



**Short Course on  
Density Functional Theory and Applications  
III. Implementations**

**Samuel B. Trickey**

©Sept. 2008

Quantum Theory Project

Dept. of Physics and Dept. of Chemistry

**[trickey@qtp.ufl.edu](mailto:trickey@qtp.ufl.edu)**



## *KS $E_{xc}$ and $v_{xc}$*

- **The exchange-correlation potential is the functional derivative of the exchange-correlation energy  $E_{xc}$  with respect to the density (or spin density):**

$$v_{xc} [n(\mathbf{r})] = \frac{\delta E_{xc} [n]}{\delta n(\mathbf{r})}$$

- **For physically and/or chemically realistic systems, only approximations to the exchange functional  $E_x[n]$  and the correlation functional  $E_c[n]$  are known. Often they used in fixed combinations for error compensation:**

$$E_x[n] + E_c[n] = E_{xc}[n] = \int d\mathbf{r} n(\mathbf{r}) u_{xc}(\mathbf{r})$$

$u_{xc}[n]$  is the exchange-correlation energy density

Credit: N. Rösch



## What is the Scale of $E_{xc}$ ?

- Here is a table of various contributions to the energy functional (in eV) from DFT calculations on selected atoms using the local density approximation (see below) and 6-31G basis sets

Atom	$\langle v_{ext}n \rangle$	$T_s[n]$	$E_{ee}[n]$	$E_x[n]$	$E_c[n]$	$E_{tot}[n]$
H	-26.8	13.2	8.4	-7.2	-0.6	-13.0
He	-180.3	75.2	54.9	-23.7	-3.0	-76.9
Ne	-8 451.7	3 385.4	1 799.7	-300.0	-20.3	-3 486.9
Ar	-34 136.6	14 321.5	6 301.7	-757.8	-38.9	-14 310.1
Kr	-178 995.5	74 857.2	31 884.6	-2 409.9	-89.4	-74 753.0

- For a given density  $n$ , the energy contributions for the external potential, the KS kinetic energy, and the classical Coulomb energy are known exactly.
- As usual, approximations were used for the exchange and the correlation energy contributions.
  - Except for H and He, the exchange energy is about 5-10% or less of the total energy.
  - For larger atoms, the correlation energy is less than 1% of the total energy

Credit: N. Rösch



## What is the Scale of $E_{xc}$ ?

- Here is the same table. *Caution!* There is something strange here

Atom	$\langle v_{ext} n \rangle$	$T_s [n]$	$E_{ee} [n]$	$E_x [n]$	$E_c [n]$	$E_{tot} [n]$
H	-26.8	13.2	8.4	-7.2	-0.6	-13.0
He	-180.3	75.2	54.9	-23.7	-3.0	-76.9
Ne	-8 451.7	3 385.4	1 799.7	-300.0	-20.3	-3 486.9
Ar	-34 136.6	14 321.5	6 301.7	-757.8	-38.9	-14 310.1
Kr	-178 995.5	74 857.2	31 884.6	-2 409.9	-89.4	-74 753.0

**NOTE** the hydrogen atom in the foregoing table!! A one-electron system without exchange and correlation has **NON-ZERO** values for both!!

The classical Coulomb energy  $E_{ee}[n]$  includes, **spuriously**, the **self-interaction of the electron charge distribution**. One task of  $E_x[n]$  is to remove this artifact. Approximate functionals achieve this removal only incompletely – a major source of errors in KS calculations.

Credit: N. Rösch

## *KS $E_{xc}$ and $v_{xc}$*

- **Functionals are developed**
  - from the XC functional form for the *homogeneous electron gas* (electrons moving in the field of a positive homogeneous background charge): analytic form (Dirac) of the exchange energy, accurate (Monte-Carlo) calculations of the correlation energy;
  - by application of scaling relations and rigorous bounds to the gradient expansion for the XC energy of the weakly inhomogeneous electron gas;
  - by considering *the XC holes of the electron pair distribution*, in particular by using exact asymptotic and scaling properties of the hole functions;
  - by using model forms of  $u_{xc}[n]$  derived from accurate calculations on small systems;
  - by fitting experimental data (geometries, binding energies, ionization potentials, electron affinities) to DFT results, adjusting parameters introduced in model forms of  $u_{xc}[n]$ .

Credit: N. Rösch



## *KS $E_{xc}$ in Idealized Systems: Homogeneous Electron Gas Exchange*

Put  $N_e$  electrons in a cubic box, volume  $L^3$ , density  $n = N_e/L^3$

Offset their mutual repulsion with a uniform positive background

They therefore are non-interacting;  $E_{tot}[n] = T + E_{xc}$   
the **ONLY** interaction is quantum mechanical!

Calculate the restricted HF ground state energy per unit volume in the thermodynamic limit:  $\lim_{\substack{N_e \rightarrow \infty, L^3 \rightarrow \infty, \\ n = \text{constant}}} \mathcal{E}_{0,RHF}$

and extract the exchange energy density  $u_x = -\frac{3}{4} \left( \frac{3}{\pi} \right)^{1/3} n^{1/3}$

**Remarks:** This calculation is exact and not too demanding. Units here are Hartree a.u.

## The First Local Density Approximations for $E_x$ : HFS Exchange and $X\alpha$

- Slater's audacious suggestion for simplifying HF [Phys. Rev. 81, 385 (1951)] was to average the exchange potential and then replace the result with the HEG RHF exchange potential for the density at each point.

*This assumes* that the X potential of electrons at the point  $\mathbf{r}$  is the same as that of a HEG with the density  $n(\mathbf{r})$ . The result is the so-called Hartree-Fock-Slater or “statistical” exchange potential.

$$v_{xHFS}(\mathbf{r}) = -\frac{3}{2} \left( \frac{3}{\pi} \right)^{1/3} n^{1/3}(\mathbf{r})$$

- In the late 1960s it began to be recognized that better one electron eigenvalues were obtained by scaling this potential with a parameter  $0 < \alpha \leq 1$ .

$$v_{X\alpha}(\mathbf{r}) = -\frac{3}{2} \alpha \left( \frac{3}{\pi} \right)^{1/3} n^{1/3}(\mathbf{r})$$

- At about the same time, Slater's co-worker Wilson realized that there was a variational total energy expression that corresponded to this potential. In modern notation it is:

$$E_{X\alpha}[n] = T_S[n] + E_{ee}[n] - \alpha \frac{9}{8} \left( \frac{3}{\pi} \right)^{1/3} \int d\mathbf{r} n^{4/3}(\mathbf{r}) + E_{ext}[n]$$

- **NOTICE:** the reasoning was “backward”: from the potential to the total energy

## The Original Kohn-Sham Local Density Approximation

- As might be expected, Kohn and Sham [Phys. Rev. **140**, A1133 (1965)] approximated the exchange energy, not the potential. So they wrote (the subscript notation is informative but not standard)

$$E_x \approx \int d\mathbf{r} n(\mathbf{r}) u_{xHEG}(\mathbf{r}) = -\frac{3}{4} \left( \frac{3}{\pi} \right)^{1/3} \int d\mathbf{r} n(\mathbf{r}) n^{1/3}(\mathbf{r})$$

$$E_{KSLDA}[n] = T_S[n] + E_{ee}[n] - \frac{3}{4} \left( \frac{3}{\pi} \right)^{1/3} \int d\mathbf{r} n^{4/3}(\mathbf{r}) + E_{ext}[n]$$

- The result is an **X** potential

$$v_{XKSLDA}(\mathbf{r}) = -\left( \frac{3}{\pi} \right)^{1/3} n^{1/3}(\mathbf{r}) = \frac{2}{3} v_{xHFS}(\mathbf{r})$$

- From the perspective of the  $X\alpha$  workers, this is just  $\alpha=2/3$ . It took a long time and considerable friction to come to the realization that  $X\alpha$  is simply a one-parameter Local Density Approximation. There is a great deal of confusion in the literature about how  $X\alpha$  is a separate theory, etc.

Notice that these simple models actually use an  $E_x$  approximation to handle all of  $E_{xc}$

## The Modern Local Density Approximation

- Modern LDAs use “Slater exchange” plus a parameterization of Monte Carlo results for the correlation energy of the H.EG.

$$E_{xc}^{\text{LDA}}[n_{\uparrow}(\mathbf{r}), n_{\downarrow}(\mathbf{r})] = \int d\mathbf{r} n(\mathbf{r}) \left\{ u_x[n_{\uparrow}(\mathbf{r})] + u_x[n_{\downarrow}(\mathbf{r})] + u_c[n_{\uparrow}(\mathbf{r}), n_{\downarrow}(\mathbf{r})] \right\}$$

$$u_x[n_{\sigma}(\mathbf{r})] = -\frac{3}{2} \left( \frac{3}{\pi} \right)^{1/3} \frac{n_{\sigma}^{4/3}(\mathbf{r})}{n(\mathbf{r})}$$

$$u_c[n_{\uparrow}(\mathbf{r}), n_{\downarrow}(\mathbf{r})] = u_{c\text{VWN}}[n_{\uparrow}(\mathbf{r}), n_{\downarrow}(\mathbf{r})] \quad \text{or} \quad u_{c\text{PZ}}[n_{\uparrow}(\mathbf{r}), n_{\downarrow}(\mathbf{r})]$$

- **NOTICE the peculiar convention for the X energy density! The literature is obscure about this.**
- **Here we have a difference between physics and chemistry communities. The underlying Monte Carlo calculations on  $E_c$  are by Ceperley and Alder [Phys. Rev. B 18, 3126 (1978), Phys. Rev. Lett. 45, 566 (1980)]. Chemists commonly use the parameterization by Vosko, Wilk, and Nusair,  $u_{c\text{VWN}}$ . [Can. J. Phys. 58, 1200 (1980)] Physicists more commonly use the parameterization by Perdew and Zunger,  $u_{c\text{PZ}}$ . [Phys. Rev. B 23, 5048 (1981)] There are newer parameterizations; see below.**
- **The VWN paper has generated some confusion. In particular, the Gaussian-03™ input denotes this as “SVWN5”.**

Credit: N. Rösch



## The Modern Local Density Approximation

- The PZ parameterization of the Ceperley-Alder Monte Carlo results for the correlation energy of the H.EG. usually is presented in terms of the Wigner electron radius and the net spin polarization:

$$r_s := \left( \frac{3}{4\pi} \right)^{1/3} n^{-1/3}; \quad \zeta := (n_\uparrow - n_\downarrow) / n$$

$$u_{cPZ}^i[n] = \gamma_i / \left( 1 + \beta_1^i \sqrt{r_s} + \beta_2^i r_s \right); \quad r_s \geq 1$$

$$u_{cPZ}^i[n] = A_i \ln r_s + B_i + C_i r_s \ln r_s + D_i r_s; \quad r_s < 1$$

$$i = U, P \Rightarrow \zeta = 0, 1$$

$$u_{cPZ}[n, \zeta] = u_{cPZ}^U[n] + f(\zeta) \left( u_{cPZ}^P[n] - u_{cPZ}^U[n] \right)$$

$$f(\zeta) = \frac{(1 + \zeta)^{4/3} + (1 - \zeta)^{4/3} - 2}{2^{4/3} - 2}$$

Parameter	U	P
A	0.0311	0.01555
B	-0.048	-0.0269
C	0.0020	0.0007
D	-0.0116	-0.0116
$\gamma$	-0.1423	-0.0843
$\beta_1$	1.0529	1.3981
$\beta_2$	0.3334	0.2611

- **Note:** For the sake of consistent notation in these presentations, this  $u$  is what PZ call  $\varepsilon$ , NOT what they call  $\mu$ .

## *The Modern Local Density Approximation*

- A more modern parameterization of the H.E.G. Monte Carlo data is “PW-92” [J.P. Perdew and Y. Wang, Phys. Rev. B 45, 13244 (1992)]
- Considering its origin, LSDA works very well for solids and ultra-thin films, and surprisingly well for molecules.
  - Good for relatively modestly inhomogeneous electron densities (e.g. bulk alkali metals)
  - Yields accurate geometries and vibrational frequencies of molecules
  - *Major limitation:* binding energies often are (*notably*) *overestimated (10-15%)*
  - *Surprise failures happen:* the ground state of solid Fe is predicted to be fcc structure and paramagnetic (experiment: bcc and ferromagnetic)
- The reason LSDA works is summarized by Perdew and Kurth [in “A Primer in Density Functional Theory” Springer 2003, Chap. 1] : LSDA has *many* correct formal features.

Credit: N. Rösch



## *KS $E_{xc}$ in Idealized Systems: Hooke's Atom*

For a two-electron singlet system for which the ground-state density is known independently, the KS equation can be rewritten to give

the KS potential  $\left\{ -\left(\frac{1}{2}\right) \nabla^2 + v_{ext}(\mathbf{r}) + v_{ee}(\mathbf{r}) + v_{xc}(\mathbf{r}) \right\} \varphi_0(\mathbf{r}) = \varepsilon_0 \varphi_0(\mathbf{r})$

$$\Rightarrow v_{xc}(\mathbf{r}) = \varepsilon_j - v_{ext}(\mathbf{r}) - v_{ee}(\mathbf{r}) + \frac{\nabla^2 \varphi_0(\mathbf{r})}{2\varphi_0(\mathbf{r})}$$

$$\varphi_0(\mathbf{r}) = n^{1/2}(\mathbf{r})$$

This fact is valuable to development of XC functionals because of Hooke's atom. It is two electrons confined by a harmonic potential (rather than attracted to a nucleus).

$$\hat{H}_{Hooke} = -\left(\frac{1}{2}\right) \left( \nabla_1^2 + \nabla_2^2 \right) + \left(\frac{1}{2}\right) k \left( r_1^2 + r_2^2 \right) + 1/|\mathbf{r}_1 - \mathbf{r}_2|$$

For certain values of the coupling constant  $k$ , the ground state of this Hamiltonian can be found exactly. (For all other values, highly accurate numerical solutions are obtainable.) Therefore the density  $n(\mathbf{r})$  is known and the exact KS potential for this density can be found and compared with approximate functionals, e.g. LDA.

## *KS $E_{xc}$ in Idealized Systems: Hooke's Atom (continued)*

Here is a comparison of the LDA and exact X potentials for  $k=10$ , [P.M. Laufer and J.B. Krieger, Phys. Rev. A 33, 1480 (1986)]

### Remarks:

- (a) Notice that LSDA falls off too fast.
- (b) By HK-II, the Hooke's atom X and C potentials apply to the Helium atom and to the  $H_2$  molecule.

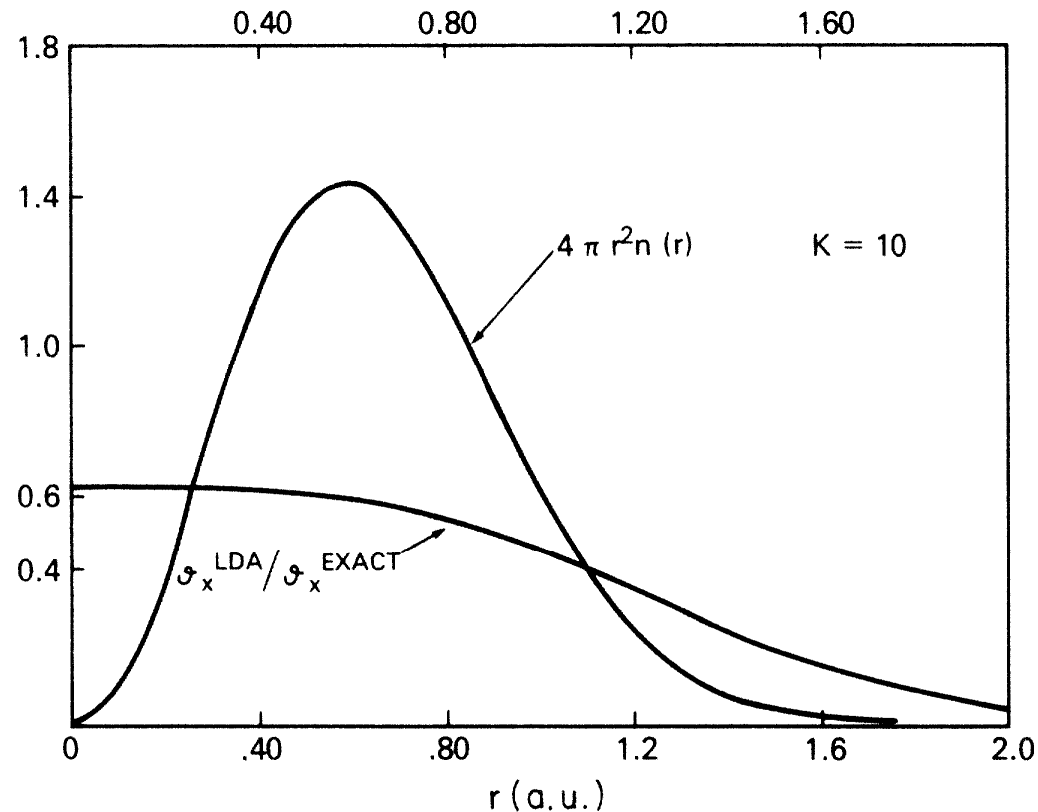


FIG. 5. Ratio of LDA to exact exchange potential for  $k = 10$ .

## LSDA - Bulk Al Equation of State

At what pressures does Al undergo crystalline phase changes?

[J.C. Boettger, and S.B.T. ,Phys. Rev. B 53, 3007 (1996); Phys. Rev. B 51, 15623 (R) (1995) ]

TABLE IV. LCGTO-FF predictions (this work) for the static lattice structural phase transition pressures ( $P$ ; in GPa) and relative volumes ( $V/V_{300}$ ;  $V_{300}=112.0$  a.u.) are compared with previous calculations using the GPT (Ref. 1), LMTO-ASA (Ref. 1), AP (Ref. 2), and LCGTO (Ref. 3) methods. An experimental lower bound for the room-temperature fcc $\rightarrow$ hcp transition from Ref. 7 is given also.

	Fcc $\rightarrow$ hcp		Hcp $\rightarrow$ bcc		Fcc $\rightarrow$ bcc	
	$P$	$V/V_{300}$	$P$	$V/V_{300}$	$P$	$V/V_{300}$
LCGTO-FF	205 $\pm$ 20	0.510	565 $\pm$ 60	0.364	340 $\pm$ 15	0.436
GPT	360		560			
LMTO-ASA	120		200			
AP	220	0.50	380	0.40	300	0.45
LCGTO					330	0.446
Expt.	>219	<0.50				

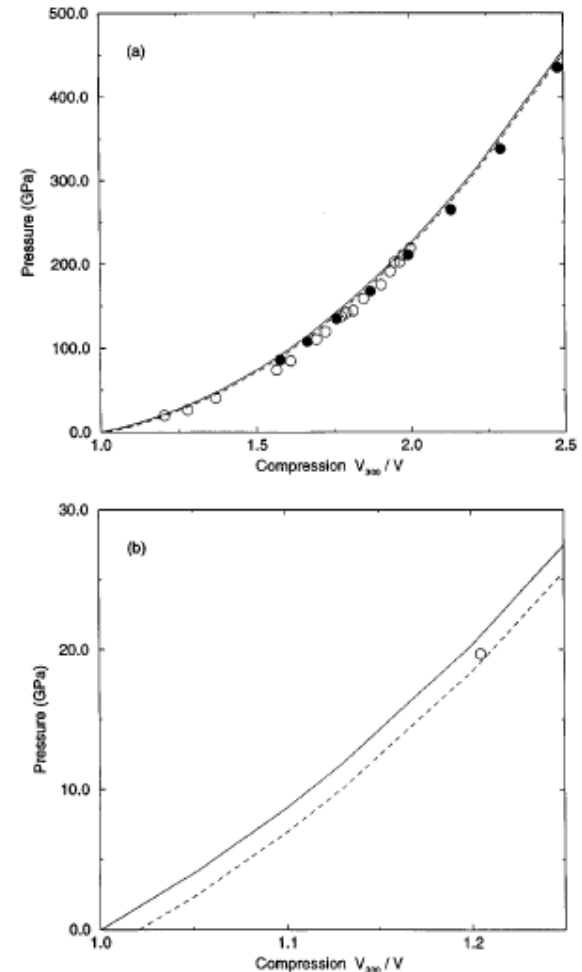


FIG. 1. The theoretical static-lattice 0-K isotherm calculated here (dashed line) and the 300-K isotherm derived from it (solid line), compared with room-temperature diamond-anvil-cell measurements (Ref. 7, open circles) and a 300-K isotherm deduced from shock data (Ref. 26, solid circles); (a) over the full range of the data and (b) for the low-pressure region. Compressions are given relative to the measured zero pressure volume at 300 K;  $V_{300}=112.0$  a.u.

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	Fcc→hcp		Hcp→bcc		Fcc→bcc	
	$P$	$V/V_{300}$	$P$	$V/V_{300}$	$P$	$V/V_{300}$
LCGTO-FF	205±20	0.510	565±60	0.364	340±15	0.436
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LCGTO					330	0.446
Expt.	>219	<0.50				

PRL 96, 045505 (2006)

PHYSICAL REVIEW LETTERS

week ending  
3 FEBRUARY 2006

### Evidence of a fcc-hcp Transition in Aluminum at Multimegabar Pressure

Y. Akahama,\* M. Nishimura, K. Kinoshita, and H. Kawamura

Graduate School of Material Science, University of Hyogo, 3-2-1, Kouto, Kamigohri, Hyogo 678-1297, Japan

Y. Ohishi

Japan Synchrotron Radiation Research Institute, 1-1-1, Kouto, Mikazuki, Hyogo 679-5198, Japan

(Received 28 July 2005; revised manuscript received 21 November 2005; published 3 February 2006)

The structure phase transition and the equation of state (EOS) of the third-period simple metal Al were investigated at pressure up to 333 GPa by powder x-ray diffraction experiments. The theoretically predicted fcc-hcp transition was observed at the reduced volume  $V/V_0$  of 0.509(1), corresponding to the pressure of  $217 \pm 10$  GPa. From the obtained pressure-volume data, the pressure derivative of the bulk modulus  $K_0'$  for the EOS of fcc-Al was determined to be 4.83(3) by fitting to the Vinet formulation with a fixed value 72.7 GPa of  $K_0$  obtained from previous ultrasonic experiments.

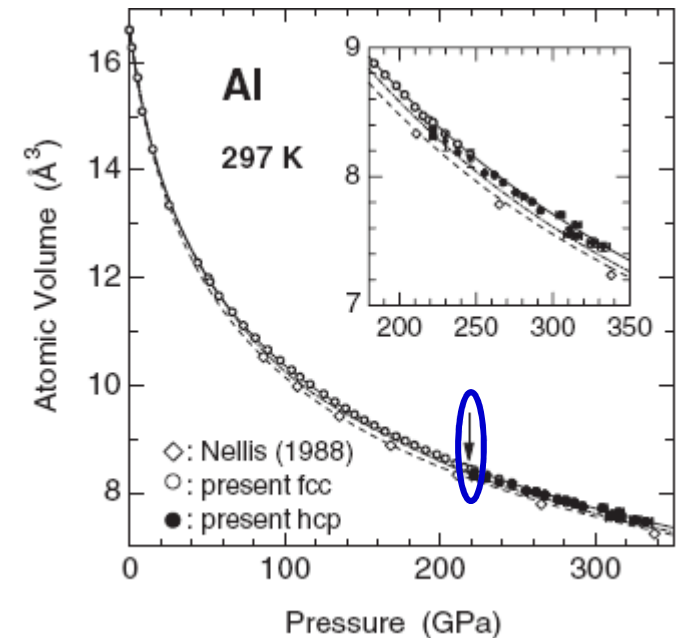


FIG. 4. The pressure dependence of the atomic volume  $V_A$  of Al at 297 K compared with previous data. Open and solid circles show the present data of fcc-Al and hcp-Al, respectively. The solid line represents the result of a least-squares fit of the equation of states (EOS) by Vinet [11] to the data for fcc-Al, where  $K_0$  is the fixed value of 72.7 GPa and  $K_0'$  is 4.83. The estimated volume reduction of the fcc-hcp phase transition from the compression curves was about 1% at the transition pressure of 217 GPa. Diamonds show a 300 K isotherm deduced from shock-compression data by Nellis *et al.* (Ref. [6]). The broken and the single-dotted broken lines indicate the EOS obtained from previous x-ray diffraction experiments at room temperature by Greene *et al.* (Ref. [5]) and the 300 K isotherm derived from the theoretical calculation by Boettger and Trickey (Ref. [4]), respectively.

## Gradient Expansions of XC

- Since LSDA is based on the HEG, an obvious route for improving LSDA is consider the gradient expansion (Taylor series) of the XC energy of the weakly inhomogeneous electron gas. **Beware**: as counter-intuitive as it might seem, done straightforwardly this strategy **fails**.
- There is a huge literature on the gradient expansion of the WIEG. A few key equations are as follows. First, there are two dimensionless variables that appear:

$$s(\mathbf{r}) := \frac{|\nabla n|}{2(3\pi^2)^{1/3} n^{4/3}}; \quad t(\mathbf{r}) := \left(\frac{\pi}{4}\right)^{1/2} \frac{|\nabla n|}{2(3\pi^2)^{1/6} n^{7/6}}$$

Second, because there is no preferred direction in the HEG, the gradient expansions cannot have a linear term in either  $s$  or  $t$ . The second-order gradient expansion (SGA) is

$$E_x = C_x \int d\mathbf{r} n^{4/3}(\mathbf{r}) \left[ 1 + a_{2x} s^2 + \dots \right]$$

$$E_c = C_c \int d\mathbf{r} n(\mathbf{r}) \left[ u_c^{HEG}[n] + a_{2c}[n] t^2 + \dots \right]$$

Using  $E_{xc}$  by keeping the terms shown is worse than LDA. The reason has been traced [roughly stated] to misbehavior of the electron pair density at large pair separations. See Perdew and Kurth [in “A Primer in Density Functional Theory” Springer 2003, Chap. 1] and references therein.

## Generalized Gradient Approximations

Generalized Gradient XC approximations incorporate gradient corrections but do not use the SGA coefficients

$$E_x^{GGA} [n_\uparrow, n_\downarrow] = \int d\mathbf{r} n(\mathbf{r}) u_x^{HEG} [n, \zeta] F_x [s]$$

$$E_c^{GGA} [n_\uparrow, n_\downarrow] = \int d\mathbf{r} n(\mathbf{r}) [u_c^{HEG} [n, \zeta] + H[n, \zeta, t]]$$

Broadly there are two routes to determining the  $X$  enhancement factor,  $F_x$ , and  $C$  gradient functional,  $H$ .

- a) Determination by constraining to HEG limits, jellium surface energies, scaling inequalities, bounds, and other exact results. Functionals in this category include: Perdew-Wang 91, Perdew-Burke-Ernzerhof, PBEsol, etc.
- b) Determination, in whole or in part, by fitting to atomization energies. This category includes functionals by Becke, Truhlar, etc.

## Generalized Gradient Approximations – A Few Examples of Constraints

In a short treatment, it is not possible to explore the large literature of scaling and exact bounds on  $X$  and  $C$  functionals. Here are a few examples actually used in constructing the PBE functional. [Phys. Rev. Lett. 77, 3865 (1996); erratum 78, 1396 (1997)]

$$n_\gamma(\mathbf{r}) := \gamma^3 n(\gamma\mathbf{r}) \Rightarrow E_x[n_\gamma] = \gamma E_x[n] \quad \text{Homogeneous scaling}$$

$$n_\gamma(\mathbf{r}) := \gamma^3 n(\gamma\mathbf{r}); \gamma \rightarrow \infty \Rightarrow H \rightarrow \gamma \phi^3(\zeta) \ln t^2$$

$$\phi(\zeta) := \left\{ (1 + \zeta)^{2/3} + (1 - \zeta)^{2/3} \right\} / 2 \quad \text{High density limit to cancel log singularity in HEG } u_c$$

$$s \rightarrow 0 \Rightarrow F_x[s] \rightarrow 1 + \mu s^2 \quad \text{To recover LSDA for nearly homogeneous systems}$$

$$\frac{E_{xc}[n]}{E_x^{LDA}[n]} \geq \lambda_{LO} = 2.2733; \quad E_x^{LDA}[n] = -\frac{3}{4} \left( \frac{3}{\pi} \right)^{1/3} \int d\mathbf{r} n^{4/3}(\mathbf{r}) \quad \text{Lieb-Oxford bound}$$

## Generalized Gradient Approximations (continued)

### Reminders about GGAs:

- The XC energy density  $u_{xc}(\mathbf{r})$  is not just a function of the local value of the electron density  $n(\mathbf{r})$ , but also depends also on the local absolute value of the density gradient  $|\nabla n|$ .
- As always in the KS formalism, the resulting exchange-correlation potential is local, i.e. it acts as a multiplicative factor on a KS orbital  $v_{xc}^{\text{GGA}}[n](\mathbf{r})$
- **GGA exchange and correlation functionals**
  - **BLYP** Becke X functional (1988) combined with the Lee, Yang, Parr (1988) C functional
  - **BP86** Becke X combined with the Perdew (1986) C
  - **PW91** Perdew, Wang (1991)
  - **PBE** Perdew, Burke, Ernzerhof (1996); simplified form of PW91
  - **PBEN** PBE functional modified by Hammer, Hansen, Norskov (1999)
  - **PBEsol** PBE functional modified (2008) to perform better in extended systems
  - . . . . Many more functionals have been proposed.

Credit: N. Rösch



## Generalized Gradient Approximations – Performance on Hooke’s Atom

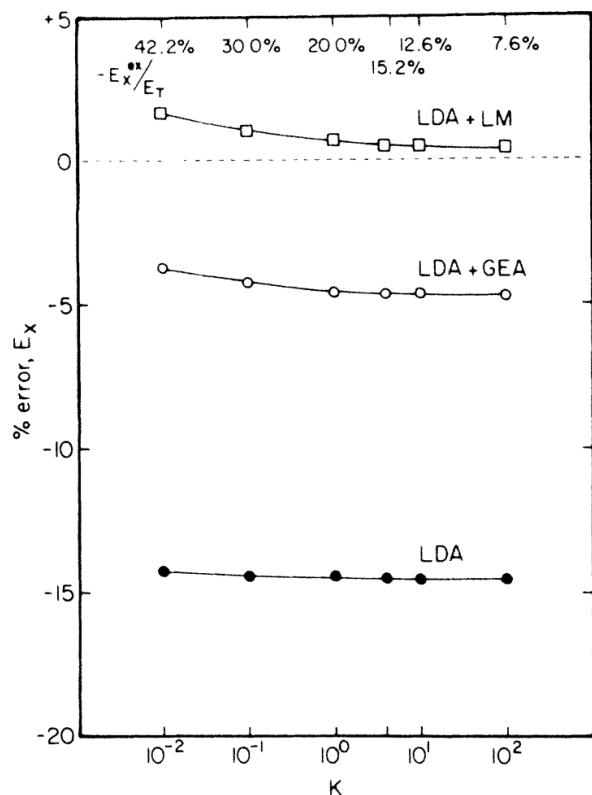


FIG. 8. Percentage error in the exchange energies.

**Gradients improve  $X$  more than  $C$  in Hooke’s atom**

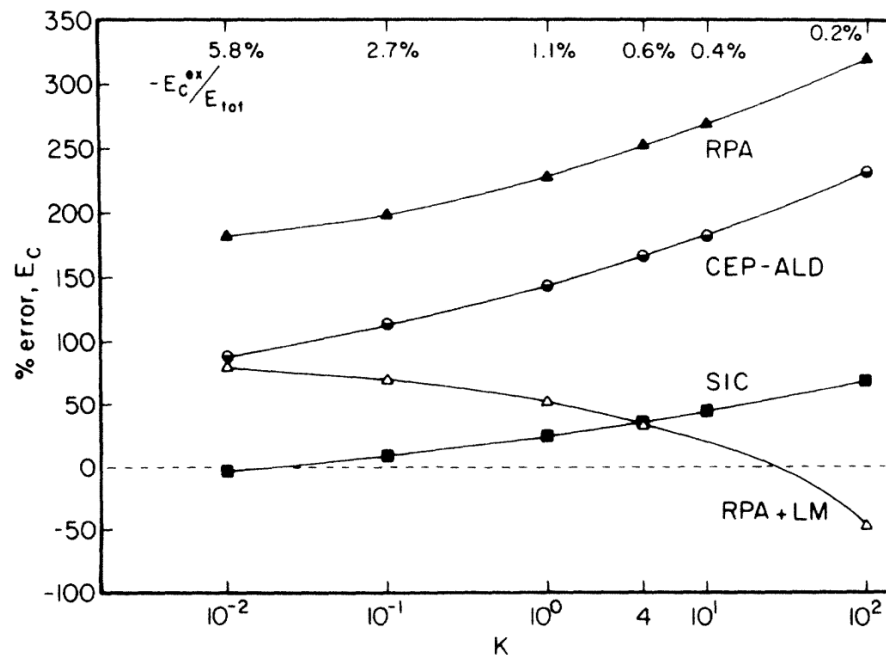


FIG. 10. Percentage error in the correlation energies.

**Errors as a function of coupling constant  $k$ . GEA = 2<sup>nd</sup> order gradient approx. LM= Langreth-Mehl GGA, CEP-ALD = Ceperley-Alder, SIC = self-interaction corrected [P.M. Laufer and J.B. Krieger, Phys. Rev. A 33, 1480 (1986)]**

## Generalized Gradient Approximations – Performance on Molecules

Comparison of structural and energetic properties (average deviation, AD, and average absolute deviations, AAD, from experiment) for 32 small molecules as calculated with various DF and wave function based methods. [Adapted from B.G. Johnson, P.M.W. Gill and J.A. Pople, *J. Chem. Phys.* **98**, 5612 (1993)]

Method	Bond distances (pm)		Bond angles (degree)		Harmon. vibrational frequencies (cm <sup>-1</sup> )		Atomization energies (kJ mol <sup>-1</sup> )	
	AD	AAD	AD	AAD	AD	AAD	AD	AAD
SVWN	1.4	2.1	-0.74	1.93	-51	75	149	149
BVWN	1.8	1.8	-0.76	1.99	-47	61	0.4	18
BLYP	2.0	2.0	-1.61	2.33	-63	73	4	23
HF	-1.0	2.0	0.11	1.99	165	168	-359	359
MP2	1.0	1.4	-0.87	1.78	69	99	-94	94
QCISD	1.2	1.3	-0.89	1.79	12	42	-120	120

SVWN = Slater X, VWN C  
BVWN = Becke X, VWN C  
BLYP = Becke X, LYP C  
1 pm = 0.01 Å  $\approx$  0.0189 au

HF = Hartree-Fock  
MP2 = 2<sup>nd</sup> Order Many-Body Pert. Theory  
QCISD = Quadratic CI with singles & doubles  
1 kJ/mol  $\approx$  0.0104 eV/atom  $\approx$  0.239 kcal/mol

## Generalized Gradient Approximations – Performance on Molecules (cont'd.)

Comparison of average absolute deviations (AAD) of enthalpies calculated from four first principles XC models relative to experiment, for the five subsets of molecular types which comprise the G2 neutral test set (non-hydrogen molecules, hydrocarbons, substituted hydrocarbons, radicals, and inorganic hydrides). [Adapted from Görling, Gisdakis, Trickey, and Rösch (1999), based on data from L.A. Curtiss, K. Raghavachari, P.C. Redfern, and J.A. Pople, *J. Chem. Phys.* **106**,1063 (1997).] All values in kJ mol<sup>-1</sup>.

	35 Non-H	22 H-C	47 Subst. H-C	29 Radicals	15 Inorg. H
SVWN	308	559	520	228	141
BP86	69	108	112	66	34
BPW91	51	20	33	27	18
BLYP	43	34	26	25	13
G2	11	5	8	6	4

## Generalized Gradient Approximations – Performance on Molecules (cont'd.)

**Comparison of constraint-based XC (PW91, PBE) approximations to HF and LSDA for small molecules [Perdew, Burke, and Ernzerhof, Phys. Rev. Lett. 77, 3685 (1996)]. UHF values for Be<sub>2</sub>, F<sub>2</sub>, and P<sub>2</sub> are for symmetry-preserving; symmetry breaking gives +7, -20, +41 respectively. [erratum, Phys. Rev. Lett. 78, 1396 (1997)]**

TABLE I. Atomization energies of molecules, in kcal/mol (1 eV = 23.06 kcal/mol).  $E_{XC}$  has been evaluated on self-consistent densities at experimental geometries [33]. Nonspherical densities and Kohn-Sham potentials have been used for open-shell atoms [34]. The calculations are performed with a modified version of the CADPAC program [35]. The experimental values for  $\Delta E$  (with zero point vibration removed) are taken from Ref. [36]. PBE is the simplified GGA proposed here. UHF is unrestricted Hartree-Fock, for comparison.

System	$\Delta E^{UHF}$	$\Delta E^{LSD}$	$\Delta E^{PW91}$	$\Delta E^{PBE}$	$\Delta E^{expt}$
H <sub>2</sub>	84	113	105	105	109
LiH	33	60	53	52	58
CH <sub>4</sub>	328	462	421	420	419
NH <sub>3</sub>	201	337	303	302	297
OH	68	124	110	110	107
H <sub>2</sub> O	155	267	235	234	232
HF	97	162	143	142	141
Li <sub>2</sub>	3	23	20	19	24
LiF	89	153	137	136	139
Be <sub>2</sub>	-7	13	10	10	3
C <sub>2</sub> H <sub>2</sub>	294	460	415	415	405
C <sub>2</sub> H <sub>4</sub>	428	633	573	571	563
HCN	199	361	326	326	312
CO	174	299	269	269	259
N <sub>2</sub>	115	267	242	243	229
NO	53	199	171	172	153
O <sub>2</sub>	33	175	143	144	121
F <sub>2</sub>	-37	78	54	53	39
P <sub>2</sub>	36	142	120	120	117
Cl <sub>2</sub>	17	81	64	63	58
Mean abs. error	71.2	31.4	8.0	7.9	...

## Generalized Gradient Approximations – Performance on Solids

**Alteration of just one parameter each in PBE X and C (to meet different constraints) yields a major improvement in the description of solids at the cost of a poorer description of molecules. Note that TPSS is a meta-GGA, not yet discussed.**

[Perdew, et al. Phys. Rev. Lett. **100**, 136406 (2008) ].

TABLE I. Errors in equilibrium lattice constants (in  $\text{\AA} \times 10^{-2}$ ) on our data set of 18 solids, relative to experiment with estimates of the zero-point anharmonic expansion removed [28].

Class	LSDA	PBE	TPSS	PBEsol
Mean error				
4 simple metals	-9.0	2.9	5.3	-0.3
5 semiconductors	-1.1	7.9	6.2	3.0
5 ionic solids	-8.4	8.5	6.8	2.0
4 transition metals	-4.0	6.4	2.5	0.0
Total	-5.5	6.6	5.4	1.3
Mean absolute error				
4 simple metals	9.0	3.4	5.3	2.3
5 semiconductors	1.3	7.9	6.2	3.0
5 ionic solids	8.4	8.5	6.8	2.7
4 transition metals	4.0	6.4	2.7	1.9
Total	5.6	6.7	5.4	2.5

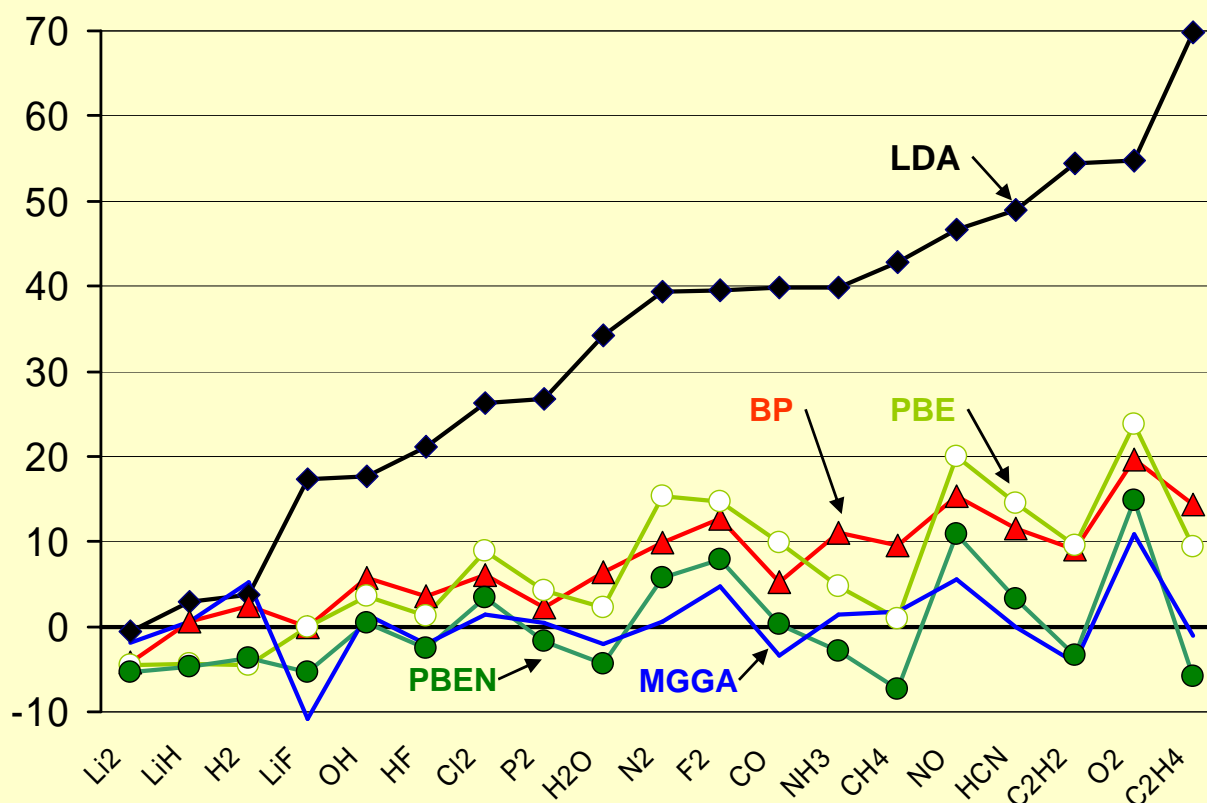
TABLE II. Errors in atomization energies (eV) for the AE6 set of molecules, using the 6-311 +  $G(3df, 2p)$  basis set.

Error	LSDA	PBE	TPSS	PBEsol
Mean error	3.35	0.54	0.18	1.56
Mean abs. error	3.35	0.67	0.26	1.56

## GGA vs LSDA – Atomization Energies of Molecules

- Deviations of atomization energies from experiment (in kcal mol<sup>-1</sup>) calculated by various exchange-correlation functionals at experimental geometries
  - Large GTO basis sets: H (8s,4p,3d), 2nd row (14s,9p,4d,3f), 3rd row (17s,12p,5d,4f)

[A. Matveev, M. Staufer, M. Mayer, and N. Rösch, *Int. J. Quantum Chem.* **75**, 863 (1999)]



LDA = PW92  
PBE: Phys. Rev. Lett. **77**, 3685 (1996), **78**, e1396 (1997)  
BP=B88P86  
PBEN= RPBE: Hammer et al., Phys. Rev. B **59**, 7413 (1999);  
MGGA=PKZB Perdew et al., Phys. Rev. Lett. **82**, 2544 (1999)

Credit: N. Rösch

## GGA vs LSDA – Atomization Energies of Molecules

- **Cross correlation of average absolute deviations (AAD) and average deviations (AD) of atomization energies (kcal/mol) between experiment and results of various exchange-correlation functionals**

AAD	Exp.	LDA	BP	PBE	AD	Exp.	LDA	BP	PBE
LDA	33.0				LDA	33.0			
BP	7.9	25.5			BP	7.4	25.5		
PBE	8.2	26.1	3.7		PBE	7.1	25.8	0.5	
PBEN	5.0	33.7	8.2	7.7	PBEN	-0.4	33.3	7.8	7.6

- **LDA (LSDA)**
  - Atomization energies much too large, not useful for chemical accuracy
- **GGA (spin polarized where necessary)**
  - Significant improvements by gradient-corrections, but overall energies still somewhat too large
  - Accuracy of BP and PBE quite comparable
  - Modified GGA functional PBEN shows further improvement
  - Dissociation energy of O<sub>2</sub> presents a problem for all GGA methods (O atom !)

Credit: N. Rösch



## *Simple XC Approximations – Some Insights*

- **The LSDA is remarkably successful: It is particularly good for the structures of extended systems, does fairly well for cohesive energies (but typically overbinds).**
- **The LSDA is not adequate for atomization energies of molecules. It is particularly bad for reaction barriers.**
- **GGA XC models generally improve on LSDA for atomization energies; bond lengths are a mixed story.**
- **But GGAs run into the “no free lunch” problem – there are more constraints on XC that are physically relevant than can be satisfied.**