CLIMBING THE LADDER OF DENSITY FUNCTIONAL APPROXIMATIONS

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THANKS TO MANY COLLABORATORS, INCLUDING

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AN OVERVIEW OF GROUND-STATE DENSITY FUNCTIONAL THEORY, INCLUDING RECENT DEVELOPMENTS AND CONTINUING DIRECTIONS

FOR MANY OF US, DFT IS A USEFUL TOOL. FOR SOME OF US, IT IS A CONTINUING OBSESSION.

KOHN-SHAM DENSITY FUNCTIONAL THEORY IS NOW THE MOST WIDELY-USED METHOD OF ELECTRONIC STRUCTURE CALCULATION IN MATERIALS SCIENCE AND QUANTUM CHEMISTRY.

10 OF THE 18 MOST-CITED PHYSICS PAPERS 1981-2010 ARE DENSITY FUNCTIONAL THEORY PAPERS.

MATERIALS (ATOMS, MOLECULES, NANOSTRUCTURES, SOLIDS, SURFACES) ARE SYSTEMS OF MANY INTERACTING ELECTRONS AND NUCLEI. THE NUCLEI ARE HEAVY AND ALMOST CLASSICAL, BUT THE ELECTRONS ARE QUANTUM MECHANICAL. WE ARE USUALLY INTERESTED IN MEASURABLE GROUND-STATE PROPERTIES:

TOTAL ENERGIES E AND CHANGES ΔE.
ELECTRON DENSITY $n(\vec{r})$ OR SPIN DENSITIES $n_{\uparrow}(\vec{r}), n_{\downarrow}(\vec{r})$.
EQUILIBRIUM NUCLEAR POSITIONS.
NUCLEAR VIBRATION FREQUENCIES.

DIRECT QUANTUM MECHANICAL APPROACH USING CORRELATED WAVEFUNCTIONS

$$\hat{H}\Psi = E\Psi$$

$$\hat{H} = \sum_{i=1}^{N}\left[-\frac{1}{2}\nabla_i^2 + v_{ext}(\vec{r}_i)\right] + \frac{1}{2}\sum_{i\neq j}\sum_{j}\frac{1}{\left|\vec{r}_i - \vec{r}_j\right|} + \frac{1}{2}\sum_{l\neq l`}\sum_{l`}\frac{Z_l Z_{l`}}{\left|\vec{R}_l - \vec{R}_{l`}\right|}$$

$$v_{ext} = \sum_{l}\frac{-Z_l}{\left|\vec{r}_i - \vec{R}_l\right|}$$

$$\Psi = \Psi(\vec{r}_1\sigma_1, \vec{r}_2\sigma_2, \ldots \vec{r}_N\sigma_N)$$

$$n(\vec{r}) = N\sum_{\sigma_1\ldots\sigma_N}\int d^3r_2 \ldots d^3r_N \left|\Psi(\vec{r}\,\sigma_1, \vec{r}_2\sigma_2 \ldots \vec{r}_N\sigma_N)\right|^2$$

THE MOTION OF EACH ELECTRON IS COUPLED TO THE MOTION OF EVERY OTHER ELECTRON.

COMPUTATIONAL COST SCALES UP RAPIDLY WITH N, THE ELECTRON NUMBER.

KOHN-SHAM DENSITY FUNCTIONAL THEORY 1965

(NOBEL PRIZE IN CHEMISTRY 1998)

WE CAN IN PRINCIPLE FIND THE EXACT GROUND-STATE ENERGY E AND GROUND-STATE DENSITY $n(\vec{r})$ BY SOLVING AN EFFECTIVE ONE-ELECTRON SCHRÖDINGER EQUATION

$$\hat{h}\psi_{\alpha\sigma} = \varepsilon_{\alpha\sigma}\psi_{\alpha\sigma}$$

$$\hat{h} = -\frac{1}{2}\nabla^2 + v_{ext}(\vec{r}) + \int d^3r` \frac{n(\vec{r}`)}{|\vec{r}`-\vec{r}|} + v_{xc}(\vec{r})$$

$$n(\vec{r}) = \sum_{\substack{\alpha\sigma \\ \varepsilon_{\alpha\sigma}<\mu}} |\psi_{\alpha\sigma}(\vec{r})|^2$$

$$E = \sum_{\substack{\alpha\sigma \\ \varepsilon_{\alpha\sigma}<\mu}} \left\langle \psi_{\alpha\sigma} \left| -\frac{1}{2}\nabla^2 \right| \psi_{\alpha\sigma} \right\rangle + \int d^3r n(\vec{r}) v_{ext}(\vec{r}) + \frac{1}{2}\sum_{l\neq l`}\sum_{l`} \frac{Z_l Z_{l`}}{|\vec{R}_l - \vec{R}_{l`}|} + \frac{1}{2}\int d^3r \int d^3r` \frac{n(\vec{r})n(\vec{r}`)}{|\vec{r}`-\vec{r}|} + E_{xc}[n]$$

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

$E_{xc}[n]$ IS THE EXCHANGE-CORRELATION ENERGY AS A FUNCTIONAL OF THE DENSITY-A RULE THAT ASSIGNS AN ENERGY E_{XC} TO EACH ELECTRON DENSITY $n(\vec{r})$.

$E_{xc}[n] < 0$ REPRESENTS THE LOWERING OF THE TOTAL ENERGY DUE TO THE TENDENCY OF ELECTRONS TO AVOID EACH OTHER AS THEY MOVE THROUGH THE DENSITY – JUST AS BEES IN A BEESWARM AVOID BUMPING INTO ONE ANOTHER.

$E_{XC}[n]$ IS "NATURE`S GLUE", BINDING ATOMS INTO MOLECULES AND SOLIDS.

THE EARLIEST APPROXIMATION WAS THE NONEMPIRICAL LOCAL DENSITY APPROXIMATION OF KOHN & SHAM 1965:

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

WHERE $\varepsilon_{xc}^{unif}(n)$ IS THE EXCHANGE-CORRELATION ENERGY PER ELECTRON OF AN ELECTRON GAS OF UNIFORM DENSITY *n*. (NOW ACCURATELY KNOWN).

LDA IS CORRECT FOR DENSITIES THAT VARY SLOWLY OVER SPACE, BUT IS USEFULLY ACCURATE FOR REAL SOLIDS WITH VERY NONUNIFORM DENSITIES. THIS WAS EXPLAINED BY THE FACT THAT LDA SATISFIES "EXACT CONSTRAINTS" ON $E_{xc}[n]$ FOR ALL DENSITIES $n(\vec{r})$. FUNCTIONALS THAT SATISFY ADDITIONAL EXACT CONSTRAINTS DEFINE A LADDER OF NON-EMPIRICAL APPROXIMATIONS.

JACOB`S LADDER OF DENSITY FUNCTIONAL APPROXIMATIONS

$$E_{xc}[n] = \int d^3 r n(\vec{r}) \varepsilon_{xc}^{approx}\left(n(\vec{r}), \nabla n(\vec{r}), \tau(\vec{r}), \ldots\right)$$

unoccupied KS orbitals

exact x info.

τ

∇n

n

RPA-LIKE

HYBRID

meta-GGA

GENERALIZED-GRADIENT APPROX. (GGA)

LOCAL DENSITY APPROX. (LDA)

HERE $\tau(\vec{r}) = \frac{1}{2} \sum_{\substack{\alpha\sigma \\ \varepsilon_{\alpha\sigma} < \mu}} \left|\nabla \psi_{\alpha\sigma}(\vec{r})\right|^2$ POSITIVE KE DENSITY.

BY ADDING INGREDIENTS, WE CAN SATISFY ADDITIONAL EXACT CONSTRAINTS AND ACHIEVE GREATER ACCURACY, FOR SOME INCREASE IN COMPUTATIONAL COST.

EXACT CONSTRAINTS ON $E_{XC}[n]$ (LANGRETH, PERDEW, GUNNARSON, LUNDQVIST, LEVY,…)

FORMALLY EXACT (BUT NOT COMPUTABLE) EXPRESSIONS FOR $E_{xc}[n]$ IMPLY EXACT CONSTRAINTS ON E_{XC} , E.G.,

$$E_{xc} = \frac{1}{2}\int d^3 r n(\vec{r}) \int d^3 r` \frac{n_{xc}(\vec{r},\vec{r}``)}{\left|\vec{r}-\vec{r}`\right|} = E_x + E_c$$

$n_{xc}(\vec{r},\vec{r}``) =$ DENSITY AT $\vec{r}`$ OF THE XC HOLE AROUND AN ELECTRON AT $\vec{r}$

$$n_x(\vec{r},\vec{r}``) \le 0$$

$$\int d^3 r` n_x(\vec{r},\vec{r}``) = -1$$

$$\int d^3 r` n_c(\vec{r},\vec{r}``) = 0.$$

THESE AND OTHER EXACT CONSTRAINTS EXPLAIN WHY LDA WORKS BETTER THAN EXPECTED, AND SUGGEST APPROXIMATIONS BEYOND LDA.

OTHER EXACT CONSTRAINTS:

DENSITY GRADIENT EXPANSIONS FOR SLOWLY-VARYING DENSITIES $n(\vec{r})$.

SCALING RELATIONS FOR $E_X + E_C$ *WHEN* $n(\vec{r})$ *IS SCALED.*

LIEB-OXFORD LOWER BOUND ON $E_{XC}[n]$, *ETC.*

THE HIGHER-LEVEL APPROXIMATIONS KEEP THE CONSTRAINTS OF THE LOWER-LEVEL ONES, AND ADD MORE CONSTRAINTS.

SPIN-DENSITY FUNCTIONAL THEORY

IN THE PRESENCE OF EXTERNAL FIELDS THAT COUPLE TO THE Z-COMPONENT OF THE ELECTRON SPIN, WE NEED

$$E_{xc}[n] \rightarrow E_{xc}[n_{\uparrow}, n_{\downarrow}]$$

EVEN IN THE ABSENCE OF SUCH FIELDS, WE USE SPIN DENSITY FUNCTIONALS TO ACHIEVE HIGHER ACCURACY AT A GIVEN LEVEL OF APPROXIMATION, AND TO PREDICT SPONTANEOUS MAGNETIZATION. SPURIOUS SPIN-SYMMETRY BREAKING CAN IMPROVE THE APPROXIMATE ENERGY (AS IN STRETCHED H_2).

TO SIMPLIFY OUR NOTATION, WE WILL NOT SHOW $n_{\uparrow}$ AND $n_{\downarrow}$ EXPLICITLY.

THREE DESIRED PROPERTIES OF AN APPROXIMATE FUNCTIONAL:

1) IT SHOULD BE NONEMPIRICAL, CONSTRUCTED FROM EXACT CONSTRAINTS OR DERIVATIONS AND NOT FROM FITTING TO DATA SETS.

NONEMPIRICAL FUNCTIONALS TEND TO BE MORE UNIVERSALLY USEFUL, AND THEY BETTER TEST OUR UNDERSTANDING OF THE PHYSICS OF E_{XC}.

WE HAVE NONEMPIRICAL CONSTRUCTIONS FOR THE SEMILOCAL FUNCTIONALS (LDA,GGA,META-GGA).
EXISTING HYBRID FUNCTIONALS HAVE AT LEAST ONE AND AS MANY AS 40 EMPIRICAL FIT PARAMETERS. THE RANDOM-PHASE APPROXIMATION (RPA) IS NONEMPIRICAL, BUT SOME CORRECTIONS TO IT ARE EMPIRICAL.

2) IT SHOULD BE COMPUTATIONALLY EFFICIENT.

THE SEMILOCAL FUNCTIONALS (LDA,GGA,meta-GGA) CONSTRUCT THE XC ENERGY DENSITY AT EACH POSITION IN SPACE FROM THE DENSITY OR ORBITALS IN AN INFINITESIMAL NEIGHBORHOOD. THEY FIND EXC FROM A SINGLE NUMERICAL INTEGRATION OVER 3D SPACE.

HYBRID FUNCTIONALS, WHICH REQUIRE AN EXACT EXCHANGE INGREDIENT (ENERGY, ENERGY DENSITY, OR HOLE) CAN BE 10 OR 100 TIMES SLOWER, DEPENDING ON THE PROGRAM AND SYSTEM.

RPA CAN BE 100 TIMES (OR MORE) SLOWER THAN SEMILOCAL FUNCTIONALS.

3) IT SHOULD BE USEFULLY ACCURATE.

LDA (OR LSDA) SATISFIES THE XC HOLE SUM RULES.
IT IS EXACT FOR UNIFORM DENSITIES. IT SATISFIES SOME OF THE SCALING RELATIONS, PLUS THE LIEB-OXFORD BOUND. IT IS ACCURATE FOR THE LINEAR RESPONSE OF A UNIFORM DENSITY.

LDA IS USEFUL FOR SOME SIMPLE SOLIDS.
IT PREDICTS LATTICE CONSTANTS THAT ARE 1% TO 2% TOO SHORT, AND TOTAL SURFACE ENERGIES THAT ARE REALISTIC.

BUT LDA STRONGLY OVERBINDS ATOMS INTO MOLECULES & SURFACES, SO IT IS NOT MUCH USED IN CHEMISTRY.

GGA`S (GENERALIZED GRADIENT APPROXIMATIONS) CAN BE CONSTRUCTED TO SATISFY DIFFERENT SETS OF EXACT CONSTRAINTS.

THE STANDARD PBE (PERDEW-BURKE-ERNZERHOF) GGA RECOVERS THE SECOND-ORDER GRADIENT EXPANSION FOR CORRELATION WHILE PRESERVING THE ACCURATE LSDA XC LINEAR RESPONSE OF A UNIFORM DENSITY. IT ADDS A SCALING RELATION FOR CORRELATION.

PBE SUBSTANTIALLY REDUCES AND IMPROVES THE OVERBINDING OF ATOMS IN MOLECULES & SOLIDS.
BUT IT OVERCORRECTS LATTICE CONSTANTS, MAKING THEM ONLY A LITTLE BETTER THAN IN LDA.
IT IMPROVES THE SEPARATE X AND C CONTRIBUTIONS TO SURFACE ENERGIES, BUT WORSENS THE TOTAL.

PBEsol GGA IS A VARIANT OF PBE THAT RECOVERS THE SECOND-ORDER GRADIENT EXPANSION OF THE EXCHANGE ENERGY OVER A WIDE RANGE OF SLOWLY-VARYING DENSITIES. PBEsol IS IN A SENSE “BETWEEN” LDA AND PBE.

PBEsol GIVES ACCURATE LATTICE CONSTANTS AND SURFACE ENERGIES. IT CAN BE USEFUL FOR MANY SOLID-STATE PROBLEMS, BUT NOT FOR CHEMISTRY, WHERE IT OVERBINDS LESS THAN LDA BUT MORE THAN PBE.

IF WE WANT AN ACCURATE DESCRIPTION OF TYPICAL ATOMS, MOLECULES & SOLIDS NEAR THEIR EQUILIBRIUM GEOMETRIES, WE HAVE TO GO TO THE META-GGA LEVEL.

META-GGA`S CAN RECOVER THE FOURTH-ORDER GRADIENT EXPANSION FOR EXCHANGE WHILE PRESERVING AN ACCURATE LINEAR RESPONSE OF THE UNIFORM DENSITY. THEY CAN ALSO ZERO OUT THE CORRELATION ENERGY OF A ONE-ELECTRON DENSITY, MAKE THE EXCHANGE ENERGY EXACT FOR A ONE-ELECTRON ATOM, ETC.

BY MAKING USE OF τ AS WELL AS n AND ∇n, A META-GGA CAN RECOGNIZE REGIONS OF SPACE IN WHICH ONE ORBITAL SHAPE DOMINATES THE DENSITY, AND TREAT THEM DIFFERENTLY FROM REGIONS OF SLOWLY-VARYING DENSITY EVEN WHEN $\nabla n \to 0$.

THE revTPSS (REVISED TAO-PERDEW-STAROVEROV-SCUSERIA) META-GGA GIVES SIMULTANEOUSLY ACCURATE LATTICE CONSTANTS, SURFACE ENERGIES, AND BINDING ENERGIES OF ATOMS, AS WELL AS BINDING ENERGIES OF MOLECULES TO SURFACES.

A RECENT “META-GGA MADE SIMPLE” CAN EVEN DESCRIBE THE INTERMEDIATE-RANGE VAN DER WAALS INTERACTIONS THAT ARE IMPORTANT FOR THE CHEMISTRY AND PHYSICS OF “SOFT MATTER”.

FOR A SYSTEM NEAR MECHANICAL EQUILIBRIUM, THE META-GGA COMES CLOSE TO SATISFYING OUR CRITERIA:

IT IS TYPICALLY NONEMPIRICAL.

IT IS COMPUTATIONALLY EFFICIENT.

IT IS USEFULLY ACCURATE FOR ATOMS, MOLECULES, SOLIDS, SURFACES,….

THE revTPSS META-GGA IS AVAILABLE IN MANY STANDARD CODES, INCLUDING VASP AND GAUSSIAN.

WE ARE SEEKING A STILL-BETTER META-GGA THAT WILL SATISFY ALL THE EXACT CONSTRAINTS THAT A META-GGA CAN SATISFY, INCLUDING THE TIGHT LIEB-OXFORD LOWER BOUND ON THE EXCHANGE ENERGY OF ANY ONE-ELECTRON DENSITY, NON-UNIFORM DENSITY SCALING, ETC.

WE EXPECT THAT SUCH A META-GGA WILL BE USEFUL IN ITSELF, AND ALSO AS A BASIS FOR THE CONSTRUCTION OF MORE ACCURATE FULLY NONLOCAL FUNCTIONALS, SUCH AS:

PERDEW-ZUNGER SELF-INTERACTION CORRECTION,
HYBRID META-GGA`S,
RPA-LIKE APPROXIMATIONS INCLUDING THE SHORT-RANGE CORRECTION TO RPA.

STRETCHED BONDS AND NONLOCALITY

WHEN BONDS ARE STRETCHED, THE EXACT XC HOLE CAN SPREAD OUT OVER TWO OR MORE ATOMIC CENTERS. (E.G., STRETCHED H_2^+). SEMILOCAL APPROXIMATIONS CANNOT CAPTURE THIS EFFECT; THEY LOCALIZE THE APPROXIMATE HOLE AND MAKE THE ENERGY TOO LOW. THIS IS A TYPICAL SELF-INTERACTION ERROR.

STRETCHED BONDS ARISE IN BINDING ENERGY CURVES, AND IN THE TRANSITION STATES OF CHEMICAL REACTIONS (WHERE SEMILOCAL APPROXIMATIONS MAKE THE ENERGY BARRIERS TOO LOW.)

IN SYSTEMS WITH ATOMIC-LIKE *d* AND *f* ELECTRONS, THE *d* AND *f* BONDS ARE STRETCHED EVEN AT EQUILIBRIUM ("STRONGLY CORRELATED SYSTEMS").

SOME STRETCHED BONDS (THOSE IN WHICH ELECTRONS ARE SHARED BETWEEN DISTANT ATOMIC CENTERS) REQUIRE FULLY NONLOCAL FUNCTIONALS, SUCH AS HYBRIDS OR RPA-LIKE FUNCTIONALS.

HYBRID FUNCTIONALS INCLUDE AN EXACT-EXCHANGE INGREDIENT. ONE OF THE SIMPLEST AND BEST HYBRIDS IS PBE0:

$$E_{xc}^{PBE0} = aE_x^{exact} + (1-a)E_x^{PBE} + E_c^{PBE}$$

WHERE $a = 0.25$. HERE E_x^{exact} IS A FOCK INTEGRAL OF KOHN-SHAM ORBITALS.

THE EXACT-EXCHANGE MIXING PARAMETER *a = 0.25* IS CHOSEN NON-EMPIRICALLY TO GIVE GOOD MOLECULAR ATOMIZATION ENERGIES, BUT FOR OTHER APPLICATIONS IT MUST BE REGARDED AS EMPIRICAL.

PBE0 IS USUALLY MUCH MORE ACCURATE THAN PBE FOR THE ATOMIZATION ENERGIES OF MOLECULES AND THE LATTICE CONSTANTS OF SOLIDS. IT ALSO IMPROVES SURFACE ENERGIES AND ENERGY BARRIERS OVER PBE. IT GIVES BETTER (BUT STILL NOT VERY GOOD) DISSOCIATION LIMITS THAN SEMILOCAL FUNCTIONALS DO.

THE NONLOCALITY PRESENT IN THE HARTREE-FOCK POTENTIAL (NOW 25% OF THE EXCHANGE POTENTIAL) CAN MIMIC THAT OF THE SELF-ENERGY TO PREDICT ACCURATE ENERGY GAPS.

CRITICISM OF HYBRIDS:

ALL SUCCESSFUL HYBRIDS HAVE AT LEAST ONE EMPRICAL PARAMETER, AND SOME HAVE AS MANY AS 40. THOSE WITH 40 PARAMETERS CONTAIN UNPHYSICAL OSCILLATIONS.

THE AMOUNT OF EXACT EXCHANGE ADMIXED IS TYPICALLY ENOUGH TO IMPROVE EQUILIBRIUM PROPERTIES AND ENERGY BARRIERS, BUT NOT NEARLY ENOUGH FOR DISSOCIATION LIMITS OF BINDING ENERGY CURVES.

WE ARE TRYING TO DEVELOP NON-EMPIRICAL HYBRIDS THAT USE THE EXACT EXCHANGE HOLE DENSITY AS AN INGREDIENT OF THE APPROXIMATE XC HOLE DENSITY.

RPA-LIKE APPROXIMATIONS

RPA IN A DENSITY FUNCTIONAL CONTENT WAS PROPOSED BY LANGRETH AND PERDEW IN THE 1970`S. IT IS A **MANY-BODY APPROXIMATION THAT EMPLOYS EVEN THE UNOCCUPIED KOHN-SHAM ORBITALS AND IS NEARLY EXACT FOR THE LONG-RANGE PART OF THE XC HOLE, ALTHOUGH NOT FOR THE SHORT-RANGE PART**. IT MAKES A LARGE -0.5 eV/ELECTRON ERROR IN THE TOTAL CORRELATION ENERGY, BUT THIS ERROR IS ONLY WEAKLY DENSITY - DEPENDENT.

IN THE 1990`S, YAN,KURTH & PERDEW CONSTRUCTED LDA AND GGA CORRECTIONS TO RPA WHICH SUGGESTED THAT THE ERROR OF RPA MIGHT LARGELY CANCEL OUT OF ENERGY DIFFERENCES THAT CONSERVE THE ELECTRON NUMBER IN THE GROUND STATE.

IN THE 2000`S, FURCHE **APPLIED RPA TO MOLECULES**.
HE FOUND THAT MOST OF THE RPA ERROR CANCELLED OUT OF ATOMIZATION ENERGIES, BUT ENOUGH ERROR REMAINED TO REQUIRE A CORRECTION, AND THE LDA AND GGA CORRECTIONS WERE NOT HELPFUL. THEN KRESSE **APPLIED RPA TO SOLIDS**, AND FOUND A MUCH MORE NEARLY-PERFECT ERROR CANCELLATION. RPA CAN YIELD VERY ACCURATE LATTICE CONSTANTS, SURFACE ENERGIES, COHESIVE ENERGIES, AND SOLID-STATE REACTION ENERGIES (INCLUDING STRUCTURAL PHASE TRANSITIONS UNDER PRESSURE).

RPA (AND HYBRIDS) ARE AVAILABLE IN VASP.
WE WILL TRY TO CONSTRUCT A NONLOCAL CORRECTION TO RPA.

SUMMARY

KOHN-SHAM DENSITY FUNCTIONAL THEORY IS THE MOST WIDELY-USED METHOD OF ELECTRONIC STRUCTURE CALCULATION IN MATERIALS SCIENCE, CONDENSED MATTER PHYSICS, AND QUANTUM CHEMISTRY.

IT HAS A RIGOROUS FOUNDATION FOR GROUND-STATE ENERGIES, ELECTRON DENSITIES, AND GEOMETRIC STRUCTURES. AND IT HAS A HIERARCHY OF APPROXIMATIONS OF INCREASING SOPHISTICATION FOR THE EXCHANGE-CORRELATION ENERGY AS A FUNCTIONAL OF THE DENSITY.

MUCH HAS BEEN DONE, BUT MORE REMAINS TO BE DONE, TO MAKE THESE APPROXIMATIONS AS ACCURATE AND AS NONEMPIRICAL AS POSSIBLE.