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IMPROVING DENSITY  
FUNCTIONALS FOR SOLIDS

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### ③ KOHN-SHAM DENSITY FUNCTIONAL THEORY 1965

AN EXACT-IN-PRINCIPLE SELFCONSISTENT  
FIELD THEORY FOR THE GROUND-STATE  
DENSITY  $n(\underline{r})$  AND ENERGY  $E$  OF  
ELECTRONS IN AN EXTERNAL POTENTIAL  
 $v(\underline{r})$ :

$$n(\underline{r}) = 2 \sum_{\alpha} |\psi_{\alpha}(\underline{r})|^2 \Theta(\mu - \epsilon_{\alpha})$$

$$\left\{ -\frac{1}{2} \nabla^2 + v(\underline{r}) + \int d\underline{r}' \frac{n(\underline{r}')}{|\underline{r} - \underline{r}'|} + v_{xc}(\underline{r}; n) \right\} \psi_{\alpha}(\underline{r}) = \epsilon_{\alpha} \psi_{\alpha}(\underline{r})$$

$$E[n] = T_S[n] + \int d\underline{r} n(\underline{r}) v(\underline{r})$$

$$+ \frac{1}{2} \int d\underline{r} \int d\underline{r}' \frac{n(\underline{r}) n(\underline{r}')}{|\underline{r} - \underline{r}'|} + E_{xc}[n]$$

$$T_S[n] = 2 \sum_{\alpha} \int d\underline{r} \psi_{\alpha}^{\dagger}(\underline{r}) \left( -\frac{1}{2} \nabla^2 \right) \psi_{\alpha}(\underline{r}) \Theta(\mu - \epsilon_{\alpha})$$

$$v_{xc}(\underline{r}; n) = \frac{\delta E_{xc}}{\delta n(\underline{r})}$$

④ IN PRACTICE, THE EXCHANGE-CORRELATION  
ENERGY  $E_{xc}[n]$  (OR REALLY  $E_{xc}[n_{\uparrow}, n_{\downarrow}]$ )  
MUST BE APPROXIMATED.

$E_{xc} < 0$  IS THE LOWERING OF THE  
ENERGY DUE TO THE TENDENCY OF  
ELECTRONS TO AVOID ONE ANOTHER.

THE EARLY APPROXIMATIONS WERE  
MOTIVATED BY THE NEEDS OF SOLID  
STATE PHYSICS:

LOCAL DENSITY APPROXIMATION (LDA) 1965

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

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## GENERALIZED GRADIENT APPROX. (GGA)

1970's + EARLY 1980's: LANGRETH, PERDEW, ...

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

IN THE 1980'S AND LATER, FUNCTIONALS WERE DEVELOPED WITH THE NEEDS OF CHEMISTRY (ESPECIALLY ATOMIZATION ENERGIES OF MOLECULES) IN MIND:

PERDEW 1986

BECKE 1986, 1988

PERDEW, BURKE, &amp; ERNZERHOF 1996

## META-GGA's

$$E_{xc}^{MGGGA}[n] = \int d^3r n \epsilon_{xc}^{MGGGA}(n, |\nabla n|, \tau)$$

$$\tau = 2 \sum_{\alpha} \frac{1}{2} |\nabla \psi_{\alpha}|^2 \Theta(\mu - \epsilon_{\alpha}) > 0$$

= POSITIVE ORBITAL KE DENSITY

BECKE, PERDEW, TRUHKAR, ...

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## SEMI-LOCAL FUNCTIONALS:

LDA, GGA, META-GGA

$\epsilon_{xc}(r)$  DETERMINED BY OCCUPIED Kohn-Sham orbitals in an infinitesimal neighborhood of  $r$ .

COMPUTATIONALLY EFFICIENT.

POTENTIALLY ACCURATE WHEN THE EXACT EXCHANGE-CORRELATION HOLE IS WELL-LOCALIZED ABOUT ITS ELECTRON, AS IN MOST EQUILIBRIUM SITUATIONS.

CAN FAIL FOR STRETCHED BONDS OVER WHICH ELECTRONS ARE SHARED.

## HYBRID FUNCTIONALS

$$E_{xc}^{hyb} = a E_{xc}^{std} + (1-a) E_{xc}^{GGA} + E_c^{GGA}$$

(a ~ 0.2)

BECKE, ...

LDA IS CONSTRUCTED NONEMPIRICALLY,  
AND IS UNIQUE.

GGA AND META-GGA CAN BE CONSTRUCTED  
NONEMPIRICALLY (BY CONSTRAINT  
SATISFACTION) OR EMPIRICALLY  
(BY DATA FITTING). AT THE  
GGA LEVEL, ONE MUST CHOOSE  
AMONG COMPETING CONSTRAINTS.

HYBRIDS HAVE AT LEAST ONE  
EMPIRICAL PARAMETER.

## PROBLEM:

STANDARD FUNCTIONALS IMPROVE  
UPON LDA FOR MOLECULES, BUT  
NOT ALWAYS FOR SOLIDS (WHICH  
SHOULD BE "EASIER" THAN MOLECULES).

LDA LATTICE CONSTANTS ARE TYPICALLY  
1% TOO SHORT. THE PBE GGA  
LATTICE CONSTANTS ARE ABOUT 1%  
TOO LONG (AND OTHER STANDARD  
GGA'S ARE WORSE). NONEMPIRICAL  
META-GGA'S CAN BE SLIGHTLY BETTER  
THAN PBE, AND HYBRIDS CAN BE MUCH  
BETTER (BUT AT GREAT COMPUTATIONAL  
COST FOR LARGE UNIT CELLS).

①  
 THE SURFACE ENERGY OF JELLIUM  
 IS KNOWN APPROXIMATELY FROM THE  
 WORK OF LANGRISH, PERDEW, ...  
 (LONG-RANGE CORRECTION OF GGA, ETC.),  
 AND FROM A RECENT IMPROVED  
 QUANTUM MONTE CARLO (FOLKES...),  
 STANDARD GGA'S MAKE THE SURFACE  
 ENERGY TOO LOW (BUT BETTER THAN  
 THE OLD GMC). META-GGAS CAN BE  
 ACCURATE. HYBRIDS ARE BETTER  
 THAN STANDARD GGAS, BUT TOO LOW.

NO STANDARD FUNCTIONAL IS REALLY  
 SATISFACTORY FOR LATTICE CONSTANTS  
 AND SURFACE ENERGIES OF SOLIDS.

NEW TREND: "GGA'S FOR SOLIDS" ②③

(A) GGA'S BASED ON THE AIRY-GAS  
 REFERENCE SYSTEM

VITOS... 2000

ARMIENTO + MATTESSON 2005

(B) GGA'S BASED ON CONSTRAINT SATISFACTION

WU + COHEN 2001

PERDEW... 2008 (PDESOL)

GGAS FOR SOLIDS: ACCURATE LATTICE  
 CONSTANTS + SURFACE ENERGIES, BUT  
 VERY POOR ATOMIZATION ENERGIES  
 OF MOLECULES (CORRECTING ONLY  
 ABOUT HALF OF THE LARGE LDA  
 ERROR).

⑩  
 LIKELY EXPLANATION: THE GGA FORM IS TOO LIMITED TO ACHIEVE HIGH ACCURACY FOR ATOMS, MOLECULES, & SOLIDS FROM THE SAME GGA.

SECOND NEW TREND: RESTORING THE GRADIENT EXPANSION FOR EXCHANGE OVER A WIDE RANGE OF DENSITIES

PERDEW, BURKE, ... 2006 REALIZED THAT THE PBE GGA, BY ITS SELECTION OF CONSTRAINTS, WAS BIASED TOWARD A CORRECT DESCRIPTION OF ATOMS & NOT OF SOLIDS.

⑪  
 FOR A SLOWLY-VARYING DENSITY,  

$$E_x[n] = E_x^{\text{LDA}}[n] + C_x \int dr^3 \frac{|\nabla n|^2}{n^{4/3}}$$
 THE PBE GGA GRADIENT COEFFICIENT  $C_x$  IS ABOUT TWICE THE FIRST-PRINCIPLES ONE, AND IS APPROPRIATE FOR THE ENERGY OF AN ATOM OF LARGE ATOMIC NUMBER.

RESTORING THE FIRST-PRINCIPLES GRADIENT EXPANSION OVER A WIDE RANGE OF DENSITIES (AS IN PBEsol) PRODUCES MUCH BETTER LATTICE CONSTANTS & SURFACE ENERGIES.

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WE NEED A GOOD SIMULTANEOUS DESCRIPTION OF ATOMS, MOLECULES, & SOLIDS, TO DEAL WITH COMPLEX PROBLEMS LIKE

- (1) CLUSTERS & NANOMATERIALS
- (2) LARGE ORGANIC MOLECULES
- (3) ATOMS AND MOLECULES REACTING ON SURFACES.

GGA'S APPEAR TO BE TOO LIMITED IN FORM. BUT META-GGA'S (EMPLOYING  $n$ ,  $|v_n|$ , AND  $\tau$ ) MAY BE FLEXIBLE ENOUGH TO DESCRIBE ALL THESE SYSTEMS CLOSE TO EQUILIBRIUM.

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A NONEMPIRICAL META-GGA WAS DEVELOPED BY TPSS 2003 (TAY, PERDEW, STAROVSKY, SCHUEPPI). IT SATISFIED MANY EXACT CONSTRAINTS, INCLUDING

- (i) EXACT FOR UNIFORM-DENSITY LIMIT.
- (ii) RECOVERY OF THE CORRECT SECOND-ORDER & FOURTH-ORDER GRADIENT EXPANSIONS FOR EXCHANGE.
- (iii) NO DIVERGENCE OF THE EXCHANGE POTENTIAL AT THE NUCLEUS.
- (iv) ZERO CORRELATION ENERGY FOR ANY ONE-ELECTRON DENSITY.

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A META-GGA PROVIDES DIFFERENT  
GGA DESCRIPTIONS FOR DIFFERENT LIMITS:

(I) SLOWLY-VARYING LIMIT (MANY ORBITAL  
SHAPE OVERLAPPED)

$$r \rightarrow r_{\text{unif}} = \frac{3}{10} (3\pi^2 n)^{2/3}$$

OR MORE GENERALLY

$$\alpha \equiv \frac{r - r_w}{r_{\text{unif}}} \rightarrow 1.$$

IMPORTANT REGIONS OF SOLIDS & SURFACES  
HAVE  $\alpha \approx 1$ .

(II) ISO-ORBITAL LIMIT (ONE ORBITAL SHAPE)

$$r \rightarrow r_w = \frac{|D|}{8n} \quad \text{OR} \quad \alpha \rightarrow 0.$$

IMPORTANT REGIONS OF ATOMS AND  
MOLECULES HAVE  $\alpha \approx 0$ .

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THE TPSS META-GGA GAVE:

(i) VERY ACCURATE ATOMIZATION  
ENERGIES OF MOLECULES (MUCH  
BETTER THAN GGAs).

(ii) ACCURATE SURFACE ENERGIES FOR JELLIUM.

(iii) LATTICE CONSTANTS SLIGHTLY  
SHORTER (THUS SLIGHTLY BETTER  
THAN PBE GGA).

THE LATTICE-CONSTANT ERRORS APPEAR TO

ARISE FROM THE FACT THAT THE

TPSS EXCHANGE DEPARTS TOO FAST

FROM ITS SECOND-ORDER GRADIENT

EXPANSION AS THE REDUCED GRADIENT

$$s = \frac{|D|}{2(3\pi^2 n)^{1/3} n} \quad \text{INCREASES.}$$



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## REVISED TPSS OR REVTPSS META-GGA 2009

KEEP ALL TPSS CONSTRAINTS, WITHOUT EMPIRICAL PARAMETERS. CHANGE THE FORM OF TPSS EXCHANGE TO RECOVER THE FIRST-PRINCIPLES GRADIENT EXPANSION OVER A WIDER RANGE OF REDUCED DENSITY GRADIENTS. \* INTRODUCE THE KNOWN (HU-LANGSOTH 1986) DENSITY DEPENDENCE OF THE GRADIENT COEFFICIENT FOR CORRELATION. \* FOR  $\alpha = 1$ .

PERDEW, RUZSINSKY, CSOZKA, CONSTANTIN,  
+ SUN, PHYSICAL REVIEW LETTERS  
103, 026403 (2009).

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## RESULTS FROM REV-TPSS

- (i) JELLIUM SURFACE ENERGIES ARE STILL CORRECT, WITHIN THE 3% UNCERTAINTY OF THE EXACT  $\epsilon_{xc}$ .
- (ii) ATOMIZATION ENERGIES OF MOLECULES ARE EVEN MORE ACCURATE THAN THOSE OF TPSS.

MEAN ABSOLUTE ERROR (kcal/mol) FOR THE 223 MOLECULES OF THE G3 SET.

LDA	121.9
PBE GGA	22.2
TPSS META-GGA	5.7
REV-TPSS META-GGA	4.8

(iii) LATTICE CONSTANTS ARE AS  
ACCURATE AS THOSE OF THE  
"GGA'S FOR SOLIDS"

MEAN ABSOLUTE ERROR (Å) FOR 21 SOLIDS

LDA	0.079
PBE GGA	0.065
TPSS META-GGA	0.047
REV-TPSS META-GGA	0.036
"GGA'S FOR SOLIDS"	
AM05 GGA	0.039
PBEsol GGA	0.038

HAVE WE GONE AS FAR AS WE  
CAN AT THE SEMI-LOCAL (GGA  
OR META-GGA) LEVEL?