

Exchange-Correlation Functionals

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Elementary Quantum Mechanics

The one-electron Schrödinger equation:

$$\left[-\frac{\hbar^2 \nabla^2}{2m} + v(\mathbf{r}) \right] \Psi(\mathbf{r}) = E \Psi(\mathbf{r})$$

The many-electron Schrödinger equation:

$$\left[\sum_i^N \left(-\frac{\hbar^2 \nabla_i^2}{2m} + v(\mathbf{r}) \right) + \sum_{i < j} U(\mathbf{r}_i, \mathbf{r}_j) \right] \Psi(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N) = E \Psi(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N)$$

$\sum_{i < j} U(\mathbf{r}_i, \mathbf{r}_j) \Rightarrow$ electron - electron interactions

$v(\mathbf{r}) \Rightarrow$ electron - nuclear attraction

$v(\mathbf{r}) \Rightarrow \Psi(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N) \Rightarrow$ observable properties

Density Functional Theory

$$n(\mathbf{r}) = N \iint \dots \int \Psi^*(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N) \Psi(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N) dr_2 dr_3 \dots dr_N$$

Hohenberg-Kohn Theorem

1. The ground state wave function is a unique function of the ground state density.

$$n(\mathbf{r}) \Rightarrow \Psi(\mathbf{r}) \Rightarrow v(\mathbf{r}) \Rightarrow \text{observable properties}$$

2. The ground state energy has the variational property that

$$E_{\nu}[n_0] \leq E_{\nu}[n']$$

Density Functional Theory

3. The total energy of the system can be written as

$$E_{\nu}[n] = T[n] + U[n] + V[n]$$

where

$T[n]$ - the kinetic energy of the system

$U[n]$ - electron-electron interaction

$$V[n] = \int d^3r n(\mathbf{r}) \nu(\mathbf{r})$$

4. The ground state density uniquely defines the ground state potential

$$\nu(\mathbf{r}) = \nu[n_0](\mathbf{r})$$

Density Functional Theory

$$E[n] = T[n] + U[n] + V[n]$$

We don't know the kinetic energy for a set of interacting electrons, nor do we know the potential energy for the electron-electron interactions...

1. Approximate the kinetic energy as the kinetic energy of a set of non-interacting electrons.

$$T[n] \approx T_S[n] = -\frac{\hbar^2}{2m} \sum_i^N \int d^3r \phi^*(\mathbf{r}) \nabla^2 \phi(\mathbf{r})$$

2. Approximate the electron-electron interactions by using the classical electrostatic interaction energy.

$$U[n] \approx U_H[n] = \frac{q^2}{2} \int d^3r \int d^3r' \frac{n(\mathbf{r})n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|}$$

Density Functional Theory

$$E[n] = T_S[n] + U_H[n] + E_{xc}[n] + V[n]$$

$E_{xc}[n]$ contains $T - T_S$ and $U - U_H$

$$E_{xc}[n] = E_x[n] + E_c[n]$$

The Hohenberg-Kohn theorem is an existence proof. It doesn't tell us anything about what the functional looks like. The art of density functional theory is designing good functionals.

Exchange Energy

- Exchange effects are due to the Paul Exclusion principle
- The exchange energy can be written exactly as a function of the single particle orbitals.

$$E_x = -\frac{q^2}{2} \sum_{jk} \int d^3r \int d^3r' \frac{\phi_j^*(\mathbf{r}) \phi_k^*(\mathbf{r}) \phi_j(\mathbf{r}) \phi_k(\mathbf{r})}{|\mathbf{r} - \mathbf{r}'|}$$

- Exchange effects are substantially larger than correlation effects
- ‘exchange hole’ - region of reduced probability for encountering a second electron around a given reference electron, due to the fact that two electrons with the same spin cannot occupy the same point in space.

Correlation Energy

- The energy lowering that occurs due to the mutual avoidance of electrons to lower the Coulomb repulsion energy.
- Accounts for quantum fluctuations
- ‘correlation hole’ - region of reduced probability for encountering a second electron around a given reference electron, due to the fact that electrons avoid each other due to having the same charge.

The practical advantage of writing the total energy as:

$$E[n] = T_S[n] + U_H[n] + E_{xc}[n] + V[n]$$

is that $E_{xc}[n]$ is typically much smaller than the other terms

	Total Energy	E_{xc}	Exchange	Correlation	% Exchange	% Correlation
He	-2.9065	-1.0619	-1.0182	-0.0437	35.0316	1.5041
Ne	-128.9577	-12.4733	-12.0902	-0.3830	9.3754	0.2970
Ar	-527.5412	-30.8663	-30.1150	-0.7513	5.7086	0.1424
Kr	-2753.8291	-95.5146	-93.7655	-1.7490	3.4049	0.0635

Jacobs Ladder of DFT

As you go up the rungs of Jacob's Ladder the functional forms get more complex but the energies get more accurate (and more expensive to compute)

'Heaven'
Chemical Accuracy

fully non-local

hybrid meta GGA

hybrid GGA

meta GGA

GGA

LSDA

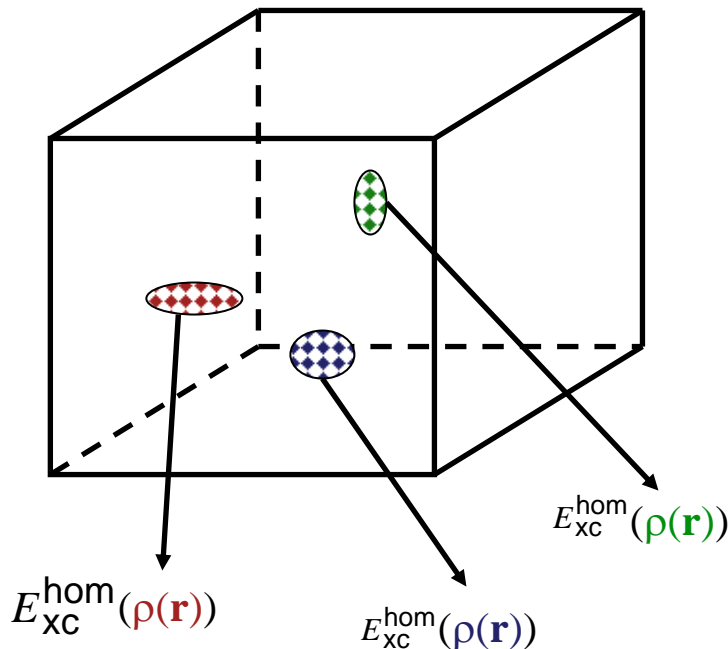


'Earth'
Hartree Theory

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.
 - ρ must be single-valued at every point in space

$$E_{xc}^{\text{LSDA}} = \int \rho(\mathbf{r}) \varepsilon_{xc}^{\text{hom}}(\rho(\mathbf{r})) d\mathbf{r} = \int \rho(\mathbf{r}) [\varepsilon_x^{\text{hom}}(\rho(\mathbf{r})) + \varepsilon_c^{\text{hom}}(\rho(\mathbf{r}))] d\mathbf{r}$$



- Exchange Energy

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

- Correlation Energy

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

Local Spin Density Approximation - Performance

- Structural properties are often good
 - usually underestimates bulk lattice constants by a small amount
 - 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.

Why does LSDA work?

- Many metallic systems are similar to a homogenous electron gas.
- One might expect it to fail for molecular systems (it does!)

What are its shortcomings?

- self-interaction

Generalized Gradient Approximation

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

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

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.

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

Generalized Gradient Approximation

The Hohenberg-Kohn theorem is an existence theorem - it tells us nothing about how to actually write the exchange correlation functional.

$$E_{\text{xc}}^{\text{GGA}}[\rho(\mathbf{r})] = \int \rho(\mathbf{r}) \varepsilon_{\text{x}}^{\text{LSDA}}(\rho(\mathbf{r})) F_{\text{xc}}^{\text{GGA}}(\rho(\mathbf{r}), \nabla \rho(\mathbf{r})) d\tau$$

Becke88 Exchange Functional

1. Obey the uniform electron gas limit

$$\lim_{\nabla \rho \rightarrow 0} E_{\text{xc}} = E_{\text{xc}}^{\text{LSDA}}$$

2. Obey the exact asymptotic behavior of the exchange-energy density.

$$\lim_{r \rightarrow \infty} U_{\text{x}} = -\frac{1}{r}$$

3. Obey the asymptotic behavior of the spin density.

$$\lim_{r \rightarrow \infty} \rho = e^{-ar}$$

4. Introduced one empirical parameter, β , to reproduce the exchange energy of the six noble gas atoms.

Becke88 Exchange Functional

The B88 exchange functional has the form:

$$F_x = 1 + \frac{2}{3} \left(\frac{4\pi}{3} \right)^{1/3} \beta \frac{x(\mathbf{r})^2}{1 + 6\beta x(\mathbf{r}) \sinh^{-1} x(\mathbf{r})}$$

$$\beta = 0.0042 E_h$$

β was fit to reproduce the exact exchange energy of the set of six noble gas atoms.

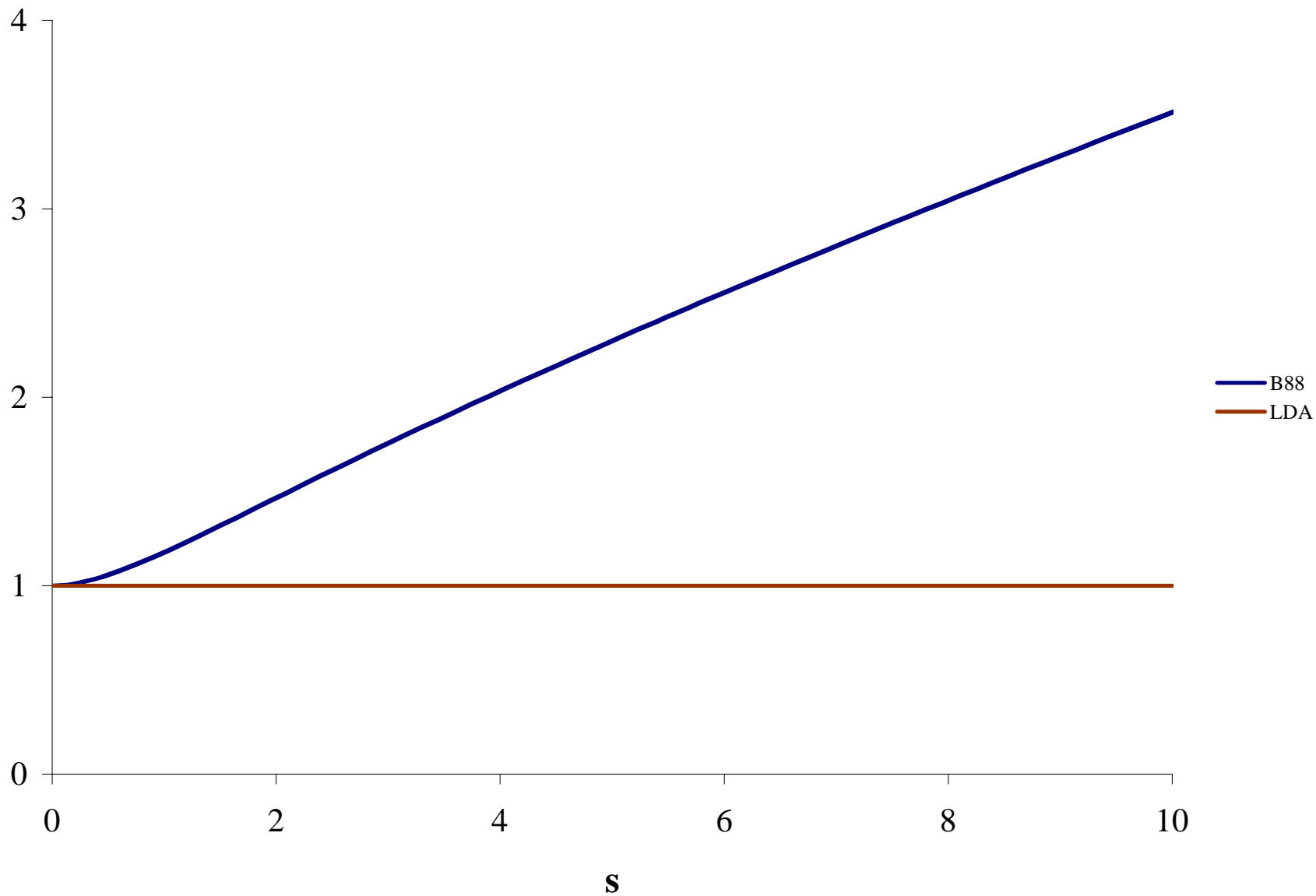
We define the reduced gradient for the system as

$$x(\mathbf{r}) = \frac{|\nabla \rho(\mathbf{r})|}{\rho(\mathbf{r})^{4/3}}$$

And the scaled density gradient as

$$s = \frac{|\nabla \rho(\mathbf{r})|}{(48\pi^2)^{1/3} \rho(\mathbf{r})^{4/3}}$$

Becke88 Exchange Functional



PW91 Exchange Functional

- The PW91 exchange functional was constructed by introducing real-space cut-offs to the long-range part of the density gradient expansion for the exchange and correlation hole.

$$F_X(x) = \frac{bx^2 - (b - \beta)x^2 \exp[-cx^2] - 10^{-6}x^d}{1 + 6b \sinh^{-1}(x) - \frac{10^{-6}x^d}{A_x}}$$

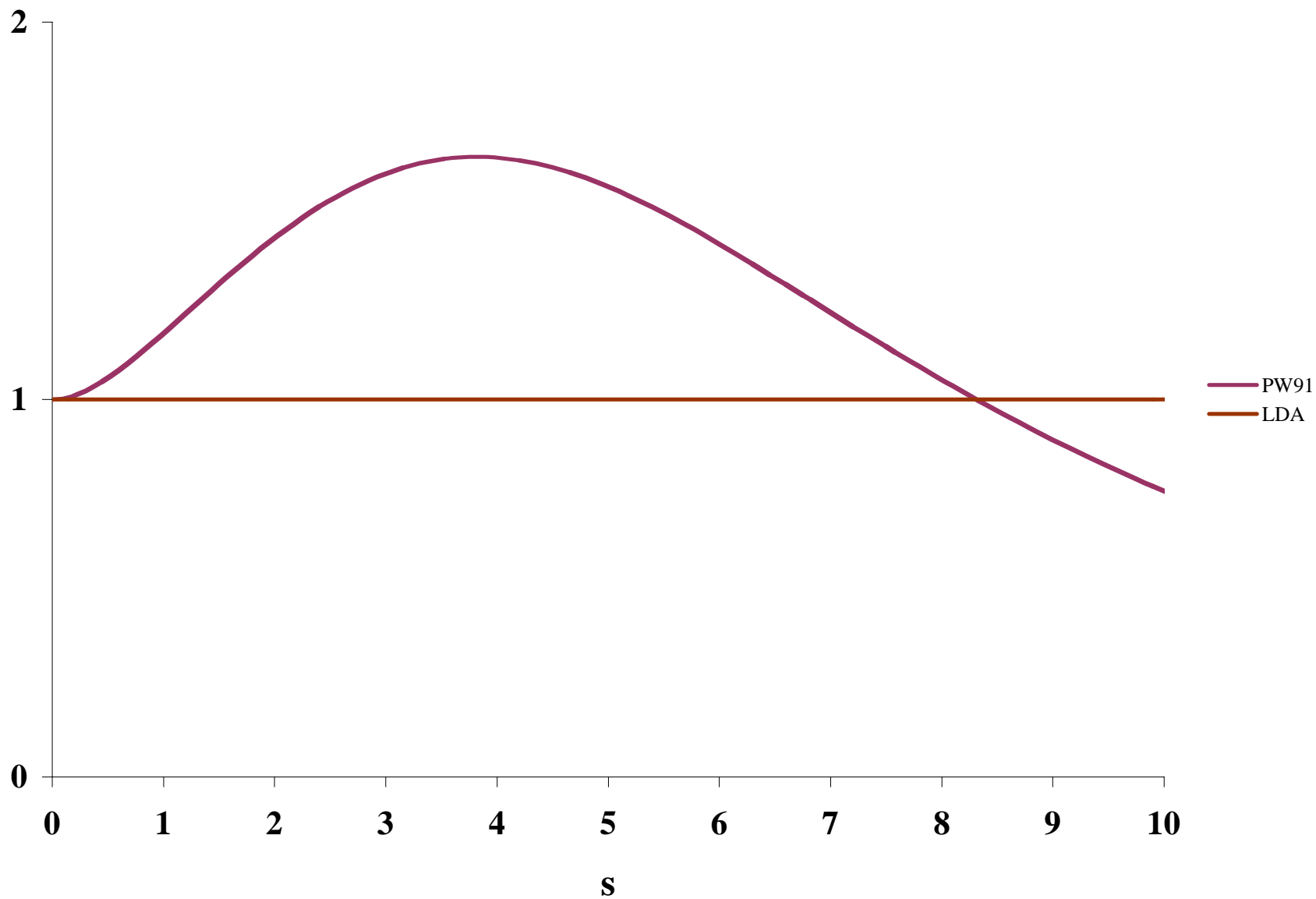
$$b = 0.0042 \quad \beta = 5(36\pi)^{-5/3}$$

$$c = 1.6455 \quad A_x = -\frac{3}{2} \left(\frac{3}{4\pi} \right)^{1/3}$$

$$d = 4.00$$

- The cutoff procedure was designed to obey as many of the known features of the exact exchange and correlation energy.
- Has spurious wiggles in the derivative to large and small values of s .

PW91 Exchange Functional



*m*PW Exchange Functional

- The modified PW91 exchange functional (*m*PW) has the same functional form as the PW91 model, however the parameters were refit

$$F_X(x) = \frac{bx^2 - (b - \beta)x^2 \exp[-cx^2] - 10^{-6}x^d}{1 + 6b \sinh^{-1}(x) - \frac{10^{-6}x^d}{A_x}}$$

$$b = 0.0046$$

$$\beta = 5(36\pi)^{-5/3}$$

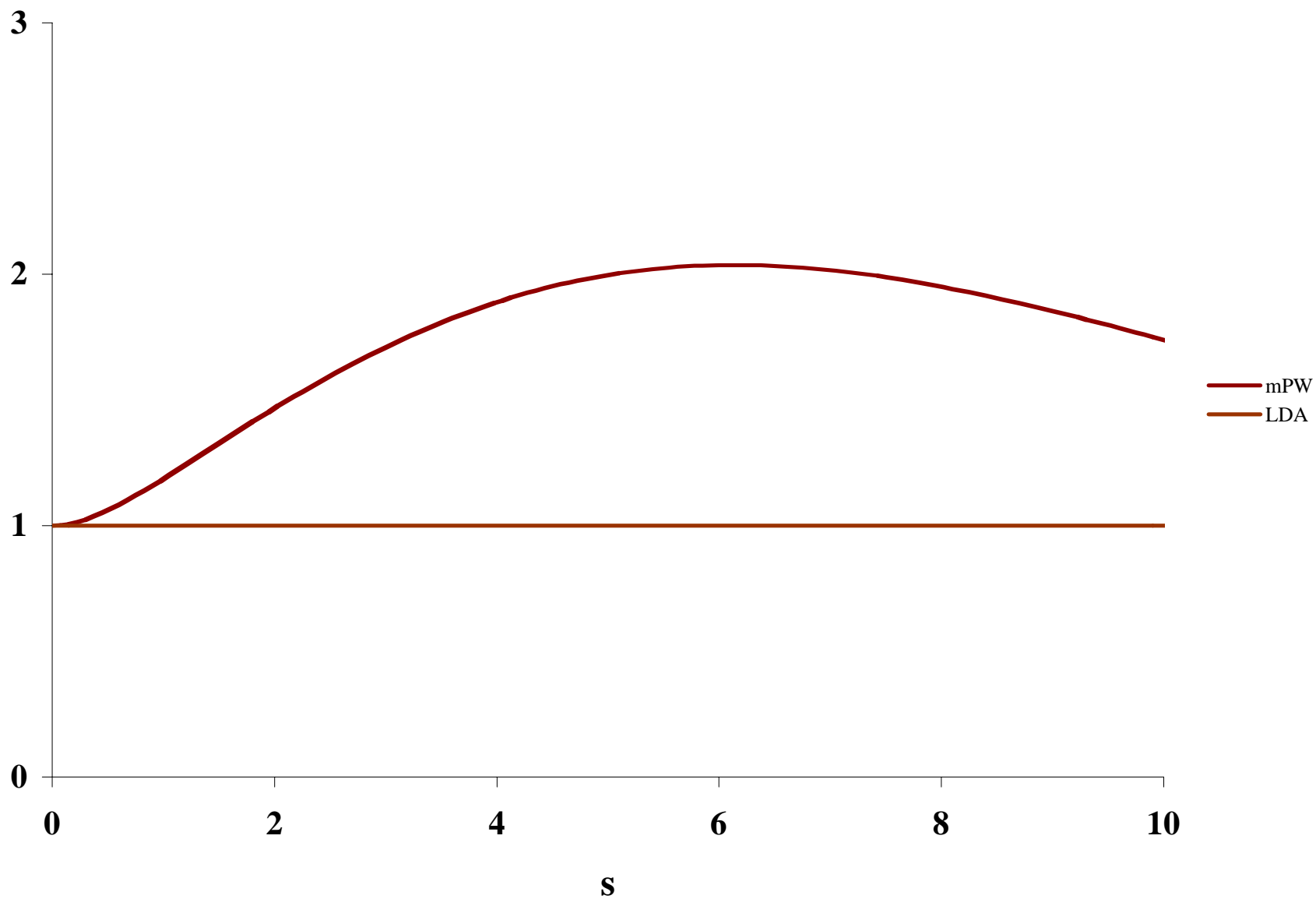
$$c = 1.6455$$

$$A_x = -\frac{3}{2} \left(\frac{3}{4\pi} \right)^{1/3}$$

$$d = 3.73$$

Fit to the exchange energies of the atoms in the 1st and 2nd rows.
Fit to the differential exchange energies of the rare gas dimers.

mPW Exchange Functional



PBE Exchange Functional

- Designed only to reproduce those features of the exchange energy which are energetically significant.
- All parameters are fundamental constants.

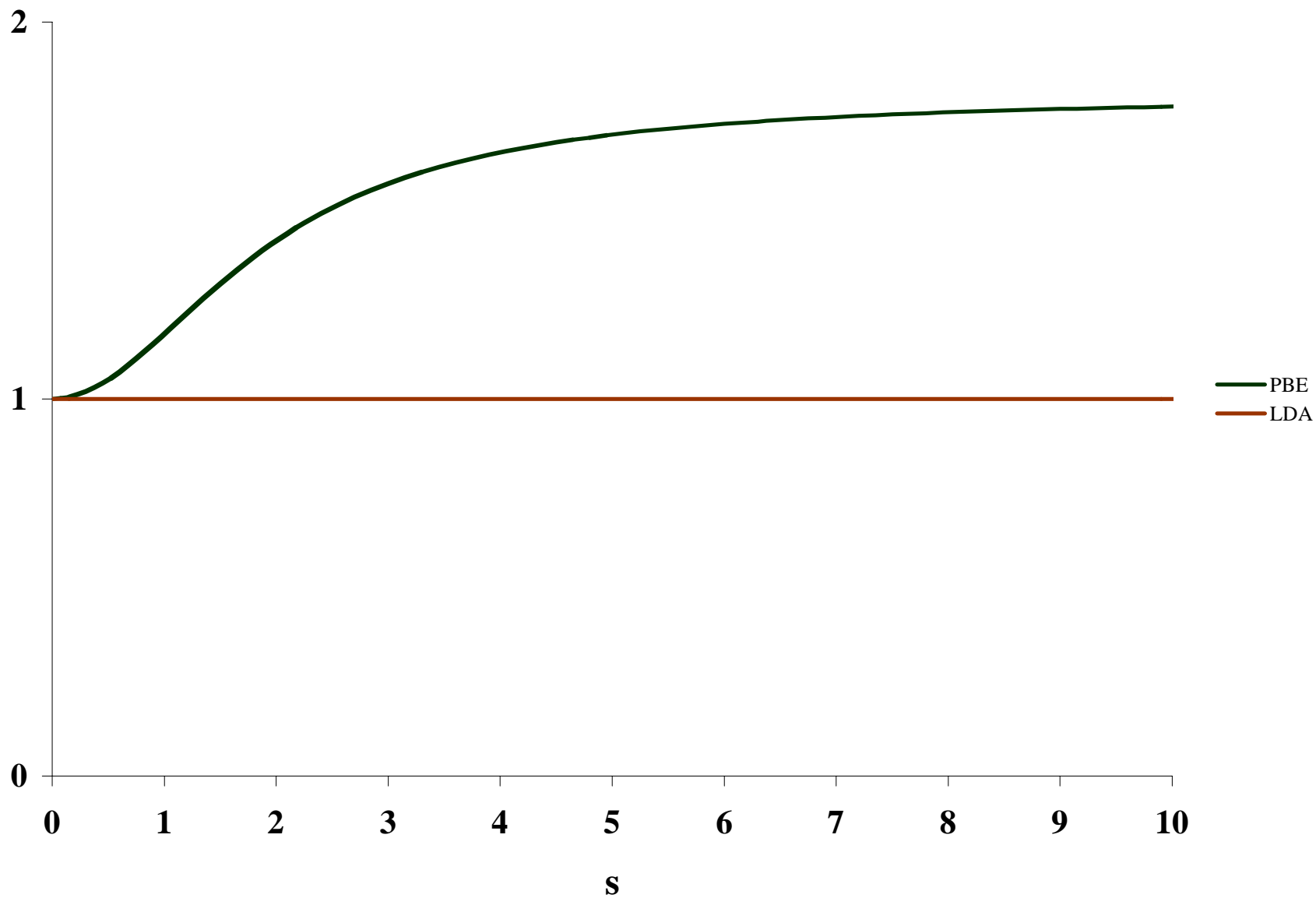
$$F_x(x) = 1 + \kappa - \frac{k}{1 + \left(\frac{\mu x^2}{\kappa (48 \pi^2)^{2/3}} \right)}$$

$$\mu = 0.235$$

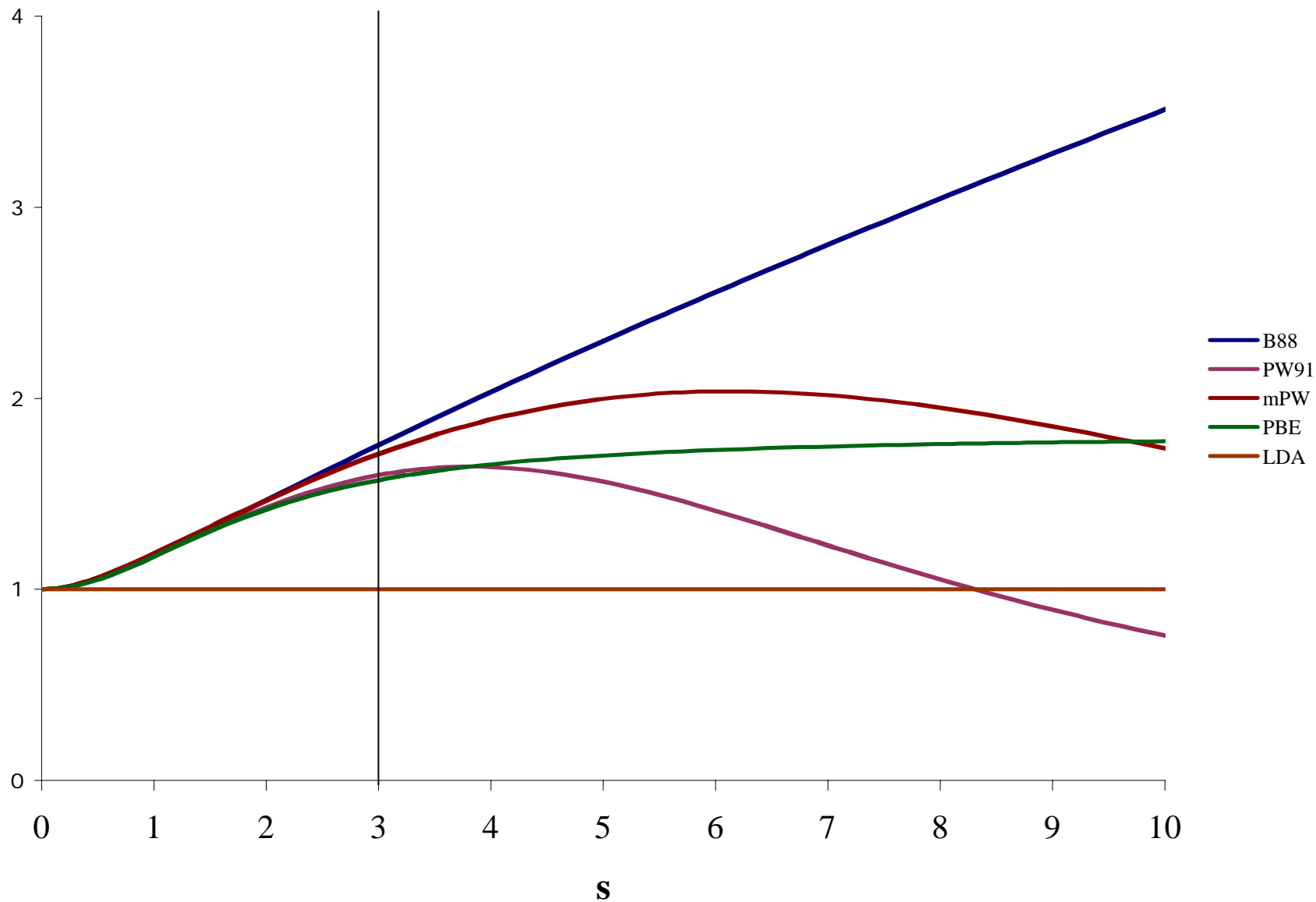
$$\kappa = 0.967$$

- Fixes many of the problems associated with PW91
- The most popular GGA functional in use today.

PBE Exchange Functional



Generalized Gradient Approximation



Correlation Functionals

Correlation is harder to put into a functional form, but it also contributes far less to the total energy.

As $s \rightarrow \infty$ $E_c \rightarrow 0$

- All correlation functionals are qualitatively the same.

PBE correlation functional designed to complement the PBE exchange functional.

Based on three conditions:

1. The second order gradient expansion
2. As $s \rightarrow \infty$ $E_c \rightarrow 0$
3. In the high density limit $E_c \rightarrow$ constant

LYP correlation functional of Lee, Yang, and Parr

- Based on a functional fit to helium, and parameterized to fit atoms with more electrons.
- Computes E_c in total, does not split it up into LSDA and GGA

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.

Problems with **LSDA** and **GGA**

One electron problems - self interaction

- In Hartree–Fock theory the self-interaction term from the Coulomb is exactly cancelled by the self-interaction term in the exchange energy.
- For LSDA and GGA functionals the self-interaction term is not exactly cancelled by the exchange and correlation functionals.
- It is unphysical to introduce a correlation functional into a one-electron system.

Exchange and Correlation from a Hydrogen atom

	Exact	LSDA	PBE	BLYP
Exchange	0.3125	0.2680	0.3059	0.3112
Correlation	0.0000	0.0222	0.0060	0.0000

How do you fix the **Self Interaction Problem**?

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.

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.

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.

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

It turns out that the Laplacian of the density is hard to numerically converge.

$$\tau(\mathbf{r}) = \sum_i^{\text{occupied}} \frac{1}{2} |\nabla \psi_i(\mathbf{r})|^2$$

- Addition of kinetic energy density is used to satisfy additional constraints on E_{xc} such as the self-interaction energy

- $E_c[n] = 0$

- $E_x[n] = -E_H[n]$

- Exchange Functionals

- B95, B98, KCIS, τ HCTH, TPSS

- Correlation Functionals

- B98, KCIS, τ HCTH, TPSS

Hybrid Functionals

$$E_{xc}^{\text{hybrid DFT}} = (1-a)E_x^{\text{LSDA}} + aE_x^{\text{HF}} + b\Delta E_x^{\text{NL}} + E_c^{\text{LSDA}} + c\Delta E_c^{\text{NL}}$$

- Functionals:

B3PW91, B3LYP, O3LYP, X3LYP

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

- Functionals:

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

Hybrid meta Functionals

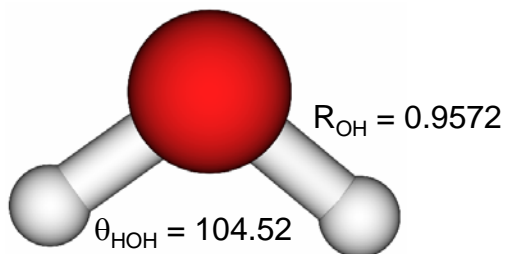
- Hybrid functionals that contain kinetic energy density, in addition to Hartree–Fock exchange.

Hybrid Functionals

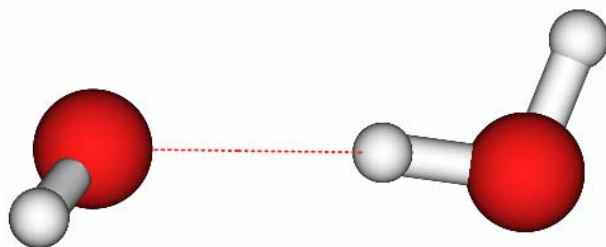
What's the rationale for adding Hartree–Fock exchange??

- 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)	$\Theta(\text{H-O-H})$
LSDA	0.9701	104.9605
PBE	0.9690	104.2068
BLYP	0.9706	104.5230
PBE1PBE	0.9575	104.9051
B3LYP	0.9604	105.1265
Hartree–Fock	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 known, 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.

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.
- Dispersion forces are not built in (except through empirical parameters) so many DFT functionals fail for complexes held together by dispersion forces.
- Kohn-Sham orbitals do not have the same interpretation as Hartree–Fock orbitals.
- Information about excited states is meaningless.

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

Energetics

1. Hybrid and meta-GGA are the most efficient, and offer improvement over corresponding pure DFT functionals. Often they show accuracy that is similar to highly correlated wave function methods.
2. Increasing basis set size does not always improve the accuracy of the DFT model, although it does lead to a converged result
3. GGA models offer substantial improvement over LSDA models.

Geometries

1. Performance is good for predicting minimum energy structures.
2. The use of GGA over LSDA does not greatly improve performance.
3. GGA functionals overestimate bond lengths.
Hartree–Fock underestimates bond lengths.
Hybrid functionals do well for bond lengths.
4. Accuracies in bond angles are typically $\sim 1^\circ$.
5. Many popular functionals fail for systems containing third row atoms.
6. In general, DFT does well for metal systems, particularly GGA and meta-GGA methods.

Summary

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