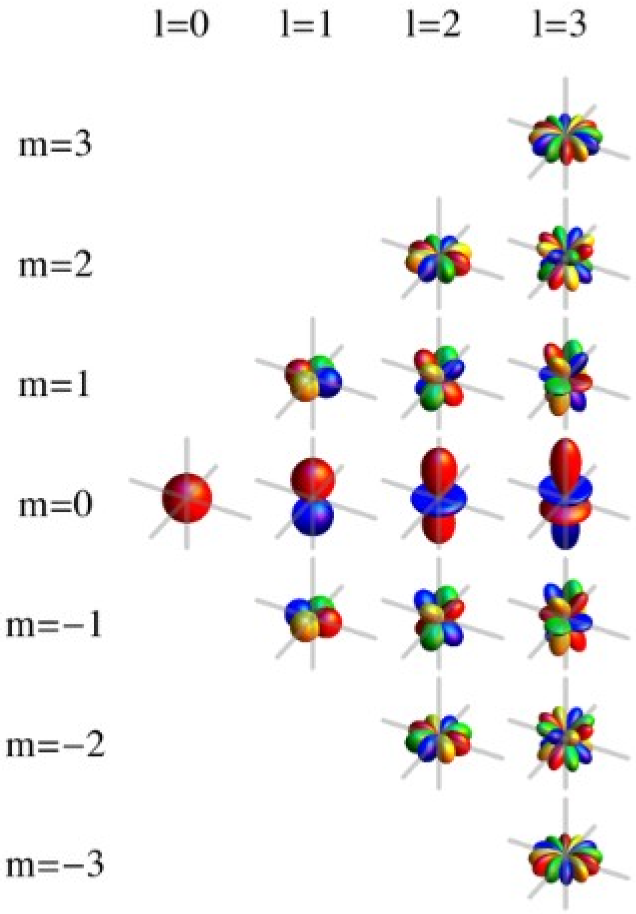
An isolated atom in DFT

For a one-electron atom, the Coulomb potential,
is **spherically symmetric**

$$V(\vec{r}) = V(r) = -Z/r$$

The solutions may be split into a **radial** and an **angular** part

$$\psi_{nlm}(\vec{r}) = \psi_{nl}(r)Y_{lm}(\theta, \phi) = r^{-1}\phi_{nl}(r)Y_{lm}(\theta, \phi)$$



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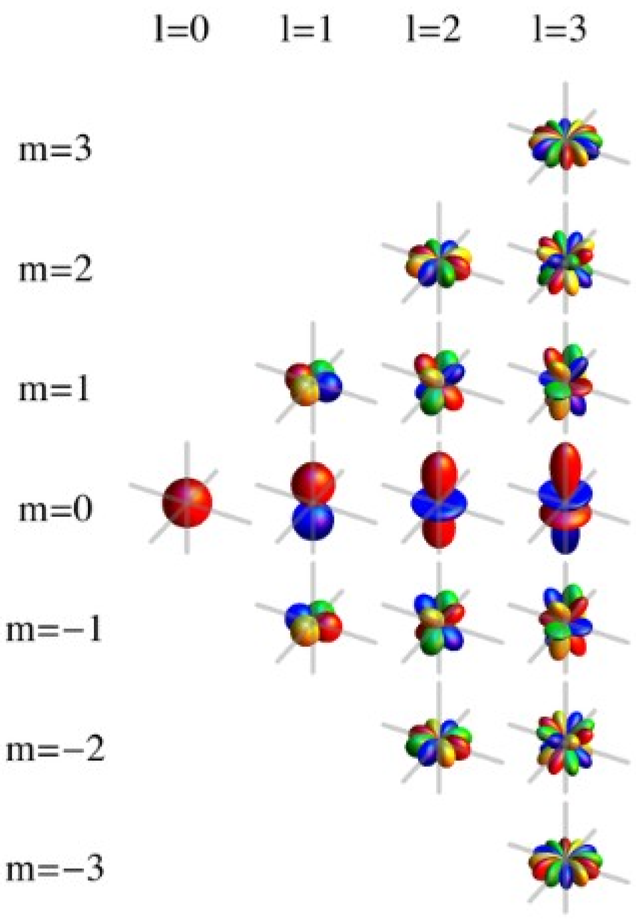
Withint DFT the **independent-particle Kohn-Sham states may be classified by the angular quantum numbers**, subject to the effective potential

$$V_{eff}(r) = V_{ext}(r) + V_H(r) + V_{xc}(r)$$



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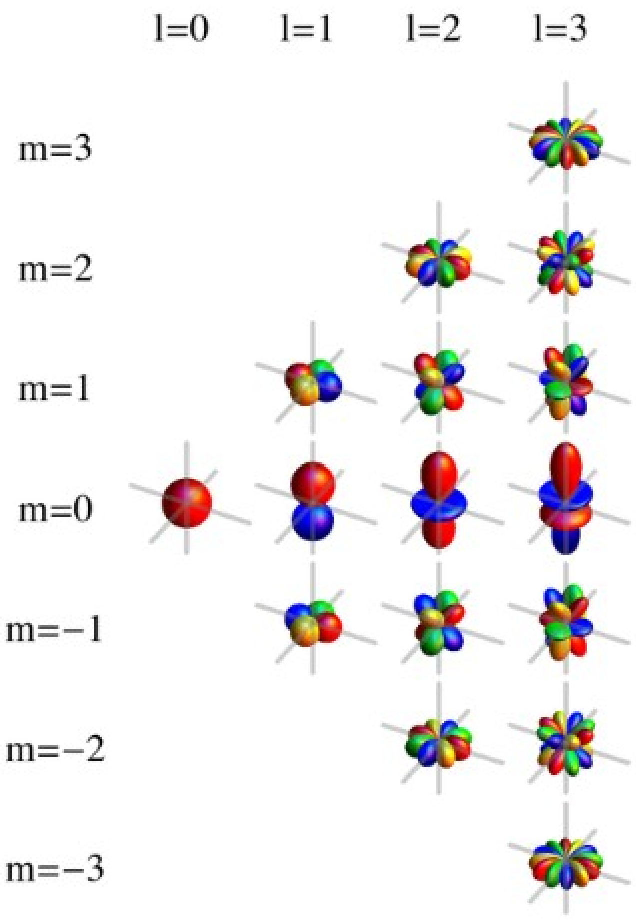
A one particle equation analogous to the Schrödinger equation for the one-electron atom, can be written as:

$$-\frac{1}{2}\frac{d^2}{dr^2}\phi_{nl} + \left[\frac{l(l+1)}{2r^2} + V_{eff}(r) - \epsilon_{n,l}\right]\phi_{n,l} = 0.$$



Pseudopotential idea 1/2

Replacing the effects of the core electrons with an effective potential.

We rewrite the valence states as a smoother function and the remaining portion in terms of core states :

$$|\psi\rangle = |\phi\rangle + \sum_{n}^{\text{core}} a_n |\chi_n\rangle$$

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Next, we consider the product with one of the core states. Because the valence state has to be orthogonal to the core states, we have

$$\langle\chi_n|\psi\rangle = \langle\chi_n|\phi\rangle + \underbrace{\sum_{n}^{\text{core}} a_n \langle\chi_m|\chi_n\rangle}_{a_m} = 0$$

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$$|\psi\rangle = |\phi\rangle - \sum_{n} \langle\chi_n|\phi\rangle |\chi_n\rangle$$

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Applying the Hamiltonian we get

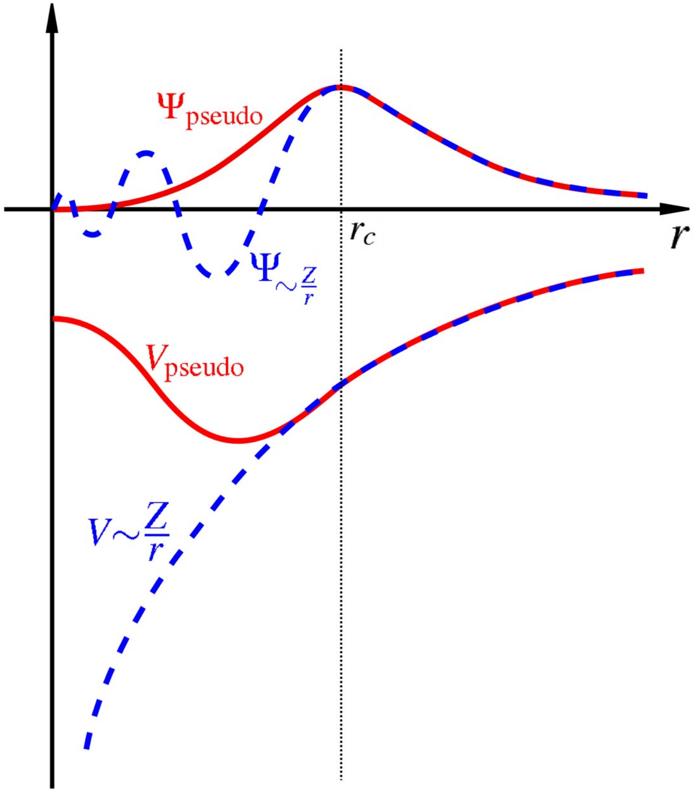
$$\hat{H}|\phi\rangle + \sum_{n}^{\text{core}} (E - E_n)|\chi_n\rangle\langle\chi_n|\phi\rangle = E|\phi\rangle \quad \Longrightarrow \quad \left(\hat{H} + \hat{V}_{nl}\right)|\phi\rangle = E|\phi\rangle$$

Pseudopotential idea 2/2

All-electron and pseudo **eigenvalues agree for the reference configuration**.

$$\hat{H}|\psi_{nl}^{AE}\rangle = \epsilon_{nl}|\psi_{nl}^{AE}\rangle$$

$$\left(\hat{H} + \hat{V}_{nl}\right)|\psi_{nl}^{PS}\rangle = \epsilon_{nl}|\psi_{nl}^{PS}\rangle$$



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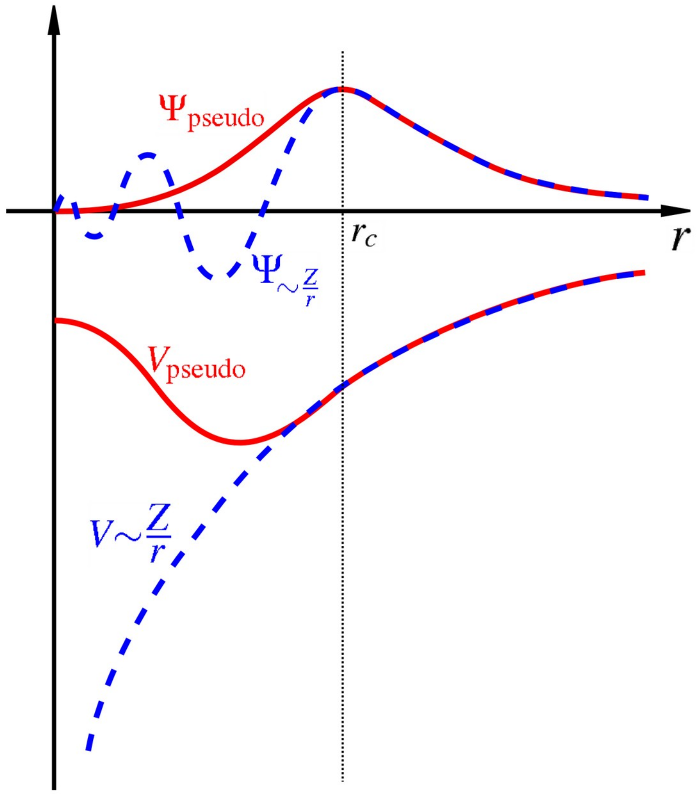

All-electrons and pseudo-wavefunctions agree beyond a certain cutoff, r_c

$$\psi_{nl}^{AE}(r) = \psi_{nl}^{PS}(r) \quad \text{for} \quad r \geq r_c$$

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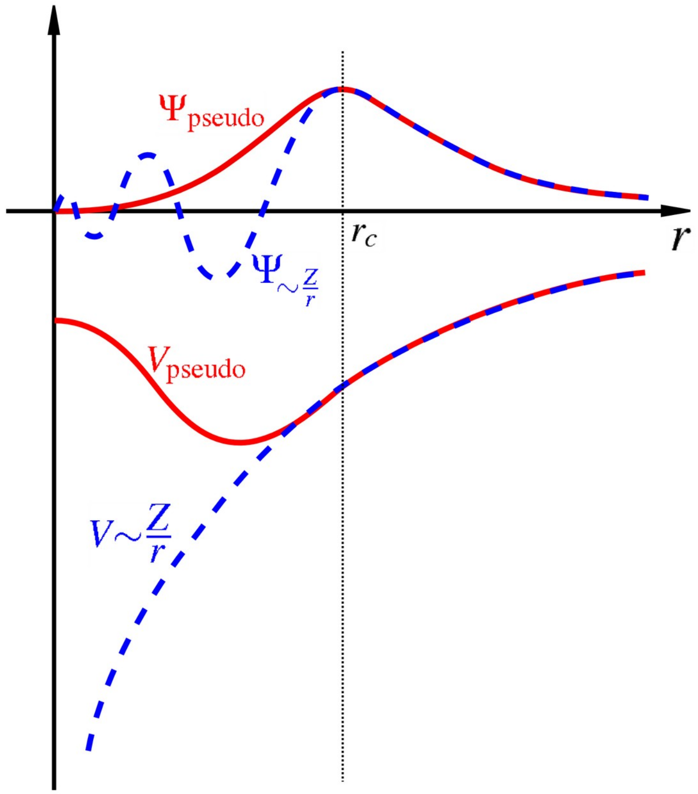

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Real and pseudo norm squares integrated from 0 to R for all R < r_c agree

$$\int_0^R |\phi_{nl}^{AE}|^2 r^2 dr = \int_0^R |\phi_{nl}^{PS}|^2 r^2 dr$$

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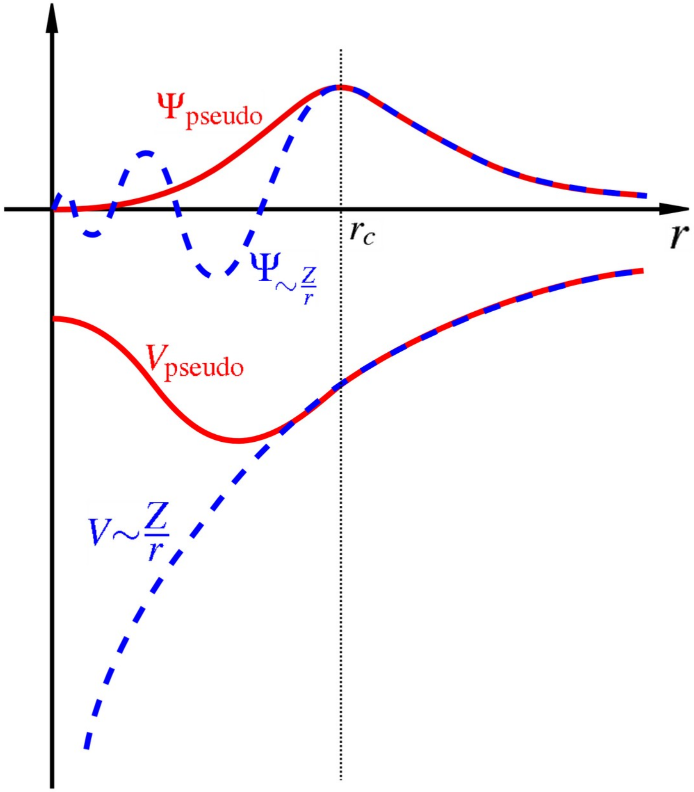

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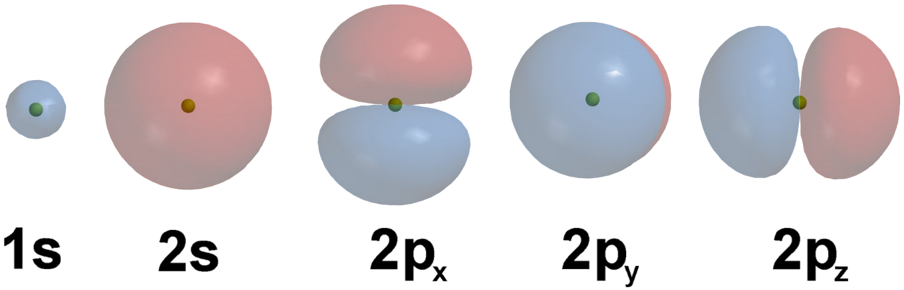
Additional condition for **transferability** [see PRL **43**, 1494 (1979)]

$$\left[(r\phi^{AE}(r))^2 \frac{d}{dE}\frac{d}{dr}\ln\phi^{AE}(r)\right]_R = \left[(r\phi^{PS}(r))^2 \frac{d}{dE}\frac{d}{dr}\ln\phi^{PS}(r)\right]_R$$

How a pseudopotential is constructed

1) Solve the all-electron atomic system



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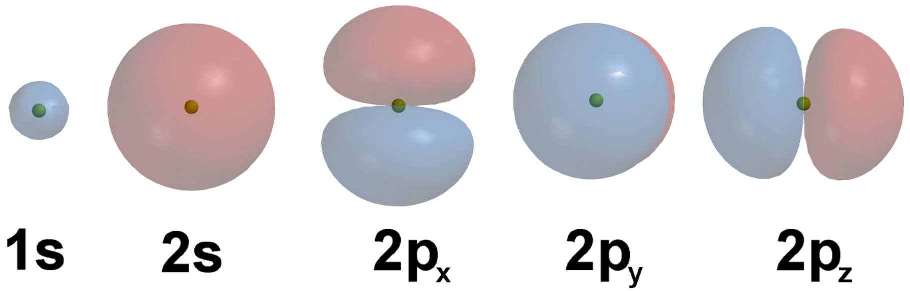
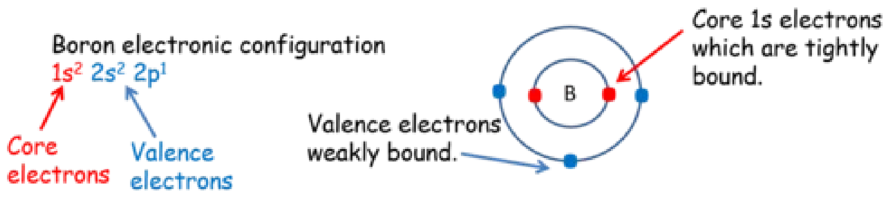


2) Decide which of the states are to be taken as core and which are to be taken as valence



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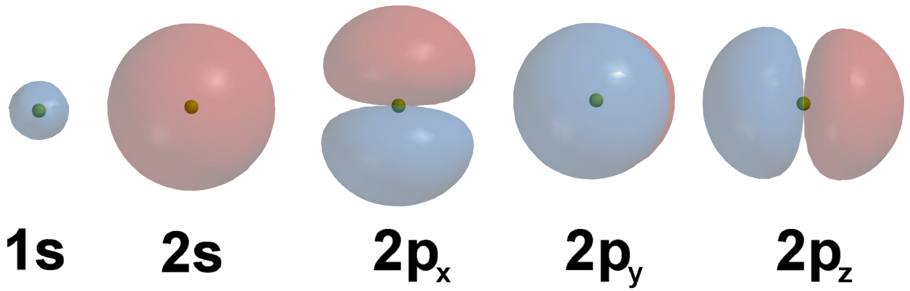

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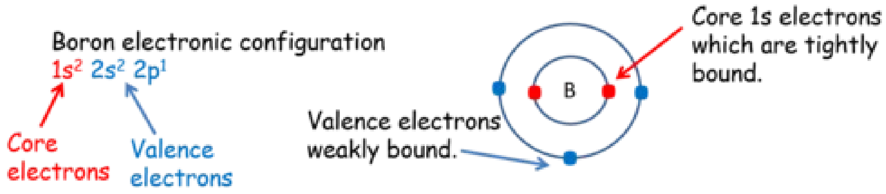
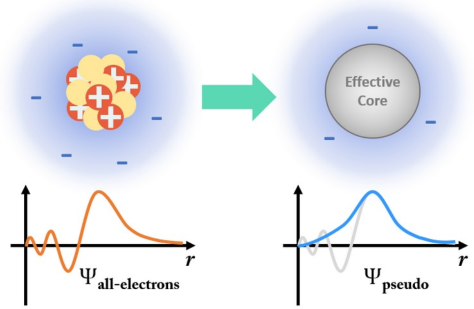


3) Generate the pseudopotentials, $V_{nl}(r)$, for the valence states.



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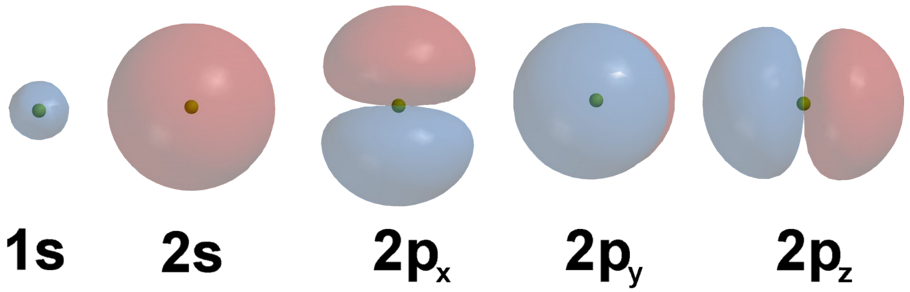

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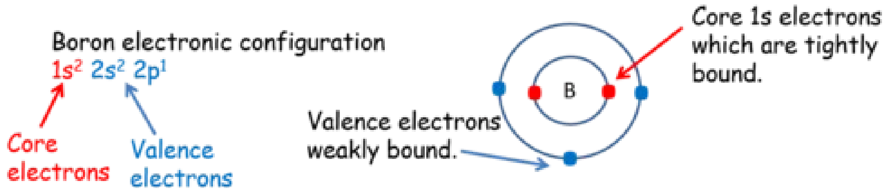

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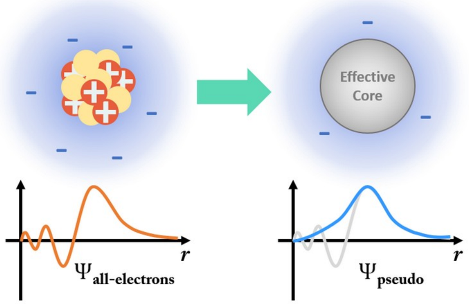


There is no unique way to determine the V_{nl} 's. There are two opposing considerations :

1. Good transferability ⇒ small r_c .
2. Large r_c ⇒ smoother pseudopotentials.

Exchange-correlation functions

‘Heaven’
Chemical Accuracy

fully non-local

hybrid meta GGA
hybrid GGA

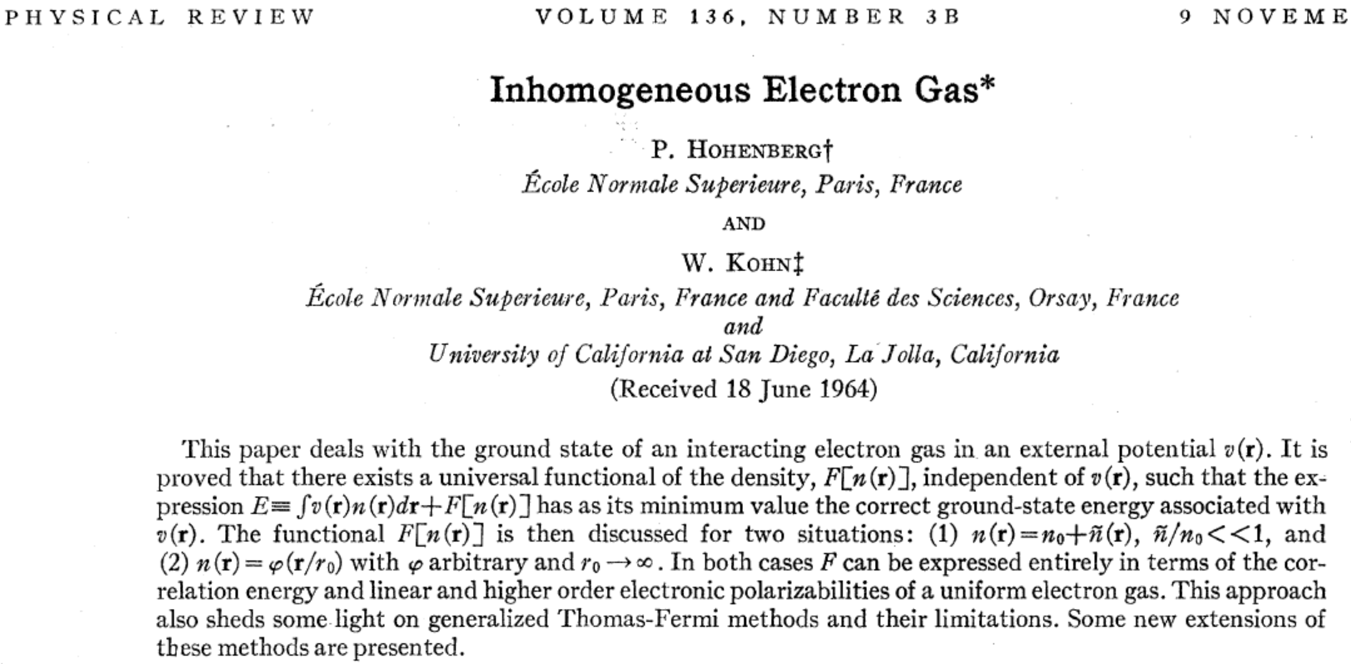
meta GGA

GGA

LSDA

‘Earth’
Hartree Theory

Exchange-correlation functionals



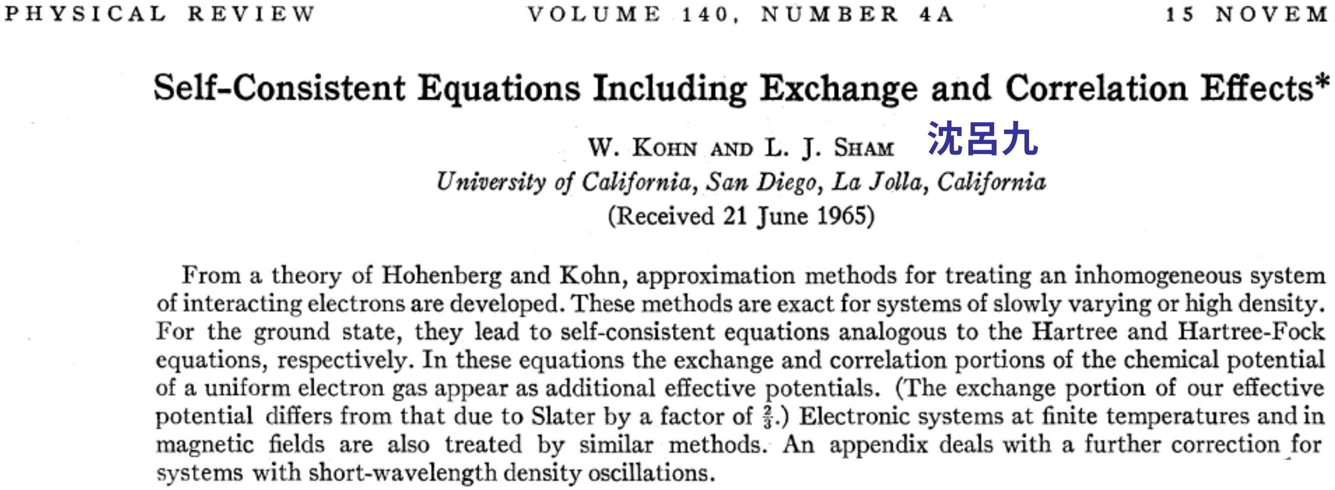
PHYSICAL REVIEW VOLUME 136, NUMBER 3B 9 NOVEMEBR 1964

Inhomogeneous Electron Gas*

P. HOHENBERG†
École Normale Superieure, Paris, France
AND
W. KOHN‡
École Normale Superieure, Paris, France and Faculté des Sciences, Orsay, France
and
University of California at San Diego, La Jolla, California
(Received 18 June 1964)

This paper deals with the ground state of an interacting electron gas in an external potential $v(\mathbf{r})$. It is proved that there exists a universal functional of the density, $F[n(\mathbf{r})]$, independent of $v(\mathbf{r})$, such that the expression $E\equiv\int v(\mathbf{r})n(\mathbf{r})d\mathbf{r}+F[n(\mathbf{r})]$ has as its minimum value the correct ground-state energy associated with $v(\mathbf{r})$. The functional $F[n(\mathbf{r})]$ is then discussed for two situations: (1) $n(\mathbf{r})=n_0+\tilde{n}(\mathbf{r})$, $\tilde{n}/n_0<<1$, and (2) $n(\mathbf{r})=\varphi(\mathbf{r}/r_0)$ with φ arbitrary and $r_0\rightarrow\infty$. In both cases F can be expressed entirely in terms of the correlation energy and linear and higher order electronic polarizabilities of a uniform electron gas. This approach also sheds some light on generalized Thomas-Fermi methods and their limitations. Some new extensions of these methods are presented.

Cited **8578** times (by 11/2011)



PHYSICAL REVIEW VOLUME 140, NUMBER 4A 15 NOVEMBER 1965

Self-Consistent Equations Including Exchange and Correlation Effects*

W. KOHN AND L. J. SHAM 沈呂九
University of California, San Diego, La Jolla, California
(Received 21 June 1965)

From a theory of Hohenberg and Kohn, approximation methods for treating an inhomogeneous system of interacting electrons are developed. These methods are exact for systems of slowly varying or high density. For the ground state, they lead to self-consistent equations analogous to the Hartree and Hartree-Fock equations, respectively. In these equations the exchange and correlation portions of the chemical potential of a uniform electron gas appear as additional effective potentials. (The exchange portion of our effective potential differs from that due to Slater by a factor of $\frac{2}{3}$.) Electronic systems at finite temperatures and in magnetic fields are also treated by similar methods. An appendix deals with a further correction for systems with short-wavelength density oscillations.

Cited **18298** times (by 11/2011)

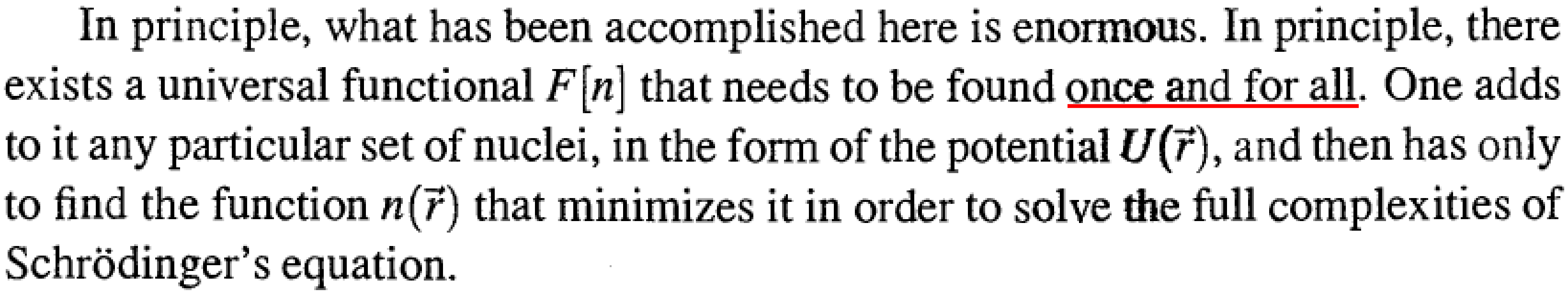
PROBLEM: HK theorem is not a constructive theorem!!

The energy functional

$$
\begin{aligned}
E_G[n] &= T[n] + V_{ee}[n] + U[n] \\
&= F[n] + U[n]
\end{aligned}
$$

$$U[n] = \int d^3r\, n(r) U(r)$$

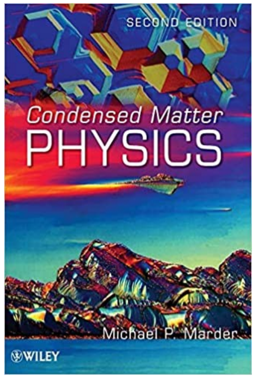
The *F* [n] functional is the same for all electronic systems.



In principle, what has been accomplished here is enormous. In principle, there exists a universal functional $F[n]$ that needs to be found once and for all. One adds to it any particular set of nuclei, in the form of the potential $U(\vec{r})$, and then has only to find the function $n(\vec{r})$ that minimizes it in order to solve the full complexities of Schrödinger's equation.

"No ones knows the true *F* [n], and no one will, so it is replaced by varios uncontrollable approximations."

(Marder, p.247)



We split the problem in various parts….

$$F[n]=T_S[n]+U_H[n]+E_{XC}[n]$$

- **Kinetic energy functional**

$$T_S[n]=\sum_i^{N_v}\langle\phi_i\left|\frac{-1}{2}\nabla_i^2\right|\phi_i\rangle$$

where ϕ_i are KS orbitals

- **Hartree energy functional**

(exact)

$$U_H[n]=\frac{e^2}{2}\int\int d^3r\,d^3r'\,\frac{n(r)n(r')}{|r-r'|}$$

- **Exchange correlation functional**

(unknown)

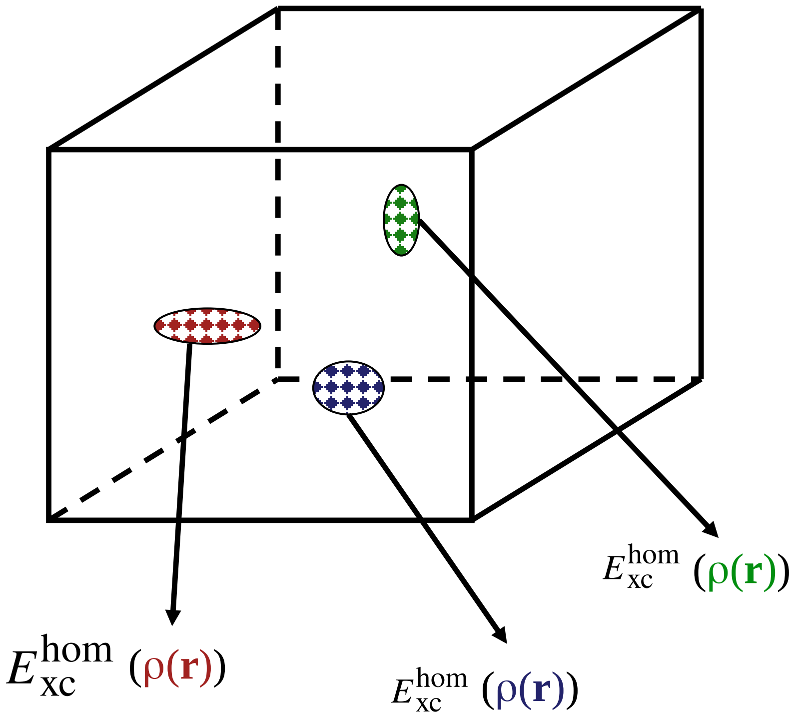
$$E_{XC}[n]$$

$E_{\mathrm{xc}}[n]$ contains $T-T_{\mathrm{s}}$ and $U-U_{\mathrm{H}}$

Local Spin Density Approximation

The value of ε_{xc} at any position $\mathbf{r}$ is calculated using only the value of ρ at that point.

$$E_{\mathrm{xc}}^{\mathrm{LSDA}}=\int \rho(r)[e_x^{\mathrm{hom}}(\rho(r))+e_c^{\mathrm{hom}}(\rho(r))]dr$$

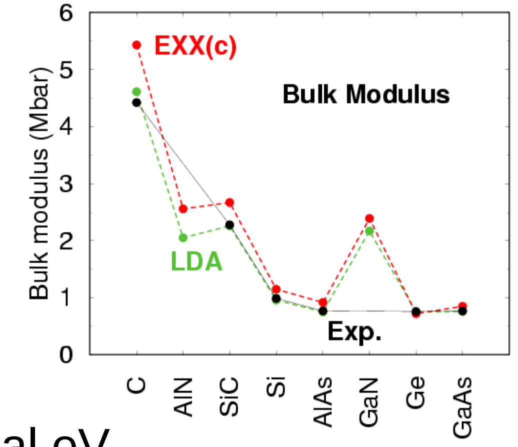


- Exchange Energy

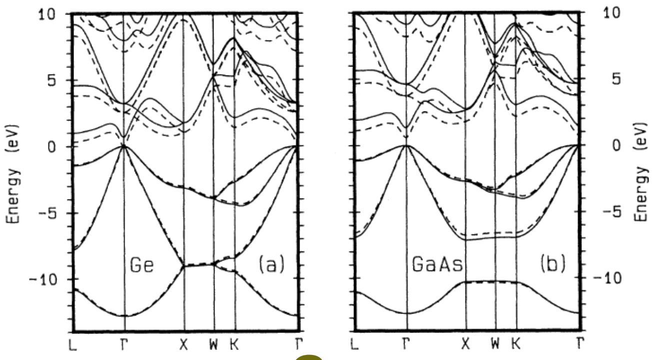
$$E_x[\rho(r)]=\int -\frac{9\alpha}{8}\left(\frac{3}{p}\right)^{1/3}\rho^{4/3}(r)\,dr$$

- Correlation Energy
  - no analytic function for the uniform electron gas. (Cerperley Alder)
  - Vosko, Wilk, Nusair functionals
  - PZ, PW

Local Spin Density Approximation - Performance



- **Structural properties are often good**
  - usually slightly underestimates bulk lattice constants
  - bulk moduli are slightly too large
  - phonons too stiff
- **Binding energies are too negative**
  - overbinding of molecular and metallic solids, up to several eV
  - molecular atomization energies have a large error
- **Activation energies for chemical reactions are unreliable**
- **Relative stabilities of bulk phases can be wrong.**
- **Density of states and band structure are okay but….**



Ge

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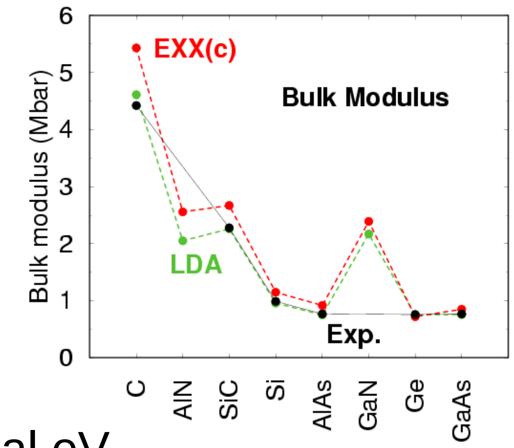

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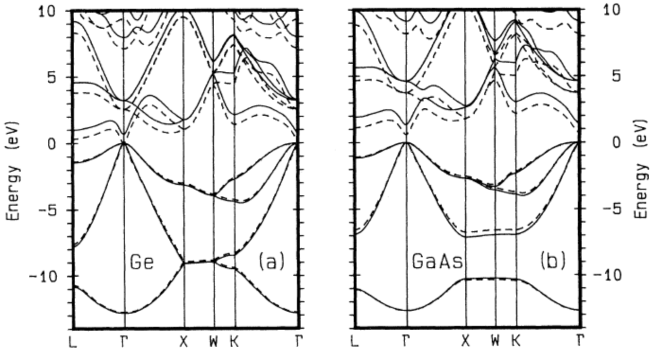

Ge

Why does LSDA work?
- Many metallic systems are similar to a homogeneous electron gas.
- One might expect it to fail for molecular systems (it does!)

What are it’s shortcomings?
- self-interaction

Generalized Gradient Approximation

Based on the idea of doing a Taylor expansion of the density:

$$f(\rho) = f(\rho_0) + f'(\rho_0)(\rho - \rho_o) + \frac{f''(\rho_0)(\rho - \rho_o)^2}{2!} + \ldots$$

it turns out that a simple Taylor expansion does not improve upon LSDA because it violates several of the constraints that the exchange-correlation functional is known to observe.
Also the gradients in real materials are often large enough that the Taylor expansion breaks down.

$$E_{\mathrm{x/c}}^{\mathrm{GGA}}[\rho(\mathbf{r})] = E_{\mathrm{x/c}}^{\mathrm{LSDA}}[\rho(\mathbf{r})] + \Delta E_{\mathrm{x/c}}\left[\frac{|\nabla\rho(\mathbf{r})|}{\rho^{4/3}(\mathbf{r})}\right]$$

Obey the uniform electron gas limit:

$$\lim_{\nabla\rho \to 0} E_{\mathrm{xc}} = E_{\mathrm{xc}}^{\mathrm{LSDA}}$$

Development of Exchange and Correlation Functionals

Empiricism

- We don’t know the exact form of the exchange-correlation functional so write down a form and parameterize it to fit to a set of experimental or high-level *ab-initio* data.

- B88, *m*PW, LYP

Nonempiricism

- The exchange and correlation functional should be developed from first principles by incorporating known constraints. Once the right constraints are met the rest will come out right.

- Often times the functional forms used are the same as, or based on those from empirically based functionals.

- PW91, PBE

Generalized Gradient Approximation

- Bulk lattice constants increase compared in LSDA
- Cohesive energies decrease compared to LSDA
- Atomic and molecular energies are improved
- Corrects over binding of LSDA
- Improves activation barriers, but they’re still too low.
- Improved relative stability of bulk phases.

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Problems with LSDA and GGA

- Self interaction
- Neglect of strong correlations
- Exchange-splitting underestimated for narrow *d*- and *f*-bands.
- Many transition-metal compounds are Mott-Hubbard or charge-transfer (not described by LDA/GGA)

beyond GGA ……   1/2

Meta-GGA Functionals

If we're interested in following the Taylor-like expansion of the density the next logical step is the Laplacian of the density.

$$E[\rho(\mathbf{r})] \Rightarrow \nabla^2\rho(\mathbf{r})$$

B95,B98,KCIS,τHCTH,TPSS

beyond GGA …… 1/2

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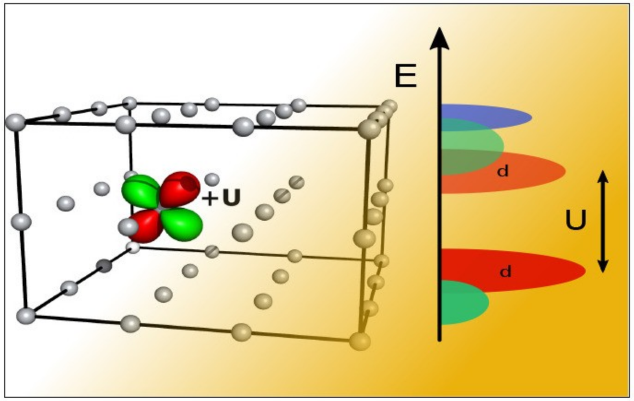
B95,B98,KCIS,τHCTH,TPSS

LDA+U Method

- A generalization of the LSDA method that takes into account orbital dependencies of the exchange and Coulomb interactions.
- The correction is usually only considered for highly localized atomic-like orbitals on the same site.
- The added term serves to shift the energies of the localized orbitals it is applied to relative to the other orbitals.

..it requires U parameter...



SIC -Self-Interaction Correction

Methods that use approximate functionals and add in a “**self-interaction correction**” to correct for the unphysical self-interaction that is present in many functionals.

beyond GGA …… 2/2

Hybrid Functionals (scaling behaviour N^4)

$$E_{\mathrm{xc}}^{\mathrm{hybrid\ DFT}} = (1-a)E_x^{\mathrm{LSDA}} + aE_x^{HF} + bDE_x^{\mathrm{NL}} + E_c^{\mathrm{LSDA}} + cDE_c^{\mathrm{NL}}$$

- Functionals:

  B3PW91, B3LYP, O3LYP, X3LYP

$$E_{\mathrm{xc}}^{\mathrm{hybrid\ DFT}} = (1-a)\left(E_x^{\mathrm{LSDA}} + DE_x^{\mathrm{NL}}\right) + aE_x^{HF} + E_c^{\mathrm{LSDA}} + DE_c^{\mathrm{NL}}$$

- Functionals:

  B1PW91, B1LYP, B1B95, *m*PW1PW91, PBE1PBE

Hybrid meta Functionals (scaling behaviour N^4)

- Hybrid functionals that contain kinetic energy density, in addition to Hartree–Fock exchange.

beyond GGA …… 2/2

Hybrid **F**unctionals (scaling behaviour N⁴)

$$E_{\mathrm{xc}}^{\text{hybrid DFT}} = (1-a)E_{\mathrm{x}}^{\mathrm{LSDA}} + aE_{\mathrm{x}}^{\mathrm{HF}} + b\Delta E_{\mathrm{x}}^{\mathrm{NL}} + E_{\mathrm{c}}^{\mathrm{LSDA}} + c\Delta E_{\mathrm{c}}^{\mathrm{NL}}$$

- Functionals:

  B3PW91, B3LYP, O3LYP, X3LYP

$$E_{\mathrm{xc}}^{\text{hybrid DFT}} = (1-a)(E_{\mathrm{x}}^{\mathrm{LSDA}} + \Delta E_{\mathrm{x}}^{\mathrm{NL}}) + aE_{\mathrm{x}}^{\mathrm{HF}} + E_{\mathrm{c}}^{\mathrm{LSDA}} + \Delta E_{\mathrm{c}}^{\mathrm{NL}}$$

- Functionals:

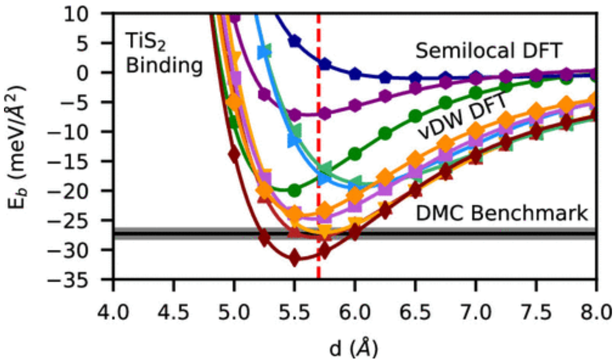
  B1PW91, B1LYP, B1B95, *m*PW1PW91, PBE1PBE

Hybrid meta **F**unctionals (scaling behaviour N⁴)

- Hybrid functionals that contain kinetic energy density, in addition to Hartree–Fock exchange.

Van der Walls **F**unctionals

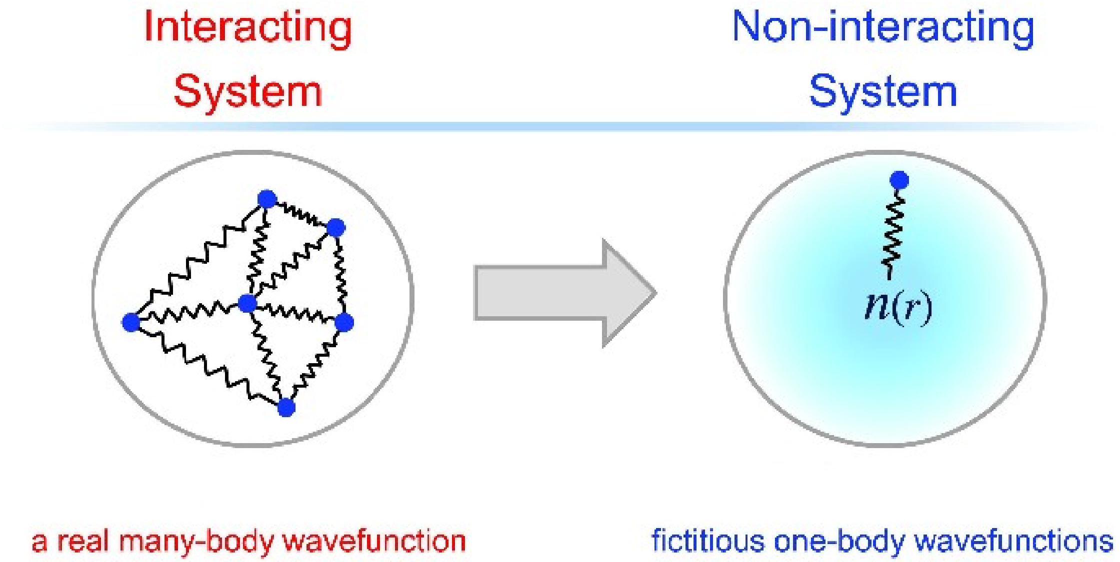
Special functionals designed to give a better description of dispersion (van der Waals) interactions in DFT calculations



Miscellaneous

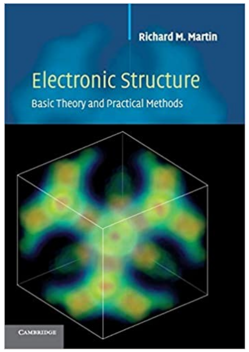
V-representability

The central assumption of KS is that such an equivalent system of non-interacting electrons always exists, i. e., that all interacting density can be represented by a non-interacting one



"a number of 'reasonable' looking densities that have been shown to be impossible to be the ground state density for any V."

R. Martin



Temperature and particles

In a statistical mechanical framework the focus is on the grand canonical potential. Here, the **grand canonical Hamiltonian** plays an analogous role as the one played by the Hamiltonian for the ground-state problem.

$$\hat{\Omega} = \hat{H} - \tau \hat{S} - \mu \hat{N}$$

Where the entropy operator is defined as

$$\hat{S} = -\ k_B \ln \hat{\Gamma} \qquad \hat{\Gamma} = \sum_{N,i} w_{N,i} |\Psi_{N,i}\rangle\langle\Psi_{N,i}|$$

$$\Omega^{\tau}_{v-\mu} = \min_n \left\{ F^{\tau}[n] + \int d^3r\ n(\mathbf{r})(v(\mathbf{r}) - \mu) \right\}$$

Kohn-Sham equations **at non-zero temperature**, and the density

$$n(\mathbf{r}) = \sum_i f_i |\varphi_i(\mathbf{r})|^2 \qquad f_i = \left(1 + e^{(\epsilon_i^{\tau} - \mu)/\tau}\right)^{-1}$$

Thermal Density Functional Theory in Context, https://arxiv.org/abs/1309.3043

Summary

- As one climbs the **Jacob's ladder** of density functionals, the **complexity** and cost of the calculation increase, as does the **accuracy**.
  - LSDA ⇒ density only
  - GGA ⇒ density and gradient of the density
  - metaGGA ⇒ density, gradient of the density, kinetic energy density
  - hybrid ⇒ density, gradient of the density, Hartree–Fock exchange
  - meta hybrid ⇒ density, gradient of the density, kinetic energy density, Hartree–Fock exchange.

- **Different functionals within the same class can give very different results**.
  - its not enough to say that you used GGA. You must specify the use of PBE, BLYP, etc.

Limitations of DFT

- Some systems **cannot be well described by a single Slater determinant**.
- Its hard to know **how to systematically** improve DFT functionals.
- Does **not obey the variational principle**.

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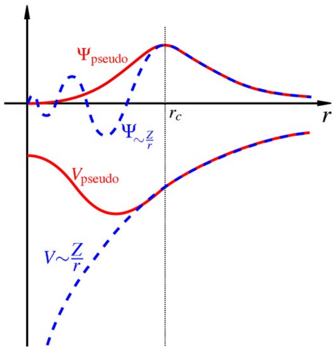
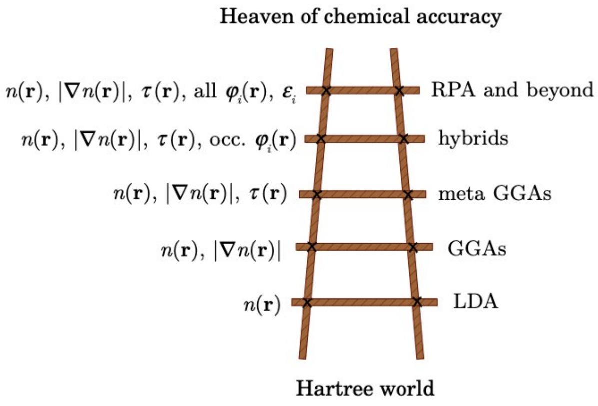


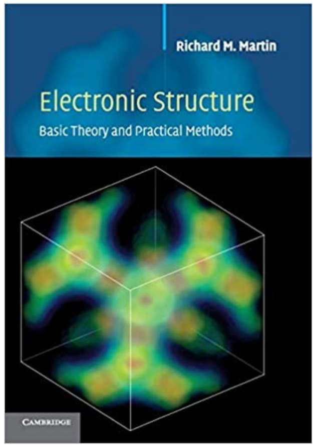
Exchange-correlation funcitions

- Review of approximations for the exchange-correlation energy in density-functional theory
  https://arxiv.org/abs/2103.02645
- Progress in the development of exchange-correlation functionals
  https://www.sciencedirect.com/science/article/pii/B9780444517197500676

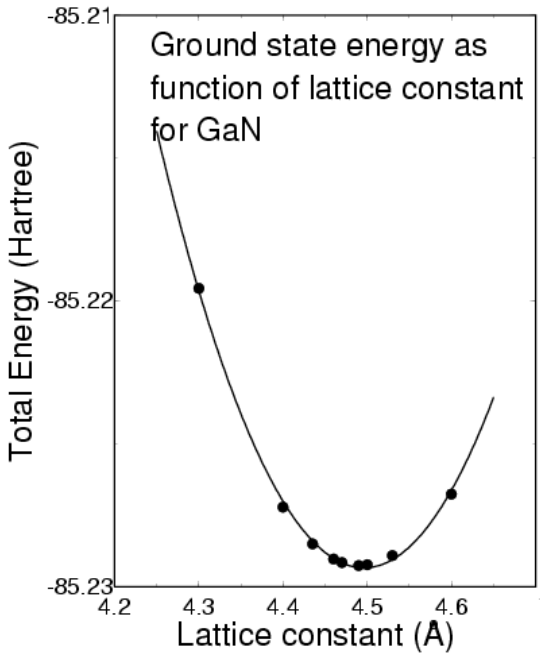


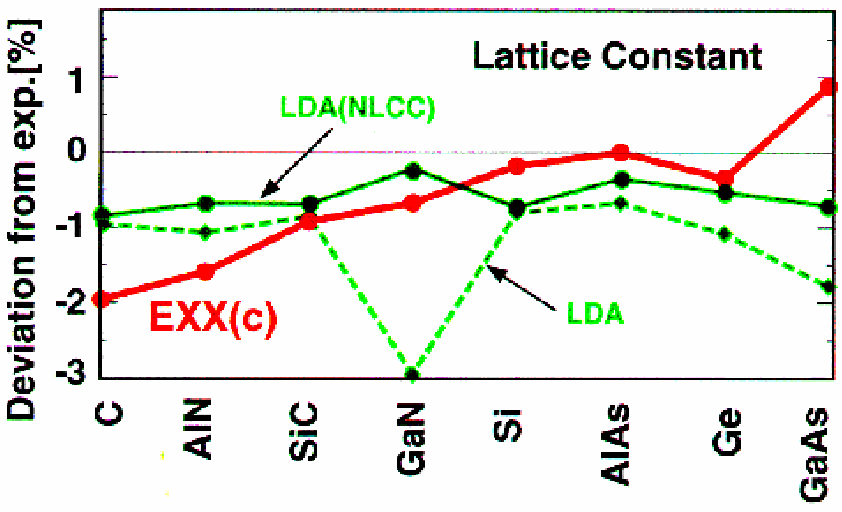
Miscellaneous

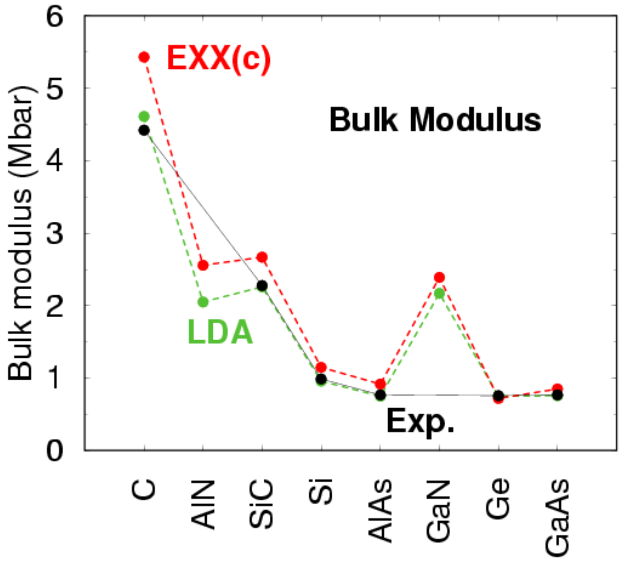
- Thermal Density Functional Theory in Context, https://arxiv.org/abs/1309.3043

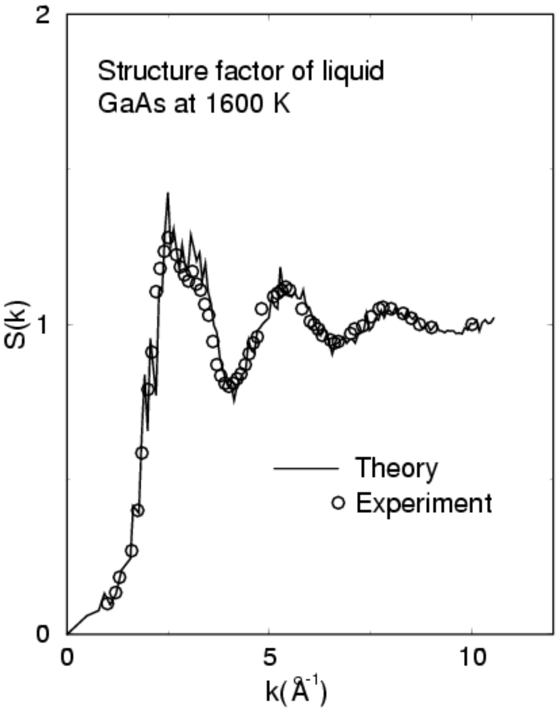


Strength of DFT









From W.Aulbur's slides

Weakness of DFT

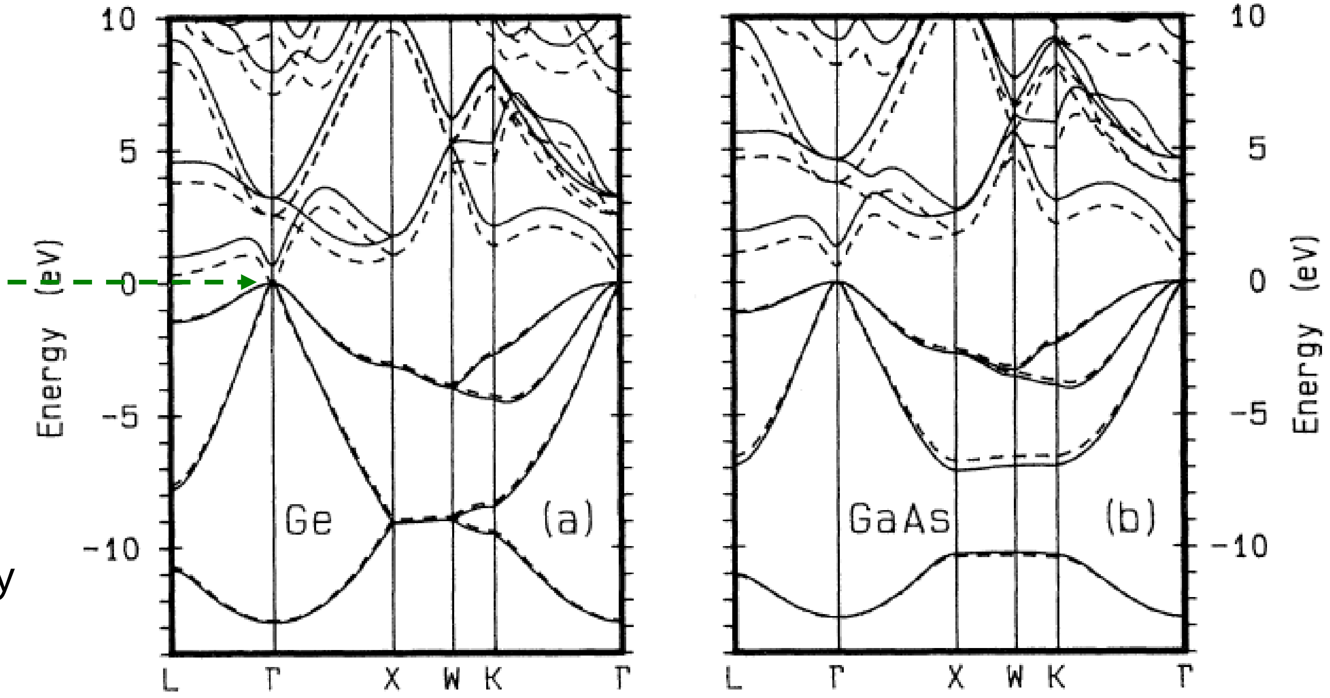
- Band-gap problem: HKS theorem not valid for excited states.

  Band-gaps in semiconductors and insulators are usually underestimated.

LDA DFT Calcs.
(dashed lines)

Metal in "LDA"
calculations

Can be fixed by
GWA…etc



Rohlfing and Louie PRB 1993

- Neglect of strong correlations

  - Exchange-splitting underestimated for narrow *d*- and *f*-bands.
  - Many transition-metal compounds are Mott-Hubbard or charge-transfer insulators, but DFT predicts metallic state.

LDA, GGAs, etc. fail in many cases with strong correlations.

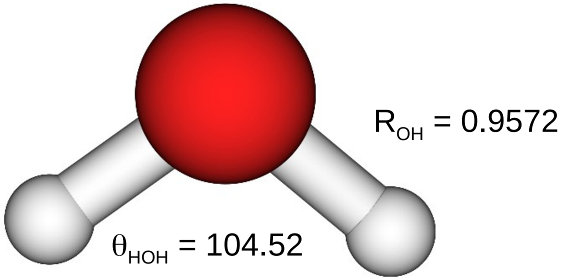
From J. Hafner's slides

Hybrid Functionals

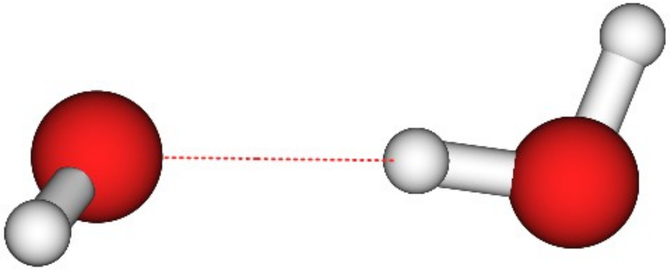
What's the rationale for adding Hartree–Fock exchange??

- LSDA and GGA overbind.
- Hartree–Fock theory underbinds.
- LSDA and GGA give bond lengths that are too long.
- Hartree–Fock theory gives bond lengths that are too short.

Perhaps if we mix the two together we'll get numbers in the middle…



	R(O-H)	Θ(H–O–H)
ΛΣΔΑ	0.9701	104.9605
ΠΒΕ	0.9690	104.2068
ΒΛΨΠ	0.9706	104.5230
ΠΒΕ1ΠΒΕ	0.9575	104.9051
Β3ΛΨΠ	0.9604	105.1265
Ηαρτρεε–Φοχκ	0.9399	106.2709



	Ebind (kcal/mol)
LSDA	7.95
PBE	5.05
BLYP	4.16
PBE1PBE	4.96
B3LYP	4.57
Hartree–Fock	3.49
Accurate	4.99

Hybrid methods also help correct the self-interaction problem, since in Hartree–Fock theory it cancels out.

How do you Determine the Percent of HF Exchange?

- The most common way to determine the amount of Hartree–Fock exchange to include it to treat it as an optimizable parameter.
  - Take a set of molecules for which the atomization energy, ionization potential, and proton affinities are well knows, as well as atomic total energies, and vary the percent of HF exchange until you minimize the unsigned error over this data set.
  - B3PW1, B3LYP,O3LYP, X3LYP

- There are some “parameter free” hybrid density functionals, where the percentage of Hartree–Fock exchange was determined based on a perturbation-theory argument
  - B1B95, *m*PW1PW91, PBE1PBE (PBE0), B1LYP
  - in reality the percentage of HF exchange used cannot be determined nonempirically.

Scaling Behavior

Scaling Behavior	Method
N^3	DFT(LSDA,GGA,meta)
N^4	HF, DFT(hybrid,hybrid meta)
N^5	MP2
N^6	MP3, CISD, MP4DQ, CCSD, QCISD
N^7	MP4,CCSD(T),QCISD(T)
N^8	MP5,CISDT,CCSDT
N^9	MP6
N^{10}	MP7,CISDTQ,CCSDTQ